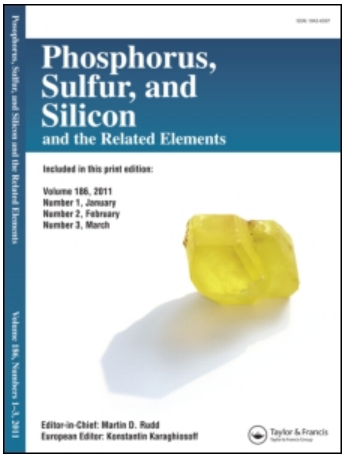

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Poster

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MONOETHYLPHOSPHITE QUANTITATIVE DETERMINATION BY USING GAS-CHROMATOGRAPHY, IN DIFFERENT REACTION SYSTEMS

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The present paper aims at establishing a G.C. proceeding for monoethylphosphite quantitative determination in different reaction systems, after a previous derivatization with CH_2N_2 in etheral solution, with the purpose of blocking the acid P-OH functions.

The reactions under investigation are as follows:

-diethylphosphite dealkylation with HCl[1,2]

-diethylphosphite reaction with H_3PO_3[3] and inferior carboxylic acids[4]

-hydrolyse of monoethyldichlorophosphite.

The performance of this method lies in the accuracy of monoethylphosphite determination, making evident the decomposition forms, as well as the stopping of the development of reactions at the every moment of collecting the samples designated to analysis.

The application of this method allows the synthesis conditions in which monoethylphosphite represents a majority, to be found, by avoiding the decomposition products. It may be also used to the interphasic control of the technology of obtaining some practical interest fungicides based on phosphorous esters[5].

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SYNTHESIS OF ETHER THIOPHOSPHOLIPIDS WITH C-S-P BOND

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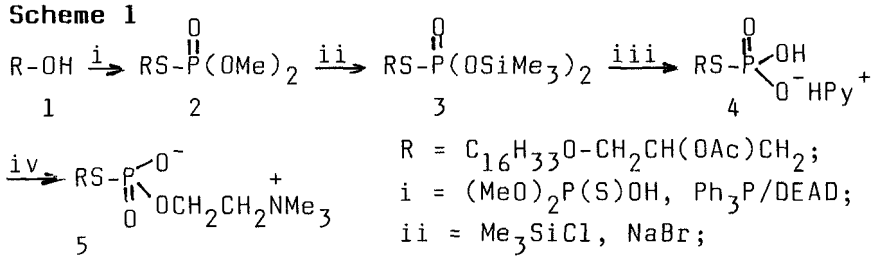
Żwirki 36, 90-924 Łódź, POLAND

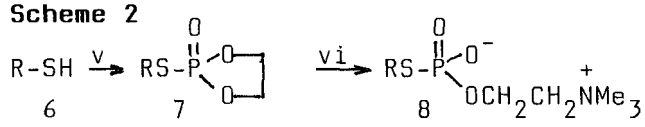
Three types of the title compounds 5, 8a and 8b (Scheme 1 and Scheme 2) were synthesized starting from glycerol, thioglycerol and dithioglycerol derivatives with different substituents at C-1 and C-2.

Scheme 1



R = $C_{16}H_{33}O$-$CH_2CH(OAc)CH_2$;
i = $(MeO)_2P(S)OH$, Ph_3P/DEAD;
ii = Me_3SiCl, NaBr;
iii = MeOH, Py; iv = choline tosylate, condensing agent.

Scheme 2



R = $C_{16}H_{33}Y$-$CH_2CH(OMe)CH_2$, Y=O [(6,7,8)a]; Y=S [(6,7,8)b].
v = 2-chloro-2-oxo-1,3,2-dioxaphospholane, Et_3N; vi = Me_3N.

Thiophosphorylation of 1 with dimethylthiophosphoric acid gives 2 in 80% yield. The reactions sequence 2-3-4 was carried out by analogy to lit.[1]. Condensation of 4 with choline tosylate gives Thio-PAF 5 in 72% yield. The ether thiophospholipids 8a and 8b were obtained in good yield (85%) from the thiols 6a and 6b respectively. The thiols have been hitherto unknown. The structure of the final thiophospholipids 5, 8a and 8b was confirmed by using ^1H-, ^{13}C- and ^{31}P-nmr spectroscopy.

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Phosphorus, Sulfur, and Silicon, 1993, Vol. 77, p. 143
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REACTIONS BETWEEN TRIPHENYLPHOSPHINE AND BROMOFORM A RE-EXAMINATION.

NEIL MCKELVIE

Department of Chemistry, The City College of the City University of New York, New York, NY 10031, USA

ABSTRACT

Ramirez and McKelvie in 1957 proposed the following propagation steps for a free-radical reaction between triphenylphosphine and excess bromoform.

(1) $(C_6H_5)_3P + \cdot CHBr_2 \longrightarrow (C_6H_5)_3P^{\cdot}\text{-}CHBr_2$

(2) $(C_6H_5)_3P^{\cdot}\text{-}CHBr_2 + CHBr_3 \longrightarrow (C_6H_5)_3P^{+}\text{-}CHBr_2\ Br^{-} + \cdot CHBr_2$.

This paper did not mention that the triphenylphosphine had to be carefully purified, to remove an unspecified inhibitor present in ordinary samples. Triphenylphosphine has to be recrystallised under nitrogen and then dried over H_2SO_4 *in vacuo* in order to obtain reproducible results . However, the reaction is inhibited not only by known radical inhibitors such as diphenylamine but also by phenol and, less effectively, by ethanol and by H_2O.

The above phosphoranyl radical cannot be an intermediate because addition of an electron to dibromomethyltriphenylphosphonium bromide leads to reduction of a carbon-bromine bond. We now propose the following mechanism :

(1) $(C_6H_5)_3P: - 1e^{-} \longrightarrow (C_6H_5)_3P^{\cdot +}$ (or other radical initiation)

$(C_6H_5)_3P^{\cdot +} + HCBr_3 \longrightarrow (C_6H_5)_3PH^{+} + \cdot CBr_3$

(2) $(C_6H_5)_3P: + \cdot CBr_3 \longrightarrow (C_6H_5)_3P^{+}\text{—}CBr_3^{-\cdot}$

$\longrightarrow (C_6H_5)_3P^{+}\text{-}CBr_2\cdot\ Br^{-}$

(3) $(C_6H_5)_3P^{\pm}CBr_2\cdot\ Br^{-} + HCBr_3 \longrightarrow (C_6H_5)_3P^{\pm}CHBr_2\ Br^{-}\ \cdot CBr_3$

The oxidation of pure triphenylphosphine in solution by O_2 is self-limiting, and we have isolated very small amounts (<0.1%) of phenol. If excess triphenylphosphine is present, reaction with the monophosphonium salt leads to bis-phosphonium salts and ylides. UV irradiation of a solution of pure triphenylphosphine and bromoform in anhydrous ether goes mostly according to the following equation.

$5\ (C_6H_5)_3P + 2\ CHBr_3 \longrightarrow (C_6H_5)_3P^{\pm}CH_2P^{\pm}(C_6H_5)_3\ (Br^{-})_2 +$

$(C_6H_5)_3P^{\pm}CBr^{=}P^{+}(C_6H_5)_3\ Br^{-} + (C_6H_5)_3P^{\pm}Br\ Br^{-}$ If a small amount of H_2O is present, then this reacts with triphenylphosphine dibromide to give HBr which produces an equimolar mixture of $(C_6H_5)_3P^{\pm}CH_2P^{\pm}(C_6H_5)_3(Br^{-})_2$ and $(C_6H_5)_3P^{\pm}CHBrP^{\pm}(C_6H_5)_3\ (Br^{-})_2$. With a further equivalent of triphenylphosphine and HBr, the product becomes entirely $(C_6H_5)_3P^{\pm}CH_2P^{\pm}(C_6H_5)_3\ (Br^{-})_2$

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AMBIDENT ELECTROPHILICITY OF ALKYL ARYL PHOSPHATES

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Department of Chemistry, University of Pretoria, Pretoria 0002, South Africa

Dimethyl aryl phosphates, $(MeO)_2P(O)OAr$, where ArO group is derived from N-methyl-8-hydroxyquinolinium or 4-hydroxy-(N,N,N-trimethyl-anilinium) ion, offer two electrophilic centres of comparable reactivities: the phosphorus atom and the methyl carbon atoms. The hydrolysis of these substrates proceeds with the cleavage of the P—OAr and Me—O bonds, and was studied in D_2O solutions by ^1H NMR spectroscopy. The effect of external factors on the relative contributions of those two reaction pathways (k_P *vs* k_C) was investigated. The increase in temperature favors, owing to the difference in activation entropies, the reaction at carbon. The addition of acetone to the aqueous reaction medium slows down the reaction at carbon more rapidly than the reaction at phosphorus indicating higher hydration requirements of the dealkylation transition state. In water - trifluoroacetic acid mixtures only the P—OAr bond cleavage is acid catalysed; the catalytic effect is superimposed on the general, decelerating, medium effect. Specific nucleophilic catalysis was demonstrated for the Me—O bond fission by thiosulfate ion (*ca* 60-fold acceleration), and for the reaction at phosphorus by fluoride ion (*ca* 500-fold acceleration).

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C.C.P. Wagener, A.M. Modro, T.A. Modro, *J. Phys. Org. Chem.*, **4**, 516 (1991).

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STRUCTURE AND REACTIONS OF DIHALOGENOPHOSPHANYL PHOSPHORINANES AND PHOSPHOLANES

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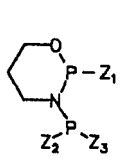
Fachbereich Chemie der Humboldt-Universität,
0-1040 Berlin, Federal Republic of Germany

The results of investigations concerning the structure and the behaviour of the 5- and 6-membered heterocyclic phosphanyl compounds (I-IV) formed by the reaction of PCl_3 or PBr_3 with bifunctional protic nucleophiles like propanolamine-1.3, ethanolamine, ethylenediamine and diaminopropane-1.3 are presented.



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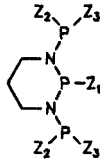

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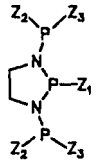

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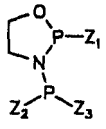

IV

Especially the exact determination of the structure of the 2-chloro-3-dichlorophosphanyl-1.3.2-oxazaphosphorinane (Ia: Z= Cl) could be realised by ^{31}P, ^{15}N, ^{1}H and ^{13}C- NMR- spectra and elemental analysis.

Furthermore derivatisation reactions of Ia with the Franz-reagent $NEt_3 \cdot 3HF$ leading to the corresponding cyclic fluoro derivative (Ib: Z= F), with $HNEt_2$ forming the expected cyclic amino-compounds (Ic: Z_1, Z_2, Z_3= NEt_2; Id: Z_1= Cl; Z_2, Z_3= NEt_2; Ie: Z_1, Z_2= Cl; Z_3= NEt_2) and with EtOH forming the cyclic ethoxy derivatives (If: Z_1, Z_2, Z_3= OEt; Ig: Z_1= Cl; Z_2, Z_3= OEt) were investigated.

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IONISATION OF PHOSPHOROCHLORIDITES. IDENTIFICATION OF PHOSPHORUS CATIONS STABILIZED BY DONOR-ACCEPTOR BONDS

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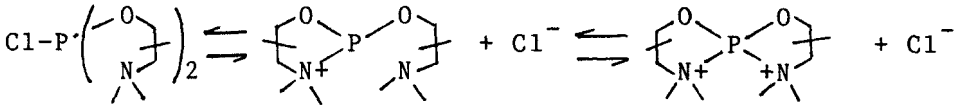
Laboratoire de Synthèse, Structure et Réactivité de Molécules Phosphorées; UA au CNRS N°454 - Université Paul Sabatier - 118 route de Narbonne - 31062 Toulouse Cedex - France

Phosphorochloridites exist as potential equilibria with phosphorus cations and chloride anion. We pointed out equilibria where cationic species are stabilized by P←N bonds :



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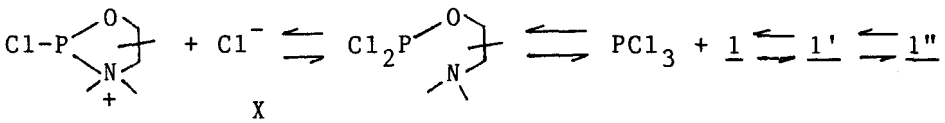
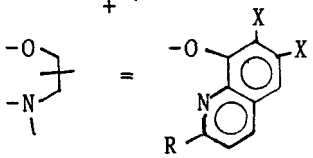
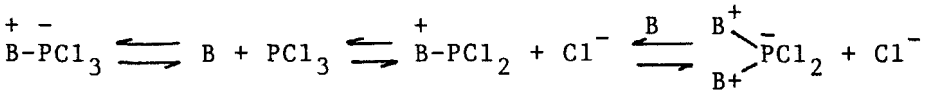




R = H, Me; X = H, Br

On the other hand, ^{31}P NMR signal of PCl_3 in presence of bases B (NMe_3, DBU, quinuclidine), in $CDCl_3$, CH_2Cl_2 or toluene solution, is splitted, at low temperatures, into two, three and even four signals. Equilibria have been proposed to explain these phenomena :



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FLUORINATED KETOENOLS IN PHOSPHORUS CHEMISTRY

ROLF-DIETER HUND, GEORGIOS BEKIARIS, and GERD-VOLKER RÖSCHENTHALER*
Institute of Inorganic and Physical Chemistry,
University of Bremen, Leobener Straße,
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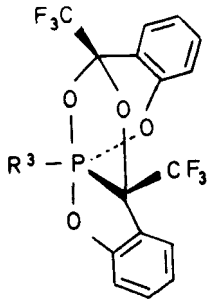
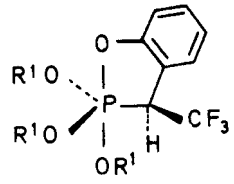
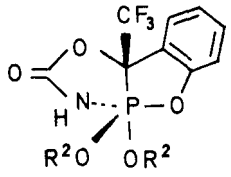
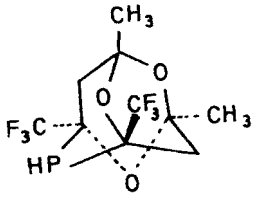
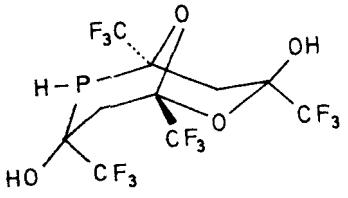
Fluorinated ketoenols and 2-trifluoracetylphenol are versatile multifunctional reactants. They were allowed to react with triorganylphosphites, $(R^1O)_3P$, isocyanatophosphites, $(R^2O)_2PNCO$, phosphonous acid chlorides R^3PCl_2, and with PH_3. Products were monocyclic, bicyclic and tricyclic compounds:











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GAS PHASE THERMOLYSIS OF ALLYL AND t-BUTYL PHOSPHINES.

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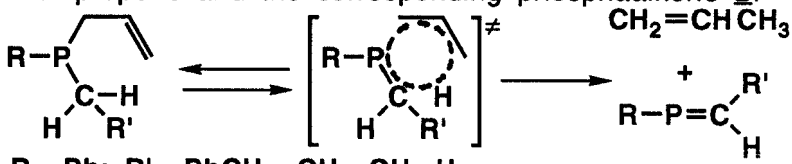
Centro de Química. Instituto Venezolano de Investigaciones Científicas.Aptdo 21827. Caracas 1020A. VENEZUELA.

The pyrolysis of the allyl phosphines **1**, in a stirred flow reactor at 380-450º C/6-20 torr using toluene as carrier gas, lead to the formation of propene and the corresponding phosphaalkene **2**.



R= Ph; R'= $PhCH_2$, CH_2=CH, H

R= TMP, Mes, iPr_2N; R'= CH_2=CH

When R= Ph, kinetic studies show that this reaction proceeds via an unimolecular elimination that involves a six-center cyclic transition state mechanism.

When the substituent R on the phosphorus atom is a Mesityl (Mes) or a Tetramethylpiperidino (TMP) group, we observe radical splitting as competitive reaction. Perhaps, the steric hindrance of these bulky group is responsible for this behaviour, preventing the molecule from reaching the appropiate transition state geometry.

In the case of R= iPr_2N, we observed besides the corresponding phosphaalkene, the formation of an iminophosphine produced most likely via a radical reaction.

In the same conditions,the pyrolysis of t-Butyl diallylphosphine vproceeds in a 60% extent via similar six center cyclic transition state elimination of propene. In a 40% extent it proceeds via t-Butyl moiety splitting, forming 67% isobutene plus 33% isobutane. This C_4 hydrocarbon ratio suggest the occurrence of both unimolecular, four-center cyclic transition state, and radical mechanisms for isobutene formation.

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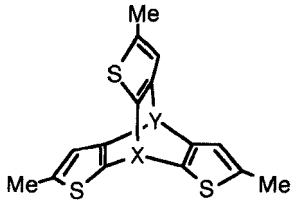
SYNTHESES AND REACTIONS OF PHOSPHA- AND DIPHOSPHA-THIOPHENETRIPTYCENES

AKIHIKO ISHII, IKUO TAKAKI, JUZO NAKAYAMA AND MASAMATSU HOSHINO
Department of Chemistry, Faculty of Science, Saitama University, Urawa, Saitama 338, Japan

Abstract 4-Phospha, 8-phospha, and 4,8-diphospha-4,8-dihydro-4,8[3',2']-thiophenobenzo[1,2-*b*:5,4-*b*']dithiophenes (thiophenetriptycene) are prepared by the reactions of the corresponding trilithium salts with triphenyl phosphite.

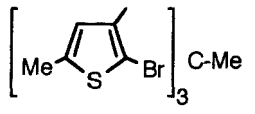
There has been great interest in chemical and physical properties of a phosphorus atom in a rigid ring system. Substitution of bridgehead carbons of **1**[1] with one or two phosphorus atoms produces **2**, **3**, and **4**, where the phosphorus atom(s) of **2** and **4** are not only fixed in the rigid ring system but also surrounded with three thiophene sulfur atoms. We report the syntheses and some reactions of such interesting compounds.

The reaction of the trilithium salt, prepared from a tribromide **5**, with $P(OPh)_3$ in THF gave desired **2** in 16% yield. In a similar manner, **3** and **4** were obtained from **6** and **7**, respectively. Reactions of **2** with *m*-CPBA, S_8, and Se provided **8**, **9**, and **10**, respectively, in good yields. Oxidation of **4** with 2 equiv of *m*-CPBA gave a bis(phosphine oxide) **11**.



1 : X=C-OH, Y=C-Me
2 : X=P, Y=C-Me
3 : X=C-Me, Y=P
4 : X=Y=P

8 : X= P=O, Y=C-Me
9 : X= P=S, Y=C-Me
10 : X= P=Se, Y=C-Me
11 : X=Y= P=O



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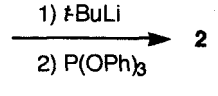

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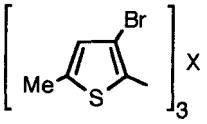

6 : X=C-Me, **7** : X=P

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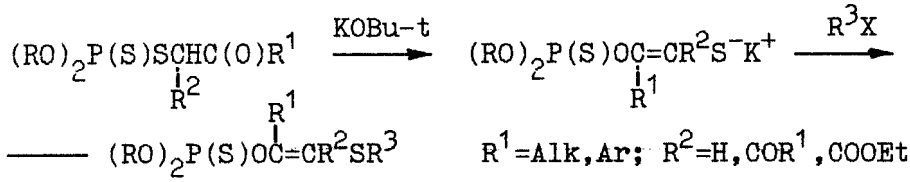
PHOSPHORYLATED VINYLSULPHIDES

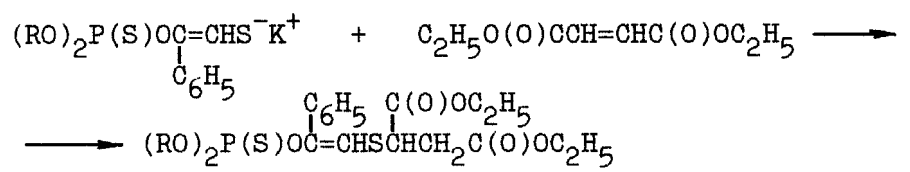
C.G.CHURUSOVA, O.A.KONONOVA, C.V.YAROVENKO, V.A.KOZLOV, V.V.NEGREBETSKII, E.B.PUTSIKINA, A.F.GRAPOV, N.N.MELNIKOV

Scientific Research Institute of Plant Protecting Chemicals, Ugreshskaya 33, Moscow 109088, Russia

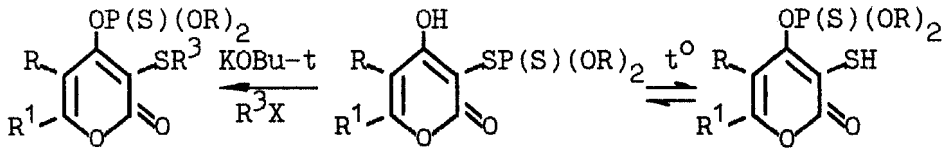
The method for preparation of phosphorylated vinylsulphides, based on the alkylation and acylation of the enthyolates, formed by isomerisation of thiophosphorylthio mono- and di-carbonyl compounds at the conditions of the base catalysis, is proposed.



The intermediate enthiolates are able to react with compounds containing activated double bonds.



It was shown by NMR ^{1}H, ^{13}C and ^{31}P that cyclic 3-thiophosphorylthio-4-oxy-pyrone and coumarin are transformed into corresponding mercapto-derivatives under action of the bases and\or high temperature. The mechanism of reversible thermal migration of thiophosphoryl groups is discussed in accordance with obtained activation parameters.



Phosphorus, Sulfur, and Silicon, 1993, Vol. 77, p. 151
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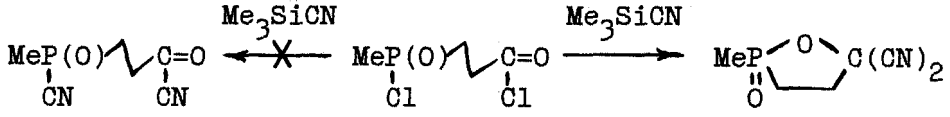
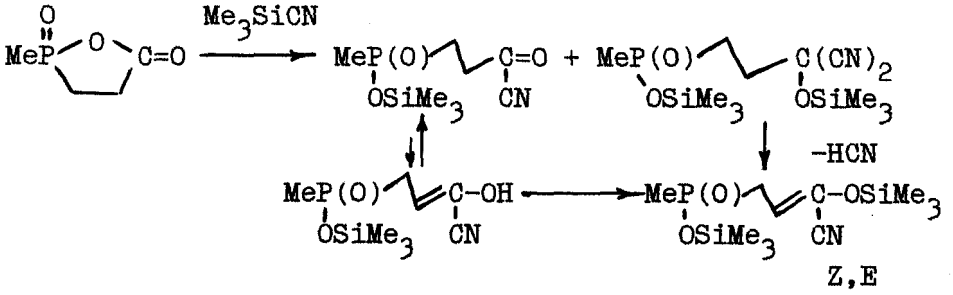
SYNTHESIS AND SOME PROPERTIES OF FUNCTIONALIZED DERIVATIVES OF 3-PROPYLPHOSPHINIC ACIDS

IRENE L. ODINETS, EUGENE A. ANTONOV, PAVEL V PETROVSKY, BORIS I. FREGER, PAVEL V. KAZAKOV, LEONID V. KOVALENKO, TATYANA A. MASTRYUKOVA, MARTIN I. KABACHNIK
A.N.Nesmeyanov Institute of Element-Organic compounds, Russian Academy of Sciences, Vavilov str. 28, Moscow 117813, Russia

We have studied reactions of some derivatives of (2-carboxyethyl)-methylphosphinic acid with Me_3SiCN. Dichloroanhydride of this acid reacts with Me_3SiCN to afford not the expected cyanophosphineoxide, but cyclic 5,5-dicyano-1,2-oxaphospholane.



An inner anhydride of the acid named interacts with Me_3SiCN to open a cycle in contrast to carboxylic acids anhydrides, which don't react with Me_3SiCN. The reaction leads to three silyl esters of phosphinic acids, which ratio depends on the conditions of the process: the catalyst the reactants ratio, temperature and time of the procedure.



The mechanism of the reactions is discussed.The hydrolysis of synthesized products and tautomerism of acids obtained were investigated.

Phosphorus, Sulfur, and Silicon, 1993, Vol. 77, p. 152
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A NEW, UNEXPECTED COURSE OF THE REACTION OF PHOSPHINOCHLORIDOTHIONATES WITH ARYLALKYL ETHERS

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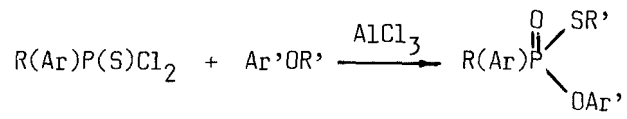
The phosphinylation of aromatic derivatives occuring in the presence of Lewis acids constitutes one of the most important methods for the construction of C-P bond.[1]

During our work[2] on the synthesis of chiral chlorophosphines we have found that arylalkyl ethers react with phosphono- or phosphinochloridothionates under the Friedel-Crafts conditions to form the corresponding phosphono(phosphino)thiolates, according to the general equation shown below:



We suppose that the reaction course consists of the following sequences: 1.formation of a complex of ether and $AlCl_3$, 2.alkylation of phosphinochloridothionates, 3.displacement of chloride by the phenoxy group in chloromethylthiophosphonium salt, 4.hydrolysis of the salt to the final product.

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Phosphorus, Sulfur, and Silicon, 1993, Vol. 77, p. 153
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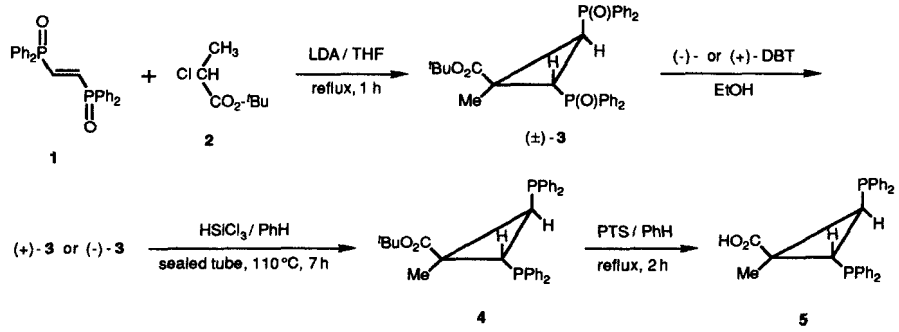
A NOVEL TYPE OF CHIRAL DIPHOSPHINE LIGAND, TRANS-2,3-BIS(DIPHENYLPHOSPHINO)-1-METHYL-1-CYCLOPROPANECARBOXYLIC ACID AND ASYMMETRIC ALLYLIC ALKYLATION BY THE USE OF ITS PALLADIUM COMPLEX

Yoshiharu OKADA, Toru MINAMI, and Junji ICHIKAWA
Department of Applied Chemistry, Kyushu Institute of Technology, Sensuicho 1-1, Tobata, Kitakyushu 804, Japan

We have recently reported a simple method for the synthesis of chiral 2-functionalized (diphenylphosphino)cycloalkanes and utilization for their transition metal complexes catalyzed asymmetric reactions. We report here synthesis and resolution of a novel type of diphosphine bearing a carboxyl group, which have been utilized as a ligand for the catalytic asymmetric reactions.

Reaction of trans-1,2-bis(diphenylphosphinyl)ethene **1** with *t*-butyl 2-chloropropionate **2** in the presence of LDA gave racemic *t*-butyl trans-2,3-bis(diphenylphosphinyl)-1-methyl-1-cyclopropanecarboxylate **3**. Resolution of (±)-**3** with (+)-dibenzoyltartaric acid [(+)-DBT] gave the optically active (-)-**3**. Reduction of (-)-**3** with trichlorosilane, followed by acidic treatment gave a new type of chiral (-)-trans-2,3-bis(diphenylphosphino)-1-methyl-1-cyclopropanecarboxylic acid (-)-**5**.



Reaction of 2-cyclohexenyl acetate with *l*-menthyl sodiodiethylphosphonoacetate in the presence of catalytic amount of palladium acetate-(-)-**5** complex (1.5 %mol, 1:0.8) gave the allylic alkylation product in quantitative yield (61 %ee).

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PHOSPHORYLNITRILOXIDES: SYNTHON APPROACH TO THE SYNTHESIS OF NEW PHOSPHORYLATED HETEROCYCLIC AND POLYFUNCTIONAL COMPOUNDS

V.A.PAVLOV, A.I.KURDJUKOV, N.V.ARISTOVA, B.I.GORIN, V.V.MOSKVA, F.R.FAZLEJEVA

Institute of Chemical Technology, Kazan, Russia

The nitrosation reaction of phosphorylacetaldehydes $(RO)_2P(O)$-CHX-CHO leads depending on R or X to either phosphorylated nitroso-(I) and nitronenols(II)[1] or oximes of phosphorylcarbonylhalogenides(III)[2] or halogenoglyoxylic monooxime(IV) and monomeric metaphosphoric acid(V)[2] which can be used as phosphorylating agent in mild conditions.

The processing of (III) by bases results in the formation of high reactivity phosphorylnitrileoxides $(RO)_2P(O)C{\equiv}N{\rightarrow}O$ (VI)[3] which either polymerize or dimerize to furoxan(VII) at room temperature. SCF ab initio molecular orbital calculations have been carried out for the phosphorylnitrileoxide with the ST04-31G* basis set. Comparison of calculations done by ab initio and by MNDO demonstrated that MNDO can be used for optimization of the transition state of dimerisation products. It was shown the consecutive mechanism of dimerisation.

The cycloaddition reactions of (VI) to alkynes and alkenes (including norbornenes and cyclopropenes) and the interaction of (VI) with oxigen-, sulfur-, nitrogen- or phosphorus containing nucleophiles have been investigated. The mechanism of novel reaction of the oximes of phosphorylcarbonylhalogenides(III) with thioureas in alcoholic medium resulting to phosphorylthioncarbamates was studied.

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PHOSPHINE-BORANES IN SYNTHESIS EASY ACCESS TO FUNCTIONALIZED DIPHENYLPHOSPHINES.

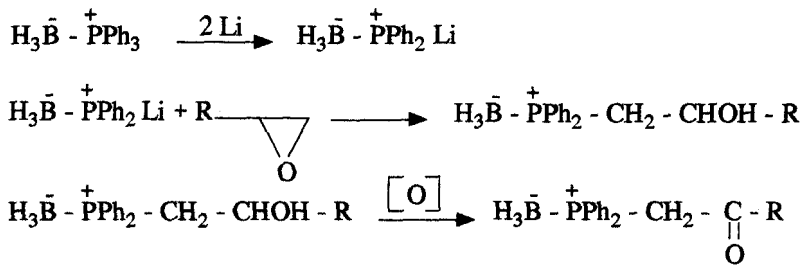
P. PELLON and M. LE CORRE
Laboratoire de Synthèse Organique, Associé au CNRS, Avenue du Général Leclerc 35042 Rennes FRANCE

Abstract Oxidation of the hydroxyalkylphosphine-borane complexes by usual oxidizing agent can lead to the phosphine-boranes bearing an aldehyde, a ketone or an acid function on the side chain.

The peculiar chemical properties, reactivity and stability, of phosphine-boranes have attracted the attention of chemists[1-3].

We report here our recent results, which show that P-B bond offers great resistance to usual oxidation.

This result allows the use of phosphine-boranes in organic syntheses and, starting from commercially available triphenylphosphine-borane we can obtain hydroxy, carbonyl or carboxy-diphenylphosphines by an original way.



If R = H, Corey's oxidation with P.C.C. give an aldehyde and, Jones' oxidation give an acid.
If R ≠ H, Corey's or Jones' oxydation give a ketone.

The decomplexation, in quantitative yields, of phosphine-boranes in phosphines was carried out using diethylamine[3].

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2. A. Peltev, R. Rosser and S'. Mills, J.C.S. Chem. Commun (1981), 1014.
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SOME ASPECTS OF REACTIVITY OF PHOSPHONIC DICHLORIDES TOWARDS ALKOXYLIC AROMATIC COMPOUNDS

OANA PETREUS
"Petru Poni" Institute of Macromolecular Chemistry
Iaşi - Romania

Abstract

The synthesis of polyphosphate esters attracts the interest of specialists due to the particular characteristics of these compounds, such as nonflammability, thermal stability high melting points, etc.[1,2,3]
The research deals with the reaction betwen phosphonic dichlorides and aromatic diols containing halogen atoms in nucleus, SO_2 group in the chain or imide groups.
Using chemical or spectroscopic methods (IR, H'-NMR) we determined the transformation degree and the reaction rate constante and we observed that the structure of monomers had a great influence on the kinetic behaviour of condensation.
As a result of our investigations we can conclude that the structure of phosphonic component influence the rate of reaction towards aromatic diols in a decreasing way for thiophosphonic dichlorides. In the case of aryloxyphosphonic dichlorides we also observed a lower stability of the product of reaction.
At the same time the chlorine atoms introduced in the aromatic ring of the diol and the internal SO_2 group having a strong electronic withdrawing effect, decrease their reactivity against phosphonic dichloride. As a results, the reaction parameters are drasticaly influences. The ethoxylic group positioned betwen the halogenated aromatic nucleus and the reactive OH group leads to an increase of reactivity. Similarly of reaction rate constants of cyclohexylphosphonic dichloride with two different diols (tetrachlorinated bisphenol and dihidroxydiphenyl sulfone, respectively) has permited the synthesis of some polyphosphonates with chlorinated aromatic ring alternating with aromatic sulfonic ones.

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CONSTRUCTION OF THE PHOSPHOLENE RING-SYSTEM FROM DIPHENYLVINYLPHOSPHINE

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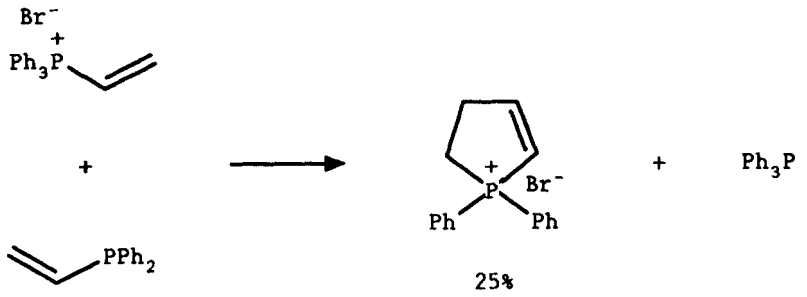
Centre of Molecular and Macromolecular Studies, The Polish Academy of Sciences, Sienkiewicza 112, 90-363 Łódź, Poland

An exploratory experiment sketched below has revealed that conditions exist under which diphenylvinylphosphine cycloadds to activated olefins with concomitant elimination of the auxiliary electrofugal group to form directly unsaturated cyclic five-membered phosphonium salt.



Efforts to make such a reaction more efficient as well as more general are presented.

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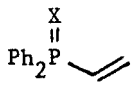
DIELS-ALDER STEREOCHEMISTRY OF PHOSPHINYLETHENES

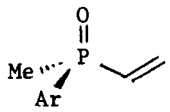
K.M.PIETRUSIEWICZ[1], W.WIŚNIEWSKI[1], W.WIECZOREK[2] and A.BRANDI[3]

[1]Centre of Molecular and Macromolecular Studies, The Polish Academy of Sciences, Sienkiewicza 112, 90-363 Łódź, Poland. [2]Institute of General Chemistry, Technical University of Łódź, Żwirki 36, 90-924 Łódź, Poland. [3]Dipartimento di Chimica Organica, Universita di Firenze, G.Capponi 9, 50121 Firenze, Italy

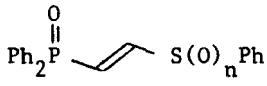
Stereochemical course of thermal Diels-Alder reactions of cyclopentadiene with phosphinylethenes 1 and 2 was studied and the effects of phosphorus substituents on the endo/exo product ratio and on the reaction diastereofacial selectivity were revealed.



1 X=O,S,Se



2 Ar=Ph, 2,4,6-$Me_3C_6H_2$



3 n=0,1,2

Selenoxy derivative 1 gave the highest endo/exo product ratio whereas mesityl derivative 2 favored the formation of the exo products the most. The diastereofacial selectivity in cycloadditions involving P-chiral dienophiles 2 was only moderate. In the most favorable case the selectivity was higher for the exo than for the endo approach. As judged from the structure of the major cycloadducts (^{1}H NMR, X-ray), the preferred reactive conformation of phosphinylethenes 2 in the studied cycloadditions was s-trans. Complete stereochemical assignment to all the products will be presented and attempts to control the endo/exo as well as diastereofacial selectivity in the above reactions by means of an auxiliary directing substituent (as in 3), or by means of Lewis acid catalysts (e.e., $AlCl_3$), will be discussed.

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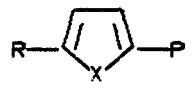
PHOSPHORYLATION OF HETEROAROMATIC COMPOUNDS BY HALOGENANHYDRIDES OF P(III) ACIDS

A.A. TOLMACHEV, S.P. IVONYN, A.A. YURCHENKO,
A.I. SVIRIDON, E.S. KOZLOV, A.M. PINCHUK

Institute of Organic Chemistry of the Akademy of Sciences of Ukraine, Murmanskaya Str. 5, Kiev 253660, Ukraine

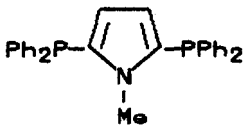
We have shown that halogen anhydrides of P(III) acids in pyridine solutions can be used as sufficiently active phosphorylating reagents in respect to wide range of heteroaromatic compounds, inclined to electrophilic substitution reactions. The best preparative results were obtained using PBr_3.

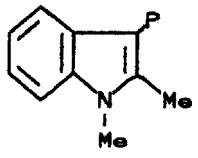
Phosphorylated pyrroles, furans, thiophenes, indoles, indolizines, pyrimidazoles, pyrazoles and indazoles were synthesized with high yields. In some cases one, two or three heteroaryl substituents can be successively introduced to phosphorus atom.

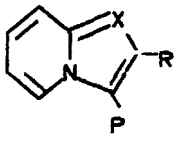


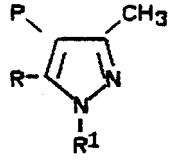
X = O; S; NMe

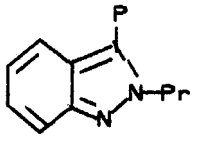
R = H, Me, -CH=NNMe$_2$











X = CH, N; R = Ph, Me R = Me, OMe; R^1 = Me, Ph

Indolizines are found to undergo phosphorotropic rearrangement in mild conditions.

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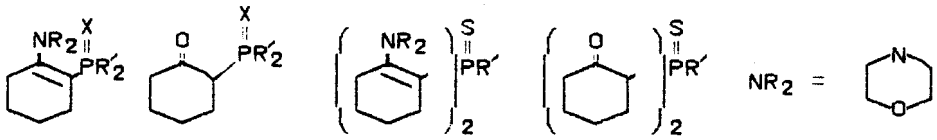
PHOSPHORYLATED DERIVATIVES OF 1-MORPHOLINOCYCLOHEXENE, CYCLOHEXANONE AND AZAENAMINES

A.A.Tolmachev, A.N.Kostyuk, E.S.Kozlov, A.M.Pinchuk
Institute of Organic Chemistry of the Akademy of Sciences
of Ukraine, Murmanskaya Str. 5, Kiev, Ukraine 253660

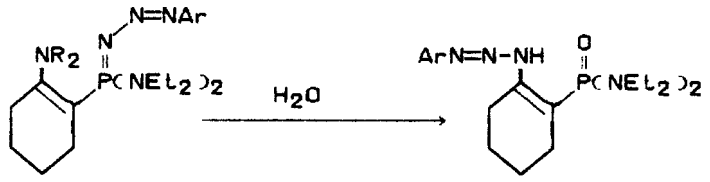
Phosphorylation of 1-morpholinocyclohexene with phosphorus trichloride in the presence of triethylamine was carried out yielding dichloro- and chlorophosphines which served as reagents for preparation of different phosphorylated derivatives.



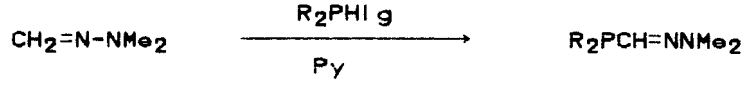
R′ = Cl, NEt_2, OEt; X = lone pair, O, S, N_3Ar, NH, NPh

The possibility of the second phosphorylation was found for some monophosphorylated 1-morpholinocyclohexenes.

On the hydrolysis of phosphazides, the unexpected rearrangement occurs accompanied by the migration of a triazene group from phosphorus to carbon atom. The structure of the hydrolyzed products was established by NMR and X-ray spectroscopy.



Azaenamines including hydrazones of aldehydes are readily phosphorylated with phosphorus (III) halogenides



Phosphorus, Sulfur, and Silicon, 1993, Vol. 77, p. 161
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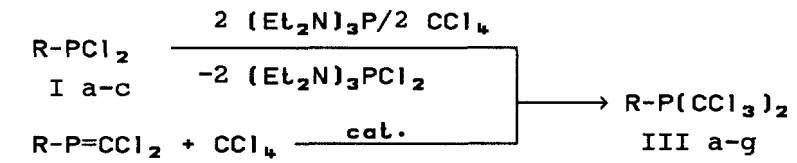
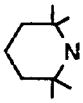
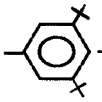
BIS(TRICHLOROMETHYL)PHOSPHINES

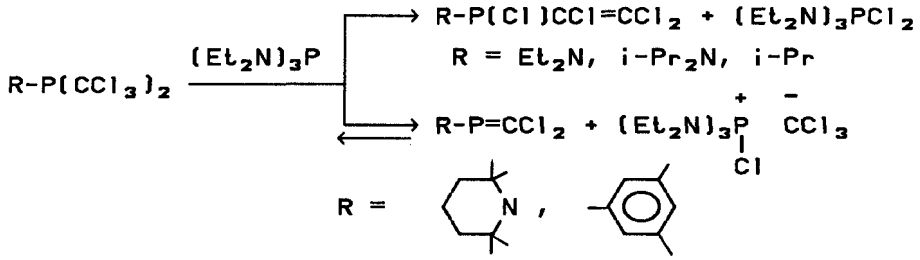
A.P.MARCHENKO, G.N.KOIDAN, G.O.BARAM, A.M.PINCHUK
Institute of Organic Chemistry of the Akademy of Science of Ukraine, Murmanskaya Str.5, Kiev, Ukraine

Accessible methods of synthesis of previously unknown polyfunctional phosphine III (a-g), containing two trichloromethyl groups, have been developed.



R = Alk(a), Ph(b), Alk_2N(c), t-Bu_2N (d),  (e),
 (f),  (g) ; cat.= $(Et_2N)_3P$, $LiCCl_3$

Like CCl_4, phosphines (III) interact with triamidophosphites by galogenophilic mechanism. Composition and structure of reaction products depend on electronic and steric properties of substituent R.



Bis(trichloromethyl)phosphine / triamidophosphite binary system is an active phosphodichloromethylating reagent in respect to various electrophiles and this allows to obtain C-substituted phosphine derivatives.

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RADICAL REACTION CHEMISTRY OF $RE(CH_2CH=CH_2)_2$ AND $R_2E(CH_2CH=CH_2)$. (E=N,P; R=ALKYL)

COLLEEN MICKLETHWAITE, ALLAN ROBERTSON
Cyanamid Canada, Inc., P.O. Box 240, Garner Road, Niagara Falls, Canada

Abstract The radical reaction chemistry of $RE(CH_2CH=CH_2)_2$ with secondary phosphines and $R_2E(CH_2CH=CH_2)$ with primary phosphines where E=N,P and R=alkyl is shown to generate tridentate ligands as well as cyclic and bicyclic byproducts.

Tridentate ligands with two three-carbon backbones of the type $RE(CH_2CH_2CH_2E'R'_2)_2$ (E=N, E'=P, or E=P, E'=N, or E=E'=P; R,R'=alkyl) commonly form coordination complexes with transition metals. Two possible routes to form tridentate ligands are the radical reaction of 1.) $R_2E(CH_2CH=CH_2)$ with primary phosphines, or 2.) $RE(CH_2CH=CH_2)_2$ with secondary phosphines.

The intermediate transition radical E-CC(·)C-P undergoes a reversible radical reaction by fission of the P-C bond to regenerate a phosphine radical and allylphosphine or allylamine. Since the nitrogen-carbon bond is more stable than the phosphorus-carbon bond, the N-C bond fission does not occur in the amine-phosphine system and thus always regenerates the starting reagents. However, the P-C-C·-C-P radical is unique in that either P-C bond may be broken.

The radical intermediate $(H_2C=CHCH_2)RECH_2C(\cdot)HCH_2PR'_2$ reacts intramolecularly with the allyl group to cyclize in addition to abstracting a hydrogen from another reactive phosphine. The cyclic radical further cyclizes to form a bicyclic compound and alkane. In order to reduce the number of byproducts in the phosphine-phosphine systems, the R substituent must be the same.

The reaction between dialkylallylamine and a primary phosphine produces a clean product and the other three methods produce a complex mixture of bidentate and tridentate ligands.

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EASY ACCESS TO α-FLUORINATED PHOSPHONIC ACID ESTERS

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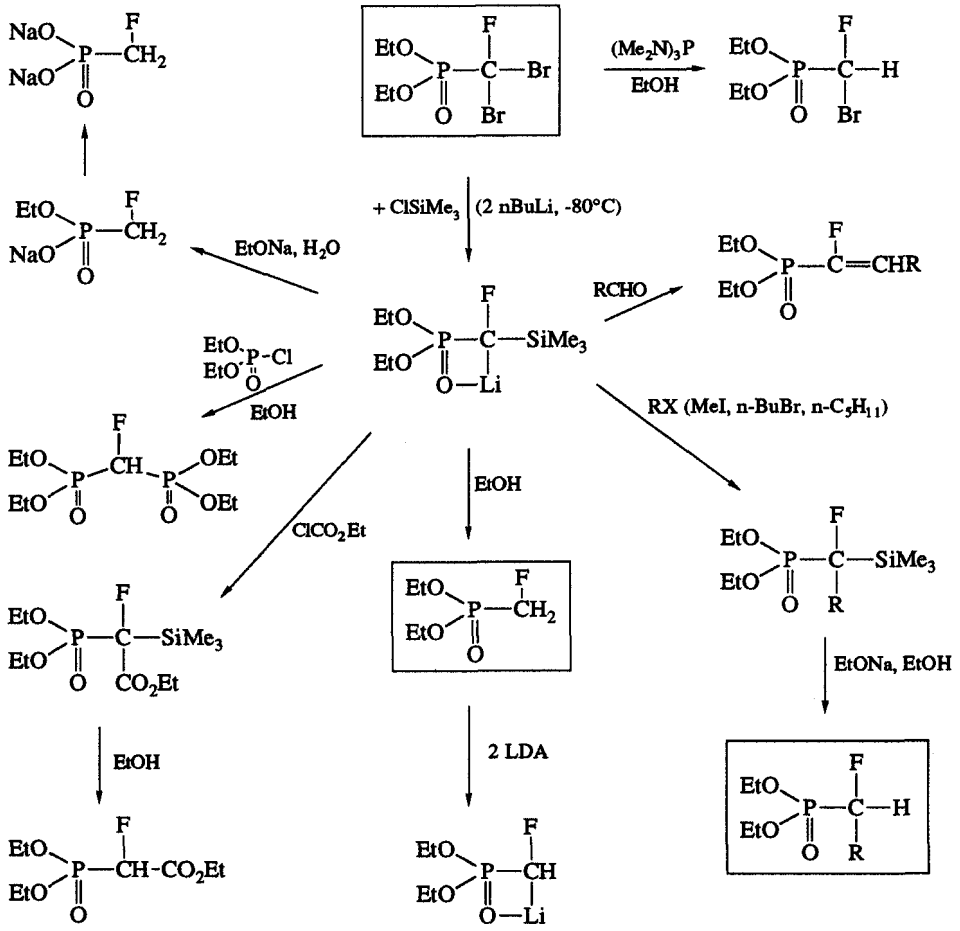
Hétéroatomes et Coordination, URA 1499, DCPH Ecole Polytechnique, F-91128 Palaiseau CEDEX

Phosphonates bearing one or two fluorine atoms at the α position have met great interest due to their potential as bioactive compounds. Blackburn *et al.* have demonstrated that P(O)CHF and $P(O)CF_2$ are better analogues of P(O)O than is $P(O)CH_2$. We wish to report here an attractive route to functionalised fluorinated phosphonates that render them available under very simple experimental conditions. Our starting fluorine containing product is commercially available fluorotribromomethane, which is an easy to use liquid. We now prepare in quantitative yields dibromofluoromethyl diethylphosphonate via an Arbuzov-like reaction in THF (improved procedure after D.J. Burton and R. Flynn, J. Fluorine Chem., 1977, **10**, 329).This phosphonate is then reduced or hemi-reduced quantitatively and can be easily functionalised.



