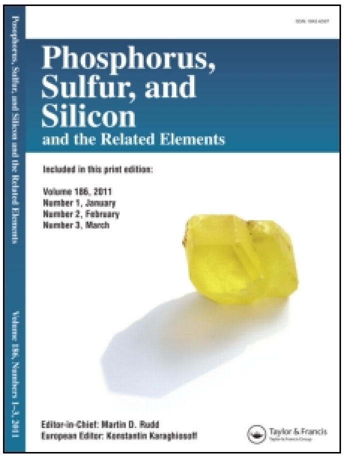
This article was downloaded by:
On: *30 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Structures, Reactivity, Mechanisms in Organophosphorus Chemistry

To cite this Article (1983) 'Structures, Reactivity, Mechanisms in Organophosphorus Chemistry', Phosphorus, Sulfur, and Silicon and the Related Elements, 18: 1, 435 — 450

To link to this Article: DOI: 10.1080/03086648308076052

URL: http://dx.doi.org/10.1080/03086648308076052

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Phosphorus and Sulfur, 1983, Vol. 18 pp. 435-450
0308-664X/83/1801-0435/$18.50/0

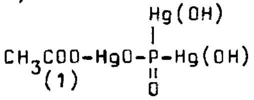
© 1983 International Union of Pure and Applied Chemistry
Printed in the United States of America

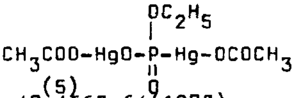
MERCURATION OF UNSATURATED β-BROMO PHOSPHONITE AND α-CHLORO PHOSPHONATE

William I.Awad,Emtithal A.El-Sawi and Tahia B.Mostafa.
Chem.Dept.Univ.Coll.for women Ain Shams Univ.Cairo,EGYPT.

The present work deals with mercuration of diethyl(2-bromo-1-phenyl, vinyl)phosphonite and diethyl(1-chloro-1-phenyl,vinyl)phosphonate with mercuric acetate at different temperatures,solvent and ratios of the reagents.Different mercurated products were obtained some of them were due to cleavage of P-C bond with the formation of mercurated aliphatic phosphonites and phosphonates.The others were formed through substitution and addition reactions.The new compounds prepared in these studies,their melting points and their analysis have been collected.

Compound no.(1)is predominant in the case of phosphonite while compound no.(5)is prevalent with phosphonate. The latter was previously described[1].In all cases infra-red spectra are consistant with the proposed structures.It is clear that in this type of reaction cleavage of C-P bond usually occurs.


$$CH_3COO{-}HgO{-}\underset{\underset{O}{\|}}{\overset{\overset{Hg(OH)}{|}}{P}}{-}Hg(OH)$$
(1)


$$CH_3COO{-}HgO{-}\underset{\underset{O}{\|}}{\overset{\overset{OC_2H_5}{|}}{P}}{-}Hg{-}OCOCH_3$$
(5)

1-W.I.Awad,M.El-DeeK&E.El-Sawi,Tetrahed.lett.,47,4663-64(1973).

Downloaded At: 10:14 30 January 2011

SPECTRES DE MASSE SOUS IONISATION CHIMIQUE DE COMPOSES DIASTEREOISOMERES EN SERIE DIOXA ET OXAZAPHOSPHORINANE.

D. BOUCHU, H. HALIMI, P. LHOSTE, D. FRAISSE et J. DREUX.
Université Claude Bernard Lyon I, Labo. de synthèse et de Chimie Organique Appliquée, 43 Bd du 11 novembre 1918, 69622 Villeurbanne Cédex, France.

L'étude en spectrométrie de masse de la fragmentation sous impact éléctronique des esters cycliques des acides phosphoriques et thiophosphoriques est maintenant bien documentée. Nous avons pour notre part montré que cette technique pouvait, grâce à la mise en évidence de relations entre les fragmentations et la stéréochimie de composés diastéréoisomères, être un moyen utile d'attribution de la configuration.

Nous avons maintenant prolongé cette étude par l'enregistrement de spectres d'ionisation chimique d'un certain nombre de composés en série dioxa et oxazaphosphorinane en faisant varier le gaz ionisant. Nous avons ainsi recherché s'il pouvait exister des différences entre les spectres d'ionisation chimique des diastéréoisomères qui seraient dues à des différences de réactivité de ceux-ci :

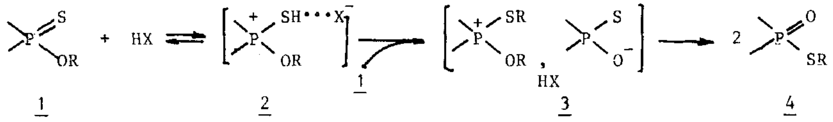
- soit lors du processus d'ionisation chimique par le gaz réactif,
- soit lors de la décomposition unimoléculaire qui fait suite à l'ionisation,
- soit encore lors de réactions bimoléculaires après ionisation.

Les spectres de collision (CID) des adducts obtenus après ionisation par un mélange d'ammoniac et de pyridine ont été enregistrés pour deux paires de composés épimères au niveau de l'atome de phosphore en série dioxaphosphorinane. Ils consistent essentiellement dans la formation de l'ion moléculaire protoné des esters phosphorés et de l'ion pyridium. Les valeurs des rapports de ces ions sont en bon accord avec la basicité plus grande d'une liaison P=O axiale en série dioxaphosphorinane.

ALKOXYPHOSPHONIUM SALT INTERMEDIATES IN THE THIONO-THIOLO REARRANGEMENTS OF PHOSPHYLTHIONATES IN PROTIC ACID MEDIA

Karol S. Bruzik and Wojciech J. Stec
Polish Academy of Sciences, Centre of Molecular and Macromolecular Studies,
90-362 Łódź, Boczna 5, Poland

According to the earlier proposed mechanism for the thiono-thiolo rearrangement of O-alkyl phosphylthionates 1 in protic acid solutions alkoxyalkylthiophosphonium salts 2 and 3 are the key intermediates in this reaction (Bruzik, K.S., Stec, W.J. (1979) J.Org.Chem. 44, 4488; ibid, 1981, 46 1618; ibid, 1981, 46, 1625).



