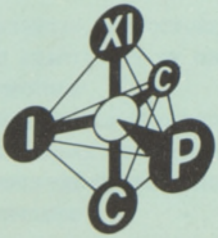
XI. INTERNATIONAL CONFERENCE ON PHOSPHORUS CHEMISTRY



TALLINN, USSR
JULY 3 - 7, 1989

ABSTRACTS OF LECTURES

CONFERENCE CHAIRMAN
M.VEIDERMA

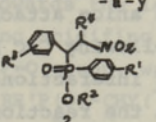
SCIENTIFIC PROGRAM

SECTION 1	SYNTHESIS, STRUCTURE, STEREOCHEMISTRY AND REACTIVITY OF ORGANOPHOSPHORUS COMPOUNDS
SECTION 2	CHEMISTRY OF PHOSPHORUS COMPOUNDS IN PARTICULAR COORDINATION AND BONDING
SECTION 3	CHEMISTRY OF PHOSPHORUS COORDINATION COMPOUNDS
SECTION 4	BIOCHEMICAL ASPECTS OF PHOSPHORUS CHEMISTRY
SECTION 5	CHEMISTRY OF PHOSPHATES, INCLUDING CONDENSED PHOSPHATES AND APATITES AND OTHER INORGANIC PHOSPHORUS COMPOUNDS

1-1 SYNTHESIS AND STEREOCHEMISTRY OF α-ARYL-β-NITROALKYL PHOSPHINATES

<u>Y. G. LI</u> and Y. S. LIU
Institute of Elemento-Organic Chemistry, Nankai
University, Tianjin, China (PRC)
F. M. MIAO and X. L. LIU
Tianjin Normal University, Tianjin
J. H. CAO and W. ZHOU
Academy of Military Medical Science, Beijing

This paper studies the One-pot reaction of O-alkyl phenylphosphonites with α-aryl-β-nitroalkenes (β-nitrostyrenes) in the presence of trimethylsilyl chloride and triethylamine(1). Twenty-three new α-aryl-β-nitroalkyl phosphinates $\underline{3}_{a-y}$ were synthesized in high yield under



$\underline{3}_{a-y}$

R^1, R^4 : H, Me, R^2 : Alkyl
R^3 : H, p-MeO, p-OH, m-C_6H_5O,
p-Me_2N, 3, 4 $<^{O-}_{O-}$

very mild condition. It is found that the compounds $\underline{3}$ consist of two racemic isomers (A) and (B)(2). The racemic (A) $\underline{3k}$ (R^1, R^2, R^3, R^4 : H, Pr^i, p-OH, H) was separated by recrystallization and its structure was determined by x-ray diffraction on single crystal. Thus, the Newman's projective torsion angles of (A) $\underline{3}$k (R_PS_C) have been calculated and in which the angle of O(1)-P(1)-C(21) is the smallest one. The conformation of molecule can be considered as antiperiplanar and a pair of racemic isomder (A) (R_PS_C and S_PR_C) becomes the stable preferential conformation.

There is a good linear relation between the values of $\delta_{^{31}P}$ of (A) or (B) and Taft constants (δ^*), and the line of (A) runs parallel to that of (B). The structures of all compounds were confirmed by elemental analysis, IR, ^1H, ^{13}C, ^{31}P NMR and MS.

(1) Y. G. Li, G. H. Wang, D. K. Chang, F. M. Miao, X.L. Liu, J.H. Cao and H.Z. guo, ICHAC Kobe 87, OLA21.
(2) R. D. Gareev, A. N. Pudovik, Zh. Obsch. Khim., 56 (2) 241 (1986).

1-2 KINETICS AND MECHANISM OF THE PUDOVIK REACTION

R.A.CHERKASOV, V.I.GALKIN, A.B.KHABIBULLINA, and Khalil Al Kurdi
V.I.Ulyanov-Lenin Kazan State University, 18 Lenin St.,
Kazan 420008, USSR

The kinetics and mechanism of the Pudovik reaction have been studied spectrophotometrically in alcoholate catalysed addition reaction of dialkylphosphorous acids to the α,β-unsaturated carbonyl compounds. The influence of substituents on the reaction rate and direction has been investigated for both substrates. The factors which determine locoselectivity of the process and the reactivity of the compounds are established. It is shown that the reaction is initiated by the dialkylphosphite anion attack on the carbonyl group of the α-enone with following C=C bond involvement. Strong electronic and steric interactions may block the carbonyl group participation in the reaction and direct the attack of the phosphite anion to the C=C bond. It has been established that reactivity of dialkylphosphites is controlled by the steric effect of the phosphorus substituents. The influence of the solvent alcohol and the catalyst on the kinetical parameters of the Pudovik reaction has been studied. A common scheme of the reaction has been suggested which is in good agreement both with the kinetic results and literature data on the addition of hydrophosphoryl compounds to α,β-unsaturated aldehydes and ketones.

1-3 ENOLYZATION OF THE PHOSPHORYL GROUP

T.A.MASTRYUKOVA

A.N.Nesmeyanov Institute of Organo-Element Compounds,
Academy of Sciences of the USSR, 28 Vavilova Str., Moscow
117813, USSR

Easy enolysation of β-dicarbonyl compounds is well-known. Their phosphorus analogs with the P=O group instead of the the C=O group were obtained by A.E.Arbuzov 60 years ago. Although the problem of enolysation of the P=O group was put forward at that time, the phenomenon itself has not been observed up till now.

The present study is based on the concept of tautomery as an acid-base protolytic process with equilibrium shifted towards the least acid form. Thus, a system with two strong acidifing groups at the carbon atom, adjacent to the P=O group, was chosen:

$$RR'P(O)\text{-}CHY({}^{+}PPh_3)X^{-} \rightleftharpoons RR'P(OH)=CY({}^{+}PPh_3)X^{-},$$

where $Y={}^{+}PPh_3$, CN, Ts, COOEt and also COPh, COMe; R, R'=PhO, AlkylO, Ph, Alkyl; X=Cl, Br, ClO_4, BF_4 - aniones.

Investigation has shown that enolization of the P=O group is dependent on the nature of substituents primarily at the carbon and then at the phosphorus atoms, the character of the anion (taking into account its ability to form H-bonding with the P=O group) and, finally, the nature of the solvent and temperature are also essential for enolization.

In the systems with Y=COPh and COMe three tautomeric forms, the phosphoryl (CH), phosphaenol (P-OH) and enol (=C-OH), are observed.

Compounds with the enolizing phosphoryl group turned out to be strong CH-acids with pKa 2.5-10.5 (determined by pH-method in nitromethane) which in strength exceed carbon acids.

1-4 MECHANISM OF THE CHLOROLYSIS REACTION OF P-S BOND IN PHOSPHORUS THIOLOESTERS. THE EFFECT OF THE SUBSTITUENT AT SULFUR ATOM ON THE STEREOCHEMISTRY

B.KRAWIECKA and E.WOJNA-TADEUSIAK

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

In our previous work (1) we have shown that the chlorination reaction of phosphorus thioloesters, $>P(O)SR$ involves the formation of two types of reactive intermediates: chlorosulfonium salts, $>P(O)\overset{+}{S}(Cl)R\ Cl^-$ and phosphonium salts, $>\overset{+}{P}(SR)OP(O)<\ Cl^-$. This knowledge has been utilized to find a rationalization for the inexplicable stereochemical results (2) caused by the effect of the substituent bonded to sulfur atom. As the model phosphorus thioloesters we have used the series of S-methyl (ethyl), S-2-chloroethyl and S-phenyl phosphoro-, phosphono- and phosphinothioates, which have been reacted with sulfuryl chloride and elemental chlorine in methylene chloride. The reaction course has been monitored at variable temperatures by ^{31}P NMR. The experimental results have confirmed the importance of the formation of chlorosulfonium salts $>P(O)\overset{+}{S}(Cl)R\ Cl^-$ in the crucial reaction step. It was found that substituents decreasing electron density at the sulfur atom dramatically reduce the reaction rate. It is proposed that the stereochemistry of the examined reaction is the result of the competition of the various possible reaction pathways. The contribution of the substituents effect favouring particular path of the reaction will be discussed.

(1) B.Krawiecka, J.Michalski, E.Wojna-Tadeusiak, J.Org.Chem. 51, 4201 (1986).

(2) J.Michalski, A.Ratajczak, Roczniki Chem., 37, 1185 (1963).

1-5 SIGMATROPIC REARANGEMENTS IN PHOSPHORYLATED 2-AZAALLYLIC SYSTEMS

P.P.ONYS'KO, T.V.KIM, E.I.KISELEVA, and A.D.SINYTSA
Institute of Organic Chemistry of the Ukrainian Academy of Sciences, Murmanskaya Str. 5, Kiev 252660, USSR

The 1,3-migrations of the proton, phosphoryl, thio- and dithiophosphate groups in the 2-azaallylic triad were considered. The methylene-azomethine triad is one of the least labile triad systems. The introduction of the phosphorus-containing group leads to the fact that 1,3-H-shifts occur under the mild conditions, even in the absence of bases. The general rules for 1,3-prototropic shifts in the C=N-C triad were formulated. Influence of the electronic and steric properties of substituents on the rate and direction of the 1,3-H-shifts was studied. The importance of the conjugation of substituent with C=N bond for the stabilization of isomeric forms was demostrated. The factors determining thermodynamic and kinetic stability of the potentially tautomeric forms were considered. The high stereoselectivity of the proton transfer process leading to asymmetric induction at the chiral centre, formed as a result of rearrangement, was found. Thus, stereospecificity of proton transfer in the α-phosphorylated imines, models of biochemical trans-amination reactions, may be accomplished without any participation of enzymes. The 1,3-migration of the phosphoryl groups in 2-azaallylic triad was accompanied by the splitting and formation of the P-C bond. The ability to migration increases in the series $(RO)_2P(O)<(Me_3SiO)_2P(O)<Ph_2P(O)<Ph_3\overset{+}{P}$. Migration of the thio- and dithiophosphate groups in the azaallylic triad is accompanied by a migration of the phosphoryl group in the S-N-C triad.

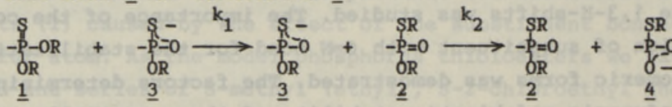
(1) P.P.Onys'ko, T.V.Kim, E.I.Kiseleva, A.D.Sinytsa, Zh.Obshch.Khim., 57, 1233 (1987).

1-6 MECHANISM OF THIONO-THIOLO ISOMERIZATION OF THIOPHOSPHATES. KINETIC EVIDENCE FOR HILGETAG'S HYPOTHESIS

W. Reimschüssel, J. Adamuś

Institute of Applied Radiation Chemistry,
Technical University, Żwirki 36, 90-924 Łódź, Poland

Thiono-tiolo isomerization of O-alkyl esters of phosphorus thioacids leading to S-alkyl isomers is of a great importance in phosphorus chemistry and biochemistry. For the isomerization effected by organic bases such as amines and phosphines two alternative mechanisms have been proposed. The firs one involves intramolecular realkylation of an anion 3 by an alkylonium species. The other one suggested by Hilgetag (1) for the isomerization in the presence of alkylammonium species involves a reaction of an anion 3 with a reactant 1 leading (k_1) to the same anion 3 and thioloisomer 2.



In the case of O-alkyl diesters the anion isomerization 3 ⟶ 4 can also apear (k_2). To examine the reaction mechanism operating in the presence of an anion 3 with tetramethyl or trimethyl cation we have undertaken systematic kinetic studies by radioactive tracer methods. In this communication kinetic data are presented for the reactions of malathion 1a, methylparathion 1b, 5,5-dimethyl-2-methoxy-2-thio-1,3,2-dioxaphosphorinane 1c, O-methyl-O,O-diphenylthiophosphate 1d and corresponding S-methyl isomers 2a, 2b with tetramethylammonium salts 3a-3d, and trimethylammonium salt 3d, respectively. The results have fully proved Hilgetag's conception showing an exactly bimolecular reaction between 1 and 3being first-order ($^{1}k_1 = {}^{2}k_1 \cdot c_3$) owing to the constant concentration of 3. The anion isomerization 3 ⟶ 4 is also bimolecular first-order reaction ($^{1}k_2 = {}^{2}k_2 \cdot c_2$). The reactivity of the anion 3 in ion-pair form of the triethylammonium salt is more then ten times smaller compared the free anion.

(1) G. Hilgetag, G. Lehman, J. Prakt. Chem., 12, 6 (1960).

1-7 REARRANGEMENT AND FRAGMENTATSION REACTIONS OF α-HYDROXYIMINOPHOSPHINATES. ON THE NATURE OF THE METAPHOSPHONATE INTERMEDIATE INVOLVED IN PHOSPHONYLATIONS BY α-HYDROXYIMINOPHOSPHINATE

Ada SCHLOSSMAN, Dan GIBSON, and Eli BREUER
Department of Pharmaceutical Chemistry, The School of Pharmacy, The Hebrew University of Jerusalem, Jerusalem, Israel

α-Hydroxyiminophosphorus derivatives are of interest on the one hand because of their potential to serve as metal chelators, and on the other hand because they have been shown to act as phosphorylating agents.[1] From kinetic data it was concluded that their phosphorylating reactions take place via metaphosphate intermediates.[1]

Here we report results from our study of some α-hydroxyiminophosphinates. The chemical properties of the two geometrical isomers of these are functions of their steric structures. While the (Z) oxime undergoes thermal fragmentation to benzonitrile and to methyl hydrogen phenylphosphonate, heating of the (E) isomer leads to the formation of an N-phosphonylated amide, by a Beckmann rearrangement.

(E)-α-Hydroxyiminobenzylphenylphosphinic acid undergoes fragmentation in alcoholic solvents to benzonitrile and alkyl hydrogen phenylphosphonates, and thus acts as a phosphonylating agent. These reactions are interpreted in terms of a dissociative type mechanism assuming the formation of a metaphosphonate intermediate.

Results from further phosphonylation experiments will be described and discussed.

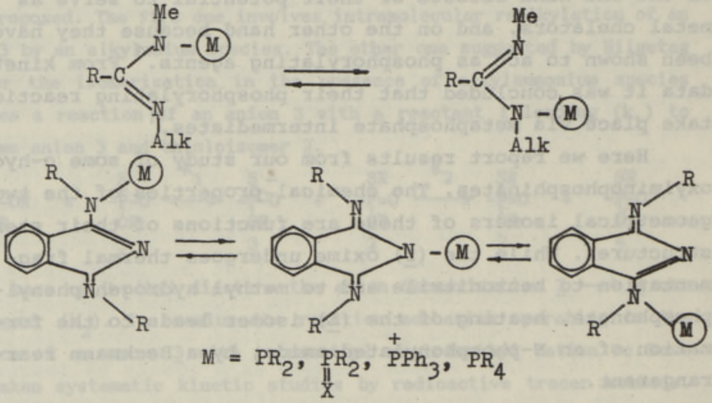
Acknowledgement: This research was supported by the U. S.-Israel Binational Science Foundation (B.S.F.), (to E.B.), and by a grant from the Joint Research Fund of the Hebrew University and Hadassah (to D.G.).

1. E.Breuer et al., J.C.S. Chem. Comm., 1987, 671; 1988, 504.

1-3 PHOSPHOROTROPIC TAUTOMERISM IN AMIDINE SYSTEMS

L.N.MARKOVSKY, V.I.KALCHENKO, and V.V.NEGREBETSKY
Institute of Organic Chemistry, Academy of Sciences of the Ukrainian SSR, Murmanskaya Str. 5, Kiev-94 252660, USSR

Reversible migrations of groups with tri-, tetra- and pentacoordinated phosphorus in N-C-N amidine triad and N-C-N-C-N pentad of 1-amino-3-iminoisoindolenines were studied by dynamic ^{1}H, ^{13}C and ^{31}P NMR (1, 2).



$M = PR_2,\ \underset{X}{\overset{\|}{P}}R_2,\ \overset{+}{P}Ph_3,\ PR_4$

The migrations occur by the intramolecular mechanism with formation of cyclic hypervalent intermediates while stereochemical configuration of phosphorus is retained. The kinetic, activation and thermodynamic parameters of the migrations were determined for amidines and isoindolenines. Free activation energy $\Delta G^{\neq}$ depends upon the nature of substituents at phosphorus, carbon and nitrogen atoms and varies in wide range of 8-26 Kcal/mol.

(1) V.I.Kalchenko, V.V.Negrebetsky, R.B.Rudy, L.N.Markovsky, Zh.Obshch.Khim. 58, 1216 (1988).
(2) V.V.Negrebetsky, V.I.Kalchenko, O.V.Balitskaya, L.N. Markovsky, M.Yu.Kornilov, Zh.Obshch.Khim. 56, 113 (1986).

1-9 POLYPHOSPHORUS COMPOUNDS: RECENT SYNTHETIC AND STRUCTURAL RESULTS

M. BAUDLER

Institute of Inorganic Chemistry, University of Köln,
Greinstraße 6, D-5000 Köln 41, FRG

A selection of recent results concerning the following classes of polyphosphorus compounds will be presented:

(1) Neutral Monocyclic Phosphanes: Detection and characterization of the perhalogenated cyclophosphanes $(PX)_6$ (X = Cl, Br); synthesis of various reaction products in which the ring size is preserved;

(2) Metal Polyphosphides Obtainable from Solutions: Formation and properties of the alkali-metal pentaphosphacyclopentadienides M^IP_5 and the alkali-metal hydrogen bicyclo[1.1.0]tetraphosphides M^IHP_4 (M^I = Li, Na, K);

(3) Three-membered Phosphorus Ring Compounds: Synthesis and structural features of the phosphinidenediphosphirane $(t\text{-}BuP)_2C{=}P\text{-}(2,4\text{-}tBu_2\text{-}6\text{-}MeC_6H_2)$ and the tris(cyclotriphosphanyl)stibane $[(t\text{-}BuP)_2P]_3Sb$;

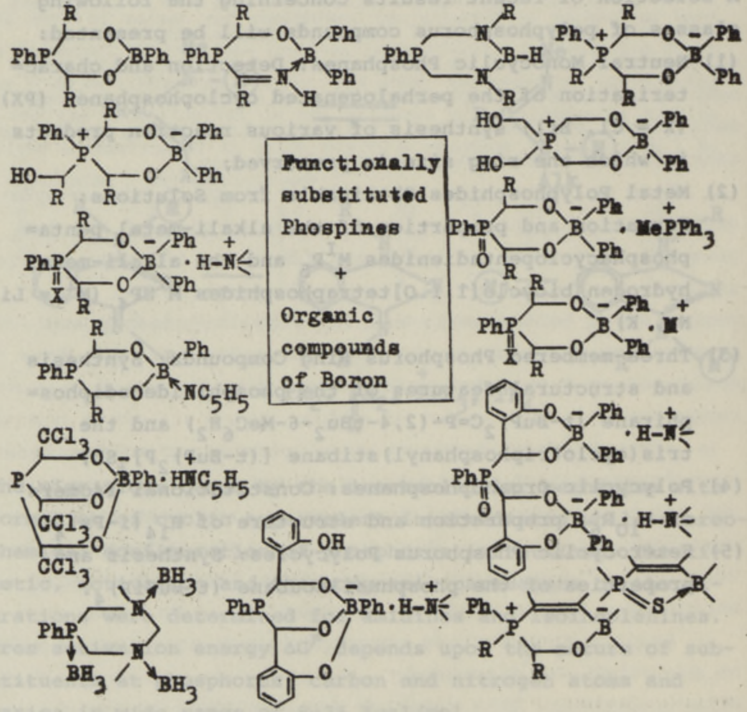
(4) Polycyclic Organophosphanes: Constitutional isomers of $P_{10}R_6$; preparation and structure of $P_{14}(i\text{-}Pr)_4$;

(5) Heterocyclic Phosphorus Polycycles: Synthesis and properties of the phosphasilacubane $(t\text{-}BuSiP)_4$.

1-10 P,B-CONTAINING HETEROCYCLES

B.A.Arbuzov, G.N.Nikonov, O.A.Erastov, S.N.Ignat'eva,
A.S.Balueva, and A.A.Karasik
A.E.Arbuzov Institute of Organic and Physical Chemistry,
Arbuzov Str. 8, 420083 Kazan, USSR

Reactions with functionally substituted phosphines with organic compounds of boron proves to be the way of synthesying new heterocycles.



Involvement of various types of functionally substituted phosphines in this reaction, as well as the introduction of additional reagents, opens up broad vistas for the synthesis of new phosphorus-containing heterocycles.

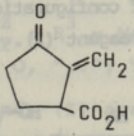
1-11 α-PHOSPHORYL CYCLOPENTANONES AS POSSIBLE INTERMEDIATES IN THE TOTAL SYNTHESIS OF SARKOMYCIN

M.MIKOŁAJCZYK, P.KIEŁBASIŃSKI, R.ŻURAWIŃSKI
and M.W.WIECZOREK[a]

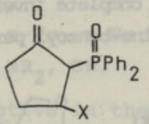
Centre of Molecular and Macromolecular Studies,Polish Academy of Sciences, Sienkiewicza 112,90-362 Łódź, Poland

[a]Institute of General Chemistry, Technical University, Żwirki 36, 90-362 Łódź, Poland

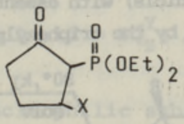
As part of our program on the synthesis of biologically active cyclopentanones and cyclopentenones we turned our attention on sarkomycin (1) - a well-known antitumor agent.



1



2 $X=C(SMe)_3$
CO_2Me



3 $X=CH_2{=}CH$
CO_2Me

In this communication we would like to report the synthesis of α-phosphoryl cyclopentanones 2 and 3 which may be transformed into sarkomycin 1. The synthesis of 2 was accomplished from cyclopentenone via C-phosphorylation of the enolate anion. The cyclopentanone 3 was prepared from β-oxophosphonate. The most important step in this synthesis was intramolecular cyclization reaction of the corresponding α-diazo-β-oxophosphonate.

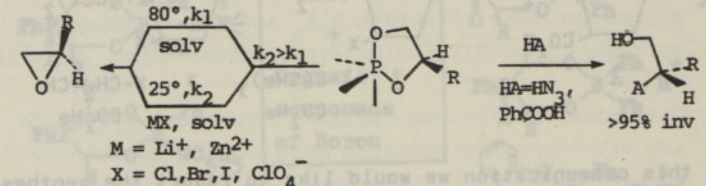
Spectroscopic and X-ray analyses data of 2 and 3 as well as attempted synthesis of sarkomycin 1 will be discussed.

1-12 REACTIVITY AND SYNTHETIC UTILITY OF 1,3,2λ^5-DIOXAPHOSPHOLANES

W. T. MURRAY, A. PAUTARD-COOPER, N. A. ESKEW, and S. A. EVANS, JR.

Department of Chemistry, CB# 3290, The University of North Carolina,
Chapel Hill, North Carolina 27599-3290. U.S.A.

The kinetics of Lewis acid-mediated decomposition and a definition of the synthetic potential of 1,3,2λ^5-dioxaphospholanes for the synthesis of highly-hindered epoxides is described. The kinetic data emphasizes (i) coordination potential (i.e., cationic charge) of the metal ion, (ii) methyl group substitution within the 1,3,2λ^5-dioxaphospholanyl substructure, and (iii) changes in solvent polarity (1). The second aspect of the presentation involves a discussion of the mechanism of the stereospecific benzoylation of secondary carbinol stereocenters (i.e., 1,2-chiral diols) with essentially complete inversion of configuration initiated by the triphenylphosphine-benzoyl peroxide reagent (2). These findings are novel and important because expansion of this basic concept allows for insertion of different nucleophiles at the secondary stereocenters without prior protection, thus demonstrating an exciting use of 1,3,2λ^5-dioxaphospholanes in the development of new synthetic methods. Finally, the unique phosphoranylation and highly diastereoselective cyclodehydration of methyl α-D-glucopyranoside is also discussed (3).



(1) W. T. Murray, S. A. Evans, Jr., Nouv. J. Chem., in press, 1989; W. T. Murray, S. A. Evans, Jr., J. Org. Chem., in press, 1989.

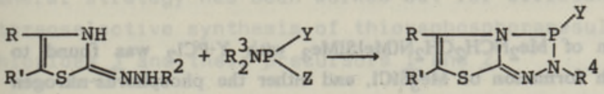
(2) A. M. Pautard, S. A. Evans, Jr., J. Org. Chem., 53, 2300 (1988); Chem & Eng News, 66:20, 23 (1988); W. T. Murray, A. M. Pautard, S. A. Evans, Jr., "7th IUPAC Conference on Organic Synthesis".

(3) J. W. Kelly, S. A. Evans, Jr., J. Am. Chem. Soc., 108, 7681 (1986).

1-13 THE CHEMISTRY OF FUSED CYCLOTRIAZAPHOSPHOLES

JING-LIN ZHANG, WEI XU, XIAO-BO MA, HAI-YAN LU, and
JINGIAO LU
Institute of Organic Synthesis, Huazhong Normal University,
Wuhan, Hubei, P.R.C.

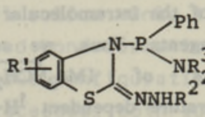
Fused cyclotriazaphospholes are interesting series in the phosphorus heterochemistry. A method has been developed for the synthesis of different derivatives of fused tricyclotriazaphosphole and fused dicyclotriazaphosphole.



R = Me, Ph; R' = H, Me, R, R' = -CH=C-CH=CH—; R^2 = Ac, H;
$X = P{<}^{Z}_{Y}$; R^3 = Me, Et, n-Pr, n-Bu; R^4 = Ac, $X = P{<}^{Y}_{Z}$, Ar;
X = S, O, ".."; Y, Z = NR_2, OR.

Compounds (I) are selective in their nucleophilic substitution reactions, like the Arbuzov reaction, Perkow reaction and sulfidation, but are nonselective in electrophilic reactions as alcoholysis.

An acyclic compound (II) was obtained when $PhP(NR_2)_2$ was used as reagent in reaction (1). It is probably the intermediate of this reaction. A mechanism of this cycloconcensation reaction has been suggested.



Conformation of some products was investigated, by IR, MS and ^1H, ^{13}C and ^{31}P NMR spectra.