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SYNTHESIS AND PROPERTIES OF PHOSPHORYLATED DONOR-ACCEPTOR SUBSTITUTED ALKENES

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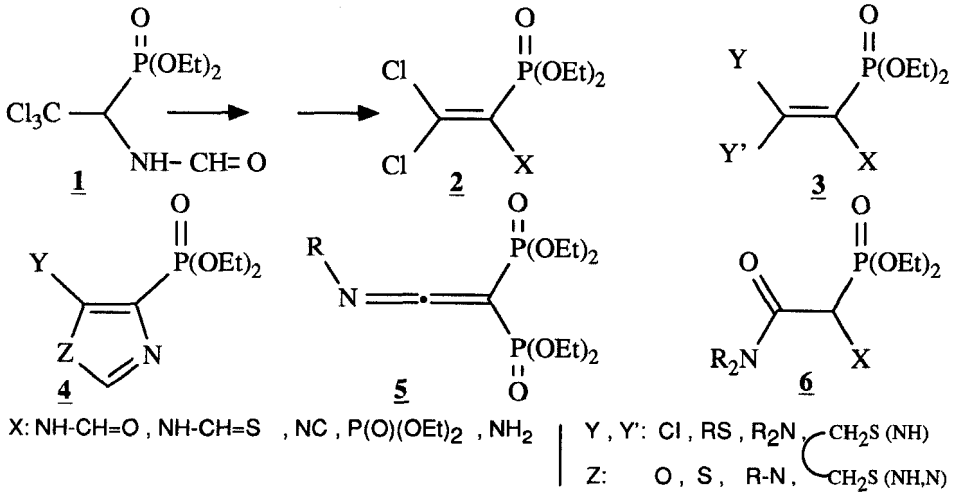
O-1199 Berlin, FRG

The chemical behaviour of phosphorylated dono-acceptor substituted alkenes 2 has been investigated. Compounds 2 are easily available from 1 by simple procedures.[1,2] Dependent on the nature of the X-group sequential chlorine substitution with N- or S-nucleophiles on C-2-atom takes place. In some cases the X-group of 2 itself has nucleophilic properties and therefore a ring closure to phosphonosubstituted heterocycles is possible. So reacts 2 (X: NH-CH=O) with amines or by uv-irradiation to oxazoles 4 (Y: NR_2,Cl). Acidic cleavage of this oxazoles gives phosphonoglycine amides 5 (X: NH_2). Thiazole 4 (Y:Cl) is obtained from 2 (X: NH-CH=S) by simple HCl-elimination. Prim. amines react with 2 (X: NC) to form imidazoles 4 (Y: RNH). Bifunctional N,N- or N,S-nucleophiles react differently, either to isonitriles 3 (X: NC) or imidazoles 4 (Z: NH). The hitherto unknown bisphosphonates 6 (X: $P(O)(OEt)_2$) are synthesized from 2 by a substitution/hydrolysis sequence on C-2-atom via keteneimines 5.



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FLUOROPHOSPHONIC ACID, HOPH(O)F, A NEW EDUCT FOR THE PREPARATION OF ORGANOFLUOROPHOSPHONATES

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Phosphonic Acid, H_3PO_3, reacts quantitatively with acetic anhydride and hydrofluoric acid or potassium fluoride at room temperature under formation of fluorophosphonic acid and potassium fluorophosphite, respectively.
The reaction proceeds via acetylphosphites and diphosphites as intermediates. The crystalline KOPH(O)F was isolated from the acetic acid/-anhydride solution by precipitation with diethyl ether and digestion of the oily precipitate with methanol/diethyl ether (yield 60 %).

$$H_2PHO_3 + (CH_3CO)_2O \xrightarrow{\text{fast}} HPHO_2(OCOCH_3) + CH_3COOH$$

$$HPHO_2(OCOCH_3) + KF \xrightarrow{\text{very fast}} K^+ + PHO_2F^- + CH_3COOH$$

The crystalline potassium salt is stable in absence of moisture. KOPH(O)F reacts with alcohols in alkaline solutions to monoalkylphosphites and F^-. Mechanical activation of a mixture of alkali phosphates and KOPH(O)F yields P^{III}-O-P^V compounds.
Fluorophosphonic acid is a weak donor and reacts similar as phosphonic acid with reactive carbonyl compounds under formation of organo fluorophosphonic acids.
For example, on heating (60 °C, 24 h) a mixture of acetic anhydride, H_3PO_3 and KF the crystalline potassium salt of acetoxyethan-bis-fluorophosphonat solvated with acetic acid is formed.

$$2\,H_3PO_3 + 2\,KF + 3\,CH_3\text{-}\overset{\overset{O}{\|}}{C}\text{-O-}\overset{\overset{O}{\|}}{C}\text{-}CH_3 \xrightarrow{\text{fast}}$$

$$K^+ + \underset{H}{\overset{O^-}{OPF}} + 2\,CH_3COOH + 2\,(CH_3CO)_2O \xrightarrow{\text{slow}}$$

$$K_2\left[\begin{array}{c} O \\ | \\ OPF \\ | \\ CH_3\text{-}C\text{-O-}C\text{-}CH_3 \\ | \\ OPF \\ | \\ O \end{array}\right] \cdot 2\,CH_3COOH$$

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PHOSHPHOROTROPIC ISOMERIZATIONS IN THE C=N-C TRIAD

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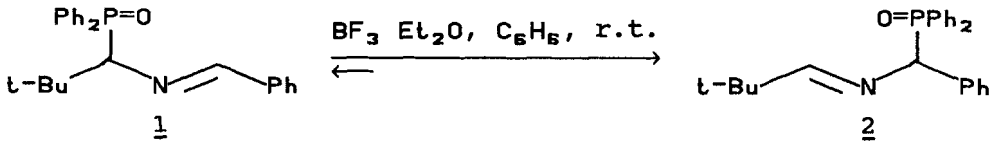
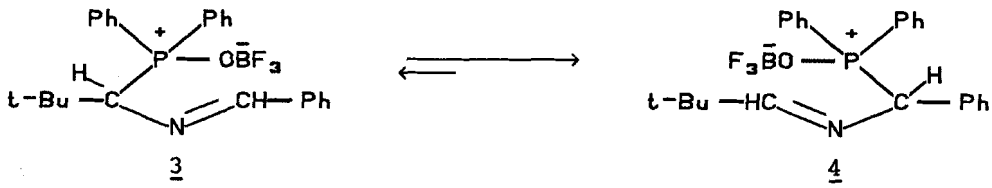
Institute of Organic Chemistry, Academy of Sciences of the Ukraine, Kiev 253660

We wish to report on a novel 1,3-phosphorotropic migration in C=N-C triad. This unusual rearrangement proceeds on heating (150-200) and is accompanied by cleavage of the C-P-bond. We have found that boron trifluoride etherate essentially facilitates the rearrangement.



1 2

The isomerization is reversible (K = 2/1 = 15 at r.t.) and proceeds by an intramolecular mechanism in the complexe formed with participation of a phosphorylated imine P=O group.



3 4

Both thermal and BF_3-induced phosphorotropic migrations in the 1.3-diarylsubstituted α-phosphorylated imines proceed not so easily as in the case of 1. The comparative data for thermal and catalytic phosphorotropic isomerizations are discussed.

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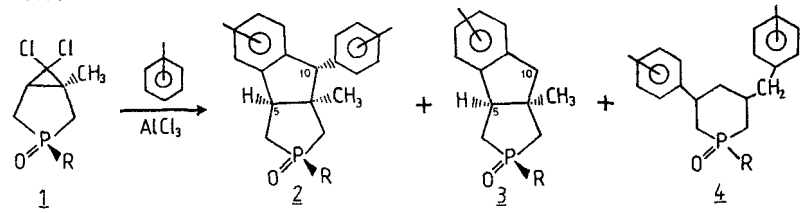
STEREOSTRUCTURE OF BENZO [f] -3-PHOSPHABICYCLOOCT--6-ENE 3-OXIDES FORMED IN THE FRIEDEL-CRAFTS REACTION OF 2,5-DIHYDRO-1H-PHOSPHOLE 1-OXIDE-DICHLOROCARBENE ADDUCTS

LÁSZLÓ TŐKE, GYÖRGY KEGLEVICH, ATTILA KOVÁCS,
KÁLMÁN ÚJSZÁSZY, GÁBOR TÓTH
Department of Organic Chemical Technology, Technical University of Budapest, 1521 Budapest, HUNGARY

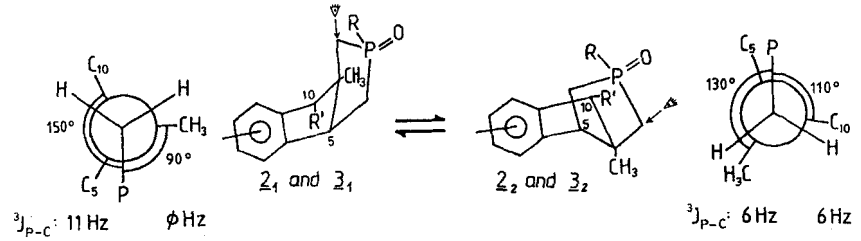
The reaction of dichlorocarbene adducts 1 with substituted benzenes in the presence of $AlCl_3$ results in the formation of benzo-phosphabicyclooctenes 2 and 3 and, in certain cases, hexahydrophosphinine 4. 2 and 3 are formed by the rarely occuring opening of the cyclopropane ring, while 4 by ring expansion.



1 2 3 4

A reduction step must also be assumed to explain the formation of 3 and 4. The excess of the aromatic substrate is responsible for the reduction by giving biaryl-derivative in Scholl-reaction.

The conformation of products 2 and 3 was elucidated by NOE measurements and stereospecific couplings. In most of the cases conformer A predominates.



$^3J_{P-C}$: 11 Hz ϕ Hz $^3J_{P-C}$: 6 Hz 6 Hz

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Stereoselective Synthesis of a Poly-unsaturated Fatty Acid Ester by Horner - Wittig Chemistry

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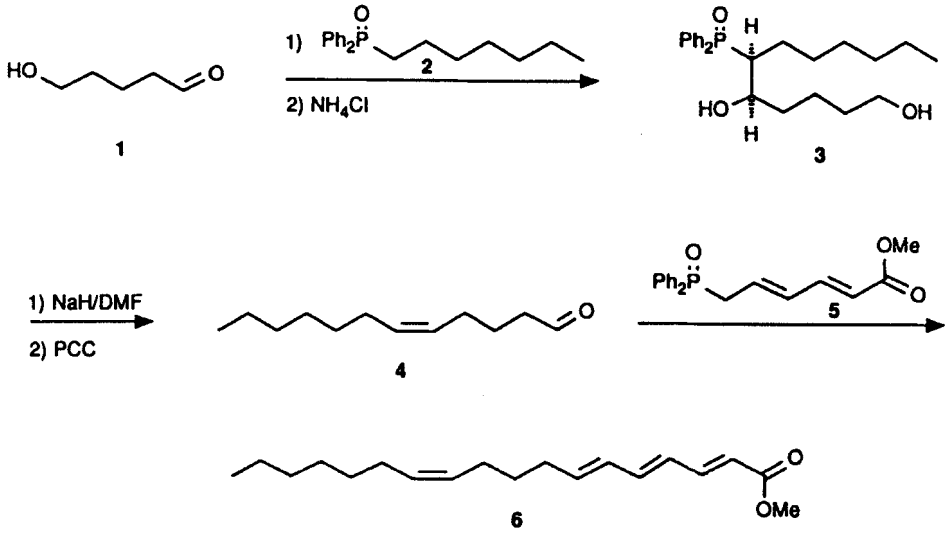
Recently, the presence of a unique, highly unsaturated fatty acid moiety has been demonstrated in the lipo-oligosaccharide signals that determine host specificity in Rhizobium leguminosum[1]. An efficient, highly stereoselective, synthesis of the methyl ester of this fatty acid (**6**) is reported here.

The reaction sequence starts with conversion of the easily available 5-hydroxypentanal (**1**) with the anion of heptyldiphenylphosphine oxide **2** to a mixture of diastereomeric adducts, containing a large preponderance of the *erythro* isomer **3**. Employing the methodology developed by Warren et al.[2], **3** is converted to the *Z*-olefin, which is easily oxidized to the aldehyde **4**. It is worthy of note that, contrary to literature reports[3], conversion of **1** with the phosphonium ylide corresponding to **2** affords a large preponderance of the *E*-isomer of **4**. In a last step, the aldehyde **4** is directly converted into the methyl ester of the desired 2*E*, 4*E*, 6*E*, 11*Z*-octadecatetraenoic acid **6**, by a Horner-Wittig reaction, using the newly developed dienoic phosphine oxide reagent **5**. The identity of **6** with the naturally occurring compound was confirmed by NMR-spectroscopy.



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ACTION OF THE TRICOORDINATED GROUP 15 ELEMENTS AMINODERIVATIVES ON PYRYLIUM SALTS. SYNTHESIS OF NEW AZODYES

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Myriam RAMAROHETRA, Corinne PAYRASTRE

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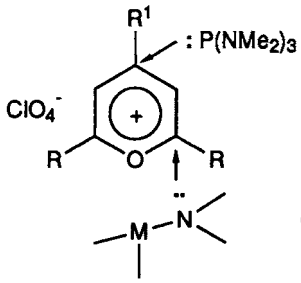
We recently discovered a new type of pentamethinium (azodyes) salts synthesis by action of trisdialkylaminoarsanes on pyrylium salts[1]. Owing to the interest of this new series including dyes, synthetic intermediates, anthelmintics and materials for non linear optics, we describe here the new results obtained in this field :

- we first proved that $Sb(NMe_2)_3$ reacts like $As(NMe_2)_3$, giving the same azodyes,
- with $P(NMe_2)_3$, the C-4 attack is always favoured whereas it is only observed in arsenic series with 2,6-alkylsubstituted salts.

The principal features of the reactivity of the pyrylium salts are gathered in the scheme :



if R = alkyl, C-2 or C-4 positions are deactivated

New salts with various substitutions were obtained with expected modified structures and physical properties as compared to the known planar *trans-trans* configuration of the previously described compounds. Particuliarly, 2,6-aryl functionnalized pyrylium salts afford starting materials for further reactivity leading to polymeric or macrocyclic compounds.

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SOME SYNTHETIC UTILITIES OF CYCLIC PHOSPHONIUM SALT

TETSUYA FUJIMOTO, YUKIHARU TAKEUCHI, HISASHI TAKEUCHI KOH-ICHI KAI, YOH-ICHI KODAMA, KAZUCHIKA OHTA, AND IWAO YAMAMOTO

Department of Functional Polymer Science, Faculty of Textile Science and Technology, Shinshu University, Ueda, Nagano 386 Japan

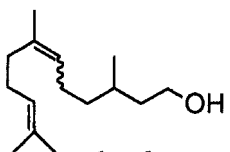
ABSTRACT

Synthesis of E- and Z-dihydrofarnesol and cycloheptenyl phosphine oxides from cyclic phosphonium salts are described.

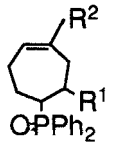
RECENTLY we reported that the tandem Wittig reactions of cyclic phosphonium ylides provided a versatile procedure for synthesis of unconjugated dienes and enones[1]. In this paper , we applied these method to syntheses of E- and Z-dihydrofarnesol **1a,b** and cycloheptenyl phosphine oxides **2**.

A Wittig olefination of 1,1-diphenylphospholanium perchlorate with acetone in the presence of t-BuOK gave a phosphine oxide having a terminal isopropylidene moiety **3** in 75 % yield. Subsequent methylation and a further Wittig-Horner reaction with 6-(t-butyl-dimethylsiloxy)-4-methyl hexanal(LDA, THF, -78°C) afforded a mixture of diastereomers of β-hydroxyphosphine oxide **4**. After separation, each of the pure diasteromeric phosphine oxide was treated with sodium hydride in DMF to give pure E- and Z-dihydrofarnesol **1a,b**, respectively.

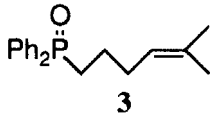
On the other hand, the reaction of the ylide with conjugated enones afforded cycloheptenyldiphenylphosphine oxide **2** via Michael-intramolecular-Wittig reactions.



1a,b



2



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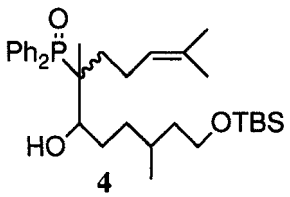

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SELECTIVE PHOSPHORYLATION OF AMINO AND HYDROXYL GROUP BY DIALKYL PHOSPHITES

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* Beijing Xing-Da Scientific System Corporation, Beijing 100084

Abstract Trcing the reaction media in different system and condition with ^{31}PNMR, it was found that the dialkylphosphite specifically reacted with amino group but not with the hydroxyl group.

(a) The reaction of the $(RO)_2P(O)H$ with CCl_4 and NEt_3 produced the $(RO)_2P(O)Cl$ at RT. It showed that the reaction rate of the $(MeO)_2P(O)H$ was twice as the $(EtO)_2P(O)H$ and thirty times as the $(i\text{-}PrO)_2P(O)H$.
(b) Selective phosphorylation of amine and alcohol by $(i\text{-}PrO)_2$ P(O)H was studied by ^{31}PNMR at different temperature. It was found that in general the amine was phosphorylated first, and at 0℃ there was the cleanest reaction with no oxygen-phosphorylation at all.
(c) Among the mixture of the amino acids (Ala, Ser, Cys, His), H_2O, EtOH, CCl_4 and NEt_3 only the amino group was phosphorylated at 0℃. In general, the $(i\text{-}PrO)_2P(O)H$ was a much cleaner reagents for only (4-17%) hydrolysis occurred but no mereapto and imidozol was phosphorylated.
(d) The competitive reaction of $(MeO)_2P(O)H$ and $(i\text{-}PrO)_2P(O)H$ with Alanine in the system (H_2O, EtOH, CCl_4 and NEt_3) was studied. It was found that the formation of N-diisopropylphosphoryl-Alanine was much more than the N-dimethylphosphoryl-Alanine.

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NOVEL CYCLOADDITION REACTIONS OF $Bu^n_3P.CS_2$: FORMATION AND REACTIVITY OF NEW RING SYSTEMS

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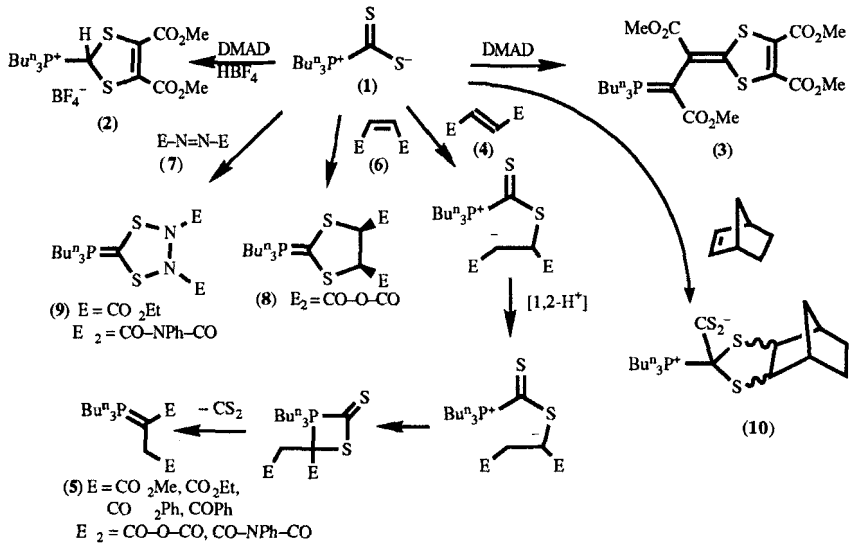
Department of Chemistry, University of St. Andrews, North Haugh, St. Andrews, Fife, KY16 9ST, UK.

Although the crystalline adduct (**1**) of Bu^n_3P with CS_2 has been known for over 100 years the only cycloaddition reaction reported is with DMAD to give salt (**2**) in the presence of HBF_4. We recently reported[1] that in neutral solution a stable crystalline 1 : 2 adduct (**3**) is formed and the structure and reactivity of this novel compound have been examined. With electron-poor double bonds a complex pattern is emerging: fumarates and other compounds with an *E*-double bond (**4**) give mainly the stabilised ylides (**5**) in which CS_2 has been lost. It seems likely that these are formed as shown rather than by



direct reaction of (**4**) with Bu^n_3P from decomposition of (**1**). Hydrolysis of (**5**) in D_2O provides a convenient synthesis of 1,1-dideuteriosuccinates. The corresponding *Z*-compounds (**6**) also give (**5**) but for maleic anhydride only, another product is formed which appears to be (**8**). With (**7**) unstable adducts are formed which may well be (**9**). Reaction with norbornene gives a 2:1 adduct which has lost Bu^n_3P and most likely has the novel structure (**10**).

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PHASE TRANSFER CATALYSIS IN THE SYNTHESIS OF ORGANOPHOSPHORUS COMPOUNDS

WEIZHEN YE, XIUGAO LIAO, GUIYUN SUN, YUNFANG QIAN, CHENGYE YUAN
Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai, 200032 China

Abstract A facile method for the preparation of alkyl alkoxycarbonylmethanephenylphosphinates, alkoxy carbonylmethanediphenylphosphine oxides, dialkyl alkoxymethanephosphonates and dialkyl alkylphosphonates under phase transfer catalytic conditions is described. Crown ether was found to catalyze the P-alkylation of dialkyl phosphite salt with inactive alkyl halide.

P-Alkylation of diphenylphosphine oxide, alkyl phenylphosphonites and dialkylphosphites using a quaternary ammonium salt as catalyst:

$$R^1_{R^2}P(O)H + ClCH_2X \xrightarrow[60\text{-}88\%]{Q^+X^-,\ aq.NaOH,\ 0\text{-}15^\circ} R^1_{R^2}P(O)CH_2X$$

R^1 = Ph, R^2 = Ph, OC_3H_7-i, OC_4H_9-n, OC_4H_9-i; X = $COOR^3$
R^3 = C_2H_5, i-C_3H_7, n-C_4H_9, i-C_4H_9, t-C_4H_9, cyclo-C_6H_{11}, n-C_6H_{13}, i-C_8H_{17};
R^1 = R^2 = OC_2H_5, OC_4H_9-n, OC_4H_9-i, OC_4H_9-s, OC_8H_{17}-i;
X = OC_4H_9-n, OC_8H_{17}-i

Crown ether is successfully applied in P-alkylation of dialkylphosphite.

$$(R^1O)_2P(O)Na + R^2X \xrightarrow[50\text{-}90\%]{\text{Crown ether},\ 50^\circ C} (R^1O)_2P(O)R^2$$

R^1 = C_2H_5, n-C_4H_9, i-C_8H_{17}; R^2 = n-C_4H_9, i-C_4H_9, s-C_4H_9
X = Cl, Br.

In the absence of crown ether, no significant reaction can be found.

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Heterocyclic Synthesis from the Reaction of Dicyanomethyleneacenaphthen-2-one with Phosphorus Ylides.

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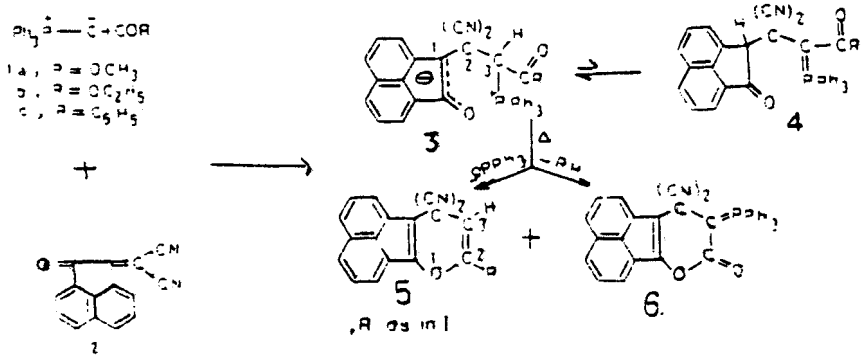
Dept. of Pesticide Chemistry, National Research Centre, Dokki, Cairo, Egypt.

Extending our work on the synthesis of newer heterocycles from β-unsaturated ketones,[1] the Witting reaction of the titled compound 2 with alkoxycarbonylmethylenetriphenylphosphorane 1 a,b has been investigated, and the reaction products; ylides (3 a,b), pyrans (5 a,b) and pyrone (6) were isolated and identified. On the other hand, reaction of 2 with benzoylmethylenetriphenylphosphorane (1c) proceeded only at drastic conditions, yielding 4 c and 5 c.

Reaction mechanisms and spectral data are discussed, and synthetic utility of the products were tested.

It is also worth noting that the polarity of the solvent and the temperature of the reaction play only a very limited role whereby, they affect only the ratio of the products to each other.



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THIOESTERS OF TRIVALENT PHOSPHORUS ACIDS - AS NEW LIGANDS IN CYMANTHRENE

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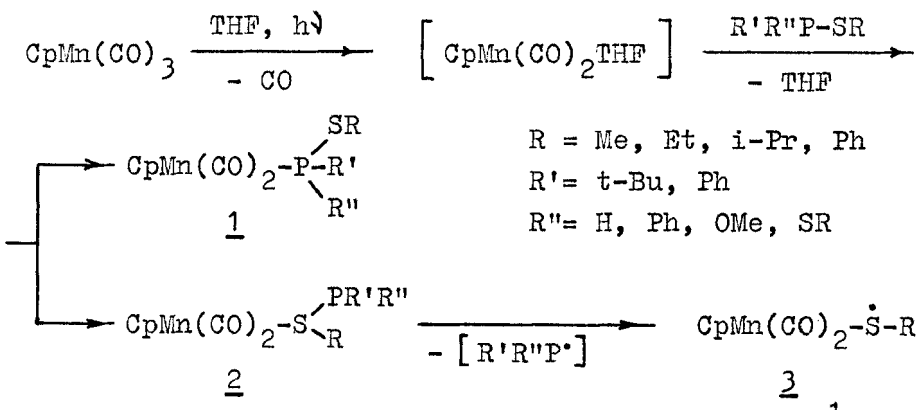
Abstract New cymanthren derivatives, containing P(III) acid thioesters as ligands, synthesized for the first time.

Complexes of transition metals, containing trivalent phosphorus acid thioderivatives as ligands, have been insufficiently studied as yet. New cymanthren derivatives (1) were synthesized by us via photochemical substitution of CO-group by thioesters P(III) acid.



The structure of complexes (1) was verified by IR, ^{1}H and ^{31}P NMR spectroscopy, by mass-spectrometry and X-ray study. The formation of labile S-coordinated complexes (2) takes place together with compounds (1). They are identified by IR and ^{31}P NMR spectroscopy. In transition reactions they are partially transformed into metal sulfur-centred radicals (3), identified by IR and EPR spectra.

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SYNTHESIS OF 1,1-DIHALOGENO 2-PHENYLETHYLENE BY ELECTROCHEMICAL WITTIG REACTION

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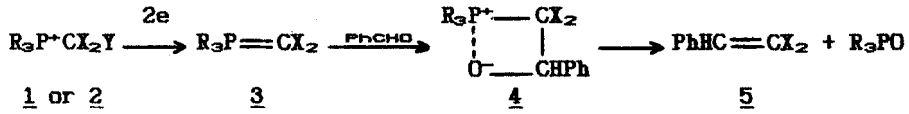
Laboratoire des Composés Organophosphorés, INSA-IRCOF, BP 08
Place E. Blondel, 76131 Mont-Saint-Aignan Cedex, France.

The development of electrolysis techniques makes it possible for Electrochemistry to become a competitive method for organic synthesis. However, the electrochemical way has not so far been experimented in the Wittig reaction, though it has appeared as both simple and efficient in the Horner reaction as well as the electroreduction of phosphonates carried out in our laboratory[1,2].

In the present study, we succeeded in the synthesis of 1,1-dichloro and 1,1-difluoro 2-phenylethylenes.

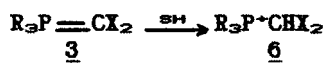
The electrochemical reduction of phosphonium salts 1 or 2 was performed by an initial bielectronic step producing ylide 3. In an aprotic medium (DMF, MeCN), this ylide reacted with the benzaldehyde present in the electrolysis cell giving , the corresponding olefin 5 through an intermediate betaïn 4 :



1 or 2 3 4 5

1: X = Y = Cl ; 2: X = F , Y = Br.

In a protic medium, the ylide 3 was protonated to give phosphonium salt 6:



3 6

The best results were obtained with controled current electrolysis in a one-compartment cell (X=F) or a two-compartments cell (X=Cl).

$PhHC{=}CCl_2$	R = 80%
$PhHC{=}CF_2$	R = 69%

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SYNTHESIS, METALATION AND FUNCTIONALISATION OF DIETHYL TOLYLPHOSPHONATES

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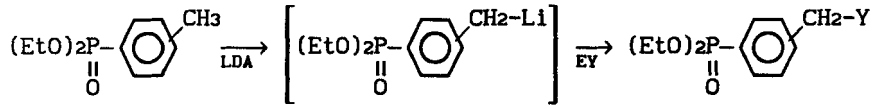
Laboratoire des Composés Organophosphorés, INSA-IRCOF, BP 08
Place E. Blondel, 76131 Mont-Saint-Aignan *Cedex*, France.

In connection with our recent work on the synthesis of phosphonophenylalanines[1], we studied the functionalisation of diethyl tolylphosphonates 1, readily prepared from halotoluenes by an adapted procedure of the $S_{RN}1$ photostimulated phosphonylation[2]. For this purpose, we submitted the phosphonotoluenes 1 to the "metalation - functionalisation" sequence. Among the various metalating systems we tested (n-, sec-, or ter-BuLi; n-BuLi-TMEDA; LTMP; LDA), LDA (2eq. in THF at -60°C) gave the best results. The intermediate carbanions 2 were reacted with different electrophiles EY [Me_3SiCl, R_3SnCl, CO_2, EtOC(O)OEt, EtOC(O)C(O)N$(CH_2)_5$] giving the corresponding diethyl tolylphosphonates 3 functionalised on the side chain. The yields in purified compounds 3 were excellent (80-98%) for the ortho- and para-isomer. For the meta-derivatives however, the yields were generally lower than 50%.



1 2 3

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SYNTHESIS AND USE OF NEW α-PYRAZOLYLALKYLPHOSPHONATES

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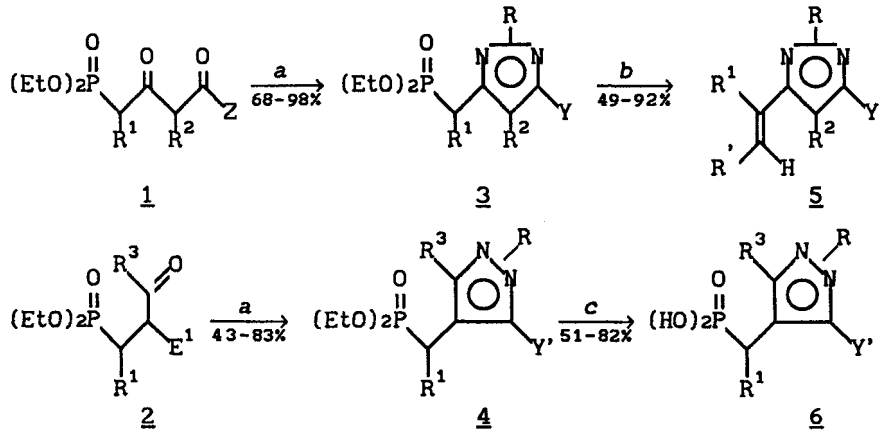
We report a straighforward synthesis of two series of new α-pyrazolylalkylphosphonates (3 and 4) obtained by cyclocondensation of hydrazines with bis-electrophilic phosphonates 1 and 2, respectively. We illustrated some synthetical potentialities of these pyrazolylalkylphosphonates by preparing new α-alkenylpyrazoles 5 from 3 and new α-pyrazolylalkylphosphonic acids 6 from 4. Advantages of the proposed method include accessibility to the starting phosphonates[1], structural diversity of the substituents [R^1,R^2= H,alkyl,Phe; R^3= H,Me,Phe,CH(OEt)2; R = H,Me,Phe; Y = H, alkyl,Phe,OH; Y'=Me,Phe,OH,NH2; R'=aryl,alkyl], chemoselectivity and efficiency of the steps.



a) R-NH-NH2/EtOH,reflux; *b)* R'CHO/KH/THF,reflux; *c)* HCl 8M,reflux.

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Phosphorus, Sulfur, and Silicon, 1993, Vol. 77, p. 179
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FUNCTIONALLY SUBSTITUTED DERIVATIVES OF TRIVALENT PHOSPHORUS THIOACID

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Abstract The use of functionally substituted derivatives instead of P(III) acid thioesters results in formation of new phosphorus and sulfur containing compounds with preservation of P-S bond.

A study of reactions of thioesters of trivalent phosphorus acids - $(RS)_3P$, with a wide range of electrophilic reagents has shown that as a rule the Arbuzov reaction as distinct from some oxygen P(III) esters is not observed where as the rupture of P-S bond proceeds with the substitution of the RS-group at the phosphorus atom. Consequently obtaining organophosphorus compounds on their basis with preservation of the P-S bond involves is extremely difficult. The presence of functional groups should promote the course of the Arbuzov reaction and formation of products with P-S bond. In fact $(RS)_2POSiMe_3$ synthesized by us for the first time, react with many electrophylic reagents - alkyl and acylhalides, aldehydes, azomethynes, ethoxyacetylene, with migration Me_3Si- or Alk-group and formation of alkylthio or thiophosphonates. In contrast, interaction of $(RO)_2P$-S-C(O)R' with electrophylic reagents proceeds mainly with formation of thiophosphorylation products. Alkylthiophosphines react with carbonyl and α,β-unsaturated compounds with migration of hydrogenous atom and preservation involving the formation of corresponding thiophosphinites and phosphonites, i.e. with preservation of P-S bond. It is of interest that insertion of RC(O)-, NR_2- and Cl-groups into the molecule of dithiophosphorous acid instead of the ether group brings about the repture of P-E bond (E = O,N,Cl) in the reaction and preservation of P-S bond

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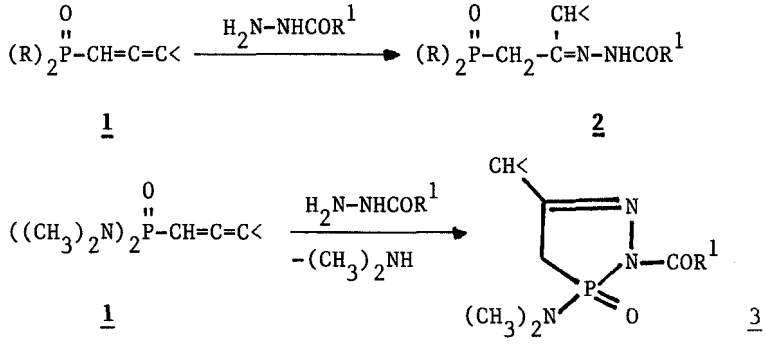
SYNTHESIS OF β-PHOSPHOHYDRAZIDES (2) AND $\Delta^5$2-ACYL 3-DIMETHYLAMINO 3-OXO 1,2,3 DIAZAPHOSPHOLINE (3).

A. BEN AKACHA; M. BOUKRAA; A. HFIDH; B. BACCAR
Laboratoire de Synthèse Organique, Département de Chimie, Faculté des Sciences de Tunis 1060 Tunis (TUNISIA).

The monoacylhydrazides recently synthetized in our laboratory[1], as well as hydrazines[2], react with phosphoallenic derivatives 1 to lead to the β-phosphohydrazides 2 (yield ≃ 70%). It has been found that when R=$(CH_3)_2N$ group, the heating of the compound 1 with monoacylhydrazides in refluxing toluene leads to obtaining compound 3 (yield ≃ 40%). The structure of these compound is further confirmed by IR, ^1H NMR and ^{31}P NMR spectra.



1 2

1 3

R = C_6H_5
R^1= C_6H_5, i-C_3H_7, t-C_4H_9
R^2= CH< = CH_3, i-C_3H_7, c-C_6H_{11}

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Phosphorus, Sulfur, and Silicon, 1993, Vol. 77, p. 181
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EFFICIENT METHOD FOR SYNTHESIS OF α-KETOPHOSPHONATES AND REACTIVITIES.

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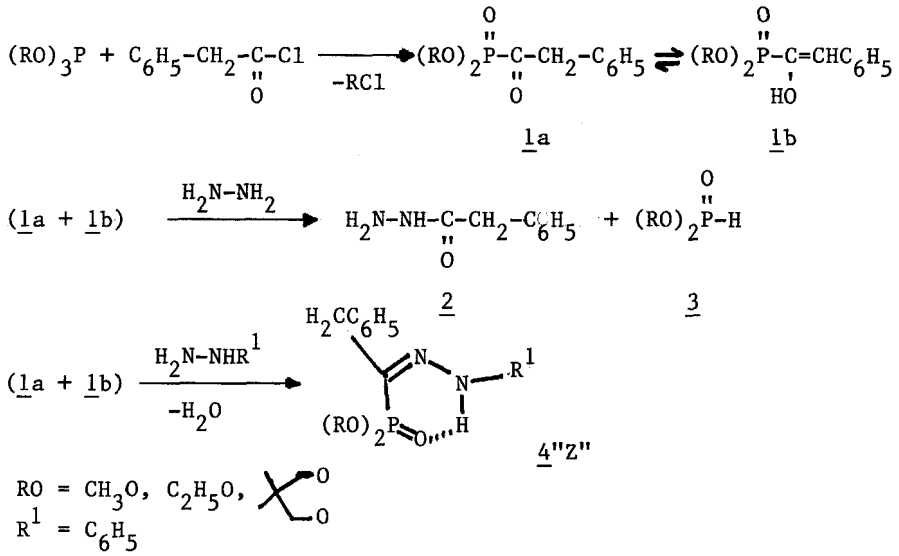
Laboratoire de Synthèse Organique, Departement de Chimie, Faculté des Sciences de Tunis 1060 Tunis (TUNISIA).

We have successfully improved the results first reported by costisella and al.[1], when preparing the compound 1 by increasing the yield from 30-40% to 90%. We show that we can similarly obtain the phenylacetichydrazide 2 and dialkylphosphite 3 after cleavage of P-C bond[2]. The synthesis of α-phosphonylhydrazones 4 was discribed. The products 1 (a-b), 2 and 4 are characterised by IR, ^{1}H NMR and ^{31}P NMR spectra.



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PHOSPHORUS SUBSTITUATED ACETYLENES - A VERSATILE STARTING MATERIAL FOR THE SYNTHESIS OF PHOSPHOPRYLATED COMPOUNDS

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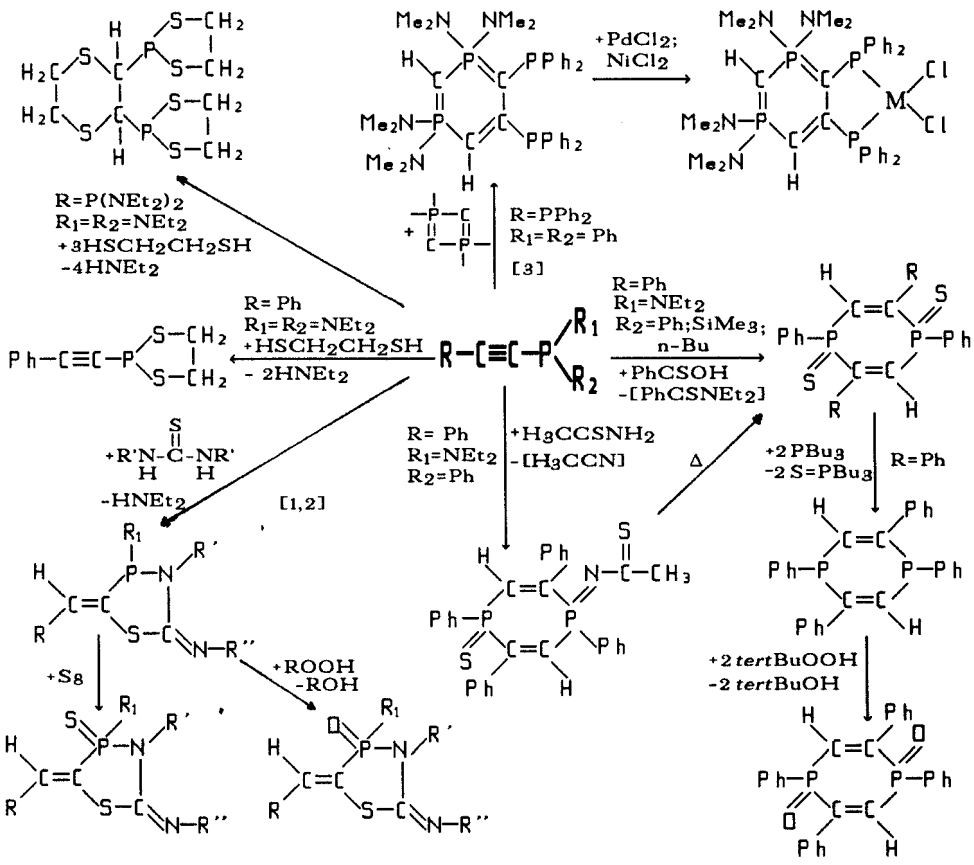
GMELIN-Institute for Inorganic Chemistry of the Max-Planck Society, Frankfurt
Institute for Inorganic Chemistry, Stuttgart

Abstract: Some reaction of phosphorylated acetylenes with nucleophiles are shown. They lead to thiazaphospholidines, dithiaphospholidines, diphosphorines and phosphorylated diphosphabenzenes. From the primary products derivatives could be obtained.



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THE INFLUENCE OF STRUCTURE ON THE REARRANGEMENT AND FRAGMENTATION OF α-HYDROXYIMINOPHOSPHONATES

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Department of Pharmaceutical Chemistry, The Hebrew University School of Pharmacy, Jerusalem, Israel

We reported previously that α-hydroxyiminophosphonate esters show stereoselectivity in their tendency to undergo either fragmentation or Beckmann rearrangement,[1] while α-hydroxyiminobenzylphosphonic acids undergo fragmentation to metaphosphate species.[2] In an effort to improve our understanding of the chemistry of α-hydroxyiminophosphonates, we examined the influence of structure on the behavior of these types of compounds. We studied the following types of derivatives: α-hydroxyiminobenzylphosphonates substituted in the aromatic ring, others esterified with aryl groups as well as polyhaloalkyl groups, and also α-hydroxyiminophosphonamidates. We found that the behavior of the compounds depends on the substituent on the phosphorus. In contrast to the dimethyl ester which exhibits stereoselective behavior, either geometrical isomer of methyl 2,2,2-trifluoroethyl α-hydroxyiminobenzylphosphonate undergoes fragmentation. In contrast, phosphonamidates underwent rapid Beckmann rearrangment, thus providing a simple and convenient synthetic approach to novel peptide transition state analogs starting from N-(α-hydroxyiminoalkylphosphonyl)amino acids. A kinetic study on the acid catalyzed fragmentation in water showed that electron withdrawing groups retard and electron releasing groups accelerate the fragmentation. The reaction rate is influenced only to a small extent by the various substituents. The enthalpy and entropy of activation are consistent with a preassociative reaction mechanism.

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MOLECULAR STRUCTURE OF FOUR-MEMBERED PHOSPHAZA CYCLES

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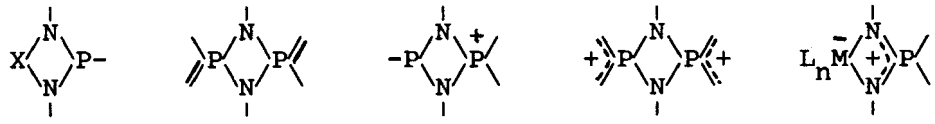
The main reguliarities and characteristic features of the molecular structure of 4-membered phosphaza cycles A-E have been discussed on the basis of wide-range X-ray diffraction studies. In diazaphosphetidine systems A and B the P-N_{endo} bonds (1.70-1.76 and 1.68-1.73 Å) are considerably longer whereas the P-N_{exo} bonds (1.65-1.71 and 1.63-1.65 Å) are shorter as compared with the analogous acyclic compounds, due to sterical and electronic [rehybridization of P and N atoms at cyclization, repulsion between LP(P) and LP(N) etc.] factors. These proportions are retained in structures C, but the presence of a phosphonium centre causes shortering both *endo* and *exo* P^{IV}-N bonds (1.64-1.66 and 1.60-1.62 Å) (due to contraction of the phosphorus bonding AO-s and lowering of their energy). Delocalization of the positive charge on *exo* bonds due to the electrostatic repulsion $P^{+}\cdots P^{+}$ in dicationic structures D leads to shortening of *exo* bonds (1.58-1.60 Å) as compared with P-N_{endo} (1.65-1.68 Å) whereas quite opposite bond lengths distribution is observed in zwitter-ionic cycles E: delocalization of the positive charge on *endo* bonds causes their considerable shortening 1.59-1.62 Å) as compared with P-N_{exo} (1.63-1.68 Å).



A B C D E

(X = C, O, N, P, Si; M - transition metal atom; L - ligand)

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PHOSPHORYLATED N-PROPARGYLAMINES - SYNTHESIS AND REACTIONS

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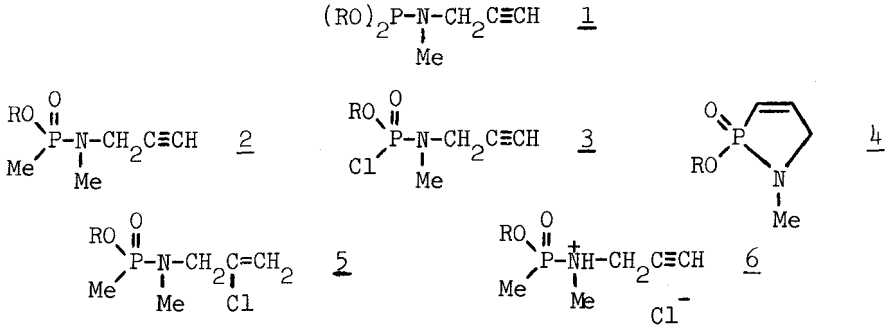
Abstract Synthesis and some reactions of phosphorylated N-propargylamines are discussed.

N-Propargylaminophosphites 1 are readily available compounds from dialkylchlorophosphites and N-propargylamine [1]. Treatment of the phosphites 1 with methyl iodide leads to the phosphonates 2. In similar way, investigation between 1 and sulfuryl chloride gives the phosphates 3 (Arbuzov type reactions). In the reaction of 1 with methyl iodide in the presence of $Et_3N.HCl$ three transformations proceed: (1) heterocyclization of 1 with HCl of $Et_3N.HCl$ affording the azaphospholes 4; (2) Arbuzov reaction of 1 with methyl iodide giving the phosphonates 2; and (3) addition of HCl upon the triple bond of compounds 2 leading to the N-allylaminophosphonates 5. Treatment of the phosphonates 2 with HCl leads to the phosphorylated N-propargylammonium salts 6, but no the adducts 5.