The existence of two types of transient alkoxyphosphonium intermediates is postulated; 2 with thiophosphoryl sulfur being protonated and 3 formed by alkylation of the neutral substrate molecule 1. Direct evidences for the involvement 2 and 3 in the promotion of alkyl group transfer from oxygen to sulfur atom of 1 are presented. Alkylation of the phosphylthioate anion vs. neutral phosphylthionate by the alkoxyphosphonium salt in acidic media and its consequences for the reaction mechanism is discussed.

THE INTERACTION OF SOME P(III) COMPOUNDS WITH SILYL HALIDES

J.Chojnowski, M.Cypryk, J.Michalski
Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences
90-362 Lodz, Boczna 5, Poland

Though the interaction of P(IV) compounds with compounds of silicon having a polarizable substituent was recently studied little is known about the similar interaction involving compounds of tricoordinate phosphorus. This knowledge is necessary for a better understanding of both the reactivity of various P(III) compounds towards silicon reagents as well as the behaviour of compounds bearing P(III) and Si centres. We found that various classes of P(III) compounds among which are phosphorous acid triamides, esters of diorganophosphinic acids and trialkyl phosphines are able to form ionic complexes with some triorganosilyl halides An example is 1/1 complex formed as a result of the addition of equimolar amounts of Me_3SiI to $P(NMe_2)_3$ solution in CH_2Cl_2 at -50°C. In an excess of $P(NMe_2)_3$ both the amide and the complex give separate ^{31}P NMR signals indicating that the exchange is slow as compared with the NMR time scale, what is in contrast to HMPT/Me_3SiI system showing only one averaged signal. After rising the temperature the following reaction occurs :

$$Me_3SiI + 2P(NMe_2)_3 \xrightarrow[-Me_3SiNMe_2]{} [(NMe_2)_3P\text{-}P(NMe_2)_2^{+}]I^- \xrightarrow[-Me_3SiNMe_2]{Me_3SiI} 2(Me_2N)_2PI$$

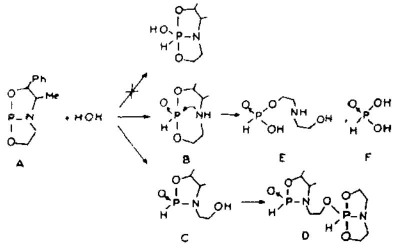
The reaction proceeds quantitatively and may serve as a convenient synthetic route to $IP(NMe_2)_2$.

Downloaded At: 10:14 30 January 2011

HYDROLYSE D'UN AMINO-PHOSPHITE BICYCLIQUE CONTRAINT

OUSMANE SEYDOU DIALLO ET RAYMONDE MATHIS, Laboratoire des Hétérocycles du Phosphore et de l'Azote, Université Paul Sabatier, 118 route de Narbonne 31062 Toulouse Cédex .

L'étude en spectrographies infrarouge et de résonance magnétique nucléaire montre que l'hydrolyse du phosphite à liaison P_{III}-N, A, conduit aux composés $[P_{IV}]$, B et C, C réagissant aussitôt sur A pour donner le composé mixte $[P_{IV}, P_V]$, D, puis à des produits de dégradation E ou F. On n'observe jamais la formation d'un composé d'addition de type $N\text{-}P_{(V)}\begin{smallmatrix}H\\OH\end{smallmatrix}$, analogue à ceux que l'on détecte dans des réactions d'alcoolyse $N\text{-}P_{(V)}\begin{smallmatrix}H\\OR\end{smallmatrix}$



Le proton (N)H de B est relativement acide en raison de la conjugaison transannulaire entre l'atome d'azote et l'atome de phosphore $[\nu_{NH}(CCl_4) - \nu_{NH}(pyridine) = 117\ cm^{-1}]$

Downloaded At: 10:14 30 January 2011

CARBENE INTERMEDIATES IN THE REACTION OF TRIALKYL PHOSPHITES WITH DIALKYL AROYLPHOSPHONATES

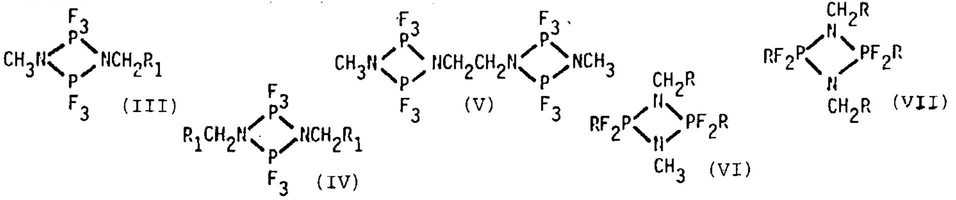
D.V. Griffiths, University of Keele, Staffordshire, England ST5 5BG.
J.C. Tebby, North Staffordshire Polytechnic, Stoke-on-Trent, England.

The reaction of trialkyl phosphites with a number of 2- and 4-substituted dialkyl benzoylphosphonates have been investigated both in the presence and absence of electrophiles. In both cases the reaction products are best explained by proposing an initial attack by the trialkyl phosphite on the carbonyl oxygen of the aroylphosphonate to give an anionic intermediate. At room temperature reaction only proceeds further at a significant rate if a suitable electrophile, such as a proton donor, is present to trap the anionic intermediate as it forms. The resulting quasi-phosphonium salt then undergoes dealkylation to form either a diphosphorus compound or a phosphonate plus trialkyl phosphate. In the absence of an electrophile the reaction only proceeds further at a significant rate above about 80°C. Under these conditions we believe that the anionic intermediate undergoes cleavage of the αC-O bond to give a carbene. If a suitable "ortho" substituent is present on the aryl ring a carbene insertion reaction can occur to give a cyclic system. If no such group is present the carbene is trapped by the trialkyl phosphite present to give novel quasi-phosphonium ylide phosphonates which in some cases rearrange to give diphosphonates.

NUCLEOPHILIC SUBSTITUTION REACTIONS OF $ClCH_2(NPF_3)_2CH_3$(I)AND $(ClCH_2NPF_3)_2$(II)WITH SELECTED ORGANOMETALLIC REAGENTS.