REFERENCE

1. J.L.Zhang, Z.S.Cao, Synthesis, 1985, 10, 1067.
2. J.L.Zhang, Z.S.Cao, Kexue Tongbao, 1986, 6, 432.

1-14 PROPERTIES AND REACTIONS OF 3-AZA-1-AZONIA-1,1,3-TRIMETHYL-$2\lambda^3$PHOSPHOLIDINES (INTRAMOLECULARLY STABILIZED PHOSPHENIUM CATIONS)

WILFRIED BECKER[a], DIETMAR SCHOMBURG[b], PETER G. JONES[a]
AND REINHARD SCHMUTZLER[a]

Institut für Anorganische und Analytische Chemie der Technischen Universität, Hagenring 30, D-3300 Braunschweig, BRD[a] *— Gesellschaft für Biotechnologische Forschung m.b.H., Mascheroder Weg 1, D-3300 Braunschweig, BRD*[b]

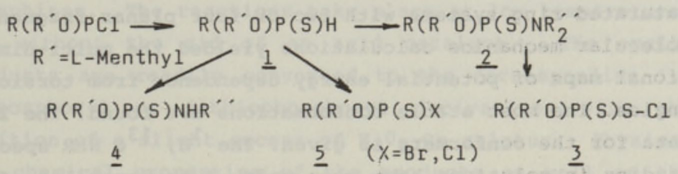
The reaction of $Me_2NCH_2CH_2N(Me)SiMe_3$ with $Y\text{-}PCl_2$ was found to proceed with formation of Me_3SiCl, and either the phosphorus-nitrogen bonded compounds, $Me_2NCH_2CH_2N(Me)P(Y)Cl$ (in the case of Y = Me, Ph, Bu^t, CCl_3, and CF_3) or the ionic, intramoleculary coordinated compounds $[Me_2\overline{NCH_2CH_2N(Me)P}(Y)]^+\ Cl^-$ (for Y = Cl, Br, OMe, OPh, and NEt_2). During the reaction of several of these trimethylethylendiamino-substituted phosphines with sodium tetraphenylborate the intramolecularly coordinated compounds, $[Me_2\overline{NCH_2CH_2N(Me)P}(Y)]^+\ [BPh_4]^-$ (Y = Me, Ph, Bu^t, CCl_3, OMe, OPh, and NEt_2) were formed. The temperature dependent ^1H-NMR-spectra of these chlorides and tetraphenylborates suggest differences in the stability of the nitrogen-phosphorus donor-acceptor bond, depending on the nature of the substituent Y on phosphorus. The coordinative $Me_2N \rightarrow P$ bond could be established by x-ray determination for $[Me_2\overline{NCH_2CH_2N(Me)P}(Cl)]^+\ Cl^-$ and $[Me_2\overline{NCH_2CH_2N(Me)P}(Ph)]^+\ [BPh_4]^-$, with P-N distances of 184.2 pm and 188.2 pm, respectively. Some of the intramolecular complexes were shown to react with oxidizing agents. Thus, we could obtain the 3,5-di-tert-butyl-o-quinone adducts of $[Me_2\overline{NCH_2CH_2N(Me)P}(Y)]^+\ [BPh_4]^-$, with Y = Me, Ph (temperature dependent ^1H-NMR spectrum), and Bu^t. Treatment of $[Me_2\overline{NCH_2CH_2N(Me)P}(OMe)]^+\ [BPh_4]^-$ with N_3Ph resulted in the formation of a four-memdered ring, with phosphorus-oxygen double bonds (P=O 145.3 pm) and two $Me_2NCH_2CH_2NMe_3^+$-units, as shown by x-ray structure determination. The structure and identity of the sulfide, $[Me_2\overline{NCH_2CH_2N(Me)P}(:S)Me]^+\ [BPh_4]^-$, could also be established by x-ray structure determination.

1-15 RECENT PROGRESS IN STEREOCHEMISTRY OF CHIRAL THIOXAPHOSPHORANESULPHENYL HALIDES AND THEIR PRECURSORS. NEW STEREOCHEMICAL PROBE FOR NUCLEOPHILIC SUBSTITUTION AT SULFENYL SULFUR

JAN MICHALSKI, ANDRZEJ ŁOPUSIŃSKI and LESZEK ŁUCZAK

Centre of Molecular and Macromolecular Studies,
Polish Academy of Sciences, 90-362 LODŹ, Boczna 5.

General strategy has been worked out for efficient fully stereoselective synthesis of thioxaphosphoranesulfenyl chlorides 3 and their precursors 1 and 2.



$$\begin{tikzcd}[column sep=small] R(R'O)PCl \arrow[r] & R(R'O)P(S)H \arrow[dl] \arrow[d] \arrow[r] & R(R'O)P(S)NR''_2 \arrow[d] \\ R(R'O)P(S)NHR'' & R(R'O)P(S)X & R(R'O)P(S)S\text{-}Cl \end{tikzcd}$$

R'=L-Menthyl

1 2

4 5 (X=Br,Cl) 3

Stereoselective synthesis of 3 is based on separation of diastereoisomers 1 R_p and S_p or 2 R_p and S_p.
The compounds 4 were obtained by Staudinger's and 5 by Todd-Atherton's reactions. The high optical purity of 1 - 5 was confirmed by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy as well as by chemical correlations. The chlorides 3 serve as stereochemical probe for nucleophilic substitution at sulfenyl sulfur. Only these reactions which proceed by concerted bond formation or bond breaking are expected to preserve configuration at P atom. On contrary, dissociative processes, both ionic and radical should lead to the 1:1 mixture of diastereoisomers R_p and S_p.
E.g.: The reaction of 3 with amines led to the sulfenamides 2 of the same optical purity as those which were employed for the conversion 2→3. In highly polar solvents where S^+ species are likely to be formed, no stereoselectivity at P centre was observed.

1-16 EIGHT-MEMBERED PHOSPHORUS HETEROCYCLES: SYNTHESIS, THREE-DIMENSIONAL STRUCTURE AND STEREOELECTRONIC EFFECTS

R.P.ARSHINOVA and B.A.ARBUZOV
A.M.Butlerov Chemical Research Institute of Kazan State University, Lenin Str. 18, Kazan 420008, USSR

In the first part of the report a general analysis of the methods of synthesis of the phosphorus-containing 8-membered heterocycles is given. The second and the third part are devoted to recent advances in the field of conformational analysis and electronic structure of 8-membered species with P^{III} and P^{IV} (organic and inorganic, saturated and unsaturated ring systems with two or four planar fragments). Molecular mechanics calculations yielded the multi-dimensional maps of potential energy dependence from torsion angles. The most stable conformations are found. The X-ray data for the conformers is given. The ^1H, ^{13}C NMR spectral studies in solutions have been made. A few examples of complex multicomponent equilibria are considered.

General conclusions on conformational characteristics are given. The effects produced by the nature of heteroatoms, planar fragments, their number and localization have been taken into account. The role of stereoelectronic effects in the formation of three-dimensional structure is discussed.

1-17 SYNTHESIS OF 1,4-DIALKYL 1,4-DI-PHOSPHA 2,3,5,6-TETRAHYDROXYCYCLOHEXANES

A.J.ROBERTSON
Cyanamid Canada Inc., Welland Plant, Garner Road,
P.O. Box 240, Niagara Falls, Ontario, Canada L2E 6T4

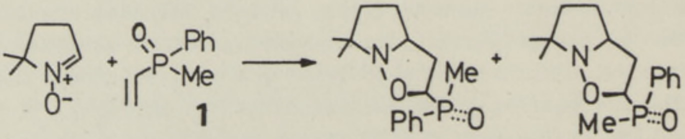
High yields of 1,4-dialkyl 1,4-diphospha 2,3,5,6 tetrahydroxycyclohexanes are produced when equal molar portions of glyoxal are added to primary alkylphosphines. The reactions take place at low temperatures and without the aid of an acid catalyst. The cyclic products are readily converted to the corresponding 1,4 diphosphoryl or dithiophosphoryl derivatives with the addition of a slight excess of H_2O_2 or sulphur. Physical and chemical properties of the products as well as the reaction conditions are discussed. Of particular importance in the order and rate of additions of the two reagents. Reversal of the addition of the reagents results in an entirely different product. This synthesis offers an easy route to 1,4-diphosphacyclohexanes. In addition the oxides of the lower homologs have utility as flame retardants for polypropylene and polyester fibers.

1-18 PHOSPHINO ISOXAZOLIDINES: AN APPROACH TO REGIO AND STEREOSELECTIVE SYNTHESIS

A.BRANDI, K.M.PIETRUSIEWICZ[a]
Department of Chemistry, University of Basilicata, 85100 Potenza, Italy and Centre of Heterocyclic Compounds, CNR, Department of Organic Chemistry, University of Firenze, 50121 Firenze, Italy.
[a] Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Boczna 5, 90-362 Lodz, Poland.

The 1,3-dipolar cycloaddition of nitrones to vinyl phosphorus derivatives, mainly phosphines and their oxides and sulfides, has been studied. In general, unsubstituted vinyl phosphorus compounds gave preferentially 5-substituted isoxazolidines in high yields (60-90%). Only nitrones having a high energy HOMO (e.g. C,N-diphenyl nitrone) gave adducts with inverted regioselectivity. Complete inversion is observed in the case of phosphine sulfide and selenide cycloadditions with the same nitrone. The studied 2-alkyl substituted vinyl phosphine oxides gave the 4-phosphinyl substituted isoxazolidines regiospecifically. ^{13}C-NMR spectroscopy has been the best means to assign unequivocally the regiochemistry to the products.

The cycloaddition to the chiral (racemic) methylphenylvinylphosphine oxide and sulfide occurs with considerable diastereofacial selection. The assignment of the preferred stereochemistry was as shown below.



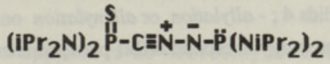
Similar diastereoselectivity was observed in cycloadditions of 1 with nitrile oxides. In one case the assignment was confirmed by single crystal X-ray diffraction analysis.

The possible transition states for the cycloadditions will be discussed.

1-19 USE OF PHOSPHORUS FOR STABILIZING HIGHLY REACTIVE ORGANIC SPECIES: NITRILEIMINES AND PSEUDODIAZOALKENES

Antoine BACEIREDO, Michel GRANIER, Florence CASTAN, Jean Marc SOTIROPOULOS, Ghislaine SICARD and Guy BERTRAND*.
Laboratoire de Chimie de Coordination, 205, route de Narbonne, 31077 Toulouse Cédex, France.

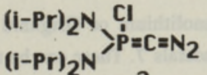
Nitrile imines, first prepared by Huisgen *et al* have been widely used in organic synthesis, in regioselective 1,3 dipolar cycloadditions. Up to now, they have only been observed by IR and UV in 85K matrix, or by mass and real time photoelectron spectroscopy in the gas phase. We will present the synthesis, reactivity and X-ray crystal structure of the perfectly stable C-thiophosphino N-phosphino nitrileimine **1** (mp 100°C without decomposition). The role of a phosphorus atom, in various coordination states, in the stabilization of other 1,3 dipoles will be discussed.



$$(iPr_2N)_2\overset{S}{\overset{\|}{P}}-C\equiv\overset{+}{N}-\overset{-}{N}-\ddot{P}(NiPr_2)_2$$

1

Diazo derivatives and Wittig reagents are among the most useful building blocks not only in organic, but also in inorganic chemistry. Diazoalkenes (>C=C=N_2) have attracted considerable interest in the last few years as potential generators of unsaturated carbenes, but have never been spectroscopically characterized. We will report the synthesis and reactivity of a new type of stable phosphacumulene **2** possessing both phosphorus-ylide and diazo moieties. Since a Wittig reagent displays, to some extent, a double-bonded character, this is also an approach to stable unsaturated diazo derivatives.



$$\left.\begin{array}{l}(i\text{-}Pr)_2N\\(i\text{-}Pr)_2N\end{array}\right> \overset{Cl}{\overset{|}{P}}=C=N_2$$

2

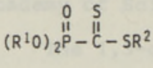
Of particular interest, 2 appeared to be a precursor of diazocarbene (:CN_2) or naked carbon and the trapping of these extremely reactive molecules will be presented.

1-20 REACTIONS OF PHOSPHONODITHIOFORMATES WITH NUCLEOPHILIC REAGENTS: POTENTIAL SYNTHETIC USES

A. BULPIN, S. MASSON and A. SENE

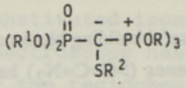
Laboratoire de Chimie des Composés Thioorganiques (U.A. CNRS 480), ISMRA,
Université, F-14032 CAEN, France.

Phosphonodithioformates **1** are readily available compounds from dialkylphosphites and carbon disulphide. The reactions of these non-enethiolisable dithioesters with nucleophilic reagents (trialkylphosphites, organometallics, thiolates) were investigated.

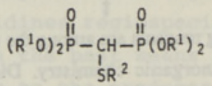

$(R^1O)_2\overset{O}{\overset{\|}{P}}-\overset{S}{\overset{\|}{C}}-SR^2$ $R^1 = Et, iPr$; $R^2 = CH_3, CH_2OCH_2CH_2OCH_3, C_{12}H_{25}$, crotyl

1

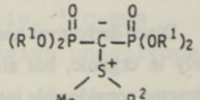
Treatment of dithioesters **1** by two equivalents of a trialkylphosphite led to the stabilized phosphonium ylids **2**. These can be used as precursors of substituted methylene bis-phosphonates (compounds of biological interest) through the following reactions : *-protonation* (by addition of a hydracid) on the central carbon atom of **2** with simultaneous dealkylation of the alkoxyphosphonium group, leading to compounds **3** ; *-methylation* (with MeI) on the sulfur atom of **2** and the same dealkylation leading to the very stable sulfonium ylids **4** ; - *allylation* or *allenylation* on the central carbon of **2** by reaction with allylic or propargylic bromides (bis-phosphonates **5** and **6**).


$(R^1O)_2\overset{O}{\overset{\|}{P}}-\underset{SR^2}{\underset{|}{\overset{-}{C}}}-\overset{+}{P}(OR)_3$

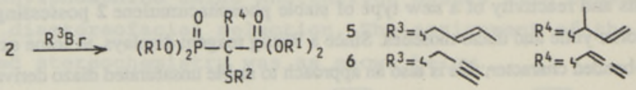
2


$(R^1O)_2\overset{O}{\overset{\|}{P}}-\underset{SR^2}{\underset{|}{CH}}-\overset{O}{\overset{\|}{P}}(OR^1)_2$

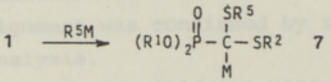
3

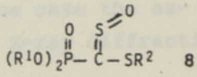


4



Thiophilic addition of organolithium or Grignard reagents to dithioesters **1** led to metallated phosphonodithioacetals **7**. These can be trapped by electrophiles or used as Wittig-Horner reagents for the synthesis of ketene dithioacetals. Similar results were obtained from sulfines **8**. Base catalyzed thiophilic addition of thiols to **1** was also observed.


$1 \xrightarrow{R^5M} (R^1O)_2\overset{O}{\overset{\|}{P}}-\underset{M}{\underset{|}{\overset{SR^5}{\overset{|}{C}}}}-SR^2$ 7

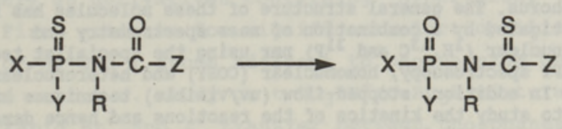

$(R^1O)_2\overset{O}{\overset{\|}{P}}-\overset{S=O}{\overset{\|}{C}}-SR^2$ 8

1-21 A NEW ROUTE TO PHOSPHORYL THIOCARBONYL MIXED IMIDES - STRUCTURE LIMITATIONS

K. E. DeBruin and E. E. Boros

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523, USA

Thiophosphoryl carbonyl mixed imides (**I**) have been observed to undergo a spontaneous, uncatalyzed rearrangement. The rearrangement results in the thiophosphoryl sulfur atom and the carbonyl oxygen atom exchanging positions and forming phosphoryl thiocarbonyl mixed imides (**II**).



I **II**

A substituent on nitrogen appears to be necessary for a facile rearrangement; with a reactivity order of **Ia** (R = H) << **Ib** (R = Me) < **Ic** (R = Ph). Rearrangement occurs faster with alkoxy groups on phosphorus giving a reactivity order of **Ic** (X = Y = MeO) > **Id** (X = Ph, Y = MeO) > **Ie** (X = Y = Ph). Benzoyl imides **Ic** (Z = Ph) rearrange much faster than acetyl imides **If** (Z = Me) or carboalkoxy imides **Ig** (Z = OiBu). A possible mechanism for the rearrangement based on these structure effects will be presented.

1-22 THE KINETICS AND MECHANISM OF THE REACTION OF ONIUM CYCLOPENTADIENYLIDES WITH TETRAHALO-p-BENZOQUINONES

by C. Dennis Hall* and Peter Speers
Department of Chemistry, King's College, Strand, London WC2R 2LS

Rosa Valero and Francisco Perez Pla,
Department of Physical Chemistry, University of Valencia,
Burjassot, Spain,
and Donald B. Denney,
Department of Chemistry, Rutgers, The State University of New
Jersey, Piscataway, N.J., 08903, U.S.A.

Abstract

The reaction of triphenylphosphonium cyclopentadienylide (1) with halogen-substituted p-benzoquinones (4) is shown to give a new class of dipolar (zwitterionic) dyes (5) containing phosphorus. The general structure of these molecules has been investigated by a combination of mass spectrometry and multinuclear (^{1}H, ^{13}C and ^{31}P) nmr using the specialist techniques of DEPT spectroscopy, homonuclear (COSY) and heteronuclear 2-D nmr. In addition, stopped-flow (uv/visible) techniques have been used to study the kinetics of the reactions and hence demonstrate that the rate-limiting step is nucleophilic addition of the ylid nucleophile to the quinone, followed by a rapid loss of halide ion. This mechanism follows the classical pattern associated with nucleophilic aromatic substitution in activated aryl halides.

1-23 NOVEL PROPERTIES OF IODOPHOSPHONIUM IONS: KINETICALLY LABILE BEHAVIOUR AND SECONDARY BONDING

M. BÄTCHER, W.-W. DU MONT, S. POHL and W. SAAK

Fachbereich Chemie, Universität Oldenburg
Carl-von-Ossietzky-Strasse 9-11, D-2900 Oldenburg,
F.R. Germany

Neutral species R_3PX_2 in equilibria with halogenophosphonium ions $R_3PX^+X^-$ have for long time been understood exclusively as derivatives containing "hypervalent" phosphorus. First evidence for significant electrophilic properties of Br and I atoms adjacent to phosphonium centers came from an n.m.r. study on $t\text{-}Bu_3PX^+/t\text{-}Bu_3P$ mixtures showing rapid Br^+ and I^+ transfer between phosphanes (fluxional P^{III}/P^V systems").

1-H, 13-C and 31-P-n.m.r. spectra and X-ray crystal structures of iodophosphonium salts with anions of variing donor properties reveal that central iodine is linear dicoordinate in all cases ($\measuredangle$ P-I-X>170°).

$$R_3P—\ddot{\underset{..}{I}}\longleftarrow :X \qquad X = I^-,\ I_3^-,\ I\text{-}ML_n^-,\ BF_4^-$$

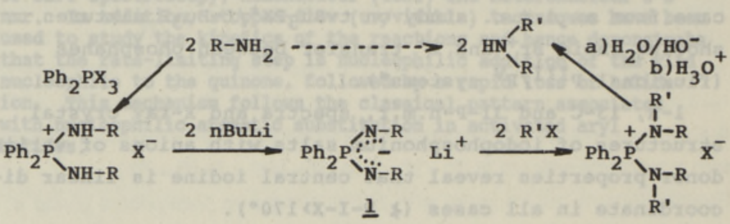
Strong I···X interaction (X = I^-) leads to lengthening of the covalent P-I bond, but even weakly coordinating anions (like BF_4^-) obey the linear coordination geometry at "hypervalent" iodine. Secondary X I-PR_3 interaction is the primary step of nucleophilic substitution reactions at iodine with PR_3 as leaving group, like I^+-cation transfer reactions between phosphanes or like the decomposition of PI_4^+ by nucleophilic attack of I^- to give PI_3 interacting weakly with iodine molecules. The role of donor substituents R at phosphorus for I···X interactions will be discussed.

1-24 PHOSPHONIUM DIAZA-DIYLIDS AND AZA-YLDIID AS NEW AND EFFICIENT REAGENTS FOR PRIMARY AND SECONDARY AMINES SYNTHESIS

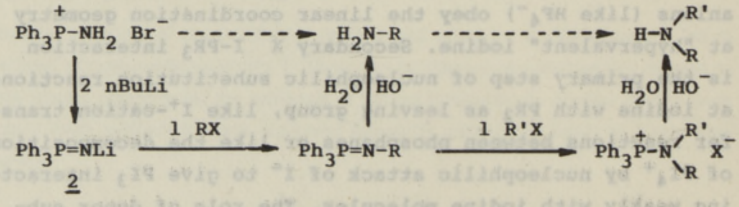
H.-J. CRISTAU, C. GARCIA, J. KADOURA and E. TORREILLES

Laboratoire de Chimie Organique ENSCM (Unité Associée
au CNRS n° 458), 8 rue de l'Ecole Normale.
34075 MONTPELLIER CEDEX (France)

A large range of phosphonium diaza-diylids 1 are prepared from primary amines and afford, after alkylation and hydrolysis, secondary amines in high yields.



In a similar way, the phosphonium aza-yldiid 2, prepared directly from ammoniac afford either primary or secondary amines.



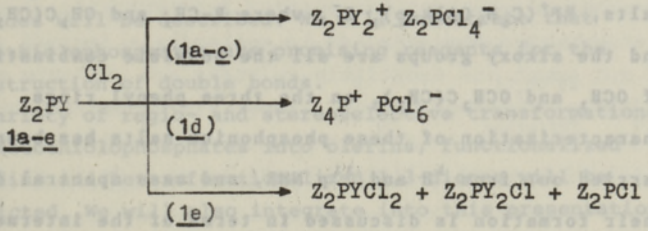
In both cases, the method can be applied to various alkyl-, aryl- or functional amines.

1-25 LIGAND EXCHANGE BY HALOGENATION OF P^{III} COMPOUNDS

J. GLOEDE

Central Institute of Organic Chemistry, Academy of
Sciences of the GDR, Rudower Chaussee 5, Berlin 1199,
GDR

With halogenes triphenyl phosphite gives tetraphenoxyphosphoniumsalts (1,2). We found, that the other P^{III}-compounds <u>1a-e</u> react with halogenes (0°C) to phosphonium phosphates or halogenophosphoranes in the same manner.



<u>1</u> (Z_2/Y): <u>a</u> 2Cl/OPh <u>b</u> 2Cl/NMe_2 <u>c</u> o-$C_6H_4O_2$/NMe_2
<u>d</u> 2PhO/Cl <u>e</u> o-$C_6H_4O_2$/OPh

We assume, that the first step is the addition of halogene and the second step is a ligand exchange reaction with the P^{III} compound <u>1</u>.

$$\underline{1} \xrightarrow{X_2} \begin{matrix} Z_2PYX^+\ X^- \\ \text{or} \\ Z_2PYX_2 \end{matrix} \xrightarrow{\underline{1}} \begin{matrix} Z_2PY_2^+\ X^- \\ \text{or} \\ Z_2PY_2X \end{matrix} + Z_2PX$$

We tested this assumption by reaction of <u>1</u> with P^Vcompounds and by reaction of <u>1</u> with half a mole of chlorine.

(1) C. T. Tseng, J. Org. Chem. <u>44</u>,2793 (1979).
(2) J. Michalski, M. Pakulski, A. Skowronska, J. Gloede, H. Groß, J. Org. Chem. <u>45</u>, 3122 (1980).

1-26

FORMATION AND REACTIONS OF PHOSPHONIUM INNER SALT, $\geqslant P^{+}C_{6}H_{4}O^{-}$-p

Gurdial Singh

Pioneering Research Laboratory, Fibers Department,
Experimental Station, E. I. du Pont de Nemours & Company,
Wilmington, Delaware 19898 (U.S.A.)

Abstract: A reaction between bis(p-methoxyphenyl)phosphine and neopentyl iodide has given eight phosphonium salts, $RP^{+}(C_{6}H_{4}OAlk\text{-}p)_{3}\ I^{-}$, where $R{=}CH_{3}$ and $CH_{2}C(CH_{3})_{3}$, and the alkoxy groups are all the possible combinations of OCH_{3} and $OCH_{2}C(CH_{3})_{3}$ on the three phenyl rings. Characterization of these phosphonium salts has been carried out from ^{1}H and ^{31}P NMR, and mass spectral data. Their formation is discussed in terms of the intermediacy of phosphonium inner salt, $\geqslant P^{+}C_{6}H_{4}O^{-}$-p. In addition, the thermolysis of methyltris(p-methoxyphenyl)phosphonium iodide, and its reaction with triphenylphosphine, will be reported. Spectral evidence for structures of the reaction products will be discussed in the light of the phosphonium inner salt.

1-27 KETOTHIOLOPHOSPHATES AS EFFICIENT REAGENTS IN ORGANIC SYNTHESIS

Aleksandra SKOWRONSKA and Piotr DYBOWSKI.

Centre of Molecular and Macromolecular Studies,
Polish Academy of Sciences, 90-362 Lodz, Boczna
5, Poland.

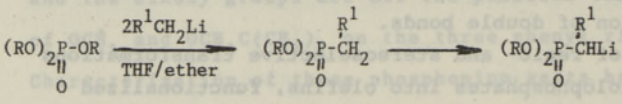
Recent results concerning the chemistry of ketothiolophosphates 1 will be presented.
A new synthesis of compounds 1 based on the reaction of silyl enol ethers with oxo- and thioxophosphoranesulfenyl halides will be described. We will demostrate that ketothiolophosphates are promising reagents for the construction of double bonds.
A variety of regio- and stereoselective transformations of ketothiolophosphates into olefins, functionalized olefins and heterofunctionalized 1,3-dienes will be depicted. We will also integrate into this presentation our results involving Diels-Alder reaction of some new heterofunctionalized 1,3-dienes.

1-28 NUCLEOPHILIC DISPLACEMENT REACTIONS ON TETRAVALENT PHOSPHORUS ESTERS BY LITHIUM REAGENTS. A POWERFUL TOOL IN ORGANIC SYNTHESIS

PHILIPPE SAVIGNAC and MARIE-PAULE TEULADE

Laboratoire de Chimie du Phosphore et des Métaux de Transition
DCPH, Ecole Polytechnique, 91128 Palaiseau Cédex, France

Alkyllithium reagents in excess smoothly convert symmetrical trialkylphosphates to α-lithioalkylphosphonates quantitatively in a THF/ether system. Altough a critical search for optimum conditions failed with methyl lithium all alkyllithium compounds, linear or ramified, were shown to attack phosphorus in simple or hindered phosphates. Metalation of aliphatic carbon attached to phosphorus is the key step.



$$(RO)_2\underset{\underset{O}{\|}}{P}\text{-}OR \xrightarrow[\text{THF/ether}]{2R^1CH_2Li} (RO)_2\underset{\underset{O}{\|}}{P}\text{-}\overset{R^1}{\overset{|}{C}}H_2 \longrightarrow (RO)_2\underset{\underset{O}{\|}}{P}\text{-}\overset{R^1}{\overset{|}{C}}HLi$$

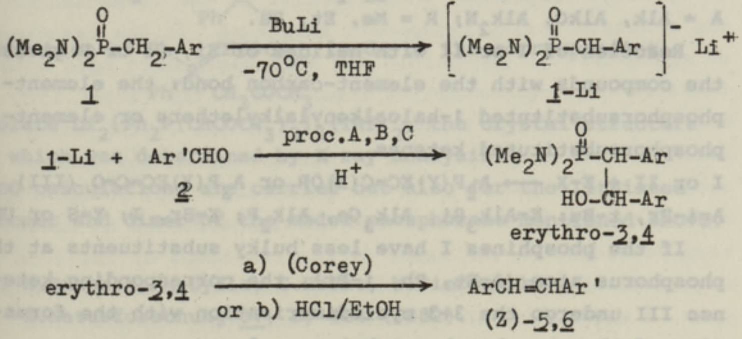
Good yields of alkylphosphonates are possible after hydrolysis. From treatment of α-lithioalkylphosphonates with functional precursors (EX) in the presence of LDA α-substituted phosphoryl stabilized anions are directly obtained. They react "in situ" with electrophiles (R^2CHO) to give α-substituted α, β-insaturated esters, acids, amides, aldehydes etc... Extension of the reaction sequence to bis-(dimethylamino) chlorophosphates provides a useful route to stable α-lithioalkylphosphonamides without side reactions. Etoxy-2 oxo-2 N,N-dimethyl-1,3 diazaphospholane-1,3,2 is also explored. It is, shown to react with lithium compounds as efficiently as trialkylphosphates. For example the stable α-lithioalkylcyclophosphonamides react at low temperature with ketones to give a β-hydroxy alcool able on hydrolysis to loose the phosphonamide moiety by cleavage of the carbon-phosphorus bond thus realizing the transfer of a methylene group. From treatment with chloroformates stable enolates are obtained which on reaction with aldehydes conduce to α-substituted ($R^1=CH_3$, C_2H_5, ${}_nC_3H_7$) α, β-unsaturated esters of (Z) geometry.

