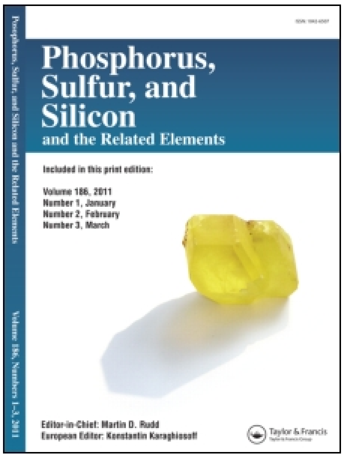

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Carboranyl Phosphonates

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CARBORANYL PHOSPHONATES

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Thomas O. McCullough, Xavier University, Cincinnati, Ohio

Mono and bis substituted carboranyl phosphonates have been synthesized via the phosphoroethylation of o-carboranes ($B_{10}H_{10}C_2R_2$ R=H,CH_3). In a quaternary ammonium hydroxide catalyzed Michael addition, o-carboranes attack diethylvinylphosphonate. Mono and bis substituted carboranyl diphosphonates have also been prepared via Michael addition. This reaction involves the attack of carboranyl carbanions on tetraethylvinyldiphosphonate. These compounds, both esters and acids, have been characterized by ^1H, ^{13}C, ^{31}P, and ^{11}B NMR as well as by elemental analysis.

Carboranyl phosphonates ($B_{10}H_{10}C_2(R)CH_2CH_2PO_3H_2$, R=$CH_3$, $CH_2CH_2PO_3H_2$) and carboranyl diphosphonates ($B_{10}H_{10}C_2(R)CH_2CH(PO_3H_2)_2$, R=$CH_3$,$CH_2CH(PO_3H_2)_2$) are stable water soluble polyprotic acids that could have utility as agents for B-10 neutron capture therapy of certain soft and hard tissue tumors.

SYNTHESES AND NMR SPECTROSCOPIC CHARACTERISTICS OF ISOMERIC S,N- AND N,N-DISUBSTITUTED PHOSPHINO-THIOIMIDOESTERS AND -THIOFORMAMIDES

A. Bruns and U. Kunze, Universität Tübingen, Institut für Anorg. Chemie,D-74 Tübingen (F.R.G.)

S-methyl phosphino-thioimidoesters have been prepared by alkylation of secondary phosphino-thioformamides with methyliodide under alkaline conditions.

$$Ph_2P\text{-}C(S)\text{-}NHR + MeI \xrightarrow{(base)} Ph_2P\text{-}C(NR)\text{-}SMe \quad \begin{array}{l} R = Me\ (n\text{-}BuLi) \\ R = Ph\ (KOH) \end{array}$$

The hitherto unknown tert. phosphino-thioformamides have been synthesized by reaction of N,N-disubstituted thiocarbamoylchlorides with diphenylphosphide.

$$R^1R^2N\text{-}C(S)\text{-}Cl + LiPPh_2 \xrightarrow[-LiCl]{} Ph_2P\text{-}C(S)\text{-}NR^1R^2 \quad \begin{array}{l} R^1_2 = Me,Ph \\ R^2 = Me \end{array}$$

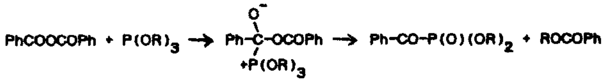
The new compounds provide an excellent means for the simultaneous observation of cis- and trans-P long-range NMR-coupling. The P=O and P=S derivatives of the imidoesters and formamides show unexpected steric effects.

THE REACTION OF TRIALKYL PHOSPHITES WITH BENZOIC ANHYDRIDE

K. M. Higgins and M. Murray, University of Bristol, England

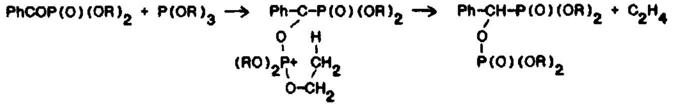
The reaction of trialkyl phosphites, $P(OR)_3$ with benzoic anhydride in refluxing chloroform has been shown to yield phosphate phosphonates, PhCHXOX, where X = $-P(O)(OR)_2$. This is in contradiction of the work of Burn, Cadogan, and Bunyan (J.C.S. 1963, 1527), who reported the product as a triphosphonate, $PhCX_3$.

The initial stage of the reaction is the formation of the carbonyl phosphonate by nucleophilic attack of phosphite at carbon, followed by alkyl group transfer.



$$PhCOOCOPh + P(OR)_3 \rightarrow Ph-\underset{+P(OR)_3}{\overset{O^-}{C}}-OCOPh \rightarrow Ph-CO-P(O)(OR)_2 + ROCOPh$$

The second stage involves proton capture, and we have shown by deuteration experiments that this does not come from the solvent. The most likely source is the alkyl groups of the phosphite, as has been shown for the similar reaction of trialkyl phosphites with aryl acetylenes (Griffin and Mitchell, J.Org.Chem. 1965, (30), 1935). The intermediate Zwitterion is probably formed by attack of phosphite on the carbonyl oxygen of the carbonyl phosphonate, though rearrangement of a product of attack at carbon cannot be ruled out.



REACTIONS OF PHOSPHORUS HALOGENIDS WITH AMINALES - A NEW METHOD OF $P-NR_2$ BOND FORMATION.