HEINRICH HAHN,WOLFGANG MEINDL,KURT UTVARY,INSTITUTE OF INORGANIC CHEMISTRY, TECHNICAL UNIVERSITY OF VIENNA,AUSTRIA.

Photochemical chlorination of $(CH_3NPF_3)_2$ yields I and II,which are valuable compounds to obtain a number of new N-substituted fluorodiazadiphosphetidines by reaction with organometallics.By this method it is possible to synthesize unsymmetric N-substituted hexafluorodiazadiphosphetidines(III) without the difficulties of former methods.Depending on the nucleophilic strength of the used organometallic reagents the chlorin atom of the$>N-CH_2Cl$ group can be selectively substituted versus an organic rest without side-reaction at the phosphorus atom.The reaction of I with magnesium leads to the dimerizationproduct(V).With $LiOCH_3$ or $LiSCH_3$ the corresponding N-and P-substituted diazadiphosphetidines(VI)and(VII)are formed.



(III) (IV) (V) (VI) (VII)

CONFORMATIONAL ANALYSIS OF PHOSPHORUS SX-DERIVATIVES

E.A.Ishmaeva, I.I Patsanovsky, A.N.Pudovik
A.E.Arbuzov Institute of Organic and Physical Chemistry AS USSR
Kazan State University

Conformations of phosphorus thioesters of type $R^1R^2P(Y)SX$, where R^1, R^2 = Alk, OAlk, SAlk; X = Alk, $SiAlk_3$, $SnAlk_3$, Cl; Y = lone pair, O, S, determined by use of set of physicochemical data, including vibrational spectroscopy, electric and electrooptical properties. General principles are suggested for investigation of conformations of molecules with several internal rotation axes.

The preference of the forms with trans and gauche orientations of SX bonds in relation to lone electron pair or P=Y bond is typical for all compounds investigated. Results are compared with data for similar compounds having P(Y)-OX fragment. Coordination of phosphorus and the nature of R^1, R^2, X groups determine preferences of conformers in equilibrium, relative role of steric, electrostatic, and resonance interactions.

Conformations of molecules with one axis of internal rotation are retained essentially in compounds containing two or three fragments P-SX both in presence and in absence of other internal rotations, e.g. about P-OAlk bond.

The preference of staggered bond orientations is the general conformational rule for phosphorus thioesters.

Downloaded At: 10:14 30 January 2011

IRREVERSIBLE AND REVERSIBLE (ELEMENTOTROPIC) REARRANGEMENTS OF ELEMENT-SUBSTITUTED (P, As, Sb) CARBONYL COMPOUNDS.

I.F.Lutsenko, Z.S.Novikova, V.L.Foss, A.N.Kurkin
Moscow State Lomonosov University U.S.S.R.

Methods of synthesis of O- and C-isomeric element-substituted (P, As, Sb) carbonyl compounds were developed and their irreversible and reversible rearrangements were found.
Factors responsible for the relative thermodynamic stability of O- and C-isomers were studied. Raising enolysability of carbonyl compounds in ester-ketone-aldehyde as well as the presence of electron-acceptor substituents in the molecule of these compounds were shown to stabilize O-isomers. An increase of steric hindrances at -carbon atom of a carbonyl compound and the size of the radical at the element results in the greater destabilization of C-isomers than O-form. Reversible elementotropic transformations are observed for O- and C-derivatives of As and Sb, whose thermodynamic stabilities are close and energy rearrangement barriers are rather small. The investigation of the effect of the nature of radicals at phosphorus atom on the stability of isomers in phosphorus derivatives showed that alkyl substituents stabilize C-isomers, while dialkylamide groups reduce the energy barrier of the rearrangement and stabilize O-form.

Downloaded At: 10:14 30 January 2011

CLEAVAGE REACTIONS OF PHOSPHORAMIDITES, PHOSPHORAMIDATES, AND PHOSPHORAMIDES.

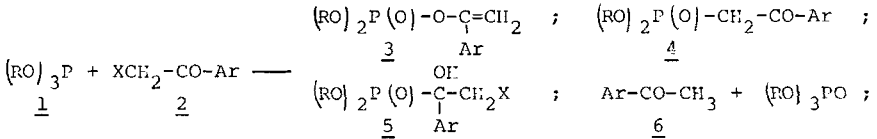
P. J. Eccles, H. R. Hudson, C. Mavrommatis, M. Pianka, and A. R. Qureshi, School of Chemistry, The Polytechnic of North London, Holloway Road, London N7 8DB, U.K.

Reactions of neopentyl *N,N,N',N'*- tetramethylphosphorodiamidite with alkyl halides show an increasing tendency to quaternization at nitrogen and P-N fission in the order I < Br < Cl. Iodomethane gave only the quasiphosphonium salt which was shown to decompose on heating by an S_N2 process to yield neopentyl iodide and methylphosphonic bisdimethylamide. On the other hand, chloromethane also gave tetramethylammonium chloride, formed by reaction at nitrogen, P-N fission, and further reaction of the so-formed trimethylamine with excess of chloromethane. Bromomethane reacted by both pathways. The results provide an example of contrasting hard and soft acid behaviour of the halogenoalkanes in their reactions with ambident P-N nucleophiles. The differing behaviour of phosphoramidates and phosphoramides in their reactions with electrophilic reagents is illustrated by their reactions with chloral. Whereas *O,O*-diethyl phosphoramidate gives a 1:1 adduct in high yield, an increasing tendency to P-N fission accompanies the replacement of RO by R_2N. The phosphoramide $(Me_2N)_2P(O)NH_2$ thus underwent cleavage with chloral to yield dimethylformamide, chloroform, polymeric phosphorus-containing products, and also $(Me_2N)_2P(O)NHCH(CCl_3)NMe_2$, whose structure was confirmed by X-ray crystallography. $(Me_2N)(RO)P(O)NH_2$ showed intermediate behaviour.

REACTIONS OF TRIALKYL PHOSPHITES WITH HALOGENO ACETOPHENONES IN PROTIC SOLVENTS.