1-29 OLEFIN SYNTHESIS VIA THE Li-DERIVATIVE OF THE N,N,N',N'-TETRAMETHYLDIAMIDES OF ARYLMETHANEPHOSPHONIC ACIDS

J. PETROVA, S. MOMCHILOVA, M. KIRILOV

University of Sofia, Faculty of Chemistry, 1 Bld
A. Ivanov, 1126 Sofia, Bulgaria

A convenient way for synthesis of (Z)-alkenes (stylbenes and β-mono and disubstituted styrenes) is proposed by achieving a high erythro-stereoselective addition of Li-N,N,N',N'-tetramethyldiamides of arylmethanephosphonic acids to aldehydes and ketones and subsequent stereospecific thermal olefination of the obtained hydroxyphosphonamide adducts. The reaction conditions are found for (Z)-stereospecific olefin formation from the erythro-adducts in acidic media. The mechanism of the aldol stage of the reaction as well as of the elimination process is discussed.



$$\underset{\underline{1}}{(Me_2N)_2\overset{O}{\overset{\|}{P}}-CH_2-Ar} \xrightarrow[-70^{\circ}C,\ THF]{BuLi} \underset{\underline{1}\text{-}Li}{\left[(Me_2N)_2\overset{O}{\overset{\|}{P}}-CH-Ar\right]^{-} Li^{+}}$$

$$\underline{1}\text{-}Li + \underset{\underline{2}}{Ar'CHO} \xrightarrow[H^{+}]{proc.A,B,C} \underset{\text{erythro-}\underline{3},\underline{4}}{\begin{array}{l}(Me_2N)_2\overset{O}{\overset{\|}{P}}-CH-Ar\\ \qquad\quad\ \ |\\ \qquad\ HO-CH-Ar\end{array}}$$

$$\text{erythro-}\underline{3},\underline{4} \xrightarrow[\text{or b) HCl/EtOH}]{\text{a) (Corey)}} \underset{(Z)\text{-}\underline{5},\underline{6}}{ArCH{=}CHAr'}$$

J.Petrova, S.Momchilova, M.Kirilov, Phosphorus and Sulfur 24,243 (1985); S.Momchilova, J.Petrova, M.Kirilov, Phosphorus and Sulfur 35, 319 (1988); J.Petrova, M.Kirilov S.Momchilova,K.Kossev, Phosphorus and Sulfur 36 (1988).

1-30 PHOSPHOR(III)- AND PHOSPHOR(IV)-SUBSTITUTED ALKOXYACETYLENES AS NEW SYNTHONS IN PHOSPHORORGANIC SYNTHESIS

M.A.KASANKOVA and N.V.LUKASHEV
Department of Chemistry, Lomonosov University, Moscow
117899, USSR

Phosphorylated alkoxyacetylenes $A_2PC\equiv COR$ (I) and $A_2P(S)C\equiv COR$ (II), a rare type of diheterosubstituted acetylenes containing the substituents with the opposite electronic properties at the triple bond, were obtained. Versatile synthetic application of such compounds is based on high reactivity. The reaction pathway is dependent on the nature of substituents at the phosphorus atom, in the alkoxygroup and the properties of reagents.

Alkylhalides and alkylsulphenchlorides attack the phosphorus atom. This reaction allows to obtain the previously unknown trialkyl-, dialkoxyalkyl-, alkylthioalkyl-, ketenylidenephosphoranes.

I or II + RBr (or RSCL) $\longrightarrow A_2P(R){=}C{=}C{=}O$ or $A_2P(SR){=}C{=}C{=}O$

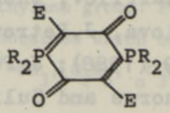
A = Alk, AlkO, Alk_2N; R = Me, Et, Bu.

Reaction of I or II with halides of Si, Ge or P gives the compounds with the element-carbon bond: the element-phosphorsubstituted 1-haloalkenylalkylethers or element-phosphorsubstituted ketenes.

I or II + E-X $\longrightarrow A_2P(Y)EC{=}C(X)OR$ or $A_2P(X)EC{=}C{=}O$ (III)

A=i-Pr, t-Bu; E=Alk_3Si, Alk_3Ge, Alk_2P; X=Br, I; Y=S or UEP.

If the phosphines I have less bulky substituents at the phosphorus atom (A=Et, Ph, i-Pr), the corresponding ketenes III undergo the 3+3 cyclodimerisation with the formation of the new phosphorus heterocycles.

I + E-X $\longrightarrow$ 

E=R_2P, R_3Si, R_3Ge

Alkoxyethynylphosphines give complexes with chromium and tungsten carbonyles which are less active and react only with the more electrophilic reagents (Me_3SiI, PBr_3).

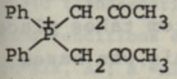
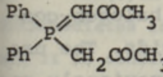
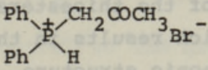
1-31 2-OXOPROPYL-2-OXOPROPYLIDENE-DIPHENYL-PHOSPHORANE AND CRYSTAL STRUCTURE OF ITS LITHIUM ENOLATE

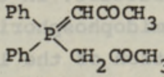
G.PETROV, E.M.KIRILOV, O.ANGELOVA, M.KIRILOV, J.KANETI[a], and J.MACICEK[b]

Department of Chemistry, Kliment Ohridsky University Sofia,
Bul. Anton Ivanov 1, Bulgaria

[a]Institute of Organic Chemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria

[b]Institute of Applied Mineralogy, Bulgarian Academy of Sciences, Sofia, Bulgaria

An assignment of the constitution of the compound  Br^- obtained in the reaction of Ph PSiMe$_4$ with BrCH$_2$COCH$_3$ and subsequent dehydrobromination  is reported. It reveals the correct reaction scheme and disproves a previously described (1) formation of the compounds  and Ph$_2$PCH$_2$COCH$_3$.

Lithiation of  leads to the corresponding enolate Li$_2$[Ph$_2$P(CHCOCH$_3$)$_2$]$_2$(THF)$_2$, the crystal structure of which was determined by X-ray analysis.

MNDO calculations are carried out also for the lithiated monomer and dimer of the model phosphorane mentioned above.

(1) H.Brunner, M.Dylla, G.Hecht, W.Pieroncyk, Z.Naturforschung 37, B, 404 (1982).

1-32 THE CHEMISTRY OF THIOLODERIVATIVES OF TRIVALENT PHOSPHORUS ACIDS

E.S.BATYEVA, O.G.SINYASHIN, and V.A.AL'FONSOV
Institute of Organic and Physical Chemistry, Kazan Branch, Academy of Sciences of the USSR, Kazan 420083, USSR

The systematic study of the chemical behaviour of the thioloderivatives of P(III) acids in the substitution and addition reactions was carried out. It was established that the scheme of the Arbuzov reaction, typical for the oxygen analogs, does not work, whereas the substitution of the alkylthio-group attached to the phosphorus(III) atom takes place with the preservation of its coordination. This was based on the investigation of the interaction of the esters and amides of the P(III) thioacids with halogens, halogen-containing electrophilic compounds and organic acids. The use of acid catalysts made possible to carry out previously unknown addition reactions of the thioesters of P(III) acids to carbonyl compounds, which results in the formation of the α-alkylthioalkylphosphonic structure. In the reactions of thioesters of phosphinic and amidophosphoric acid with oxiranes the regioselective insertion of the latter into the P-S bond of the thioderivatives of the P(III) acids was demonstrated. Original ways of synthesize of new classes of unsaturated compounds with the phosphorus(III) phosphorylated dichlorovinylsulfides and monothioacetales of ketene were developed on the basis of the reactions of thioloderivatives of the P(III) acids with some substituted acetylenes. A new method of synthesize previously unknown diamidoacetylenothiophosphonates was discovered while investigating the interaction of the thioesters of diamidophosphoric acids with chloroacetylenes.

1-33 THE TRANSESTERIFICATION OF PHOSPHORUS ESTERS WITH P-H BONDS - A ^{31}P NMR STUDY

M.J. GALLAGHER, R. GARBUTT, GUM HEE LEE and LIU YUN HUA

School of Chemistry, University of New South Wales,
P. O. Box 1, Kensington, N.S.W. 2033. Australia.

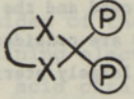
Esters of phosphorus acids RPH(O)OR' (R=H, Alk, Ar: R'Alk, Ar) undergo rapid transesterification under mild basic conditions. Under the same conditions esters of the type $(RO)_3P(O)$, $RP(O)(OR')_2$ and $R_2P(O)OR'$ (R=Alk, Ar; R'=Alk, Ar) are inert. The order of reactivity is: $H_2P(O)OR'$ > RPH(O)OR' > $HP(O)(OR')_2$. The reactions are followed and the intermediates identified by ^{31}P nmr. Possible mechanisms are considered and it is concluded that the difference in behaviour is largely steric.

1-34 NEW DIPHOSPHONATES, SYNTHESIS AND REACTIONS

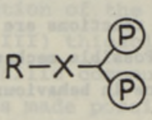
H. GROSS, S. OZEGOWSKI, S. HAUSSDÖRFER, I. KEITEL
and B. COSTISELLA

Central Institute of Organic Chemistry, Academy of
Sciences of the GDR, Rudower Chaussee 5, Berlin 1199,
GDR

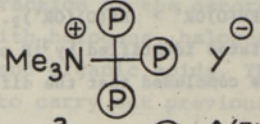
A number of new types of diphosphonates is described. In compounds of type 1 X can be O or CH_2, the R-X-group in α-position of type 2 can be aryl-NH, acyl-NH, dialkylphosphoryl-NR or aryl-O. The synthesis of the arylamino-derivatives 2 can be achieved in one step, in the other cases the phosphono-group may be introduced successively.



1



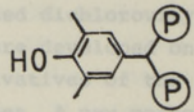
2



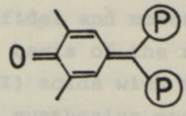
3

$Ⓟ\!- \hat{=} (EtO)_2\overset{O}{\overset{\|}{P}}-$

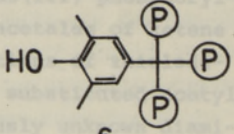
Depending on the structure of RX in 2 or on the nucleophilicity of $Y^{\ominus}$ in the quarternated triphosphonate 3 the phosphonates are either stable or show a tendency to splitt off or rearrange one phosphonyl-group. Diphosphonates 4, prepared from normally very unreactive



4



5



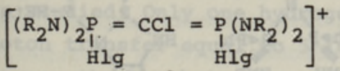
6

α-chlorobenzylphosphonates via Arbusov-reaction give the quinonmethides 5 by oxidation. The latter can be transformed to the stable triphosphonate 6.

1-35 THE REACTION OF NUCLEOPHILIC POLYHALOGENALKYLATION UNDER THE CONDITIONS OF TWO- AND THREE-COMPONENT SYSTEMS

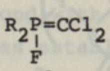
A.M.PINCHUK, A.P.MARCHENKO, and G.N.KOIDAN
Institute of Organic Chemistry of the Academy of Sciences of the Ukrainian SSR, Murmanskaya Str. 5, Kiev 252660, USSR

We have managed to perform the halophilic reaction of derivatives P^{III} of R_2PHlg (1) ($R=R_2N$, Alk; Hlg=F, Cl) type with CCl_4 and determine that, depending on the nature of these compounds 1, three types of high reactive products 2-4 are formed (1).



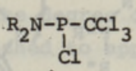
$$\left[(R_2N)_2\underset{Hlg}{P} = CCl = \underset{Hlg}{P}(NR_2)_2\right]^+ Cl^-$$

2



$$R_2\underset{F}{P}=CCl_2$$

3



$$R_2N-\underset{Cl}{P}-CCl_3$$

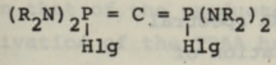
4

As a result of this research the reaction of nucleophilic tris-chloromethylation (polyhalogenoalkylation) og P-, Si- and C-halogenide in three component system was discovered.

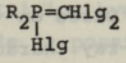
$$E\text{-}Hlg + XCHlg_3 + R_3P \longrightarrow \underset{5}{E\text{-}CHlg_2X} + R_3PHlg_2$$

$E=R_2P$, $R(Cl)P$, $Me_n(Cl)_{3-n}Si$, $RC(O)$; $X=Hlg$, CF_3, CN

Availability of the key compounds (5) makes it possible to perform the directed synthesis of different derivatives of phosphorus.



$$(R_2N)_2\underset{Hlg}{P} = C = \underset{Hlg}{P}(NR_2)_2$$



$$R_2\underset{Hlg}{P}=CHlg_2$$

$R\text{-}P=CHlg_2$

Hlg= F, Cl Hlg= Cl, Br; Hlg= F, Cl Hlg= Cl, Br, J

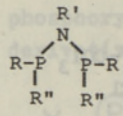
(1) G.N.Koidan, A.P.Marchenko, V.A.Oleinik, A.M.Pinchuk Zh. Obshch. Khim., 58, 1461-1468 (1988).

1-36 DIASTEREOSELECTIVE FORMATION OF FUNCTIONAL DIPHOSPH(III)AZANES

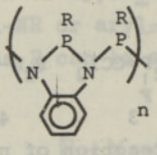
A. D. NORMAN, E. G. BENT, T. R. PROUT, AND R. C. HALTIWANGER

Department of Chemistry and Biochemistry, University
of Colorado, Boulder, Colorado 80309 USA

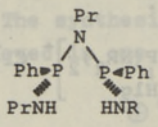
Stereoselective ⊐P-N(-)-P⊏ unit formation in bis(phosphino)amines (I), and the incorporation of these into stereoregular phosph(III)azane oligomer/polymer syntheses (II), will be discussed.



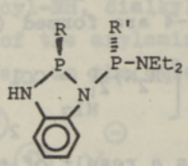
I



II



III



IV

Reactions of the chloro bis(phosphino)amine Ph(i-PrNH)PN(i-Pr)P(Ph)Cl with RNH$_2$ (R = Me, Et, i-Pr, Ph) yield bis(phosphino)amines III. Spectral and x-ray characterization show that (d,l)' diastereomers of III (Pr = i-Pr) are formed preferentially. The diazaphospholes C$_6$H$_4$(NH)$_2$PR (R = Me, t-Bu, Ph) undergo transamination with (Et$_2$N)$_2$PR (R = Me, t-Bu, Ph) to form the skeletally-stabilized bis(phosphino)amines IV, which are potential A-B monomers of [C$_6$H$_4$(N)$_2$(PR)(PR')]$_n$ polyphosphazanes. Based on ^{31}P NMR spectral correlations and x-ray characterization of C$_6$H$_4$(NH)PEtS(N)P(NEt$_2$)EtS, IV are shown to form preferentially as the (d,l) diastereomers. Reactions to use chloro(amino) or alkylamino bis(phosphino)amines (IV) as A-B type condensation monomers for polyphosph(III)azanes synthesis will be described.

1-37 NEW ASPECTS OF TRIVALENT PHOSPHORUS ACID AMIDE CHEMISTRY

E.E.NIFANTYEV, M.K.GRATCHEV, and S.Y.BYRMISTROV
V.I.Lenin Moscow State Pedagogical Institute, Malaya
Pirogovskaya 1, Moscow 119882, USSR

The interaction of proton-containing nucleophiles with trivalent phosphorus acid amides (TPAA) in the presence of weak acids is an effective method of phosphorylation, and therefore widely used to synthetic practices. Nevertheless, little is known about the chemistry of such a process. The interaction of the TPAA with amine hydrohalides was studied. Only one hydrogen bond with the degree of proton transfer equal to 5-10% was established to appear between these substances. This fact is very important and implies that: first, the TPAA are expected to enhance their reactivity proportionally to hydrohalide acidity; second, the racemic TPAA can enantioselectively phosphorylate chiral alcohols in the presence of optically active catalysts. These two facts were corroborated experimentally. Also, the TPAA were completely protonated with HBF_4 at the phosphorus atom. On heating the obtained products ^{31}P NMR spectra ceased to be doublet-shaped, which suggests the appearance of exchange processes. The phosphorylating ability of the completely protonated TPAA is far higher than that of the products containing hydrogen bonds. Acid activation of the TPAA has made it possible to find solutions to the synthetic phosphorylation and some other new problems. Thus, acid additives were found to catalyze phosphotropic processes in p,Π-conjugated TPAA, such as phosphopyrazoles, -imidazoles and -amidines. The fundamentally new conversions of the TPAA are based on the synthesis of new types of substances and methods of their effective separation from acid impurities using an interphase hydroxyl anion transfer technique.

1-38 THE EFFECT OF CHARGE DISPERSAL ON PHOSPHINE BASICITIES AND REACTIVITIES

M.TAAGEPERA, R.W.TAFT, and W.J.HEHRE
Department of Chemistry, University of California, Irvine, California, 92717, USA

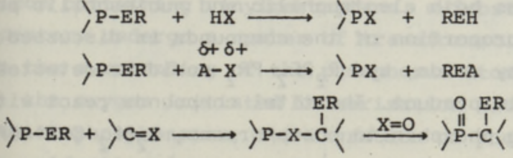
The opposing aqueous and gas phase trends in trimethyl- and triphenylphosphine basicities have both been suggested to be fundamental predictors of phosphine ligand reactivity in organometallic and coordination chemistry. (1,2) Phosphine ligand reactivities have been analyzed in terms of σ-bonding, ρ-bonding, and steric properties. σ-bonding ability in metal complexes had most commonly been estimated from basicities toward protonic acids in solution. Aqueous basicities and ligand reactivity, where σ-bonding is the predominant factor, seem to follow the electronegativity order, where the trimethylphosphine shows the greatest reactivity. In the gas phase, however, both proton affinity and UV photoelectron studies indicate that the triphenylphosphine is the stronger base. This seeming contradiction can be understood in terms of solvent attenuation, through charge dispersal from the reaction center, of reactivity parameters associated with field/inductive, resonance, and polarizability effects. (3) This study will use theoretical calculations of monohydrated cations to attempt to assess the factors involved in the better than two power of ten greater gas phase basicity of Ph_3P than Me_3P but the nearly six power of ten weaker basicity in water. The effect of charge concentration on basicities of cyclic vs. acyclic phosphines will also be discussed.

(1) R. C. Bush, R. J. Angelici, Inorg.Chem. 27, 681 (1988)
(2) R. J. Puddephatt, G. M. Bancroft, T. Chan, Inorganica Chimica Acta 73, 83 (1983).
(3) R. W. Taft, R. D. Topsom, Prog. Phys. Org. Chem. 16, 1 (1987).

1-39 RUPTURE OF THE P-E BOND IN REACTIONS OF ACIDIC DERIVATIVES OF TRIVALENT PHOSPHORUS

A.N.PUDOVIK, E.S.BATYEVA, and V.A.ALFONSOV
A.E.Arbuzov Institute of Organic and Physical Chemistry, Kazan Branch of the USSR Academy of Sciences, 8 Arbuzov Str., Kazan 420083, USSR

The reactions of the P(III) acid derivatives with the P-E bond proceeding with its cleavage, have been divided into three types: reactions of substitution by proton-containing nucleophilic reagents, reactions of substitution by aprotionic electrophilic reagents, and addition reactions with the insertion of an unsaturated fragment into the P-E bond (E - heteroatom with a lone electron pair, N, O, S)



$$\rangle P{-}ER \;+\; HX \longrightarrow \rangle PX \;+\; REH$$

$$\rangle P{-}ER \;+\; \overset{\delta+}{A}{-}\overset{\delta+}{X} \longrightarrow \rangle PX \;+\; REA$$

$$\rangle P{-}ER + \rangle C{=}X \longrightarrow \rangle P{-}X{-}\overset{ER}{\overset{|}{C}}\langle \xrightarrow{X=O} \rangle\overset{O}{\overset{\|}{P}}{-}\overset{ER}{\overset{|}{C}}\langle$$

The reactions are acid-catalysed. I can be concluded that acid-catalysis is the general feature of the reactions of the P(III) acid amides, esters and thioesters, which proceed with the cleavage of the P-E bond. The idea of applying acid catalysis to control the course of reactions and predict previously unknown transformations has proved to be effective. The possible schemes of the reactions are discussed.

1-40 SYNTHESIS AND REACTIVITY OF FLUORO(ORGANYL)PHOSPHANES

L. RIESEL and J. HAENEL

Humboldt-Universität zu Berlin, Sektion Chemie, Hessische Str. 1-2, Berlin, 1040, G.D.R.

The chemistry of fluoro(organyl)phosphanes is widely unknown caused by the considerable diffilculties in preparing these substances as well as by their small stability. We developed a new very convenient method for producing fluoro(organyl) phosphanes and succeeded in increasing their stability. Fluoro(organyl)phosphanes are produced from the corresponding chloro compounds by Cl/F-exchange using $Et_3N.nHF$ as a fluorinating agent. The reaction behaviour of fluoro(organyl) phosphanes is characterized by the fact that their phosphorus atom possesses both electrophilic and nucleophilic properties. The disproportion of the compounds is discussed. It is catalyzed by acids, and $R_2PF_2{-}PR_2$ could be detected as an intermediate product. The titel compounds react with aldehydes forming phosphinito phosphoranes, $R_2PF_2\text{-}CHR'\text{-}OPR_2$. The crystal structure of the reaction product with piperonal could be determined. The phosphinite P atom can be oxidized, such as by sulfur and covalent azides. α,β-unsaturated aldehydes react with R_2PF (R = Bu, Ph) forming oxaphospholenes. Furthermore the reactions with carboxylic acid chlorides, carbon tetrachloride, and covalent azides (aryl azides, trimethylsilyl azide), resp., are described. $R_2PF_2\text{-}COR'$ (R = Bu), R_2PF_3 (R = Ph, Bu), fluorophosphazenes, and oligomeric phosphazenes can be prepared in this way.

1-41 SYNTHESIS AND PROPERTIES OF PHOSPHORYLATED AND SILYLATED α-MERCAPTOCARBONYL COMPOUNDS

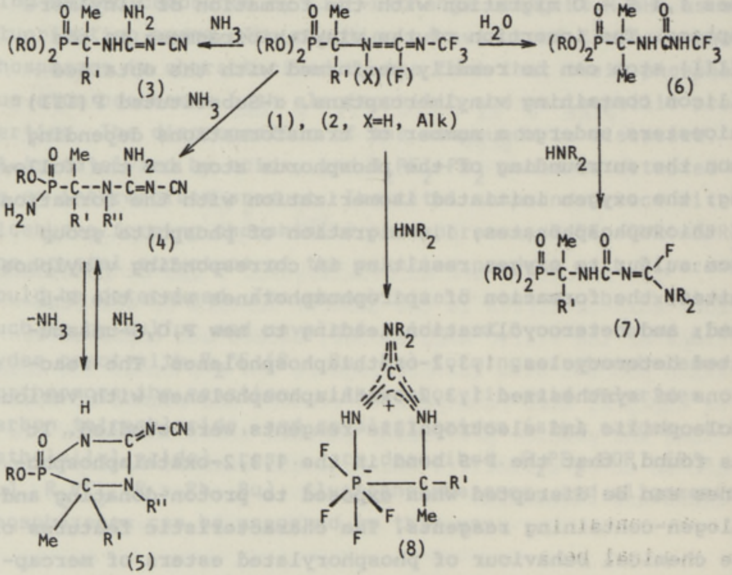
M.A.PUDOVIK, A.R.BURILOV, I.L.NIKOLAEVA, Ya.A.DROZDOVA,
D.V.CHEREPASHKIN, A.A.BARULLIN, and A.N.PUDOVIK
A.E.Arbuzov Institute of Organic and Physical Chemistry,
Kazan Branch of the Academy of Sciences of the USSR,
Arbuzov Str. 8, Kazan 420083, USSR

Silylated α-mercaptoketones, which appear to be convenient semiproducts for the synthesis of α-substituted thioesters of trivalent phosphorus, were obtained. The trimethylsilyl group in the silylated α-mercaptoketones undergoes 1,4 S → O migration with the formation of vinylmercaptans. The insertion of the vinylthiofragment to the P(III) atom can be readily performed with the obtained silicon containing vinylmercaptans. α-Substituted P(III) thioesters undergo a number of transformations depending upon the surrounding of the phosphorus atom are the following: the oxygen initiated isomerization with the formation of thioxophosphonates; 1,4-migration of phosphite group from sulfur to oxygen resulting in corresponding vinylphosphites; the formation of spirophosphoranes with the P-H bond; and heterocyclization leading to new P,O,S-unsaturated heterocycles, 1,3,2-oxathiaphospholenes. The reactions of synthesized 1,3,2-oxathiaphospholenes with various nucleophilic and electrophilic reagents were studied. It was found, that the P-S bond in the 1,3,2-oxathiaphospholenes can be disrupted when exposed to proton-donating and halogen-containing reagents. The characteristic features of the chemical behaviour of phosphorylated esters of mercaptoacetic acid were established.

1-42 PHOSPHORUS-CONTAINING N'-TRIFLUOROMETHYLCARBODIIMIDES AND N'-TRIFLUOROMETHYLFLUOROFORMAMIDINES IN REACTIONS WITH NUCLEOPHILIC REAGENTS

I.V.Martynov, A.Yu.Aksinenko, V.B.Sokolov, A.N.Chekhlov, A.N.Pushin, and O.V.Korenchenko
Institute of Physiological Active Substance of the USSR Academy of Sciences, Chernogolovka, Moscow region 142432, USSR

Interaction of 1-aminoalkylphosphonates with $CF_2=N-CF_3$ yields 1-(3-trifluoromethyl-1,3-diazaprop-2-enyl)alkylphosphonates (1) and (2), which was studied in the reactions with NH_3, R_2NH and H_2O:



Molecular structures of the compounds (2, X=H), (3, 7, 8) were determined by X-ray analysis. NMR ^{19}F and ^{31}P spectra of some compounds are discussed.

1-43 SYNTHESES WITH HYPOPHOSPHORUS ACID AND ITS DERIVATIVES

G.BORISSOV, I.DEVEDJIEV, and V.GANEV
Central Laboratory for Polymers, Bulgarian Academy of Sciences, Sofia 1040, Bulgaria

The following reactions have been investigated: hypophosphorus acid (HPA) with alcohols, polycaprolactame and formaldehyde; salts of HPA with alkylhalogenides, chlorene-containing polymers and isocyanates; and water solution of HPA with isocyanates.

It has been shown that the reaction of HPA with alcohols or HPA salts with alkylhalogenides yields phosphonous acids according to the scheme:

$$H_2P(O)OX + RY \longrightarrow RHP(O)OH,$$

where X = H for Y = OH, and X = M for Y = halogen.

A suitable method for the synthesis of 1-methylol-1,2-propadienylphosphonous acid and its hydroxyesters from epoxides, HPA, and 2-butine-1,2-diol has been proposed. The supposed mechanism of the reaction is discussed.

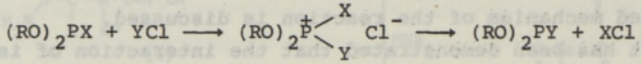
It has been demonstrated that the interaction of isocyanates with HPA salts yields phosphorus-containing products with P-C bonds. When isocyanates react with the water solution of HPA both products with P-C bonds and amides of HPA have been isolated.

The following polymers were phosphorylated: polyvinylchloride and polychloroprene rubber with some salts of HPA; polycaprolactame with HPA and formaldehyde; polyurethanes with some newly-synthesized phosphonous acids. The preliminary characterization of these polymers has been carried out.

1-44 NEW TYPES OF FUNCTIONALLY SUBSTITUTED METHYLPHOSPHONITES AND THEIR DERIVATIVES

A.A.Prishchenko, M.V.Livantsov, and I.F.Lutsenko
M.V.Lomonossov Moscow State University, Moscow 119899,USSR

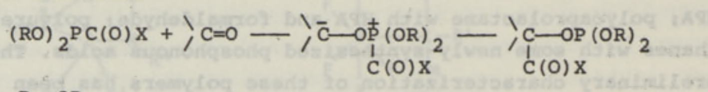
Functionally substituted methylphosphonites and their derivatives are convenient subjects for the investigation of the mutual effect of ternary coordinated phosphorus containing a functional group and heteroatoms in the α-position. They are the key compounds for the synthesis of new types of organophosphorus compounds. On the basis of hypophosphorous acid and its esters some convenient methods for synthesis of dialkoxy- and dialkylaminomethylphosphonites (I, II) as well as α-carbonylphosphonites (III) have been worked out, and a unique reactivity of these compounds in the course of various transformations is shown. A new route of Arbuzov reaction, taking place with unusual breakage of the P-C bond and retention of ternary coordinated phosphorus, is found for phosphonites (I-III).



$$(RO)_2PX + YCl \longrightarrow (RO)_2\overset{+}{P}\genfrac{}{}{0pt}{}{X}{Y}\ Cl^- \longrightarrow (RO)_2PY + XCl$$

$X = CH(OR)_2$ (I), CH_2NH_2 (II), $C(O)R$ (III);
$Y = C(O)R$, $C(O)OR$, CCl_3.