V.P. Kukhar, M.V. Shevchenko
Institute of Organic Chemistry, Acad. Sci. Ukr. SSR, Kiev, USSR

P-Halogencontaining compounds react with 1,1-bis(dialkylamino)methanes and tris(morpholino)methane yielding phosphorus amides

$$>P(X)-Hlg + >N-CH_2-N< \longrightarrow >P(X)-N< + >\overset{+}{N}=CH_2\ Cl^-$$

X : lone pair, O

Various phosphorus-III and phosphoryl compounds, chlorophosphoranes react this way. The structure of reaction products is determined by nature of phosphorus substituents and reactivity of iminium salt being formed. It is possible a sequences introduction of dialkylamino groups into PCl_3, $POCl_3$ and $RPCl_2$.

Dialkylphosphites react with bis(dialkylamino)methanes in the presence of CCl_4.

SULFURYL CHLORIDE FLUORIDE, NEW REAGENT IN ORGANOPHOSPHORUS CHEMISTRY

by A.Łopusiński and J.Michalski
Polish Academy of Sciences, Centre of Molecular and
Macromolecular Studies, Boczna 5, 90-362 Lodz, Poland

Recently we have found that sulfuryl chloride fluoride $ClSO_2F$ can be used as a new versatile fluorinating agent in organophosphorus chemistry. A variety of compounds such as thio- and selenophosphates, phosphonates, phosphinates, phosphine sulfides and selenides can be converted with high yield and under mild conditions into the corresponding fluoridates $RR'P(O)F$ or fluorophosphoranes R_3PF_2.
Stereochemical and ^{31}P nmr studies were carried out using optically active and diastereoisomeric substrates as a model compounds to obtain more information about the intermediate products and in effect to propose the reaction mechanism of fluorination.

REACTIONS OF PHOSPHORUS TRIHALIDES WITH FUNCTIONALIZED ALKENES AND ALKYNES.

I.F.Lutsenko,M.A.Kazankova,I,G.Trostyanskaya,I.L.Rodionov, E.V.Luzikova.Moscow State Lomonosov University,USSR.

Direct phosphorynation of vinil alkil ethers,ketene acetals and terminal acetilenes with phosphorus trihalides was carrides out. Noncatalised addition of phosphorus trihalides, trialkyl bromo(iodo)phosphites and dialkyl halophosphines across the triple bond was carried out in reaction with alkoxyacetylenes and element (Si,Ge)-substituted acetylenic ethers for the first time.The new tipe of phosphorus(III) and(V) derivatives - phosphorylated 1-haloalkenylalkyl ethers were prepared. Direction of the addition, effects ofreagents structure and solvent polarity are consistent with electrophylic origin of the reaction which proceeds as regio- and stereoselective anti-addition. Factors, affecting the type of fragmentamtion of P(V)- containing 1-haloalkenylalkyl ethers with the formation of phosphorylated ketenes or phosphorylated carboxylic acids halides, were studied.

THE SYNTHESIS OF N-ACYLPHOSPHYLAMIDATES

V. Mizrahi, T.F. Hendrickse and T.A. Modro, Department of Organic Chemistry, University of Cape Town, Rondebosch 7700, South Africa

The preparation of $Z_2P(O)$-NR-C(O)R' (1) from both carboxamide and phosphylamide precursors, has been investigated. The synthesis of (1) by the reaction of R'C(O)-NHR with certain phosphylating agents $Z_2P(O)Cl$ (Z = MeO, EtO) under basic conditions, is accompanied by the formation of large quantities of the corresponding tetraalkylpyrophosphate, the mechanism of which is discussed in terms of the involvement of the kinetically controlled O-phosphylimidate $Z_2P(O)$-O-C(NR)R' (2), as an intermediate in the reaction. The preparation of (1) via the N-acylation of $Z_2P(O)$-NHR is even less satisfactory, as illustrated by the outcome of the reaction of the sodium salt of $(EtO)_2P(O)$-NHMe with PhC(O)X (X = Cl, F) in benzene under reflux, in the presence of a catalytic amount of $n\text{-}Bu_4N^+Br^-$, which yields three products : $PhCO_2Et$ (3), PhC(O)-NHMe (4) and $(PhCO)_2NMe$ (5). The formation of ester (3) is explained in terms of E1cB expulsion of ethoxide ion from the phosphoramidate conjugate base. ^1H N.M.R. spectroscopy has revealed that although there is an initial rapid formation of ca. 10% (1), this species does not survive in the medium and its collapse via P-N bond cleavage provides an avenue for the formation of (4) and (5). The mechanism of the P-N cleavage reaction is discussed.

NEW CARBON-PHOSPHORUS BOND FORMATION REACTIONS

Toshikazu HIRAO, Yoshiki OHSHIRO, and Toshio AGAWA

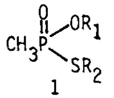
Department of Chemistry, Faculty of Engineering, Osaka University,
2-1 Yamada-oka, Suita, Osaka 565, Japan

Dialkyl arylphosphonates and vinylphosphonates are prepared by the palladium-catalyzed phosphonation of the corresponding bromides with dialkyl phosphite in the presence of triethylamine. In the latter case, the reaction proceeds stereoselectively. gem-Dibromocyclopropanes are subjected to phosphonation on treatment with triethyl phosphite, triethylamine and water to give diethyl cyclopropanephosphonates. These processes provide new and versatile methods for the carbon-phosphorus bond formation. On the contrary, gem-dibromocyclopropanes are reduced to the corresponding monobromides with dialkyl phosphite and triethylamine. 1,1-dibromo-2-trimethylsiloxycyclopropanes or α-bromo-α,β-unsaturated ketones are converted to β,γ-unsaturated ketones.

ON THE MECHANISM OF THE NUCLEOPHILIC DISPLACEMENT AT PHOSPHORUS IN THE PHOSPHOROTHIOLATE S-OXIDE INTERMEDIATE.