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

It is known from the literature, that the reaction between trialkyl phosphite and α-haloketone in protic solvent results in formation of vinyl phosphate 3, β-ketophosphonate 4, α-hydroxy phosphonate 5 and dehalogenated ketone 6 but detailed work for the product formation supported by firm mechanistic studies are missing. In this paper we present our work on the reactions of α-haloacetophenones:



$$\underset{\underline{1}}{(RO)_3P} + \underset{\underline{2}}{XCH_2\text{-}CO\text{-}Ar} \longrightarrow \underset{\underline{3}}{(RO)_2P(O)\text{-}O\text{-}\underset{Ar}{C}{=}CH_2}\ ;\ \underset{\underline{4}}{(RO)_2P(O)\text{-}CH_2\text{-}CO\text{-}Ar}\ ;\ \underset{\underline{5}}{(RO)_2P(O)\text{-}\overset{OH}{\underset{Ar}{C}}\text{-}CH_2X}\ ;\ \underset{\underline{6}}{Ar\text{-}CO\text{-}CH_3} + (RO)_3PO\ ;$$

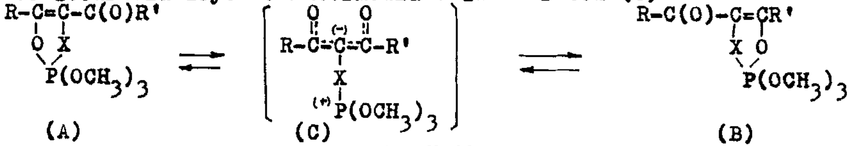
X= Cl, Br; R= Me, Et, iPr; Ar= ring substituted aryl

On the basis of kinetic and nonkinetic methods we substantiated a resonable mechanism involving common intermediate for the formation of the products. A number of new compounds were prepared and identified. The side reactions were also examined.

PHOSPHOROTROPIC TAUTOMERISM OF CYCLIC PHOSPHORANES

B.A.Arbuzov, N.A.Polezhaeva, A.V.Aganov, A.I.Khaiarov
The A.M.Butlerov Chemical Research Institute, University, Kazan, USSR

A tautomerism for series of five-members cyclic phosphoranes with an acyl group in position-4 have been discovered and studied. An equilibrium of two tautomeric forms of pentacoordinated phosphorus atom (A⇄B) is supposed to accur via acyclic intermediate zwitter-ion (C)



X=CHR'', O, NPh

The values of chemical shifts $\delta\ ^{31}P$ for the compounds studied have been shown to be unchanged in the range of temperatures from 203K to 383K. Rate constants and thermodynamic parameters of phosphorotropic rearrangemets have been determined by means of dynamic NMR (^1H and ^{13}C) spectroscopy.

Downloaded At: 10:14 30 January 2011

UTILISATION DE LA SPECTROSCOPIE DE VIBRATION A L'ETUDE DES RELATIONS PROPRIETES-STRUCTURES DES COMPOSES OXYFLUORES DU PHOSPHORE V TETRAVALENT.

SEMMOUD A. - ADDOU A. - VAST P. Laboratoire de Chimie Appliquée - Sp. In.
LEGRAND P. - L.A.S.I.R. L.P. 2641
Université de Lille 1 - 59655 - Villeneuve d'Ascq Cédex

Dans le cadre d'une étude spectroscopique des composés oxyfluorés du phosphore V, nous nous sommes intéressés aux édifices $PO_2F_2^-$, PO_3F^{--} et POF_3. Le calcul à priori des fréquences dans le champ de forces de symétrie locale a permis de proposer une description cohérente des modes normaux de vibration. Nous avons ensuite testé la transferabilité de ce champ de force sur l'espèce condensé $P_2O_3F_4$ comportant les mêmes motifs élémentaires. Ces résultats ont permis de formuler des hypothèses sur la géométrie de cette molécule dont la structure est encore inconnue. Un travail identique a été fait pour l'ion $P_2O_5F_2^{--}$. A partir de ces données nous avons montré que suivant le nombre de ligand Fluor ou d'oxygène ponté, les édifices phosphorés se contractent ou se dilatent refletant ainsi leur variation d'énergie interne.
$P_2O_3F_4$ étant un excellent agent de synthèse, nous avons obtenu de nouveaux sels, pour lesquels nous avons vérifié ces résultats.
Cette méthode d'approche reliant traitement spectroscopique et énergie des édifices phosphorés tétraédrique doit permettre une meilleure compréhension des relations propriétés-structure que nous illustrons par quelques exemples.

Downloaded At: 10:14 30 January 2011

A NOVEL BASE-PROMOTED N → O MIGRATION OF A PHOSPHONATE ESTER

by C RICHARD HALL, THOMAS D INCH and NANCY E WILLIAMS
Chemical Defence Establishment, Porton Down, Salisbury, Wiltshire SP4 OJQ England.

Cleavage of the P-N bond in basic solution in acyclic phosphoramidates where nitrogen is fully substituted does not usually occur. Thus the observation that ethyl phenylphosphonic acid was formed rapidly as the only phosphorus containing product when 2-deoxy-2-methylamino-3,4,6-tri-O-methyl-D-glucose 2-N(ethyl phenylphosphonamidate) was treated with sodium ethoxide at room temperature prompted a more detailed investigation of the reaction. The formation of the main carbohydrate product ie 3-deoxy-2-N-methyl-4,6-di-O-methyl-αβ-D-erythro-hexofuran-2-ulosylamine 1,1-diethylacetal, was consistent with P-N bond cleavage occurring following an elimination process, N to O migration of phosphorus occurring with imine formation. A series of related reactions, including stereochemical studies, which support the proposed mechanism will be reported.

THEORETICAL INVESTIGATIONS OF NUCLEOPHILIC PROPERTIES OF DERIVATIVES OF P(III) AND RELATED COMPOUNDS

A.A.Karelov, V.I.Molostov, V.F.Goncharov
Arbuzov Institute of Organic and Physical Chemistry, Kazan
Branch Academy of Sciences, USSR.