α-Carbonylphosphonites containd most labile P-C bond and are capable of smooth addition on carbonyl groups of various compounds. They can be employed as new synthons to form C-C bonds.



$$(RO)_2PC(O)X + \rangle C{=}O \longrightarrow \rangle\bar{C}{-}O\underset{C(O)X}{\overset{+}{P}}(OR)_2 \longrightarrow \rangle\underset{C(O)X}{C}{-}OP(OR)_2$$

X = R, OR

The lability of the P-C bond in functionally substituted methylphosphonites (I-III) can be widely used for various synthetic purposes.

1-45 SUBSTITUENT EFFECTS OF ORGANOPHOSPHORUS ESTERS IN STRUCTURE-REACTIVITY STUDIES

C.Y.Yuan, S.S.Li, H.Z.Feng, W.H.Hu, and X.G.Liao

Shanghai Institute of Organic Chemistry, Chinese Academy
of Sciences, 345 Lingling Lu, Shanghai 200032,
People's Republic of China

The structural effect of 4-substituted-2,6,7-trioxa-1-phosphabicyclo[2,2,2]octane-1-oxide (1), in which the influence of the steric effect of substituent on position 4 can be eliminated, was evaluated on the basis of the difference on chemical shift in ^{31}P NMR between methanol and deuterated acetone as represented by $\Delta\delta\ ^{31}P$. Thus obtained $\Delta\delta\ ^{31}P$ may be considered as a quantitative measure of the Lewis basicity of phosphoryl oxygen in compound 1. It was observed that the $\Delta\delta\ ^{31}P$ values of alkylsubstituted bicyclic phosphates are similar and linearily dependent on q_O calculated by MNDO method. In other words, the $\Delta\delta\ ^{31}P$ can really reflect the polar effect of the substituents, since $\Delta\delta\ ^{31}P$ is the function of σ_1 value. Similar results were obtained with diethyl p-substituted phenylphosphonated (2) and corresponding mono-hexyl esters (3). Our data revealed that both the inductive constant and Hammett parameter, widely used in the chemistry of carbon compounds, are applicable in correlation analyses of organophosphorus esters, probably for organophosphorus in general. Consequently, it seems unnecessary to define a new set of parameters for polaricity in phosphorus chemistry.

A significant difference of the substituent steric parameters of organophosphorus esters from carbon compounds was evidenced by poor results in regression analysis involving Taft Es and Charton's υ and log k of alkaline hydrolysis of alkylphosphonates. A new set of steric parameters was introduced based on the difference of energy between the tetra- and pentacoordinated species by molecular mechanics calculation using Allinger's 1977 force field and MM2, 1985.

1-46 CHEMISTRY OF P-HALOGENOYLIDES. SYNTHESIS AND PROPERTIES

O.I.KOLODIAZHNYI
Institute of Bioorganic Chemistry of the Ukrainian Academy of Sciences, Murmanskaya Str. 5, Kiev 252094, USSR

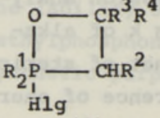
P-Halogenoylides are available reagents possessing high activity and various chemical properties. Several convenient methods for the synthesis of P-halogenoylides are discussed: reactions of tertiary phosphines with $CHlg_4$, dehydrohalogenation of halogenophosphonium salts and halogenotropic rearrangement of α-halogenoalkylphosphines.

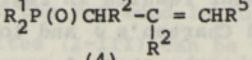
$$P(Hlg)_{3-n}{=}C \quad , \; Hlg = Br, Cl, F; \; n = 0, 1, 2$$

The reversible migration of the halogen atom from the phosphorus atom to the carbon atom proceeding with the change of phosphorus coordination number P^{IV} P^{III} is typical for the P-halogenoylides (phosphorus-carbon halogenotropic tautomerism). The detailed kinetic studied and estimation of activation parameters from temperature-dependence studies have revealed the monomolecular mechanism of the rearrangement

$$\underset{1}{R_2P(Hlg){=}CHR'} \rightleftharpoons \underset{2}{R_2PCH(R')Hlg}$$

P-Halogenoylides react readily with carbonyl compounds to give /2 + 2/-cycloaddition productes (3), which, depending on their structure, transform into different phosphorylated alkenes: allylphosphonates (4) (Hlg=F, R^4=CH_2R^5), vinylphosphonates (5) (Hlg=Cl, R^3, R^4=H, Alk, Ar) or heterocumulenes of phosphorus (6) (ketenes, thioketenes, ketenimines, Hlg=Cl or F, CR^3R^4= C=X = C=O, C=S, C=NR)


(3)



$R^1_2P(O)CHR^2{-}\underset{R^2}{C}{=}CHR^5$

(4)

$R^1_2P(O)CR^2{=}CR^3R^4$
(5)

$R^1_2P(O)CR^2{=}C{=}X$
(6)

Various protic reagents add quantitatively to the P = C double bond of P-halogenoylides to form various phosphonium salts, which are used in the synthesis.

1-47 NEW AND UNUSUAL REACTIONS IN THE CHEMISTRY OF UNSATURATED ORGANOPHOSPHORUS COMPOUNDS

B.I.IONIN and A.A.PETROV
Leningrad Lensoviet Institute of Technology,
Leningrad 198013, USSR

A series of new and unusual reactions has been disclosed in the study of unsaturated organophosphorus compounds. These are: (1) nucleophilic substitution of halogen atoms in haloethynes; (2) homolytic photo- and oxygeno-initiated addition of phosphorus trihalides to carbon-carbon double and triple bonded compounds; (3) electrophilic heterocyclization of allenic phosphonates to phospholenes; (4) acetylene-allene isomerization of propargyl hydrophosphoryl esters; (5) allene - conjugated diene (phosphonoprene) conversion of haloalkyl- and alkoxyalkylallene phosphonates; (6) formation and butadiene - cyclobutene conversion of strained 1,3-butadiene phosphonates; (7) formation, ring cleavage and isomerization of some oxyrane phosphonates; (8) competitive nucleophilic substitution, prototropic isomerization, H-Hlg elimination under the action of nucleophiles upon haloallylphosphonates; (9) Diels-Alder's cycloaddition of diene hydrocarbons to ethyne phosphonates.

Mechanisms of these reactions are discussed. The review includes application possibilities of listed reactions for the formation of C-P bond, molecular design of unsaturated organophosphorus compounds, and synthesis of organophosphorus C-functional derivatives.

1-48 INTERACTION OF PHOSPHORUS ANHYDRIDE WITH CH-, NH-, PH-, SH-ACIDS

P.M.ZAVLIN and D.A.EFREMOV
Leningrad Institute of Motion-Picture Engineers,
13 Pravda Str., Leningrad 191126, USSR

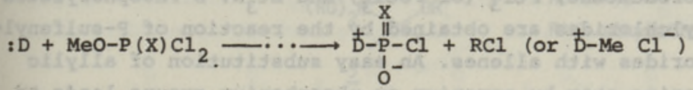
Several publications considering the reactions of phosphorus anhydride with organic substances have appeared. Most of them deal with either intramolecular or intermolecular dehydration. There are also descriptions of phosphorus anhydride interaction with alcohols, amines, ethers, orthoethers, and silanes. Anyway, no systematic investigation of P_4O_{10} synthetic potentialities in reactions with REH-acids (E = C, N, P, S) was delivered. Another present investigation aim was to synthesize different types of phosphorus organic substances, new ones included, in ecologically pure process.

We have shown that the interaction of P_4O_{10} with acid ethers which contain a mobile H-atom at the α-carbon atom results in the ethers dealcoholysis and the formation of cuntionalized ketens. Free cyanoketen, chloroketen, nitroketen, phenylketen were obtained using the described method. The chemical properties of the substances mentioned above were studied by reactions of dipolar cycloaddition, and by alcohols, amines, thiols, phosphites, and other reagents. Phosphorus anhydride reactivity was investigated with the bifunctional compounds containing competitive reaction centres, i.e. keto-enols or/and amide-imides, and also with azoles, thiols, phosphites, unsaturated substances. The main products of phosphorylation were corresponding phosphates and pyrophosphates.

1-49 PHOSPHORYLATIONS WITH ROP(X)CL$_2$: A NEW MECHANISTIC PATHWAY

H.TEICHMANN, D.WILBRANDT, and J.SCHULZ
Zentralinstitut für Organische Chemie der AdW der DDR,
Rudower Chaussee 5, Berlin-Adlershof, DDR-1199

Contrary to literature reports phosphorylations with MeOP(O)Cl$_2$ in excess pyridine to yield phosphoric diesters do not pass an N-methylpyridinium dichlorophosphate moiety as the active bifunctional phosphorylating species. Instead, a betaine (1) pathway is followed, 1 being formed here (X = O) and in the thiophosphate series (X = S), too, via phosphorylation of the pyridine donor and dealkylation by either Cl$^-$ or excess pyridine.

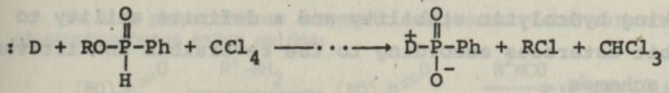


$$:D + MeO{-}P(X)Cl_2 \xrightarrow{\cdots} \overset{+}{D}{-}\underset{O^-}{\overset{\overset{X}{\|}}{P}}{-}Cl + RCl\ (\text{or } \overset{+}{D}{-}Me\ Cl^-)$$

D = C_5H_5N, 4-$Me_2NC_5H_4N$ 1

^{31}P-NMR spectra prove the presence of 1 in equimolar mixtures as well as in excess pyridine. The former release MeCl far below room temperature, to leave residues capable of converting hydroxy compounds into diesters as do betaines obtained by known routes. Isolation and full characterization (spectroscopically and by elemental analyses of 1 is best accomplished using 4-dimethylaminopyridine as a donor.

Donor-mediated phosphorylation is likewise applicable to monofunctional systems and may even be more simplified by in situ generation of the reagents, e.g.



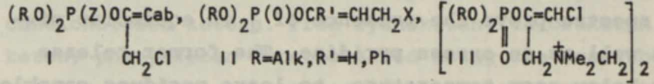
$$:D + RO{-}\underset{H}{\overset{\overset{O}{\|}}{P}}{-}Ph + CCl_4 \xrightarrow{\cdots} \overset{+}{D}{-}\underset{O^-}{\overset{\overset{O}{\|}}{P}}{-}Ph + RCl + CHCl_3$$

R = Me, SiMe$_3$

1-50 PHOSPHORYLATED ALLYLCHLORIDES: A SOURCE OF NEW STRUCTURES AND TRANSFORMATIONS

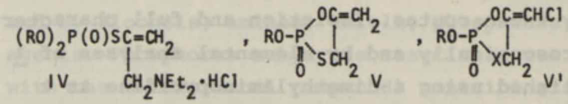
Yu.G.GOLOLOBOV, A.S.OGANESYAN, G.D.KOLOMNIKOVA, and S.A.KUZNETSOVA
Nesmeyanov Institute of Organoelement Compounds, Academy of Sciences of the USSR, Vavilov Str. 28, Moscow 117813, USSR

General methods have been elaborated for the synthesis of new types of compounds: O(or S)-phosphorylated vinylcholines (I-IV) and 5-membered heterocycles with P, O, S, N atoms in the cycle and the exo-CHX= (X=H, Cl) bond (V). The key substances, O-phosphorylated allylchlorides, are obtained either by the well known Perkov reaction or from 1,3-dichloroacetone, PCl_3 (or $POCl_3$) and Et_3N. S-Phosphorylated allylchlorides are obtained by the reaction of P-sulfenylchlorides with allenes. An easy substitution of allylic chlorine atom by ammonium or phosphonium groups leads to (I-IV).



$(RO)_2P(Z)OC(CH_2Cl)=Cab$, I; $(RO)_2P(O)OCR'=CHCH_2X$, II R=Alk, R'=H,Ph; $\left[(RO)_2P(=O)OC(=CHCl)CH_2\overset{+}{N}Me_2CH_2\right]_2$ III

$X=\overset{+}{N}Me_3Cl^-$, $\overset{+}{P}Alk_3Cl^-$, $NAlk_2\cdot HCl$; $Z=O, S, Mo(CO)_5, W(CO)_5, Cr(CO)_5$



$(RO)_2P(O)SC(CH_2NEt_2\cdot HCl)=CH_2$ IV, V, V' X=S,NPh

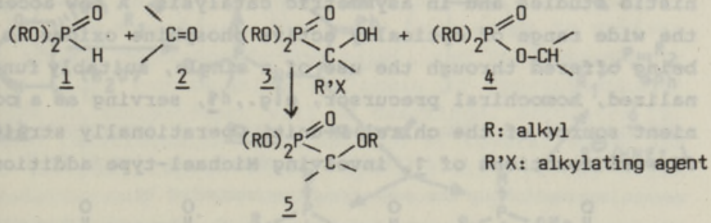
"Vinylthiocholines" (IV) can also be obtained from O,O-dialkyl-S-2,3-dibrompropylphosphate and Et_2NH. All vinylcholines obtained by this method are liable to dealkylation, which leads to a new type of betaines. Betaines display a striking hydrolytic stability and a definite ability to inhibit esterases according to the reversible and irreversible schemes.

1-51 SYNTHESIS OF ORGANOPHOSPHORUS COMPOUNDS USING PHASE TRANSFER CATALYSIS

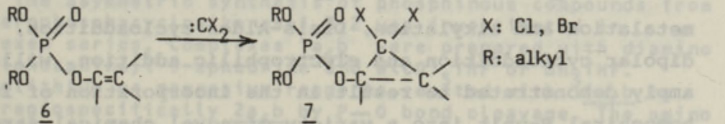
I. PETNEHÁZY, ZS. JÁSZAY, GY. KEGLEVICH, P. TÉTÉNYI, L. TŐKE
Department of Organic Chemical Technology, Technical University of Budapest
H-1521 Budapest, HUNGARY

In general it is not easy to perform any reaction on organophosphorus compounds of the ester type by classical methods without hydrolysis occuring. In this work we present some reactions using PTC conditions as a special method to prepare new derivatives.

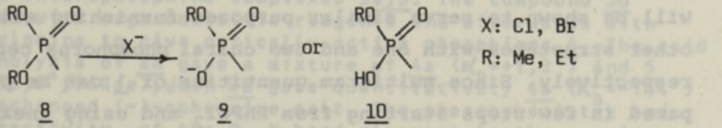
The synthesis and O-alkylation of α-hydroxyphosphonates were studied with both solid-liquid and liquid-liquid PTC. In this case a C→O 1,2-phosphoryl migration also can occur:



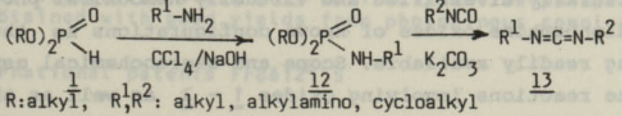
Some phosphoric acid esters of type 7 containing a cyclopropyl ring were synthetized by the addition of a dihalogeno-carbene to the vinyl phosphate in a two phase system:



Monodealkylated phosphorus esters can be produced in the mono salt or acid form from a number of organophosphorus compounds of the ester type by the action of solubilized halogenide anions:



We also prepared some unsymmetrically substituted carbodiimides via organophosphorus ester amides:



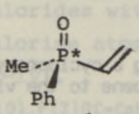
R:alkyl, R^1,R^2: alkyl, alkylamino, cycloalkyl

1-52 SYNTHESIS OF HOMOCHIRAL PHOSPHORUS COMPOUNDS: THE "CHIRON" APPROACH

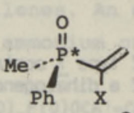
K.M.PIETRUSIEWICZ

The Polish Academy of Sciences, Centre of Molecular
and Macromolecular Studies, Sienkiewicza 112,
90-362 Łódź, Poland

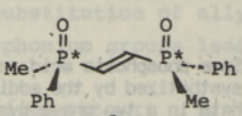
Optically active organophosphorus compounds of high optical purity are of great importance for their utility in mechanistic studies and in asymmetric catalysis. A new access to the wide range of optically active phosphine oxides is now being offered through the use of a single, suitably functionalized, homochiral precursor, e.g., 1, serving as a convenient source of the chiral P-unit. Operationally straightforward reactions of 1, involving Michael-type addition, metalation and alkylation, Diels-Alder cycloaddition, 1,3-dipolar cycloaddition and electrophilic addition, will be amply demonstrated to result in the incorporation of its homochiral P-unit into a variety of novel chemical structures. Other functionalized homochiral phosphine and diphosphine oxides, such as 2 or 3 (both derived from 1), will be shown to serve similar purposes furnishing still other structures with one and two chiral phosphorus centres, respectively. Since multigram quantities of 1 can be prepared in few steps starting from $PhPCl_2$ and using inexpensive natural menthol as the chiral auxiliary, a wealth of structurally diversified and virtually homochiral phosphine and diphosphine oxides of known configurations is thus becoming readily available. Scope and stereochemical aspects of the reactions involving oxides 1 - 3 as well as the syntheses of these oxides will be discussed in detail.



1



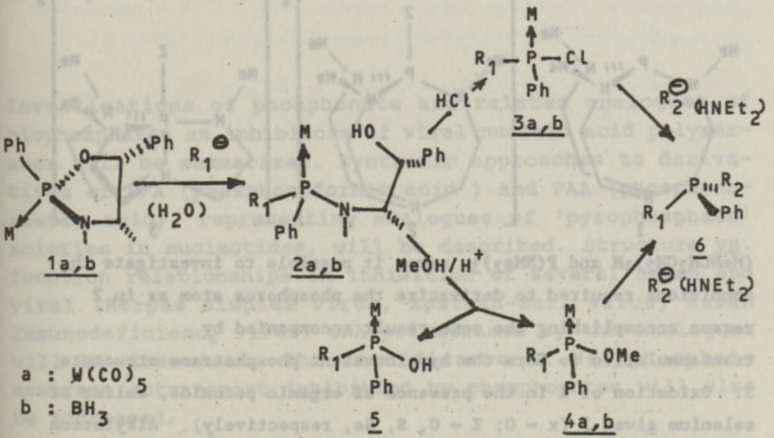
2



3

1-53 NEW ASYMMETRIC SYNTHESIS OF TERTIARY PHOSHPINES VIA PHOSPHINOUS COMPLEXES

S.JUGE*, M.STEPHAN, S.ACHI and J.P.GENET
Laboratoire de synthèse organique chimio et stéréosélective
E.N.S.C.P 11 rue P. et M.Curie 75231 Paris (France)



a : $W(CO)_5$
b : BH_3

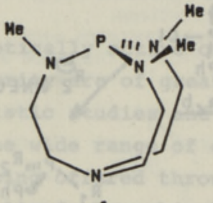
The asymmetric synthesis of phosphinous compounds from diheterophosphacycloalkanes-1,3,2 was investigated in complexed series. Complexes 1a,b were prepared with diamino phenylphosphine,(-)-ephedrine and $W(CO)_5$THF or BH_3THF. Organolithium or magnesium reagents reacted with 1a,b to give regiospecifically 2a,b by P—O bond cleavage. The amino phosphine complexes 2a,b were stereochemically stable and were used in synthetic applications (1). Thus,HCl gas reacted with 2a,b in CH_2Cl_2 or toluene to give optically active chlorophosphine complexes 3a,b. The compound 3b reacted with organometallic reagents and afterwards with diethylamine to give optically active phosphines 6. The acid methanolysis of 2a gave a mixture of 4a (α_D=+1,2°) and 5 (α_D=+16,9°;54%ee),when 2b gave quantitatively 4b (α_D=-104°) and unchanged (-)-ephedrine salt. The stereochemistry and the reactivity of the P—N bond cleavage in the amino phosphine complexed series, depend of the acid and the complexe concentrations.Highly optically active phosphines were obtained with good yields from phosphinous complexes 4b.

1)International patents Fr8612115

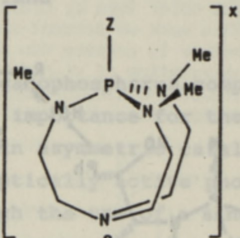
1-54 AZAPHOSPHATRANES

H. SCHMIDT, S.K. XI, C. LENSINK and J. G. VERKADE
Gilman Hall, Department of Chemistry, Iowa State University,
Ames, Iowa, 50010, USA

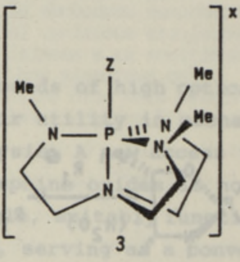
The new stable pro-azaphosphatrane 1, synthesized from $(MeNCH_2CH_2)_3N$ and $P(NMe_2)_3$, makes it possible to investigate the conditions required to derivatize the phosphorus atom as in 2 versus accomplishing the same result accompanied by transannulation to form the hypercovalent phosphatrane structure 3. Oxidation of 1 in the presence of organic peroxide, sulfur or selenium gives 3 ($x = 0$; $Z = O$, S, Se, respectively). Alkylation with RX similarly gives 3 ($x = +1$; $Z = CH_2X$, X, respectively). Proton sources readily give 3 where $x = +1$ and $Z = H$.



1



2



3

1-55 DESIGN AND SYNTHESIS OF ORGANOPHOSPHORUS COMPOUNDS WITH ANTIVIRAL AND OTHER BIOACTIVITIES

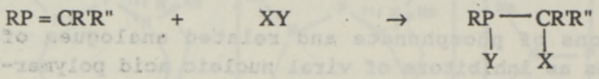
C.E.MCKENNA
Department of Chemistry, University of Southern California,
Los Angeles, CA 90089-0744, U.S.A.

Investigations of phosphonate and related analogues of biophosphates as inhibitors of viral nucleic acid polymerases will be summarized. Synthetic approaches to derivatives of PFA (phosphonoformic acid) and PAA (phosphonoacetic acid), representing analogues of 'pyrophosphate' moieties in nucleotides, will be described. Structure vs. function relationships in inhibition of several human and viral (Herpes simplex virus, Epstein-Barr virus, Human Immunodeficiency virus) DNA polymerases by the analogues will be discussed. The significance of Na^+/phosphate membrane cotransport inhibition by phosphonates will also be addressed.

2-1 THE ELECTRONIC NATURE OF THE P=C BOND

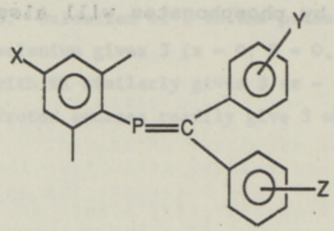
T. VAN DER DOES and F. BICKELHAUPT
Scheikundig Laboratorium, Vrije Universiteit, De Boelelaan 1083,
1081 HV Amsterdam, The Netherlands

In agreement with predictions based on electronegativity (X), the P=C double bond of phosphaalkenes behaves on addition reactions with XY (X = electrophile, Y = nucleophile) as if P (X = 2.1) is the positive end of the dipole (C : X = 2.5).

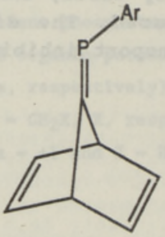


$$RP = CR'R'' \quad + \quad XY \quad \rightarrow \quad \underset{Y}{RP} - \underset{X}{CR'R''}$$

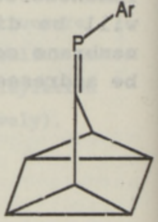
In contrast, extensive studies of ^{31}P NMR chemical shifts show that the P=C unit is electron-withdrawing, especially towards substituents at carbon. The relative importance of inductive and resonance effects in triarylphosphines I is discussed; substituents were varied on the *para*-position of the P-aryl group and in the *ortho*- and *para*-positions of the C-aryl groups.



I



II



III

Another type of strong conjugative interaction of the P=C bond was observed in a comparison between II, III and other alicyclic phosphaalkenes. Even in strongly conjugated phosphaalkenes, *cis-trans*-isomerization was not observed; this implies considerable configurational stability both towards inversion at phosphorus and towards rotation around the P=C bond.

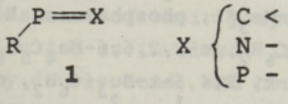
2-2 THE ELECTRON DEMAND OF LOW COORDINATED PHOSPHORUS COMPOUNDS THEORETICAL AND EXPERIMENTAL EVALUATION

J. Niemann, R. Thiele, W. Haug, T. Busch and W.W. Schoeller

Fakultät für Chemie der Universität, 4800 Bielefeld, FRG

In this contribution the following aspects will be discussed:

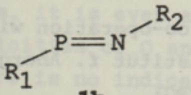
(1) The electron demand of the inorganic double bonded systems, **1**, with respect to cycloaddition reactions.



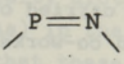
1

An experimental approach is performed via photoelectron spectroscopic measurements and low temperature cyclic voltammetric studies. For the evaluation of substituent effects a variety of model compounds were investigated, and compared with (a) corresponding results on a vareity of enamines (electron rich olefines) and also tetracyanoethylene (electron poor olefine) and (b) the expectations of theory.

(2) Theoretical evaluation of conformational aspects of iminophosphanes, diphosphenes and related isovalence electronic compounds: (a) cis-trans isomerization at nitrogen on substituted **1b**, (b) substituent effects on geometries of **1b** and **1c**.



1b



1c

2-3 PHOSPHORUS COMPOUNDS IN LOWER COORDINATION STATES: ELECTRICAL PROPERTIES AND FEATURES OF STRUCTURE

E.A.ISHMAEVA, I.I.PATSANOVSKY, V.D.ROMANENKO*, and
L.N.MARKOVSKY*
Kazan State University, Lenin Str. 18, Kazan 420008,
USSR
*Academy of Sciences, Murmanskaya Str. 5, Kiev 252094,
USSR

P^{I*} and P^{II}-derivatives were investigated by means of electrical and electro-optical methods. Experimental data on polarity and polarizability of phosphaalkynes $P\equiv CR$: R=t-Bu, Ad, phosphaalkenes $R^1P=CR^2_2$: R^1=H, Ph, Me_3Si, $R_2=Alk_2N$; R^1=t-Bu, Ph, Hlg, $(Me_3Si)_2N$, $R^2=Me_3Si$, phosphazenes $R^1P=NR^2$; $R^1=(Me_3Si)_2N$, 2,4,6-t-$Bu_3C_6H_2$, c-2,2,6,6-$Me_4C_5H_6N$, $R^2=Me_3Si$, t-Bu, PBu_2-t, $P(S)Bu_2$-t, 2,4,6-t-Bu_3-C_6H_2, diphosphenes, arsa- and stibaphosphenes $R^1P=ER^2$: E=P, As, Sb, R^1=2,4,6-t-$Bu_3C_6H_2$, $R^2=N[SiMe_2(t\text{-}Bu)]_2$ and some other P^{II}--derivatives were obtained.

Polarities of $P\equiv C$, $P=C$, $P\overset{..}{-}C$ (in λ^3-phosphabenzenes), $P=E$ (E=N, P, As, Sb) bonds were determined and the order of polarity change was established: $m(C-P) > m(C\overset{..}{-}P) > m(C=P) > m(C\equiv P)$; $m(P=N) > m(P=As) > m(P=Sb)$. The conversion of polarity of $C\equiv P$, $P=As$ and $P=Sb$ bonds was observed. Triple bond in phosphaalkynes and double bond P=N in phosphazenes are characterized by considerable anisotropy of polarizability. Phosphaalkenes $R^1P=C(NAlk_2)_2$ and diphosphadienes $(Me_3Si)_2C=P-P=C(NAlk_2)_2$ are highly conjugated systems.

---

*The research has been carried out in co-operation with professor G.Becker and co-workers (Institut f. Anorganische Chemie, Universitat Stuttgart, FRG).