Yoffi Segall, Ayala Balan, and Rivka Moalem. Israel Institute for Biological Researh, P.O.B.19, Ness-Ziona, 70450, Israel.

Phosphonothiolates (1, R_1,R_2-alkyls, δ ^{31}P 47-52 ppm), on oxidation with excess m-chloroperoxybenzoic acid (MCPBA), give new peaks in the ^{31}P NMR spectrum. The large shifts to high field of the new lines (26-29 ppm and a pair of singlets at 22 ppm), are associated with oxidized and rearranged products containing a P(O)-O bond rather than the original P(O)-S bond. The peaks at the lower field are associated with m-chlorobenzoyl ester of the phosphonic acid, as established by an independent synthesis. The pair of signals at the higher field are due to the corresponding pyrophosphorus diastereomers. As opposed to phosphorothiolates, where rearrangement to the oxysulfonate occurs following the initial oxidation step, the latter anhydride is not observed in the oxidation of phosphonothiolates. That suggests that intermediate 2 is either much more reactive, undergoing a fast nucleophilic attack, or the rearranged oxysulfonate hydrolyses very fast. MCPBA oxidation of optically active 1 (R_1=i-C_3H_7, R_2=C_2H_5) results in a mixture of m-chlorobenzoyl anhydride and i-propyl pyrophosphorus diastereomer, both of which are optically active. The resulting solution has an opposite rotation sign compared to that of 1. Therefore, 2 does not undergo recemization prior to the nucleophilic displacement, which is assumed to proceed via inversion of the configuration at phosphorus.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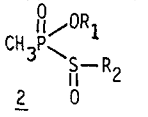
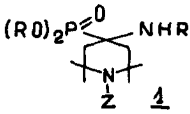

2

SYNTHESIS OF N-/2,2,6,6-TETRAMETHYL-4-PIPERIDINYL/-AMINOALKANEPHOSPHONIC ACID DERIVATIVES.

R. Skowronski, Z.H. Kudzin, J. Skolimowski.
Institute of Chemistry, University of Lodz, 90-136 Lodz, Narutowicza 68, Poland.

The main aim of this research was the synthesis of a new class of nitroxide spin markers containing aminoalkanephosphonic acids 1, 2 or thioureidoalkanephosphonic acids 3.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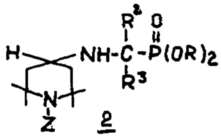
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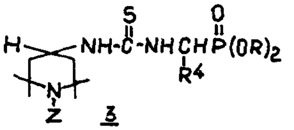
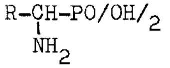

3

R = H, Et, n-Bu; R^1 = H, $PhCH_2$; R^2, R^3 = H, H; Me, H; Ph, H; Me, Me; R^4 = Me, Ph; Z = H, O•
The dialkyl esters of aminoalkanephosphonic acids 1 and 2 were obtained by the addition of dialkyl phosphites to imines of 4-amino-2,2,6,6-tetramethylpiperidine and 2,2,6,6-tetramethyl-4-piperidone derivatives. Thioureido derivatives 3 were prepared by Birum condensation with triphenyl phosphite, aldehyde and N-/2,2,6,6-tetramethyl-4-piperidinyl/thiourea. The introduction of a spin marker to the aminoalkanephosphonic acids increases the applicability of this class of compounds. Chemical and spectroscopy studies of compounds 1, 2, 3 were carried out.

RESOLUTION OF α-AMINOPHOSPHONIC ACIDS BY AMINOACYLASE I

Judit Telegdi, Ferenc Kraicsovits, László Ötvös
Central Research Institute of Chemistry, Hungarian Academy of Sciences

The α-aminophosphonic acids built in peptide chain, important in the pharmaceutical chemistry, have biological activity only in their optically active form. Therefore we have aimed at the preparation of optically active α-aminophosphonic acids through enzymatic resolution of their acyl derivatives. Some acyl aminophosphonic acids were prepared by the methods Isbell and Kabachnik:



$R-\underset{NH_2}{\underset{|}{C}}H-PO/OH/_2$ $R=CH_3$, C_2H_5, C_3H_7, C_6H_5, $C_6H_5-CH_2$, $CH_3-S-CH_2-CH_2$

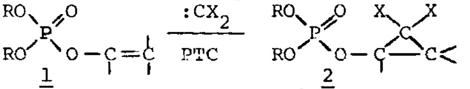
and submitted to the action of aminoacylase I according to Greenstein. As a result we obtained pure optically active aminophosphonic acids in both enantiomeric form. Comparison of the enzymatic reactivity constants of isosteric acyl aminosulfonic-, acyl aminocarboxylic and acyl aminophosphonic acids led to certain conclusions concerning enzyme stereospecificity.

We believe that our new resolution method and the systematic study on enzymatic reaction of aminophosphonic and aminosulfonic acids are important in practical and theoretical point of view, respectively.

SYNTHESIS OF ORGANOPHOSPHORUS COMPOUNDS USING PTC METHODS.

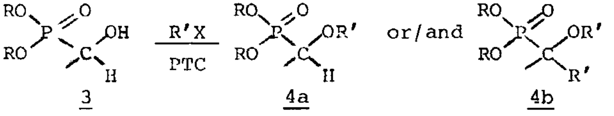
L.Tőke, I.Petneházy, Gy.Keglevich. Department of Organic Chemical Technology, Technical University Budapest, 1521 Budapest, HUNGARY

In general it is not easy to transform phosphoric acid esters to their derivatives by classical methods if hydrolysis also can occur. In these cases special methods are to be used. In recent work we present some reactions using PTC methods to get new compounds. It was synthetised some phosphoric acid esters of type 2 containing a cyclopropyl ring by the addition of dihalogeno-carbene to vinyl phosphates /1/.