Ab initio (at the STO-3G and 4-31G levels) and MNDO methods were employed for calculating the electronic and spatial structure of compounds $X-PY_2$ and X-Y, of their protonated derivatives and of the adducts of compounds PH_2-X with CH_3^+, $CH_2=OH^+$, BH_3, BF_3 (X,Y=H,Me,NH_2,NMe_2,OH,OMe,F, SiH_3,PH_2,PMe_2,SH,SMe,Cl). The following regularites were observed: a) the relative nucleophilicity of the phosphorus atom in the row does not depend on the nature of the electrophile; b) the enthalpies of the formation of the adducts of P(III) compounds with the different electrophiles are linearly related and so are the quantities of electronic transfer from ligands to the phosphonium centre; c) the influence of the substituent X on the proton affinity (PA) of the phosphorus atom in molecules PH_2-X is quantitatively similar to its influence on the PA of the atom $Z \equiv O,N,S$ in molecules H_nZ-X; d) the relative nucleophilicity of the phosphorus atom and the heteroatom in the system P-E depends both on the nature of the heteroatom and on the electrophilic reagent.

TITRE : ETUDE COMPAREE DE L'HYDROLYSE D'ESTERS PHOSPHORIQUES BASOCATALYSEE EN MILIEU ACETONITRILE - EAU ET ENZYMO CATALYSEE.

par A. MURILLO BELTRAN [a], A. KLAEBE [a], E. MONNIER[c] et J. PERIE[b]

a - ERA 926 UER PCA - Bat.II.R1 - Université Paul Sabatier
b - ERA 264 118, route de Narbonne - 31062 Toulouse Cedex
c - Ecole Normale Supérieure de FES - Maroc

Une étude préalable de l'hydrolyse baso-catalysée d'ester allophaniques (modèles de carboxybiotine) en milieu acétonitrile/eau a montré une augmentation importante de la vitesse de réaction avec la diminution de la concentration en eau dans le milieu. La variation de la constante de vitesse expérimentale passe par un maximum pour des concentrations faibles en eau puis décroit brutalement : une interprétation a été proposée.

Cette étude a été poursuivie avec les esters phosphoriques tous porteurs du même groupe partant paranitrophényle.

L'hydrolyse des triesters phosphoriques et phosphorothioïques a été étudié dans ce milieu et présente des accélérations inhabituelles.

Le monoester (dianion) a été également étudié ; des accélérations encore plus marquées ont été mesurées ($10^4 < \gamma < 10^8$) et comparées à celles obtenues par catalyse enzymatique (phosphorylase alcaline de l'intestin de veau). Des mécanismes sont proposés.

Downloaded At: 10:14 30 January 2011

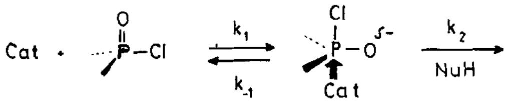
KINETIC AND STEREOCHEMICAL DISTINCTION BETWEEN A NUCLEOPHILIC ACTIVATED SUBSTITUTION, $SN_{NA}(P)$, AND A TWO STEP NUCLEOPHILIC DISPLACEMENT AT PHOSPHORUS

by R.J.P. CORRIU, G.F. LANNEAU and D. LECLERCQ
Laboratoire des Organométalliques, LA 349 - U.S.T.L. Place Bataillon, 34060 Montpellier

We have studied kinetics and stereochemistry of the reactions of alcohols and water with chlorophosphorus derivatives,activated by nucleophilic catalysts (NmI, pyridine, HMPT). Kinetics are complex, varying in a "continuum" as a function of the nucleophile, the catalyst and the phosphorus species.

$$v = k_1k_2/k_{-1}\,[P][NuH][Cat]\ ,\quad v = \frac{k_1k_2/k_{-1}\,[P][NuH][Cat]}{1 + k_2/k_{-1}\,[NuH]}\ ,\quad v = k_1[P][Cat]$$

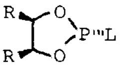
These results, plus large entropic factors (ΔS -50 u.e) associated with the stereochemical trends (chlorophosphates with retention, chlorophosphonates with inversion) are best interpreted by the so-called nucleophilic activated substitution process, $SN_{NA}(P)$.



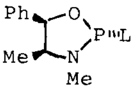
STEREOCHEMISTRY OF NUCLEOPHILIC SUBSTITUTION AT TRICOVALENT PHOSPHORUS

John Nielsen and Otto Dahl
Department of General and Organic Chemistry, The H. C. Ørsted Institute,
University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen,
Denmark

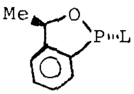
The stereochemistry of substitution of Cl, OR or NR_2 at tricovalent phosphorus in a variety of cyclic compounds (1-4) with nucleophiles (RO^-, ROH, R_2NH) has been studied. In many cases the result is clean inversion, although with good leaving groups like Cl the reactions are normally unselective.



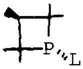
1



2



3



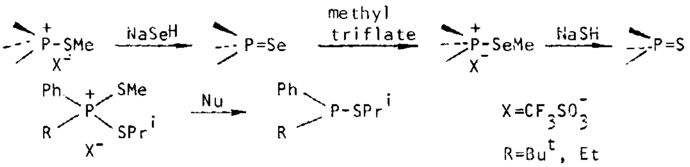
4

Downloaded At: 10:14 30 January 2011

STEREOSPECIFIC INTERCONVERSION OF THIO- AND SELENOPHOSPHORYL COMPOUNDS.STEREOSPECIFIC SYNTHESIS OF OPTICALLY ACTIVE PHOSPHINOUS ACID THIOESTERS.

J.Omelańczuk, W.Perlikowska, M.Mikołajczyk
Centre of Molec. and Macrom.Studies,Polish Acad. of Sciences, 90-362 Łódź,Boczna 5, Poland

The conversion of chiral methyl-n-propylphenylphosphine sulphide into the corresponding selenide and the reverse reaction are accomplished by teatment of the methylthio- and methylselenophosphonium salts with sodium hydrogen selenide and sodium hydrogen sulphide, respectively. Both reactions occur with retention of configuration at phosphorus. The mechanism of the reaction will be discussed. It was also found that the reaction of the optically active S-methyl-S-i-propylalkylphenylphosphonium salts with thiophilic reagents leads selectively to the corresponding optically active S-i-propyl alkylphenylphosphinites with retention of configuration and high stereospecificity.