The NMR and IR characterizations of the phosphorylated N-propargylamines as well as the possible mechanisms of their formation will be discussed.

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A SIMPLE SYNTHESIS OF ACTIVATED DIENES FROM PHOSPHONIUM SALTS

Domitila Aparicio[§] José Barluenga[#*], Isabel Merino,[#] Ana Ochoa de Retana,[§] Francisco Palacios[§*] and Gloria Rubiales[§].

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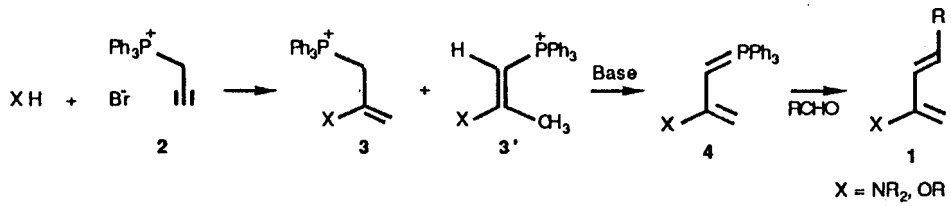
# Dpto. Química Organometálica. Facultad de Química. Universidad de Oviedo. 33071. Oviedo. SPAIN.

Phosphorus derivates such as the phosphorus ylides[1] and the isoelectronic λ^5-phosphazenes[2] have been widely used in preparative organic chemistry in recent years because of their broad range of aplications.

On the other hand, activated dienes such as alkoxy-, and siloxy-1,3-butadienes[3] as well as sulfur-[4] and amino-[5] substituted dienes represent synthetically attractive buildings blocks for the synthesis of heterocycles and complex natural products, through the Diels-Alder reaction[6]. In connection with our interest in the application of phosphonium salts[7], as intermediates in organic synthesis, we report here a very easy method of synthesis of activated dienes **1**.

Recently we reported the preparation of 2-amino-1,3-butadienes **1** from comercially available starting reagents, as propargyltriphenyl phosphonium bromide, secundary amines and aldehydes. Here, we extent this synthetic process to other nitrogen and oxigen containing nucleophiles, in which the key step involves Wittig reaction of phosphoranes generated "in situ" from the β-functionalized phosphonium salts with aldehydes.

The preparation of the desired β-sustituted phosphonium salts **3** was very easily accomplished in very high yields through nucleophilic addition of amines and alcohols, to comercially available propargyltriphenyl phosphonium bromide **2**. Wittig reaction of phosphoranes **4** generated "in situ" from β-enamino- and alkoxy- phosphonium salts **3** with a base followed by addition of aldehydes leads to 2-functionalized-1,3-butadienes **1** in excellent yields.



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KINETIC RESOLUTION OF δ-HYDROXY ALLYLIC PHOSPHINE OXIDES: A STEREOCONTROLLED ROUTE TO ALLYLICALLY FUNCTIONALISED SYSTEMS

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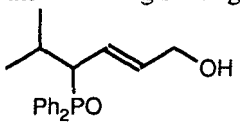
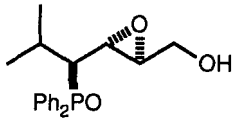
[b] Glaxo Group Research Ltd., Park Road, Ware, Herts., SG12 0DJ

Abstract: We have used a combination of phosphine oxide and Sharpless epoxidation chemistry to synthesise allylically functionalised compounds with complete control over absolute, relative and geometrical stereochemistry.

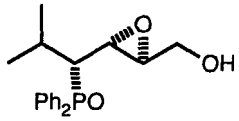
Starting material **1** were resolved kinetically by Sharpless methodology to give *anti* epoxide ***anti*-2** with good e.e. The *syn* epoxide **syn-2** was made by peracid epoxidation of the remaining starting material from the kinetic resolution.



1

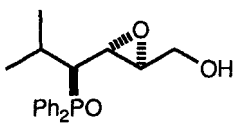


***anti*-2**



***syn*-2**

Regiocontrolled ucleophilic opening of the epoxide was controlled gave intermediates **3** which underwent stereospecific Horner-Wittig elimination to yield compounds **4** with controlled geometry double bonds and controlled absolute stereochemistry.



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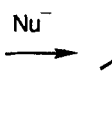

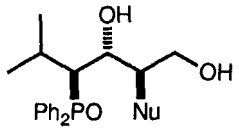

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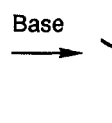
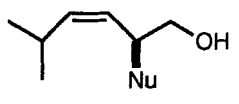
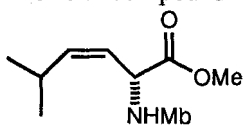




4

The method has been extended to the synthesis of unsaturated amino acids such as **5**, and compounds with further chiral centres such as **6**. Work is under way which should allow the synthesis of compounds bearing remote (1,4) chiral centres (such as **7**).



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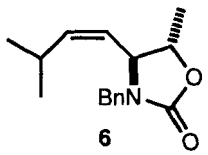

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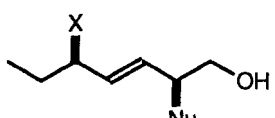

7

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NEW ROUTE TO THE PREPARATION OF 1,3,2 OXATHAPHOSPHOLANES 2-SULFIDE DERIVATIVES

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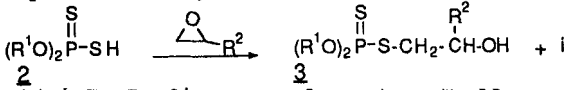
Laboratoire de Chimie Organique, Faculté des Sciences F-57045-Metz

Abstract 5-substituted 2-alkyl (or aryl, heteroaryl,...)thio 1,3,2 oxathiaphospholanes 2-sulfide 5 are readily accessible by reaction of the triethylammonium salt 1 of a diester of the phosphorotetrathioic acid with appropriate epoxide in the presence of $BF_3.Et_2O$ as catalyst.

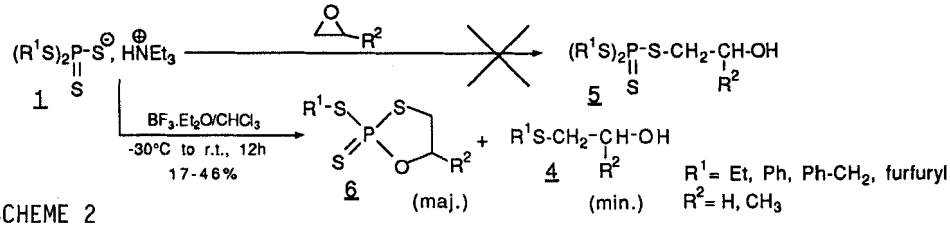
INTRODUCTION

It is known that (O,O) diesters 2 of the phosphorodithioic acid react easily with oxiranes, yielding to the addition products 3 (scheme 1). The salts 1, previously described[1], don't react in the similar way.

SCHEME 1



The use of a Lewis acid ($BF_3.Et_2O$) as catalyst doesn't allow to obtain the alcohols similar to 3 but instead 2-alkyl (or aryl,...)thio 1,3,2-oxathiaphospholanes 2-sulfide 6 are formed (scheme 2).



SCHEME 2

An important amount of phosphorus containing oligomers is formed during the reaction, which explains the moderate yields obtained.
This reaction is regiospecific but not stereoselective[2].
The salts 1 add in the same manner on thiiranes and 2-sulfide of 1,3,2-dithiaphospholane derivatives are formed but in lower yields.

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SYNTHETIC EQUIVALENTS OF γ-FUNCTIONALIZED ALLYLIC CATION INVERSION OF POLARITY APPLICATION TO ALLENYL COMPOUDS

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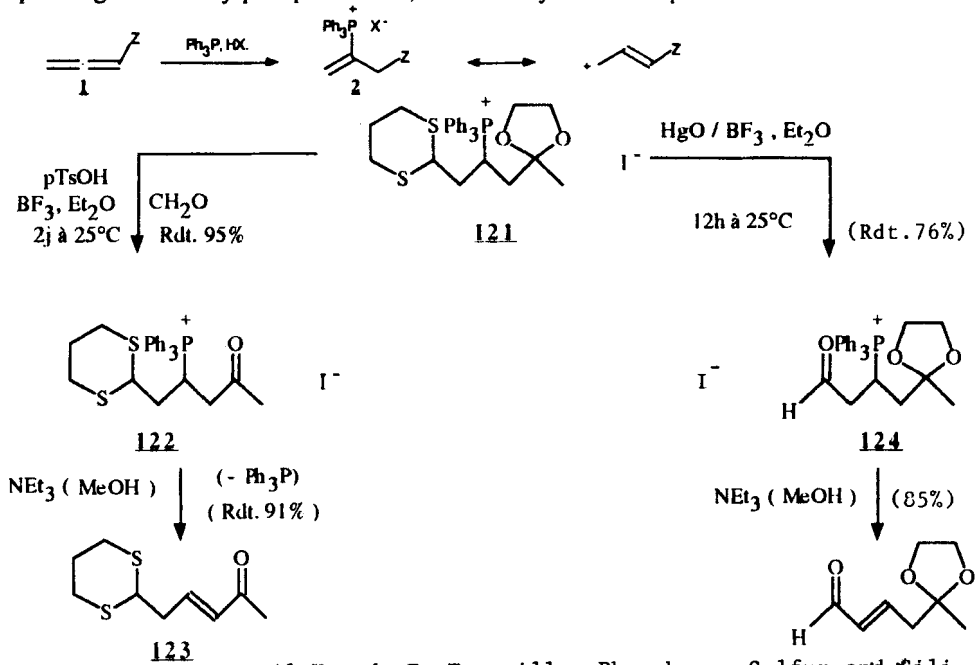
Our target was to obtain equivalents of γ-functionalized allylic cation trom allenyl derivatives **1** This involve the protection of the β−position in **1** towards nucleophiles and the inversion of the electronic character of the carbon in the γ-position, that becomes electrophile.As illustrated by the following example compound **121** results of the introduction of triphenyl phosphonio group in allenyl substrate **1** giving rise to the corresponding salt of vinylphosphonium **2**, followed by the nucleophilic addition of NuH.



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REACTION OF O- AND P-NAPHTHOFUCHSONE WITH THIOL PHOSPHORIC ACIDS AND PHOSPHORUS PENTASULPHIDE.

Ahmed El-Kateb, Ebtisam Hennawy, Rashad Shabana
and Hoda Abdel-Malek
National Research Centre, Dokki, Cairo, Egypt.

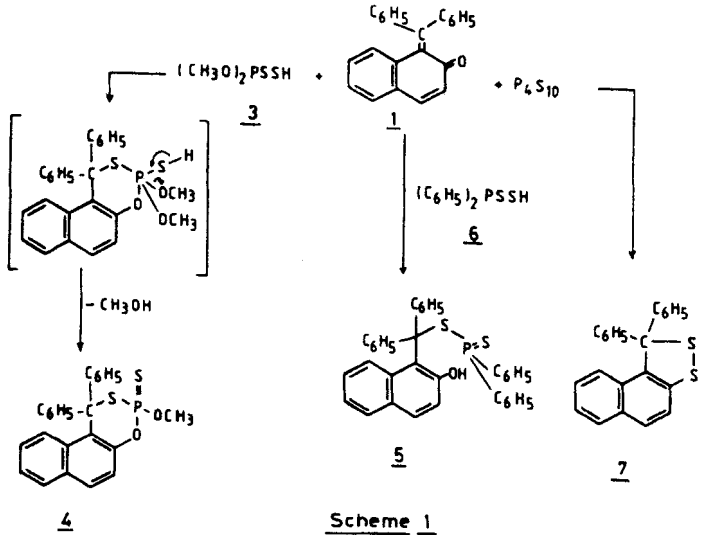
Abstract The reaction of o-, and p-naphthofuchsone with thiol phosphoric acids and phosphorus pentasulphide, was undertaken.

INTRODUCTION

Extending our work on the reaction of 0- and p-naphthofuchsone with organophosphorus reagents[1-3], we now wish to report the chemical reactivity of compounds **1** and **2** towards some thiol phosphoric acids and P_4S_{10} to synthesize a new naphthalene derivatives of expected biological activity.

RESULTS AND DISCUSSION

Naphthalenone **1** reacts with thoil phosphoric acids **3** and **6** to give adducts **4** and **5**, respectively. Reaction of **1** with P_4S_{10} gives **7**.



Scheme 1

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MASS SPECTRA OF CYCLOHEXYL- AND PHENYL THIOPHOSPHORYLIC AMIDES

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The electron impact mass spectra (70 eV) were made for two types of thiophosphorylic morpholinyl amides previously reported[1]:

$(C_6H_{11})RP(S)(N\langle\rangle O)$; R =$CH_3$,Cl,OH,$OCH_3$ (I)

$(C_6H_5)R'P(S)(N\langle\rangle O)$; R'=$CH_3$,Cl,$OCH_3$,$OC_2H_5$ (II)

The fragmentation pathways and ion structures were established by exact mass determination of peaks due to metastable transitions[2,3].

The present work is concerned with the study of the dependence of the fragmentation pathways on the nature of phosphorus-substituents: cyclohexyl and phenyl.

It was found that the dissociation pathways were strongly dependent on the saturation grade of the phosphorus-attached hydrocarbonate radical.

The main fragmentation of compound I starts with a H transfer from cyclohexyl group to thionic S, followed by elimination of neutral cyclohexene or SH radical. Rearrangements involving H transfer to S from the morpholinyl group produced low-intensity ions (3%).

For compounds II, the H transfer from morpholinyl group to S is characteristic. So, the ions resulted from molecular ion by elimination of morpholinyl group in this way exhibited an aboundance of about 10%. Anyhow phenyl-P bonds exhibited high stability.

Another series of ions is formed by simple fission of P-Cl, P-N, P-O bonds from M^+ of I and II.

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DIETHYL 1-AZIDOALKYLPHOSPHONATES AS USEFUL INTERMEDIATES: PREPARATION OF DIETHYL 1-AMINOALKYLPHOSPHONATE HYDROCHLORIDES

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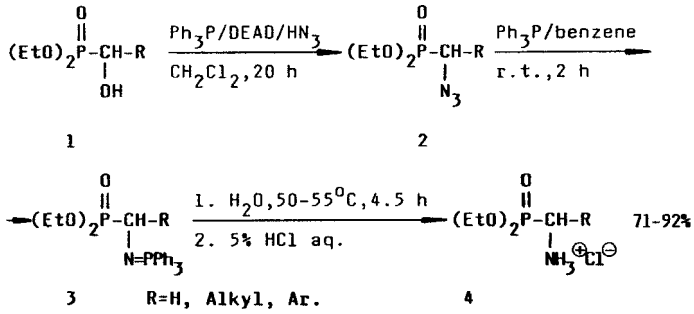
Abstract A new, simple and efficient route to the primary and secondary diethyl 1-aminoalkylphosphonate hydrochlorides has been devised.

Herein is reported a one-pot transformation of the easily available diethyl 1-hydroxyalkylphosphonates **1** into diethyl 1-aminoalkylphosphonate hydrochlorides **4**, without the necessity of isolation of the intermediate azide **2**. Similar methodology was applied by Golding et al.[1] for conversion of alcohols into amines and amino acids.



Thus, the azide **2**[2] prepared from **1** by the Mitsunobu reaction[3] is converted "in situ" by the Staudinger reaction[4] with Ph_3P into the iminophosphorane **3**. This, in turn is hydrolysed by addition of water, and transformed by treatment with HClaq. into the corresponding hydrochloride **4** in high overall yield and purity.

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THE INFLUENCE OF RADICAL CHARACTER ON THE ADDITION OF A GRIGNARD TO AN α,β-UNSATURATED PHOSPHORYL GROUP[1]

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Chemistry Division, Argonne National Laboratory, 9700 S. Cass Ave.,
Argonne, Illinois, USA

During an investigation of the substitutent effects upon the extraction of trivalent actinides by the carbamoylmethylphosphine oxides, we required a generic synthesis of alkyl substituted aromatic phosphorus compounds. Unfortunately, the literature reports of the direct addition of hypophosphorous acid to an olefinic center[2] and the addition of an organometallic reagent to phosphorus trichloride, followed by hydrolysis[3] were unsatisfactory for our purposes. An ideal approach to this class of compounds would involve the direct substitution of an alkyl group on the aromatic group of phenylphosphinic acid or an ester as this readily available starting material has been converted into the carbamoylmethylphosphine oxide extractants.[4]

We had previously observed that trace quantities of an octyl substituted phosphinic acid were prepared during the addition of octylmagnesium bromide to ethyl phenylphosphinate.[5] Extrapolation of the mechanism proposed by Ashby[6] for the addition of a Grignard reagent to a ketone suggests that if a solvent-cage radical species could be stabilized by increasing the radical character of the alkyl group of the Grignard reagent than a corresponding increase in the yield of the 1,4 or 1,6 addition product would be realized.

We began our investigation by preparing a series of Grignard reagents (RMgX) with increasing radical character (R = Me, Et, nPr, iPr, nBu, secBu, iBu, tBu, neo-Pentyl) and examining the product distribution by GC/MS and NMR spectroscopy. While the data indicates that the method is far from being synthetically useful for the preparation of these compounds it is clearly supports our belief that the direction of addition is dependent upon the radical's structure.

1. Work performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy under Contract number W-31-109-ENG-38.

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STUDIES OF THE INTRAMOLECULAR CYCLISATION REACTIONS OF THE CARBENE INTERMEDIATES FORMED BY THE ACTION OF TRIALKYL PHOSPHITES ON 2-SUBSTITUTED DIALKYL BENZOYLPHOSPHONATES

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Department of Chemistry and Biological Chemistry,
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BELINDA J. WHITEHEAD
Department of Chemistry, University of Keele,
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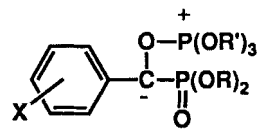
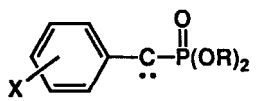
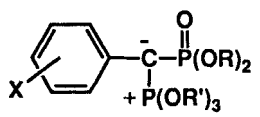
Trialkyl phosphites attack the carbonyl oxygen of dialkyl benzoylphosphonates to give anionic intermediates (**1**) which under appropriate conditions decompose thermally to give carbenes (**2**) and trialkyl phosphate. These carbenes are readily trapped by trialkyl phosphites to give ylidic phosphonates (**3**) which may undergo further rearrangement.[1]



(1)



(2)



(3)

When suitable *ortho*-substituents are present on the benzoylphosphonate intramolecular carbene insertion reactions can also occur to give cyclic systems. The dominant mode of cyclisation appears to be carbene insertion into a C—H bond to give a five-membered ring system, even in those cases where six-membered ring formation is possible. However, if this is prevented by choice of an appropriate substitutent other reaction pathways are observed.

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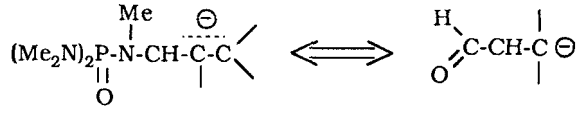
A NEW STRATEGY FOR THE PREPARATION OF DICARBONYL COMPOUNDS: THE α–ALLYL PHOSPHORAMIDO LITHIATED CARBANIONS APPROACH

Philippe COUTROT, Claude GRISON, Catherine BOMONT
Laboratoire de Chimie Organique II (URA CNRS n° 486), Domaine Scientifique Victor Grignard, Université de Nancy I

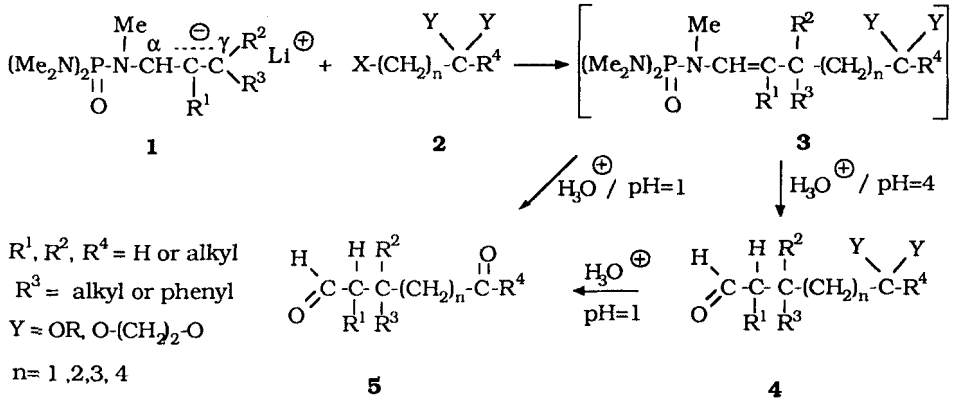
Abstract α-allylphophoramido lithiated carbanions are used as homoenolate reagents with halogenated acetals and give regioselectively γ-alkylation products. Acidic hydrolysis of the adducts is a novel route to dicarbonyl compounds.

The dicarbonyl compounds are very interesting precursors in organic synthesis, especially in the construction of cyclopentenones, cyclohexenones and heterocyclic compounds.

Previously, it has been demonstrated that the lithiated carbanions derivatived from ene-phosphoramides are excellent synthetic equivalents of homoenolate anions.



This methodology is now used in a straightforward approach to oxoaldehydes .



The synthetic potentialities of this strategy have been exploited in the synthesis of a well-known pheromone, the (E)-9-oxo-2-decenoic acid (Queen Bee substance) .

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KINETICS OF THE PTC-WITTIG REACTIONS OF 2-BUTENYL METHYLDIPHENYLPHOSPHONIUM YLIDS

WENFANG HUANG, MINGWU DING, WENJING XIAO, TIANJIE WU
Institute of Organic Synthesis, Central China Normal University, Wuhan, China 430070

Abstract The kinetics and linear free energy relationship of PTC-Wittig reaction between substituted aromatic aldehydes and title compound are discussed.

INTRODUCTION

The kinetics of PTC-Wittig reaction has been paid little attention in the past years[1]. Here we described this topic about the following reaction.

$$Ph_2\overset{+}{P}\underset{CH_3}{CH_2}CH{=}CHCH_3\,\bar{B}r + p\text{-}R\text{-}C_6H_4CHO \xrightarrow{K_2CO_3(S),\,CH_2Cl_2,\,35^{\circ}C} p\text{-}R\text{-}C_6H_4CH{=}CHCH{=}CHCH_3 + Ph_2\underset{O}{P}CH_3$$

$R{=}NO_2, Cl, H, CH_3$, t-Bu, OCH_3, $N(CH_3)_2$

KINETICS AND LFER

Results showed that there are good linear relationship between 1/c and t no matter what R is. This indicates a second order kinetic reaction.

The reaction rate increases with the increasing electron-withdrawing substituents of aldehyde. A Hammett linear relationship is observed as the following equation

$$\log k = 0.30\sigma - 1.31$$

The low reaction constant($\rho = 0.30$) implies that this PTC-Wittig reactions are not sensitive to the substituent and the reaction might take place through low polar intermediates or free radicals[2].

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KINETICS AND MECHANISM OF DECOMPOSITION OF QUASIPHOSPHONIUM INTERMEDIATES: BORDERLINE S_N1 CHARACTER OF ALKYL-OXYGEN FISSION IN s-ALKYLOXYPHOSPHONIUM SALTS AND SOLVENT EFFECTS ON THE RATE OF DECOMPOSITION OF MICHAELIS-ARBUZOV INTERMEDIATES.

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School of Applied Chemistry, The Polytechnic of North London, Holloway Road, London, N7 8DB, U.K.

We have previously isolated intermediates in Michaelis-Arbuzov reactions of phosphorus (III) esters containing sterically hindered alkyl groups and we have studied their structures and reactivities.[1] The present work describes the detection, by ^{31}P nmr spectroscopy, of short-lived s-alkyloxyphosphonium intermediates (δ_P 68.6 - 68.7 ppm) in the reactions of s-alkyl diphenylphosphinites with iodomethane. The chemical shifts are at slightly higher field than for ethoxy(methyl)diphenylphosphonium iodide (δ_P 72.4 ppm), in accord with higher electron density at phosphorus in the secondary alkoxy series. The relative rates of decomposition in $CDCl_3$ for alkyl diphenylphosphinite-methyl iodide adducts, $ROPPh_2Me\ I^-$ (Me > Et > i-Pr >> neopentyl) are in accord with S_N2-type cleavage of the R-O bond but for the secondary alkoxy series the relative rates of decomposition (i-Pr < s-Bu < 3-Pe) are in accord with an increasing tendency towards carbonium ion character as the secondary alkyl group becomes bulkier. Reactions of this type nevertheless occur with essentially total inversion of configuration and with only traces of products that could be attributed to carbonium ion rearrangement. A borderline S_N1 mechanism is indicated. In more ionising media (CD_3CN, $MeNO_2$, DMSO-d_6, and $PhNO_2$) the reaction order is intermediate between first and second. Separation of the ions in these solvents leads to a reduction in the overall rate of product formation but there is no effect on the mechanism of alkyl-oxygen fission.

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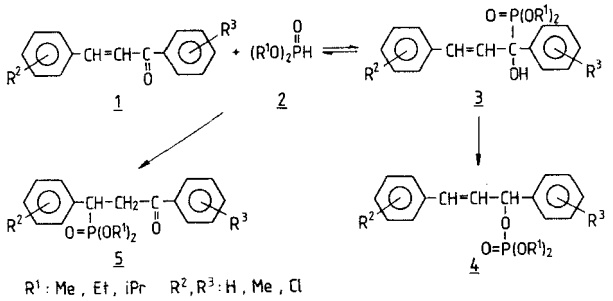
PUDOVIK REACTION UNDER PHASE TRANSFER CATALYTIC CONDITIONS

Zsuzsa M.JÁSZAY; Imre PETNEHÁZY; László TŐKE
Dept. of Organic Chemical Technology, Technical University H-1521, Budapest, HUNGARY

The reaction of dialkyl phosphites with α,β-unsaturated oxo compounds in basic circumstances has been called as Pudovik reaction by Russian authors[1]. The product depending on the structure of the starting compounds, are α-hydroxyphosphonate, γ-ketophosphonate and several diphosphonates[2,3].

We have now investigated the interaction of a series of dialkyl phosphites with chalcones using solid-liquid PTC conditions. In all cases three types of products (α-hydroxyphosphonates 3, γ-ketophosphonates 5 and phosphoric acid allylic ester 4) could be isolated and identified. The 2:1 adducts which are always formed in the reacton of two moles of dialkyl phosphites with one mole of α,β-unsaturated oxo compounds in homogenous phase never have been observed in our circumstances.



The reaction has been carried out in a nonprotic solvent as benzene or toluene using solid potassium carbonate as base in the presence of a quaternary ammonium salt as catalyst between 25-70 °C.

The differences observed in the structure of the final products in homogenous phase and in PTC conditions may be due to the solid surface of the potassium carbonate.

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(R) or (S)-MethylPhosphine-Borane Complexes: Easily accessible and versatile precursors for bidendate ligands

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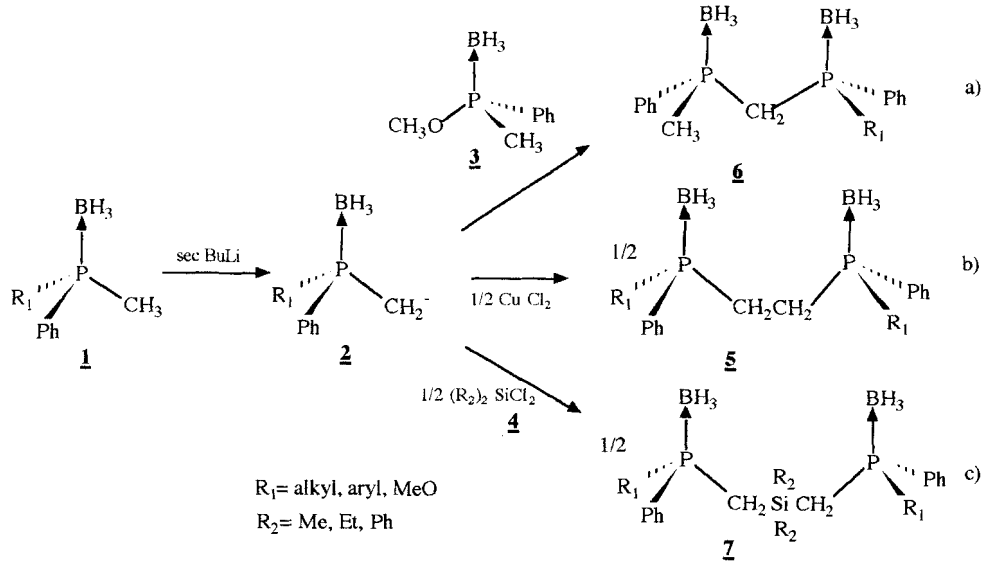
Chiral phosphine ligands are of key importance in asymmetric synthesis of optically active products, by homogeneous catalysis using organometallic species, and particularly for the industrial preparation of the desired antipode[1]. Recently, we have described[2] a new asymmetric synthesis of optically pure tertiary phosphines via an oxazaphospholidine borane complex prepared from commercially available (-)-ephedrine. The attractivity of this synthetic approach in borane complexed serie is due to the possibility to prepare the two antipodal phosphines, starting from the same precursor, and the great stability of the borane complexes which permit their easy manipulation and storage.

In our continuing program on chiral organophosphorus ligands, we described here[3] the synthesis of various chiral bidendate ligands using optically pure methylphosphine borane 1 as a chiral synthon. the compound 1 was metalated with sec-BuLi in THF at -78°C. The generated carbanion 2 could be converted into 1,2-diphosphino ethane complexes 5 by oxidative coupling using anhydrous $CuCl_2$ (scheme 1b). The reaction of 2 with the phosphinite borane complex 3 or the dichlorosilane 4, gave respectively the corresponding 1,1 6 or 1,3 - diphosphine complexes 7 without loss of chirality (Scheme 1a, c).



Scheme 1

The diphosphines were removed of their complexes on treatment with diethylamine at 50°C and with overall yields of 60-80% from 1. The efficiency of this new route permit the preparation of new class of tertiary bidendate ligands, which constitute a powerful tool for organometallic chemistry and asymmetric catalysis.

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ACID HYDROLYSIS OF IFOSFAMIDE AND RELATED DECHLOROETHYLATED COMPOUNDS

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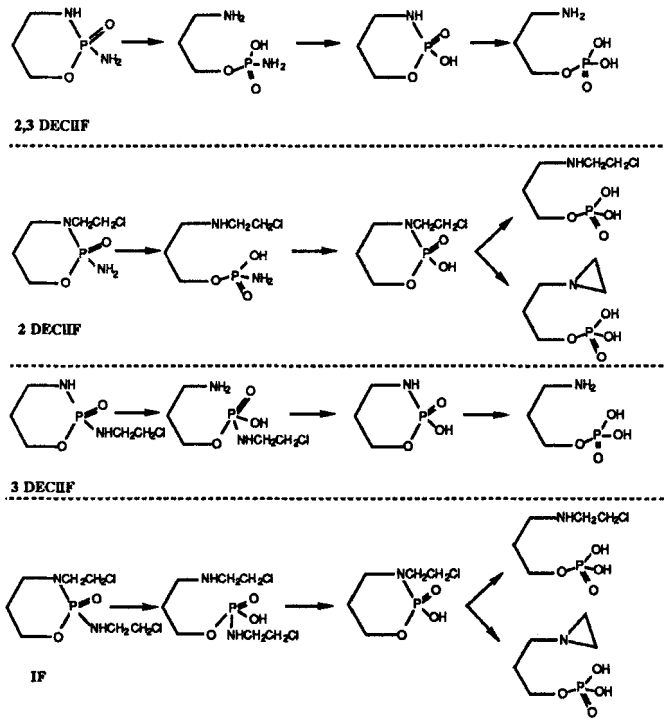
As nearly all the metabolites of the antineoplastic oxazaphosphorine drug, ifosfamide (IF), contain the phosphorus atom, phosphorus-31 NMR is a powerful, direct and simple method to determine the biotransformation of this drug. Indeed, phosphorus-31 NMR analysis of patients' urine samples allowed the detection of at least ten phosphorated compounds of unknown structure, some of them being degradation compounds of yet identified IF metabolites. To identify these compounds, we studied the acid hydrolysis of IF and its dechloroethylated related compounds, i.e. 3- and 2-dechloroethylifosfamide (3DEClIF and 2DEClIF) and 2,3-didechloroethylifosfamide (2,3DEClIF). The time course of acid hydrolysis of these compounds was followed using phosphorus-31 NMR. The structure of each intermediate formed was identified by mass spectrometry and carbon-13 NMR after their isolation. Results are reported in the following scheme.



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O-OCTYL-S-(METHOXYCARBONYLMETHYLMERCAPTOMETHYL)-METHYLPHOSPHONOTHIOATE - A SELECTIVE INHIBITOR OF INSECT CARBOXYESTERASES

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A.N. Nesmeyanov Institute of Organo-Element Compounds of the Russian Academy of Sciences, Moscow.

The compounds $Me(RO)P(O)SCH_2SCH_2COOMe$, where R = C_8H_{17} (I), C_9H_{19}, $C_{10}H_{21}$ have been erlier shown to be the active and selective inhibitors of carboxyesterases (CE) of american cockroach Periplaneta americana (nervous chain) and cereal aphids Schizaphis gramina (in toto)[1]. The differences in inhibition constants of (I) for the corresponding CE and cholynesterases (ChE) are 3 orders of magnitude.

It had to be found out whether the ability of (I) for selective CE inhibition is general for insects of other species. The composition of the esterases fractions from the tissues of the diverse organs of red cockroaches Blattella germanica and housflies Musca domestica as well as from homogenate of rat fleas Xenopsylla cheophis was electrophoretically revealed. On the basis of the differences in electrophoretic mobility and diverse substrate and inhibitor specificity of the separate esterases fractions the latter were identified as ChE, acetylesterases and CE. (I) was shown to inhibit the CE zones completely already at the concentrations $1 \cdot 10^{-7}$M (cockroaches), $1 \cdot 10^{-6}$M (fleas) and $1 \cdot 10^{-5}$M (housflies), while the corresponding ChE zones were inhibited only by solutions of 100-fold concentration.

Thus the compound (I) is one of the most active and selective inhibitors of insect carboxyesterases and can be used for the identification of these enzymes.

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SYNTHESIS AND HPLC-ANALYSIS OF N-PHOSPHORYLATED AMINOACIDS AND THEIR DERIVATIVES

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VLADIMIR A.TSYRYAPKIN, PAVEL V.PETROVSKII,
YURI A.DAVIDOVICH, TATYANA A.MASTRYUKOVA,
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A.N.Nesmeyanov Institute of Element-Organic compounds, Russian Academy of sciences, Moscow

The new procedure to prepare N-phosphorylated aminoacids is reported here, the method applied earlier [1] for the synthesis of N-acylated aminoacids being extended to organophosphoryl chlorides.The reaction of N,O-bis(trimethylsilylated) aminoacids (Gly,Ala,Val) with phosphorus acids chlorides $(RO)_2POCl$ proceeds smoothly (CH_3CN, r.t.) to give silylic esters of N-phosphorylated aminoacids $(RO)_2P(O)NHCHR'COOSiMe_3$ (I; R=Et, ^iPr; R'=H, Me, ^iPr) with quantitative yields. Esters (I) are highly hydrolyzable, then these may be used directly to prepare corresponding acids $(RO)_2P(O)NHCHR'COOH$ (2) (sometimes (I) can be distilled in vacuo).

The procedure described may be useful alternative to the direct phosphorylation of aminoacids by dialkylphosphites [2].

Anilides of (2) have been obtained also to accomplish their structural investigation.The effect close to "double magnetic non-equivalence" in ^1H-NMR-spectra of (2) may be related to inter- or intra-molecular interactions.So HPLC analysis (size-exclusion variant) of these anilides and other amides has been performed under conditions used earlier [3].The straight line (see eq.) demonstrates the absence of long-lived associates of anilides in THF.

$$\lg M = -0.0023V + 3.933 \quad (r\ 0.930,\ S_p\ 0.055)$$

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INTERMOLECULAR TRANSALKYLATION OF TRIORGANOSILYL-METHYL PHOSPHORIC ESTERS

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Moscow 117334, Russia.

We have established, by GC-MS and NMR(^{1}H,^{31}P) methods, that upon heating triorganosilylmethyl phosphoric esters the intermolecular exchange of triorganosilylmethyl groups takes place.

$$Et_3SiCH_2\text{-}OP(O)(OPh)_2 + Me_3SiCH_2\text{-}OP(O)(OCH_2CF_3)_2 \overset{150^{\circ}}{\rightleftharpoons} Me_3SiCH_2\text{-}OP(O)(OPh)_2 + Et_3SiCH_2\text{-}OP(O)(OCH_2CF_3)_2$$

After 10 h reaction mixture contains all four components in approximately equal proportions, and the mixture composition does not change with continued heating, which testifies to equlibrium process.

We studied too the thermal behaviour of $^{17/18}O$-labeled (trimethylsilylmethyl)bis(2,2,2-trifluoroethyl) phosphate, containing $^{17/18}O$-atom in P=O fragment. ^{17}O-NMR-spectral data testify to isotopic scrambling between the phosphoryl and alkoxyl positions.

$$Me_3SiCH_2OP(O^{*})(OCH_2CF_3)_2 \overset{150^{\circ}}{\rightleftharpoons} Me_3SiCH_2O^{*}P(O)(OCH_2CF_3)_2$$

A mechanistic picture, that may be constructed from our studies, suggests, that the thermal transalkylation is carried out by means of intermolecular nucleophilic attack of phosphoryl oxygen to carbon atom of $Si\text{-}CH_2\text{-}O$ -fragment.

Thus, the triorganosilylmethyl phosphoric esters exist in state of equilibrium transalkylation at temperature 150° and some above.

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STEREOCONTROLLED REDUCTIONS OF BRANCHED β-KETO PHOSPHINE OXIDES: A ROUTE TO EITHER GEOMETRY OF DISUBSTITUTED ALKENES

GORDON HUTTON AND STUART WARREN
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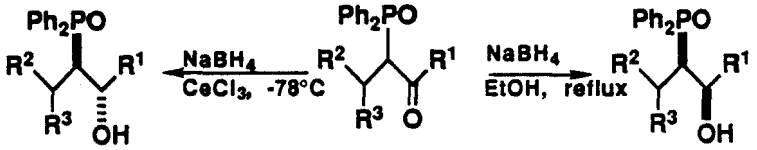
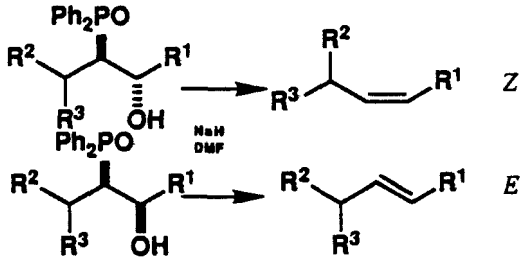
Abstract Stereoselective syntheses of precursors to either geometry of various disubstituted alkenes which are branched at least at one end are discussed.

In the Horner-Wittig reaction it has been noticed that addition of alkyl diphenyl phosphine oxides to aldehydes gives good selectivity for the *anti* isomer. However, when there is a branch β to phosphorous this selectivity is poor.This problem can be overcome by using stereocontrolled reductions of the corresponding ketones. Reduction using $NaBH_4$ in refluxing ethanol leads to the *syn* isomer in good selectivity whereas reduction using $NaBH_4$ and $CeCl_3.7H_2O$ in ethanol at –78°C leads to the *anti* isomer in excellent selectivity.



Purification to single diastereoisomers is generally easy and each undergoes a stereospecific *syn* elimination upon treatment with a sodium or potassium base to give pure *E* or *Z* alkenes.



The poster will describe work with various R^1, R^2 and R^3 where R^2 and R^3 are identical to avoid the complication of an extra chiral centre.

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ORGANOPHOSPHORUS COMPOUNDS AS INDUCTORS OF THE IODINE-AZIDE REACTION. ANALYTICAL APPLICATION AND MECHANISTIC ASPECTS

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[b] Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Sienkiewicza 112, 90-363 Lodz, Poland

Recently we have reported that thiophosphoryl compounds can induce the iodine - azide reaction . Some analytical applications of this reaction were also reported [1,2]

$$2N_3^- + I_2 \xrightarrow{\text{P-S inductor}} 3\,N_2 + 2\,I^-$$

The efficiency of these compounds as inductors was characterized on the basis of their induction coefficients defined by equation :

$$F_i = \frac{n_I}{n_i}$$

Where n_I - milimoles of iodine consumed in the induced reaction

n_i - milimoles of the inductor.

Since the induced consumption of iodine is linearly dependent on the inductor quantity (direction factor contains F_i) this effect constitutes the basis for the indirect determination of inductors. Taking into account a high induction potency of thiophosphoryl compounds, we developed three procedures for their indirect determination based on the induced iodine consumption :

a) titrimetric method (on μmole scale) ; b) spectrophotometric method (on nmole scale) ; c) coulometric method (on nmole scale).

Methodology based on the title reaction constitutes the first general method which can be applied for detection and determination of a variety of thiophosphoryl compounds in a broad analytical range from 1.0 μmole to 0.15 nmole and with high accuracy. The thiophosphoryl compounds are oxidized during the reaction to the corresponding phosphoryl compounds.

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POLAROGRAPHIC INVESTIGATIONS OF FUNCTIONALIZED ALKANEPHOSPHONIC ACIDS

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Institute of Chemistry, University of Łódź,
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The first report[1] on the polarographic reduction of nitro-substituted phenylphosphonic acids was published as early as 1957. Later on the polarographic investigations of phosphonoaldehydes[2], α-ketophosphonates[3] and alkanephosphonates bearing nitro group[4] have been reported. However in fact they were focused on the polarographic activity of the carbonyl or nitro groups. The first and still single report on the polarographic reduction of phosphonic function was presented by Tomilov and co-workers[5] almost two decades ago. They observed that at -1.62 V vs. SCE (LiCl, KCl) on the mercury electrode the cathodic wave of phosphorous acid appeared. Taking into account this observation the occurance of polarographic reduction of phosphonic function expressed by eq. 1 was postulated:

$$H_3PO_3 + 2H^+ + 2e \longrightarrow H_3PO_2 + H_2O \qquad \text{eq. 1}$$

The analytical and synthetical importance of this conversion, which steams mainly from chelating abilities of phosphonic acid and/or biological activities of their phosphinic analogs encouraged us to carry out more detailed electrochemical study of this class of compounds. The results have been presented in this communication.

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ORTHOFORMATES - THE USEFUL REAGENTS FOR DERIVATIZATION OF FUNCTIONALIZED ALKANEPHOSPHONIC ACIDS

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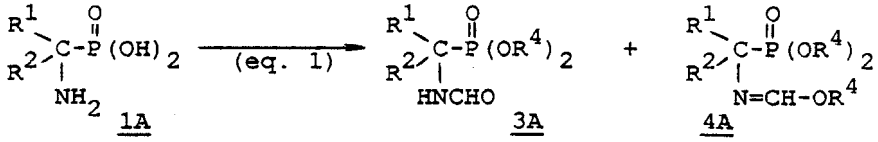
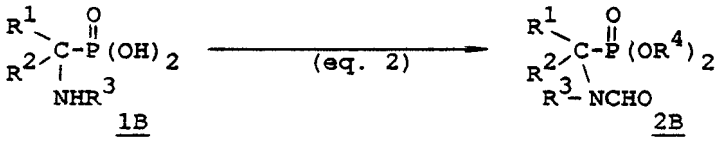
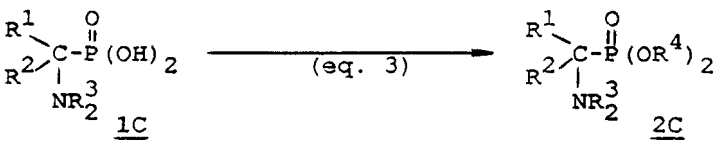
In a search for new derivatization procedure the reaction of orthoformates with functionalized alkanephosphonic acids have been investigated. Thus, 1-aminoalkanephosphonic acids 1A were found to form the mixtures of N-formyl 2A and N-forminoethoxy 3A derivatives, the ratio of which depends on the reaction conditions (eq. 1). On the other hand, the reaction of orthoformates with aminoalkanephosphonic acids having either secondary amino group 1B (eq. 2) or tertiary amino group 1C (eq. 3) afforded the corresponding N-alkyl-N-formyl derivatives 2B or N,N-dialkylaminoalkanephosphonates 2C, respectively.







R^1,R^2 = H,H; H,alkyl; H,aryl; alkyl,alkyl;

R^3 = Me, Et, n-Bu, t-Bu; R^4 = Me, Et, i-Pr;

All compounds 2, 3 and 4 have been found to be suitable for gas chromatographic (GLC) and mass spectrometric (GCMS) analysis.

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AMINOALKANEDIPHOSPHONIC ACIDS. THE SYNTHESIS VIA THIOUREIDOALKANEPHOSPHONATE METHOD.

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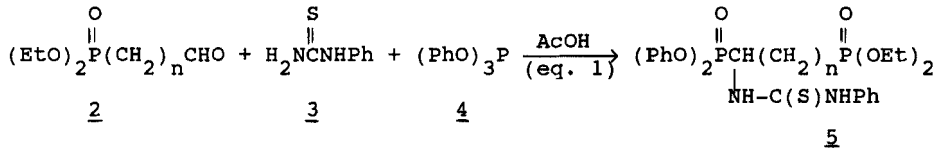
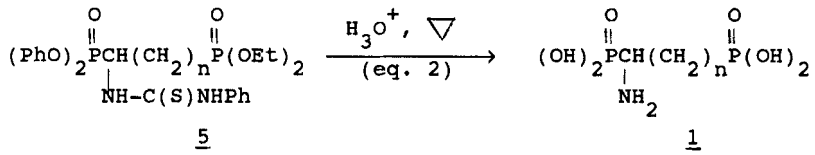
[b]Institute of Chemistry, Faculty of Pharmacy, Medical Academy of Łódź, Narutowicza 120A, 90-151 Łódź, Poland

In this paper we would like to present a new synthesis of aminoalkanediphosphonic acids described by formula 1. The procedure is based on the thioureidoalkanephosphonate metodology [1]. Thus, starting from phosphonoaldehedes 2 (n = 1, 2, 3), N-phenylthiourea (3) and triphenylphosphite (4) the corresponding intermediary thioureidoalkanephosphonates 5 have been obtained in good to high yield (eq. 1).



2 3 4 5



5 1

When these derivatives 5 were subjected to hydrolytic degradation (eq. 2) the title aminoalkanediphosphonic acids 1 [2,3] were isolated in high yields. The dissotiation costants and spectroscopic properties of amino acids 1 have been presented.

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POTENTIOMETRIC INVESTIGATION OF ACIDIC AND CHELATING PROPERTIES OF HYDROXYALKANEPHOSPHONIC ACIDS

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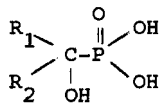
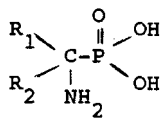
[b]Institute of Chemistry, Faculty of Pharmacy, Medical Academy of Łódź, Narutowicza 120A, 90-151 Łódź, Poland

Recently we have reported on the complexing and tensiometric abilities of 1-aminoalkanephosphonic acids [1,2]. In order to characterize the influence of other auxiliary chelating functions of the dissotiation constants and chelation properties of phosphonic acids we have examined the dissotiation and chelate formation equilibria of a series of 1-hydroxyalkanephosphonic acids 1.



1



2

where: R_1 , R_2 = H , Me , Ph

These results indicate that 1-hydroxyalkanephosphonic acids 1 have stronger acidic character than 1-aminoalkanephosphonic acids 2. Their chelating properties to metal ions such as Cu(II), Co(II), Ni(II) and Cd(II) are weaker in comparision with chelating properties of corresponding amino analogs.