X= Cl, Br;
R= alkyl

On the other hand, alkylation reactions of -hydroxy phosphonates /3/ in liquid-liquid PTC circumstances result in formation of products alkylated on the oxygen or/and on the carbon.



R= alkyl
R'X= alkylating agent

SYNTHESIS OF α-AMINOALKYLPHOSPHONIC ACIDS.

Yuan Chengye, Qi Youmao and Xiang Caili. Shanghai Institute of Organic Chemistry, Academia Sinica, 345 Lingling Lu, Shanghai 200032, CHINA.

The discovery of the biological activity and chelating ability of aminophosphonic acids and peptides stimulates the synthetic studies of these phosphorus analogues of natural amino-acids. The present paper reports the systematic investigation of the preparative reactions for α-aminoalkylphosphonic acids:

$$RCHO + H_2NC(X)Y + (RO)_2PZ \longrightarrow RCH(NH_2)PO(OH)_2$$

Where R=H, CH_3, C_2H_5, C_3H_7, C_4H_9, C_5H_{11}, C_6H_{13}, C_8H_{17}, $C_{11}H_{23}$, C_6H_5, p-ClC_6H_4, p-BrC_6H_4, p-$CH_3C_6H_4$. X = O, S. Y= NH_2, C_6H_5NH, CH_3, COOEt, CF_3. Z = OR, OH.
The influence of variation in structure of aldehyde, amino-component and phosphorus reagent on the yield of α-aminoalkylphosphonic acids was described. A reaction mechanism involving the addition of phosphorus ester to the C=N bond resulted from the condensation of aldehyde with amino-component was postulated and dicussed.

C-PHOSPHORYLATION OF COMPOUNDS WITH AN ACTIVE METHYLENE GROUP.

Yuan Chengye, Ding Yixiang, Long Haiyan and Li Shusen. Shanghai Institute of Organic Chemistry, Academia Sinica, 345 Lingling Lu, Shanghai 200032, CHINA.

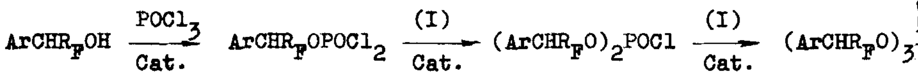
Para-substituted benzylnitrile possessing an active methylene group undergoes stepwise C-phosphorylation smoothly with diethyl phosphoryl chloride in the presence of naphthalene-sodium. Diethyl phosphinyl chloride reacts analogously. The presence of an electron withdrawing group in the benzene ring reduces the yield of phosphorylation seriously. The chemical schift of ^{31}P NMR of the resulted α-cyanobenzylphosphonates correlates linearly with the Hammett σ constants of the substituents. As indicated by ^{1}H NMR studies the protons in the ester ethyl groups are magnetically nonequivalent. These compounds could be alkylated with alkyl halide or condensed with aromatic aldehyde by Horner-Wittig type reaction due to the presence of residual active hydrogen atom.

The structure-reactivity studies of diethyl phosphoryl chloride on various β-diketones and β-keto esters as regiospecific reaction were reported. The influences of metal ions in the enolates on the reactivity of the latter were examined. Only vinyl phosphates with predominantly Z-configuration have been isolated as exclusive products. The C-atom bearing an active hydrogen in the β-diketones investigated is inert to phosphorylation. These experimental results are well supported by reaction selectivity in term of Eqo/Eco,c based on EHMO calculation.

SYNTHESIS AND STEREOCHEMICAL FEATURES OF THE DIFFERENT TYPES OF α-POLYFLUOROALKYLBENZYL PHOSPHATES WITH SEVERAL ASYMMETRICAL CENTRES.

M.I.Kabachnik, L.S.Zakharov, E.I.Goryunov, P.V.Petrovskii
Institute of Organoelement Compounds Academy of Sciences of the USSR
Moscow USSR

The new method of stepped carrying out the catalytic phosphorylation process of α-polyfluoroalkylbenzyl alcohols (I) is suggested. This method gives the possibility to synthesize previously inaccessible symmetrical and unsymmetrical bis(α-polyfluoroalkylbenzyl) chlorophosphates (II) and tris(α-polyfluoroalkylbenzyl) phosphates (III)



$$\underset{(I)}{ArCHR_FOH} \xrightarrow[Cat.]{POCl_3} ArCHR_FOPOCl_2 \xrightarrow[Cat.]{(I)} \underset{(II)}{(ArCHR_FO)_2POCl} \xrightarrow[Cat.]{(I)} \underset{(III)}{(ArCHR_FO)_3\overset{O}{\overset{\|}{P}}}$$

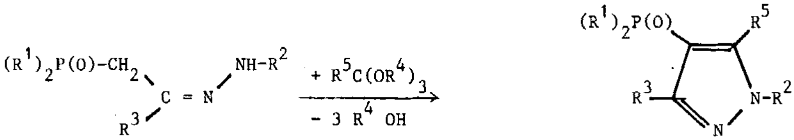
The stereochemistry of phosphates (II) and (III) is investigated by NMR spectroscopy. These compounds are the mixtures of two, three, or four diastereomers with statistical components ratio, according to the number of asymmetrical centers and the molecule symmetry. The influence of the nature of solvents, concentration and temperature on diastereomeric anisochronity value in NMR spectra of chlorophosphates (II) with pseudoasymmetrical phosphorus atom is investigated.

SYNTHESE DE PYRAZOLES PHOSPHONATES EN -4.