KINETICS OF ALKALINE HYDROLYSIS OF QUATERNARY PHOSPHONIUM SALTS. THE DEPENDENCE OF APROTIC SOLVENT EFFECTS ON THE STRUCTURE OF THE SALTS.

By J. C. Tebby, J. G. Dawber and A. A. C. Waite,
Department of Chemistry and Biology, North Staffordshire Polytechnic,
Stoke-on-Trent, ST4 2DE, U.K.

Third order rate constants have been determined for the alkaline hydrolyses of five ethyl phenyl phosphonium iodides and four benzyl phenyl phosphonium bromides in 70% methanol in water (ϵ40) and in 70% equeous tetrahydrofuran in water (ϵ20). The salts which possess one or no ethyl groups hydrolyse much more rapidly in the medium with the lower dielectric constant. However, the hydrolysis of salts which possess two, three or four ethyl groups is only slightly faster in the less polar medium. These trends are consistent with increased delocalisation of the positive charge as the number of alkyl substituents increase which leads to less specific solvation of the alkylphosphonium ions and reduced sensitivity to changes in the solvating power of the medium. The replacement of a phenyl group by a benzyl group increases the salts sensitivity to the solvating power of the medium. This appears to be due mainly to the benzyl groups inability to $d\pi$-$p\pi$ bond, which in the case of phenyl groups stabilise the positive charge on phosphorus and encourages specific solvation. Since the more aliphatic salts, which contain benzyl groups, show little sensitivity to medium effects, solvation of the transition state in the final step (which involves the ejection of the leaving group) does not appear to be very important.

Downloaded At: 10:14 30 January 2011

A DISCUSSION ABOUT THE THIONO-THIOLO REARRANGEMENT OF O-ALKYLTHIOPHOSPHORODICHLORIDES.

Hu Shui-sheng, Zhang Jing-lin, Yang Xing-yu, Department of Chemistry, Huazhong Normal University, Wuhan, Hubei, The People's Republic of China.

The rearrangement of O-methyl-, O-ethyl-, O-n-propyl- and O-isopropylthiophosphorodichlorides to corresponding S-alkyl-isomers in the presence of a catalyst or without it has been studied. The results of Gas Chromatograph being used to follow the reactions reveal that in this isomerization exist four different reactions, thiono-thiolo rearrangement, decomposition, crossed reaction and hydrolysis. The softer pyridine possesses a powerful catalytic ability than triethylamine in the first step of rearrangement to form an anionic intermediate(1). In the second step, in our opinion, there would be two competition reactions, the attack on (1) by thiophosphorodichloride itself causes the formation of the main products, and the attack on the hard P atom in (1) by chloride anion (2), produced in hydrolysis of substrate, tends to form by-products. The action of (2) has been examined. The rearrangement would become more difficult to take place as the size and the branched chain of the alkyl group are increased. Besides pyridine, however, adding isopropyl chloride to the reaction mixture of O-isopropylthiophosphorodichloride is able to reduce the quantities of by-products and to enhance the yield of S-isomer. In this way four S-alkyl isomers were prepared in comparative satisfactory yields.

Downloaded At: 10:14 30 January 2011

ELECTRONIC STRUCTURE OF SOME BORON-PHOSPHORUS POLYMERS

by D.R. Armstrong, University of Strathclyde, Scotland

The electronic structures of some boron-phosphorus polymers have been calculated by the MNDO method. The geometry of the polymeric systems $(BP)_n$ $(BHPH)_n$ and $(BH_2PH_2)_n$ have been optimised and the framework bonds are found to span 1.62A, 1.74A and 1.90A respectively while the corresponding framework angles measure 145°, 121°, and 111°. The band structures of the polymers are presented and the composition of the bands is described. All three systems have a substantial band gap. The effect on the band structures of replacing the hydrogen atoms by various substituents is reported. The calculated electron distribution of the polymers indicates that there is an electron drift towards the phosphorus atom in $(BP)_n$ and $(PHBH)_n$ while the reverse is true for $(PH_2BH_2)_n$. The calculated bond indices show that multiple bonding is present in $(BP)_n$ and $(PHBH)_n$ with values of 1.41 and 1.08 respecitvely while in $(PH_2BH_2)_n$ the boron-phosphorus index measures 0.76.

Finally, the electronic structures of the polymers are compared with those of realted molecules and ions whose geometry, electron distribution, and bonding is reported and discussed.

REACTIVITY OF VARIOUS PHOSPHITES WITH POLYHALOGENOMETHANES. ROLE OF ELECTRON TRANSFER.

BAKKAS, S., TORDO, P., BUONO, G., JULLIARD, M., CHANON, M.
Laboratoire de Chimie Inorganique Moléculaire, Rue H. Poincaré, 13397 Marseille Cedex 13

The reaction between various phosphites (RO_3P with R = Et, Methyl cyclopropyl, hexene-5 y 1-1 tertiobutyl , dimethyl-1,1 hexene-5 yl-1) and polyhalogenomethanes (CX_nY_{4-n} X=Cl, Y=Br) has been studied under photochemical and thermal conditions :

$$(RO)_3P + CCl_4 \longrightarrow CCl_3P(O)(OR)_2 + RCl$$

The use of TNCQ as scavenger, (and ESR consequences) evidence for CTC, measurement of quantum yields, observation of by products when appropriate free radical clocks are used and tentative CIDNP experiments suggest a non chain electron transfer mechanism for this type of reaction. The proposed general scheme undergoes modifications when the structure of reagents is progressively modified. These modifications will be discussed.