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TOWARDS WATER SOLUBLE PHOSPHINES

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40-006 Katowice, POLAND

Abstract Chlorosulfonated and sulfonamide substituted aromatic phosphines as precursors of water soluble phosphines have been synthesized.

INTRODUCTION

Water soluble phosphines are one of the most desired ligands for metal complexes as effective catalysts in water or water/organic solvent system. Sulfonamide substituted phosphines (and their chlorosulfonated precursors) are convenient source of such the compounds.

RESULTS

Chlorosulfonated phosphines can be obtained by controlled direct reaction of triphenylphosphine and chlosulfonic acid. Ammonia or amine treatment of chlorosulfonated phosphine leads to a variety of sulfonamide substituted aromatic phosphines. The latter can be transformed into relative alkali metal salts form:

$$Ph_3P \xrightarrow{ClSO_3H} (m\text{-}ClO_2S\text{-}Ph)_3P \xrightarrow{R'RNH}$$

$$(m\text{-}R'RNO_2S\text{-}Ph)_3P \xrightarrow{NaOH} (NaO_3S\text{-}Ph)_3P$$

R, R- Me, H

Chlorosulfonated phosphine is accompanied with its oxidized form which can undergo the same processes as former. It can be finally recovered as $(NaO_3S\text{-}Ph)_3P$ by deoxygenation with $HSiCl_3$.

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SYSTEMATIC INVESTIGATIONS IN THE SYSTEM PHOSPHANE / HALOMETHANE

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Fachbereich Chemie der Humboldt-Universität zu Berlin,
O-1040 Berlin, F.R.G.

The reaction of various phosphanes, R_3P (R = Ph, Bu, Me_2N, Et_2N), with halomethanes, CX_nY_{4-n} (X, Y = F, Cl, Br, I, H), are investigated under comparable reaction conditions. It is shown that the course of reaction and the products of interaction between phosphane and halomethane depend on steric as well as electronic effects of the substituents at carbon and phosphorus. Depending on these effects simple phosphonium salts, $[R_3PCX_3]X$, bisphosphonium salts, $[R_3P\text{-}CX_2\text{-}PR_3]X_2$, ylidic bisphosphonium salts, $[R_3P{=}CX\text{-}PR_3]X$, and/or phosphonium salts containing reduced halomethyl groups, e. g. $[R_3PCH_nX_{3-n}]X$, are formed in these systems.

The phosphonium salts show different physical and chemical properties. The triphenyl(iodomethyl)phosphonium salts, $[Ph_3PCH_nI_{3-n}]I$ (n = 0, 1) are unstable at room temperature and decompose under releasing iodine, whereas $[Ph_3PCH_2I]I$ is still stable under similar conditions. But the crystal structure of this compound already shows very short I-I distances. By heating iodine and the ylide $Ph_3P{=}CH_2$ are formed, what allows to use this compound for the olefination of carbonyl compounds (WITTIG reaction) (eq.).

$$[Ph_3PCH_2I]I \xrightarrow[-\ I_2]{} Ph_3P{=}CH_2 \xrightarrow{+\ RR'C{=}O} Ph_3P{=}O + RR'C{=}CH_2$$

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SYNTHESIS OF NEW FUNCTIONALIZED OPTICALLY ACTIVE PHOSPHINES

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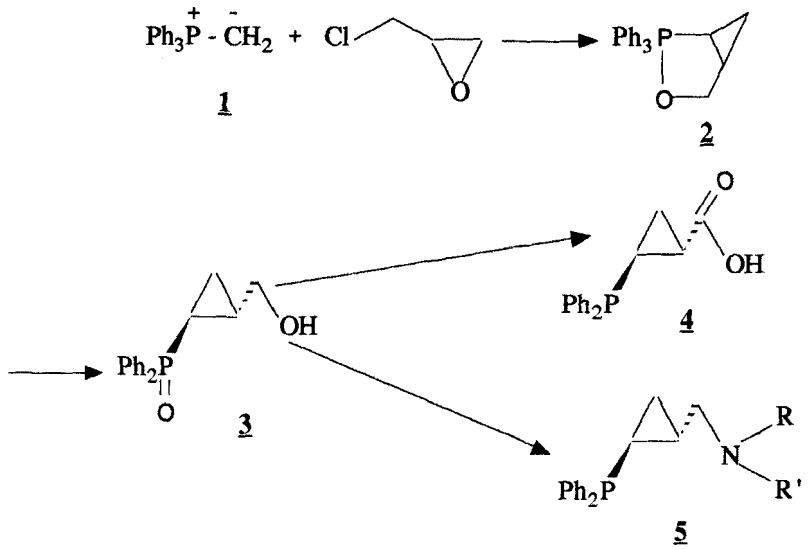
Avenue du Général Leclerc - 35042 Rennes - FRANCE

Abstract : New functionalized optically active phosphines were prepared from oxaphospholane.

Methylenetriphenylphosphorane 1 react with optically active epichlorhydrin to give in good yield oxaphospholane 2. This heterocyclic compound is a good precursor for different optically active phosphines.



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STRUCTURES AND PROPERTIES OF DEXTHOROTATORY 2,4,3-DIAZAPHOSPHABICYCLO(3.2.1)OCTANES

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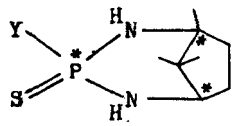
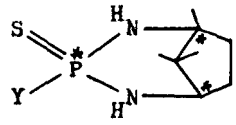
RUYU CHEN
Institute of Elemento-organic Chemistry, Nankai University, Tianjin 300071, China

ABSTRACT

The experimental data of chemical shifts of ^{31}P NMR of the two diastereomers ((1R,3R,5S) and (1R,3S,5S) isomers) of some title compounds have been determined.



1a-8a(1R,3R,5S)



1b-8b(1R,3S,5S)

Number of Compounds:	1	2	3	4	5	6	7	8
Group Y :	OMe	OEt	OPr-i	OBu-s	OPh	$OC_6H_4NO_2$-p	$OC_6H_4CH_3$-p	Ph
δ_a :	67.7	65.2	64.1	64.3	61.8	61.7	62.1	56.4
δ_b :	70.4	68.4	66.9	67.2	66.2	66.3	66.2	63.5

When regression analysis was used to the relationship between δ_a and δ_b a satisfied regression equation could be found

$$\delta_a = 1.631\delta_b - 46.15 \quad (n = 8,\ r = 0.973;\ r_8^{0.01} = 0.843)$$

It may be concluded that the (1R,3S,5S)-diastereomer should be more stable than the (1R,3R,5S)-isomer when group Y in the molecule is the same. However, the conclution is supported by some chemical experiments.

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A HIGHLY STEREOSELECTIVE APPROACH TO CHIRAL 1,3,2-OXAZAPHOSPHORINANE SYSTEM

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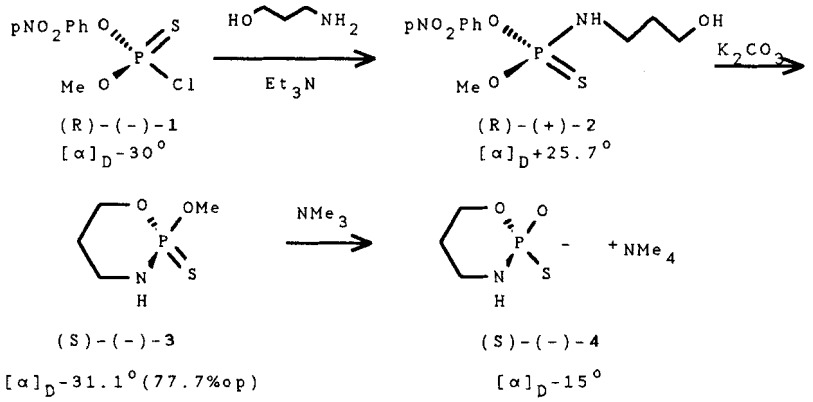
It is well known that biological activity of many 1,3,2-oxazaphosphorinane derivatives is strongly dependent on the absolute configuration of the chiral phosphorus atom[1]. For this reason, synthesis of such systems in optically active forms constitutes an interesting synthetic problem. Here we would like to report the first, highly stereoselective synthesis of the optically active 1,3,2-oxazaphosphorinane system which is based on the use of optically active methyl p-nitrophenyl phosphoro-chloridothionate (**1**)[2] as a key reagent according to Scheme 1.



Scheme 1

References

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2. A.Hirashima, M.Eto, Agric. Biol. Chem. 47, 2831,(1983).

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DIETHYL SELENITE - A NEW AND USEFUL OXIDANT FOR SELECTED ORGANOPHOSPHORUS COMPOUNDS.

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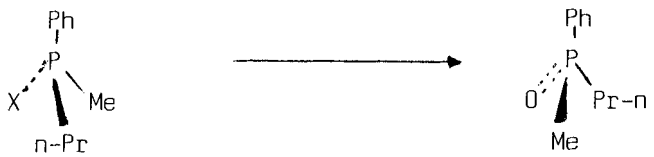
[b]Department of Chemistry, Vanderbilt University, Nashville, TN 37235, USA

Considering oxidizing properties of organic oxidants containing the polar heteroatom-oxygen bond we wondered whether the replacement of the heteroatom-carbon linkages by the heteroatom-heteroatom bonds would change oxidizing abilities of the modified compounds so that they could still be strong enough to make them useful reagents in reactions of interest in organic and bioorganic chemistry. Checking this point we have found that diethyl selenite 1, which can be very easily prepared by the reaction of selenium dioxide with ethanol, is able to convert either tio(seleno)phosphoryl compounds or trivalentphosphorus derivatives into the corresponding phosphoryl compounds.

$$\begin{matrix} R_3P{=}X \\ \text{or} \\ R_3P{:} \end{matrix} \quad + \quad (EtO)_2SeO \quad \underline{1} \quad R_3P{=}O + X + [(EtO)_2Se] \qquad X{=}S,Se$$

To determine the stereochemistry of the oxidation process, (+)-(R)-methyl-n-propylphenylphosphine 2a, (+)-(R)-methyl-n-propylphenylphosphine sulfide 2b and (+)-(R)-methyl-n-propylphenylphosphine selenide 2c were used as a substrate.



2 a X=electron pair
b X=S, c X=Se

3

The results obtained indicated that the considered oxidations take place with predominant inversion of configuration, although stereoselectivity is strongly dependent on the nature of the substrate.

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ON THE EXTENSION OF THE ATHERTON - TODD REACTION TO THE 1-ORGANYLOXY 1-HYDRIDOBICYCLOPHOSPHORANES

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U.R.A. 454 - Université Paul Sabatier F-31062 TOULOUSE CEDEX

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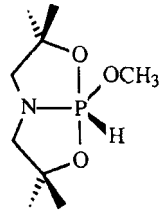
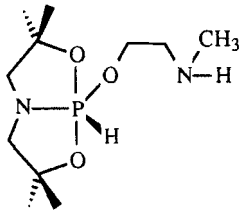
The oxidation of **1** by CCl_4 in the presence of triethylamine and a nucleophile (Atherton-Todd reaction) leads easily to the new symmetric and



1



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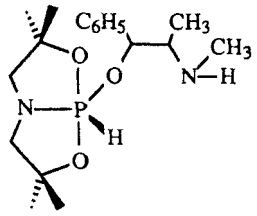

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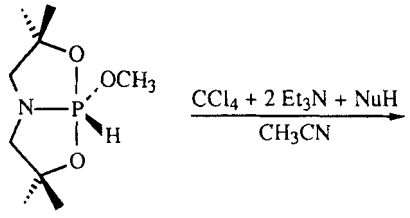
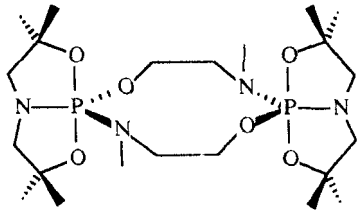
non symmetric bicyclophosphoranes **2** - **5**.



2 Nu = OCH_3
3 Nu = $OC(CH_3)_3$
4 Nu = $N(C_2H_5)_2$
5 Nu = HNC_3H_7

The same reaction, performed with the bicyclophosphoranes **6** and **7**, in the absence of another nucleophile, leads to the ten membered rings **8** and **9** which are, to our knowledge, the first bicyclophosphoranes containing ten membered rings.



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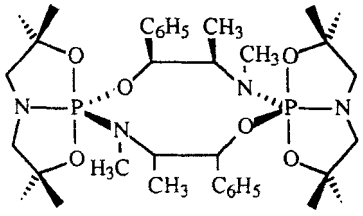

9

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NEW CHEMISTRY AND STEREOCHEMISTRY OF PHOSPHORUS SIX-COORDINATE SYSTEMS

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[1]Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Sienkiewicza 112, 90-363 Łódź, Poland

[2]Institute of General Chemistry, Technical University of Łódź, Żwirki 36, 90-924 Łódź, Poland

Recent results concerning preparation and stereochemistry of six-coordinate phosphorus compounds are described. In a number of cases the formation of isomeric species resulting from the interaction of the cyclic phosphoranes with a variety of nucleophiles has been demonstrated by means of ^{1}H, ^{19}F and ^{31}P NMR spectroscopy. Their structure and mode of isomerization will be discussed.
Special attention will be paid to:

a) the configuration and the conformation of bicyclic compounds with a six-membered ring $(RO)(R'O)(C_6Cl_4O_2)^{-}\underline{P\text{-}OCH_2CR^2R^3CH_2O}\ MH^{+}$ 1.

b) X-ray crystallographic studies of the compounds $(C_6Cl_4O_2)_2^{-}\underline{P\text{-}OCH_2CR^1R^2CH_2O}\ Et_3N^{+}H$ 2, which have a chair, twist or boat conformation of a six-membered ring depending on the nature of the ligands R^2 and R^1.

c) Kinetic data on isomerization of bicyclic compounds trans-$(C_6H_4O_2)_2^{-}P\text{-}(OAr^1)(OAr^2)\ Et_3N^{+}H$ 3 into cis-3 providing evidence for the intramolecular dissociative mechanism with heterolysis of one of P-O endocyclic bonds.

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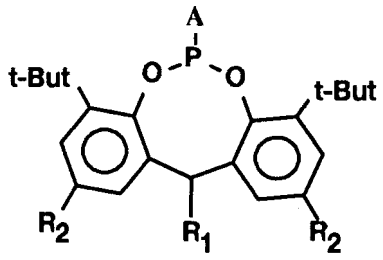
P. Hug, S. Kolly, **H.R. Meier**, R. Pitteloud, G. Rist, Ciba-Geigy AG
Marly/Switzerland

Conformational equilibria of 12-substituted and 12-unsubstituted dibenzo[d,g][1,3,2]dioxaphosphocines



B

A = Cl, F, Ph; R_1 = H, Me; R_2 = t-But

Conformational equilibria of dibenzo[d,g][1,3,2]dioxaphocines B in solution are investigated by ^{1}H-, ^{13}C-, ^{19}F-, and ^{31}P-NMR-spectroscopy.

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HIGHLY REGIOSELECTIVE AND STEREOSPECIFIC FUNCTIONALIZATION OF 1,2-PROPANEDIOL WITH TRIMETHYL(X)SILANES EMPLOYING THE 1,3,2λ^5-DIOXAPHOSPHOLANE METHODOLOGY

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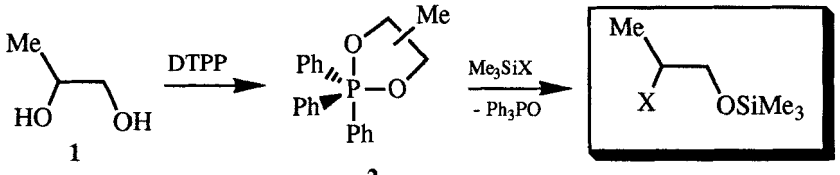
The William Rand Kenan, Jr., Laboratories of Chemistry
The University of North Carolina at Chapel Hill
Chapel Hill, North Carolina 27599-3290 U.S.A.

ABSTRACT

The regioselective ring opening of (*S*)-4-methyl-2,2,2-triphenyl-1,3,2λ^5-dioxaphospholane (**2**)[prepared from the *bis*(transoxyphosphoranylation) of (*S*)-1,2-propanediol (**1**) with diethoxytriphenylphosphorane (DTPP)] was initiated with several trimethylsilyl reagents (Me_3SiX: X= PhS, I, Br, Cl, CN and N_3) to afford the regioisomeric silyloxyphosphonium salts. A stereospecific extrusion of triphenylphosphine oxide from these oxyphosphonium salts gave predominantly the thermodynamically less stable *C*-2-X substituted derivatives with nearly complete inversion of stereochemistry at the *C*-2 stereogenic center (*i.e.*, X = PhS).

Regioselective Substitution of 4-Methyl-2,2,2-triphenyl-1,3,2λ^5-dioxaphospholane 2 with Me_3SiX



1 2

Major or exclusive product
X = Br, I, Cl, CN, SPh and N_3.

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(1) I. Mathieu-Pelta and S. A. Evans, Jr., *J. Org. Chem.*, **57**, 3409 (1992).

(2) J. W. Kelly, P. L. Robinson, W. T. Murray, N. Anderson- Eskew, A. Pautard-Cooper, I. Mathieu-Pelta, and S. A. Evans, Jr., in the ACS Symposium Series No. 486, *Phosphorus Chemistry: Developments in American Science*; E. N. Walsh, E. J. Griffith, L. D. Quin, and R. W. Parry (eds); Chapter 15, pp 186-201, 1992; American Chemical Society, Washington, DC, USA.

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NEW CONVENIENT SYNTHESIS OF PHOSPHONIC KETENE DITHIOACETALS AND THEIR REACTIONS WITH NUCLEOPHILES. SYNTHESIS OF POTENTIAL ANTIVIRAL COMPOUNDS.

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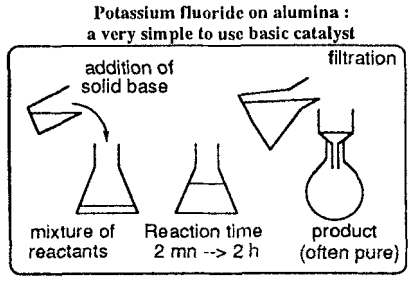
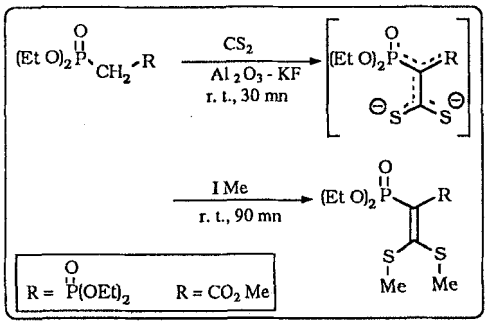
Potassium fluoride on alumina is a solid base prepared by dissolution of potassium fluoride in water and evaporation of water in the presence of chromatographic alumina. This base can be used in organic synthesis, allowing reactions otherwise hardly possible by classical ways. Its basicity is near to that of butyl lithium. Its work-up is very simple, as it only needs to be added to the mixture of acid and nucleophile, eventually with a solvent. After a reaction time from 2 Mn to 1 or 2 hours, the product is obtained by simple filtration and washing of the solid with a solvant. Reactions can be surprisingly chemoselective, and the product is often very pure : sometimes no purification is necessary.

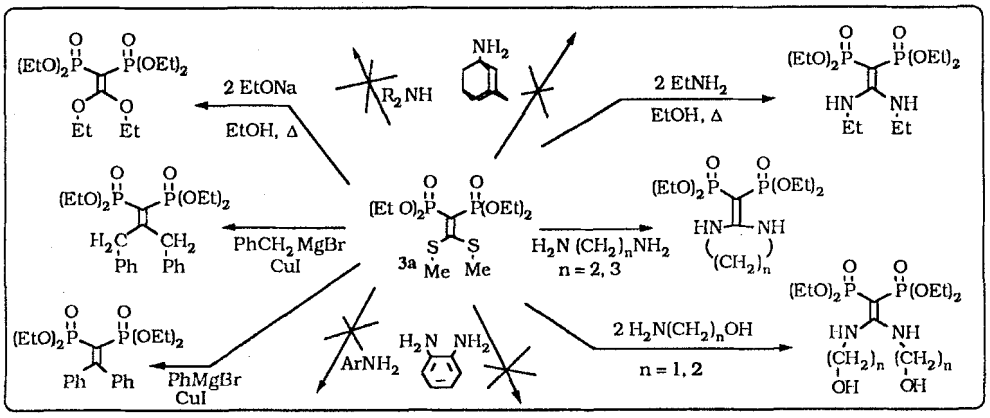




We have used this solid base to prepare phosphonic ketene dithioacetals. The yields are 90-95 %. The products are obtained upon filtration and chromatography on a short silica column.

Reaction with nucleophiles :

These compounds react with amines, on the condition that they are not too big, because of steric hindrence, and that they are nucleophilic enough (aromatic amines do not react) These compounds also react with sodium ethylate to substitute the methylthio groups by Grignard reagents.The obtained derivatives will be hydrolysed to free acids and biologically tested, for they are analogs of pyrophosphate and may have anti-viral properties.



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PHOSPHORUS CASCADE MOLECULES

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Cascade species bearing phosphorus core and branch sites have been synthesized in several categories. In prior efforts, tridirectionally or tetradirectionally elaborated cascade species have been generated from a single phosphonium ion core, with each branch point being an additional phosphonium ion site.[1,2] In each instance the phosphonium core site has been generated from tri(4-methoxymethylphenyl)phosphine by quaternization using either an alkyl halide or 4-methoxymethylbromobenzene in the presence of nickel(II) chloride. These cascade molecules have been elaborated to three generations bearing up to forty phosphonium ion sites within the covalent structure (and forty free associated iodide ions).

In the present work a phosphine oxide core has been formed based on tri(4-methoxymethylphenyl)phosphine oxide which is elaborated to further generations of the cascade structure in a manner similar to that previously reported, that is by treatment first with iodotrimethylsilane (which selectively cleaves the benzylic ether linkage leaving it as a benzylic iodide function) followed by quaternization of the resultant benzylic iodide sites using three equivalents of tri(4-methoxymethylphenyl)phosphine.

The species thus generated bears a phosphine oxide core with three surrounding phosphonium ion sites in the covalent portion of the molecule, and three free associated iodide ions. Further elaboration to a second generation cascade structure is accomplished by repetition of the two steps previously mention yielding a species with a phosphine oxide core surrounded by three first generation phosphonium ion sites and nine second generation phosphonium ion sites; twelve free associated iodide ions are also present. Although the core site might be anticipated to be buried within the expanded covalent framework of the molecule, it remains available for continued reaction. This core phosphine oxide site has been reduced to the free phosphine by treatment with trichlorosilane, and the resultant phosphine has been used in formation of a 1:1 complex with gold(I) chloride. The electronic absorption spectrum of the gold(I) complex exhibits a slight bathochromic shift from that of the corresponding complex involving triphenylphosphine. Elemental analyses and NMR spectra (H-1 and P-31) in accord with the proposed structures have been obtained for all species, the P-31 NMR spectra exhibiting definitive signals for each of the several types of phosphorus sites present within each species.

In addition, a previously reported tetradirectional cascade structure with a phosphonium ion core, tetra(4-methoxymethylphenyl)phosphonium iodide, has been converted to the penta(4-methoxymethylphenyl)phosphorane by treatment with the organolithium reagent, 4-methoxymethylphenyllithium. This phosphorane has been elaborated to a cascade structure by treatment with iodotrimethylsilane followed by quaternization of the benzylic iodide sites using tri(4-methoxymethylphenyl)phosphine. The casacde species thus generated bears a neutral core surrounded by cationic branch points. This represents the first cascade structure bearing a quinquedirectional core from a single center. This species exhibits suitable elemental analysis and NMR spectra (H-1 and P-31) for the proposed structure; again, the P-31 NMR spectrum clearly distinguishes each type of phosphorus site within the molecule.

1. K. Rengan and R. Engel, *J. Chem. Soc., Chem. Commun.*, 1084 (1990).
2. K. Rengan and R. Engel, *J. Chem. Soc., Perkin Trans. 1*, 987 (1990).

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REACTIONS OF AMINOPHOSPHINES WITH ALKYL THIOCYANATES. 1,2-BIS[(PHOSPHORANYLIDENE)AMINO]TETRACYANOETHANES - SOURCE OF NEW STABLE ORGANOPHOSPHORUS RADICALS

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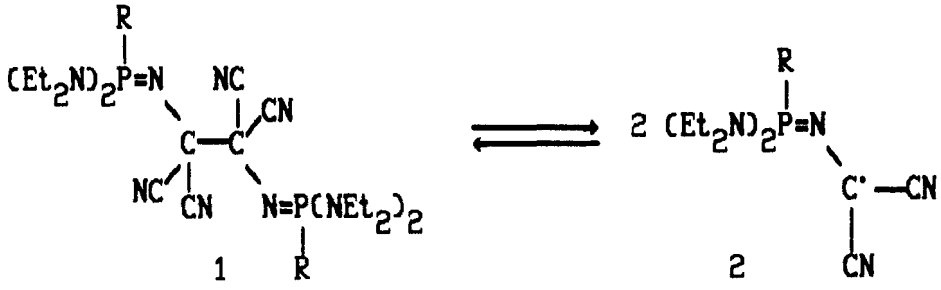
Reactions of $R\text{-}P(NEt_2)_2$ (R = Et_2N, Ph) with alkyl thiocyanates have been found to yield alongside with other products, N^2-alkyldicyanomethyl-N^1-(phosphoranylidene)cyanoformamidines and 1,2-bis(phosphoranylideneamino)tetracyanoethanes 1. These reactions were assumed to take both a heterolytic and a homolytic course.

Essential lengthening of the central C–C bond [1.609(6)A] has been found by X-Ray study of 1 and this made it possible to assume easy cleavage of this bond in 1. Actually the ESR investigation of solutions of 1 in toluene and HMP in the 300-400K temperature range has demonstrated the existence of an thermally-induced equilibrium homolytic dissociation of 1, resulting in the formation of the stable radicals 2.



The values of the dissociation enthalpy and entropy for 1 have been estimated from ESR spectra of solutions of radicals 2, which are temperature-dependent. Main changes of the spectra have been found to be due to the a^P variation.

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X-RAY STRUCTURAL STUDY OF THE NEW PHOSPHORUS-NITROGEN COMPOUNDS

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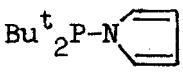
Using X-ray diffraction method a series of the new phosphorus-nitrogen compounds, products of their protonation and complexes with metals was studied.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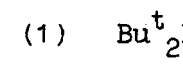
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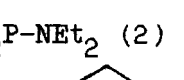
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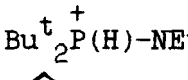
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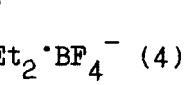
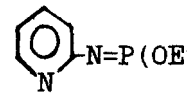

(5,6: R=3-Me,4-Me)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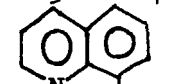
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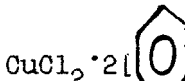
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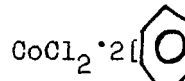
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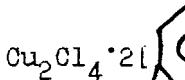
(11)

(12)

Amides (1,2) are protonated by HBF_4 with the formation of the unusual phosphonium salts (3,4) with P-H bonds. Protonation of the iminophosphine derivatives (5-8) may take place at the N-atoms of the heterocycle or imino-group. Reasons of such behavior are discussed. In metalocomplexes (9-12) Cu- and Co-atoms are coordinated by N-atoms of heterocycles and Cl-atoms. A strong additional intramolecular coordination of the metals by N-atoms of the imino-groups also take place in all structures investigated. The degree of this interaction influences on P=N bond's lengths.

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SYNTHESIS OF GEM-ORGANODISUBSTITUTED CYCLOTRIPHOSPHAZENES BEARING FUNCTIONAL GROUPS

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Abstract Various gem-organodisubstituted cyclotriphosphazenes which might be considered as precursors of bioactive phosphinic compounds have been obtained.

Cyclotriphosphazenes bearing functional substituents linked to the ring through Phosphorus-Carbon bonds are yet rather unusual[1,2]: the transient *in situ* generated tetrachlorocyclotriphosphazenes anions $(N_3P_3Cl_4R)^-$, with either Li^+ or Cu^+ cationic counterparts, are claimed as substrates of limited synthetic utility and relatively low reactivity[3].

We show that the lithiocyclotriphosphazenes with aryloxy substituents are suitable substrates for further alkylation with functionalized carbon chains. The new cyclotriphosphazenes are obtained in 60-70% yields. In the course of their structure determination, we have pointed out the existence of some virtual coupling at the $^{13}C_{Ar}$ signals .

The new synthetized compounds may be considered as precursors of the corresponding phosphinic acids, since the 1,1-diphenylcyclotriphosphazenes are known to lead to the diphenylphosphinic acid under hydrolytic conditions[4]. In this way, the progressive release of pharmaceutical and agrochemical bioactive phosphinic compounds might be looked upon.

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CONFORMATIONAL STABILITY OF SHORT-CHAIN LINEAR CHLOROPHOSPHAZENES: MNDO CALCULATIONS, ^{31}P NMR AND VIBRATIONAL SPECTRA.

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The availability of new high polymeric systems (-P(R)2=N-) (R is an organic group) based on the phosphazene backbone provides the possibility to obtain insulating, non burning and chemically stable materials suitable for a wide range of applications. Some are elastomeric at room temperature. These elastomeric properties are in relation with the flexibility of the phosphazene backbone.

Polyorganophosphazenes are unusual in polymer chemistry inasmuch as they are derived from a single polymeric intermediate, the polydichlorophosphazene $(-PCl_2=N-)_n$.

In the present work, we use the MNDO (modified neglect of diatomic overlap) method to examine the conformational stability and vibration of the linear short-chain chlorophosphazene compounds: $Cl_3PN(PCl_2N)_nP(O)Cl_2$ and $[Cl_3PN(PCl_2N)_nPCl_3][PCl_6]$ (n= 1,2,3).

The ^{31}P NMR spectra were recorded in the temperature range 183-413 K. The coalescence phenomena observed at low temperature for $Cl_3PN(PCl_2N)_nP(O)Cl_2$ (n= 2, 3) indicate the mobility of the (PN) backbone.

The Raman spectroscopy was used for the linear chain chloro-phosphazene compounds from n= 1 to n= ∞ to obtain the vibrational frequencies of the phosphazene backbone in the solid state as well as in the liquid phase.

In order to ascertain the vibrational assignment a classical normal coordinate analysis of the vibrational modes of dimeric and polymeric isolated molecules was performed.

All the experimental and calculated results are in good agreement with a *cis-trans* planar arrangement of the phosphazene backbone. It turns out that the short linear molecular oligomers are better models for the polymeric chain than cyclic oligomers or ionic derivatives.

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VIBRATIONAL AND CONFORMATIONAL PROPERTIES OF MONOMERIC PRECURSORS OF LINEAR POLYDICHLORO-PHOSPHAZENES.

Yahia Lemmouchi, Daniel Bougeard, Claude Brémard, Roger De Jaeger

Laboratoire de Spectrochimie Infrarouge et Raman, CNRS UPR 2631L Bat. C5, Université des Sciences et Technologies de Lille, 59655-Villeneuve d'Ascq Cedex, France

Polyphosphazenes represent a new class of inorganic polymers; they are characterized by a backbone of alternating phosphorus and nitrogen atoms with organic groups (R) attached to the phosphorus $(-P(R)_2=N-)_n$. The polymers are derived from a single polymeric intermediate which can be obtained through the polycondensation of the monomeric species $Cl_3P=N-P(O)Cl_2$. Some polyphosphazenes are highly elastomeric materials at room temperature and these elastomeric properties are in relation with the flexibility of the phosphazene backbone.

In the present work about the shortest linear chlorophosphazene compounds we use the semi-empirical MNDO method (modified neglect of diatomic overlap) to study the ground state structures and vibrations in order to predict the more stable conformers of $Cl_3PNP(X)Cl_2$ (X= O, S) and $[Cl_3PNPCl_3][Y]$ (Y= Cl, PCl_6).

A ^{31}P NMR study of $Cl_3PNP(O)Cl_2$ indicates that even at low temperature either one rigid species or two flexible species in very fast equilibrium exist in solution.

The Raman spectroscopy is an efficient tool to study the conformation of the polyphosphazenes in all phases. The Raman spectra of $Cl_3PNP(X)Cl_2$ (X= O, S) and $[Cl_3PNPCl_3][Y]$ (Y= Cl, PCl_6) were carried out in solution or in the molten and solid states at different temperatures. The polarized Raman spectra of $Cl_3PNP(O)Cl_2$ in the melt are in good agreement with a nearly planar structure. The number of observed Raman band demonstrates the simultaneous presence of two conformers in solution as in the solid state.

In order to ascertain these results a classical normal coordinate analysis of the vibrational modes of the $Cl_3PNP(O)Cl_2$ isolated molecule was performed. The calculated values are in good agreement with the experimental values and the calculations yield a quantitative interpretation of the vibrational spectra.

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SPECTRAL STUDY OF COPPER (II) COMPLEXES WITH POLYAZACYCLIC PHOSPHONIC ACIDS.

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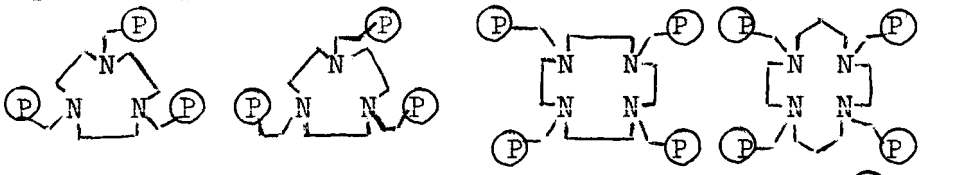
E. I.Matrosov, M.I.Kabachnik.
A.N.Nesmeyanov Institute of Organo-Element Compounds,
Russian Academy of Sciences, Vavilov str. 28, Moscow,
117334, Russia.

The complexation of tri- and tetra-azacyclic phosphonic acids (1-4) with Cu^{2+} (1:1) in the aqueous solution under different pH condition by means of UV-Vis, IR and ESR spectroscopy has been studied.



1 2 3 4 P=PO_3H_2

In the complexes under study Cu^{2+} ion is pentacoordinated by ligand donor atoms and has square-pyramidal environment. In the complexes of 1 or 2 the chromophore ($Cu2N_e2O_eN_a$) is formed, one phosphonic group is free. For ligand 2 the coordination polyhedron is more distored and flexible than for 1. In the complexes of 3 and 4 the ($Cu4N_eO_a$) chromophore is formed, three phosphonic groups are free. In the frozen solution of CuL^1 at high pH values there are two different conformation complexes.

Thus, variations of the cycle size (3 and 4) or pendant length (1 and 2), for our ligands, do not influence on the number of coordinated ligand donor atoms, but change their mutual position in coordination polyhedron.

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PREPARATION OF STERICALLY PROTECTED 3,4-BIS-(PHOSPHINIDENE)CYCLOBUTENES AND THEIR ISOMERISM

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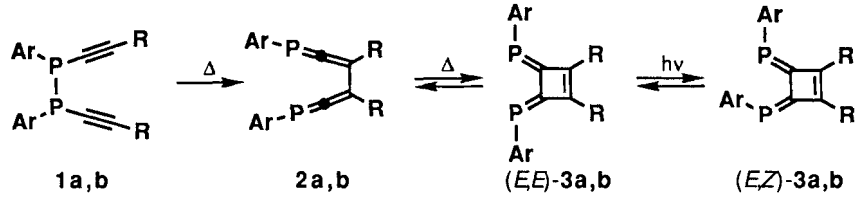
Aoba, Sendai 980, Japan

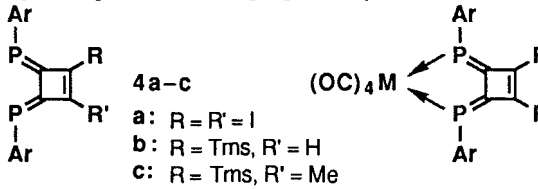
Bidentate phosphaalkene ligands having conformationally rigid skeletons are of interest since their coordination is expected to be selective in site and size. By utilizing 2,4,6-tri-*t*-butylphenyl group (abbreviated to Ar) as protecting group, we have prepared 1,2-bis(trimethylsilylethynyl)diphosphane **1b** (δ_P –38.5).[1] The diphosphane **1b** was unstable toward heat and gradually isomerized to **2b** (δ_P 42.9). On heating in refluxing toluene for 30 min **2b** gave an equilibrium mixture of **2b** and (*E*,*E*)-**3b** (δ_P 162.5). Furthermore, (*E*,*E*)-**3b** isomerized to (*E*,*Z*)-**3b** (δ_P 197.4 and 176.6, ABq, $^3J_{PP}$ = 14.6 Hz) by irradiation with a Xe lamp or sunlight.



1a,b **2a,b** (*E*,*E*)-**3a,b** (*E*,*Z*)-**3a,b**

a: R = H; **b**: R = Tms Ar = 2,4,6-Bu$^t_3$C$_6$H$_2$; Tms = SiMe$_3$

Desilylation reaction of **1b** with K_2CO_3 in MeOH gave **2a**, which was then converted to (*E*,*E*)-**3a** almost quantitatively by heating. Irradiation of (*E*,*E*)-**3a** led to the photo-equilibrium between (*E*,*E*)- and (*E*,*Z*)-**3a**. They were also obtained by the reaction of tetrabutylammonium fluoride (TBAF) with (*E*,*E*)- and (*E*,*Z*)-**3b**, respectively. Furthermore, the reaction of (*E*,*E*)-**3b** with CH_2ClI or MeI in the presence of TBAF gave **4a** and **4b** or **4b** and **4c**, respectively, as major products. The group-6 metal(0) carbonyl complexes **5** were prepared by several methods.



4a–c
a: R = R' = I
b: R = Tms, R' = H
c: R = Tms, R' = Me

5a: R = H; M = Mo
5b: R = Tms; M = Cr, Mo, W

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PHOSPHAMETALLACYCLOBUTANE- AND PHOSPHAMETALLACYCLOBUTENE DERIVATIVES BY INSERTION REACTION

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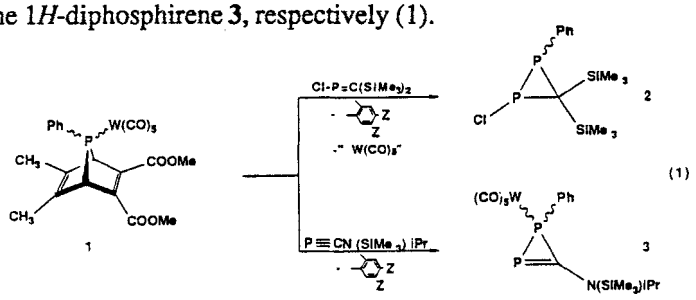
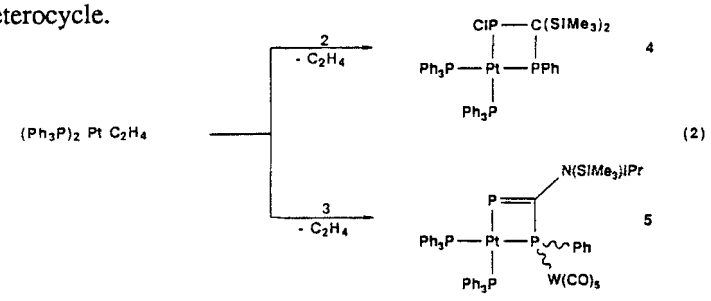
Thermal decomposition of the 7-phosphanorbornadiene-derivative **1** in toluene in the presence of either a phosphaalkene or a phosphaalkyne afforded the stable diphosphirane **2**[1] and the 1*H*-diphosphirene **3**, respectively (1).



An access to the new diphosphaplatinacyclobutane **4** as well as to the diphosphaplatinacyclobutene **5** has been achieved by reaction of the appropriate heterocycles **2,3** with the platinum complex (2). In the case of the diphosphirane **2**, the insertion of the $[(Ph_3P)_2Pt]$ fragment into the P/P-bond proceeds with the retention of the configuration of the parent heterocycle.



The products have been characterized by means of NMR, IR-spectroscopy and single X-ray cristallography in the case of **3**.

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1) M. Rahmoune, Y.Y.C. Yeung Lam Ko, R. Carrie, *New J. Chem.* **13**, 891 (1989).

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Structure of a 1,3-diphosphaallyllithium

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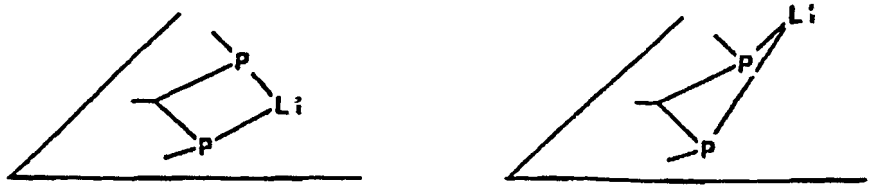
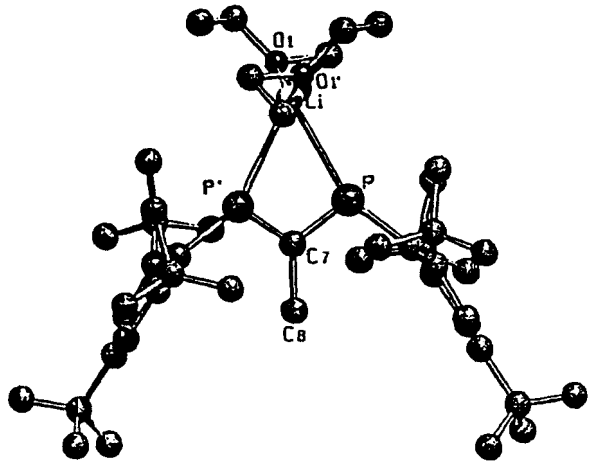
b) Université Paul Sabatier, 31062 Toulouse cedex; France
c) Universität des Saarlandes, 6600 Saarbrücken; Germany

For allyllithium compounds, the theoretical calculations, performed by R.v. Schleyer, indicate two possible structures : a σ structure with a more covalent character and a π structure with a more ionic character. According to these two calculated allyllithium structures, the π-allyl system appears more stable than the σ allyl system. Similar results have been obtained by Bachrach for the calculated 1,3-diphosphaallyllithium structures. Moreover, this author considers the π-diphosphaallyllithium as an intermediate in the 1,3-diphosphaallene formation.



We have recently determined the X-ray structure of 1,3-diphosphaallyllithium $(ArP{=}C(Me){-}PAr)^{-}(Li.\ 2\ Et_2O)^{+}$.The position of Li atom in the PCP plane (d_{PLi}=2.80 Å) involves a σ structure.Taking into account the rotation barrier around P-C bonds, we will discuss the mechanism of 1,3-diphosphaallene formation.



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EXPERIMENTS ON THE GENERATION OF 2-COORDINATE PHOSPHORYL SPECIES BY FRAGMENTATION OF 7-PHOSPHA-NORBORNENE DERIVATIVES

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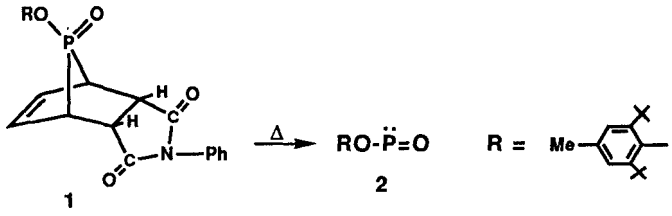
Thermolysis of the 7-phosphanorbornene (7-PNB) derivative **1** at 300°C and 0.01 mm caused release of the phosphenite **2**, which rapidly gave dimeric and trimeric condensation products.



1 **2**

A ^{31}P NMR signal at δ 238 in the product when condensed in a liquid nitrogen receiver disappears on standing or addition of ethanol, and is attributed to structure **2**. The same signal was present in the pyrolysate from a pure sample of the trimer, prepared by a different method. A calculation of the ^{31}P NMR shift for R = Ph confirmed that δ 238 is consistent with **2**. Attempts to generate this and other phosphenites, as well as thiono and P-phenyl analogs, by photolysis of 7-PNB derivatives in aprotic solvents were unsuccessful. However, as noted in the literature, photolysis proceeded readily when alcohols were present, providing H-phosphonates from the released fragment. That an alcohol is *required* for the fragmentation suggests that it first reacts with the 7-PNB, possibly to give a 5-coordinate adduct. This observation prompted an examination of the photolysis of 3-phospholene oxides, also reported in the literature to fragment photochemically. Again it was found that the reaction failed in aprotic solvents, and occurred only when an alcohol was present. An adduct of the 3-phospholene and the alcohol is suspected as the species undergoing the fragmentation.

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TRIPHOSPHORUS DISULFIDE P_3S_2 AND THIOLPHOSPHINIDENE HSP STABLE MOLECULES IN THE DILUTE GAS PHASE

HELMUT KECK[a], WILHELM KUCHEN[a], PETER TOMMES[a]
JOHAN K. TERLOUW[b] and THOMAS WONG[b]
[a]Heinrich-Heine-Universität Düsseldorf, Inst. f. Anorg. Chemie und Strukturchemie, Düsseldorf, Germany; [b]McMaster University, Department of Chemistry, Hamilton, Canada.

Abstract Generation and identification of gaseous P_3S_2 and HS-P by means of Neutralization-Reionization mass spectrometry is presented and discussed.

Neutralization-Reionization mass spectrometry (NRMS) has proved to be a powerful technique to generate highly reactive but thermodynamically stable molecules in the rarefied gas phase by reduction of their corresponding ions. We wish to report part of the results of our continuous studies concerning the generation of "non-existing" small gaseous molecules containing phosphorus by means of NRMS. The dissociative ionization of tetraphosphorus trisulfide P_4S_3 by electron impact (70 eV) yields $[P_3S_2]^+$, the connectivity of which has been determined by Collisional Activation (CA) mass spectrometry of this ion and of its isotopomer $[P_3{}^{32}S^{34}S]^+$. Using NRMS these ions can be reduced to the corresponding neutral molecules. On the basis of the CA-mass spectra and thermochemical data as well as from the results of *ab initio* MO calculations (HF/6-31G* basis set) it is concluded that both $[P_3S_2]^+$ ion and neutral molecule exist as planar five-membered rings (C_{2v}) with one P-P-bond.

The hitherto unknown thiolphosphinidene HS-P has been identified by NRMS, too. We found that radical ions of composition "$[HPS]^{+\bullet}$" can be generated by dissociative ionization (electron impact: 70 eV) of dialkylphosphanesulfides $R_2HP(S)$ ($R = C_2H_5, C_3H_7$) and by use of the methods mentioned above that both the ions and the neutral molecules have the connectivity of thiolphosphinidene HS-P (C_S).