A.BEN AKACHA, B. BACCAR, N.AYED . Laboratoire de Synthèse Organique
Faculté des Sciences de Tunis - TUNISIE-

On a déja montré que l'action de PCl_3 sur les hydrazones conduit à des diazaphospholes substitués en - 4 par un groupement oxyde de phosphine (1).

Dans ce travail,nous décrivons la synthèse de pyrazoles comportant un groupement phosphoré en - 4 par action des orthoesters sur les hydrazones des β-cétophosphonates.



Le rendement de la réaction dépend de la nature de l'orthoester utilisé et des substituants de l'hydrazone (R^1, R^2, R^3).

Avec l'orthoformiate d'éthyle ($R^4 = C_2H_5$, $R^5 = H$), les rendements dépassent les 65 %.

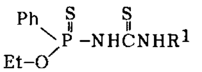
L'identification des produits obtenus a été faite grâce à l'analyse de leurs spectres I.R, R.M.N du ^{31}P, ^1H, ^{13}C et de masse.

(1) N. AYED, R. MATHIS, F. MATHIS et B. BACCAR, C.R. Acad. Sci., 292 II 187 (1981).

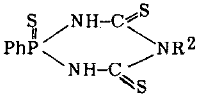
STUDIES ON THE REACTIONS OF $PhP(S)(NCS)_2$ AND (RO)PhP(S)NCS WITH AMINES.

Ru-Yu Chen, Shi-xian Hu, Institute of Elemento-Organic Chemistry, Nankai University, Tianjin, China.

In order to study further reactions of the Ph(EtO)P(S)NCS and $PhP(S)(NCS)_2$ with amines in searching for new pesticides, seven new compounds of the general formulas (I) and (II),

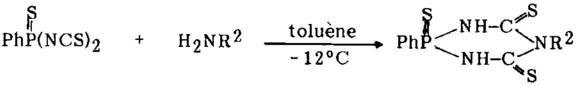


(I)



(II) where R^1=isopropyl, cyclopropyl, isoamyl, morpholinyl, p-chlorophenyl groups, R^2=isopropyl, isoamyl groups, have been synthesized by the reactions of Ph(EtO)P(S)Cl and $PhP(S)Cl_2$ with KSCN and treatment of the intermediate compounds with amines.

It was interesting that the products from $PhP(S)(NCS)_2$ and isopropyl and isoamyl amines respectively were cyclic compounds (II) as shown in the following equation :



(II)

Elemental analysis, IR, NMR, yields, and physical constants of the products (I) and (II) were given.

References : (1) Peter, E.N., Leawood, K., US3691276 (1972).
(2) Ru-yu Chen et al., Scientia Sinica B. 1983, 2 : 109-118.
(3) Shokol, V.A. et al., Zh. Obshch.Kim. 48 (7) 1978, 1656-7.

SYNTHESIS OF ARYLOXY (OR ALKYLOXY) PHENYLPHOSPHONOTHIONATES DERIVATIVES OF ETHYL GLYCINATE.

Ru-yu Chen, Jian-xing Fang, Institute of Elemento-Organic Chemistry, Tianjin, China

More than thirty new compounds of the general formula $PhP(S)(OR)NHCH_2$-COOEt, where R=low alkyl, chloroalkyl, phenyl, and substituted phenyl groups, have been synthesized (equations (1) and (2))for screening in order to find out new pesticides which will be non-toxic to mammals and highly toxic to pests.

$$PhP(S)Cl_2 + ROH \xrightarrow{Et_3N} Ph(RO)P(S)Cl + ET_3N \cdot HCl \qquad (1)$$

$$Ph(RO)P(S)Cl + H_2NCH_2COOEt \cdot HCl \xrightarrow{2Et_3N} Ph(RO)P(S)NHCH_2COOEt + 2Et_3N \cdot HCl \qquad (2)$$

The reaction intermediates, Ph(S)(OR)Cl were difficult to be purified by distillation under the pressure of 0.1mm Hg, as most of them decomposed near their boiling points under vacuum with the exception of the compound with R=Et. For this reason, one-step process without the isolation of the reaction intermediates was used.

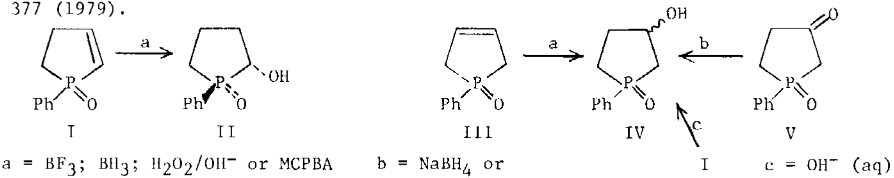
The advantages of one-step method over that of the two-steps were that higher overall yields of the products were obtained and it was more convenient to synthesize these compounds.

References: (1) Mulliez, M. Phosphorus and Sulfer, 1980, 9(2), 209-20 .
(2) Grapov, A.F., et al, U.S.S.R. 308,639 (1981).

SYNTHETIC ROUTES TO 1-PHENYL-2- & 3-PHOSPHOLANOL 1-OXIDES.

Edgar Howard, Jr., M.Z. Chen & R.E. Dagger, Dept. of Chem., Temple Univ., Philadelphia, PA 19122 U.S.A.