Downloaded At: 10:14 30 January 2011

PHOTOCHEMISTRY OF TETRA-tert-BUTYLCYCLOTETRAPHOSPHANE

A. Wallace Cordes, Willis A. Weigand, and William T. Pennington
Department of Chemistry, University of Arkansas, Fayetteville, Arkansas 72701 USA

Irradiation of tetra-tert-butylcyclotetraphosphane, $(C_4H_9)_4P_4$, I, in an ESR cavity using a broad-band high-pressure 254 nm light source results in the observation of an ESR spectrum consisting of a doublet with a splitting of 90 gauss. There is a linear decline in the intensity of this ESR signal as the irradiation continues; typical solutions (0.1 M in cyclohexane) are inactive after 40-60 min of exposure to the light. This loss of photoactivity is accompanied by a gradual decline in the intensity of the 257 and 284 nm absorption peaks of the electronic spectrum of I, and an increase in the complexity of the ^1H NMR spectrum. ^{31}P NMR spectra indicate the tetramer is converted to the trimeric cyclophosphane in good yield. Analogous experiments with tetra-n-butyl, tetraisopropyl, and hexaphenyl phosphanes do not give spectral evidence for any similar photoactivity. Traces of water and/or dissolved oxygen in the solutions of I do not appear to affect the photolysis. Irradiation of a carbon disulfide solution of I and sulfur produces a new monosulfide, $(C_4H_9)_4P_4S$; the molecular structure determination of this product reveals a new phosphane sulfide bonding arrangement which includes a non-planar P_4 central ring and an exocyclic-bonded sulfur atom.

AMINATION ELECTROCHIMIQUE DE β-CETO-PHOSPHONATES.

D. COLLETA, M. DEVAUD, N. COLLIGNON et P. SAVIGNAC, INSCIR, B.P. 08-76130 Mont St-Aignan

L'amination électrochimique de l'oxo-2 propyl phosphonate de diéthyle a été étudiée sur cathode de mercure dans les milieux $NH_3 + NH_4^+ + H_2O$ et $AcOH + AcONH_4 + EtOH$. Une étude détaillée conjointe des polarogrammes et des spectres ultra-violets des solutions a montré que l'espèce électroactive est l'ion immonium. La constante d'acidité de cet ion et la constante d'équilibre cétone-énamine ont été évaluées. Le processus électrochimique est contrôlé dans ces deux milieux par la cinétique d'isomérisation de l'ion énaminium en ion immonium. La réduction irréversible est biélectronique. Les électrolyses préparatives sont plus faciles à conduire en milieu ammoniacal. La concentration maximale en substrat est égale à 0,5 $mol.l^{-1}$; l'aminophosphonate correspondant a été isolé avec un rendement supérieur à 90 %.

L'oxo-1 éthylphosphonate de diéthyle et le (diéthoxyphosphoryl)pyruvate d'éthyle ont été aminés dans des conditions identiques.

Les réductions en présence de divers inducteurs d'asymétrie (tartrate, camphorate, N,N-diméthyléphédrinium et strychnine) n'ont conduit qu'au racémique. Les interactions trop faibles entre le substrat et l'électrode sont vraisemblablement responsables de cet échec.

L'amination électrochimique est donc une voie d'accès aux acides amino-phosphoniques, simple et nouvelle. Le mécanisme de réduction sera discuté.

Downloaded At: 10:14 30 January 2011

THE INTERACTION PHOSPHINE OXIDES AND DIPHOSPHINE DIOXIDES WITH THE STRONG ACIDS.

Matrosov E.I. Moscow, Academy of Sciences of USSR.

The structure of adducts of phosphine oxides, alkylenediphosphine dioxides and other phosphoryl compounds ($B= \geqslant P=O$) with $HClO_4$, CF_3SO_2OH, HBr and HCl (HA) has been studied by means of low-temperature PMR-spectroscopy, IR spectra and X-ray diffraction. There has been established the formation of protonated salts of two main types.

(1) Basic salts BHB^+A^- with very strong symmetrical hydrogen bond in complexes BHB^+. There complexes have an extreme short the O..O contact, a continous absorption in the IR spectra, a mobile proton signal of $\delta= 21,4$ ppm and $J= 6,8$Hz in PMR spectra. From the spectral and structural consideration one may assume a symmetrical single, flat minimum of the potential function for the proton BHB^+ complexes.

(2) Ion pairs or proton-transfer complexes $BH^+..A^-$ stabilized by a strong "inverse" hydrogen bond. Complexes of this type are characterised by the strong absorption near $1000 cm^{-1}$ IR spectra and the signal parameters of the bridging proton $\delta=15,6$ppm and $J=25$Hz (PMR spectra). The "inverse" hydrogen bond in salts of type 2 results in an incomplete protonation of the base; the protonation extent for $Ph_3POH^+..Br^-$ and $Ph_3POH^+..Cl^-$ is 0,72 and 0,68 respectively.

^{13}C N.M.R. SPECTRA OF DI- AND TRI-PHOSPHORUS COMPOUNDS

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

The spectra of ^{13}C nuclei which lie off the symmetry elements of symmetrical di- and tri-phosphorus compounds belong to the AA'X and AA'_2X spin systems ($A={}^{31}P$, $X={}^{13}C$).

The X spectrum of the AA'X spin system typically consists of 5 lines, symmetrically placed about ν_X; analytical expressions can be written for the line positions in terms of the coupling constants. From the two splittings observable it is clearly impossible to determine the three coupling constants involved, but it will be shown that the intensity ratios of the lines afford additional information, so that all three coupling constants can often be obtained from the ^{13}C spectra.

For the AA'_2X spectrum a maximum of twelve lines are expected for the X part, and in suitable cases all three coupling constants can be obtained without the use of intensity measurements. If $J_{AA'}$ is large, and $J_{A'X}=0$, the spectrum consists of four lines of equal intensity and equal separations $J_{AX}/3$.

Examples will be presented of ^{13}C spectra of organophosphorus compounds and transition metal complexes.