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Seleno Derivatives of Planar Three-coordinate Ylide-substituted Phosphorus

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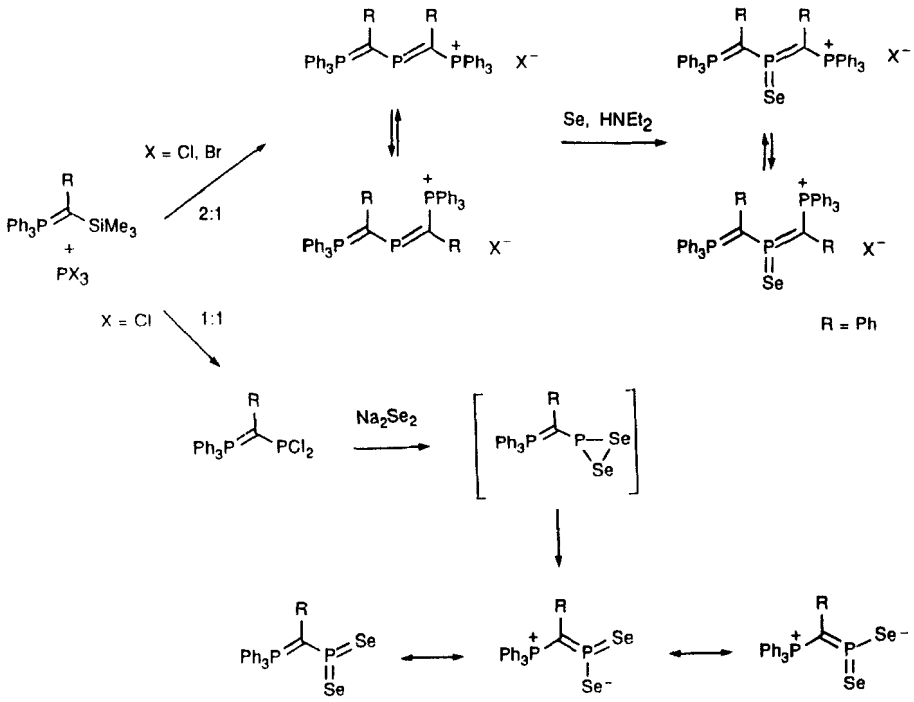
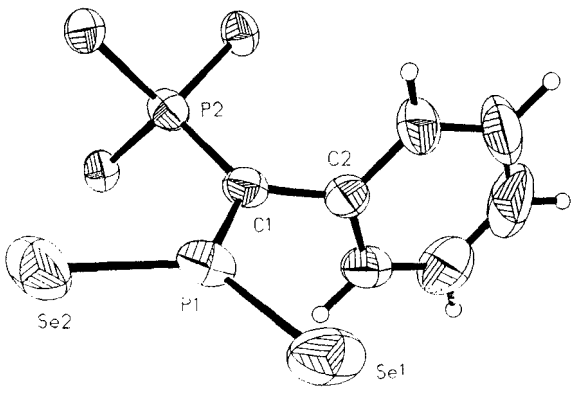
Institut für Anorganische Chemie der Universität München, Meiserstrasse 1, D-8000 München 2, Germany

Ylide substituents cause selenophosphinoyl halides to become ionic $\overset{\backslash +}{P}=Se\ X^-$ and keep diselenoxophosphoranes $-P\overset{Se}{<}_{Se}$ from becoming dimeric. Representatives can be prepared these ways:





In the crystal the PSe_2 and the CCP moieties are coplanar (dihedral angle 9°). In solution the rotation around the connecting PC bond is restricted, as documented by two ^{77}Se NMR signals and by two pairs of satellites to the ^{31}P NMR signal.

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STUDIES OF P...P BONDING THROUGH INTRABRIDGEHEAD CHEMISTRY

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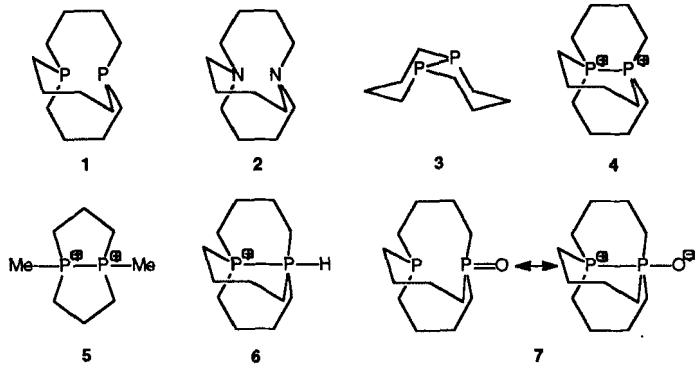
We sought to make 1,6-diphosphabicyclo[4.4.4]tetradecane **1** to compare the interactions of the P atoms with those of the N atoms in **2**.[1] Calculations show **1** is highly strained with *in,in*, *in,out*, or *out,out* lone pairs, but that derivatives such as **4**, **6** and **7** with almost any kind of P...P bonding are relatively strain-free.



1 **2** **3** **4** **5** **6** **7**

Isslieb's route to 1,5-diphosphabicyclo[3.3.0]octane[2] was modified to make **3**, shown to be thermodynamically-stable as the *cis*-isomer. Reaction of **3** with 1,4-butanediyl ditriflate yields **4** which is stable to water unlike **5**. Reaction of **4** with $NaBH_4$ yields P-P bonded ion **6**, i.e. mono-protonated **1**. Reaction of **4** with hydroxide ion yields **7**, which has some P...P bonding by ^{31}P NMR. The chemistry of these species has been studied.

References

1 For a review see: R. W. Alder, Tetrahedron, 1990, **46**, 683-713.

2 K. Issleib and P. Thorausch, Phosphorus and Sulphur, 1978, **4**, 137-144.

Phosphorus, Sulfur, and Silicon, 1993, Vol. 77, p. 235
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Substitution and Addition Reactions of 1,5-Anellated 1,3-Azaphospholes

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Meiserstraße 1, 8000 München 2, Germany

Raj K. Bansal, Neelima Gupta, Dinesh C. Sharma, Ruchi Mahnot and Vijaya Kabra

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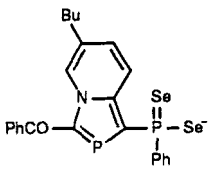
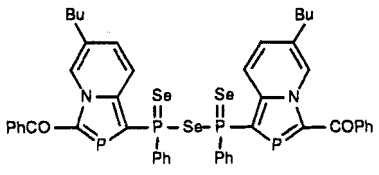
Jaipur - 302004, India

1-Unsubstituted 1,3-azaphospholo[1,5-*a*]pyridines (2-phosphaindolizines) **1** [1,2] - like indolizines - enter electrophilic substitution reactions in this position. They are brominated by Br_2/NEt_3 or NBS and yield phosphino derivatives with PCl_3 and $RPCl_2$.

With $(PhPSe_2)_2$ in the presence of NEt_3 the seleno phosphinate **2** is isolated, in absence of base the seleno anhydride **3** as a mixture of diastereomers and the zwitterion **4** are obtained. In contrast no substitution is observed with Lawesson's reagent.



2



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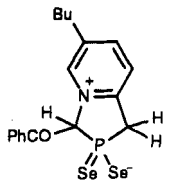
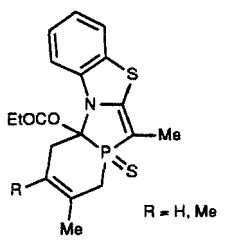


4

The sulfur analogue of **4** can be prepared from **1**, H_2S and S_8. 1-Methyl 3-carbethoxy 1,3-azaphospholo[5,1-*b*]benzothiazole yields with dimethylbutadiene/S_8 **5**, R = Me and with isoprene/S_8 regioselectively **5**, R = H.



5

References

[1] For a recent review on heterophospholes see: A. Schmidpeter and K. Karaghiosoff, in "Multiple Bonds and Low Coordination in Phosphorus Chemistry", M. Regitz and O. J. Scherer eds., Thieme, Stuttgart, 1990; p. 258.

[2] R. K. Bansal, K. Karaghiosoff, Neelima Gupta, A. Schmidpeter and C. Spindler, *Chem. Ber.*, **124**, 475 (1991).

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GENERATION OF ALKYL METAPHOSPHATES BY THERMOLYSIS OF O-ALKYL ESTERS OF PHOSPHORAMIDIC ACIDS

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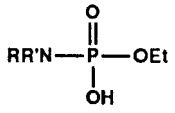
Phosphoramidic acid esters are known to be thermally unstable, and when decomposed in water or alcohols give phosphate products from replacement of the amino group. Both elimination-addition (EA) and addition-elimination (AE) mechanisms have been proposed for these solvolyses. We have now found conditions for the practical generation of alkyl metaphosphates by the EA mechanism in aprotic solvents. The thermolysis of several O-ethyl phosphoramidates was studied in various solvents (toluene, ethanol, acetonitrile, DMSO) at 45-110°C, as a possible source of ethyl metaphosphate.



1, R = mesityl, R' = H
2, R = 1-adamantyl, R' = H
3, R = phenyl, R' = H
4, R = R' = Et

From kinetics measurements, it was found that a large bulky N-substituent (as in **1** and **2**) was essential for the exclusive occurrence of the monomolecular EA process. With smaller N-substituents (as in **3** and **4**), the AE process is also sterically allowed and the bimolecular (AE) process accompanies the monomolecular process. The EA process for **1** and **2** was supported by the activation parameters, and by the kinetic isotope effects for nitrogen and hydrogen. The intermediacy of the metaphosphate was proved by trapping it through reaction with the surface OH groups on silica gel. All of **1-4** gave products with a CP-MAS ^{31}P NMR signal for a surface-bound ethyl phosphate group, with the same shift as observed when silica gel is reacted with ethyl metaphosphate generated by other processes. The method is also capable of generating other metaphosphates; thus, (-)-menthyl metaphosphate was so generated and successfully reacted with silica gel.

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^{31}P-CHEMICAL SHIFT ANISOTROPY IN $\sigma^2\lambda^3$-IMINOPHOSPHANES

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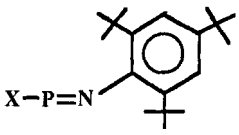
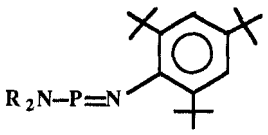
Gerhard-Domagk-Str. 1, D-5300 Bonn 1, Germany

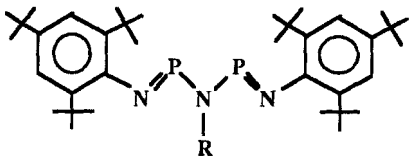
The high resolution $^{31}P\{^1H\}$-MAS-spectra spectra of the halogeno-iminophosphanes **1** (X = Cl, Br, I) as well as those of several amino-iminophosphanes and 2.4-diphospha-1.3.5-triazadienes of general formula **2** and **3**, respectively, were obtained. From the side-band intensities, the isotropic shift and the principal components of the anisotropic shielding (CSA)-tensor were determined.



1



2



3

The anisotropic chemical shift parameters show a close relation with the chemical structures. It can be shown that different types of substituents induce characteristic variations of individual tensor components. The anisotropic shift parameters further provide better understanding of substitution effects on the solution nmr data, although the observed differences of 5 - 117 ppm for the isotropic shifts give evidence that conformational relaxation processes may occur. The effect is most pronounced for the iodo-iminophosphane, whose unique solid state structure becomes also manifest in a totally different axiality of the CSA tensor.

For the amino-iminophosphanes and diphosphatriazenes **2** and **3**, respectively, a relation between the anisotropy of the chemical shift and the *cis*-or *trans*-configuration of the double bond may be estab lished. This allows the determination of the stereochemistry of these compounds exclusively on the basis of the nmr data.

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SYNTHESIS OF NOVEL BIS(PHOSPHONIO)-PHOSPHOL- AND BIS-(PHOSPHONIO)-ISOPHOSPHINDOL-CATIONS

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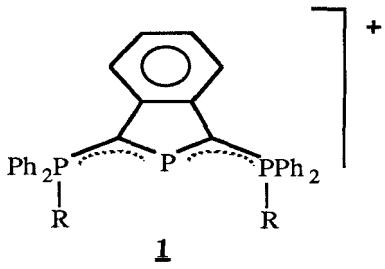
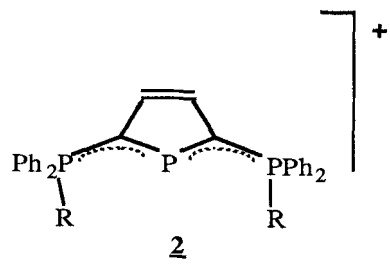
Anorganisch-Chemisches Institut der Universität Bonn,
Gerhard-Domagk-Str. 1, D-5300 Bonn 1, Germany

The synthetic approach to the Bis-(Phosphonio)-isophosphindol cation **1a** (R = Ph) by Schmidpeter and Thiele[1] is extended to the functionalized derivatives **1b** (R=2-pyridyl), **1c** (R = 2-thienyl), **1d** (R = Me), and the Bis-(phosphonio)-phosphol-cation **2** (R= pyridyl). **3** (R = pyridyl) containing a formal phosphinine ring was detected by spectroscopy.



1



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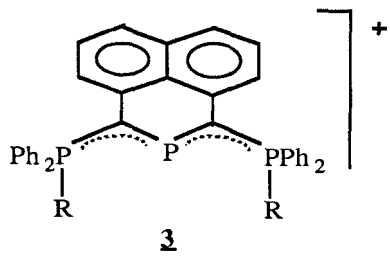

3

Even if the presence of Lewis basic centers in the pendant groups R makes **1b,c** potentially chelating ligands, the failure of **1b** to form stable transition metal complexes shows that the coordinating ability is still underdeveloped. In the reaction of **1b** with $AlCl_3$, evidence was obtained for the formation of a C-protonated product which underlines the ambident nucleophilicity of these systems.

[1] A. Schmidpeter, M. Thiele, *Angew. Chem.* **1991**, *103*, 333.

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METALLO(BISMETHYLENE)PHOSPHORANES AS BUILDING BLOCKS IN ORGANOPHOSPHORUS CHEMISTRY

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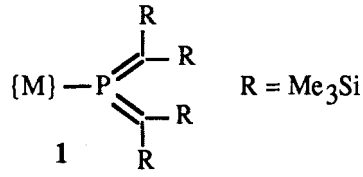
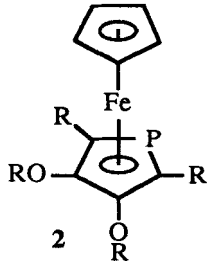
Brighton BN1 9QJ, Sussex, United Kingdom

Organometallic derivatives of bis(methylene)-phosphoranes **1** (e.g. {M}= Cp_2V (**a**), $CpFe(CO)_2$(**b**), Allyl-$Fe(CO)_3$ (**c**), Ni(Cl)PR'_3 (**d**), Pt(Cl)PR'_3 (**e**)) were obtained by nucleophilic displacement as well as insertion reactions starting from P-functionalized bis(methylene)phosphoranes.



1

The highly electrophilic phosphorus center initiates different rearrangement reactions depending on the electronic nature of the metall - ligands. By this, phospha-ferrocenes [1] (**2**), phosphole-complexes (**3**) and 2-phosphonioallene complexes of nickel and platinium (**4,5**) [2] were obtained. The reaction mechanism, spectroscopic and structural data are discussed.



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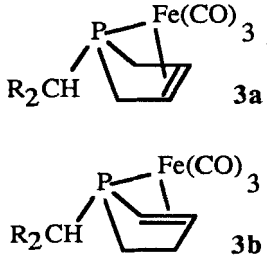
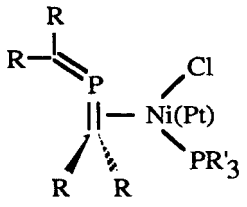


3a **3b**



4 (5)

[1] H.J. Metternich, E. Niecke, Angew. Chem. Int. Engl., **1991**, 30, 312.

[2] H.J. Metternich, E. Nicke, J.F. Nixon, R. Bartsch, P.B. Hitchcock, M.F. Meidine, Chem. Ber. **1991**, 124, 1973.

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Unusual Coordination In Phosphorus-Silicon Compounds

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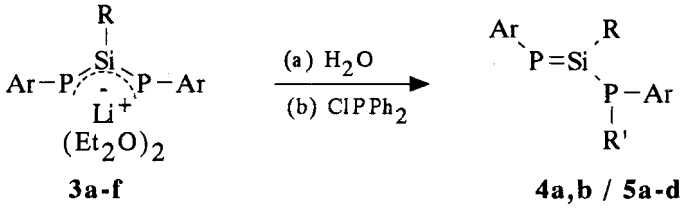
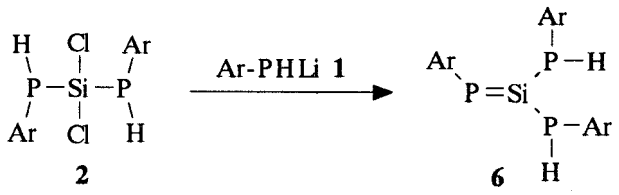
In analogy to the recently reported synthesis of the 1,3-diphospha-2-sila-allylic anion **3a** [1], the lithium salts **3b-f** have been obtained by treatment of **1** with the adequate substituted trichlorosilanes. The X-ray-structures of **3a-c** are discussed.
Mild hydrolysis (a) of **3a-d** or reaction of $ClPPh_2$ (b) with **3a,b** yields the phosphasilens **5a-d** (R'=H) and **4a,b** (R'=PPh_2). Structural investigation of **4a** leads to the first X-ray-structure of a Phosphasilene (P=Si-bond-length: 209.4pm).



3a-f **4a,b / 5a-d**

R= ^{t}Bu(**a**), Mes(**b**), Cp*(**c**), Is(**d**), Ph(**e**), OAr(**f**)

The phosphasilene **6** can easily be generated from the lithium phosphide **1** and the dichlorodiphosphinosilane **2**. The single-crystal-structure of **2** is also reported.



2 **6**

(Cp*= Me_5C_5; Is= 2,4,6-^{i}Pr$_3$C$_6$H$_2$; Ar= 2,4,6-^{t}Bu$_3$C$_6$H$_2$)

Reference:

[1] E. Niecke, E. Klein, M. Nieger, *Angew. Chem. 101*, **1989**, 792-793.

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HALOGENO-BIS(IMINOPHORANES) - SYNTHESIS, CRYSTAL STRUCTURE AND REACTIVITY

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ALEXANDER RUBAN
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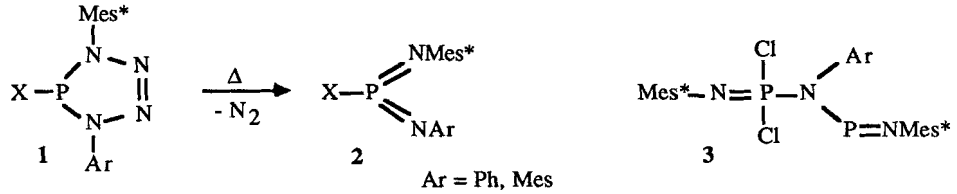
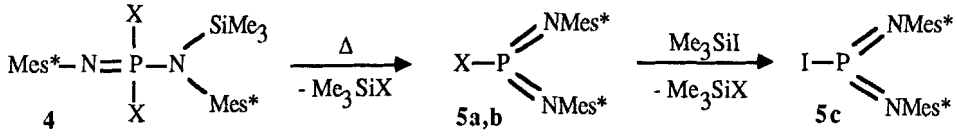
Halogeno(aryl)iminophosphines react with alkylazides[1] and arylazides at low temperature to the 4,5-dihydro-1H-tetrazaphospholes **1**. Compounds **1** can be transformed into the thermally unstable halogeno-diiminophosphoranes **2**, which have been identified by means of their n.m.r. data. In some cases they were trapped in form of the triaza λ^5,λ^3-diphosphapenta-1,4-dienes **3** by the educts.



Thermally stable P-halogeno-bis(2,4,6-tri-tert-butylphenylimino)phosphoranes **5a,b** have been obtained by thermal decomposition of corresponding $\sigma^4\lambda^5$-P,P-dihalogeno-aminoiminophosphoranes **4**. Treatment of compounds **5a,b** with excess of trimethyliodosilane leads to the formation of P-iodo-diiminophosphorane **5c**.



Mes* = 2,4,6-^{t}Bu$_3$C$_6$H$_2$; X = Cl, Br, I

The structural data of compounds **3** and **5** are discussed.

[1] E. Niecke, V. von der Gönna, M. Nieger, *Chem. Ber.*, **1990**, *123*, 2329-2333.

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TRANSITION METAL COMPLEXES OF P-FUNCTIONALIZED IMINOPHOSPHINES: SYNTHESES AND REACTIVITY

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JOHN F. NIXON*, BERNADETTE F. TRIGO PASSOS, MOHAMED F. MEIDINE
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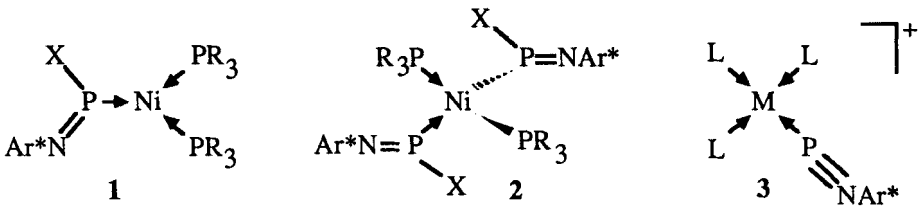
Treatment of $(PR_3)_2Ni(COD)$ with one or two equivalents of halogenoiminophosphanes produces the P-functionalized Ni-complexes **1** (R=PEt_3, PBu_3, PPh_3; X=Cl, I, Br) and **2** (R=PEt_3, PBu_3,PPh_3; X=Cl)[1]. A single-crystal X-ray diffraction study confirmes the expected tetrahedral conformation of **2** with η^1-bonded iminophosphine fragments. Similar results, established by n.m.r. data have been obtained in the Pt-systems, $Pt(X_2)(PEt_3)$(Cl-P=NAr*) [X = Cl, Br, I].



Reaction of **2** (R=Et, X=Cl) with two equivalents of a methylmagnesiumiodide results in the substitution of both chlorine atoms whereas reaction of **1** (R=Et, X=Cl) with one equivalent Grignard-Reagent in the presence of PEt_3 yields the tris(triethylphosphine)methyliminophosphine-nickel. The cationic complexes **3** (M=Ni, Pt; L=PEt_3, PBu_3, PPh_3, triphos) can be generated either by treatment of **1** with $AlCl_3$ or $NaBPh_4$ and an excess of phosphine or via *in situ* dehalogenation of the halogenoiminophosphine followed by addition of a transition metal complex. Using triphos as a ligand the bonding mode of the iminophosphine moiety has been proved to be η^1. The reaction of **2** (R=PPh_3; X=Cl) with two equivalents of $AlCl_3$ yields instead of a double charged complex *via* migration of a phenyl-group the bis(triphenylphosphine)-bis(phenyliminophosphine)-nickel.

[1] J.Hein, E.Niecke, M.F.Meidine, B.F.Trigo Passos, J.F. Nixon, J.Chem.Soc.,Chem.Commun., **1991**, 41-42.

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CYCLOADDITION REACTIONS OF METHYL- AND ETHYL(ARYL)IMINOPHOSPHINE

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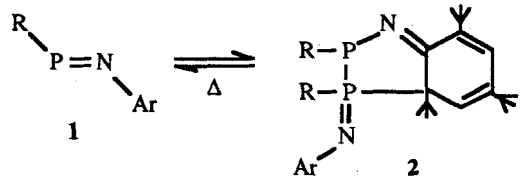
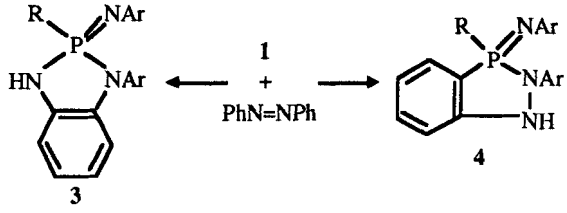
Gerhard-Domagk-Str. 1, D-5300 Bonn 1, Germany

Carbenic like alkyl(aryl)iminophosphines **1** containing a steric non protecting alkyl substituent at the phosphorus-atom, (R = Me, Et), undergo a reversible [4+1]-cycloaddition to the benzoazadiphospholes[1] **2**.



(R = Me, Et; Ar = 2,4,6-$tBu_3C_6H_2$)

1 react regioselective with *cis* and *trans* azobenzene to the azaphospholes **3** and **4**, respectively. The course of the reaction involves a [2+1]- (**3**) or [4+1]-cycloaddition reaction (**4**) of the iminophosphines[1].



The versatility of compounds **1** for the synthesis of three-membered phosphorus heterocycles has been further demonstrated by [2+1]-cycloaddition reactions with alkynes, alkenes, phosphaalkenes and iminophosphines.
The spectroscopic data of all reaction products as well as the X-ray structure of most of the ring system are discussed.

[1] E.Niecke, M. Link, M. Nieger, *Chem. Ber.*, in press.

Phosphorus, Sulfur, and Silicon, 1993, Vol. 77, p. 244
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PECULIARITIES OF THE MOLECULAR AND ELECTRONIC STRUCTURE OF $\delta^3\lambda^5$-IMINOPHOSPHORANES

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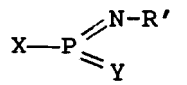
Institute of Organic Chemistry of the Ukrainian Academy of Sciences,253660,Kiev 94, UKRAINE

The main peculiarities and characteristic features of molecular and electronic structure of the $\delta^3\lambda^5$-iminophosphoranes have been studied on the basis of a large-scale X-ray diffraction and NMR (^1H, ^{13}C, ^{15}N, ^{31}P and ^{29}Si) studies. The "twisting" of the P=C double bond which indicates the p_π-p_π overlapping degree may change in an unusually wide interval (φ_{XPCR} =0-50°),depending on electronic and steric characteristics of the X substituent. However, the P=C bond length is independent of the φ value; this is connected with the peculiarities of the three-centered four-electron π-system. On the other side, the dynamic NMR data (in solution) indicate a correlation between the φ value and the rotation barrier around this bond. The cis- or trans- orientation of substituents X and R'relatively to the P=N double bond is shown to be determined by the balance of stereoelectronic (n_N-δ^*_{P-X} etc.) effects and intramolecular steric interactions. The differences in molecular and electronic structure of phosphoranes and initial compounds - iminophosphines X-P=N-R' and phosphaalkenes X-P=CR_2- are considered. On the base of the X-ray diffraction studies of products of $\delta^3\lambda^5$-phosphoranes transformation, some of their reaction pathways are revealed. In particular, the formation of four-membered zwitterionic cycles where a co-ordinatively unsaturated state of a transition metal may be stabilized, is proved at the interaction of $\delta^3\lambda^5$-phosphoranes with metal derivatives.



X = Ar, Alk, NR_2, PR_2, OR et al.
Y = CR_2, NR_2, S

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PERFLUORO-2-PHOSPHAPROPENE AND BIS(TRIFLUOROMETHYL)-DIPHOSPHENE - SYNTHONS FOR NOVEL PHOSPHA HETEROCYCLES

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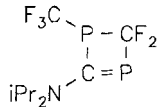
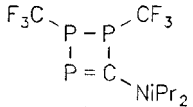
Abstract The cycloaddition reactions of $F_3CP{=}CF_2$ and $F_3CP{=}PCF_3$ with $P{\equiv}CR$ and R_2CN_2 has been investigated.

The stabilizing effect of fluorine and/or π-donor substituents is used for the preparation of E=C and E=E (p-p)π systems[1]. Thus the fluorophosphaalkene $F_3CP{=}CF_2$ and the in situ generated diphosphene "$F_3CP{=}PCF_3$" have been shown to act as excellent dienophiles and therefore are suitable synthons for the preparation of new [2+4]-cycloadducts[2].
Here we will report on the application of these reactive species in the syntheses of the novel four- and five-membered ring compounds A to C with F_3CP building units.



A



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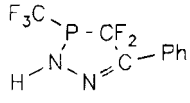
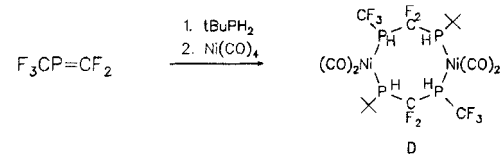


C

In addition, the preparative potential of $F_3CP{=}CF_2$ is demonstrated by the simple two-step synthesis of the macrocycle D according to the following equation:



D

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2. (a) J. Grobe, D. Le Van, W. Meyring, B. Krebs, M. Dartmann, J. Organomet. Chem., 346, 361 (1988); (b) J. Grobe, Th. Großpietsch, D. Le Van, J. Schulze, B. Krebs, M. Dartmann, ibid., 385, 255 (1990).

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2H-1,2,3-DIAZAPHOSPHOLES AND 2-METHYL-5-PHENYL-1,2,3-DIAZAARSOLE IN REACTION WITH ETHYL DIAZOACETATE

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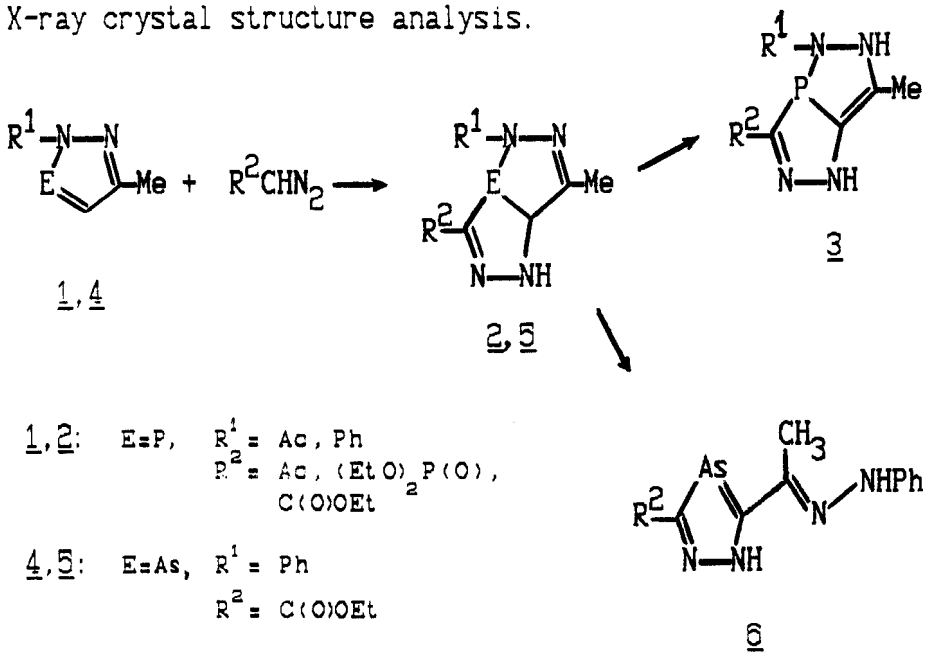
Butlerov Chemical Research Institute
of Kazan University, Russia

A comparison of 2H-1,2,3-diazaphospholes and 2H-1,2,3-diazaarsoles with monosubstituted diazocompounds is carried out herein.

2R^1-5-methyl-1,2,3-diazaphospholes 1 react with diazocompounds $RCHN_2$ (ethyl diazoacetate, acetyl diazomethane, diethoxyphosphoryl diazomethane) to form bicyclic products 2, which isomerise in crystalline form or in solutions to 3.

5-Methyl-2-phenyl-1,2,3-diazaarsole 4 in the reaction with ethyl diazoacetate yields two crystalline 1:1 products 5, 6. The structures of the both products are determined by X-ray crystal structure analysis.



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ATTEMPTS TO PREPARE METAL BASE/ACCEPTOR COMPLEXES: LIGANDS WITH TIN AS LEWIS ACIDIC CENTRE

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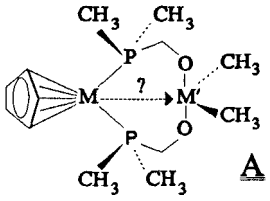
Abstract Phosphine ligands with tin as acceptor centre were coordinated to electron rich Cr(0)- and Rh(I)-compounds and examined for metal→Sn interactions.

INTRODUCTION

The spectroscopic data of succesfully synthesized complexes of type A do not give conclusive evidence for M → M' interactions[1]. In order to improve the acceptor strength of M' we recently have chosen the "soft" acceptor centre tin as partner for the "soft" metal bases. Due to the tendency of Sn to realize coordination numbers higher than 4, the synthesis of ligands with Sn acceptors is expected to be more difficult than that of the corresponding Si or Ge containing compounds[2,3].



A

CONTENTS OF THE CONTRIBUTION

- Systematic studies to produce ligands of the type $Me_3SnXCH_2PMe_2$ and $Me_2Sn(XCH_2PMe_2)_n(CH_2CH_2PMe_2)_{2-n}$ (X = O, CH_2; n = 0 - 2),
- experiments to build up donor/acceptor ligands in the coordination sphere of $Cr(CO)_5$ and the photochemical synthesis of $Cr(CO)_5L$-complexes,
- attempts to use the electron rich Rh(I)-compounds $(\eta^5\text{-}C_5Me_5)Rh(CO)_2$ and $(\eta^5\text{-}C_5H_5)Rh(C_2H_4)_2$ as partners for the Sn/P ligands,
- the complete spectroscopic investigation (^1H, ^{13}C, ^{31}P, ^{103}Rh, ^{119}Sn-NMR, Mößbauer) of the new compounds and the X-ray diffraction analysis of some representatives in order to elucidate the coordination geometry and the bonding situation at tin.

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3. E. M. Reifer, Dissertation, WWU Münster (1992).

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ARYLDITHIOXOPHOSPHORANES AND DITHIADIPHOSPHETANES - CPMAS, CV-INVESTIGATIONS, CRYSTAL STRUCTURE AND *ab initio* CALCULATIONS

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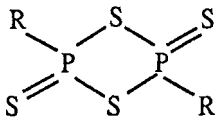
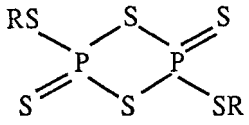
Postfach 8640, 4800 Bielefeld , Germany

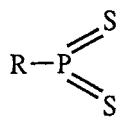
As is known the thionation of 2,6-disubstituted phenylphosphanes yields either dithiadiphosphetanes **1** or aryldithioxophosphoranes **3**. Applying 2,4-di-*tert*-butyl-6-methylphenylphosphane we were able to obtain the aryldithioxophosphorane **3** and furthermore the *cis*-and the *trans*-isomer of **1**. We have taken ^{31}P CP-MAS spectra of different compounds of type **1, 2** and **3**. These spectra are discussed considering results of IGLO-calculations.



1



2



3

Quantum chemical calculations were carried out for some selcted compounds to support the interpretation of shielding tensors. Effects of substituents and conformative changes were considered. The IGLO-calculations allow the assignment of the principal values of the tensors.

Treatment of Ar_f-PH_2 (Ar_f = 2,4,6- $(CF_3)_3$-C_6H_2, 2,6-$(CF_3)_2$-C_6H_3) or Ar_f-P=P-Ar_f with sulfur leads to corresponding dithioxophoranes **3**, the structure of which has been proven by X-ray structure analysis.
The redox behaviour of **3** (Ar = 2,4,6-tBu_3-C_6H_2) were determined by cyclic voltammetry. Quantum chemical calculations at UHF and MCSCF level on the radical anion, **3**, were carried out on its structure and electronic configuration.

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INTRAMOLECULAR DONATOR-ACCEPTOR INTERACTION - CONCEPT TO STABILIZE PHOSPHENIUM IONS AND PHOSPINIDENES

K. Diemert, G. Krautz, and W. Kuchen

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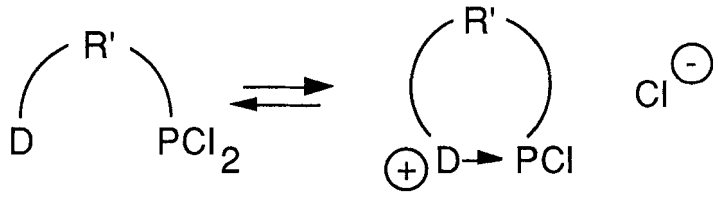
In contrast to carbenium cations the corresponding phosphenium ions could be stabilized by π-backdonating substituents [1]. A new route of stabilizing these compounds is described following the concept of intramolecular trapping [2] and donator-acceptor stabilization of low coordinated species [3].

Chlorophosphines of general type D-R'-PCl_2 **1** (R' = aliphatic or aromatic spacer group; D = group containing O, N, P as donor atoms) have been synthesized according to the following equation

$$D\text{-}R'\text{-}P(NEt_2)_2 + 2\,PCl_3 \longrightarrow \mathbf{1} + 2\,Cl_2P(NEt_2).$$

In solutions of **1** there exists an equilibrium



1 **1a**

containing first examples of well characterized phosphenium cations stabilized by intramolecular donator-acceptor interaction [1,4].

It has been shown by VT-^{31}P-NMR and conductivity measurements that the equilibrium is shifted to the right by decreasing temperature and strongly depends on solvent, donor properties of D, flexibility of the spacer R'.

By reaction of **1** with molar quantities of $AlCl_3$ in CH_2Cl_2 the corresponding phospheniumtetrachloroaluminates $[D\text{-}R'\text{-}PCl]^+[AlCl_4]^-$ are obtained.

Reduction of **1** lead only to cyclo-oligophosphines rather than to "phospinidenes" stabilized by intramolecular donation.

[1] M. Sanchez, M. - R. Mazières, L. Lamandé, R. Wolf in *"Multiple Bonds and Low Coordination in Phosphorus Chemistry"* by M. Regitz and O. J. Scherer; Thieme Verlag, **1990**, literature cited therein

[2] K. Diemert, B. Kottwitz and W. Kuchen, *Phosphorus Sulfur* **1986**, 26, 307

[3] R. Corriu, G. Lanneau and Ch. Priou, *Angew. Chem.* **1991**, 103, 1153

[4] Y. van den Winkel, J. van der Laarse, F. de Kanter, T. van der Does, F. Bickelhaupt, W. Smeets and A. Spek, *Heteroatom Chemistry* **1991**, 2, 17

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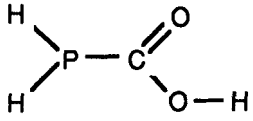
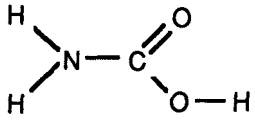
THE HITHERTO UNKNOWN PHOSPHINOFORMIC ACID H_2PCOOH - STABILIZED AS LIGAND IN A CHROMIUM(0)CARBONYL-COMPLEX

K. Diemert, T. Hahn, and W. Kuchen
Institut für Anorganische Chemie und Strukturchemie
Heinrich-Heine-Universität Düsseldorf, 4000 Düsseldorf 1, Universitätsstr. 1, FRG

Phosphinoformic acid **1** are unstable like their analogue carbamic acid **2**.



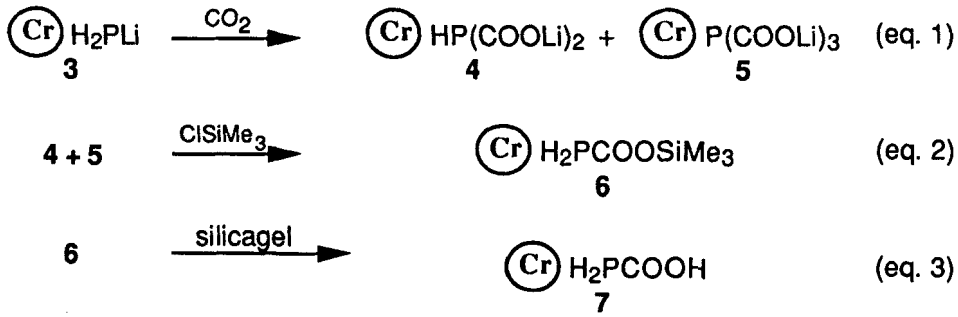
1



2

Efforts to prepare the phenyl substituted compound Ph_2PCOOH by protolysis of the corresponding alkaliphosphinoformate resulted in decarboxylation with formation of Ph_2PH [1].

We have found, however, that acids **1** can be stabilized by coordination via P to a $(CO)_5Cr$-moiety [Cr] following the procedure according to eq. 1 - 3. Thus, the reaction of **6** with silicagel at room temperature provides the mild conditions necessary to prevent the decarboxylation of the ligand in **7**.



Compound **7** is a yellow solid which is stable under nitrogen and decomposes slowly in contact with moist air. The spectroscopic data confirm the coordination via phosphorus in **6** and **7** [2].

More examples of complexes of substituted phosphinoformic acids are given.

[1] K. Diemert, T. Hahn, W. Kuchen, *Phosphorus, Sulfur Silicon Relat. Elem.* **1991**, 60, 287 - 94

[2] **6**: ∂_P = -38.3 ppm; $^1J_{PH}$ = 339 Hz; ∂_C = 170.9 ppm; $^1J_{PC}$ = 66 Hz; $\tilde{\nu}_{as,COO}$ = 1695 cm^{-1}; $\tilde{\nu}_{PH}$ = 2337 cm^{-1}. **7**: ∂_P = -37.7 ppm; $^1J_{PH}$ = 342 Hz; ∂_H(OH) = 9.1 ppm; $\tilde{\nu}_{as,COO}$ = 1665 cm^{-1}; $\tilde{\nu}_{PH}$ = 2385 cm^{-1}.

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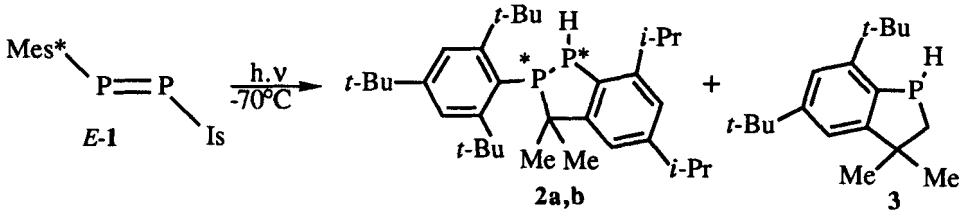
SYNTHESIS AND PHOTOREACTIONS OF *E*-1-(2,4,6-TRIISOPROPYL-PHENYL)-2-(2,4,6-TRI-*TERT*-BUTYLPHENYL)DIPHOSPHENE

CORINE M.D. KOMEN, SIMON J. GOEDE, FRIEDRICH BICKELHAUPT
Scheikundig Laboratorium, Vrije Universiteit
De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands.

Abstract The synthesis and irradiation of the title compound *E*-**1** are discussed.

The title compound *E*-**1**[1] was synthesized by reaction of Mes*PHLi (Mes* = 2,4,6-tri-*tert*-butylphenyl) with $IsPCl_2$ (Is = 2,4,6-triisopropylphenyl) followed by HCl elimination with DBU.



The main products of the irradiation (λ = 300 nm, T = -70 °C) of the title compound *E*-**1** are the diastereoisomers **2a,b**. Besides **2a,b**, some minor products were formed e.g. the cleavage product **3** ; this phosphaindane has also been obtained on irradiation of the symmetrical diphosphene Mes*P=PMes*[2].

Irradiation of *E*-**1** leads also to the thermally unstable cis-isomer *Z*-**1** which, however, rapidly reverts to the *E*-isomer at room temperature.

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2. A.-M. Caminade, M. Verrier, C. Ades, N. Paillous, M. Koenig, J.Chem.Soc., Chem. Commun., 875 (1984) ; M. Yoshifuji, T. Sato, N. Inamoto, Chem. Lett., 1735 (1988).

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SYNTHESIS AND REACTIVITY OF P-SUPERMESITYL-C-HALOPHOSPHAALKENES

SIMON J. GOEDE, HENK P. VAN SCHAIK, FRIEDRICH BICKELHAUPT
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De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

Abstract The synthesis of the title compounds in high yield via a new route are presented and their reaction with *n*-butyllithium and subsequent functionalisations is discussed.

The title compounds were synthesized in high yield via a one pot synthesis using carbenoids, generated from haloforms and bases, and Mes^*PCl_2 (Mes^* = 2,4,6-tri-*tert*-butylphenyl).

$$HCX_3 + Mes^*PCl_2 \xrightarrow[\text{or 2 LDA}]{2\ n\text{-BuLi}} \underset{\textbf{1a-c}}{Mes^*P{=}CHX} \text{ or } \underset{\textbf{2a-c}}{Mes^*P{=}CX_2} \qquad \begin{matrix}\text{a: X = Cl}\\ \text{b: X = Br}\\ \text{c: X = I}\end{matrix}$$

Reaction of (*E*/*Z*)-**1c** with *n*-butyllithium followed by electrophilic substitution of the intermediate phosphaalkenyllithium intermediate gave E/Z mixtures of new functionalized phosphaalkenes. The conformation of $(Mes^*P{=}CH)_2Hg$ was established by an X-ray structure determination. The other E/Z pairs could be identified by their ^{31}P NMR spectrum; especially the $^2J(PH)$ and $^2J(PE)$ coupling constants are diagnostic.

$$\underset{(E/Z)\textbf{-1c}}{Mes^*P{=}CHI} \xrightarrow{n\text{-BuLi}} \xrightarrow{EX} (Mes^*P{=}CH)_nE \qquad \begin{matrix}n = 1;\ X = Cl\\ \quad E = Me_3Si,\ Me_3Ge,\ Me_3Sn,\ HgCl\\ n = 2;\ X = Cl_2\\ \quad E = Hg\end{matrix}$$

The η^1-tertracarbonyliron complex of **2c** was prepared. A preliminary investigation of its reactivity towards *n*-butyllithium is presented. The formed phosphaalkenyllitiumtetracarbonyliron complex decomposes at low temperature giving $Mes^*C{\equiv}P$, presumably via a phosphorus analogue of an isocyanide intermediate, which could be observed in the ^{31}P NMR spectrum.

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(2-PHOSPHINO)PHOSPHOLYLS : A NEW TYPE OF η^1,η^5-HETERODIFUNCTIONAL LIGANDS FOR TRANSITION METAL CHEMISTRY

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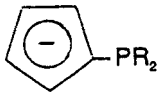
Laboratoire "Hétéroatomes et Coordination", URA CNRS 1499
DCPH, Ecole Polytechnique, 91128 Palaiseau Cedex, France

Phosphino-substituted cyclopentadienyls (1) have recently found a widespread use in coordination chemistry.[1] Their interest stems from the fact that they allow two types of transition metals to be held in close proximity in order to study their cooperativity in various reactions. On the other hand, phospholyls (phosphacyclopentadienyls) (2) have been shown to be able to replace cyclopentadienyls in a variety of η^5-complexes[2] (3) and to have the additional ability to coordinate a second metal via their phosphorus lone pair[2] (4). The previously unknown phosphino-substituted phospholyls (5) were thus a target of obvious interest for coordination chemists. We describe here the synthesis of the first such ligand, i.e. the 3,4-dimethyl-(2-diphenylphosphino)phospholyl anion (6) and some of its transition metal complexes.



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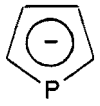

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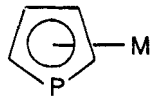

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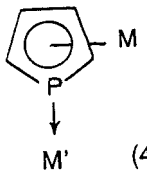

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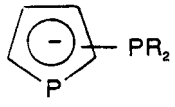

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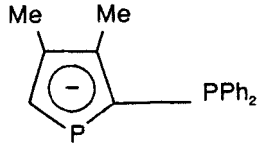

(6)

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1,3-DIPHOSPHOLYL, 1,3-ARSAPHOSPHOLYL AND 1,2,3-TRIPHOSPHOLYL : SYNTHESES AND CHARACTERIZATION.

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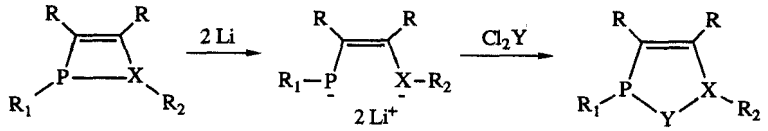
DCPH, Ecole Polytechnique, 91 128 PALAISEAU. France.

These compounds are prepared starting from 1,2-dihydro-1,2-diphosphetes and 1,2-dihydro-1,2-arsaphosphetes (**1**). Lithium and sodium metal are used to cleave the P-P or As-P bond leading to the formation of dianions **2**. The condensation of these dianions with Cl_2CH_2 or PCl_3 give rise to the five membered ring **3**.

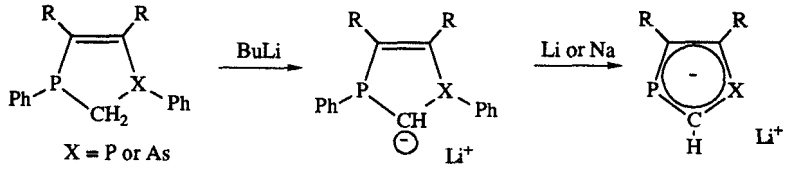


1 X = P or As

2 R = Ph, Me or Et R_1 and R_2 = Ph or Me

3a Y = CH_2
b Y = PCl

Butyllithium is used to extract a proton from compound **3a** to afford the carbanion **4**, which in the presence of lithium or sodium metal cleaves the P-Ph or As-Ph bonds leading to the desired 1,3-diphospholyl or 1,3-arsaphospholyl derivative **5**.