2-4 ARE PHOSPHORINS AND PHOSPHOLES AROMATIC?

G. P. SCHIEMENZ

Institut für Organische Chemie der Universität Kiel
Olshausenstrasse 40-60, D-2300 Kiel, Fed.Rep.Germany

In addition to (4n+2) π-electrons, planarity is a condition for aromaticity. Hence, pyrrole can be aromatic, but a phophole with tricoordinate phosphorus has been shown to be neither planar nor aromatic in the ground state (1). Since, many dicoordinate P and As compounds have been prepared, and these new systems require an independent assessment of their properties. A (p-p)π bond in which P (or As) is involved, is largely different from an ordinary double bond, and hence it cannot be taken for granted that incorporation of such a substructure into a cyclic system with a total of 6 π-electrons will create an aromatic system. Recently, 4-hydroxy-arsenins, 4-hydroxy-1,3λ^3-aza-phospholes and related condensed systems containing a pyridine ring have been prepared (2). Their As-, P-, C-, N-protonated tautomers have not been observed. This has been attributed to the incapability of these tautomers of having aromatic character and hence, implicitly, that the "heterocyolic phenols" are to some extent aromatic. The preponderance of the hydroxy forms can, however be rationalized without recourse to the concept of aromaticity. In some cases, e.g. the hydroxy vs. the phosphorus- or arsenic-protonated species, it is even a necessity dictated by the relative basicities of O and P (As) in the common anion. Hence, there is no indication that these systems are aromatic.

(1) W. Egan, R. Tang, G. Zon, K. Mislow, J.Am.Chem.Soc. 92, 1442 (1970).

(2) G. Märkl, S. Pflaum, Tetrahedron Letters 29, 3387 (1988).

2-5 PHOSPHA-CARBA-OLIGO-ENES, SYNTHESIS AND REACTIVITY

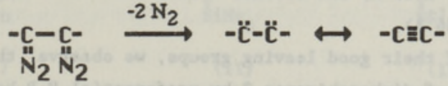
R.APPEL
Anorganisch-Chemisches Institut der Universität Bonn,
Gerhard-Domagk-Str. 1, 5300 Bonn, FRG

Phospha-carba-oligo-enes will be dealt with in this paper. This class of compounds can be deducted from oligo-enes by means of substitution of individual CH-moieties by sp^2-hybridized phosphorus atoms, creating (PC)-double bonds in conjugation with other (PC)- and (or) (CC)-sequences. In particular compounds with the skeleton of phospha-butadienes, phospha-pentadienes and phospha-hexadienes will be reported. Besides the Monophosphabutadienes, 3 differently positioned Diphosphabutadienes could be obtained. Attemps for the synthesis of a 1,2,3-Triphosphabutadienes gave the first Triphosphacyclobutane. Compounds possessing a phosphahexadiene structure are fascinating because of the uncommon affinity to pure carbon chemistry. This can be seen in a number of theoretically interesting cycloaddition and valence isomerisation reactions, pointing to a stable (2p3p)-π-bond between phosphorus and carbon. A combination of NMR-spectroscopic, X-ray and kinetic results prove the Woodward-Hoffmann-rules for pericyclic reactions to apply for this class of compounds.

2-6 SYNTHESIS AND REACTIVITY OF THE FIRST STABLE λ^5-PHOSPHAACETYLENE ($R_2P\equiv CR'$)

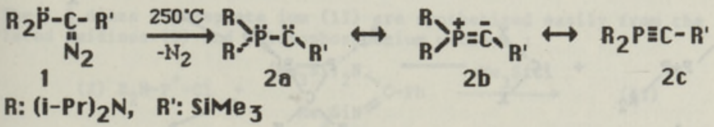
Guy BERTRAND, Alain IGAU, Antoine BACEIREDO and Hansjorg GRUTZMACHER
Laboratoire de Chimie de Coordination du CNRS, 205, route de Narbonne, 31077 Toulouse Cédex, France.

A hundred years ago, Curtius showed that α,α'-bis-diazoderivatives spontaneously lost two molecules of nitrogen giving the corresponding alkynes. Since diazo compounds are precursors of carbenes, this result clearly states that an α,α'-bis-carbene is an alkyne.



$$-\underset{N_2}{\overset{}{C}}-\underset{N_2}{C}- \xrightarrow{-2\,N_2} -\ddot{C}-\ddot{C}- \longleftrightarrow -C\equiv C-$$

Like carbenes, a tricoordinated-trivalent phosphorus atom possesses a lone pair of electron and an accessible vacant orbital and thus it was reasonable to think that an α-phosphinocarbene ($>\ddot{P}\text{-}\ddot{C}\text{-}$) would be a λ^5-phosphaacetylene ($>P\equiv C\text{-}$). We will report the synthesis of the first stable compound of this type (**2**), obtained by flash thermolysis of the corresponding α-diazophosphine **1**.

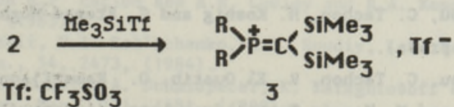


$$\underset{\mathbf{1}}{R_2\ddot{P}-\underset{N_2}{C}-R'} \xrightarrow[-N_2]{250^\circ C} \underset{\mathbf{2a}}{R_2\ddot{P}-\ddot{C}-R'} \longleftrightarrow \underset{\mathbf{2b}}{R_2\overset{+}{P}=\overset{-}{\ddot{C}}-R'} \longleftrightarrow \underset{\mathbf{2c}}{R_2P\equiv C-R'}$$

R: $(i\text{-}Pr)_2N$, R': $SiMe_3$

In contrast with carbon-carbon triply-bonded compounds, we will show that **2** can react as a λ^5-phosphaacetylene **2c** by [2+2] and [2+3] cycloadditions, but also as a carbene by CH insertion, [1+2] cycloadditions and "carbene-carbene" coupling reactions.

2 is also a good precursor for new unusually hybridized phosphorus species such as methylenephosphonium **3** which appears to be the most severely twisted valence isoelectronic olefin yet reported.



$$\mathbf{2} \xrightarrow{Me_3SiTf} \underset{\mathbf{3}}{R_2\overset{+}{P}=C(SiMe_3)_2}\ ,\ Tf^-$$

Tf: CF_3SO_3

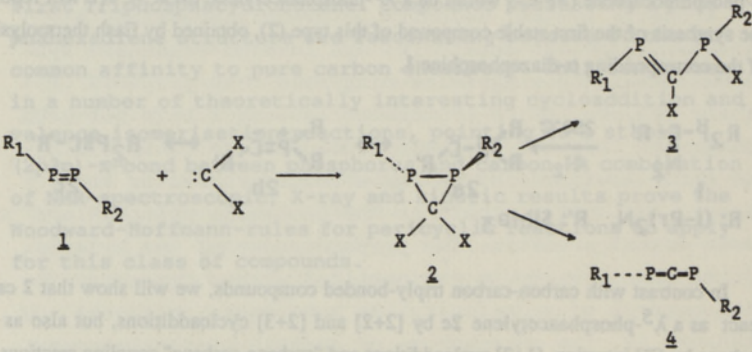
THE CARBENIC INSERTION INTO THE P-P BOND

by *M. KOENIG* [a], *M. GOUYGOU* [a], *C. TACHON* [a], *R. EL OUATIB* [a]
and G. ETEMAD-MOGHADAM [b]
[a]) UA 454 [b]) Laboratoire de Chimie de Coordination
Université Paul Sabatier 31062 Toulouse Cedex FRANCE

The reaction of different halogenocarbenes on symmetrical or unsymmetrical diphosphenes 1, leads to the stable functionalized diphosphiranes 2.

The P-P bond undergoes a lengthening by heterocyclopropanation reaction (d_{PP} = 2.25 Å) and becomes weaker than the intracyclic P-C bond (d_{PC} = 1.86 Å).

Because of their good leaving groups, we observe the ring opening reactions of diphosphiranes 2 by preferential P-P bond cleavage. We obtain the corresponding 1,3-diphosphapropenes 3 (1) or the 1,3-diphosphaallene 4 (2).



Different modes of ring opening reactions are observed (cationic, anionic, photochemical and thermal processes).

The structure of the ring opening products and the various mechanisms are discussed.

1 - M. Gouygou, C. Tachon, M. Koenig and G. Etemad-Moghadam, New. J. Chem (in press).

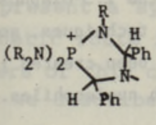
2 - M. Gouygou, C. Tachon, R. El Ouatib, O. Ramarijaona, G. Etemad-Moghadam and M. Koenig, Tetrahedron Lett. (in press).

2-8 PHOSPHORUS CATIONS IN HETEROCYCLIC CHEMISTRY

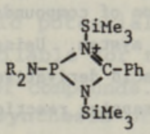
by C. Roques, T.Kim, M.R.Mazières, J.P. Majoral, R.Wolf
and M. SANCHEZ

Laboratoire Synthèse, Structure et Réactivité de Molécules Phosphorées
UA CNRS 454, Université Paul Sabatier 31062 Toulouse Cedex FRANCE

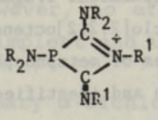
Our interest in the study of phosphorus dicoordinated cations (1)- the phosphenium $(R_2N)_2P^+$ ions (2) - bring us to report the new convenient access at three types of cationic phosphorus heterocycles :



(I)

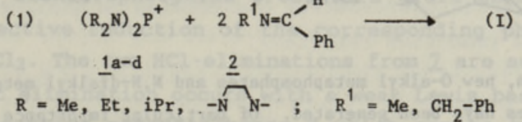


(II)



(III)

The 1,4,2 diazaphospholanium cations (I) result from the reaction of phosphenium cations 1 with aldimines ;



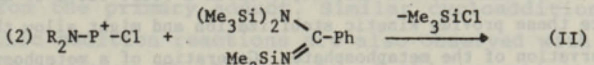
$$(1)\quad (R_2N)_2P^+ + 2\,R^1N{=}C\begin{smallmatrix}H\\Ph\end{smallmatrix} \longrightarrow (I)$$

1a-d

R = Me, Et, iPr, -N⌒N- ; R^1 = Me, CH_2-Ph

2

The 1,3 diaza 2-phosphete ium (II) are synthetized easily from the silylated amidines (3) and chlorophosphenium cations :



$$(2)\quad R_2N\text{-}P^+\text{-}Cl + (Me_3Si)_2N\text{-}C(Ph){=}NSiMe_3 \xrightarrow{-Me_3SiCl} (II)$$

The X-ray crystal structure of one compound (II) (R=iPr) will be reported and discussed.

The four membered heterocycles (III) are prepared by addition of nucleophilic isocyanides R^1NC on $(R_2N)_2P^+$. The course of the reaction depends on the nature of R and R^1 groups : when R=Me or Et and R^1 =tBu the cyclic cation (III) are isolated. The structure of the four membered rings (I, II, III) will be discussed from spectroscopic and X-ray data.

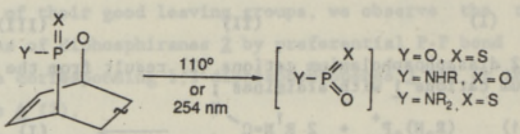
1 - M.R. Mazières, C. Roques, M. Sanchez, J.P. Majoral, R. Wolf, Tetrahedron 43, 2109, (1987).
2 - For a review on R_2P^+ cation see A.H. Cowley and R.A. Kemp, Chem. Rev. 65, 367, (1985).
3 - V.V. Negrebetskii, V.I. Kal'tchenko, R.B. Roudiy, L.N. Markowski, Zh. Obsh. Khim., 54, 2473, (1984).
- H.W. Roesky, U. Scholz, A. Schmidpeter, K. Karaghiosoff et W.S. Sheldrick, Chem. Ber., 121, 1681, (1988).

2-9 STUDIES WITH METAPHOSPHORIC ACID DERIVATIVES

L. D. QUIN, N. D. SADANANI, C. BOURDIEU, X.-P. WU AND G. S. QUIN

Department of Chemistry, University of Massachusetts, Amherst,
Massachusetts 01003, U.S.A.

Derivatives of metaphosphoric acid can be generated by either thermal or photochemical fragmentation of compounds with the 2,3-oxaphosphabicyclo[2.2.2]octene ring system. Using these techniques, several new types of metaphosphoric acid derivatives have been created in solution and identified by trapping reactions with nucleophiles.



In addition, new O-alkyl metaphosphates and N,N-dialkyl metaphosphoramidates have been generated. Of particular importance are 2,3-oxaphosphabicyclo[2.2.2]octene esters or amides with bulky groups on O (such as adamantyl or neopentyl) or on N (*tert*-butyl or mesityl) since these provide kinetic stabilization and might allow the direct observation of the metaphosphate. Generation of a metaphosphate in the gas phase by heating the solid precursors *in vacuo* has also been accomplished, and the product characterized by matrix IR. The metaphosphates are highly reactive phosphorylating agents; various synthetic applications of this reactivity are being explored.

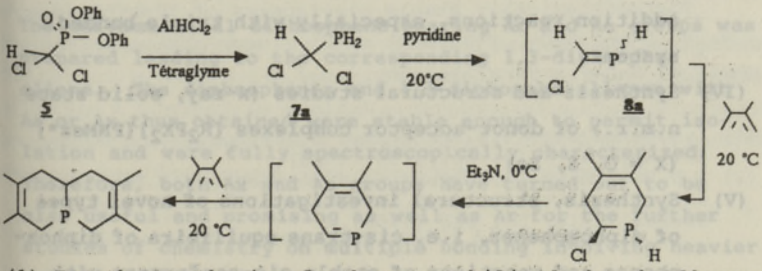
2-10 SYNTHESIS OF PRIMARY α-CHLOROPHOSPHINES, PRECURSORS OF UNHINDERED C-CHLOROPHOSPHAALKENES AND SYNTHETIC EQUIVALENTS OF λ^3-PHOSPHAALKYNES

J.M.DENIS, J.C.GUILLEMIN and M. LE GUENNEC
Groupe de Physicochimie Structurale, Université de Rennes I, Campus de Beaulie, 35042 Rennes Cedex

Recent research has demonstrated that λ^3-phosphaalkynes bearing bulky substituents are stable at room temperature and present a synthetic potential. However, no efficient synthetic route is available for the simplest and unstable members of this class of compounds.

We describe the synthesis of primary α-dichlorophosphines 7 and show that these species are precursors of unstabilized C-chlorophosphaalkenes 8 (1) and synthetic equivalents of λ^3-phosphaalkynes 9

The dichlorophosphine precursors 7 are obtained by a chemoselective reduction of the corresponding phosphonate with $AlHCl_2$. The two HCl-eliminations from 7 are selective : the first elimination occurs with a weak Lewis base leading to the reactive phosphaalkenes 8 which can be trapped in [4+2] or [3+2] cycloadditions. The second HCl-elimination occurs from the primary adduct. Similar cycloaddition or nucleophilic addition reactions are also observed with the C-methyl derivative 7b. An example of this reactivity is given on the following scheme.



---

(1) For the synthesis of other unstabilized phosphaalkenes see a)B. Pellerin, J.M. Denis, J. Perrocheau, R. Carrié, Tetrahedron Lett., 1986, 27, 5723.b) B. Pellerin, P. Guénot, J.M. Denis, Tetrahedron Lett., 1987, 28, 5811.c) S. Lacombe, D. Gombeau, J.L. Cabioch, B. Pellerin, J.M. Denis, G. Pfister-Guillouzo, J. Am. Chem. Soc., 1988, 110, 6964.

2-11 P(III)-DOUBLE BONDED SYSTEMS - RECENT DEVELOPMENTS

E. Niecke, D. Barion, M. Lysek, M. Nieger and F. Reichert

Institut für Anorganische Chemie, Universität Bonn,
Gerhard-Domagk-Str. 1, 5300 Bonn 1, FRG

Synthesis, structural elucidation, spectroscopic data and studies of reactive behaviour of novel iminophosphanes and diphosphenes, including electronegative as well as electropositive substituents at the phosphorus atom, are reported.

In detail the following aspects will be considered:

(I) Synthesis of P-functionalized iminophosphanes in a cis and trans conformation and studies on their reactivities (addition reaction).

(II) Utility of halogene-iminophosphanes as a building block for a variety of new derivatives with electropositive (electronegative) substituents, π-configurated multiple bonds as well for the formation of the extreme case of PN triple bonded systems, i.e., the [P≡NR]-cation.

(III) The carbene analogy of iminophosphanes in (n+1) cycloaddition reactions, especially with triple bonded systems.

(IV) Synthesis and structural studies (x-ray, solid state n.m.r.) of donor-acceptor complexes $[R_2PX_2][PNMes^*]$ (X = O, S, Se).

(V) Synthesis, structural investigations of novel types of diphosphenes, i.e. cis-trans equilibira of diphosphenes and reactions of stable cis-conformers with multiple bonded systems as well as transition metal complexes.

2-12 SOME NEW PROTECTIVE GROUPS FOR STABILIZING LOW COORDINATED PHOSPHORUS COMPOUNDS

M. YOSHIFUJI, S. SASAKI, D. SHIOMI, T. NIITSU, and
N. INAMOTO

Department of Chemistry, Faculty of Sicence,
The University of Tokyo, Hongo, Tokyo 113, JAPAN

2,4,6-Tri-t-butylphenyl (Ar) group is one of the most useful protective groups for stabilizing low coordinated phosphorus compounds of current interest. We now wish to report some other sterically bulky groups than Ar which might serve as alternative protective groups for kinetically stabilized multiple bonded compounds involving heavier main group elements. 2,6-Di-t-butylphenyl- (Ax; x stands for xylyl) and 2,4,6-tri-t-pentylphenyl- (Aa; a stands for amyl or pentyl) phosphonous dichlorides were synthesized from the corresponding bromobenzenes via lithiation followed by the reaction with phosphorus trichloride. The dichlorides were then converted to the corresponding diphosphenes and 1,3-diphospha-allenes by the method as employed for the Ar derivatives as follows.

$$\mathrm{ArBr} \longrightarrow \mathrm{ArPCl_2} \longrightarrow \mathrm{ArP{=}PAr} \longrightarrow \mathrm{ArP{=}C{=}PAr}$$

The unsymmetrical diphosphene bearing Ar and Aa groups was prepared leading to the corresponding 1,3-diphospha-allene. The diphosphenes and 1,3-diphospha-allenes with Aa or Ax thus obtained were stable enough to permit isolation and were fully spectroscopically characterized. Therefore, both Ax and Aa groups have turned out to be also useful and promising as well as Ar for the further studies of chemistry on multiple bonding involving heavier main group elements.

2-13 P-SUBSTITUTED λ^3-IMINOPHOSPHINES AND DIPHOSPHENES

L.N.MARKOVSKY, V.D.ROMANENKO, A.V.RUBAN, A.B.DRAPAILO,
G.V.REITEL, and T.V.SARINA
Institute of Organic Chemistry of the Ukrainian Academy of Sciences, Murmanskaya Str. 5, Kiev 252660, USSR

P-Substituted λ^3-iminophosphines, XP = NTtb (Ttb = 2,4,6-tri-tert-butylphenyl; X = Cl, R_2N, RO) were obtained by elimination of Me_3SiCl from XP(Cl)-N($SiMe_3$)Ttb. The following aspects of their chemistry will be considered in detail: a) the reactivity of ArO-P=NTtb towards various nucleophilic reagents; b) application of Cl-P=NTtb for obtaining new types of substituted iminophosphines; c) synthesis and properties of the 2-phospha-1,3-butadienes, including P=N Π-bond.

The reactions of Cl-P=NTtb with F^-, Br^-, I^-, RO^-, RS^-, R_2P^- anions lead to the corresponding λ^3-iminophosphines. The second preparative route for obtaining XP=NTtb consists of treating ClP=NTtb with O-, N- or S-silylated nucleophiles. In this way compounds like R_2C=P-P=NTtb were obtained.

The interaction of ArO-P=NTtb with TtbP(Li)H gives the iminophosphine TtbP(H)-P=NTtb, which undergoes rearrangement to diphosphene Ttb-P=P-N(H)Ttb. The latter can also be synthesized by the reaction of Cl-P=NTtb with TtbN(H)Li.

Thermodynamically stable cis-isomers of XP=NTtb (X = = Me_2N, 2-MeC_6H_4O-, T-BuS, Cl et al.) were characterized by means of X-ray crystallography.

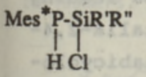
(1) L.N.Markovsky, V.D.Romanenko, A.V.Ruban, A.N.Chernega, Zh. Obshch. Khim. 58, 2758 (1988).
(2) V.D.Romanenko, A.V.Ruban, A.N.Chernega, M.I.Povolotskii, M.Yu.Antipin, Yu.T.Struchkov, L.N.Markovsky, Zh. Obshch. Khim. 58, 948 (1988).

2-14 RECENT DEVELOPMENTS IN PHOSPHASILENE CHEMISTRY

Y. VAN DEN WINKEL, H. M. M. BASTIAANS and F. BICKELHAUPT
Scheikundig Laboratorium, Vrije Universiteit, De Boelelaan 1083,
1081 HV Amsterdam, The Netherlands

Our original procedure (1) for the preparation of phosphasilenes **5** followed the sequence outlined below.

$$\underset{\mathbf{1}}{Mes^*PH_2} \xrightarrow[THF/-60^{o}C]{n\text{-BuLi}} \underset{\mathbf{2}}{Mes^*PHLi} \xrightarrow[-60^{o}C]{R'R''SiCl_2\ (3)}$$



4

$$\underset{\mathbf{4}}{Mes^*P(H)\text{-}SiR'R''(Cl)} \xrightarrow[-60^{o}C]{n\text{-BuLi}} \underset{\mathbf{5}}{Mes^*P{=}SiR'R''}$$

(Mes* = 2,4,6-tri-*tert*-butyl-phenyl)

However, depending on the nature of R' and R", several problems were encountered. For example, the combination of Is_2SiCl_2 (Is = 2,4,6-triisopropylphenyl) and the lithium phosphide was impossible, due to overcrowding. Another difficulty was encountered in the reaction of **2** with Es_2SiCl_2 (Es = 2,4,6-triethylphenyl) and *t*-$BuIsSiCl_2$. Here, **4** could not be detected; instead, **5** together with **1** was formed. After realizing that one equivalent of **2** was consumed as a base, we could increase the yield of **5** by employing the stoichiometry **2** : **3** = 2 : 1. However, this approach has the obvious drawback of yielding equimolar amounts of **1** and **5**, so that pure and crystalline **5** could not be obtained.

Recent investigation have been aimed at the synthesis of known and novel phosphasilenes **5** in pure form by variation of the bases used for coupling of **1** and **2** and for elimination of HCl from **4**. Substituents are varied both on phosphorus and on silicon. Structural and spectroscopic data will be reported, as well as an extension of the reactivity of **5** towards metal complexes, dienes, oxygen, sulfur, organolithium and protic reagents.

(1) C. N. Smit and F. Bickelhaupt, Organometallics 6, 1156 (1987).

2-15 CYCLOOLIGOMERISATION OF λ^3-PHOSPHAALKINES IN THE COORDINATIONSPHERE OF A TRANSITIONMETAL

Paul Binger*, B.Biedenbach, R.Milczarek, R.Schneider
Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, D-4330 Mülheim an der Ruhr

Cyclodimerisation and cyclotrimerisation of λ^3-phosphaalkynes, e.g. tert.-butylphosphaacetylene (1a), has been achieved in the coordinationsphere of a transition metal. The degree of cyclooligomerisation and the structure of the reaction products strongly depends on the transition metal used.

So far cyclodimerisation of 1a has been achieved leading to cyclobutadiene metal complexes 2 - 4[1,2] metalla-2,4-diphosphacyclopentadiene (5) or to 1,3-diphosphabicyclo[1.1.0]butandiylzirkonium[3] compounds (6) [scheme 1].

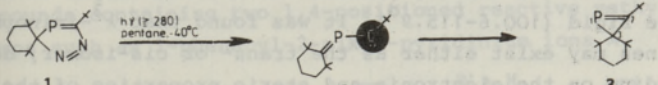
On the other hand cyclotrimerisation occours when vanadium[4] or molybdenum[5] is used as a metal centre [scheme 2]. Structure proof of all new compounds, cited in scheme 1 and 2 will be given and the reaction paths leading to these new compounds will be discussed.

1) P.Binger, R.Milczarek, R.Mynott, M.Regitz, W.Rösch, Angew. Chem. Int. Ed. Engl. 25(1986) 644. - P.Binger, R.Milczarek, R.Mynott, E.Raube, C.Krüger, M.Regitz, Chem. Ber. 121(1988) in press.
2) P.B.Hitchcock, M.J.Maah, J.F.Nixon. J. Chem. Soc. Chem. Commun. 1986, 737.
3) P.Binger, B.Biedenbach, C.Krüger, M.Regitz, Angew. Chem. Int. Ed. Engl. 26(1987) 764.
4) R.Milczarek, W.Rüsseler, P.Binger, K.Jonas, K.Angermund, C.Krüger, M.Regitz, Angew. Chem. Int. Ed. Engl. 26 (1987) 907.
5) A.R.Barrow, A.H.Cowley, Angew. Chem. Int. Ed. Engl. 26 (1987) 906.

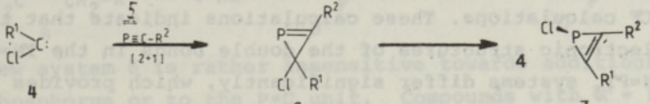
2-16 TRANSFORMATION OF PHOSPHAALKYNES INTO 2H-PHOSPHIRENES

M. REGITZ, H. HEYDT, O. WAGNER, M. EHLE AND T. WETTLING
Department of Chemistry, University of Kaiserslautern,
Erwin-Schrödinger-Straße, D-6750 Kaiserslautern,
Federal Republic of Germany

In contrast to open-chained phosphaalkenes only a few representatives of cyclic compounds possessing $\lambda^3\sigma^2$-phosphorus are described in literature. We now report on the synthesis of the parent compounds, i.e. the 2H-phosphirenes and partly on their transformation into 1H-isomers.



1 2 3



4 6 7

The spirocyclic 2H-phosphirene 3 results from the photolysis of the 3H-1,2,4-diazaphosphole 1 [accessible by [3+2]-cycloaddition of the corresponding diazo cyclohexane onto the phosphaalkyne 5 (R^2 = tBu)]. The carbene 2 is assumed to be an intermediate of the process.

Chlorocarbenes (4) - generated by thermolysis of diazirines - add onto the triple bond of phosphaalkynes (5) under the formation of the 2H-phosphirenes 6. They cannot be isolated as they rearrange quickly by chlorine shift under the formation of isomeric 1H-phosphirenes (7).

2-17 MOLECULAR AND ELECTRONIC STRUCTURE OF λ^3-IMINOPHOSPHINES

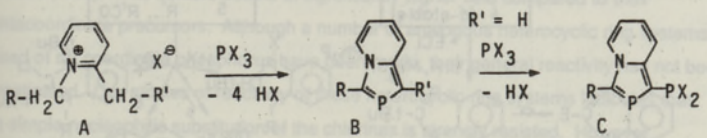
A.N.CHERNEGA[a], A.A.KORKIN, M.Yu.ANTIPIN, and
Yu.T.STRUCHKOV
Institute of Organoelement Compounds, Academy of
Sciences of the USSR, Vavilov Str. 28, Moscow 117334,
USSR
[a]Institute of Organic Chemistry, Ukrainian Academy of
Sciences, Murmanskaya Str. 5, Kiev 252660, USSR

X-Ray diffraction studies of a large number of novel λ^3-iminophosphines X-N=P-Y (X = Ar, Alk, PR_2, $P(S)R_2$, $\overset{+}{P}R_3$; Y = Ar, Alk, NR_2, PR_2, OR, SR, Hal et al.) elucidated the main characteristics of their molecular structure. Thus, it has become evident that the PNX bond angle shows great variance 114.0-173.7°, whereas the NPY bond angle is much more rigid (100.6-115.9°). It was found that λ^3-iminophosphines may exist either as the trans- or cis-isomer, depending on the electronic and steric properties of the substituents. The most favourable conformations of λ^3-iminophosphines are estimated on the basis of ab initio MO LCAO SCF calculations. These calculations indicate that the electronic structures of the double bonds in the XN=PY and $XN=PY_3$ systems differ significantly, which provides the theoretical basis for the different dependence of the P=N bond length on the PNX bond angle in these two types of compounds. It has been shown that the XN=PR and RN=PX molecules (X - donor or acceptor group) exhibit different type of conjugation. The influence of steric shielding of the reaction centres on the chemical properties of λ^3-iminophosphines is discussed. X-Ray structural studies of the λ^3-iminophosphines transformation products have been done.