ELECTRONIC STRUCTURE AND REACTIVITY OF YLIDIC SYSTEMS
XI: DICYANO-METHYLIDS, MODES OF STABILIZATION

K. A. Ostoja Starzewski*, M. Feigel and J. Rieser
Contribution from the Departments of Chemistry
at the Universities of Frankfurt, Bremen and Freiburg
*correspondence address: BAYER AG, Zentrale Forschung,
Wissenschaftliches Hauptlaboratorium, D-5090 Leverkusen

Ylids e.g. R_3PCXY are characterized by a highly polar donor-acceptor bond with partial π contribution $\overset{+}{D}\xrightarrow{\cdots}\bar{A}$.
Their photoelectron spectra not only span a new low ionization potential range on the chemical energy scale; they also illuminate aspects of carbanion and carbene stabilization. Earlier PES and C-13 NMR studies of simple and conjugated ylids showed the reduction of the carbanionic π-charge to be an efficient mode of stabilization. Interestingly, for the ylidic carbon of $Ph_3PC(CN)_2$ the C-13 chemical shift is basically unchanged compared to that of the clearly more reactive Ph_3PCH_2.

$$\left.\begin{array}{lll} Ph_3PCH_2 & \delta^{13}C = -5.3\ \text{ppm} & IE_1(n_{C^-}) = 6.62\ \text{eV} \\ Ph_3PC(CN)_2 & \delta^{13}C = 5.4\ \text{ppm} & IE_1(n_{C^-}) = 7.63\ \text{eV} \end{array}\right\} \quad \Delta IE_1 = 1.0\ \text{eV!}$$

CNDO model calculations for Me_3PCH_2 and $Me_3PC(CN)_2$ support the view of practically the same π-charge at both ylid carbanion centers. However, the HOMO of the dicyanomethylid is predicted to be energetically stabilized relative to that of the parent trimethylphosphine-methylene.

Downloaded At: 10:14 30 January 2011

α-PHOSPHONYLKETYLS : AN ESR STUDY

V. CERRI, F. GERSON*, P. TORDO,
S.R.E.P. Université de Provence, Rue H. Poincaré 13397 Marseille Cedex 13 France
* Phys. Chem. Inst. der Universität Basel, Klingelbergstrasse 80, CH-4056 Basel, Suisse

Twenty six α-phosphonyl ketyls RC(O)P(O)L_2 (R = Ar, Alkyl, L = Alkoxy, Alkyl, Ar) have been produced by electrochemical reduction or by the mirror metal technique and studied by ESR. The configuration, the spin and charge distributions as well as the conformational preference of these species have been deduced from the analysis of the ESR data.
The α-phosphonyl ketyls have a bent configuration and a large negative charge localized on the carbon of the keto group.
The decomposition of α-phosphonyl ketyls produces different secondary radicals whose nature gives some information on the reactivity of the former.

Downloaded At: 10:14 30 January 2011

AN ESCA STUDY OF THE P2p BINDING ENERGIES IN $(C_6H_5)_{3-n}PX_nCr(CO)_5$ COMPLEXES (X = Cl,Br, I, H; n = 0-3).

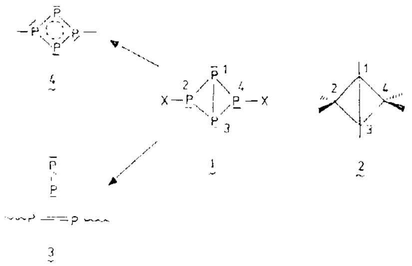
E. VINCENT, L. VERDONCK.
Laboratory for General and Inorganic Chemistry-B, Krijgslaan 281, B-9000 GENT-BELGIUM.

An ESCA study of the P2p binding energies in $(C_6H_5)_{3-n}PX_nCr(CO)_5$ complexes (X = Cl, Br, I, H; n = 0-3) provides information on the chemical bond in these compounds.
The experimental parameters are shown to be predictable following the so-called potential model equation. For X = Cl a linear correlation between the $P2p_{3/2}$ binding energy and the field and resonance parameters of the substituents on phosphorus is observed. Therefore the $P2p_{3/2}$ binding energy in the chlorine series seems to be directly related to the atomic charge on phosphorus. For X = Br, I and H however, additional variations of the relaxation energy have to be taken into account to rationalize the observed $P2p_{3/2}$ shifts.
Finally, a comparison of the data for the ligands with those for the complexes proves that, although the σ-donor effect is primarily responsible for the $P2p_{3/2}$ ESCA shift on complexation, it is certainly not the only binding energy determinating effect.

ON THE ELECTRONIC STRUCTURE OF BICYCLOTETRAPHOSPHABUTANE

W.W. Schoeller and C. Lerch, Fakultät für Chemie der Universität,
48 Bielefeld, Fed. Rep. Germany

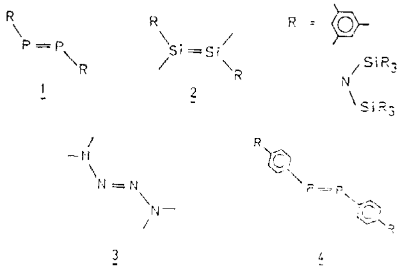
The electronic structure of bicyclotetraphosphabutane 1 is analyzed. Accordingly, π-donors (e.g. X=NR$_2$) or -acceptors decrease (increase rsp.) the central bond in the parent compound. which therefore possesses olefinic character. X exerts a new type of substituent effects, common to inorganic three-membered ring systems, spanning a Hückel system of frontier orbitals. The presence of two high lying, energetically closely spaced frontier orbitals reveals for the cation radicals various isomers, which are comparable in energy. The concerted fragmentation of 1 (R=H) to 3 is symmetry forbidden in the ground state. Similarly the reaction of 1 to 4 is forbidden in the ground state and allowed in the excited state. 4 takes up a nonplanar structure and is isovalent to S_2N_2 which is not known yet in the bicyclic form.



SUBSTITUENT EFFECTS ON THE BONDING PROPERTIES IN DIPHOSPHENES AND DISILENES

W.W. Schoeller[a] and V. Staemmler[b], (a) Fakultät für Chemie der Universität, 48 Bielefeld, Fed.Rep.Germany and (b) Abteilung für Chemie der Ruhruniversität, 463 Bochum, Fed.Rep.Germany.

The compounds 1 to 3 (R=NR$_2$) represent linear 6 electron 4 center π-systems. They possess low rotational barriers for the peripheral amino groups. The preference of a bisorthogonal over a coplanar conformation is promoted with increasing electropositive character of the central π-bonding atoms, due to increasing overlap repulsion between the lone pairs at the amino groups and the central π-bond. Electron withdrawing groups (e.g. silyl) at the amino groups promote in 1 a bisorthogonal conformation as well is the case for R= π-acceptor for 4. π-electron donors in 4 do the opposite, i.e. they promote coplanarity of the π-units. The relation of this concept to substituent effects on 3 and on 2 are drawn.



Downloaded At: 10:14 30 January 2011