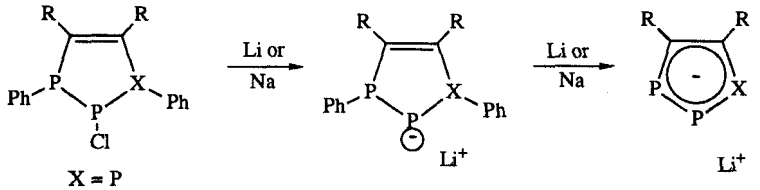


3a X = P or As

4a

5a

For compound **3b**, lithium or sodium metal affords in a first step the anion **4b**, then the 1,2,3-triphospholyl **5b**.



3b X = P

4b

5b

Compounds **5a** and **5b** react with $FeCl_2$ or $[\eta^6$-*p*-xylene$]Fe^{++}2PF_6^-$ leading to the sandwich complexes which are characterized by X-ray crystal structure analysis.

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COORDINATION CHEMISTRY OF A 2,2' BIPHOSPHININE

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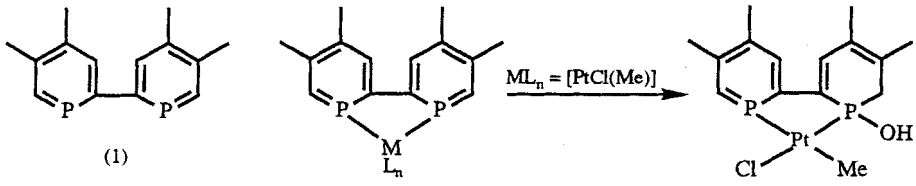
Abstract
The coordination chemistry of a 2, 2' biphosphinine is discussed.

The recent preparation of the first example of the strongly pi- accepting class of 2,2' biphosphinine ligands (1) (E^0_1 -1.85, E^0_2 -2.42V versus SCE)[1] suggests the possibility of building coordination complexes which will show interesting metal to ligand charge transfer properties when irradiated with low- energy photons. To investigate the viability of such an approach, we have prepared a number of coordination complexes $[M(L)_n(\text{biphosphinine})]$ and made comparisons of their properties.



Preliminary studies suggest that complex stability is inversely proportional to metal oxidation state for values between 0 and +2. Hence, $[Cr(CO)_4L]$ is resistant to hydrolysis, $[ReCl(CO)_3L]$ shows reasonable stability, and the platinum (II) complex $[PtCl_2L]$ (L = 4, 4' 5, 5' tetramethyl 2, 2'biphosphinine) is highly sensitive. We observe a selective hydrolysis of the phosphinine ring *trans-* to the chloride ligand in [Pt(Cl)(Me)L], which further suggests that electron density at phosphorus plays a significant role in the stability of the complexed biphosphinine ligand.

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Phosphorus, Sulfur, and Silicon, 1993, Vol. 77, p. 256
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Chirals Vectors. Synthesis of Chiral bisphospholyls and Application in Enantioselective Catalysis

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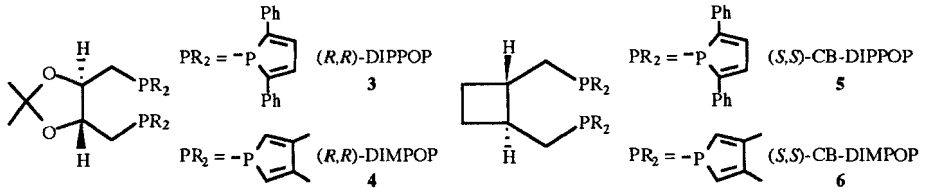
Laboratoire de Chimie de Coordination du CNRS, Unité N°8241, liée par conventions à l'Université Paul Sabatier et à l'Institut National Polytechnique, 205 route de Narbonne, 31077 Toulouse Cedex (France).

We recently reported that phospholes are very efficient ligands for the rhodium-catalyzed hydrogenation and hydroformylation of various kind of α-olefins [1]. Among the phospholes, 1,2,5-triphenylphosphole **1** and 1-phenyl-3,4-dimethylphosphole **2** appeared to present the required stereoelectronic properties to achieve high activities and regioselectivities in both the hydrogenation and the hydroformylation reactions.

Di- or polydentate ligands, especially phosphorus-containing ones, are finding increasing applications in homogeneous catalysis [2]. A large number of diphosphines bearing the PPh_2 substituents have been synthesized and successfully applied in enantioselective catalysis [3].

Chiral diphosphines bearing the dibenzophospholyl moiety have brought about efficient catalytic systems in enantioselective hydrogenation [4] and hydroformylation [5] reactions. However, as has been stated, the dibenzophospholes do not behave like typical phospholes [6].

The synthesis of the first chiral diphosphines bearing truly phospholyl moieties, (*R*,*R*)-DIPPOP **3**, (*R*,*R*)-DIMPOP **4**, (*S*,*S*)-CB-DIPPOP **5** and (*S*,*S*)-CB-DIMPOP **6**, involves the reaction of the phospholyl anion generated from **1** or **2** on the appropriate bis(tosylate) precursor.



Rhodium/**3** combinations or rhodium complexes of **3** are active catalysts for the enantioselective hydrogenation of (*Z*)-α-acetamidocinnamic acid and hydroformylation of styrene. A reversal of enantio selectivity with respect to (*R*,*R*)-DIOP, which exhibits the same absolute configuration, is observed.

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NOVEL SILYLATION OF FUNCTIONALLY SUBSTITUTED PHOSPHANES WITH HEXACHLORODISILANE

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Anionic trichlorosilylations of various functionally substituted phosphanes with Si_2Cl_6 provide new compounds with silicon to heteroatom bonds. These reductive silylations avoid the use of organometallic reagents and the addition of bases, even organic solvents may be unnecessary. The silylation of dialkylchlorophosphanes and diphosphanes provides trichlorosilylphosphanes, alkyldichlorophosphanes give bis(trichlorosilyl)phosphanes or cyclophosphanes.

$$R_2PCl + Si_2Cl_6 \longrightarrow R_2PSiCl_3 + SiCl_4 \qquad /1/$$

$$RPCl_2 \xrightarrow{Si_2Cl_6} \begin{cases} \longrightarrow RP(SiCl_3)_2 & (R= t\text{-Bu}) \\ \longrightarrow 1/n\ (RP)_n & (R= i\text{-Pr}) \end{cases}$$

Molecules with P-Si, P-Ge and P-Sn bonds are also cleaved by Si_2Cl_6 in a kind of "2+2" exchange reaction. Selective cleavage of one P-$SiMe_3$ group of t-BuP$(SiMe_3)_2$ with Si_2Cl_6 leads to chiral t-BuP$(SiMe_3)(SiCl_3)$ and oligomeric silicon chlorides Si_xCl_y, the formation of which might be due to base catalysed decomposition of $Me_3SiSiCl_3$ /2/. Contrary, the Si_2Cl_6 cleavage of organometal phosphanes $R_2P\text{-}MR'_3$ opens a completely new way to silyl-metal compounds under very mild conditions. For the recovery of R_2PMMe_3 from R_2PSiCl_3, reasonable paths have been developed.

$$R_2PMMe_3 + Si_2Cl_6 \longrightarrow Me_3MSiCl_3 + R_2PSiCl_3$$
$$M= Ge, Sn \qquad R= i\text{-Pr}, t\text{-Bu}$$

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NEW REACTIONS OF 1,1',3,3'-TETRAKIS(DIMETHYLAMINO)-1λ⁵,3λ⁵-DIPHOSPHET

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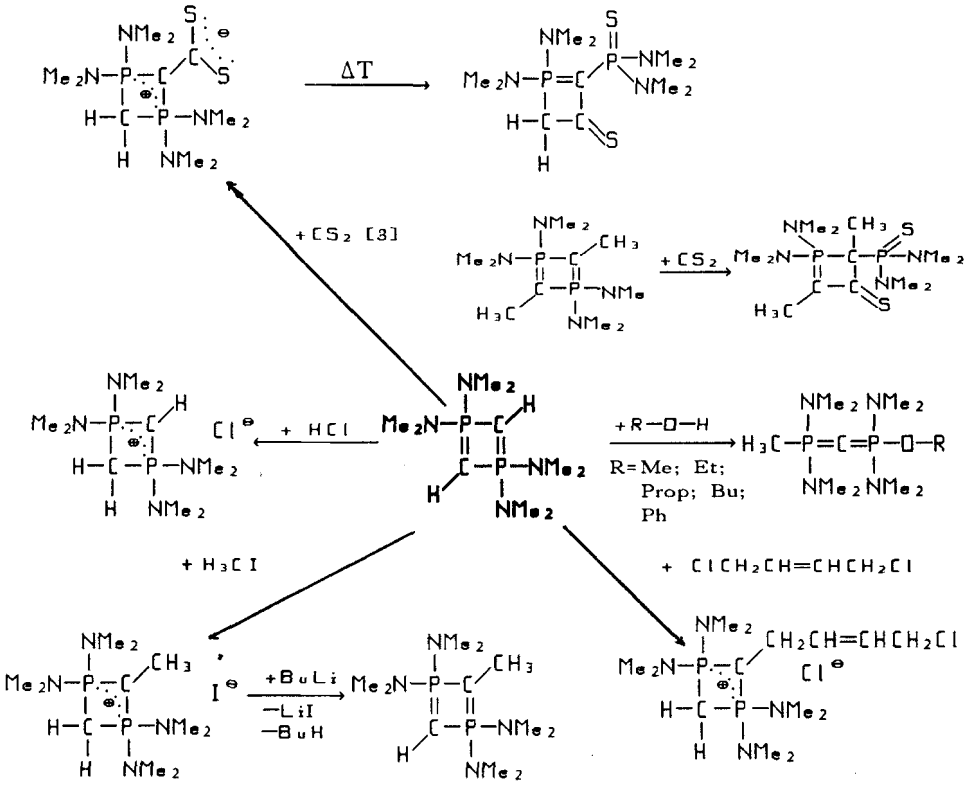
GMELIN-Institute for Inorganic Chemistry of the Max-Planck Society, Frankfurt
Institute for Inorganic Chemistry, Stuttgart

Abstract: The titel substance [1,2] reacts as a compound with high carbanionic character of the ring-C-atom. Several new reactions are shown leading to interesting products.



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MNDO, AM1, PM3 AND NMR STUDY OF THE FORMATION AND STRUCTURE OF PHOSPHONIO SUBSTITUTED ISOXAZOLINES AND ISOXAZOLIDINES

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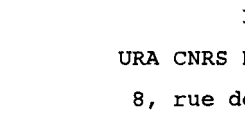
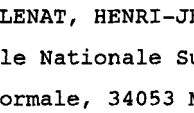
1,3-dipolar cycloaddition of nitrones and α,β-unsaturated phosphonium salts leads to a mixture of 4- and 5-phosphonio substituted isoxazolidines 4 and only 4-phosphonio substituted isoxazolines 5 in the case of ethylenic and acetylenic salts, respectively.[1]



1



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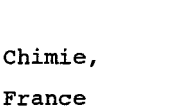

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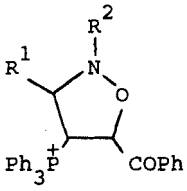

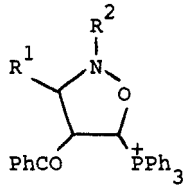

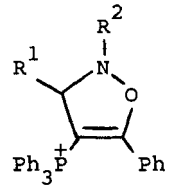

R^1 = H, Ph; R^2 = Me, tBu; R^3 = H, COPh

Some MNDO, AM1 and PM3 calculations[2] were accomplished to find the HOMO and LUMO electron density distribution for selected nitrones 1 and unsaturated phosphonium salts 2,3. Simple application of Klopman's equation did not lead to explication of the lack of regioselectivity observed for ethylenic phosphonium salts.

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APPLICATION OF AB INITIO ^{31}P NMR CHEMICAL SHIFTS CALCULATIONS

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Compounds of current research interest were chosen to investigate the influence of structure on ^{31}P NMR chemical shifts. These were calculated with the LORG[1] program.

PHOSPHAETHENES (**1**)

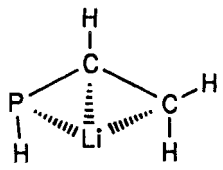
^{31}P chemical shifts of **1a** ($H-P=CH_2$) and **1b** ($Cl-P=CH_2$) with short half-lives in solution have been recently reported. Experimental and calculated LORG values are given below.

1a δ(exp.)[2] = + 230.1 ppm
δ(LORG) = + 220. ppm

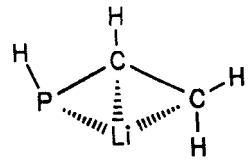
1b δ(exp.)[3] = + 300. ppm
δ(LORG) = + 304. ppm

PHOSPHA-ALLYL LITHIUM (**2**)

2a
E_{rel}= 0.00 kcal/mol
δ_{calc} (^{31}P) = - 112 ppm

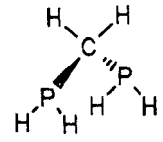


2b
E_{rel}= 0.20 kcal/mol
δ^{calc} (^{31}P) = - 100 ppm



Structure **2** (C_2H_4LiP) has two stable conformations **2a** ("cis") and **2b** ("trans"). The large dependence of the measured ^{31}P NMR shift on the solvent (δ_{exp}(^{31}P/pentane)=-82 ppm; δ_{exp}(^{31}P/THF)=-125 ppm)[4] may be due to aggregation as in similar systems studied before[5].

DIPHOSPHINOMETHANE (**3**, $H_2P-CH_2-PH_2$)



The detailed structure of **3** has not been experimentally clarified. While ab initio calculations (MP2(fu)//6-31G*) indicate 4 conformers to be minima of approximately equal energy, the chemical shifts calculated with LORG give the best agreement with experiment for the depicted rotamer with C_{2v} symmetry.

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SOLID STATE ^{31}P AND ^{13}C CP/MAS STUDY OF IONIC AND NEUTRAL RH(I) -BISPHOSPHINE-DIENE COMPLEXES

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S.AIME and R.GOBETTO University of Torino, Via P.Giuria7.,Torino 10125,Italy

INTRODUCTION: In the last decade a number of paper dealing with the solid state NMR investigations of organometallic compounds has shown the potential of this technique to get more insight into the structural and dynamic properties of such species. Due to the "narrower" significance of the term "equivalence" than in solution, high resolution solid state techniques may be particularly attractive in the investigation of the steric and electronic factors of the solid state structures of organometallic compounds.

RESULTS AND DISCUSSIONS : in solution the cationic complexes possess a C2 axis[1], however, this axis may or may not exist in the neutral complex depending on the solvent and temperature used. In solid state no element of symmetry has been observed, even the free ligand ((2S,4S) - 2,4-bis(diphenylphosphino) pentane, BDPP) exhibits two lines in the ^{31}P CP/MAS spectrum. Spectra of the ionic complexes ((Rh-BDPP-NBD)$^+$ BF_4^- and (Rh-BDPP-NBD)$^+$ ClO4-) with identical cations but different anions consist of two doublets,the nature of the latters has large impact on the chemical shifts and coupling constants. There are four doublets in the ^{31}P CP/MAS spectrum of the neutral complex (Rh-BDPP-NBD-Cl) what indicates the existence of two different molecules in the unit cell which is line with the crystal structure data[2]. The substantial difference of the chemical shifts and its principal tensor components is in support of a trigonal bipyramidal structure. **CONCLUSIONS:** It has been shown that the coordination to the Rh atom causes large increase of the chemical shift anisotropy of the phosphorus resonance , however, the determination of the tensorial components revealed that mainly the $\sigma 11$ components is affected by the coordination.

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NMR SIMULATION AND ITERATION TOOLS FOR PCs

NMR SIMULATION AND ITERATION TOOLS FOR PERSONAL COMPUTERS
Applications in Organo Phosphorus Chemistry

R. SPISKE, G. HÄGELE, H.W. HÖFFKEN, T. LENZEN, R. SPISKE,
U. WEBER, S. GOUDETSIDIS
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INTRODUCTION

Structural analysis of organo phosphorus compounds in the liquid and solution state is widely based on NMR spectroscopic methods using nuclei ^{31}P, ^{1}H and ^{13}C, in suitable cases further spin active elements like ^{19}F and others. Since modern PCs are fast enough for simulations or iterations of NMR spectra novel programs with convenient SAA user interfaces and graphical output facilities were developed. We wish to supply laboratories in research and practical applications with the following novel tools:

DSYM-PC
can be used for simulations of systems up to 8 spins with I = 1/2. The program supports chemical equivalence and both isotropic and anisotropic media.

DCYM-PC
additionally supports magnetic equivalence and nuclei with I >/= 1/2.

NMR-FILM
is a fast simulator for interactive use producing sequences of spectra varying up to six parameters in film fashion. Usefull and illustrative tool, in particular when iterations are difficult.

NMDR
is a simulator for 1D-double resonance spectra, helps to plan experimental work prior to spectrometer sessions and to understand results hereafter.

LAO
is a convenient iterator user interface to support work with the well known LAOCOON 5 by simplified data input and line assignment.

DAISY PROGRAM PACKAGE
Programs mentioned above represent parts of our strategy to implement towards the DAISY Program package on PCs. DAISY, previously designed for main frame computers allows for an almost automatical iteration even in difficult spectral situation. Practical problems will be solved.

The programs are available from the authors. Extensive references will be given in the poster.

Phosphorus, Sulfur, and Silicon, 1993, Vol. 77, p. 263
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SEMIQUANTITATIVE ANALYSIS OF OLIGOPHOSPHATE MIXTURES BY ^{31}P-^{31}P HOMONUCLEAR-2DJ NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

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Physical Sciences Center, Monsanto Corporate Research[1] and Performance Products Division, The Chemical Group of Monsanto[2], 800 North Lindbergh Blvd., St. Louis, MO 63167, USA

Abstract

One-dimensional ^{31}P NMR spectra of mixtures containing phosphate species with more than three phosphorus atoms per molecule are often complicated by overlapping resonances. In these cases, quantification can be extremely difficult. Homonuclear 2DJ-resolved spectroscopy has found widespread use because of its capacity to separate the effects of chemical shift and spin-spin coupling, although it is usually applied for structural identification of single compounds. In this work, the feasibility of applying and optimizing the 2DJ experiment for the quantitative analysis of oligophosphate mixtures is examined. The ^{31}P-^{31}P homonuclear-2DJ NMR spectrum of oligophosphate mixtures (i.e. sodium phosphate glass) when projected onto the chemical shift axis yields effectively homonuclear broadband decoupled spectra with simultaneous observation of all phosphorus-containing species. Semiquantitative determination of individual phosphate species is achieved through optimizing 1) dispersion at high magnetic fields, 2) the interpulse delay, 3) application of weighting functions to improve lineshape, and 4) curve fitting. Determination of individual species up to decapolyphosphate (n=10) is demonstrated. The average chain length determined by 2DJ NMR compares well with the value determined from elemental analysis.

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TRANSFORMATION OF WHITE PHOSPHORUS BY CARBONYL COMPLEXES

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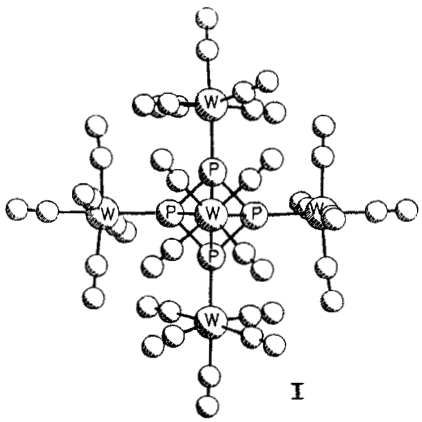
Weinbergweg 16, O-4050 Halle/S., Germany

The reactions of white phosphorus with cyclopentadienyl-carbonyl-complexes of various transition metals have been extensively studied, in contrast to the reaction of P_4 with carbonyl complexes.

The reaction of P_4-Phosphorus with $[M(CO)_5thf]$ (M = Cr or W) affords $[(CO)_4M(\eta^4\text{-}P_4\{M(CO)_5\}_4]$. The structure determination of the tungsten derivative **I** reveals a square-planar *cyclo*-P_4-ligand serving as a 12-electron donor (Fig.). This structure also exists in solution in CH_2Cl_2, whereas when a donor solvent such as thf or acetone is added, reversible changes to this structure are observed by nmr spectroscopy. The reactivity of these derivatives with tetrakis-(triorganylphosphano)-platinum(0) and phosphorus pentahalides is discussed.

The reaction of P_4 with $Fe_2(CO)_9$ gives a highly symmetrical complex $[\{Fe(CO)_4(\mu\text{-}P_2)\}_2\{\mu\text{-}Fe_2(CO)_6\}_2]$ **II** which contains a rectangular P_4-unit (Fig.) as a 16-electron donor.



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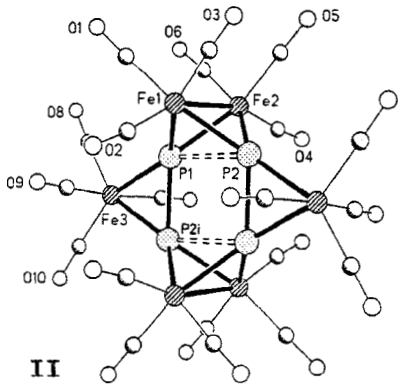

II

Phosphorus, Sulfur, and Silicon, 1993, Vol. 77, p. 265
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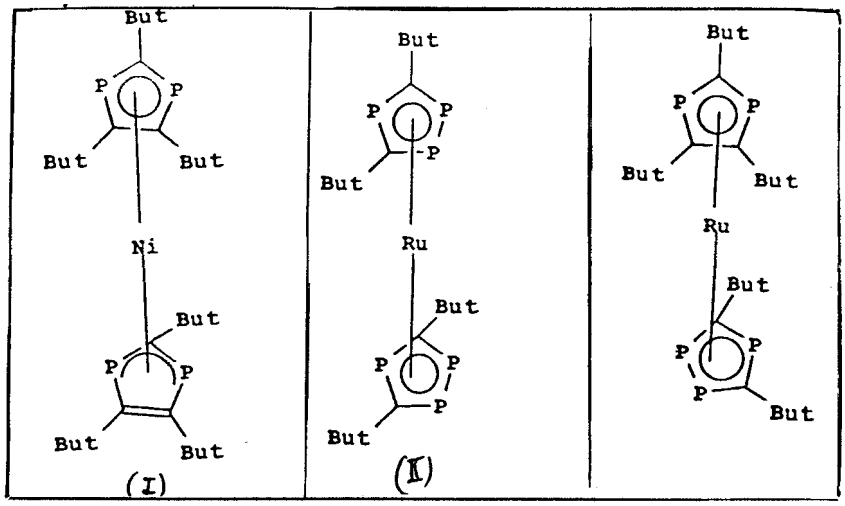
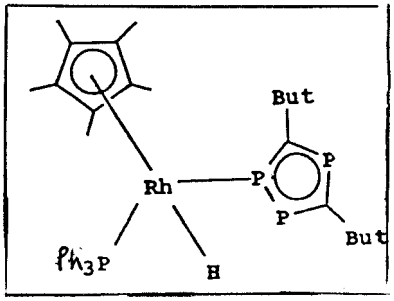
NOVEL COMPLEXES OF RHODIUM AND RUTHENIUM CONTAINING THE $P_3C_2Bu^t_2$ AND $P_2C_3Bu^t_3$ RING SYSTEMS.

By ROBSON MATOS, PETER HITCHCOCK and JOHN F. NIXON
(School of Chemistry and Molecular Sciences,
University of Sussex, Brighton, BN1 9QJ, Sussex, UK).

A variety of novel transition metal complexes typified by the selection shown below will be described and structural and spectroscopic (particularly nmr) data will be presented. Fluxional behaviour of (I) and (II) will be described. A remarkable transformation of the $P_3C_2Bu^t_2$ and $P_2C_3Bu^t_3$ ring systems in the presence of a Rh(I) complex will be described. Comparative data of $[M(\eta^5\text{-}P_3C_2Bu^t_2)_2]$, M = Fe and Ru; and the synthesis of the 'new' cage compound $P_4C_6Bu^t_6$ will also be presented and its structure discussed.





We thank CNPq for financial support (for RM)

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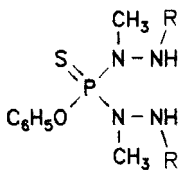
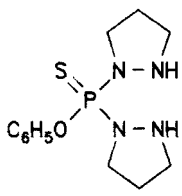
PHOSPHORIC ACID HYDRAZINE DERIVATIVES AS CHELATING LIGANDS

UDO ENGELHARDT, CHRISTINE RENZ-KREIKEBOHM AND BRIGITTE STROMBURG
Institut für Anorganische und Analytische Chemie der Freien Universität Berlin, Fabeckstr. 34-36
D-W-1000 Berlin 33, Germany

The title compounds **I** -**IV** form stable complexes with Cd- and Ni(II)-salts in alcoholic solutions. Depending on the substituents at N dimeric or polymeric complexes are found with Cl in bridging positions. The ligands are bonded via N alone or via N and S (five- and sixmembered chelate rings).



Ia : R = H
Ib : R = Me



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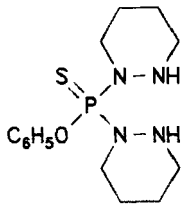
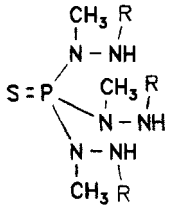
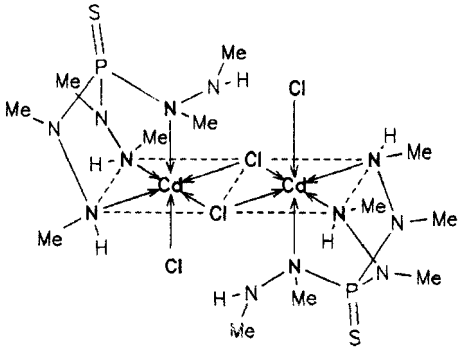


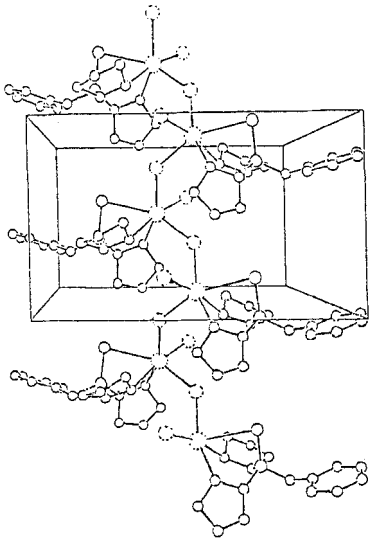
III



IVa : R = H
IVb : R = Me

X-ray structure determinations reveal octahedral or tetragonal pyramidal coordination at Cd.





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FUNCTIONALIZED PHOPHORUS HYDRAZIDES AS NOVEL CHELATING LIGANDS TO TRANSITION METALS.

K.V. KATTI,*[1] P.R. SINGH,[2] H. JIMENEZ,[2] C.L. BARNES,[2]
A.R. KETRING,[3] AND W.A. VOLKERT.[4]

Center for Radiological Research, Departments of Radiology[1] and Chemistry,[2] Research Reactor,[3] University of Missouri and Research Service, H.S. Truman Memorial VA Hospital,[4] Columbia, MO 65211. USA

Abstract There is current interest in the development of new bifunctional chelates (BFC's) of late transition metal radioisotopes (eg., ^{67}Cu, ^{105}Rh, ^{109}Pd) for radioimmunotherapeutic purposes. The ligating properties of π-acid phosphines have been extensively used to stabilize different oxidation states of electron rich late transition metals. However, the chemical inflexibility and the difficulty to derivatize the traditional phosphine based ligands has necessitated the search for new multifunctional ligand systems to produce immunoconjugates of ^{109}Pd, ^{105}Rh and ^{67}Cu for radioimmunotherapy (RIT). The physical properties of Pd-109 ($t1/2$ = 13.5 h, $E\beta$ = 1030 keV) makes it a potential candidate for RIT. We are currently interested in the development of new bifunctional chelating agents (BFCA's) for labeling proteins with Pd-109. In this connection, we have investigated the fundamental coordination chemistry of the functionalized phosphorus hydrazides ($RP(S)[NMeNH_2]_2$) and their carboxylate derrivatives with Pd(II) precursors. The extension of this chemistry to produce new bifunctional chelates of Pd-109 which contain a carboxylate group as a reactive moiety is described. The reactivity of these BFC's towards aliphatic amines has been evaluated as a model for the preparation of new bioconjugates. The utility of a carboxylate functionalized BFC to label human IgG with Pd-109 is also demonstrated.

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[2+2] PHOTOCYCLOADDITIONS OF [CpRu(DMPP)$_2$L] PF_6

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Department of Chemistry, University of Nevada, Reno, Nevada 89557

JEAN FISCHER
Laboratoire de Cristallochimie et de Chimie Structurale (URA 424 du CNRS)
Université Louis Pasteur, 67070 Strasbourg Cedex, France

Abstract A series of [CpRu(DMPP)$_2$L] PF_6 complexes, DMPP = 1-phenyl-3,4-dimethylphosphole, L = CH_3CN, Ph_3P, $PhSO_2CH{=}CH_2$, $(CH_3)_2NC(O)CH = CH_2$, PhN ≡ C, CO, pyridine and $P(OCH_3)_3$ were found to undergo sunlight initiated [2+2] photocyloadditions only when L is a good π- acceptor ligand. These [2+2] cycloadditions are accompanied by [4+2] cycloadditions. The ratio of the [2+2] to the [4+2] cycloaddition product is a function of the steric bulk of L. The reactive photo excited state is probably a ML charge transfer state. The complexes have been characterized by elemental analyses, infrared, electronic and ^1H, $^1H\{^{31}P\}$, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopy and in one case by single crystal X-ray crystallography.

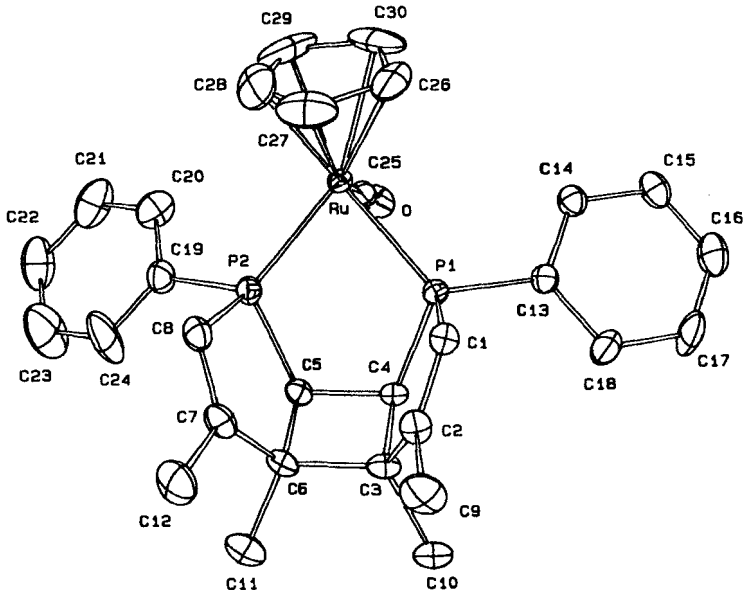

Figure 1 Ortep plot of the cation of the [2+2] photoproduct of [CpRu(DMPP)$_2$(CO)] PF_6

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UNEXPECTED BREAKDOWN OF A P-C BOND WHEN ATTEMPTING TO SYNTHESIZE THE CADMIUM SALT OF BUTANE-HYDROXY-1 AMINO-4 DIPHOSPHONIC-1 1' ACID.

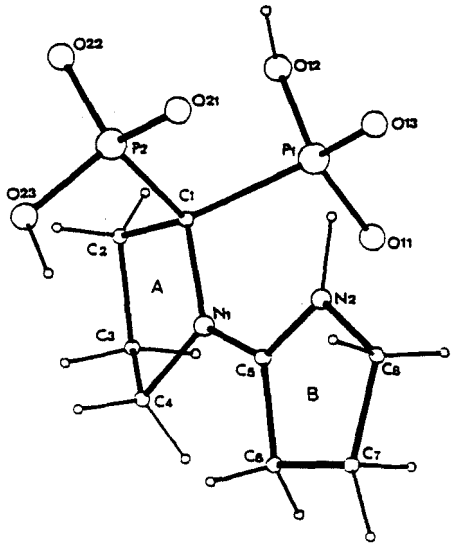
D. EL MANOUNI, Y. LEROUX, T. PRANGE, A. NEUMAN and H. GILLIER

Laboratoire de Chimie Structurale Biomoléculaire, (U.R.A. 1430 CNRS), 74, rue Marcel Cachin 93012 BOBIGNY CEDEX, FRANCE

Structure of the Cupric salt of butane-hydroxy-1 amino-4 diphosphonic-1, 1' acid is shown in poster n° X. Attempting to synthesize the Cd salt of the same acid through the Cd carbonate gives an example of an unexpected break down of the P-C bond of the diphosphonic acid.

The cristalline product obtained is the Betaine of Bis (dihydroxy phosphinoyl)-2,2' N(2',3',4'-H pyrrolyl)pyrrolidine.

NMR Data and mechanism of this surprising reaction is discussed. Biological aspects of the toxicity of Cd salts are also presented.



Phosphorus, Sulfur, and Silicon, 1993, Vol. 77, p. 270
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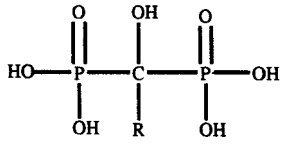
FUNCTIONNALIZATION INFLUENCE ON THE COORDINATION SCHEME OF SUBSTITUTED H.E.D.P Cu (II) SALTS.

Yves LEROUX, Alain NEUMAN, Hélène GILLIER, Driss EL MANOUNI and Thierry PRANGÉ

Laboratoire de Chimie Structurale Biomoléculaire, (U.R.A. 1430 CNRS), 74, rue Marcel Cachin, 93012 BOBIGNY CEDEX, France

In the course of a general study on complexed hydroxydiphosphonic acids, three Cu(II) complexes of differently subtituted HEDP's were prepared and investigated by X-ray diffraction methods.



R : CH_3 HEDP I
$(CH_2)_n$- NH_2 n = 3 II
n = 5 III

The HEDP methyl substitution in (**I**) by an aminopropyl (**II**) or an aminopentyl (**III**) chain, led to a drastic modification of the complex structures :

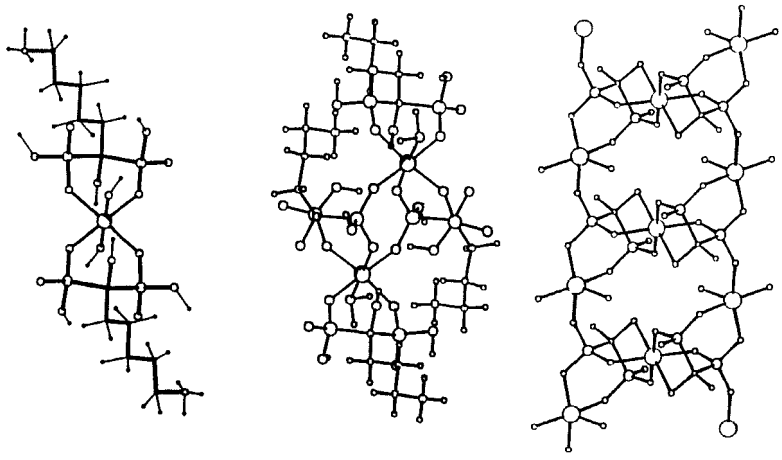
I : $Cu_3^{2+}((C(CH_3)(OH)(PO_3^{2-})(PO_3H^-))_2, 6H_2O$

II : $Cu^{2+}(C((CH_2)_3NH_3^+)(OH)(PO_3H^-)_2)_2, 2H_2O$

III : $Cu^{2+}(C((CH_2)_5NH_3^+)(OH)(PO_3H^-)_2)_2, 4H_2O$

The organisation of polyhedral complexation network around the Cu(II) has been found completely different in the three cases : a polymeric chain association (**I**), a tetrameric (**II**) and dimeric (**III**) arrangements.

On the basis of the molecular X-ray structures, a model including
i) the aliphatic chain elongation and
ii) the influence of the terminal ammonium group, which prevent for further Cu(II) coordinations, is proposed.



III II I

Phosphorus, Sulfur, and Silicon, 1993, Vol. 77, p. 271
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PALLADIUM AND PLATINUM PROMOTED DIASTEREOSELECTIVE INTRAMOLECULAR [4+2] CYCLOADDITIONS

WILLIAM L. WILSON and JOHN H. NELSON
Department of Chemistry, University of Nevada, Reno, Nevada 89557

NATHANIEL W. ALCOCK
Department of Chemistry, University of Warwick, Coventry CV47AL, England

Abstract Dichlorobis-(1-phenyl-3,4-dimethylphosphole) palladium (II), **1**, and dichlorobis-(1-phenyl-3,4-dimethylphosphole) platinum (II), **2**, react with two equivalents of $AgBF_4$ in CH_3NO_2 to form the $[(DMPP)_2Pd(BF_4)_2]$, **3**, and $[(DMPP)_2Pt(BF_4)_2]$, **4**, complexes containing very weakly bound BF_4^- ligands. These BF_4^- ligands are quantitatively displaced by 2-vinylpyridine, N,N-dimethylacrylamide, vinyldiphenylphosphine and divinylphenylphosphine to produce equilibrium mixtures of *cis*- and *trans*- $[(DMPP)_2ML_2](BF_4)_2$. Each of these complexes undergo intramolecular [4+2] Diels-Alder cycloadditions, producing racemic mixtures of cis $[(L - L')_2M](BF_4)_2$. The absolute stereochemistry of the first metal-promoted intramolecular [4+2] cycloaddition dictates, by virtue of interligand steric interactions, the absolute stereochemistry of the second [4+2] cycloaddition on the same metal center.

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NOVEL SYNTHESIS OF AN η^1-PHOSPHINIDENE OXIDE, (RP=O, R = Bu^tCH_2-) COMPLEX OF RHENIUM(I) FROM A PHOSPHA-ALKYNE PRECURSOR. CRYSTAL AND MOLECULAR STRUCTURE OF $[ReCl(Ph_2PCH_2CH_2PPh_2)_2(\eta^1\text{-}P(O)CH_2Bu^t)]$

By PETER B. HITCHCOCK, JULIAN A. JOHNSON, M. AMÉLIA N.D.A. LEMOS, MOHAMED F. MEIDINE, JOHN F. NIXON[a] and ARMANDO J.L. POMBEIRO[b]

[a] School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, E. Sussex, UK.

[b] Centro de Quimica Estrutural, Complexo 1, Instituto Superior Tecnico, 1096 Lisbon Codex, Portugal

Tervalent phosphorus compounds having the two-coordinate structure RP=O are rare and highly reactive species, which readily undergo cyclic head-to-tail trimerisation.[1] Compounds of the type X-P=O (X = F, Cl, Br) have been generated by the action of silver on appropriate phosphorus oxide trihalides at high temperatures and low pressures, and the gaseous products characterised by mass, photoelectron or IR spectroscopy. Alkyl- and aryl-phosphinidene oxides, RP=O (R = Ph, Bu^t), can be generated by several methods and trapped with a variety of reagents;[1] however, examples of metal complexes containing RP=O ligands are extremely rare.

Generation and stabilisation of RP=O (R = Pr^i_2N) within the coordination sphere of a transition metal was first reported by Niecke *et al.*[2] by the treatment of $Pr^i_2NP{=}NBu^t$ with $[Cr(CO)_6]$ followed by treatment with SO_2, and the *P*-bonded (κP) ligating mode was confirmed by a single-crystal X-ray diffraction study. Marinetti and Mathey[3] proposed the intermediacy of a κP-tungsten pentacarbonyl complex $[W(CO)_5\text{-}P(O)Ph]$ in the thermal fragmentation of the phosphinidene complex $[W(CO)_5PPh]$ in the presence of phenyloxirane, but its low stability prevented full characterisation.

We now report a stable *P*-bonded phosphinidene oxide complex of rhenium(I), which results from a completely different route to any previously described. It was formed upon N_2 replacement by $P{\equiv}CBu^t$[4-7] from *trans*-$[ReCl(N_2)(dppe)_2]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) in tetrahydrofuran (thf), presumably followed by addition of H_2O across the activated P≡C triple bond of the phosphaalkyne-κP coordinated to the bulky rhenium centre (Scheme 1).

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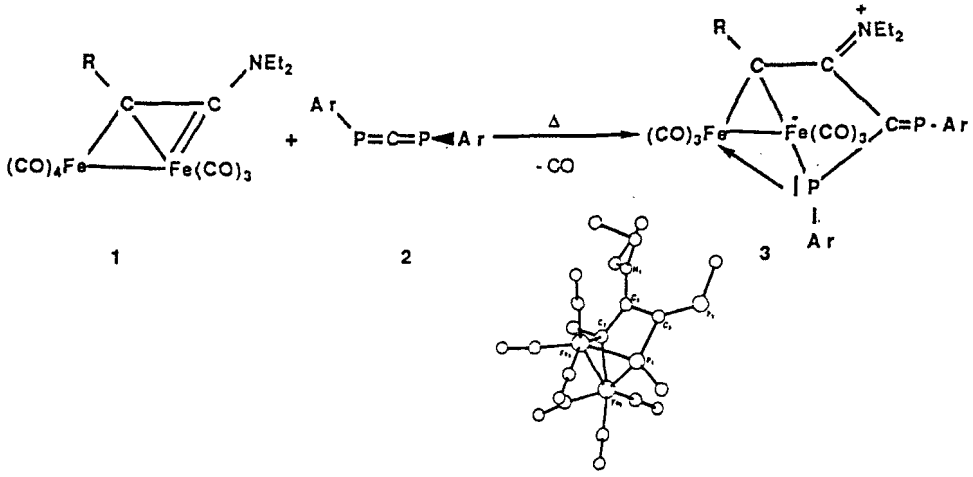
REACTION OF DI-IRON AMINOCARBENE COMPLEX WITH 1,3-DIPHOSPHAALLENE

MARYSE GOUYGOU, JEAN-CLAUDE DARAN, BERND HEIM, RENE THOUVENOT AND YVES JEANNIN.
Laboratoire de Chimie des Métaux de Transition, URA 419, Université Pierre et Marie Curie, 75252 Paris Cedex 05, FRANCE.

The reaction of dinuclear aminocarbene complex[$Fe_2(CO)_7\{\mu,\eta$-C(R)C(NEt_2)}]**1**,with various heterocumulenes (S=C=S , R'-N=C=X ; X=O, S, Se, N-R') normally involves the terminal carbene function but occasionally attack occurs at the bridging carbene function.

The reaction of complex **1** may be extented to the analogous phosphorus cumulene. The 1,3-diphosphaallene **2** reacts with **1** to yield complex **3** as the major product.



Complex **3** has been isolated and its X-ray crystal structure determined. The formation of **3** results from cycloaddition between the Fe=C and the P=C bonds with a subsequent C-C coupling. This compound can be viewed as a basket-like structure with the two Fe-C-Fe and Fe-P-Fe triangles forming the basket and the fragment C(NEt_2)C(PAr) providing the handle.

Phosphorus, Sulfur, and Silicon, 1993, Vol. 77, p. 274
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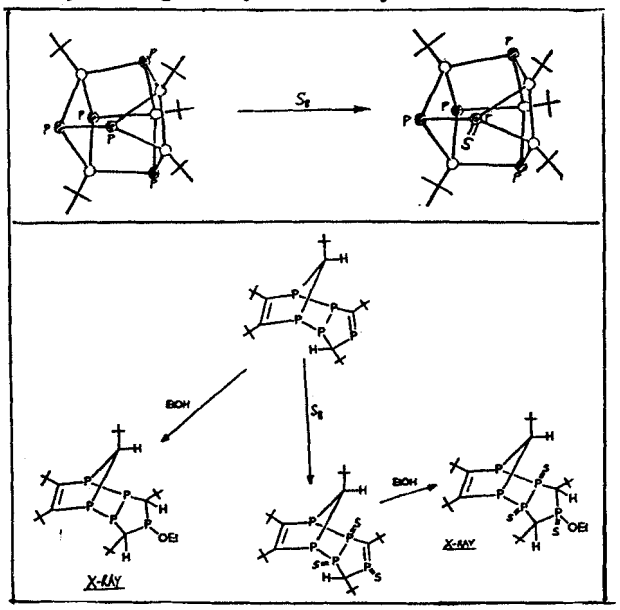
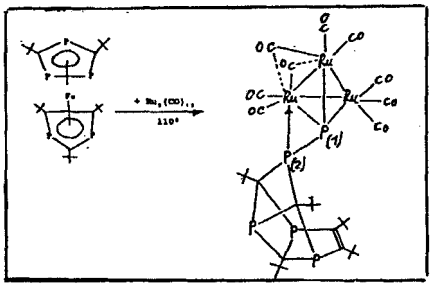
SOME NOVEL CAGES CONTAINING PHOSPHORUS DERIVED FROM PHOSPHA-ALKYNES INCLUDING AN UNUSUAL PHOSPHINO-PHOSPHINIDENE COMPLEX.

By RAINER BARTSCH, PETER HITCHCOCK and JOHN F. NIXON
(School of Chemistry and Molecular Sciences,
University of Sussex, Brighton, BN1 9QJ, Sussex, UK).

The novel cyclic and cage compounds shown below react with sulphur to give interesting products shown below and evidence for their structures will be discussed. A surprising reaction, involving loss of Fe from the sandwich complex $[Fe(\eta^5\text{-}P_2C_3Bu^t_3)(\eta^5\text{-}P_3C_2Bu^t_2)]$, generates the first example of a phosphino phosphinidene complex, which has been structurally characterised by a single crystal *X*-ray diffraction study.





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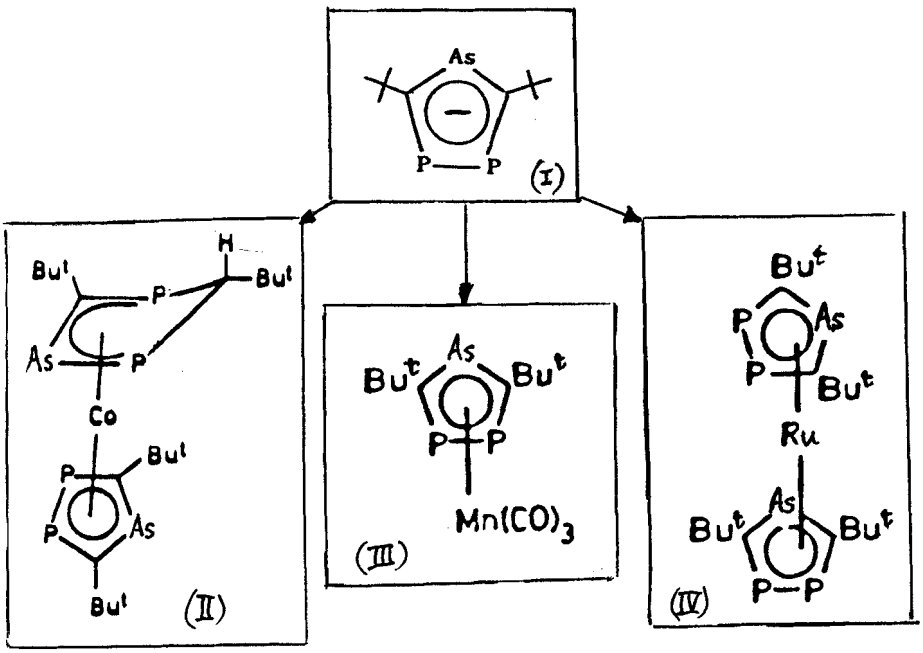
SYNTHESIS OF THE FIRST 4-ARSA-1,2-DIPHOSPHACYCLOPENTADIENYL ANION ($AsP_2C_2Bu^t_2$)- AND ITS COORDINATION TO TRANSITION METALS.