1-Phenyl-3-phospholanol 1-oxide, IV, first prepared by addition of OH^- to I (R.S.Jain, this lab) has also been made by reduction of the ketone V and hydroboration-oxidation of III. Although early work suggested that nucleophilic attack of I & V was sterically controlled by phenyl, later work has shown that even hindered hydrides give diastereomers of IV. Hydroboration of the C=C in I and III was a synthetic challenge because of the competition of P=O for BH_3, leading to ring-opened products. Protection of P=O by prior addition of 1.0 equiv of BF_3:Et_2O (0.5 hr; rt) to a $CDCl_3$ solution of III, then 1.0 equiv BH_3-THF (9 hr; rt), followed by H_2O_2/OH^- or MCPBA workup gave 33-54% of a 57:43 Z/E mixture of IV. Similar protection of I in $CDCl_3$ with BF_3:Et_2O, then BH_3-THF (72 hr; rt), followed by oxidative workup gave 14% pure II, Z-isomer only. This compares favorably with an alternate synthesis of II, Musierowicz et al., Phos. & Sulfur, 5, 377 (1979).



a = BF_3; BH_3; H_2O_2/OH^- or MCPBA

b = $NaBH_4$ or K-Selectride

c = OH^- (aq)

SYNTHETIC APPROACHES TO DIPHENYLPHOSPHINO-SUBSTITUTED 2-PHOSPHOLENES AND PHOSPHOLES.

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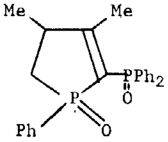
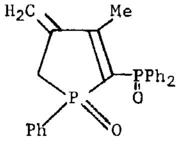
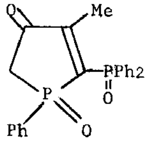
Further to our studies of the coordination chemistry of phospholes, we have carried out a preliminary investigation of the synthesis of diphenylphosphino-substituted 2-phospholenes and phospholes. Among the structures synthesized are those shown below.



I



II



III

Structure II is formed from I (briefly reported earlier by Mathey) by an allylic photobromination - dehydrobromination sequence. III is of great interest since it forms from II in air in the solid state in the dark under refrigeration. A free-radical O_2 oxidation is suggested on the basis of AIBN catalyzed oxidations of II which give III in good yield. The generality of this reaction will be discussed as will other reactions of III and NMR spectroscopic data for all products.

FORMATION D'OLEFINES SUBSTITUEES AU COURS D'UNE REACTION D'ARBUZOV.

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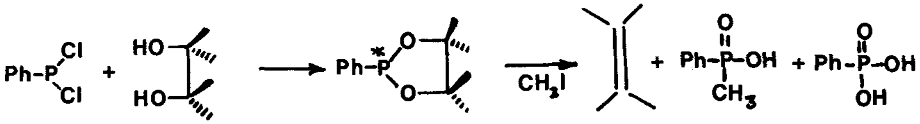
La réaction de diols-1,2 dérivés d'acide lactique ou de la camphoquinone avec la dichlorophénylphosphine ,conduit à de nouveaux dioxaphospholanes-1,3,2 optiquement actifs. Leur réaction avec l'iodure de méthyle donne facilement une élimination et la formation d'oléfines substituées:



Dans les mêmes conditions, l'hydrobenzoïne d,l ou méso conduit à un mélange de cis/trans stilbène 15-85 .La généralisation de cette réaction ,et le mécanisme ,sont étudiés.

REACTIONS OF α,β-UNSATURATED PHOSPHORUS (III) DERIVATIVES WITH ELECTROPHILIC SYSTEMS

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Kazan State University

The general method of synthesis for a new fivemembered nitrogen phosphorus containing heterocycles was worked out on the basis of reaction of α,β-unsaturated P(III) derivatives with wide range of electrophilic agents.Isocyanatophosphites, their thioanalogues and substituted methylenamidophosphites can act as specific 1,3-dipoles towards the majority of systems with C=O, C=N and C=C bonds.

Two-stated mechanism for cycloaddition is proposed.The scheme involves the formation of bipolar ions with P-C or P-O-C bonds and azaphospholenes followed by their stabilization via imide-amide and imide-imide rearrangement, dimerization or hydrolises depending on the structure of imidophosphorus compound. Reactions between the P(III) compounds mentioned and α-halogen carbonyl compounds may proceed via cycloaddition as well as via Perkov rearragement. Reactions of dialkylisocyanatophosphites with α-dicarbonyl and α,β-unsaturated carbonyl compounds involve phosphorus atom only, NCX-group acting as pseudohalogen and undergoing nucleophilic substitution.

PHOSPHORUS-CONTAINING DERIVATIVES OF THE DIENE-DIOL FORM OF ACETYLACETON

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Reactions of dichlorides of P(III) and P(IV) with acetylacetone in the presence of the base, stdied by us, showed, that it is possible to obtain structures, derived from the hypothetical diene-diol form of acetylacetone - 2-substituted 4-methylen-6-methyl-I,3,2-dioxaphosphorines. Detailed investigation of the effect of acetylacetone on the mono- and dichlorides of P(III) and P(IV) in the presence of a base made it possible to establish the regularities, determining the formation of either the derivatives of enol form (open-chain β-acetylisopropenylphosphites) or the derivatives of the diene-diol form (cyclic 4-methylen-I,3,2-dioxaphosphorines). The formation of cyclic phosphorus-containing substances was found to proceed stepwise. Firstly open-chain β-acetylisopropenylphosphites derived from the enol form of β-dicarbonylic compound are formed. Then, if the conformation of the β-acetylisopropenyl radical is cis-S-cis, the formation of the ring systems is possible, but it is the presence of definite substituents, attached to the phosphorus atom, the acidic impurities in the reaction mixture and the temperature that are the the decisive factors in this process.