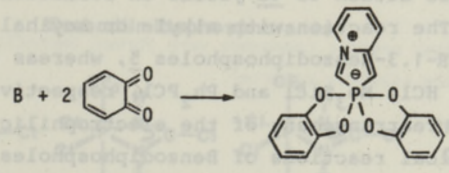
2-18 AZAPHOSPHOLES: STATE AND ADVANCES

A.SCHMIDPETER, R.K.BANSAL, K.KARAGHIOSOFF and F.STEINMÜLLER
Institute of Inorganic Chemistry, University of Munich,
Meiserstrasse 1, D-8000 München 2, FRG

A variety of routes has been developed for the synthesis of azaphospholes (1) by cyclocondensation or cycloaddition reactions. The phosphorus ring member in most cases is introduced as PCl_3, $P(NMe_2)_3$ or $P(SiMe_3)_3$. Syntheses of ring systems with only carbon adjacent to phosphorus were so far restricted to the latter. We now demonstrate the synthesis of the 1,3-azaphosphole ring by condensing PCl_3 with compounds containing two 1,4-positioned reactive methylene groups such as 1-phenacyl-2-alkyl-pyridinium ions A.



The new system B is rather insensitive towards additions to the phosphorus or to the P=C unit. Compounds with R' = H easily undergo substitution reactions however, as exemplified by the reaction with excess PX_3 to give C and further products. Strongly oxidizing orthoquinones in a twofold addition yield zwitterionic derivatives with six-coordinate phosphorus.



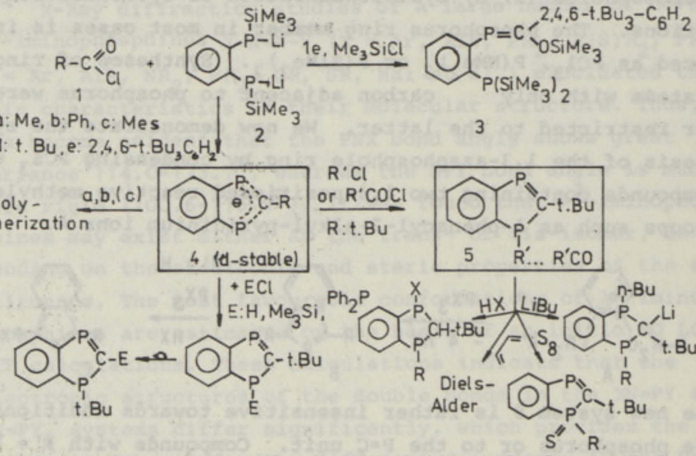
Including recently available systems and new investigations the azaphosphole reactivity will be compared. With 1,2,4,3-triazaphospholes a unique cycloaddition to phosphorus has been found.

(1) A. Schmidpeter, Phosphorus Sulfur 28, 71 (1986)

2-19 1.3-BENZODIPHOSPHOLES - SYNTHESIS AND REACTIONS

K.Issleib, H.Schmidt and E.Leißring
Department of Chemistry, Martin-Luther-University
Halle-Wittenberg, Weinbergweg 16, 4010 Halle/S., GDR

Depending upon the nature of the substituent R, the reaction of carbonic acid chlorides 1a-1e with the diphosphide 2 can be classified as follows:



With the bulky 1e ring formation fails and after silylation the acyclic phosphaalkene 3 is formed. 1a-1d are reacting with 2 to produce 1.3-Benzodiphospholate anions 4, but only 4d is a stable anion, 4a-4c lead to polymers. Electrophilic attack to 4d yields in formation of the title compounds. The reaction with alkyl- or acylhalides results in stable 1R-1.3-Benzodiphospholes 5, whereas the substitution with HCl, Me_3SiCl and Ph_2PCl, respectively, is followed by rearrangement of the electrophilic group to form 7. Typical reactions of Benzodiphospholes like 5 are shown above. 5 adds electrophiles as well as nucleophiles, sulfurization occurs at the σ^2-phosphorus, and with dienes [2+4]-cycloaddition is observed. Reaction behaviour and spectroscopic data are in agree with a nonaromatic stabilization of phosphorus heterocycles like 5.

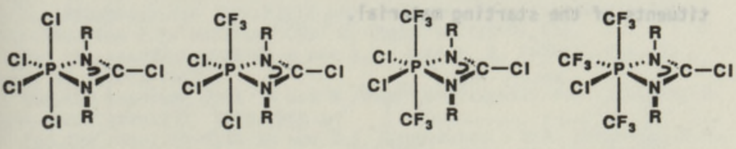
2-20 NEUTRAL SIX COORDINATE CARBODIIMIDE DERIVATIVES OF PHOSPHORUS

Ronald G. Cavell and Dietmar K. Kennepohl

Department of Chemistry, University of Alberta
Edmonton, Alberta
CANADA T6G 2G2

Neutral six coordinate phosphorus compounds (1 to 8) of the general formula $(CF_3)_xCl_{4-x}\overline{PN(R)C(Cl)N}R$ (x = 0 - 3, R = cyclohexyl or isopropyl) have been prepared, quantitatively and directly, from the reaction of the λ^5-phosphorane and the bidentate carbodiimide. These octahedral compounds, which are all stable crystalline solids with melting points of 90 to 150°C, have been fully characterized by multinuclear NMR, IR and mass spectroscopies. Characteristically, ^{31}P NMR shifts of these highly oxidized phosphorus centers occurs at significantly higher field compared to their pentacoordinate precursors. Although a number of analogous heterocyclic ring systems based of six coordinate phosphorus have been made, their general reactivity has not been investigated. Our studies of reactivity of these heterocyclic ring systems indicates that the simple nucleophilic substitution of the chlorines is strongly resisted. However, $Cl_4\overline{PN(R)C(Cl)N}R$ may be fluorinated, in a metathesis reaction with AgF, generating $FCl_3\overline{PN(R)C(Cl)N}R$ and $F_2Cl_2\overline{PN(R)C(Cl)N}R$ (R = isopropyl). Other reactants such as $NaOCH_2CF_3$, CH_3Li or C_6H_5Li are potentially able to react with the chlorine on the phosphorus or the ring carbon. We shall desribe the structure, chemistry and reactivity behavior of these systems.

Carbodiimidephosphoranes



1, 2   3, 4   5, 6   7, 8

R = cyclohexyl or isopropyl

2-21 THERMAL BEHAVIOUR OF SOME ORGANO PHOSPHORUS COMPOUNDS

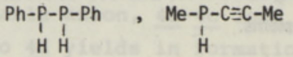
O.S.DIALLO, L.LOPEZ and J.BARRANS
Laboratoire des Hétérocycles du Phosphore et de l'Azote - UA CNRS 454 - Université Paul Sabatier, 118 Route de Narbonne 31062 Toulouse Cedex

Laboratoire des Hétérocycles du Phosphore et de l'Azote - UA CNRS 454 - Université Paul Sabatier, 118 Route de Narbonne 31062 Toulouse Cedex

So far, organo-phosphorus chemists have been interested in synthesizing low coordinated phosphorus compounds and in studying their reactivity often in solution and rarely at high temperature (e.g above 300 °C).

As a matter of fact there are few reports on the behaviour of dicoordinated phosphorus molecules at temperatures above 500 °C under low pressure.

We have been dealing with such molecules as diaza and triazaphospholes. Some results showed that transient species could have been formed and the method has revealed itself to be a new synthetic route to stable and unstable higher coordinated phosphorus compounds such as phosphine and diphosphine derivatives :

e.g 

$$\underset{H}{Ph\text{-}P}\text{-}\underset{H}{P}\text{-}Ph \ , \ Me\text{-}\underset{H}{P}\text{-}C{\equiv}C\text{-}Me$$

Other organic compounds were formed depending on the substituents of the starting material.

2-22 PENTAOXYPHOSPHORANES WITH SIX-MEMBERED RINGS

K. C. KUMARA SWAMY, ROBERTA O. DAY, and ROBERT R. HOLMES

Department of Chemistry, University of Massachusetts, Amherst,
MA, 01003 U.S.A.

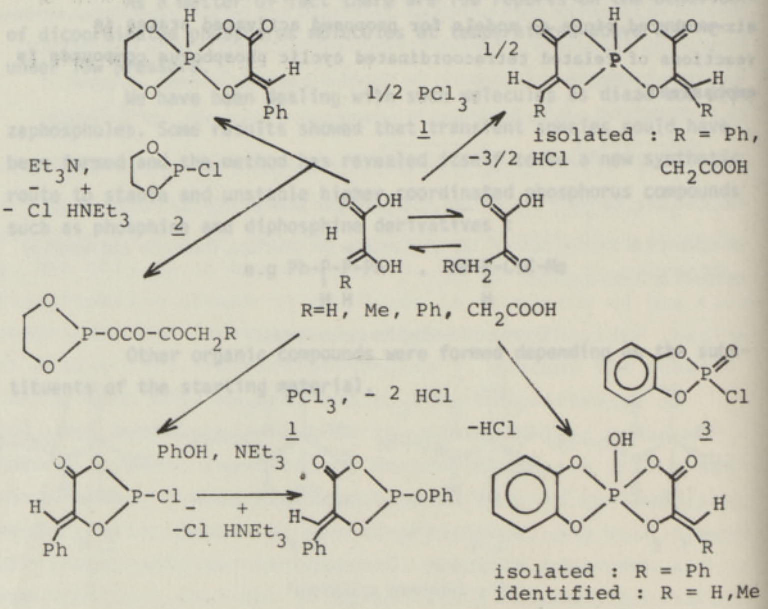
The synthesis and X-ray structural studies of the pentaoxyphosphoranes, $[(3,5\text{-}(t\text{-}Bu)_2C_6H_2O_2)(2,6\text{-}Me_2C_6H_3O)\overline{POCH_2CMe_2CH_2O}]$ (2) and $[(2,6\text{-}Me_2C_6H_3O)_3\overline{POCH_2CMe_2CH_2O}]$ (3), have been performed. An oxidative addition reaction between an *o*-quinone and a P(III) compound gave 2, and a coupling reaction between a diol and a P(III) compound in the presence of N-chlorodiisopropylamine produced 3. The structures both are trigonal bipyramids with the six-membered rings spanning apical-equatorial positions. Distortions are noted along a pseudorotational coordinate leading to diequatorial placement of the six-membered rings suggesting a low energy barrier to the formation of this structural arrangement. The usefulness of phosphoranes containing six-membered rings as models for proposed activated states in reactions of related tetracoordinated cyclic phosphorus compounds is emphasized.

2-23 NEW PHOSPHORUS COMPOUNDS INVOLVING PYRUVATE MOIETY. HYDROXYPHOSPHORANES MODELS OF INTERMEDIATE PHOSPHORANES IN NUCLEOPHILIC SUBSTITUTION REACTIONS ON PHOSPHORIC ESTERS OF ENOL PYRUVIC ACID

A. MUNOZ and LYDIA LAMANDE

UA au CNRS N° 454, Université Paul Sabatier, 118 route de Narbonne, 31062, Toulouse, Cedex, France

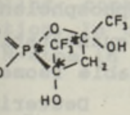
α-ketonic acids, in their enolic form, react on phosphorus compounds 1 - 3 giving hydrido or (and) hydroxyspirophosphoranes, or (and) mixed anydrides of phosphorous and ketonic acids, or (and) cyclic phosphorochloridites, or (and) cyclic phosphites. Hydroxyphosphoranes represent good models of intermediates postulated in the substitution reactions involving phosphoric esters of enol-pyruvic acid.



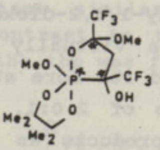
2-24 PHOSPHITES AND HEXAFLUOROACETONE-HEXAFLUOROACETYLACETONE : A COMPARISON

R. FRANCKE, J. HEINE and G.-V. RÖSCHENTHALER
Institute of Inorganic and Physical Chemistry,
University of Bremen, Leobener Straße, D-2800 Bremen 33,
Federal Republik of Germany

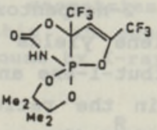
Phosphites $(RO)_2PX$ [X = Cl(1), OH(2)[1], OMe(3), $OSiMe_3$(4), NCO(5); R = Me(a), Et(b), R-R=CH_2CH_2(c), CMe_2CMe_2(d)] were allowed to react with hexafluoroacetone (6) (1,1,1,3,3,3-hexafluoropropane-2-one) and the enol (7a) (Z-1,1,1,5,5,5-hexafluoro-4-hydroxy-3-propene-2-one) or its O-silylated derivative 7b [E-1,1,1,5,5,5-hexafluoro-4-(trimethylsiloxy)-3-propene-2-one] to investigate the influence of R and X on the product formation. Phosphites $(RO)_2POC(CF_3)_2Cl$ (8a- d) were found besides other products from the interaction of 1a-d and 6. In an Arbuzov reaction 3a converted 8c and d to give $(MeO)_2P(O)C(CF_3)_2OP(OR)_2$, whereas with 1a and b $(MeO)_2P(O)OC(CF_3)_2P(OR)_2$ were obtained. Dialkylphosphites 2a, b, d furnished α-hydroxyphosphonates with 6[2] and 7a. The chiral compounds Z-$(RO)_2P(O)C(CF_3)(OH)CH{=}C(OH)CF_3$ (9a, b) rearranged to the ketophosphonates $(RO)_2P(O)C(CF_3)(OH)CH_2C(O)CF_3$ (10a, b) which upon heating gave four diasteromeric oxaphospholanes (11a, b). Thermally unstable $\lambda^5\sigma^5$-oxaphospholenes 13a-d were obtained from 3a-d and 7a. Compound 13d was trapped by addition of methanol to give the oxaphospholane 14d. The phosphites 4a-d and 6 or 7b reacted to yield α-trimethylsiloxy-phosphonates (in the case of 7b E-isomers). The fluorinated ketones 6[3] and 7a[4] and 5a-d underwent (3+2) and (2+2) cycloaddition to form $\lambda^5\sigma^5$P bicyclic ring systems (16a-d for 7a). The molecular structure of the phosphoranes 16a-d is that of a slightly distorted trigonal-bipyramide with carbon in axial position. Reacting the E-isomer 7b with 5d resulted in the formation of the isolable $\lambda^5\sigma^4$ phosphorane imine 17d.



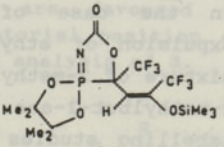
11



14d



16



17d

[1] Dialkylphosphites $(RO)_2P(O)H$ may react in their tautomeric form $(RO)_2POH$, see J.P. Guthrie, Can. J. Chem. 57 (1979) 236.

[2] For the reaction with 2a,b see A.F. Janzen, R. Politt, Can. J. Chem. 48 (1970) 1987.

[3] For the reaction with 5b see E. Duff, S. Tripett, P.J. Whittle, J. Chem. Soc. Perkin I, 1973, 972.

[4] For the reaction with 5a see I.V. Konovalova , L.A. Burnaeva, N.M. Kashtanova, R. Gareev, A.N. Pudovik, Zh. Obshch. Khim. 54 (1984) 2445.

2-25 ABSTRACTION *VERSUS* ELECTROPHILIC SUBSTITUTION: METAPHOSPHATE-MEDIATED REACTIONS IN THE GAS PHASE

Malcolm R. Banks,[a] J.I.G. Cadogan,[b] Ian Gosney[a]*,
Philip K.G. Hodgson[b] and David R. Rodger[a]

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

[b] B.P. Research Centre, Chertsey Road,
Sunbury-on-Thames, Middlesex TW16 7LN, England

When subjected to gas-phase thermolysis 2-aryl-1,3,2-dioxaphospholanes (aryloxyphosphites) extrude ethylene to generate highly electrophilic arylmetaphosphates ($ArOPO_2$) which cyclise by intramolecular C-H insertion (phosphonylation) to produce cyclic phosphonic monoesters in one step and good yields [1]. This process usually poses a difficult problem since known phosphonylating agents are not as a rule sufficiently electrophilic [2]. For analogous alkoxyphosphites bearing α, β, and/or γ-abstractable hydrogens, thermal breakdown leads to a different reaction pathway in which the metaphosphate intermediate rearranges by cycloelimination of HPO_3 to form alkenes exclusively [3]. In the case of 2-neopentoxy-1,3,2-dioxaphospholane, expulsion of ethylene yields a virtually quantitative mixture of 2-methylbut-1-ene and its more stable isomer, 2-methylbut-2-ene in the ratio of 2.0:1. Deuterium labelling studies show these products as being formed from a thermally generated metaphosphate moiety by a cyclic, concerted elimination reaction involving as the key step an unusual 1,2-methyl shift induced by a combination of competing α- and γ-hydrogen abstraction reactions with concomitant loss of metaphosphoric acid.

---

[1] Cadogan, J.I.G., Cowley, A.H., Gosney, I., Pakulski, M., Wright, P.M., Yaslak, S., J. Chem. Soc. Chem. Commun., 1685, (1986).

[2] Effenberger, F., Kottmann. H., Tetrahedron, 41, 4171, (1985), and references therein.

[3] Cadogan, J.I.G., Gosney, I., Wright, P.M., Phosphorus and Sulfur, 30, 397, (1987).

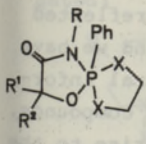
2-26 SYNTHESIS AND X-RAY ANALYSIS OF NEW SPIROPHOSPHORANES

B. KÖLL, K. TOTSCHNIG, J. VÖGEL, P. PERINGER, E.P. MÜLLER*
Institut für Organische und Pharmazeutische Chemie,
Universität Innsbruck, Innrain 52a, A-6020 Innsbruck, AUSTRIA

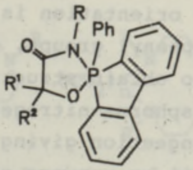
M. FISCHER, W. PETTER
Institut für Kristallographie und Petrographie, Eidgenössische
Technische Hochschule, CH-8092 Zürich, SWITZERLAND

Spiro[4.4]oxaza-λ^5-phospholidinones and spiro|4.5|oxaza-λ^5-phosphinanones |1| were prepared by Staudinger reaction of 2- and 3-hydroxycarboxylic acid azides with several cyclic phosphorus(III)compounds. In solution, the equilibrium between the spirophosphoranes and their monocyclic valence tautomers is strongly influenced by the solvent and the kind of the reacted phosphine: thus, both species are observed in the n.m.r. spectra of compounds **1**, whereas in the cases of **2-4** only the spirocycle is detectable. In the crystalline state, however, the spirocyclic form is obtained, except for compounds **5**, which exclusively occur as phosphoranylidenamides.

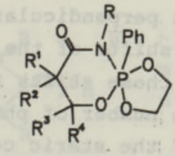
Deprotonation under proper conditions leads to the anions of **1-5**, which, according to ^{31}P n.m.r., exist in the spirocyclic form. By addition of methylating agents, the latter are converted into N-methyl spirophosphoranes. X-ray analyses of **6**, **7** and **8** showed slightly distorted trigonal bipyramidal structures with an unexpected apical position of the N-atom. As indicated by the value of the $^3J_{PNCH}$ coupling constant, similar geometries are favoured in solution. In contrast to this, an equatorial position of the N-atom in the tbp was found by X-ray analysis of **3**.



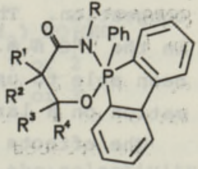
1 R=H; X=CH$_2$
2 R=H; X=O
6 R=CH$_3$; X=CH$_2$
7 R=CH$_3$; X=O



3 R=H
8 R=CH$_3$



4 R=H
9 R=CH$_3$



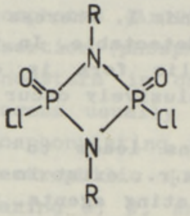
5 R=H
10 R=CH$_3$

[1] P. Pöchlauer, W. Petter, P. Peringer, E.P. Müller,
J. Chem. Soc., Chem. Commun. 1985, 1764.

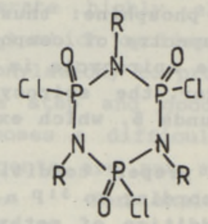
2-27 STERIC CONGESTION AND REACTIVITY IN CYCLOPHOSPHAZANES

M. MURRAY and G. WOODWARD.
Department of Chemistry, University of Bristol,
Cantocks Close, Bristol, BS8 1TS, ENGLAND.

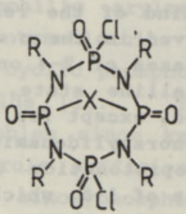
Dimeric chlorocyclophosphazanes (I) are reactive compounds because of the ring strain, which is relieved by formation of the pentacoordinate intermediate in the SN2(P) substitution reaction. The trimers (II) and the bicyclic compounds (III) which we have recently prepared are much less reactive.



(I)



(II)



(III)

X-ray crystallographic studies of both isomers of (II) reveal that the phenyl groups are perpendicular to the planes of the nitrogen atoms, presumably because of steric congestion. This perpendicular orientation is reflected in the ^{13}C n.m.r shifts of the phenyl groups, and we have been able to use these shifts to obtain structural information on a large number of phosphorus-nitrogen compounds.

The effects of the steric congestion giving rise to the unusual orientation of the phenyl groups are seen in the reactivity of compounds of type (II) and (III). Nucleophilic substitution leads to cleavage of the rings, apparently by a trans-annular attack of nitrogen on phosphorus.

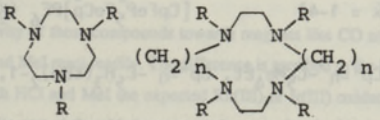
3-1 ORGANOPHOSPHORUS COMPLEXONES. EFFECTIVENESS AND SELECTIVITY OF COMPLEX FORMATION

M.I.KABACHNIK
A.N.Nesmeyanov Institute of Organoelement Compounds, Academy of Sciences of the USSR, Vavilov Str. 28, Moscow 117334, USSR

Organophosphorus complexones (OPC) have been known since 1949 (G.Schwarzenbach). We began systematic studies on OPC in 1958. We devided OPC into 3 types: I, OPC with flexible atom chains; II, OPC with limited conformational mobility; and III, cyclopentade OPC. Type I compounds resemble the carbon prototypes in their effectiveness of complex formation, but exceed them in their selectivity. Lower effectiveness and higher selectivity of complex formation are characteristic of type II OPC. Type III OPC can display both high effectiveness and selectivity of action.

The effectiveness of OPC is connected with the cationophilicity of the $-PO_3^{2-}$ anion, exceeding that of the $-COO^-$ group. The flexibility of the chain accounts for a weak selectivity of the type I OPC. High selectivity of cyclopentade OPC is results from the correspondence between the ligand contour and the coordinated polyhedrons of the cations. This explanation is supported by the calculations of the molecular mechanics.

The following types of cyclopentade OPC were investigated:



$R = -(CH_2)_mPO(OH)_2$
$m = 1$ or 2
$n = 2$ or 3

An explanation of the differences in the selectivity and effectiveness of complex formation is given.

1. M.I.Kabachnik, Yu.M.Polikarpov, Zhurn. Obsch. Chim. 58, 1937 (1988).

3-2 UNUSUAL PHOSPHORUS LIGANDS

O. J. SCHERER, J. BRAUN, Th. BRÜCK, T. DAVE, M. SWAROWSKY,
H. SWAROWSKY and G. WOLMERSHÄUSER
Fachbereich Chemie, Universität Kaiserslautern
D-6750 Kaiserslautern, Germany (F.R.G.)

The interaction of white phosphorus, P_4, with $[\mathrm{Cp''}_2M(CO)_2]$, M = Zr,Hf and $[\mathrm{Cp^*}M(\mu\text{-}CO)]_2$, M = Co,Rh,Ni affords complexes with the polyphosphides $P_4^{\,n-}$ [n = 2 (A, B); n = 4 (C); n = 6 (D, nickelaphosphacubane)] as ligands.

$[\mathrm{Cp''}_2MP_4]$	$[\mathrm{Cp^*}(CO)MP_4]$	$[\mathrm{Cp^*}_2(CO)_2Co_2P_4]$	$[\mathrm{Cp^*}_3Ni_3P_5]$
A (M=Zr,Hf)[1]	B (M=Co[2],Rh)	C [2]	D [3]

P_4 and $[\mathrm{Cp'}M(CO)_2]$, M = Co,Rh as well as $[\mathrm{Cp''}Ni(\mu\text{-}CO)]_2$ react with formation of E (cyclo-P_5 as 7e donor), F (isomer of $P_4^{\,2-}$) and the cyclo-P_3 sandwich G.

$[\mathrm{Cp'}_2Co_2P_5]_2$	$[\mathrm{Cp'}(CO)RhP_4Rh\mathrm{Cp'}]$	$[\mathrm{Cp''}Ni(\eta^3\text{-}P_3)]$
E	F [1]	G [3]

Starting with the pentaphosphaferrocene $[(\eta^5\text{-}P_5)Fe\mathrm{Cp^*}]$ and $[\mathrm{Cp}Mn(CO)_2(thf)]$ or $[\mathrm{Cp}Fe(C_6H_6)]PF_6$ further coordination (H) and build up of the 30 VE triple-decker sandwich K can be realized.

$[\mathrm{Cp^*}FeP_5\{Mn(CO)_2\mathrm{Cp}\}_x]$ (H, x = 1-4) $[\mathrm{Cp}FeP_5Fe\mathrm{Cp^*}]PF_6$ (K)

$\mathrm{Cp}=\eta^5\text{-}C_5H_5$, $\mathrm{Cp^*}=\eta^5\text{-}C_5Me_5$, $\mathrm{Cp'}=\eta^5\text{-}C_5Me_4Et$, $\mathrm{Cp''}=\eta^5\text{-}C_5H_3(tBu)_2\text{-}1,3$

(1) O. J. Scherer, M. Swarowsky, H. Swarowsky, G. Wolmershäuser, Angew. Chem. 100, 738 (1988); Angew. Chem. Int. Ed. Engl. 27, 694 (1988).

(2) O. J. Scherer, M. Swarowsky, G. Wolmershäuser, Organometallics, in press.

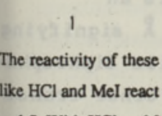
(3) O. J. Scherer, T. Dave, J. Braun, G. Wolmershäuser, J. Organomet. Chem. 350, C 20 (1988).

3-3 NEW ORGANOMETALLIC AND COORDINATION COMPOUNDS OF IMINOPHOSPHORANYLMETHANES WITH RHODIUM AND IRIDIUM

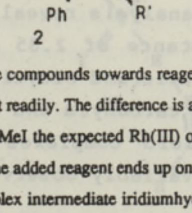
C.J. Elsevier and P. Imhoff.

Anorganisch Chemisch Laboratorium, Universiteit van Amsterdam,
Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands.