By RAINER BARTSCH, JULIAN A. JOHNSON and JOHN F. NIXON
(School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, E. Sussex, UK)

The new $AsP_2C_2Bu^t_2^-$ anion (I), which has been synthesised from Bu^tCP and $LiAs(SiMe_3)_2$, reacts with (i) $CoCl_2$ in dimethoxyethane to give the red complex $[Co(\eta^5\text{-}AsP_2C_2Bu^t_2)(\eta^4\text{-}AsP_2C_2Bu^t_2H)]$ (II), (ii) $[Mn(CO)_5Br]$ to give the orange oil $[Mn(CO)_3(\eta^5\text{-}AsP_2C_2Bu^t_2)]$ (III), and (iii) $[RuCl_2(PPh_3)_3]$ to give the sandwich complex $[Ru(\eta^5\text{-}AsP_2C_2Bu^t_2)_2]$ (IV), all of which have been structurally characterised by ^{31}P nmr and mass spectroscopy.



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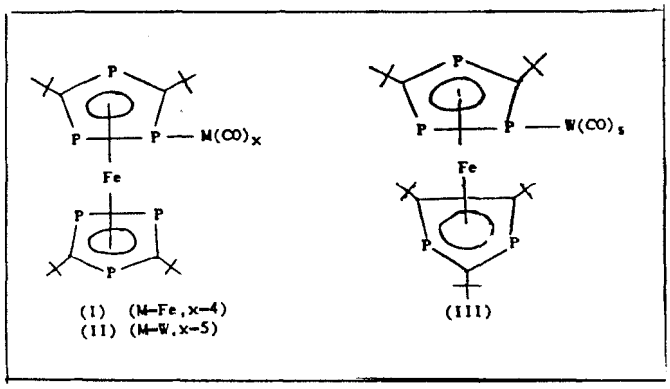
PENTA- AND HEXAPHOSPHORUS FERROCENES AS LIGANDS: CRYSTAL AND MOLECULAR STRUCTURES OF $[Fe(\eta^5\text{-}P_3C_2Bu^t_2)_2W(CO)_5]$, $[Fe(\eta^5\text{-}P_3C_2Bu^t_2)(\eta^5\text{-}P_2C_3Bu^t_3)W(CO)_5]$ AND THE NOVEL TRIRUTHENIUM CARBONYL CLUSTER COMPLEX $[Fe(\eta^5\text{-}P_3C_2Bu^t_2)_2Ru_3(CO)_{10}]$ CONTAINING TWO INTERLINKED $\eta^5\text{-}P_3C_2Bu^t_2$ RING SYSTEMS.

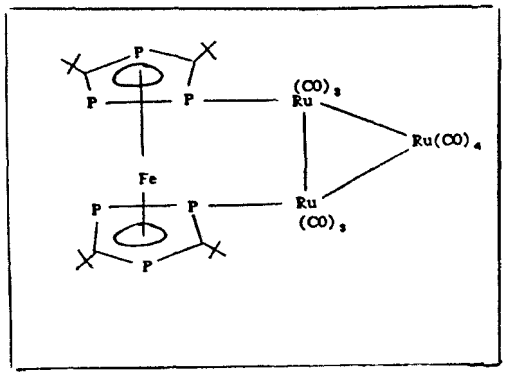
By RAINER BARTSCH, ACHIM GELESSUS, PETER B. HITCHCOCK and JOHN F. NIXON
(School of Chemistry and Molecular Sciences, University of Sussex, Brighton, BN1 9QJ, Sussex, UK).

The lone-pair electrons of one of the two directly bonded phosphorus atoms of the $P_3C_2Bu^t_2$ ring in the penta- or hexaphosphaferrocene complexes $[Fe(\eta^5\text{-}P_3C_2Bu^t_2)(\eta^5\text{-}P_2C_3Bu^t_3)]$ and $[Fe(\eta^5\text{-}P_3C_2Bu^t_2)_2]$ can ligate to other metal centres to afford novel bi- and tetrametallic complexes, whose structures have been elucidated by nmr and single crystal *X*-ray crystallographic studies.



(I) (M=Fe, x=4)
(II) (M=W, x=5)

(III)



Phosphorus, Sulfur, and Silicon, 1993, Vol. 77, p. 277
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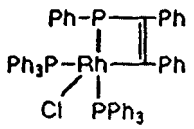
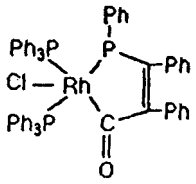
INSERTION REACTIONS OF THE [RhCl(PPh$_3$)$_2$] FRAGMENT INTO A PHOSPHIRENE RING, AND CARBONYLATION OF THE RESULTING Rh(III) COMPLEX. CRYSTAL AND MOLECULAR STRUCTURES OF [RhCl(PPhCPh=CPh)(PPh$_3$)$_2$],[RhCl(PPhCPh=CPhCO)(PPh$_3$)$_2$] AND THE DIMERIC COMPLEX [{RhCl(PPhCPh=CPhCO)(PPh$_3$)}$_2$].

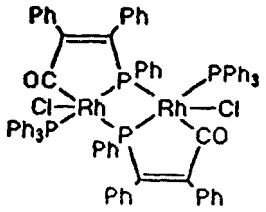
By FLORENCE A. AJULU[a], DUNCAN CARMICHAEL[a], PETER B. HITCHCOCK[a] FRANÇOIS MATHEY[b], MOHAMED F. MEIDINE[a], JOHN F. NIXON[a], LOUIS RICARD[b], AND M. LOUISE RILEY[a].

[a] (School of Chemistry and Molecular Sciences, University of Sussex, Brighton, BN1 9QJ, Sussex, UK).
[b] (Laboratoire de Chimie du Phosphore et des Metaux de Transition, DCPH Ecole Polytechnique, 91128 Palaiseau Cedex, France)

The first example of insertion of the d^8 Rh(I) fragment [RhCl(PPh$_3$)$_2$] into a phosphirene ring system results in a 5-coordinate Rh(III) complex, which undergoes insertion of carbon monoxide to give either monomeric [RhCl(PPhCPh=CPhCO)(PPh$_3$)$_2$] or dimeric [{RhCl(PPhCPh=CPhCO)(PPh$_3$)}$_2$], whose structures have been elucidated by nmr spectroscopy and single crystal *X*-ray diffraction studies.







The novel 8-membered ring complexes resulting from unusual insertion reactions of the opened phosphirene ring into the Pt-Cl bond of [PtCl$_2$(NCR)] complexes will also be presented and discussed. (Studies carried out in collaboration with Professor A.J.L. Pombeiro, Lisbon and Professor R. Michelin, Padova.)

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THE NATURE OF PHOSPHINE LIGANDS AS PROBED BY MOLYBDENUM-95 NMR SPECTROSCOPY

ELMER C. ALYEA AND SHUQUAN SONG
Guelph-Waterloo Centre for Graduate Work in Chemistry, Guelph Campus, Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada, N1G 2W1.

Abstract The ^{95}Mo chemical shifts for an extensive series of fac-$Mo(CO)_3(PY_3)_3$ (Y = R, Ar, OR, NR_2, halide) complexes, which occur over a 950 ppm range downfield from $\delta(^{95}Mo)$ for $Mo(CO)_6$ (-1857 ppm), prove a sensitive probe of the nature of the phosphorus(III) ligand. Correlations of $\delta(^{95}Mo)$ with various ligand parameters will be described. Correlation of $\delta(^{95}Mo)$ with Kabachnik's parameter ($\Sigma\sigma^{ph}$) provides a differentiation of the σ-donor and π-acceptor ability of the PY_3 ligands. The surprisingly low downfield position of $\delta(^{95}Mo)$ for the PCl_3 complex (-910 ppm vs -1860 for the PF_3 analogue) refutes the common literature description, deduced from infrared carbonyl data, of PCl_3 as a good π-acceptor. Our ^{13}C, ^{31}P and ^{95}Mo NMR evidence that PCl_3 is both a weak σ-donor and π-acceptor is consistent for the series of $Mo(CO)_{6-n}L_n$ (L = $PCl_{3-n}Ph_n$, n = 0-3) complexes as well as some related PBr_3 and $AsCl_3$ complexes and is readily explicable in terms of shielding theory for the quadrupolar ^{95}Mo nucleus. Similarly, the ^{95}Mo NMR data for their molybdenum carbonyl complexes allows an assessment of the coordinating ability of some unusual phosphorus(III) ligands undergoing complexation studies in our laboratory, i.e. bis(diphenylphosphinomethyl)dimethylsilane, 5-phenyldibenzophosphole (PhDBP) and 1,3,5-triaza-7-phosphaadamantane (PTA).

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METAL COMPLEX CATALYSTS WITH PHOSPHONIC ESTER PHOSPHANE LIGANDS FOR CARBONYLATION OF METHANOL

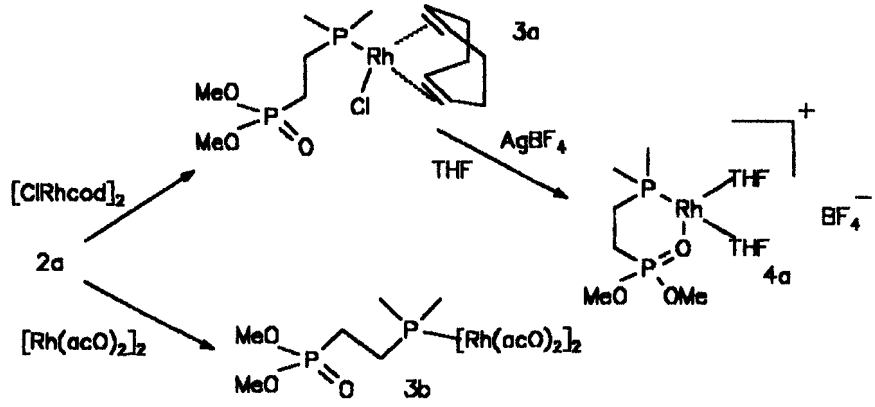
Axel Weigt[a], Jürgen Freiberg[a] and Herbert Dilcher[b], Germany;
[a] Gesellschaft zur Förderung der Umwelttherapie e.V., Berlin;
[b] Zentrum für Heterogene Katalyse, Berlin.

The treatment of technically available 2-(chloroethyl)phosphonic acid dimethylester (1) with diphenylphosphane and potassium-tert.-butylate affords 2-(diphenylphosphanoethyl)phosphonic acid dimethylester (2a) in a simple manner.

$$(MeO)_2P(O)CH_2CH_2Cl \xrightarrow{HPPh_2/KOC(CH_3)_3} (MeO)_2P(O)CH_2CH_2PPh_2$$

(1) (2a)

2a can be used as a hemilabile complex ligand by phosphane and phosphoryl group and it contains an ester function for anchoring of complexes on a catalyst support. Acyclic rhodium complexes 3a, 3b and cyclic complex 4a were obtained from 2a.



3a and 3b exhibit excelent catalytic properties in the liquid-phase carbonylation of methanol to acetic acid (MeOH-conversion 100%, AcOH-selectivity >90%, TOF 1800 gAcOH/gRh/h, at 180°C, 4,5 MPa, MeOH:MeI=8:1, Rh-concentration 200 ppm) [1].

1. J. Freiberg, A. Weigt, H. Dilcher, Chemiker Zeitung **1992** in print

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PHOSPHOROUS-31 NMR STUDIES OF THE HYDROLYSIS OF 'NORMAL' ZINC(II) *O,O*-DIALKYLDITHIOPHOSPHATE LUBRICATING OIL ADDITIVES AND RELATED COMPOUDS

ALAN J. BURN[a], IAN GOSNEY[b], PAUL S.G. TAN[b], AND JOHN WASTLE[b]

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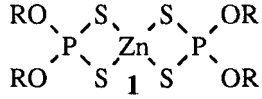
[b]Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, Scotland.

We have shown by ^{31}P NMR techniques that Zinc(II) bis(*O,O*-dialkyldithiophosphates), $Zn[S_2P(OR)_2]_2$, **1** (ZDTPs) undergo a complex hydrolytic process involving attack at zinc by water to form the intermediary *O,O*-dialkyldithiophosphoric acid, $PS_2(OR)_2$,



1

followed by further hydrolysis to thiophosphoric acid, $PS(OH)_3$. This species is then either hydrolysed further to give phosphoric acid, $PO(OH)_3$, the major product, or undergoes a series of transesterification reactions with the *O,O*-dialkylthiophosphoric acid to give the minor products *O*-alkylthiophosphoric acid, $PS(OH)_2(OR)$, *O,O*-dialkylthiophosphoric acid, $PS(OH)(OR)_2$, and *O*-alkylphosphoric acid, $PO(OH)_2(OR)$.

A number of ZDTPs bearing the following alkyl groups have been studied: R= ethyl, 2-propyl, 2-butyl, n-hexyl, 4-methyl-2-pentyl and 2-ethylhexyl. Kinetic studies show the reaction to be acid catalysed and that the size and nature of the alkyl group have little or no bearing upon the rate of hydrolysis. This constancy, besides providing further evidence for attack by water at the zinc centre rather than at phosphorous, also shows that for a given ZDTP, its structure represents no steric or hydrophobic hindrance to attack by water, presumably due to the remoteness of the alkyl groups from the tetrahedral zinc atom. We attribute this inability to provide a protective shield by the longer alkyl groups to hydrophobic interactions (otherwise called hydrophobic bonding). We have also observed that in the presence of its 'basic' form, $Zn_4[S_2P(OR)_2]_2O$, hydrolysis of 'normal' ZDTP is inhibited. This effect is asribed to the interaction between the O,O-dialkyldithiophosphoric acid formed during hydrolysis of 'normal' ZDTP and zinc oxide, a product of the decomposition of the 'basic' ZDTP.

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POLYMERIZATION OF β–PROPIOLACTONE CATALYZED BY NICKEL CARBOXYLATE - TRIBUTYLPHOSPHINE COMPLEX - DETERMINATION OF THE INITIATION STEP.

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Laboratoire de Chimie Macromoléculaire, Université Pierre et Marie Curie, Tour 44 , 4 Place Jussieu, F-75252 Paris Cedex 05, FAX : (33) (1) 44 27 70 89

INTRODUCTION

The anionic polymerization of 3,3-disubstituted β-propiolactones has been studied with tetraalkylammonium salt type initiators[1,2] and the propagation was found not to be stereoselective. In order to improve this stereoselection nickel carboxylates-tributylphosphine complexes were used[3], but in this case a new initiation step had to be determined.

RESULTS

The initiation was studied by infrared, ^1H NMR and UV light. Since the complex is not destroyed, no initiation occurs. Therefore it has been found: i- The colour diminishes gradually with time giving free phosphine and nickel carboxylate. ii- During this period, all the free nickel carboxylate is complexed by the lactone. Then iii- The free phosphine reacts with the "activated" lactone to give the true initiation and the first zwitterion $R_3P^+ (CH_2)_2COO^-$. iv- An order 2 with respect to monomer has been found. v- The rate of the initiation is given by the rate of the complex decomposition (point i) since points ii and iii are very fast. The initiation is faster in THF than in toluene and the rate depends strongly on the concentrations of the complex and/or of the lactone.
In conclusion, a new mechanism of initiation has been elucidated in the BPL polymerization catalyzed by nickel carboxylate-tributylphosphine complex and a new initiation rate constant k_i has been calculated.

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1- F.J. Carrière, C.D. Eisenbach Makromol. Chem., 182, 325 (1981)
2- F.J. Carrière, R. Blottiau, H. Sekiguchi Europ.Polym.J., 22, 285(1986)
3- F.J. Carrière, R. Blottiau, H. Sekiguchi Makromol.Chem.189,717(1988)

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To OPTIMIZE THE CRYSTALLIZATION PROCESS OF THE $CaO-P_2O_5-SiO_2$ GLASSES

JIA-HENG YEH and CHIN-WANG HUANG
Department of Chemistry, Chung Yuan Christian University,
Chung-Li 320, Taiwan, R.O.C.

Abstract The crystallization mechanism for five various SiO_2 content in $CaO-P_2O_5-SiO_2$ glass are discussed. By using nonisothermal technique, the activation energy of crystallization are from 66.7 to 92.6 $Kcal \cdot mol^{-1}$ and the parameter n are from 0.50 to 2.32. The microstructures and crystalline phases are also investigated base on SEM pictures and XRD patterns.

INTRODUCTION

On kind of glass-ceramic materials is prepared by the controlled crystallization of calcium phosphate glasses for use in prosthetic bone replacement.

EXPERIMENTAL

Glasses are prepared by melting the raw materials (Table I) in a mullite crucible at 1250 to 1350°C for two hours.

Table I The composition of the raw materials (in gram)

	$Ca(H_2PO_4)_2 \cdot H_2O$	$CaCO_3$	SiO_2
A	123.79	4.91	0
B	123.79	4.91	2.56
C	123.79	4.91	5.26
D	123.79	4.91	8.11
E	123.79	4.91	11.11

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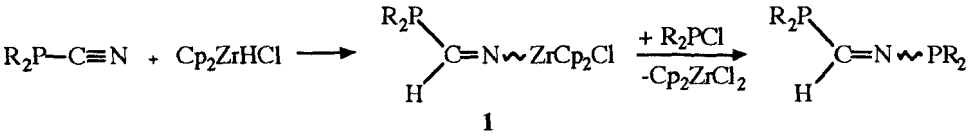
GROUP 4 ELEMENTS, TOOLS IN MAIN GROUP ELEMENT CHEMISTRY

Alain IGAU, Nathalie DUFOUR, Tom STRAW, Mike DEWEY, Florence BOUTONNET, Armelle MAHIEU, Maria ZABLOCKA and Jean Pierre MAJORAL*
Laboratoire de Chimie de Coordination du CNRS, 205, Route de Narbonne
31077 TOULOUSE Cédex, FRANCE

Titanium and zirconium species when reacted with unsaturated phosphorus compounds give rise to a large variety of original metallated (or not) phosphorus derivatives difficult or impossible to obtain via classical routes. Oxophilicity, halophilicity of group 4 elements, weakness of Zr-C, Ti-C bonds are the driving force of most of these reactions.
Some example :



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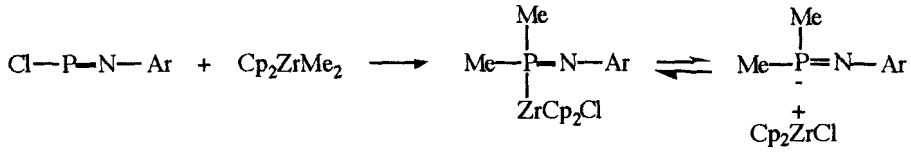

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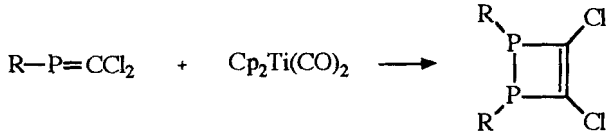

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The reactivity of compounds **1** to **3** will be reported. Evidence for the formation of the first zircona phosphene Cp_2Zr=P-R will also be given.

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HYDRAULIC CEMENT FOR ORTHOPAEDIC USES

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Calcium phosphates are largely used in orthopaedy and stomatology for bone defect filling, hip coating, etc . A new development has recently occurred : self-setting cements.
In addition to total biocompatibility, these cements require various specific properties such as a suitable setting rate and strengh, a good resorption rate.
We studied the synthesis, the physico-chemical characterization and the mechanical properties, of a cement prepared from dicalcium phosphate dihydrate (DCPD) and tetracalcium phosphate (TTCP). A mixture of these two reagents added to water forms an hydroxyapatite as follows :

$$2\ Ca(HPO_4).2H_2O + 2\ Ca_4(PO_4)_2O \text{ ------> } Ca_{10}(PO_4)_6(OH)_2 + 4\ H_2O$$

We examined the influence of the proportions of the reactants , the solid/solution ratio, pH, addition of H_2O_2, amino acid addition, and temperature on self-hardening and compressive strengh.
As a general rule, particle dimensions, in the range 20/120 μm, the solid/solution ratio and pH have no marked influence on the self-setting rate ; temperature however has a large influence : the duration of setting is about 3 hours at 25°C and 1 hour at 37°C. The addition of NH_4OH decresases the self-setting rate but increases the hardness. On the opposite, H_3PO_4 addition decreases the setting time from 3 hours to 10 minutes ; we can propose the formation of an intermediate $Ca(HPO_4),2H_2O$ phase which binds the particles. H_2O_2 addition does not affect the physical properties of the cement but can improve biological effects.
Biological tests, cell culture and biocompatibility tests were performed on the most promising samples.

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A SIMPLE METHOD OF PROVING THE INTRODUCTION OF URANIUM IN THE APATITIC STRUCTURE

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Apatites, Me10 (XO4)Y2, are well known to be the mineral host of uranium ; however no definitive proof have never confirmed the introduction of uranium ions in asignificant amount in the apatitic structure. In this study, uranium (IV) - containing silicoapatites were prepared and localization of uranium is proposed.

Apatite synthesis was carried out realized by a solid state reaction at high temperature (1000°C) and high pressure (60 kbars) according to the reaction :

$$3\ Ca\ SiO_3 + 3\ La_2O_3 + 3\ SiO_2 + CaF_2 \text{ -----> } Ca_4La_6(SiO_4)_6F_2$$

Uranium-containing britholite were prepared by a convenient replacement of calcium fluoride with uranium fluoride to obtain compounds containing 0.005%, 0.05%, 0.5% of uranium (atomic ratio). X-ray diffraction data confirm the formation of apatites for all the concentrations.

The registration of fissions tracks from the thermal neutron-induced fission of U^{235} in this material have been used to confirm the introduction of uranium in the apatitic structure, to study its distribution and to determine quantitatively its concentration. The presence of fission tracks in the heart of crystallites and the quasi linear variation of their density vs uranium content correlate with the progressive introduction of this element in the crystal lattice. Nevertheless one can observe that the fission track density reaches a constant level at 6000 ppm : this can be correlated with a limit to the amount of substituted uranium (0.6 % weight or 0.04 ion/unit cell. Furthermore, the decrease of the crystallite size seems also to be correlated with the introduction of uranium.

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SURFACE MODIFICATIONS OF HYDROXYAPATITE CERAMICS IN AQUEOUS AND BIOLOGICAL MEDIA.

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INTRODUCTION

Hydroxyapatite ceramics are widely used for orthopedic applications because they readily form physico-chemical bonds with bony tissue and promote bone formation (Bioactivity). Bioactivity is conditioned by the characteristics of the calcium phosphate-biological media interface and especially the surface alterations of hydroxyapatites ceramics. This report presents data on the chemical modifications of apatite ceramic surfaces in aqueous media

TECHNIQUES

Sintered hydroxyapatite pellets (relative density 95%) have been exposed at room temperature, to a series of aqueous solutions which varied in ionic strength, PH, and composition. The surface changes were determined by chemical analyses of the solutions, and direct examination of the surface using ESCA and IR reflectance spectroscopy.

RESULTS AND INTERPRETATIONS

Exposure to aqueous media modified the surface composition of sintered hydroxyapatites. ESCA studies showed Ca/P ratios as low as 0,9 compared to 1,6 for the original sintered material. ESCA angular analysis confirmed that only the first few atomic layers were altered. This phenomenon was interpreted as a surface hydrolysis of $PO4^{3-}$ groups to $HPO4^{2-}$, followed by a preferential release of calcium ions which ensures electrical neutrality of the surface. Experiments in saturated solutions showed however that the surface hydrolysis was not necessary linked to the dissolution of the apatite but probably arose from a surface equilibration process at the calcium phosphate surface. The $HPO4^{2-}$ surface groups were observed in several favourable cases by IR reflectance spectroscopy. The features of The IR spectra did not reveal, however , specific environments of these ions such as that of dicalcium phosphate dihydrate or octacalcium phosphate postulated by different authors.
In biological media the surface Ca/P ratio was also found to be very low. However, these media are generally supersaturated with respect to hydroxyapatite, and the surface hydrolysis was hidden by the formation of a neo-formed carbonate apatite exhibiting a low surface Ca/P ratio. Bone samples studied by the same technique also showed a very low surface Ca/P ratio consistent with those observed for all aqueous apatite surfaces in this study.

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STRUCTURE/TRANSITIONS/RELAXATIONS RELATIONSHIPS IN CARBONATED APATITES

Alain LAMURE*, Fatiha MISKANE**, Amina BENNIS**, Najia HITMI**, Mireille VIGNOLES*** and Colette LACABANNE*
* Paul Sabatier University, Toulouse (France)
** Mohammed V University, Rabat (France)
***E.N.S.C.T., Toulouse (France)

Apatitic structures are characterized by tunnels in which ions principally OH^- have two equilibrium positions. Reorientations of the related dipoles are responsible for the structural monoclinic-hexagonal transition T_t observed at 211.5 °C in hydroxyapatites. Previous studies by Thermally Stimulated Current (TSC) spectroscopy have shown that these reorientations are also at the origin of dielectric relaxations. Morover, these movements inside tunnels are cooperative and the compensation temperature T_c deduced from the analysis of TSC spectra has been found equal to the T_t temperature. This result shows that the kinetic of polarization phenomena can be used as fingerprint of hydroxyapatite structures. Complementary studies of carbonated hydroxyapatites and carbonated fluorohydroxyapatites have been investigated. The aim of this work was to precise the relationships between atomic arrangements and dipolar reorientations in carbonated apatites.

Comparative studies of stoichiometric hydroxyapatites and carbonated hydroxyapatites show the influence of $CO_3^{2-} \rightarrow PO_4^{3-}$ substitutions. These substitutions are evidently acompanied by defects (water, lacunae,...) in the apatitic structure. Analysis of the compensation temperatures T_c shows that carbonate ions facilitate the cooperativity of hydroxyl reorientations. A contrario, anionic substitutions inside tunnels like $F^- \rightarrow OH^-$ in carbonated fluorohydroxyapatites restrain the OH^- ions cooperativity. The existence of F···H-O and O-H···F hydrogen bonds prevents probably the hydroxyl reorientations.

These studies of carbonated hydroxyapatites confirm that like in hydroxyapatites the mobility of hydroxyl ions inside tunnels is governed by interactions of OH^- with ions inside and outside tunnels.

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Influence of Ca/P ratios on the Transitions of Hydroxyapatites by T.S.C.

A. Lamure*, A. Bennis***, F. Miskane***, N. Hitmi***,
M. Vignoles****, M. Heughebaert**** and C. Lacabanne*

*Paul Sabatier University, Toulouse (France)
***Mohammed V University, Rabat (France)
****E.N.S.C.T., Toulouse (France)

Natural filler of calcified tissues are non stoichiometric apatites characterized by a Ca/P ratio larger or lower than 1.66 (stoichiometric ratio). Structural studies of hydroxyapatites have shown that synthetic hydoxyapatites can occur in two phases - monoclinic or hexagonal- according to preparation method, approach to stoichiometry and thermal treatment. The transition from one phase to the other is of the order-disorder type. Previous works by Thermally Stimulated Current (TSC) spectroscopy have shown that the reorientation movements and arrangement of the OH^- ions in the apatitic tunnels can be characterized by a compensation temperature deduced from the analysis of TSC spectra. The aim to this work is to determine the influence of defects on the mobility of hydroxyl ions.

Calcium deficient hydroxyapatites have a TSC relaxation map quite analogous with the stoichiometric hydroxyapatites one : only one compensation phenomenon is observed. In that case, the non stoichiometry is only characterized by a lowering of the compensation temperature. This result shows that $HPO_4^{2-} \rightarrow PO_4^{3-}$ substitutions and presence of lacunae in calcium sites facilitate hydroxyl ions mobility. A contrario, in hydroxyapatites with calcium in excess, TSC relaxation map shows the existence of two compensation phenomena. In that case the non stroichiometry induces two phases.

As defects, responsible for modification of the crystalline structure, can be eliminated by annealing apatites at various temperatures, pretreated samples of non stoichiometric hydroxyapatites have been also studied By coupling pretreatment and relaxation map analysis, the origin of defects (hydrogenophosphate or water) has been determined.

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MAGNESIA AMIDOIMIPOLYPHOSPHATE CEMENTS.

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Mortars and concretes made from magnesia-phosphates cements are beeing used increasingly for rapid repairs. These cements provide a workable mix which sets within 15 minutes at 20°C, and hardens to over 20 MPa within 1 hour.
We propose a new magnesia-phosphate cement using amidoimidopolyphosphates.
By heating diamidophosphoric acid at 110°C[1], we obtain a mix of : ammonium hydrogeno diamido 1, 2 imidodiphosphates and ammonium salt of trimetaphosphimic acid.
Amidoimidopolyphosphate compounds are known to be converted in aqueous basic solution firstly into amidophosphates, then to ammonium orthophosphates[2]. So the magnesia-amidoimidopolyphosphate cement have a long setting time : 8 days, due to the gradual hydrolysis during the hardening reaction. This long setting time results in a decrease of the heat and loss of ammonia during the setting.
It have been shown that amidoimidopolyphosphates are more complexing than the corresponding polyphosphates[3]. Amidoimidopolyphosphates increase internal cohesion, and the cement have a greater mechanichal strength than the equivalent polyphosphates cements : 30 MPa.
We investigated the mechanism of hardening by X ray powder diffraction, ^{31}P nuclear magnetic resonance and infra-red spectroscopy. The mechanism of setting presents two steps :

- hydrolysis of the amidoimidopolyphosphate
- complexation of amidoimidophosphates by magnesium.

The resulting species are : monoamidophosphates, orthophosphates, ammonium hydrogeno diamido 1, 2 imidodiphosphates, pyrophosphates and polyphosphates.

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FORMATION AND CRYSTALLIZATION OF AMORPHOUS CALCIUM PHOSPHATE

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Studies were made to investigate the synthetic conditions of amorphous calcium phosphate (ACP) obtained by hydrolyzing calcium dihydrogenphosphate monohydrate (MCP) solution with aqueous ammonia and the crystallization of the ACP at a certain condition.
A strong point of the present work was to obtain ACP in various atomic ratios of Ca/P 1.25 1.55 by controlling the synthetic conditions such as temperature, pH, aging time, concentrations of MCP solution and aqueous ammonia. Also the crystallization of ACP in relative hummidity of 80% and in aqueous solution (pH 4 10) was discussed.

The MCP solution (0.005 0.07mol dm) was kept at 0 , and the aqueous ammonia (0.3 15N NH OH) was added quickly to the solution in the specified volume ratio (MCP/NH OH: 80/1 2/1, addition rate: 40cm min) with ranging from pH 6 to 12 and an gelatinous precipitate was obtained. The gel was separated from the mother liquor by filtering and then it was washed with cold aqueous ammonia and acetone.

The ACP in the present work could be roughly divided into three kinds of the low calcium type (L-ACP) and high calcium type (H-ACP), middle calcium type (M-ACP) between the both. The kinds of L-ACP (Ca/P atomic ratio: 1.25 1.30), M-ACP (Ca/P atomic ratio: 1.30 1.40) and H-ACP (Ca/P atomic ratio: 1.40 1.55) form respectively at pH 6, pH 8.5 and pH 11, but ACP becomes unstable with changing from the high pH to the low pH. The present work are emphasized to confirm the presence of unknown ACP of low calcium type and middle calcium type.

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SYNTHESIS AND THERMAL TRANSFORMATIONS OF Ca,Mg - CARBONATEAPATITE

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Ca,Mg-fluorohydroxycarbonateapatite was synthesized by the precipitation method. Na_2HPO_4, $CaCO_3$, $MgCO_3$, $Mg(OH)_2$, NaOH and KF were used as reagents. The formation of apatite proceeded through the stage of amorphous phase which evolves partly in the initial mixture and completely during heating into crystalline form. The samples obtained were studied by methods of chemical and thermal analysis, x-ray diffraction and IR spectroscopy. In spite of the different molar ratios Mg:Ca and CO_3:PO_4 in the reaction mixture these ratios in products are approximately equal (0.5:9.5 and 0.5:5.5, respectively). Under thermal influence the structure of the apatite obtained is relatively labile and undergoes changes of all its anion groups, especially in the part of carbonate-ions. The phenomena of the relocation of CO_3^{2-} ion and the forming of gaseous CO_2, the distortion of PO_4-groups and the appearance of P-O-P bonds, formation of OH...F hydrogen bonds and others were revealed.

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COMPOSITION AND PROPERTIES OF THE HEATING PRODUCTS OF CALCIUM PHOSPHATE - ALUMINOSILICATE MIXTURES

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For obtaining thermophosphate fertilizers from phosphate rock, the use of natural aluminosilicates (nepheline, glauconite a.o.) as reagents is possible. To determine the influence of different reagents on the composition and properties of the products, model mixtures on the basis of $Ca(H_2PO_4)_2 \cdot H_2O$ and $CaCO_3$ (with molar ratio CaO : P_2O_5=2.8 - 3.2), with natural aluminosilicates and pure SiO_2, $Al(OH)_3$, Fe_2O_3 and MgO, were prepared. The mixtures were calcinated at 1300 - 1400°C. The products were studied by chemical, x-ray and IR methods. By adding aluminosilicates (in amounts 6 -8%) to the calcium phosphates, products with 89 - 96% solubility in 2 % citric acid were obtained. The principal phases of the products are α- and β-$Ca_3(PO_4)_2$, with various substituents in the structure , as well the solid solutions of α-$Ca_3(PO_4)_2$ and α-Ca_2SiO_4.The 2% content of MgO or Fe_2O_3 in the mixtures of calcium phosphate with 4% SiO_2 decreases the solubility of P_2O_5 by 25% and 10% correspondingly. Al_2O_3 has no influence on the solubility of P_2O_5 in these mixtures.

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MIXED COBALT PHOSPHATES AND THEIR INFLUENCE ON THE CORROSION INHIBITION

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Abstract Pyrophosphates $Ca_xCo_{2-x}P_2O_7$ and tetrametaphosphates $Ca_xCo_{2-x}P_4O_{12}$ were prepared and verifying their presumed corrosion-inhibition properties.

EXPERIMENTAL AND RESULTS

Products were prepared by thermal dehydration of double hydrogen phosphates or corresponding mixtures of phosphoric acid with suitable calcium and cobalt compounds. The obtained condensed phosphates were thermally stable, water insoluble and slightly soluble in hydroxides and dilute acids (tetrametaphosphates). The paints used for the trials were prepared from medium alkyd resins. The anticorrosion performance of the paints was tested both in shortened laboratory tests, including salt-spray tests, sulphur dioxide tests, and long-term outdoor weathering tests in heavily-polluted industrial areas. The mechanical properties of the paints were evaluated as well. The protective performance of the new condensed phosphate pigments was better than that of zinc phosphate available on the market.

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MIXED METAPHOSPHATES AS ANTICORROSIVE PIGMENTS

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Abstract The metaphosphates are synthesized as new mixed compounds. The products are tested as stable compounds with anticorrosive properties.

RESULTS

Products represent the cyclo-tetraphosphates of bivalent cations $M^{II}_{2-x}Me^{II}_{x}P_4O_{12}$ (M^{II} is Zn, Me^{II} is Mn or Mg) in the whole range x, i.e. (0,2). In case of the products containing calcium the mixed compounds $M^{II}_{2-x}Ca_xP_4O_{12}$ is formed until molar ratio $Ca/M^{II}=1$ is reached. If the cations are trivalent metals like Al, Fe, Cr, mixed metaphosphates of $/(M^{III}_{1-x}Me^{III}_{x})(PO_3)_3/_n$ type are formed in the whole range of i.e.(0,1). If combined with bivalent metals (Al-Mg, Fe-Mg, Al-Zn), the products are mixed metaphosphates $/(M^{III}_{1-x}Me^{II}_{3x/2})(PO_3)_2/_n$ and or mixed cyclo-tetrametaphosphates$(M^{III}_{1-x}Me_{3x/2})_4(P_4O_{12})_3$. All these products due to their exellent special properties are very perspective. The results of corrosion tests are very good and comparable with classical Pb containing pigments.

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MIXED MAGNESIUM TETRAMETAPHOSPHATES

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Abstract Tetrametaphosphates (cyclo-tetraphosphates) of the type c-$Mg_{2-x}M^{II}_xP_4O_{12}$, where $x \in (0,2)$ and M^{II} = = Cu, Mn, Ni, Co, have been synthetized as new mixed (binary) compounds.

EXPERIMENTAL AND RESULTS

Procedure for the preparation of mixed magnesium tetrametaphosphates is based on a two-step thermal synthesis. The first step starts from pure tetrametaphosphates of the two bivalent metals which are melted in air and then abruptly cooled to give a vitreous amorphous product composed of higher linear polyphosphates. In the second step this product is repeatedly heated to a suitable temperature and recrystallized to give microcrystalline product - mixed tetrametaphosphates. The structure of the products belongs to the monoclinic system in the whole range of x. The volume of elementary cells of the mixed Mg-Mn and Mg-Co products quite regularly increases with an increase in the M^{II} content (x) (0.8433 to 0.9068 resp.0.8497 nm^3), in case mixed Mg-Ni products volume cell slightly decreases(0.8433 to 0.8278 nm^3) and in case of mixed Mg-Cu products slightly fluctuates in the x range (0.8405 to 0.8523 nm^3).

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ON THE DISSOLUTION OF APATITIC OCTACALCIUM PHOSPHATE

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INTRODUCTION :

Octacalcium phosphate exhibits interesting compression properties which could allow its use as a biocompatible and biodegradable material for osseous defect repair. The biodegradibility is closely related to the solubilities properties. As a prelimary study, we examined the dissolution of this phosphate in an unbuffered aqueous solution .

EXPERIMENTAL :

Powdered octacalcium phosphate was stirred in 500 ml of water at 37°C, and the composition (calcium and phosphate) and the pH of the solution were determined as a function of time. The modification of the solid phase was studied after filtering, by various techniques: X-ray diffraction, IR, Chemical Analysis, and Electron Spectroscopy for Chemical Analysis .

RESULTS AND DISCUSSION :

With regard to the solution, the calcium and phosphate release rates decrease with time, but the Ca/P ratio remain at a value of 0.5. Furthermore, a decrease of pH is observed. In the solid the Ca/P atomic ratio, initially equal to 1.33, increases with time, up to a value of 1.66 which is the Ca/P ratio of pure HAP, the most stable phase in solution. FTIR and ESCA studies reveal that the concentration of HPO_4^{2-} ions decreases; while the amount of apatitic OH^- ions increases.
The invariance of Ca/P atomic ratio in the solution during dissolution and the decrease of pH, can be explained by considering apatitic octacalcium phosphate to be transformated directly .
into HAP, without intermediate stages. The following equation is proposed for this process :

$$7\ Ca_8(HPO_4)_{2,5}(PO_4)_{3,5}(OH)_{0,5} \xrightarrow{6.5H_2O} 5\ Ca_{10}(PO_4)_6(OH)_2 + 6\ Ca^{2+} + 12\ H_2PO_4^-$$

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CATION-EXCHANGE CHARACTERISTICS OF SILICATE-CONTAINING APATITES

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ABSTRACT During investigation of the surface characteristics of various synthetic hydroxyapatites [$Ca_{10}(PO_4)_6(OH)_2$], we have discovered that cations in aqueous solution are held on some synthtic hydroxyapatites at room temperature and the behavior is not merely an adsorption effect but a type of ion-exchange reaction between cations in solution and lattice Ca^{2+} ions of the apatites. We have therefere begun to examine the feasibility of employing the apatites as a new inorganic "lattice cation ion-exchanger"* for the treatment of various toxic cations in solution. The purpose of the present paper is to examine an interesting removal behavior of Cd^{2+}, Zn^{2+} and Mn^{2+} ions in solution by newly-synthesized silicate-containg apatites. Two silicate-containing apatites (SiAp1 and SiAp2) were hydrothermally synthesized at 150 ℃ under saturated steam pressure for 4 days. The syhthetic samples were characterized by XRD and IR, and their chemical analyses were made by ICP. The removal characteristics of Mn^{2+}, Zn^{2+} and Cd^{2+} ions in aqueous solutions by the apatite samples were examined by using a normal batch method at 25 ℃. The analytical results showed that the chemical compositions of SiAp1 and 2 were $Ca_{10}(PO_4)_{5.3}(SiO_4)_{0.8}(OH)_{0.9}$ and $Ca_{10}(PO_4)_{4.2}(SiO_4)_{1.7}(OH)_{0.6}$, respectively. The specific surface areas of SiAp1 and SiAp2 were measured to be 17 and 19 m^2/g, respectively. It was found that the cation-exchange characteristics of lattice Ca^{2+} ions in the apatite samples for Mn^{2+}, Zn^{2+} and Cd^{2+} ions in solution were enhanced with increasing SiO_4^{4-} ions for PO_4^{3-} ions and especially SiAp2 shows 8 times larger amount of cation-exchange removal characteristics for Mn^{2+} ions compared with that of original hydroxyapatites [$Ca_{10}(PO_4)_6(OH)_2$]. The superior cation-exchange characteristics seem to be due to a produced "activated Ca^{2+} ions" in the apatite samples by a loosening effect on the skeletal structure of the apatite by the substitution of SiO_4^{4-} for PO_4^{3-} ions, assisted by attacking effect of H_2O molecules and other cations in aqueous solution. * T. Suzuki, T. Hatsushika and M. Miyake in New Developments in Ion Exchange, edited by M. Abe, T. Kataoka and T. Suzuki (Kodansha and Elsevier, Tokyo-Amsterdam, 1991), P.401.

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CHEMICO-PHYSICAL CHARACTERIZATION OF Na-POLY[BIS(CARBOXYLATOPHENOXY)PHOSPHAZENE] IN WATER SOLUTIONS

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In the present work Na-poly[bis(carboxylatophenoxy)phosphazene) (PCBPP-Na), which was first synthesized by Allcock[1] and whose potential biological applications were pointed out[2], is characterized in dilute aqueous solutions.

Two samples with different molecular weight of the charged polymer (PCBPP1-Na and PCBPP2-Na) have been characterized by means of viscosity measurements at 25°C in aqueous solutions at different ionic strength (NaCl) and the data obtained have been elaborated as proposed by Smidsrod[3]. The rigidity parameter B is found to be the same for the two samples and equal to 0.26, which is one of the highest values observed for polyelectrolytes, indicative for a high degree of flexibility.

Weight average molecular weight (M_w), radius of giration ($\langle R_g^2 \rangle_z^{1/2}$) and second virial coefficient (A_2) for the high molecular weight sample PCBPP1-Na were obtained by light scattering measurements performed in 0.12 N NaCl aqueous solutions. The best fitting of the extrapolated points at C=0 is obtained using a P(θ) function for polydisperse coil.

Preliminary results on the interactions of PCBPP-Na with Methylene-Blu (Mb) are also presented. A behaviour similar to Na-polystyrenesulfonate is found. The results obtained on addition of KCl to polyanion-dye system seem to indicate that the binding of Mb to PPCBP-Na is even stronger than that of Mb to Na-polystyrenesulfonate.

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CRYSTALLINE NITRIDOOXOPHOSPHATES DERIVED FROM PHOSPHORUS NITRIDE OXIDE

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Nitridooxophosphates [1-4] are hitherto described to exist as two crystalline types: $Na_nP_nO_{3n-3}N_2$ (n = 4-6); $M^I_3M^{III}P_3O_9N$ (M^I = Na, K; M^{III} = Al, Ga, Fe, Cr, Mn) and $M^I_2M^{II}_2P_3O_9N$ (M^I = Na, M^{II} = Mg, Co) [4]. In the present paper we report on a new type of crystalline nitridooxophosphates of the general formula

$$(MPN_2)_a \cdot PXN \cdot b\ H_2O,$$

wherein M = $K_{0.6} + H_{0.4}$; $Rb_{0.7} + H_{0.3}$; $Na_{0,5} + Cs_{0.5}$, X = O; $O_{0.9} + (NCN)_{0.1}$, a = 1, 2; b = 0 - ≈ 1.2.
The novel nitridooxophosphates which all belong to the same structure type can be considered as derivatives of $(PON)_n$ which bridging oxygen is partially substituted by -NM- groups. A general way to prepare these nitridooxophosphates is the heating of suitable mixtures containing compounds as sources of the alkali metal, of phosphorus, and of nitrogen; the maximum temperature may be 800 - 900 °C. Excellent nitriding agents - which should be used in excess - are nitrogen derivatives of carbonic acid, preferably melamine; their use is the cause of NCN content in reaction products. The obtained compounds are sparingly soluble in water, the K- and the Rb-salt have ion exchange properties.

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Solid solution Nasicon in the system Ca - Na - Ti - (PO_4) : Application for the elaboration of multicomponent phosphate bioceramics.

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Bioactive glasses in the phosphate system are use as implant materials for medical device.We presently observe the development of bioglass ceramics like CaO / P2O5 glasses containing TiO_2. Titanium oxide is used to form biocompatible Nasicon like compounds.We develop biomaterials from soft chemistry precursor:the polyphophates coacervates. When adding Anatase in suspension in the solution of Graham's salt, the coacervate precipitates after addition of multivalent cations (Ca, Mg) with the totality of TiO_2. After drying and grinding, we obtain a ceramic after heating at 900°C with this chemical composition : 13,5CaO, 12MgO, $8Na_2O$, $31,5TiO_2$, $34P_2O_5$. The thermal evolution can be summarized as following : In a first step, the phosphate chains are subjected to hydrolysis and led to amorphous hydrogen phosphate at 130°C.Afterwards thermal condensations and crystallisations occur at 400°C. The free and bonded waters are releasedbetween 80 and 400°C. For the coacervate without anatase, we obtain at 500°C two major compounds: Calcium sodium trimetaphosphate and magnesium sodium trimetaphosphate and also a little calcium metaphosphate. With anatase, we have a reaction above 700°C which gives sodium titanium orthophosphates - $NaTi_2(PO_4)_3$ Nasicon like compound. The formation of Nasicon phasis may be controlled in order to obtain a good biomaterial by this way. This lead us to study more particularly the comportement of these orthophosphates in the system Ca - Na - Ti - (PO4)

A complete solid solution has been prepared between $CaTi_4(PO_4)_6$ and $Na_2Ti_4(PO_4)_6$ by solid state reaction from stoechiometric mixture of Na_2CO_3, $Ca(PO_4)_2$, TiO_2 and $(NH_4)_2HPO_4$ at 970°C during 16 hours. In the range $0,5< x <1$, the X ray powder patterns are indexed with the space group R3c, on contrary, in the range of $0< x < 0,5$, extra lines led us to reassign the space group R3 , thus Ca and Na atoms are partly ordered. Infra Red study confirm the existence of a complete solid solution.Sodium ions can be totally exchange for calcium in Ca Ti4(PO4)6 using molten NaNO3 at 350°C. Reverse exchange failed.

This study of the formation of Nasicon solid solution shows the possibility of sodium ratio control in the glass phasis of multicomponent phosphate ceramic obtained by coacervate process. Thus it is possible to obtain adaptable durability of phosphate ceramic in biomedical application.

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A SIMPLE METHOD TO STUDY THE DISSOLUTION OF APATITIC MATERIALS IN ACID SOLUTIONS

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INTRODUCTION

Over the last two decades, the dissolution of synthetic or natural apatitic materials has been extensively studied. This work concerns the study of the digestion step of the production process of phosphoric acid. Over 90% of the phosphoric acid produced worldwide is manufactured by digestion of phosphate rock (apatite forms) with sulfuric acid; phosphoric acid is then separated from the resultant calcium sulfate slurry by filtration. Several processes are available; we focus our attention specially on the dihydrate process. The dissolution of phosphate rocks in acid solutions is essentially a surface solid-liquid reaction. When sulfate ions are present in solution, as in the dihydrate process, a solid product, i.e., calcium sulfate, is formed simultaneously with the digestion of the phosphate. This solid formation (crystallization) originates a solid-solid-liquid system (phosphate-calcium sulfate-solution) which is much more complicated to deal with than the basic solid-liquid system. The complexity of the system is even more important since the produced calcium sulfate may form solid layers around the phosphate particles (coating phenomenon) and block partially or completely the development of the reaction.
To isolate the dissolution phenomenon in order to study it separately from the calcium sulfate formation, we have replaced sulfuric by hydrochloric acid. The phosphate material used in our experiments is synthetic hydroxyapatite (HAP).