SYNTHESIS AND STRUCTURE OF N-ALKOXY OR N-HYDROXY 1,4-AZAPHOSPHORINANE

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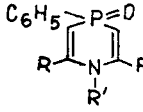
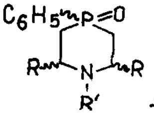
The process studied was the synthesis of N-hydroxy or N-alkoxy 1,4-dihydro-1,4-azaphosphorine 1a derivatives as a result of cyclisation of monoacetylene phosphonium salts or as a result of oxidation of 2,4,6-trisubstituted 4-oxo-1,4-dihydro-1,4-azaphosphorinanes 1b by dibenzoyl peroxide.



1



2

R = C_6H_5,t-C_4H_9

1a R' = OH,$C_6H_5CH_2O$,CH_3O

1b R' = H

The reduction of compounds 1 was studied with the aid of formic acid or $NaBH_3CN$ and $NaBH_4$ in acetic acid. This reduction leads to 1,4-aza-phosphorinanes 2. As a result of oxidation of 2/R=OH/ with PbO_2 or HgO in organic solvents, unstable nitroxides were generated. The compounds obtained were studied with the use of ^1H and ^{31}P NMR spectroscopy or ESR spectroscopy for paramagnetic compounds.

LE P TRICHLORO N DICHLOROPHOSPHORYLE MONOPHOSPHAZENE, CARREFOUR DE LA CHIMIE DES PHOSPHAZENES.

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Plusieurs groupes de réactions originales de $Cl_2(O)PNPCl_3$ ont été étudiées. Il s'agit essentiellement de substitutions nucléophiles, montrant que le groupement = $NPCl_3$ présente une réactivité particulière.

- L'hydrolyse dont P_2NOCl_5 est la première étape si l'on part de $(NP_2Cl_6)^+PCl_6^-$; se fait par l'intermédiaire de deux étapes essentielles : $HN(P(O)Cl_2)_2$ et $HN(P(O)(OH)_2)_2$
- Par action de sels oxygénés XOM(X=NO,NO_2,AcO ; M=Na,K,NH_4,Pb) avec ou sans solvant; on remplace 1 Cl par OM. Le sel obtenu, pourrait être considéré comme un di(dichlorophosphoryle)imidate, identifié par des réactions caractéristiques ainsi que par IR et RMN. La pyrrolidine donne un pyrrolidinyl dichloro et un dipyrrolidinyl chloro N dichlorophosphoryle monophosphazène.

Le di(chloroéthyl)amine donne de même les dérivés mono et di|di(chloroéthyl)|amino phosphazènes.

Le trifluoroéthanol conduit à un mono et à un diester dont les propriétés sont d'un grand intérêt.

Par pyrolyse contrôlée on obtient des polychlorophosphazènes linéaires de longueur variable allant au moins jusqu'à 2000 motifs et modulables à volonté.

Techniques de caractérisation utilisées : RMN ^{31}P, ^{1}H, ^{13}C-IR - spectrométrie de Masse.

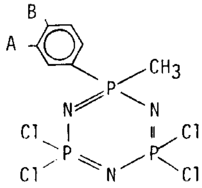
RECENT SYNTHETIC ADVANCES DESIGNED TO PROBE THE BONDING WITHIN CHLOROCYCLOTRIPHOSPHAZENES.

Paul J. Harris and Kenneth B. Williams. Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061.

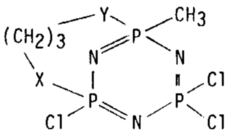
Several new synthetic advances toward the preparation of molecules designed to probe the bonding in phosphazene compounds will be presented. Specifically, the synthesis and physical properties of aryl substituted phosphazenes of type I, and ANSA phosphazenes of type II will be discussed. Compounds I are designed to probe the possibility of chlorophosphazene-aryl group interactions by the use of IR, NMR, UV, and PES techniques. ANSA compounds of type II are designed to probe the possibility of a delocalized π system within the phosphazene ring.

A=H,B=F,Me,etc.

B=H,A=F,Me,etc.



I



II

X=Y=NH_2

Y=NH_2,X=O

NEW PHOSPHAZENE POLYMERS DERIVED FROM THE FRIEDEL CRAFTS REACTION OF HEXA(ARYLOXY)CYCLOTRIPHOSPHAZENES.

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Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012, India.

The reactions of hexa(aryloxy)cyclotriphosphazenes, $N_3P_3(OR)_6$ (R = C_6H_5, C_6H_4Me-p) with polyhaloalkanes in the presence of anhydrous aluminium chloride yield new crosslinked phosphazene polymers. The thermal stability of the polymers derived from various haloalkanes increased in the order

$$1,2\text{-}ClCH_2CH_2Cl > CHCl_3 > CH_2Cl_2 > CCl_4.$$

The thermal stability also increased with increasing amounts of the catalyst, reaching a maximum at 1:10 mol ratio ($N_3P_3(OPh)_6$:$AlCl_3$) and remaining constant with further increase in the amount of the catalyst. These crosslinked phosphazene polymers exhibit much greater thermal stability compared to that of the linear polyorganophosphazenes, $|R_2P{=}N|_n$ (R = OPh, Ph or SCN) and also the polymers prepared by the Friedel Crafts reaction of (O)P(OPh)$_3$ or (O)P(OC$_6$H$_4$Me-p)$_3$ with halo-alkanes. The results show that the side-group modification of readily available organophosphazenes can provide a useful method for the synthesis of phosphazene polymers and for crosslinking linear polymers in a subsequent curing process. The preparation, characterisation and the thermal analysis of this new class of polyorganophosphazenes will be discussed.

PHOSPHAZENE COMPOUNDS AS FLAME RETARDANTS OF POLYESTER FIBERS.