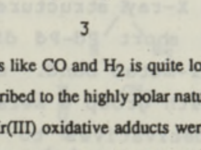
The chemistry of polyfunctional iminophosphorans $R'N=PR_2-CH_2-Y$ ($Y=PR_2$, $PR_2=NR'$ etc.) has been elaborated to some extent. Their novel organometallic and coordination chemistry, particularly aimed at catalytic and conductivity properties, currently receives attention from several groups [1-3]. We report the synthesis, structure and reactivity of a new class of organorhodium and -iridium compounds based on iminophosphoranylmethanes. Reaction of the bis(iminophosphoranyl)methanes $(R'N=PPh_2)_2CH_2$ 1 (R=para-substituted aryl) with the electron-rich d^8 complexes $[MCl(COD)]_2$ or $[MCl(CO)_2]_2$ (M=Rh, Ir) gives rise to the formation of new four- and six-membered metallacycles, 2 and 3, containing σ–N, σ–C or σ-N, σ-N' coordinated ligands. Lithiated compounds $[(R'N=PPh_2)_nCH_{(3-n)}-Li]$ (n=1, 2) provide upon reaction with the same d^8 complexes the unique four-membered metallacyclic iminophosphoranylmethanide compounds $L_2\overline{M-CH_2-PPh_2=N}R'$ (4) and $L_2\overline{M-CH(PPh_2=N}R')-PPh_2=NR'$ (5). The compounds 2, 4 and 5 contain a sp^3-carbon-to-metal bond that is stabilized by intramolecular coordination of the electron-rich nitrogen of the iminophosphoranyl moiety to the metal. The stabilization by the P=N moiety is very effective since the Rh-C and Ir-C bond remains intact even under harsh conditions such as reaction with HCl in benzene or ether.



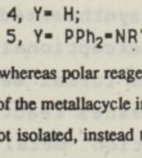
1



2



3



4, Y= H;
5, Y= $PPh_2=NR'$

The reactivity of these compounds towards reagents like CO and H_2 is quite low, whereas polar reagents like HCl and MeI react readily. The difference is ascribed to the highly polar nature of the metallacycle in 4 and 5. With HCl and MeI the expected Rh(III) or Ir(III) oxidative adducts were not isolated, instead the electrophylic part of the added reagent ends up on the nitrogen atom(s) of the ligand. In the reaction of HCl with the iridium complex intermediate iridiumhydrides, in which the H-atom is in cis-position to N, have been observed. Apparently, oxidative addition occurs first, followed by a H-shift from the metal to nitrogen. X-ray crystallographic studies, solid state and solution ^{31}P as well as ^{103}Rh NMR data will be presented.

[1] K.V.Katti, H.W.Roesky and M.Rietzel; Z.Anorg.Allg.Chem. 553, 123 (1987)
[2] K.V.Katti and R.G.Cavell; Organometallics; 7, 2236 (1988)
[3] P.Imhoff and C.J.Elsevier; J.Organomet.Chem.; in press

3-4 DIPHOSPHAZANES AS LIGANDS: LINKS BETWEEN PHOSPHORUS CHEMISTRY AND ORGANOMETALLIC CHEMISTRY

M.S. Balakrishna, T.K. Prakasha and S.S. Krishnamurthy

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

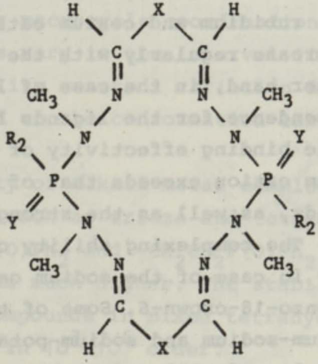
Several new acyclic, cyclic and bicyclic diphosphazanes have been synthesized and their organometallic chemistry has been explored. Acyclic diphosphazane ligands, $X_2PN(R)PX_2$(L) (R = alkyl, aryl ; X = aryl, alkoxy, aryloxy) react with group 6 metal carbonyl derivatives to yield mainly cis-chelated complexes, $M(CO)_4L$. Hepta-coordinated species of the type $M(CO)_3I_2L$ (M = Mo, W) have also been isolated and the structure of the tungsten complex $W(CO)_3I_2[PhN(P(OPh)_2)_2]$ has been confirmed by single crystal X-ray analysis. Reactions of iron pentacarbonyl with L yield complexes in which both chelating and bridged bidentate modes of coordination of the ligands are observed. Reactions of MCl_2(COD) (M = Pd or Pt, COD = 1,5-cyclooctadiene), $[RhCl(COD)]_2$ and $[RhCl(CO)_2]_2$ afford complexes in which the diphosphazane acts as a chelating or a bridging ligand. A novel dinuclear Pd(0) complex, $Pd_2[X_2PN(R)PX_2]_3$ (R = Me, X = OPh), has been synthesized ; X-ray structure analysis reveals an exceptionally short Pd-Pd distance of 2.85 Å signifying a formal metal-metal bond. Cyclic and bicyclic diphosphazanes react with group 6 metal carbonyls and other transition metal derivatives to yield complexes in which a monodentate coordination is invariably observed.

3-5 POLYAZAPHOSPHORUS MACROCYCLES

Jean Pierre MAJORAL*, Myriam BADRI, Anne Marie CAMINADE,
Alain GORGUES, Michel DELMAS, Antoine GASET
Université Paul Sabatier, 118 Route de Narbonne
31062 Toulouse Cedex France

The development of synthetic methods concerning phosphorus macrocycles has been slow and concern mainly P-C, P-O or P-S containing macrocycles. Indeed very few investigations were devoted to the preparation of polyazaphospho-macrocycles.

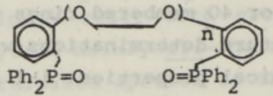
We will report the high yields one pot synthesis of stable 18, 20 or 22 membered rings of the type I. The preparation of the corresponding 30 or 40 membered rings will be also investigated. X ray structure determinations will be presented as well as some chemical properties: 1-2 addition on carbon carbon double or triple bonds included in the macrocycle, substitution reactions, ring contraction, complexations, transmetallations etc...



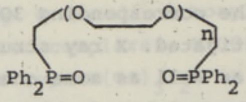
3-6 READILY AVAILABLE PHOSPHORUS-CONTAINING COMPLEXING AGENTS

E.N.TSVETKOV
Institute of Physiologically Active Substances, Academy of Sciences of the USSR, Chernogolovka, Moscow region 142432, USSR

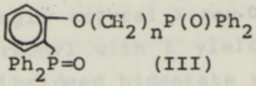
This study is aimed to finding effective and selective complexing agents towards the alkali metal cations in a series of phosphine oxides. The conductometric method in tetrahydrofuran-chloroform (4:1) and acetonitrile was used to determine the stability constants of complexes of the ligands I-IV with the alkali metal cations.



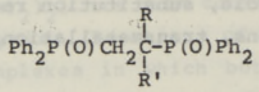
(I), n=1-5



(II), n=1-5



(III)



$$Ph_2P(O)CH_2\overset{R}{\underset{R'}{C}}-P(O)Ph_2$$

(IV), R=H, R'=Alk, R=R'=Me

For the potassium, rubidium and cesium cations the complexing properties increase regularly with the value of n in I and II. On the other hand, in the case of lithium and sodium cations the dependence for the ligands I and II has a maximum at n=3. The binding effectivity of ligand I (n=3) towards the lithium cation exceeds that of 15-crown-5 and 18-crown-6 compounds, as well as the strongest phosphorus containing agents. The complexing ability of ligands II (n=3, 4) is higher in case of the sodium cation, being not lower that of dibenzo-18-crown-6. Some of the ligands I and II show high lithium-sodium and sodium-potassium selectivity. Less effective ligands III and IV have high selectivity for the lithium cation.

3-7 COORDINATION COMPOUNDS OF ALKALI METAL IONS WITH PHOSPHORYL GROUPS CONTAINING LIGANDS

K.B.YATSIMIRSKII
L.V.Pisarzevsky Institute of Physical Chemistry, Ukrainian Academy of Sciences, Prospekt Nauki 31, Kiev 252028, USSR

Phosphoryl groups containing ligands form coordination compounds with alkali metal ions. The coordination number of 1a group elements increases from Li to Cs as a consequence of increasing radii and number of virtual orbitals. The coordination polyhedrons of the corresponding complexes become more complicated in the same order. The influence of virtual orbitals is especially revealed in the case of metal ion and polydentate ligand interaction because of the spatial arrangement of donor atoms requiring the definite set of virtual orbitals.

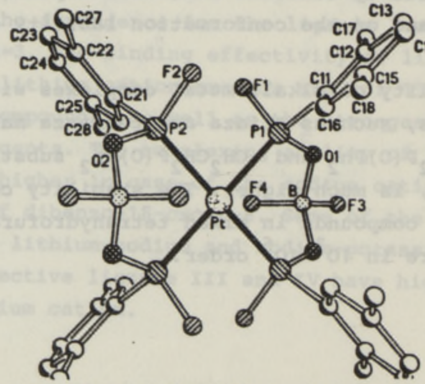
Stable coordination compounds of alkali metal ions form in cases where several phosphoryl groups are present, and especially if they are included into the macrocycles or pseudomacrocycles. The stability constant values of phosphoryl-containing macrocycle coordination compounds with alkali metal ions vary in the interval $10-10^4$. The character of the stability constant variation depends on the cavity dimension and on the conformation lability of macrocycle.

The stability of alkali metal complexes with cyclopendant ligands, such as triaza and tetraaza macrocycles containing $-CH_2P(O)Ph_2$ and $-CH_2CH_2P(O)Ph_2$ substituents at nitrogen atoms, is much higher. The stability constants values of such compounds in mixed tetrahydrofuran-chloroform solvent are in 10^3-10^6 order.

3-8 REACTIVITY AND STRUCTURE OF DIFLUOROPHOSPHINE COMPOUNDS AND THEIR PLATINUM COMPLEXES

L.Heuer[a], P.G.Jones[a], D.Schomburg[b], and R.Schmutzler[a]
[a]Institut für Anorganische und Analytische Chemie der Technischen Universität, Hagenring 30, 3300 Braunschweig, FRG
[b]Gesellschaft für Biotechnologische Forschung mbH, Mascheroder Weg 1, 3300 Braunschweig, FRG

Various novel organodifluorophosphines involving aromatic, unsaturated and aliphatic substituents were prepared and used as ligands in reactions with $(COD)PtCl_2$ or K_2PtCl_4; complexes of the type *cis*-dichloro-bis(organyldifluorophosphine)platinum(II) or tetrakis (organyldifluorophosphine)platinum(0) were formed. The ^{31}P-n.m.r. data of these complexes were correlated with the Pt-P bond length found in X-ray diffraction studies. The hydrolysis of RPF_2 and $Pt(RPF_2)_4$ with water lead to the formation of RP(F)(O)(H) or $[RP(F)(OH)]_2[RP(F)(O)]_2Pt$. Both products were characterized by n.m.r. spectra and X-ray structure determination. $[RP(F)(OH)]_2[RP(F)(O)]_2Pt$ also was reacted with $BF_3{*}Et_2O$ to form *meso*-bis{bis(2,5-dimethylphenylfluorophosphinito)-difluoroborato)} platinum(II), characterized by a single crystal X-ray diffraction study.



1 L.Heuer, M.Sell, R.Schmutzler, D.Schomburg, *Polyhedron 6*, (1987) 1295.

2 L.Heuer und R.Schmutzler, *J.Fluorine Chem.*, *39* (1988) 197.

3-9 SYNTHESIS AND CHARACTERIZATION OF DIRHODIUM COMPLEXES CONTAINING μ-SO, μ-S_2, AND μ-SH GROUPS STABILIZED BY THE TRIPODAL LIGAND $CH_3C(CH_2PPh_2)_3$

C. BIANCHINI, A. MELI, C. MEALLI, M. PERUZZINI, and F. VIZZA
Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione, CNR, Via J. Nardi, 39 - 50132 Firenze, Italy.

The genesis and chemistry of the coordinatively and electronically unsaturated μ-sulphido Rh(III) complex $|(triphos)Rh(\mu\text{-}S)_2Rh(triphos)|(BPh_4)_2$, triphos = $CH_3C(CH_2PPh_2)_3$, is presented and discussed.

Complex 1 reacts with samll molecules such as O_2 and H_2 or with S^{2-} anions to form $|(triphos)Rh(SO)|_2(BPh_4)_2$, $|(triphos)RhH(SH)|_2(BPh_4)_2$, $|(triphos)Rh(S_2)|_2(BPh_4)_2$, respectively.

All of the compounds have been characterized by means of chemical-physical measurements, including spectroscopic techniques. ^{31}P NMR studies have shown that all of the compounds are fluxional. The dynamic behaviour has been studied in detail and compared with that shown by the related derivatives $|(triphos)Rh(Se_2)|_2(BPh_4)_2$, and $|(triphos)Rh(SO_2)|_2(BPh_4)_2$, containing bridging Se_2 and SO_2 ligands, respectively.

Complete X-ray diffraction analyses have been carried out for all of the complexes, which share the same primary geometry, i.e. two $|(triphos)RHX_2|$, $X_2=S_2, Se_2, SO, SO_2, H(SH)$, subunits are linked together by a donor atom from each X_2 group.

3-10 P-RICH SILYLPHOSPHANES; SYNTHESIS AND REACTIONS

G. Fritz, H. Bauer, S. Lang, E. Layher, B. Mayer,
M. Jarmer, J. Reuter, T. Vaahs
Inst.f. Anorg. Chemie d. Universität, D-7500 Karlsruhe

It is reported on:

1. Synthesis and complexchemical properties of the Heptaphospha-nortricyclenes P_7R_3 ($R=SiMe_3, SiPh_2Me, SiPhMe_2, P(tBu)_2$), as well as of the functional Tri- and Tetraphosphanes (tBu, $SiMe_3$, H, Me).
2. Synthesis of Silylphosphanes of adamantane structure.
3. Reactions of functional Diphosphanes.
4. Formation and decomposition of $(tBu)_2P\text{-}P{=}P(tBu)Br$ LiBr and detection of the intermediate Phosphiniphosphinidene $(tBu)_2\text{-}P\text{-}P$ by derivatives.

ad 1: Starting from investigations on the formation of complexes of P_7Et_3 with $Cr(CO)_5THF$ the influence (sterical and electronical) of the substituents was examined in the compounds $P_7(SiPh_3)_3$, $P_7(SiPh_2Me)_3$, $P_7(SiPhMe_2)_3$. The synthesis of $P_7[P(tBu)_2]_3$ offers the chance to investigate the effect of the PR_2-substituent of the P_7-cage on its complexing properties and thus on the electronic system of this cage. Using differently substituated di-, tri- and tetraphosphanes (the substituents being $SiMe_3$, tBu, Ph, Me, H) as model compounds for the formation of complexes of non-cage-compounds it is observed, that the complexation of $Cr(CO)_5THF$ preferably occurs at the silylated P-atom.

ad 2: Li_3P_7, $P_7(SiMe_3)_3$, $P_4(SiMe_2)_3$ can be obtained by the reaction of P_4 with Na/K or LiR. It is shown, that a molar ratio P_4:Na/K of 1:3 diminishes the formation of a nortricyclene-cage, while adamantane structures, like $(Et_2Si)_6P_4$, $[(Et)(Me)Si]_6P_4$, $[(Ph)(Me)Si]_6P_4$, $[(Me)(H)Si]_6P_4$ or $[(Vinyl)(Me)Si]_6P_4$ are obtained.

ad 3: Since the introduktion of one tBu-group is sufficient to obtain Li-phosphides like $(tBu)(Me_3Si)P\text{-}P(Li)(SiMe_3)$, that are stable in ether solution, it is through the reaction of such lithiated diphosphanes with RPX_2 that functional triphosphanes like $(tBu)_2P\text{-}P(SiMe_3)\text{-}P(Cl)(tBu)$ or $(tBu)_2P\text{-}P(Cl)\text{-}P(SiMe_3)_2$ are available. Eliminating Me_3SiCl these compounds lead to $(tBu)_2P\text{-}P{=}P\text{-}tBu$ or $(tBu)_2P\text{-}P{=}PSiMe_3$ respectively, which finally yield the cyclotetraphosphanes $P_4(tBu)_2[P(tBu)_2]_2$ and $P_4(SiMe_3)_2[P(tBu)_2]_2$. The access to triphosphanes of the $R(Me_3Si)P\text{-}P(Cl)\text{-}P(SiMe_3)R'$-type and the reaction of these with Li-phosphides enable the synthesis of iso-tetraphosphanes. Formations and reactions of PF-containing triphosphanes are described.

ad 4: $(tBu)_2P\text{-}P{=}P(tBu)_2Br$ LiBr, generated from $[(tBu)_2P]_2PLi$ with 1,2-dibromoethane, decomposes at 20°C to give $(tBu)_2PBr$, LiBr and the cyclophosphanes $P_4[P(tBu)_2]_4$ and $P_3[P(tBu)_2]_3$. The intermediate phosphinophosphinidene $(tBu)_2P\text{-}P$ is proven by trapping with both 2,3-dimethyl-1,3-butadiene and cyclohexene.

3-11 THE REACTIONS OF ALKYNLCYCLOPHOSPHAZENES WITH METAL CARBONLYS

Christopher W. Allen*, Pauline Malik, Adam Bridges, James Desorcie and Brian Pellon, Department of Chemistry, University of Vermont, Burlington, VT 05405 USA

ABSTRACT The reactions of $N_3P_3F_5C\equiv CR$ (R=Ph, Me_3Si, n-C_4H_9) with $Co_2(CO)_8$ lead to $N_3P_3F_5C\equiv CR\bullet Co_2(CO)_6$. The corresponding reaction with 2,2-$N_3P_3F_4(C\equiv CPh)_2$ produces the novel, structurally characterized, tetracobalt species 2,2-$N_3P_3F_4(C\equiv CPh.Co_2(CO)_6)_2$. In the case of the previously reported $N_3P_3F_5C\equiv CPh$ complex, we now report that reaction with excess ligand leads to the cyclotrimerized material 1,2,4-$(N_3P_3F_5)_3Ph_3C_6$(I). Detailed dynamic ^{19}F NMR spectroscopy studies of this material shows detectable barriers to rotation about the phosphorus-carbon bond of the central arene. The reaction of a more reactive catalyst, η^5-$C_5H_5Co(CO)_2$, with $N_3P_3F_5C\equiv CPh$ gives rise to a variety of cyclooligomerized products. A cyclodimerized material, $(N_3P_3F_5)_2Ph_2C_4$(II) is isolated as the colbalt stabilized entity II•CoCp. The carbonyl insertion product of the cyclodimerized complex has been isolated as well as I and its colbalt complex I•CoCp (which is believed to contain an η^4 arene). The reaction of $Fe(CO)_5$ with $N_3P_3F_5C\equiv CPh$ gives the iron stabilized cyclodimer, II•$Fe(CO)_3$. The corresponding reaction with $Fe_2(CO)_9$ gives a plethora of products including the cyclodimerized material noted above and its carbonyl insertion product. Other characterized products include I•$Fe(CO)_3$ (also believed to be an η^4 material), an iron containing metallocycle and unique derivative in which the alkyne bridges iron and cyclopentadienone fragments.

3-12 A TERTIARY PHOSPHINE METAL COMPLEX, $[Ir(Cl)(CO)(Ph_3P)_2]$: DISCOVERY, MECHANISM OF FORMATION, AND CATALYTIC PROPERTIES

L. VASKA

Department of Chemistry, Clarkson University, Potsdam, New York 13676, USA

Phosphorus ligands - especially triphenylphosphine (Ph_3P) - impart important properties to certain low-valent and coordinatively unsaturated transition metal complexes, such as the ability to reversibly activate small molecules, act as catalysts for a variety of chemical reactions, and provide simple models related to some biological processes. Since the discovery of the title compound nearly 30 years ago (1), research involving this complex and analogous species continues unabated. In this paper, the history of the synthesis of and some unique properties of trans-$[Ir(C\ell)(CO)(Ph_3P)_2]$ are reviewed. New results to be presented and discussed embrace mechanistic aspects of the formation of trans-$[Ir(C\ell)(CO)(Ph_3P)_2]$ from $IrC\ell_3$, Ph_3P and alcohols, and the catalytic activation of carbon dioxide, water and other molecules by the same iridium complex. The latter reactions include evolution of hydrogen from H_2O-DMF solutions, and the synthesis of triazine ($C_3H_3N_3$) from CO_2, NH_3 and H_2 via formamide ($HC(O)NH_2$) intermediation.

(1) L. Vaska, J.W. DiLuzio, J. Am. Chem. Soc. 83, 2784 (1961).

3-14 PHOSPHORUS METAL DOUBLE BOND COMPLEXES: FUNCTIONAL AND CHIRAL SPECIES $Cp(L)(L')M=PR_2$ (M = Mo, W) AND THE IRON DERIVATIVE $Cp(CO)Fe=PMes_2$

Wolfgang Malisch, M. Märkl, S. Amann, U. Hirth and M. Schmeußer,
Institut für Anorganische Chemie, Universität Würzburg,
Am Hubland, D-8700 Würzburg, FRG

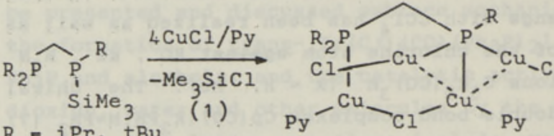
Functional metal phosphorus double bond complexes $Cp(CO)_2M=P(R)X$ (1) (X = H, Cl; R = alkyl, aryl, alkoxy, dialkylamino; M = Mo, W) can be synthesized either via decarbonylation of the corresponding metallo-phosphanes $Cp(CO)_3M-P(R)X$ (2) or via the dehydrochlorination of the bifunctional phosphane complexes $Cp(CO)_2M(Cl)-P(H)(R)X$ (3). In special cases side reactions give rise to the formation of the metallacycles $Cp(CO)_2M-P(t-Bu)(X)-P(t-Bu)$ (4) or the dinuclear M=P complex $Cp(CO)_2M=P(Mes)-M(CO)_2[P(Mes)H_2]Cp$ (5). Compounds of the type 1 are extremely reactive concerning the exchange of P-bonded hydrogen or chlorine. In this context H/Cl-exchange with CCl_4 has been realized as well as the substitution of the chlorine atom against RO^-, RS^-, R_2N^- and the metal anions $C_5R_5(CO)_3M^-$ (R = H, Me). The chiral metal phosphorus double bond complexes $Cp(CO)(R_2PH)M=PR_2$ (7) ($R_2P = Ph_2P$, t-Bu(Ph)P) are obtained via dehydrohalogenation of $Cp(CO)(R_2PH)_2MCl$ (6) with $Me_3P=CH_2$. 7 can be further deprotonated to the anionic diphosphametalla-allyl species $[Cp(CO)(R_2P)_2M]^-$ (8), which represents an attractive building block in cluster synthesis. Dehydrobromination of $Cp(CO)(HMes_2P)Fe-Br$ yields $Cp(CO)Fe=PMes_2$ (9), the first example of an iron phosphorus double bonded species. Due to the low coordination number of its metal centre, 9 exhibits high reactivity towards S_8, Se_8, $R(H)CN_2$, $MeO_2CC\equiv CCO_2Me$ and PhN_3 leading to the formation of three four and five membered metallacycles $Cp(CO)Fe-PMes_2X$ (X = S, Se, NPh, CH_2, $CHCO_2Et$, $MeO_2CC=CCO_2Me$, N(Ph)N=N).

3-15 COPPER(I) COMPLEXES WITH ELECTRON DEFICIENT μ_3PRR' BRIDGING - A NOVEL COORDINATION MODE OF SECONDARY PHOSPHIDO GROUPS IN TRANSITION METAL CHEMISTRY

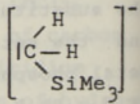
D. J. BRAUER, P. C. KNÜPPEL and O. STELZER

Fachbereich 9, Anorg. Chemie, Bergische Universität-GH
Wuppertal, Gaußstr. 20, D-5600 Wuppertal 1, BRD

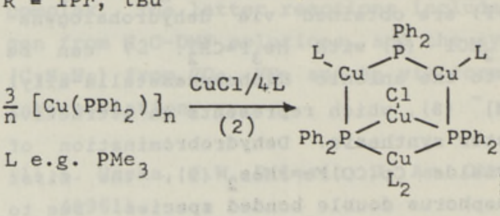
Phosphido groups PRR' with their two lone electron pairs typically act as bridging ligands forming M-PRR'-M units with two electron precise M-P bonds. However, μ_2 bridging of transition metals may also be achieved by ligands X providing only one electron pair for bonding in M-X-M units (e.g. $[Cu(CH_2-SiMe_3)]_4$). By analogy with the iso-electronic carbanions $CH_2SiMe_3^-$ (A) the copper(I) phosphido species PRR'Cu (B) may be expected to bind two additional Cu(I) ions forming electron deficient [Cu-(PRR'Cu)-Cu] bridges. Copper(I) complexes containing these novel μ_3-PRR'Cu_3 bridges (e.g. 1) have been obtained by P-Si cleavage reactions (1) and depolymerisation (2) of polymeric Cu(I) phosphides by Lewis bases (e.g. 2).



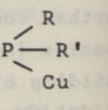
1



A



2



B

The copper(I) μ_3-PRR' phosphido complexes obtained were characterised by elemental analysis, molecular weight determinations, $^{31}P\{^1H\}$- and ^1H-NMR spectra in solution. Crystal structures of 1, 2 and related species will be discussed and a bonding scheme for the μ_3-PRR'Cu_3 units will be presented.

3-16 DECISIVE INFLUENCE OF PHOSPHORUS LIGANDS ON O_2 OXIDATIONS OF ALKENES IN THE PRESENCE OF THE IRON NITRATO/IRON NITROSYL COUPLE

M. POSTEL, F. TOMI, H. LI KAM WAH and P. GUILLAUME

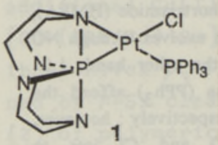
Laboratoire de Chimie Moléculaire , Unité Associée au C.N.R.S. n 426,
Université de Nice, 06034 Nice, France.

We have demonstrated that the iron-nitrato/iron nitrosyl couple constitutes a new alternative for the O_2 oxidation of alkenes. In this system, the nitrosyl ligand, N-bonded to iron, is oxidized by O_2 into a nitrato group, bidentate, O-bonded to iron, which, in turn, transfers oxygen to alkenes or phosphines and is thus reduced to the initial nitrosyl group. Phosphorus ligands were found to play a key role in the different steps of this cycle. Their influence is decisive for the oxygen transfer capacility of the Fe-NO/Fe-NO_3 system. Thus : The nitrosyl dimer $[Fe(NO)_2(Cl)]_2$ 1 in the presence of hexamethylphosphortriamide (HMPA), yields the unstable compound 5, $Fe(NO)_2(Cl)(HMPA)$, which evolves through NO dissociation to give 6, $Fe(NO)(Cl)_2(HMPA).\frac{1}{2}(HMPA)$. On the other hand, 1,2-bis(diphenylphosphino)ethane (dppe) and triphenylphosphine (PPh_3) afford the stable $[Fe(NO)_2Cl]_2(\mu\text{-dppe})$, 2, and $Fe(NO)_2Cl(PPh_3)$, 1a, respectively ; however, in the presence of dppe, 2 evolves with both NO and Cl loss to $Fe(NO)Cl_2(Odppe)$ and $Fe(NO)_2(dppe)$, while, in the presence of PPh_3, 1 evolves through loss of Cl only to yield $Fe(NO)_2(PPh_3)_2$. All these nitrosyl complexes activate molecular O_2 to yield **nitrato** - and not nitro- iron(III) complexes. Formation of $Fe(NO_3)(Cl)_2(HMPA).\frac{1}{2}(HMPA)$, 11, $Fe(NO_3)_2(Cl)(HMPA)_2$, 8, and $Fe(NO_3)(Cl)_2(HMPA)_2$, 12, in the presence of HMPA. The molecular structure of 8 has been determined by X-ray diffraction and shows a "normal" NO_3 moiety. The 8 and 12 nitrates only are capable of oxygen transfer and only to phosphines. On the other hand, in the presence of PPh_3 or $OPPh_3$ a single nitrato complex $Fe(NO_3)_2X(OPPh_3)_2$, 7 is obtained : 7 **selectively epoxidizes cyclohexene** and this is the first example of oxygen transfer from a nitrato ligand to an olefin. The X-ray structure of 9 shows a most original asymmetric bidentate nitrato group : the terminal N-O bond is longer than the other two N-O's, which is contrary to what has so sfar been observed in nitrato complexes.