EXPERIMENTS AND RESULTS

Several publications concern the dissolution of apatitic minerals although no agreement has been achieved concerning the rate-controlling step: diffusion of calcium ions away from the particle, diffusion of hydrogen ions towards the particle, and chemical reaction of the acid with the ore. The complete dissolution of HAP in hydrochloric acid solutions was studied in order to verify the rate controlling step of this phenomenon.
A weighted amount of HAP was put to react with a 5 % excess of hydrochloric acid in dilute conditions (1.5 % of solids in mass). The time for complete dissolution of the HAP powder was measured by visual observation. All experiments were achieved at 75°C. Increasing amounts of calcium were established by adding calcium chloride ($CaCl_2.2H_2O$) into the solution. Similarly, different amounts of phosphorus were considered by addition of phosphoric acid into solution. Increasing amounts of calcium slow down the dissolution since it increases the time for complete dissolution. On the other hand, the presence of phosphoric acid shows an analogous effect on the dissolution kinetics. The study of the dissolution of calcium hydroxyapatite powder in the presence of various concentrations of calcium and phosphorus points out that the controlling step of the process is the diffusion of products (calcium and/or phosphate) from the solid-liquid surface to the bulk of the solution. Some complementary experiments (different temperatures, solutions of various viscosities) are to be carried on, in a similar way as herein described, to implement the study of the dissolution rate. The time for complete dissolution (100 % conversion) will be used to calculate the dissolution rate constant assuming a shrinking particle behaviour controlled by diffusion.

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STUDY OF THERMAL STABILITY OF CALCIUM HYDROXYLAPATITES.

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Thermal stability of the defect calcium hydroxylapatites (DCHA) $Ca_{10-x}(HPO_4)_{6-x}(OH)_{2-x}$, where $0 \le x \le 2$, with various degree of defectiveness was investigated by the method of high-temperature rentgenography.

It is known, that when heated acidic phosphate groups HPO_4^{-2} turn into pyrophosphate ions:

$$2HPO_4^{-2} = P_2O_7^{-4} + H_2O, \qquad (1)$$

which subsequently react with structural hydroxyls giving ß-$Ca_3(PO)_4$.

$$P_2O_7^{-4} + 2OH^- \text{ ----> } 2PO_4^{-3} + H_2O$$

Thermal stability of DCHA was estimated according to a content of ß-$Ca_3(PO)_4$ in calcinated samples with the help of high-temperature rentgenography.

It was shown that, when increasing DCHA defectiveness, thermal stability of DCHA would also be increasing. For instance, at temperature of 700°C, the DCHA sample with molar CaO/P_2O_5 ratio of 2.96 is converted to ß-$Ca_3(PO)_4$ during 60 minutes, while DCHA with molar CaO/P_2O_5 ratio of 2.72 does the same in 220 min.

With the same duration of thermal treatment, full conversion of DCHA into ß-$Ca_3(PO)_4$ in the second sample is achieved at the temperature 40-50°C higher than in the first sample.

The data obtained can be used for purposeful search of new thermostable catalysts for petrochemical processes.

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INHIBITION OF AMINOPEPTIDASES BY PHOSPHONIC AND PHOSHINIC ACID ANALOGUES OF ASPARTIC AND GLUTAMIC ACIDS

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Aminopeptidases are a diverse group of enzymes that catalyze the hydrolysis of the amino-terminal residue from a peptide chain. Since these enzymes appear to be involved in important biological processes, compounds that inhibit the aminopeptidases may have therapeutic applications. Although the substrate specificities of these enzymes are well understood the mechanistic details of their action are not and the enzyme inhibitors can provide mechanistic information regarding enzyme catalysis. Thus, the development of synthetic inhibitors of aminopeptidases is an active field of research that has provided insight into the nature of enzyme-substrate interactions during catalysis.

Our approach to new inhibitors of cytosolic (EC 3.4.11.1) and microsomal (EC 3.4.11.2) aminopeptidases was to replace the scissile amide bond in a substrate by phosphonic acid function, moiety which effectively mimics the putative tetrahedral transition-state of catalytic process involving the direct attack of water molecule on the amide linkage of the substrate. Thus, for better understanding of the structure-activity relationship, as well as the structural requirements of catalytic and binding subsites of both enzymes, we have synthesized more than 30 phosphonic and phosphinic acid analogues of aspartic and glutamic acids and evaluated their inhibitory properties. Among all the compounds tested only those in which α-carboxylic function was replaced by phosphonic or related moiety were found to inhibit, to some extent, at least one of the enzymes studied.

Although the analogues of aspartic and glutamic acids are modest inhibitors of both aminopeptidases the obtained data provide the basis for the structure-activity relationship discussion.

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DEGRADATION OF ORGANOPHOSPHONATES BY FUNGI

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Organophosphonates are of great economical and environmental importance since they are used worldwide in massive quantities as plasticizers, flame retardants, corrosion inhibitors and pesticides. Although the phosphorus-to-carbon (P-C) bond is resistant to chemical degradation (either hydrolytically, thermally or photochemically) organophosphonates are widely regarded as environmentally nonpersistent. Thus, one would expect that there exists a great number of microorganisms containing suitable catabolic pathways for biodegradation of such compounds. Thus, the ability of five fungal isolates to utilize structurally diverse organophosphonates as a sole source of phosphorus, nitrogen or carbon was studied.

The microorganisms used include: *Penicillium citrinum* isolated from soil during the studies on selection and characterization of lipolytic fungi; *Penicillium verrucosum*, also a soil isolate, which was a generous gift from Dr. H. Sztajer (Gesellschaft fur Biotechnologische Forschung, Braunschweig, Germany); *Penicillium* sp. which grew spontaneously on a solid sample of di-*n*-butyl 9-hydroxy-fluoren-9-ylphosphonate and unidentified yet strains of like-yeast and *fungi imperfecti* (probably *Chladosporium* sp.) which spontaneously grew in aqueous solutions of 6-amino-6-phosphonohexanoic acid.

With the exception of the representative of *fungi imperfecti* which grew well on 2-aminoethylphosphonic acid (ciliatine) as the sole source of nitrogen, the strains studied in this work did not utilize any of the phosphonates as the sole source of nitrogen or carbon. All the fungi, however, utilized a range of phosphonates as the sole source of phosphorus for growth.

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FAILURE OF AMINOPHOSPHONATE SYNTHESIS DUE TO FACILE HYDROXYPHOSPHONATE - PHOSPHATE REARRANGEMENT.

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Aminophosphonates and aminophosphonic acids have received their great interest due to their biological activity [1].

One of the very useful methods of aminophosphonates synthesis appears to be the one described by Kabachnik, Medved and Fields [2-4] in a reaction between ammonia or amine, dialkyl phosphite and corresponding carbonyl compound. It was postulated that the reaction undergoes via imines [4], or hydroxyphosphonates due to reversibility of their formation from ketone [5].

Observed yields of aminophosphonates vary from 85% (acetone) 40-47% (acetophenone) 12% (benzophenone) to 0% (fluorenone derived substrates), when aliphatic amines are used [6,7].

We found that in the case of aromatic ketones (especially fluorenone derivatives) and aliphatic amines, the formation of hydroxyphosphonates is very fast. The reaction rates are in the range 0.2 to 1.7 [sek^{-1}]. It should still allow the formation of aminophosphonates as long as formation of hydroxyphosphonate is reversible. This reversibility was observed monitoring fluorenone formation at λ = 400 nm when the excess of amine (100 times) was added to the solution of hydroxyphosphonate The complete reversibility should be manifested by formation of the corresponding amount of fluorenone. For all studied diesters and amines the reversibility was lower than 20%. The major reaction was irreversible formation of phosphates followed by their decomposition to many products and not towards starting ketone. Nothing or little of aminophosphonate was formed in the presence of aliphatic amines.

Aromatic amines like aniline, or N-methylaniline are too weak bases and they catalyse neither the hydroxyphosphonate formation nor their rearrangement to phosphate. In this case the yields of the aminophosphonates were satisfactory (above 65%).

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ALKYLATING PROPERTIES OF DIALKYL PHOSPHITES

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Dialkyl phosphites are used as reagents in many reactions involving amine as a another substrate. The reaction proceeds , in general, without complications. However, there are several examples of failure with the formation of some unidentified product [1]. We found that in some cases the N-alkylation of amine could be a serious problem especially when methyl phosphite or phosphonites are used. Diethyl phosphites are not so powerfull alkylating agents. However when methanol is used as a reaction mixture component the methylation proceeds via transestrification of dialkyl phosphite to mono- or dimethyl derivatives, which act as methylating agents.

In this communication we report the studies on the reaction of phosphites, amines and methanol or water. The mixture of butylamine, diethylphosphite and methanol was left in room temperature for several days. The NMR spectrum (in C_6D_6) was taken at certain periods of time. After several days the very complicated mixture of many compounds was found.

The transestrification rate constants are: 2.7×10^{-2}, 4×10^{-2} [min^{-1} mol^{-2}], for monomethyl and dimethyl ester formation respectively. The corresponding equilibria constant are: 0.80 and 0,34. Monoesters have not alkylating properties. Even after 30 days at room temperature no further reaction was observed.

The mono-, di-, and trialkylated butylamine derivatives are formed with the estimated rate constants 1.0×10^{-4}, 3.0×10^{-4}, 5.1×10^{-4} [min^{-1} mol^{-2}] respectively.

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NEW SYNTHETIC METHODS FOR PHOSPHONOPEPTIDES*

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A three-component condensation involving halogenated acylamide, substituted benzaldehyde and dialkylphosphite in the presence of acetic anhydride containing ethanolic hydrogen chloride gave α-(2-haloacylamino)-substituted benzylphosphonate in good yield. The latter on amidation by a modified Gabriel procedure provided protected phosphonopeptide -- a backbone for the formation of oligophosphonopeptides by prolongation either from N- or from P-terminus in the usual manner.

Pentachlorophenyl ester of protected amino acid was prepared conveniently either in situ or by isolation as crystalline compound upon condensation of N-protected amino acid with pentachlorophenol with the aid of DCCI. The resultant active ester underwent coupling smoothly with aminophosphonate to provide phosphonopeptides in excellent yields.

A novel and direct synthesis of p-nitrophenylethyl hydrogen benzylphosphonate consisting the reaction of benzylcarbamate, substituted benzaldehyde and phosphorus trichloride in the presence of acetyl chloride followed by subsequent alcoholysis with p-nitrophenylethanol was reported. As protection group of the phosphonic acid function, p-nitrophenylethyl group is easily removed by treatment with DBU via β-elimination reaction under mild conditions, suitable for the preparation of phosphonopeptide with phosphonamide linkage.

*This project was supported by National Natural Sciences Foundation of China.

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SYNTHESIS OF myo-INOSITOL-1,3,5-O-PHOSPHATE, AS A NEW TYPE OF CAGE-PHOSPHATE*

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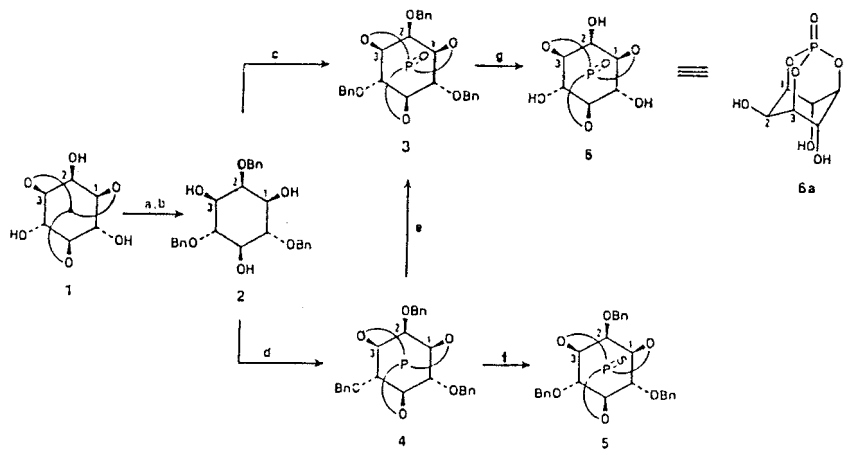
Since myo-inositol-1,4,5-O-trisphosphate (IP_3) behaves as second messager in cellular signal transduction, synthetic study of myo-inositol phosphate became an area of active investigations. Studies on the possibilities of using phosphoryl moiety as protection group for the multi-hydroxyl functions in the synthesis of various inositol phosphate derivatives is therefore a problem of synthetic importance. Herein we wish to report a new synthetic method leading to myo-inositol-1,3,5-O-phosphate(**6**), a compound with cage-phosphate structure and resemble to adamantane **6a** by the following sequence of reactions.



Reagents and conditions: a-NaH,DMF,imidazole,BnBr,r.t.; b-36%HCl, MeOH,reflux; c-$POCl_3$,pyridine,100°C; d-$P(NEt_2)_3$,dioxane,110°C,18h; e-H_2O_2(30%),THF,reflux; f-S,PhOMe,150°C; g-H_2(17atm),10%Pd/C,r.t..

*This project was supported by National Natural Science Foundation of China.

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DIRECT PHOSPHORYLATION OF NUCLEOSIDES

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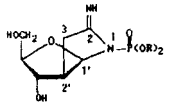
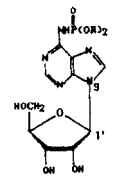
In our laboratory, since all of the naturally occuring amino acids have been successfully N- phosphorylated by the dialkylphosphite[1], it would be useful if this new method could be extended to N-phosphorylation of the nucleosides. By the literature[1], the oxazoline or adenosine was phosphorylated by one equivlent of dialkylphosphite.



phosphorylated oxazoline



phosphorylaind adenosine

The ^{31}P-NMR spectrum of phosphorylated oxazoline shows peak at 6.19ppm, it suggested that the phosphoryl group is at the imino or amino group other than the hydroxyl group. Additionally, the FAB- MS showed that the dialkylphosphoryl group was added to the oxazoline. Also, in the ^{13}C-NMR spectrum, the C_2 and $C_{1'}$ as well as the first two carbon atoms in the butyloxy group were splited into doublet by the phosphorous atom, this concluded that the amino group was phosphorylated.

The FAB- MS of phosphorylated adenosine shows the molecular ion, as well as the fragment ions at m / z 98 and 298. The peak at m / z 98 could be asscribed for ($HO)_2P(O)NH$ other than $(HO)_3P(O)$ (m / z 99), it implies that the phosphoryl group is connected to the amino group in the base. The ion at m / z 298 produced by $C_{1'}$-N_9 cleavage provides more evidence for the conclusion. Moreover, the two hydrogens in the base shifted more than any others in the ^1H -NMR spectrum after phosphorylation, it again ensures the proposed structure. The nucleoside and the analogue without protection were able to be N- phosphorylated by the dialkylphosphites in the aqueous basic condition, this might provide a novel new stratgy to synthesizing the N-phosphoryl nucleoside.

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Hydrophobic peptides induce phospholipid flip-flop in bilayers

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The synthetic amphipathic peptide (GALA) designed to serve as a model for triggered fusogenic peptides, exists as a random coil at pH 7.4. At pH 5.0 it is transformed to an amphipathic α helix and its ability to partition into membranes increases about 5,000 fold. In the membrane, GALA organizes into a pore containing 8-12 peptides. Interaction with the membrane result in leakage of vesicles contents and membrane fusion for small unilamellar vesicles.

We have examined the effect of GALA on the flip-flop of N-4-nitrobenzo-2-oxa 1,3 diazole phosphatidylcholine (C_{12}-NBD-PC) in large unilamellar vesicles (LUV) that contain an asymmetrical distribution of the NBD-PC. Asymmetrical vesicles with NBD on the inner monolayer were prepared and NBD-PC flip-flop was measured by following the quenching of fluorescence of NBD that results when probe molecules that have flipped to the outer monolayer spontaneously transfer to a 10-fold excess of vesicles containing Rhodamine-Phosphatidylethanolamine (Rh-PE). The asymmetrical NBD vesicles were incubated with various peptides under various conditions and then an excess of the Rh-PE was added. Moderate mole ratios of GALA to lipid induce complete flip-flop of the probe. The dose dependence of flip-flop is similar to that observed for leakage of the contents. pH-jump experiments which cause dissociation of GALA from the membrane indicate flip-flop occurs sooner than 10 seconds after GALA addition. LAGA, a control peptide with a 30 fold lower affinity for the membrane, was about 30 fold less potent in causing flip-flop. The flip-flop activity of melittin, a peptide that self-associates in the membrane, was similar to that of GALA. Gramicidin and Valinomycin, peptides that do not form water-filled pores in the membrane were orders of magnitude less potent, despite their high level of association with the membrane. These data suggest that only peptides that self-associate to form pores provide a low energy path for the phospholipid headgroups to cross the hydrocarbon interior of the bilayer in significant quantities. Such an effect may be in part responsible for their fusogenic properties [Supported by Fondation pour la Recherche Thérapeutique (EF) and NIH GN 30163 (FCS)].

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PHOSPHONOACETALDEHYDE HYDROLASE : AN ENZYME THAT CLEAVES THE C-P BOND

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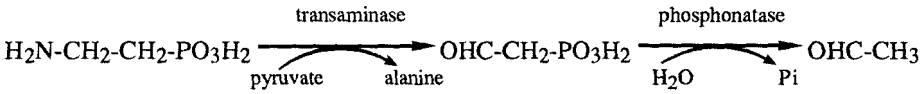
Although a number of natural and synthetic organophosphonates are degraded by soil microorganisms, few enzymes have been isolated and characterized.

Phosphonoacetaldehyde hydrolase (EC 3.11.1.1) from *Pseudomonas aeruginosa*, inducible by 2-aminoethylphosphonic acid, catalyses the C-P bond cleavage of phosphonoacetaldehyde into acetaldehyde and orthophosphate following the scheme.



This enzyme has a homodimeric structure with a subunit of Mr 30 000 and an isoelectric point of 5.2 ; it exhibits apparent Michaelis-Menten saturation kinetics with a K_m value of 200 µM and a catalytic-centre activity of 300 min^{-1}. The hydrolysis proceeds *via* an imine formation between the aldehyde group of the substrate and a lysine of the active site (*Bacillus cereus* [Olsen *et al.*, Biochemistry, 27, 2229 (1988)]). The enzyme is very specific for its substrate.

A series of alkylphosphonic acids from C_1 to C_4 behave as allosteric modulators of the hydrolase. Phosphite inactivates the enzyme in a time dependent process. This inhibition is pH-dependent and exhibits a pKa value of 7.70.

P. aeruginosa is able to grow, as many other soil microorganisms, in the presence of a number of alkylphosphonates as sole phosphorus source showing the existence of other catalytic systems which failed to be isolated from cellular extracts.

Recently a complex system has been discovered from a crude extract of *Enterobacter aerogenes* [Murata *et al.*, Biochem. Biophys. Res. Commun., 157, 190 (1988)] : this system has a broad specificity since it recognized structurally different phosphonic acids as methylphosphonic acid, phosphonoacetic, phenylphosphonic acid.

An increasing number of toxic synthetic organophosphonates are being introduced into the environment. The cleavage of the C-P bond by soil microorganisms is an important process for nature detoxification and maintenance of the ecosystems.

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Studies on the Synthesis of Nucleoside Esters of Trifluoromethanephosphonic acid as Nucleotide Analogues

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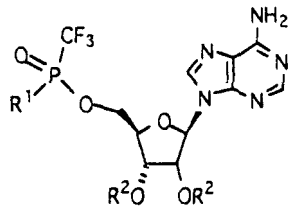
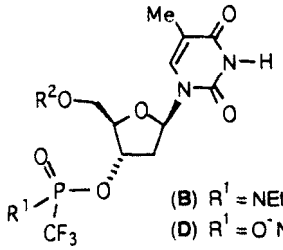
We have employed diethylamino trifluoromethylphosphorus bromide,[1] $CF_3P(Br)NEt_2$, as a synthon for the preparation of analogues of phosphate esters. In it, the bromine can readily be replaced by the 5'- or 3'-oxygen of a suitably protected nucleoside to give trifluoromethylphosphonamidite species, $CF_3P(NEt_2)OR$, which are close relatives of the intermediates used in P(III) oligonucleotide synthesis. These phosphonamidites can be oxidised by *t*-butyl hydroperoxide to the corresponding phosphonamidates for both adenosine (**A**) and deoxythymidine species (**B**). Unfortunately, these analogues of nucleoside phosphoramidates did not behave as expected and showed P-O rather than P-N cleavage under certain conditions of transformation.



(**A**) $R^1 = NEt_2$; $R^2 = >CMe_2$. (**C**) $R^1 = OH$; $R^2 = H$



(**B**) $R^1 = NEt_2$; $R^2 = DMT$
(**D**) $R^1 = O^-NH_4^+$; $R^2 = H$

We therefore turned to the use of trifluoromethylphosphorus dibromide,[2] prepared by a new and convenient route, for access to trifluoromethanephosphonate diesters.[3] This reacts with triazole to give the bistriazolide which behaves as a standard phosphorus (III) reagent towards 5'-dimethoxytritylthymidine and 2',3'-di-*O*-ethoxymethylideneadenosine to afford the corresponding 3- and 5'-mononucleotides (**C**) and (**D**) respt. The latter can conveniently be used to build $dTp_{CF_3}rA$, the phosphonate analogue of deoxythymidylyl-(3'→5')-adenosine. Progress towards the incorporation of the trifluoromethanphosphonate linkage into oligonucleotides in a stereospecific fashion will be reported.

Lastly, in the course of conversion of (**D**) into its sodium salt for NMR analysis, it was observed that prolonged exposure to Chelex^R resin resulted in the selective hydrolysis of (**D**) by P-C cleavage to give thymidine-3'-phosphate. The significance of this observation will be discussed.

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PHOSPHONOPEPTIDES AND CHELATED PHOSPHONOPEPTIDES AS HAPTENS FOR GENERATING CATALYTIC ANTIBODIES

By Professor G.Michael Blackburn and Dr.Deng Shi-Xian

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Monoclonal antibodies have been shown to be capable of the catalysis of a relatively large number of different chemical transformations[1] since the first examples were discovered[2,3] in 1986. The task of cleaving the amide bond remains one of the most difficult to accomplish by a catalytic antibody.

The general target is the synthesis of stable haptens of lifetime at least one day *in vivo*, which will mimic the tetrahedral intermediates that are characteristic of the hydrolysis of the amid bond. We have designed phosphonopeptides and chelated phosphonopeptides as haptens to elicit the production of monoclonal antibodies capable of amide scission similar to that seen in aminopeptidases. Phosphonate esters, phosphonamides, and phosphinic acids containing P(O)-C-, P(O)-N-, and P(O)-O- surrogates for the peptide linkage have been prepared and conjugated to the carrier proteins, keyhole limpet haemocyanine (KLH) and bovine serum albumin (BSA) through their carboxyl terminus. In addition, specific stable metal chelate complexes have been prepared and characterised by ^{31}P NMR to demonstrate the nature of the metal ligands from the peptide mimetic and these also have been conjugated to carrier protein.

The hapten-KLH conjugates are being used to immunise mice and monoclonal protein is being prepared by standard hybridoma technology.[4] Results on the screening of clones for catalytic activity will be reported.

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AMINOOXYPHOSPHONATES AS SLOW BINDING INHIBITORS OF ASPARTATE- AND ALANINE- AMINOTRANSFERASES

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** Technical University of Wroclaw - 50-370 Wroclaw - Poland

Aminooxymethylphosphonic (AOMP) and 1-aminooxyethylphosphonic (AOEP) acids were synthetized following the scheme :

$$\mathrm{RCH(OH)\text{-}PO(OC_2H_5)_2} \xrightarrow{a} \mathrm{RCH(ONPhth)\text{-}PO(OC_2H_5)_2} \xrightarrow{b}$$

$$\mathrm{RCH(ONH_2)\text{-}PO(OC_2H_5)_2} \xrightarrow{c} \mathrm{RCH(ONH_2)\text{-}PO(OH)_2} \quad (\mathrm{R = H \text{ or } CH_3})$$

and their interaction with cytosolic aspartate- (EC 2.6.1.1) and alanine- (EC 2.6.1.2) aminotransferases from porcine heart was investigated.

These compounds exhibit a time dependent inhibition with biphasic reaction kinetics. The formation of an initial, rapidly reversible enzyme-inhibitor complex (EI) is followed by the conversion to a tighter complex (EI*) which dissociates slowly.

$$\mathrm{E + I} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \mathrm{EI} \underset{k_6}{\overset{k_5}{\rightleftharpoons}} \mathrm{EI^*}$$

[Morrison and Walsh, Adv. Enzymol. 61, 201-301 (1988)]

The kinetic parameters of Asp-AT and Ala-AT determined by the onset of inhibition, preincubation enzyme-inhibitor studies and reversal of inhibition indicate that AOMP and AOEP are potent slow-binding inhibitors of both enzymes. The inhibition constants are in the nanomolar range for AOMP and in the micromolar range for AOEP. The half-times for the recovery of activity of fully inhibited-enzymes varie from 0.25 to 11.3 hours.

The spectra of Asp-AT monitored before and after addition of AOEP show a shift from 362 nm, the absorption band of the internal aldimine between PLP and lysine 258, to 380 nm, characteristic of an oxime formation.

These compounds ($\mathrm{NH_2\text{-}O\text{-}R\text{-}PO_3H_2}$) were compared to their carboxylic analogues ($\mathrm{NH_2\text{-}O\text{-}R\text{-}COOH}$) as well as to the corresponding aminophosphonates ($\mathrm{NH_2\text{-}R\text{-}PO_3H_2}$).

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THE SYNTHESIS OF SMALL MOLECULE PHOSPHORYL-CHOLINE COMPOUNDS FOR USE IN BIOCOMPATIBILITY APPLICATIONS

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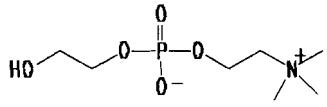
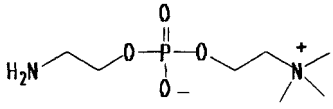
Phosphorylcholine treated surfaces confer biocompatibility by mimicking the outer membrane of the red blood cell. To this end a series of functionally active phosphorylcholine derivatives have been prepared for covalent attachment to surfaces.

In particular two compounds (1,2) have been shown to be key intermediates to the synthesis of a wide range of derivatives and for directly attaching to surfaces.



(1)



(2)

Single step syntheses of these compounds are presented, thereby circumventing longer routes already described in the literature[1,2]. The starting materials are cheap and readily available. Each route depends on the initial formation of a tetraalkylammonium salt of the phosphate which then undergoes nucleophilic displacement of an epoxide, or halide.

Each method utilises water as the solvent, with the tetraalkyl-ammonium species being totally extracted using dichloromethane. This methodology is applicable to a range of different molecules.

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CONCISE SYNTHESES OF HOMOCHIRAL INOSITOL PHOSPHATES FROM *MYO*-INOSITOL

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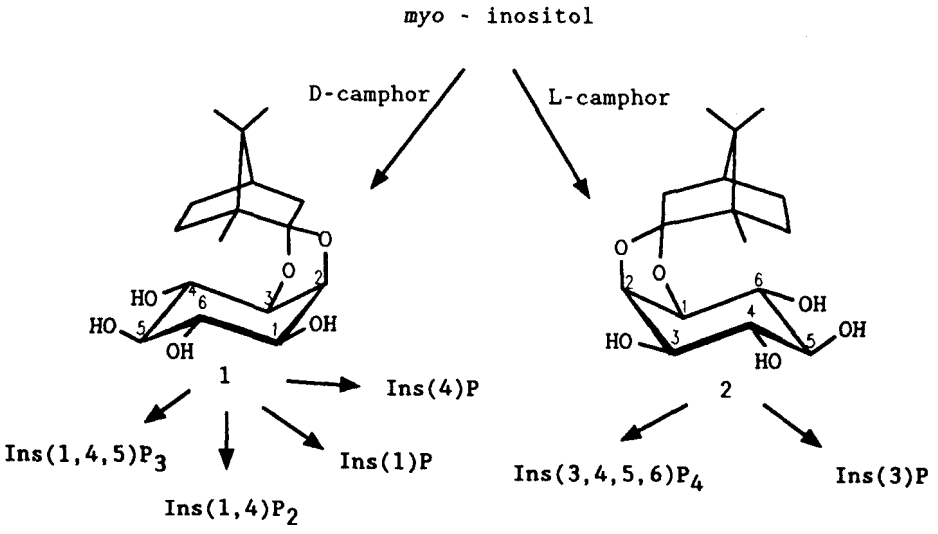
Centre of Molecular and Macromolecular Studies, The Polish Academy of Sciences, Sienkiewicza 112, 90-363 Łódź, Poland

A new synthetic protocol for efficient conversion of *myo*-inositol into homochiral inositol phosphates is presented and is illustrated with six syntheses of naturally occurring inositol phosphates, specified in the Scheme.

Scheme



The syntheses start with selfresolving *myo*-inositol camphanylidene *cis*-monoacetals 1 and 2, which are obtained in one step from the parent cyclitol and D- or L-camphor dimethyl acetal, respectively, and are harvested conveniently by means of a precipitation driven equilibration. The syntheses feature in the key steps the selective monophosphorylation, selective bissilylation and selective trisacylation of tetrols 1 and 2, as well as the use of dibenzyl phosphorochloridate and 2-dimethylamino-5,6-benzo-1,3,2-dioxaphosphepane for effecting mono and polyphosphorylations, respectively.

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SYNTHESIS OF NOVEL INOSITOL POLYPHOSPHATE ANALOGUES AT THE 1-POSITION

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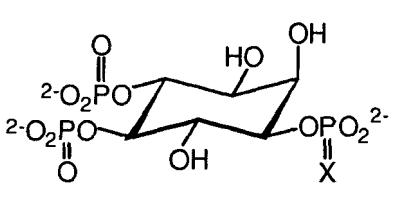
Abstract The synthesis of novel inositol tris- and tetrakisphosphate analogues modified at the 1-position is reported.

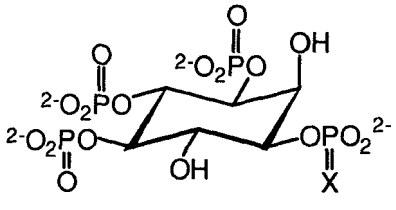
D-*myo*-inositol 1,4,5-trisphosphate Ins(1,4,5)P_3 (1) is a hydrophilic second messenger which is generated by agonist-stimulated, G-protein coupled, phospholipase C-catalysed cleavage of the minor membrane lipid phosphatidylinositol 4,5-bisphosphate. Ins(1,4,5)P_3 releases Ca^{2+} from an intracellular store via a receptor which has now been isolated, cloned, sequenced and which, when reconstituted, mediates Ca^{2+} release in response to Ins(1,4,5)P_3. A major challenge is now the elucidation of the structural basis for the interaction of Ins(1,4,5)P_3 with its receptor and with the metabolic enzymes 5-phosphatase and 3-kinase and the rational chemical design of agonists, antagonists and enzyme inhibitors. We have addressed this challenge in several ways by the synthesis of inositol phosphates and a variety of chemically modified inositol phosphate analogues.

The biochemical interest in Ins(1,4,5)P_3 and D-*myo*-inositol 1,3,4,5-tetrakisphosphate Ins(1,3,4,5)P_4 (3), which also has a possible second messenger function, has created a demand for analogues of these compounds possessing reporter groups. Substitution of the 1-phosphate group by a phosphorothioate moiety allows facile attachment of reporter groups.

Starting from *myo*-inositol, D-*myo*-inositol 1-phosphorothioate 4,5-bisphosphate (2) and *myo*-inositol 1-phosphorothioate 3,4,5-trisphosphate (4) have been synthesised employing different protecting groups and a P(III) approach followed by oxidation/sulphoxidation to give (2) and (4) after deblocking.



X = O (1)
X = S (2)



X = O (3)
X = S (4)

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C-FLUORINATED AMINOPHOSPHONIC ACID ESTERS

C-FLUORINATED AMINOPHOSPHONIC ACID ESTERS

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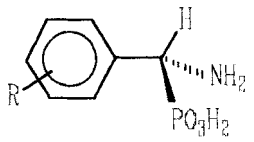
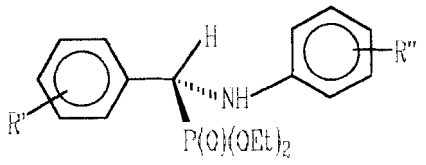
INTRODUCTION

Aminophosphonic acids, the phospha analogues of aminocarboxylic acids, play an important role in biological and biochemical processes. Especially fluorinated aminophosphonic acids and aminophosphonates are of current biological interest having potential antibacterial, fungicide, herbicide and insecticide activities [1].

RESULTS AND DISCUSSION

Here we present three synthetic routes (several new variations to known reactions [2-4]) leading to fluorinated 1-amino-1-arylmethanephosphonic acids 1 and 1-N-arylamino-1-arylmethanephosphonic acid diethylesters 2 :





1 2
R = 4-, 3-,2-, (F, CF_3, OCF_3) ; R',R" = H, 4-, 3-, 2-, (F, CF_3, OCF_3) ; 3,4-F_2

Using the oxime method and amidoalkylation techniques free acids of type 1 were obtained, while the addition of diethylphosphite to Schiff bases yielded the esters of type 2. It is not trivial to cleave the esters 2 to parent acids. Fluorinated substituents exert considerable influence on preparative yields of 2 : the highest reactivities were observed for para-substituted educts, while the ortho-effect gave rise to modest yields only. All compounds were investigated by ^1H-, $^1H\{^{31}P\}$-$^{13}C\{^1H\}$-, ^{19}F- and $^{31}P\{^1H\}$-NMR in one dimensional methods. Selected samples were subjected to advanced techniques in 2 D NMR and high resolution NMR-spectra were analyzed and iterated using new program systems DSYM-PC [5] and LAO5PC [6] developed in Düsseldorf. Specific data for chemical shift and coupling constants were obtained for the aromatic ring systems and molecular dynamics were calculated by using force field- and semi-empirical-programs (DISCOVER, VAMP and MOPAC). External biological studies are in progress.

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[5] G. Hägele, S. Goudetsidis, University of Düsseldorf
[6] G. Hägele, R. Spiske, University of Düsseldorf

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N-(PHOSPHONOACETYL)-L-ASPARTIC ACID

PALA, N-(PHOSPHONOACETYL)-L-ASPARTIC ACID, A POTENT ATCase INHIBITOR

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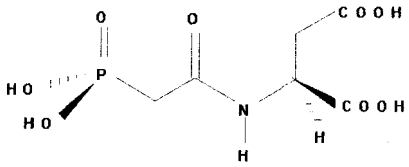
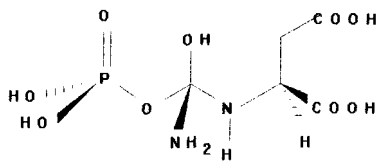
INTRODUCTION

Since the early 1970ies PALA is known as a potent inhibitor of ATCase [1]. ATCase (Aspartate Transcarbamylase) is the key enzyme in pyrimidine and DNA biosynthesis and therefore of great importance for the reproduction of cells. PALA's tumorostatic properties, especially in Lewis lung carcinoma, are due to complete inhibition of ATCase in cancer cells. Unfortunately it exhibits strong mutagenic and teratogenic effects [2] and was withdrawn from cancer chemotherapy. Nevertheless PALA remains an interesting and instructive model for enzyme inhibition by " transition state analogues " (Figure 1).



(1)



(2)

PALA N-(Carbamylphosphate)-L-aspartic acid

FIGURE 1 PALA as "transition state analogue"

RESULTS AND DISCUSSION

The main difference between PALA and the natural transition state is the replacement of easily hydrolizable P-O-C bond in (2) by a non hydrolizable P-C-C bond in PALA (1). This replacement shows a principle widely used in the design of anti cancer drugs. In spite of these facts only few material on NMR and structural data has been published so far. Aiming at NMR and structural studies we investigated several methods for the preparation of PALA. In our poster we critically review results from preparative studies and discuss the influence of pH on the synthesis of PALA [1]. With the aid of the molecular modelling program DISCOVER [3] we were able to find the main conformation of aspartic residue in PALA.Rotameric populations and the Karplus -type function for the aspartic residue in PALA were calculated.

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[3] Program DISCOVER, BIOSYM,(based on force field and semi empirical methods)

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POLYFUNCTIONAL PHOSPHONIC AND PHOSPHINIC ACIDS: SYNTHESIS, STRUCTURE, NMR AND ANALYTICAL PROPERTIES

G. HÄGELE, M. ACKERMANN, M. BATZ, R. FUHLER, H.W. KROPP, H. PAPADOPOULOS, U. PRIOR, J. OLLIG, E. WILKE, M. MURRAY
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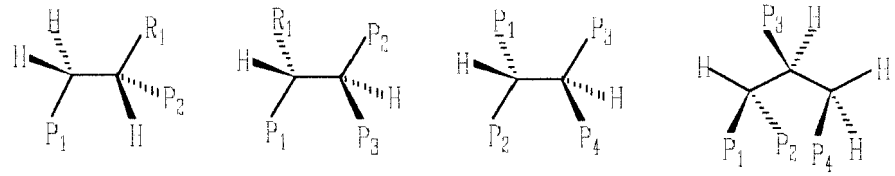
School of Chemistry, University of Bristol, Cantocks Close, Bristol BS8 1TS, Great Britain

INTRODUCTION

Several synthetic routes lead to polyfunctional acids of type:



P_1 - P_4 = PO_3H_2 , R_2PO_2H ; R_1 = H, Me, t-Bu, Ph, Mes; R_2 = Me, t-Bu, Ph

FIGURE 1 Polyfunctional phosphonic and phosphinic acids

RESULTS AND DISCUSSION

The compounds shown in FIGURE 1 represent the phospha-analogues of polycarboxylic acids with unusual protonation and complex formation properties. Corresponding esters are obtained by Pudovik-addition and methods called "anomalous Michaelis Becker reactions". Molecular modelling is used to support postulated reaction mechanisms. Esters and in some cases the parent acids and anions as well, are sterically overcrowded exhibiting several specific rotameric forms at room temperature, as observed by NMR studies and predicted by modelling using molecular mechanics and dynamics. Special force field parameters were determined to simulate phosphonate and phosphinate structures. Individual rotameric forms were identified by a novel technique called "P,P - ROESY spectroscopy". Exchange between rotamers was monitored by EXSY-spectra in collaboration with K. Orrel, Exeter.

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NMR a. STRUCTURAL INVESTIGATIONS OF PHOSPHOPEPTIDES

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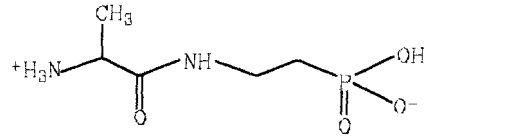
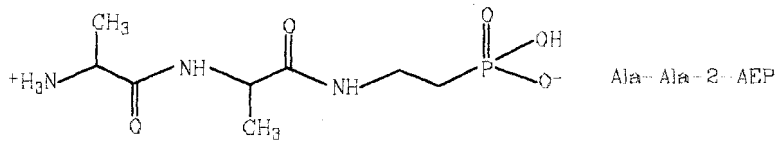
INTRODUCTION

Phosphopeptides are small linear peptides containing one or more aminophosphonic acids as building units. Because of the stability of the P-C bond against hydrolysis they are of particular interest as substrates and inhibitors in biochemical pathways. Therefore it is important to elucidate their structure in aequeous solution. It can be determined using 1D and 2D NMR techniques as well as molecular dynamics and force field calculations. The Phosphopeptides investigated so far are shown in FIGURE 1.:[1]





STRUCTURAL ANALYSIS

1. 1D spectral analysis and iterativ refinement of ^1H chemical shifts and coupling constants [2].
2. COSY and related techniques (double quantum filtered COSY) for the assignment of alanine units (Ala).
3. C,H-correlation and COLOC for analyzing the aminoacid sequence (both peptides are insoluble in aprotic solvents. Therefore C_a-H-NH coupling constants can not be used on this purpose.).
4. NOE measurements (H,H-NOESY; P,H-HOESY) for elucidating three dimensional structure in aqueous solution.

RESULTS AND DICUSSION

These well known methods were applied to the structure elucidation of phosphopeptides for the first time. While the AEP subunit occupies the typical antiperiplanar conformation the flexibility of the remaining skeleton of these short peptides is high at room temperature. Further investigations will include cyclic phosphopeptides as well as phosphorus containing macrocycles

REFERENCES

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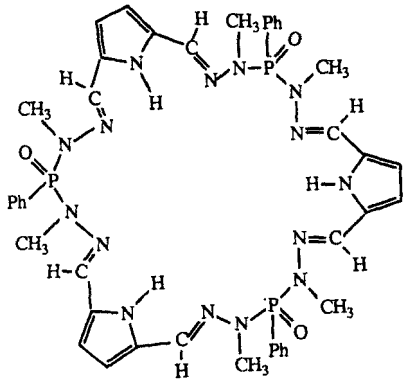
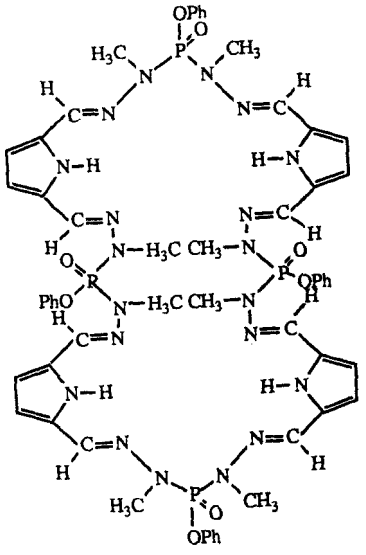
PYRROLE-CONTAINING MACROCYCLES DERIVED FROM [2+2], [3+3], [4+4] CYCLOCONDENSATIONS

Boualem OUSSAID[a], Bernard GARRIGUES[a*] and Anne-Marie CAMINADE[b]
[a] Laboratoire Synthèse, Structure et Réactivité de Molécules Phosphorées, URA 454, Université Paul Sabatier, 118 Route de Narbonne, 31062 Toulouse Cédex, France
[b]Laboratoire de Chimie de Coordination du CNRS, 205 Route de Narbonne 31077 TOULOUSE Cédex, FRANCE

Addition of phosphodihydrazides R-P(O)[NMe-NH_2]$_2$ to pyrrole 2,5-dicarboxaldehyde or N-methylpyrrole 2,5-dicarboxaldehyde led to a mixture of 20, 30 and 40 membered-rings. All these compounds resulted from [2+2], [3+3] and [4+4] cyclocondensations . In one case, a linear compound obtained *via* a [4+4] condensation is isolated.

Some examples :





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PHOSPHOHYDRAZIDES AS BUILDING BLOCKS FOR POLYNUCLEAR COMPLEXES

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The synthesis of redox-active molecules in which a redox center is in close proximity to a host binding site is actually an increasing field of activity. The condensation of phosphohydrazides $XP(N(CH_3)NH_2)_3$ or $PhP(X)(N(CH_3)NH_2)_2$ (X = O, S) with ferrocene carboxaldehyde could lead to such type of compounds.

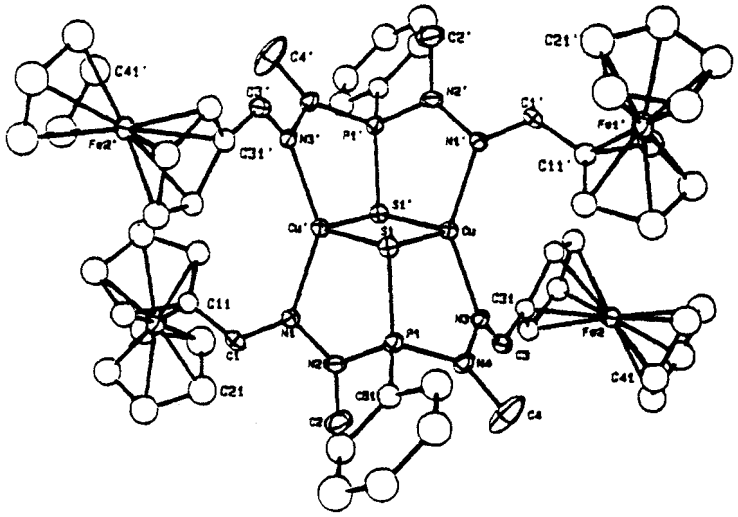
This condensation reaction gives quantitatively new phosphohydrazideq compounds according to the reaction:

$$n\ CpFeC_5H_4CHO + Ph_{3-n}P(X)(N(CH_3)NH_2)_n \longrightarrow [CpFeC_5H_4CH{=}NN(CH_3)]_nP(X)Ph_{3-n}$$

n = 2,3

When n = 2 their complexing properties have been checked toward copper(I) triflate and the products obtained depend of the ligand/metal ratio.

In the 1/1 case the structure of the complex has been established by an X-ray study.



In the 2/1 ratio the spectroscopic studies are in agreement with the complexation of the ligand through sulfur atom and one nitrogen of one imino group.

The same compounds can be made first by complexation of $PhP(S)(N(CH_3)NH_2)_2$ with copper triflate and then condensation with ferrocene carboxaldehyde.

Properties and electrochemical studies of the various complexes will be presented.

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A NEW REARRANGEMENT IN PHOSPHORUS CHEMISTRY

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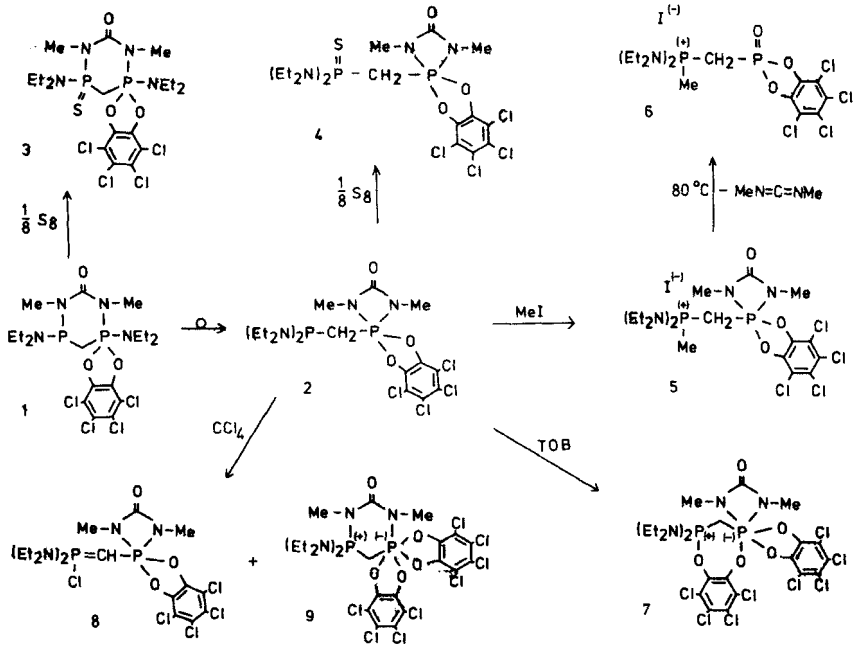
Institut für Anorganische und Analytische Chemie der Technischen Universität, 3300 Braunschweig, GERMANY

The transformation of the spirophosphorane **1** into the isomer **2** constitutes a new type of rearrangement in phosphorus chemistry. **1** and **2** react with sulfur to give the structural isomers, **3** and **4**, which exhibit no tendency to undergo mutual isomerisation.

The methylenephosphinophosphorane, **2** is a new type of compound, possessing unusual chemical properties. With MeI it gives the salt, **5** which, when heated, loses dimethylcarbodiimide with formation of **6**. Tetrachloroorthobenzoquinone (TOB) adds to the two phosphorus atoms of **2** giving the unusual zwitterionic compound, **7**. The reaction of **2** with CCl_4 leads to the P-chloroylide, **8** as well as to another compound, **9** isomeric to **7**, also containing two phosphorus atoms of opposite formal charge and different coordination number. Isomers **7** and **9** exist independently of each other and do not undergo mutual isomerisation.



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