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Several bromophenoxyphosphazene compounds have been synthesized in the laboratory and as well as pilot scale, mainly hexa (2,3,4,5,6-pentabromophenoxy) - phosphazene, hexa - (2,4,6-tribromophenoxy) - phosphazene and hexa - (4-bromophenoxy) - phosphazene. Synthesis of mentioned compounds was carried out by different methods with 85-92% yield. The quality of the obtained products has been estimated on basis of elemental analysis, IR spectrum, 31P NMR and thermal analysis. The thermal destruction of above phosphazene derivatives was over 300°C, which recommended these compounds as flame retardants for polyester fibers. Bromophenoxyphosphazenes have been introduced to polyethyleneterephtalate in the different stages of the synthesis or to the granulated polymer before extrusion and spinning of the fibers. This flame retardant of polyethyleneterephthalate was used for spinning of the fibers at a speed of 800 m/min. The fibers and the fabrics produced from these fibers have the oxygen index LOI=26-28.

STUCTURAL STUDIES ON SPIRO DERIVATIVES OF HEXACHLOROCYCLOTRIPHOSPHAZATRIENE - Sorab R. Contractor,* Michael B. Hursthouse,[1] Leylâ S. Shaw*[1] Robert A. Shaw,* and Hamza Yılmaz* - Department of Chemistry, Birkbeck College, (University of London) Malet Street, London, WC1E 7HX, U.K.; Queen Mary College (University of London), Mile End Road, London, E1 4NS, U.K.

Spiro derivatives of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$, with ethylene glycol, 1,3-propylene glycol and 1,4-butylene glycol have been prepared and subjected to X-ray crystallographic analysis. The structures of the resultant compounds which contain a six-membered phosphorus-nitrogen ring, a phosphorus atom of which is at the same time also part of a 5-,6-, and 7-membered ring will be presented. The structures and conformations of these spiro compounds will be discussed and compared with those of related compounds. An attempt will be made to relate the structures to physical properties and chemical reactivity.

THE REACTION OF OCTACHLOROCYCLOTETRAPHOSPHAZATETRAENE WITH TRIFLUOROETHOXIDE - [+]A GC-MS STUDY, K.C. Kumara Swamy, S.S. Krishnamurthy, Robert A. Shaw[+], A.R. Vasudeva Murthy and Michael Woods[+], Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012, India; [+]Department of Chemistry, Birkbeck College, (University of London), Malet Street, London, WC1E 7HX, U.K.

The reaction of octachlorocyclotetraphosphazatetraene ($N_4P_4Cl_8$) with sodium trifluoroethoxide in diethyl ether has been investigated. The formation of more than twenty trifluoroethoxy derivatives, $N_4P_4Cl_{8-n}(OCH_2CF_3)_n$ (n = 1-8) is revealed by a gas chromatography cum mass spectrometric (GC-MS) analyses of the reaction mixtures. To alleviate the problems associated with the extreme hydrolytic instability of chloro(trifluoroethoxy)cyclotetraphosphazatetraenes, the reaction mixtures are subjected to "exhaustive dimethylaminolysis". Separation of the dimethylaminated reaction mixtures by column chromatography is partially successful; the efficiency of separation and the purity of the products can be monitored by Gas Liquid Chromatography (GLC). The retention times of (trifluoroethoxy)cyclotetraphosphazatetraenes (OV17 on Diatomite CQ column) decrease drastically with the increase in the number of trifluoroethoxy groups. Structural elucidation of the products by NMR spectroscopy and the chlorine replacement pattern are discussed.

CONTROLLED HYDROLYSIS OF INORGANIC RING SYSTEMS.

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The hydrolysis of $(NPCl_2)_3$, ultimately leading to NH_3 and H_3PO_4, has been suggested to proceed via geminal forms of $N_3P_3Cl_4(OH)_2$ and $N_3P_3Cl_2(OH)_4$, but lack of stability has prevented the characterization of these compounds. In order to gain more insight in the hydrolysis pathway we have conducted a number of reactions of $(NPCl_2)_3$ and the related ring systems *$NPCl_2(NSOX)_2$ and $(NPCl_2)_2NSOX$ (X = Cl, Ph) with water in* acetonitrile in the presence of Ph_4AsCl or 18d6-crownether $(C_{12}H_{24}O_6)$/KCl. The reactions afforded stable mono- and disubstituted products, all of them salts of hydroxy derivatives.

It appeared that the disubstituted derivative of $(NPCl_2)_3$ had a non-geminal structure, whereas the analogous derivative of $(NPCl_2)_2NSOCl$ had a geminal structure (^{31}P NMR, X-ray analysis). The strikingly dissimilar behaviour of the two ring systems towards H_2O *is ascribed to the larger basicity of* $(NPCl_2)_3$ with respect to $(NPCl_2)_2NSOCl$. This greatly affects the charge distribution within the reaction intermediates, leading to essentially different substitution pathways.

ALKYL AND ARYL SUBSTITUTED POLYPHOSPHAZENES: SYNTHESIS AND REACTIVITY.

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Further studies of the condensation polymerization of N-silylphosphinimines, $Me_3SiN{=}P(OCH_2CF_3)RR'$, have resulted in the preparation of new polyphosphazenes, $(RR'PN)_n$, with alkyl and/or aryl groups directly bonded to phosphorus through P-C bonds. The most recent of these include polymers and copolymers with various combinations of substituents (R,R' = Me, Et, Ph, CH_2Ph, n-Pr, $CH_2CH = CH_2$). The synthesis and characterization of the polymers, as well as the synthesis of some of the precursors will be discussed. Recent results of our investigation of the chemical reactivity of poly(dimethyl)phosphazene will also be given. These will include reactions with MeI, CF_3COOH, CH_3COOH, and n-BuLi.