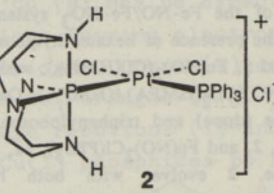
3-17 REACTIONS OF A CYCLENPHOSPHORANIDE PLATINUM (II) COMPLEX AND THE ROLE OF HIGHLY NUCLEOPHILIC SUBSTITUENTS AT THE AXIAL POSITIONS OF A TRIGONAL BIPYRAMID

DILIP V. KHASNIS, MICHAEL LATTMAN, AND UPALI SIRIWARDANE
Department of Chemistry, Southern Methodist University, Dallas, Texas 75275, USA

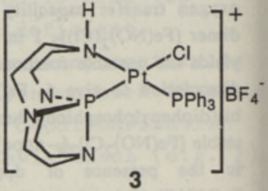
(η^2-cyclenP)Pt(Cl)PPh$_3$ **1** exhibits a large variety of selective reactions due to the platinum metal and cyclenphosphoranide ligand, cyclenP. Moreover, the cyclenP ligand is capable of altering many of the usual reactions and/or mechanisms at square planar platinum (II) complexes. The addition of HCl to **1** results in cleavage of the Pt-N bond and dual protonation at the axial positions of the cyclenP ligand yielding *cis*-[Cl$_2$Pt(H$_2$cyclenP)PPh$_3$]X **2**. Protonation of **1** using HBF$_4$, an acid with a noncoordinating anion, allows isolation of [(η^2-HcyclenP)Pt(Cl)PPh$_3$]BF$_4$ **3**, a complex in which cyclenP is ligated in the "open" form.



1



2



3

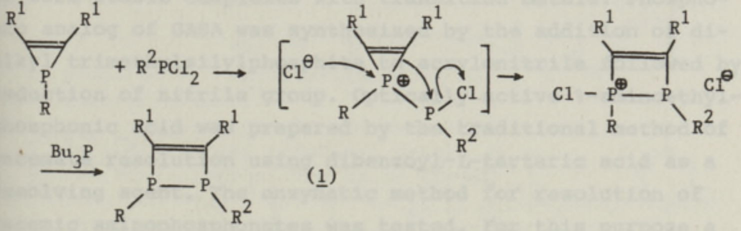
Further reaction of **3** with HCl yields [(H$_2$cyclenP)PtCl$_2$PPh$_3$]BF$_4$ **4**, which is the BF$_4$ salt of the cation of **2**. Treatment of **3** with another equivalent of HCl results in disproportionation, yielding **1** and **2**. While very strong electrophiles, such as the above protic acids, attack the cyclenP ring, nucleophiles lead to ligand substitution at platinum. For example, reactions of **1** with Na[Co(CO)$_4$], NaSMe, KI, and KBr, gave the chloride substitution products, (η^2-cyclenP)PtLPPh$_3$, where L = Co(CO)$_4$ **5**, SMe **6**, I **7**, and Br **8**. Neutral donors, on the other hand, appear to favor PPh$_3$ displacement: reaction of **1** with CH$_2$(PPh$_2$)$_2$ (dppm) led to (η^2-cyclenP)Pt(Cl)PPh$_2$CH$_2$PPh$_2$ **9**, in which the dppm is monodentate. No reaction was observed between **1** and HC≡CPh, even in refluxing THF. However, addition of NaBPh$_4$ to the reaction led to both P-N bond cleavage and Pt-C bond formation, yielding [(η^2-HcyclenP)Pt(C≡CPh)PPh$_3$]BPh$_4$ **10**.

3-18 THE CHEMISTRY OF 1,2-DIHYDRO-1,2-DIPHOSPHETES

FRANCOIS MATHEY, CLAUDE CHARRIER, NICOLE MAIGROT, LOUIS RICARD

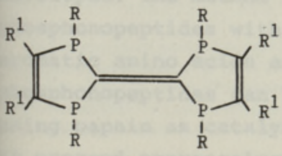
Laboratoire de Chimie du Phosphore et des Métaux de Transition
DCPH, Ecole Polytechnique, 91128 Palaiseau Cédex, France

For a long time, the preparation of 1,2-dihydro-1,2-diphosphetes (1) has remained a difficult task since no general and performing synthesis of these species was known. Recently, we have discovered a simple and general ring-expansion of phosphirenes by dichlorophosphines which affords 1,2-dihydro-1,2-diphosphetes with a variety of substituents :

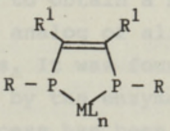


(1)

This discovery has allowed us to develop a systematic study of the chemistry of these interesting heterocycles. Starting with this ring, it has been possible to prepare some exciting new species such as tetraphosphafulvalenes (2) and 2,1,3-metalladiphospholenes (3)



(2)



(3)

We have also demonstrated that 1,2-dihydro-1,2-diphosphetes may act as masked 1,4-diphosphadienes under selected conditions.

3-19 COORDINATION CHEMISTRY OF UNSATURATED ORGANOPHOSPHORUS LIGANDS

John F. Nixon

School of Chemistry and Molecular Sciences
University of Sussex, Falmer, Brighton, BN1 9QJ UK.

The preparation of transition metal complexes containing η^1-, η^3- and η^5- ligated ($P_3C_2R_2$) ring systems will be described and structural features discussed. Spectroscopic properties (such as n.m.r., P.E. and Mössbauer) will be reported. Fluxional behaviour of the η^1- metal complexes will also be reported.

4-1 SYNTHESIS AND PROPERTIES OF AMINOPHOSPHONIC ACIDS AND PHOSPHONOPEPTIDES

V.P.KUKHAR and V.A.SOLODENKO

Institute of Bioorganic Chemistry of the Ukrainian Academy
of Sciences, Murmanskaya Str. 5, Kiev 252660, USSR

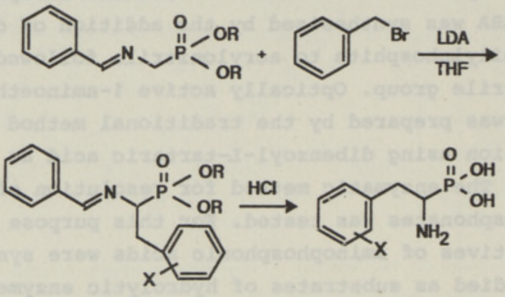
Phosphorus analogs of natural iminocarboxylic acid homoproline were prepared by the iminoalkylation of organophosphorus compounds containing P(O)H fragment with trimer of tetrahydropyridine. Some properties of these compounds were investigated. Piperidine-2-phosphonic acid was found to form stable complexes with transition metals. Phosphonic analog of GABA was synthesized by the addition of dialkyl trimethylsilylphosphite to acrylonitrile followed by reduction of nitrile group. Optically active 1-aminoethylphosphonic acid was prepared by the traditional method of racemate resolution using dibenzoyl-L-tartaric acid as a resolving agent. The enzymatic method for resolution of racemic aminophosphonates was tested. For this purpose a number of derivatives of aminophosphonic acids were synthesized and studied as substrates of hydrolytic enzymes. The results of this study are discussed. The method of phosphonopeptide synthesis using pivaloyl chloride was developed. The method was applied to obtain a number of phosphonopeptides with phosphonic analog of aliphatic and aromatic amino acids at P-terminus. It was found that phosphonopeptides can be obtained by the enzymatic route using papain as catalyst. The process has been determined to proceed stereoselectively in regard to aminophosphonates. The bioactive phosphonopeptide alafosfalin was obtained by this method. The application of enzymes as useful tools in the chemistry of aminophosphonic acids is discussed.

4-2 SYNTHESIS AND PROPERTIES OF 1-AMINO-2-ARYLETHYLPHOSPHONIC AND -PHOSPHINIC ACIDS AS WELL AS -PHOSPHINE OXIDES*

by Ludwig MAIER
CIBA - GEIGY Ltd., Division Agro, 4002 Basel, Switzerland

Abstract

The preparation, physical and spectroscopic properties of 1-amino-2-arylethylphosphonic- and -phosphinic acids as well as phosphine oxides, the phosphorus analogues of phenylalanine are described. A general synthesis of 1-amino-2-arylethylphosphonic acids consists in the treatement of the Schiff'base of aminomethyiphosphonates with a strong base and substituted benzylhalides, followed by hydrolysis.



1, X= F
2a, X= 2-CH_3
2b, X= 3-CH_3
2c, X= 4-CH_3

The reactions of 1-amino-2-(4-fluorophenyl)ethylphosphonates with acetals, isocyanides, esters, acids anhydrides, activated aromatic nitro- and halogen compounds, and with N-protected alanine are also reported.

It is shown that several of the 1-amino-2-arylethyl-phosphonic acids are strong inhibitors of PAL and anthocyansynthesis and also are quite active botryticides, the order of activity being comparable to the inhibition constants of PAL. Among the active compounds were 1-amino-2-(4-fluorophenyl)ethylphosphonic acid, 1, and the methylsubstituted compounds 2a, 2b and 2c. The fluoroderivative 1 was also effective as a seed dressing agent in barley showing a 100% protection against the fungus Fusarium nivale.

---

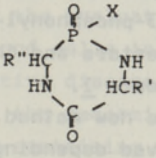
*Extended version of a lecture given at the First National Phosphorus Congress, Chinese Chemical Society, Beijing May 30 to June 2, 1988.

4-3 DIPEPTIDES OF α-AMINO ALKYLPHOSPHONIC ACID AND THEIR CYCLIC COMPOUNDS

Ru-yu Chen and Shi-cain Dan

Institute of Elemento-Organic Chemistry
Nankai University, Tianjin, PRC

In order to find out the biololgical activity of phosphonic peptides with P-C bond we synthesized a series of new compounds with the general formula $H_2NCH(CH_3)P(O)(OEt)NHCHR'COOR$ (I), where $R'=CH$, $R=CH_3$; $R'=H$, $R=C_2H_6$ and (II) where $R'=H, CH_3, CH_2PH$; $R''=CH_3$, $n-C_3H_7$, C_4H_9; $X=OEt$, Ph.


(II)

I was prepared (1) by esterification of $CbzNHCH(CH_3)P(O)(OH)_2$ (III) which was obtained by the reaction of benzoyl amide with acetaldehyde and triphenyl phosphite and carbobenzyloxylation of the amino group, (2) saponification of the diethyl ester of III to get its mono ester which was then converted into the corresponding phosphonyl chloride with thiony chloride followed by coupling with an α -amino acid ester and finally deprotection of the amino group with 5% Pd-C and H_2. The cyclophosphonodipeptides (II) were synthesized by reflux of I in n-butanol-toluene (3:1) solution for 30-60 hours. All the products have been confirmed by the elemental analysis and 'HNMR, IR, MS.

References:

(1) T.Hori; et al., J. Biol. Chem. 258,2239(1983).
(2) H. Seto; T. Sasak, J. Antibiotics, 98(1983).
(3) M. Yamuto; T. Koguchi, J. Antibiotics, 39(1), 44 (1986).
(4) W.J. Greenlee Teaneck; et al., U.S. Patent 4379146 (1983).

4-4 SYNTHESES AND STEREOCHEMICAL STUDIES OF P-ANALOGUES OF ASPARTIC ACID DERIVATIVES

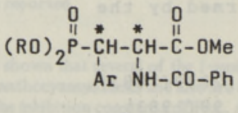
K. Kellner, C. Preußler, M. Dargatz

Martin-Luther-Universität Halle-Wittenberg
Sektion Chemie, Halle(S.), 4010, GDR

A simple approach is reported for the synthesis of both 3-phosphonyl-3-aryl-2-benzoylamino propionic acid esters and their derivatives by using a one-pot procedure 1.

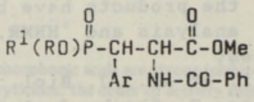
By the new method a diastereoselective reaction is observed depending on reaction conditions. Pure diastereoisomeres are isolated. Isomer assignments were made using an extensive data base of nmr spectra. In some cases x-ray analyses support the proposed structures.

The method allowed a large variation of substituents at the phosphorus atom 2, at the C-3 carbon atom 3 and at the carboxyl group 4 too.



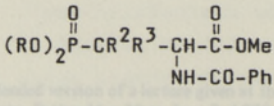
$(RO)_2\overset{O}{\overset{\|}{P}}-\overset{*}{\underset{Ar}{C}}H-\overset{*}{\underset{NH-CO-Ph}{C}}H-\overset{O}{\overset{\|}{C}}-OMe$

1



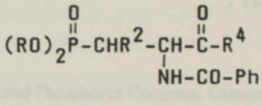
$R^1(RO)\overset{O}{\overset{\|}{P}}-\underset{Ar}{C}H-\underset{NH-CO-Ph}{C}H-\overset{O}{\overset{\|}{C}}-OMe$

2



$(RO)_2\overset{O}{\overset{\|}{P}}-CR^2R^3-\underset{NH-CO-Ph}{C}H-\overset{O}{\overset{\|}{C}}-OMe$

3



$(RO)_2\overset{O}{\overset{\|}{P}}-CHR^2-\underset{NH-CO-Ph}{C}H-\overset{O}{\overset{\|}{C}}-R^4$

4

4-5 ^{31}P NMR STUDY OF BIOLOGICAL STRUCTURES IN NORMAL AND PATHOLOGICAL STATE

L.A.SIBELDINA, U.EICHHOFF*, T.L.KNUBOVETS, N.A.SEMENOVA,
D.S.KHRISTIANOVICH, V.E.YUCHMANOV, and S.S.LIKHODIJ
Institute of Chemical Physics of the USSR Academy of Sciences, 4 Kosygin Str., Moscow 117977, USSR
*Bruker Analytische Messtechnik GmbH, Karlsruhe, W.Germany

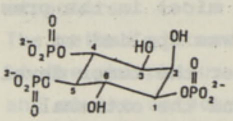
^{31}P NMR spectroscopy can be applied to studying a wide range of biological tissues and to solving various biomedical problems. ^{31}P NMR was applied for the evaluation of the functional activity of human red blood cells in the normal state and during lymphoproliferative diseases. ^{31}P NMR (a surface coil probe) was used for the determination of the change in the pool of phosphorus-containing metabolites in tumor cells at different stages of developing melanoma B-16 in mice in vivo. ^{31}P NMR was employed to study the kinetics of phosphorus-containing metabolites in tumor cells of ascite hepatoma 22 A (in mice) in the presence of antitumor antibiotics. ^{31}P NMR was applied to study the metabolic damage of liver under the tumor development (Leukemia La, Lymphoma L-1210) and the extremal exposures (administration of cycloheximide, high doses of adrenaline, etc.). ^{31}P NMR in vitro was applied to evaluate the phosphate compounds content in the native bile of patients with primary biliary cirrhosis, and of healthy subjects. ^{31}P NMR was employed to investigate the influence of cryoprotectants on the cellular energetics, and to assess the metabolic changes occurring during erythrocytes cryoconservation and subsequent preparation for the transfusion. ^{31}P NMR in vivo was used to study the dynamics of changes in the level of phosphorus-containing metabolites of rat brain under ischemia.

4-6 PHOSPHOROTHIOATE ANALOGUES OF MYO-INOSITOL 1,4,5-TRISPHOSPHATE

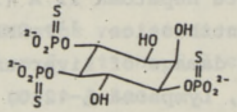
A.M. COOKE, L. JAMES AND B.V.L. POTTER

Department of Chemistry, University of Leicester,
Leicester, LE1 7RH, U.K.

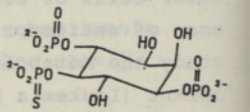
D-Myo-inositol 1,4,5-trisphosphate (IP$_3$, 1) is a biological second messenger which mediates the mobilisation of calcium from intracellular stores in stimulated cells. In order to investigate the biological actions of IP$_3$ we have chemically synthesized novel IP$_3$ analogues possessing phosphorothioate groups instead of phosphate groups. Thus, we have prepared myo-inositol 1,4,5-trisphosphorothioate (IPS$_3$, 2) and myo-inositol 1,4-bisphosphate-5-phosphorothioate (IP$_3$-5S, 3).



(1)



(2)



(3)

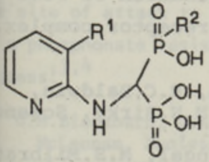
These compounds are of interest because the substitution of phosphorothioate for phosphate confers resistance to phosphatases. Thus, IP$_3$ and IP$_3$-5S are full agonists for calcium release, and only some 3-fold less potent than IP$_3$. However, these compounds are not degraded by the IP$_3$ specific 5-phosphatase, are the most potent competitive inhibitiors of this enzyme known and give rise to novel effects in biological systems. Additionally, we have prepared the novel analogue myo-inositol-1-phosphorothioate -4,5-bisphosphate, which should be of use in attaching reporter groups to IP$_3$ without markedly affecting calcium-releasing ability. The synthesis and novel biological effects of these analogues will be discussed.

4-7 THE DESIGN AND SYNTHESIS OF BONE ACTIVE PHOSPHINIC ACID ANALOGUES: I. THE PYRIDYLAMINOMETHANE PHOSPHONOALKYLPHOSPHINATES

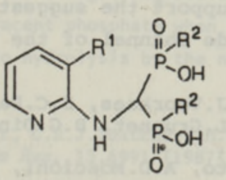
Frank H. Ebetino and Laura A. Jamieson

Product Development, Norwich Eaton Pharmaceuticals, Inc.
A Procter and Gamble Company
P.O. Box 191, Norwich, N.Y. 13815

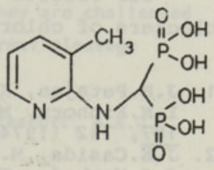
In the last 20 years the bisphosphonic acids and their salts, the bisphosphonates, have been the subject of study by a number of research groups for their marked ability to modulate bone metabolism. We have recently designed a related novel class of bone active agents, the pyridylaminomethane phosphonoalkylphosphinates I! The preparation and biological evaluation of phosphinic acid analogues of the known bisphosphonates is discussed. Initially, the pyridylaminomethane bisphosphinic acid analogues II were demonstrated to be inactive as inhibitors of the bone metabolic processes of mineralization and resorption. However, the pyridylaminomethane phosphonoalkylphosphinates were shown in subsequent studies to have good antiresorptive activity despite exhibiting greatly reduced bone affinity as compared to the analogous bisphosphonic acids III. This novel discovery, subsequent analogue preparation, and a novel synthetic sequence to the pyridylaminomethane phosphonoalkylphosphinate series is discussed. A brief description of the biological and physical chemical activity of these analogues is also included.



Ia $R^1=CH_3$, $R^2=CH_3$
Ib $R^1=H$, $R^2=CH_3$
Ic $R^1=CH_3$, $R^2=n$-butyl
Id $R^1=CH_3$, $R^2=$phenyl-butyl



IIa $R^1=CH_3$, $R^2=CH_3$
IIb $R^1=CH_3$, $R^2=n$-butyl
IIc $R^1=H$, $R^2=CH_3$
IId $R^1=H$, $R^2=n$-butyl



III

4-8 PHOSPHOTRIOXABICYCLOOCTANES, A NEW GROUP OF PHOSPHORUS COMPOUNDS WITH HIGH TOXICITY

S.RUMP and W.RASZEWSKI
Department of Pharmacology and Toxicology, Military Institute of Hygiene and Epidemiology, Kozielska 4, 01-163 Warszawa, Poland

In the early seventies there were reported severe poisonings due to smoke inhalation of combustion products of a fire retarded polyurethane foam.[1] In the next years the chemical structure of these toxic agents were established and some of them were synthesized in the laboratory.[2] These agents were called phosphotrioxabicyclooctanes (PTBO) or bicyclic organophosphates, and they produce severe convulsions which led to death.

PTBO have no inhibitory influence on acetylcholinesterase and it was suggested they are specific blockers of GABA receptors. Therefore it was supposed that GABA-mimetics should demonstrate a therapeutic effect in these poisonings. Some classic anticonvulsants, as barbiturates, should be proved also.

It was shown that the highest antidotal potency exhibits diazepam. Progabide (a GABA-mimetic) and phenobarbital have rather small therapeutic value in these poisonings Diazepam blocked also almost immediately the convulsive activity due to PTBO.

Our results support the suggested mechanism of PTBO as blockers of chloride channel of the GABA receptor complex.

1. J.H.Petajan, K.J.Voorkees, S.C.Packham, R.C.Baldwin, I.N.Einhorn, M.L.Grunnet, B.G.Dinger, M.N.Birky, Science 187, 742 (1974).
2. J.E.Casida, M.Eto, A.D.Moscioni, J.L.Engel, M.S.Milbrath, J.G.Verkade, Toxicol. Appl. Pharmacol. 36, 261 (1976).

4-9 SYNTHESES AND ENZYMIC STUDIES ON ISOSTERIC AND ISOPOLAR PHOSPHONATE ANALOGUES OF BIS(5'-ADENOSYL)-P^1,P^4-TETRAPHOSPHATE, ApppppA, USING THE SPECIFIC ApppppAases FROM *ARTEMIA* AND *E.COLI*

G.MICHAEL BLACKBURN, ANDRZEJ GURANOWSKI, MAO-JUN GUO,
SANY McLENNAN* and GRAHAM E.TAYLOR
Department of Chemistry, Sheffield University, Sheffield S3 7HF, U.K.
**Biochemistry Department, Liverpool University, Liverpool L69 3BX, U.K.*

We have recently reported the synthesis and separation of three diastereoisomers of diadenosine 5',5'''-P^1,P^4-(P^1,P^4-dithio-P^2,P^3-methylene)-tetraphosphate ($Ap_spCH_2pp_sA$) and demonstrated their resistance to hydrolysis by and competitive inhibition of the *asymmetrical*-NppppNase from *Artemia*[1] while Guranowski *et al.*,[2] have studied the ability of four phosphonate analogues of ApppppA to act as substrates and inhibitors of the lupin and *E.coli* NppppNases, lupin phosphodiesterase 1, and the yeast ApppppA phosphorylase.

We have now synthesised a wider range of phosphonate analogues of ApppppA having CHF, CF_2, CCl_2, and CH_2CH_2 bridges in the $P^1,P^2,(P^3,P^4)$- and P^2,P^3-positions in the tetrapolyphosphate chain to give both isosteric and isopolar analogues. These compounds have been studied as modified substrates for the ApppppAases from *Artemia* and *E.coli*. The results give some mechanistic insights into the nature of the enzyme-catalysed mechanism of hydrolysis. Unexpectedly, they show that these enzymes can manifest changed regioselectivity by adapting the site of attack to an adjacent phosphate when they are challenged by a phosphonate resistant to hydrolysis by the normal cleavage process![3,4]

1. G.M.Blackburn, G.E.Taylor, G.R.J.Thatcher, M.Prescott, & A.G. McLennan, *Nucleic Acids Res.*,15,6991 (1987).
2. A.Guranowski, A.Biryukov, N.B.Tarussova, R.M.Khomutov, & H.Jakubowski, *Biochemistry*,26,3425 (1987).
3. A.G.McLennan, G.E.Taylor, M.Prescott, and G.M.Blackburn, *Biochemistry*, submitted for publication.
4. A.Guranowski, E.Starzynska, G.E.Taylor, and G.M.Blackburn, *Biochem.J.*, submitted for publication.

4-10 SYNTHETIC POLYPHOSPHONATES, POLYPHOSPHATES, AND PHOSPHONOCARBOXYLATES AS ALLOSTERIC EFFECTORS OF HEMOGLOBIN

D. Currell, H. Goldwhite, S. Lim, and N. Patel

Department of Chemistry and Biochemistry, California State University, Los Angeles, 5151 State University Drive, Los Angeles, California 90032, U. S. A.

The effects of alkane diphosphonic and some triphosphonic acids on the oxygen affinity of human hemoglobin were determined and compared with those of the naturally occurring effectors 2,3-diphosphoglycerate, ATP, and ADP. Alkane diphosphonic acids were more active effectors than phosphonocarboxylic acids, but less active than the naturally occurring phosphates. Of the alkanediphosphonic acids studied the most active was ethane 1,2-diphosphonic acid. While nitrilotris(methylene)triphosphonic acid was a more active effector than ethane 1,2-diphosphonic acid, the apparently similar tris(phosphonomethyl)phosphine oxide produced an increase in oxygen affinity of hemoglobin. Inorganic triphosphate and diphosphate were more powerful effectors than ATP and ADP respectively. Inorganic triphosphate was almost as powerful an effector as the naturally occurring 2,3-diphosphoglycerate.

4-11 FROM MOLECULAR CONFORMATION TO PHOSPHOLIPID BILAYER ORGANIZATION

K.S.BRUZIK, G.M.SALAMOŃCZYK, B.SOBOŃ

Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, 90-362 Łódź, Poland

The organization of phospholipid bilayer assembly is thought to be mainly ruled by the balance of the phospholipid headgroup polarity, its size and the hydrophobicity of fatty acid in the 1,2-diacylglycerol or ceramide moiety. Our present work on the stereoisomers of sphingomyelin: D-erythro- and L-threo-2,N-stearoylsphingosyl-1-phosphocholine and their phosphorothioyl analogues suggests, that the morphology and the dynamics of the bilayer is also affected by the more subtle factors, such as the conformation of the headgroup of the monomeric phospholipids. The two stereoisomers of sphingomyelin were shown to differ in their headgroup dynamics. The natural D-erythro-sphingomyelin displayed hindered rotation about C1-C2 bond of sphingosine, rendering its phosphocholine headgroup more rigid than this of analogous L-threo-sphingomyelin.

The results obtained by means of differential scanning calorimetry, wideline ^{31}P nmr spectra and solid-state high resolution ^{13}C nmr spectra of both isomers indicate the existence of highly ordered rigid gel phase in the case of D-erythro-sphingomyelin. L-threo analogue behaves in a similar fashion to a saturated lecithins.

The effect of cholesterol on the formation of the rigid gel phase was also studied. The substitution of the phosphoryl oxygens with sulfur had much more serious consequences in D-erythro- than in L-threo- series.

These results provide and evidence for control of the phospholipid bilayer morphology, among other factors, by the conformation of the unaggregated phospholipid molecule.

4-12 PHOSPHOLIPASE A_1 ACTIVITY AND CATALYTIC MECHANISM OF PANCREATIC CHOLESTEROL ESTERASE

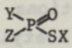
D. M. Quinn,[a] L. D. Sutton,[a] J. S. Stout[a] and H. S. Hendrickson[b]

[a]Department of Chemistry, The University of Iowa, Iowa City, Iowa 52242, USA. [b]Department of Chemistry, St. Olaf College, Northfield, Minnesota 55057, USA

Pancreatic cholesterol esterase (CEase) catalyzes the hydrolysis of fatty acyl ester bonds of emulsified lipids (triacylglycerols, cholesteryl esters and phospholipids) in the intestinal tract, and is necessary for the absorption of cholesterol and other dietary fats. We have investigated the phospholipase A_1 mechanism of CEase by using mixed micelles of triton X100 and di(decanoylthio)phosphatidylcholine as substrate. The interfacial Michaelis Menten parameters are $k_{cat} = 0.8 \pm 0.1\ s^{-1}$ and $K_m = 17 \pm 2$ mole%. The k_{cat} is within a factor of two of that for CEase-catalyzed hydrolysis of mixed micellar *p*-nitrophenyl decanoate, a reaction that is rate limited by acylenzyme turnover. Hence, the phospholipase A_1 activity must be similarly rate limited by hydrolysis of the decanoyl-CEase intermediate. Solvent isotope effects for k_{cat} and k_{cat}/K_m of 2.3 ± 0.1 and 3.6 ± 0.3, respectively, are consistent with chemical transition states for acylation and deacylation that are stabilized by general acid-base catalysis. Proton inventory experiments further indicate that CEase stabilizes the acylation transition state by multifunctional proton transfer catalysis. These results and those for CEase-catalyzed hydrolysis of lipid *p*-nitrophenyl esters are interpreted in terms of a serine esterase catalytic mechanism. This mechanism serves as the basis for the rational design of CEase inhibitors that may prove useful in preventing intestinal absorption of dietary lipids, particularly cholesterol. Such inhibitors include phosphates, enolphosphates, haloketones, boronic and borinic acids, and carbamates.

4-13 QSAR IN REACTIONS OF ORGANOPHOSPHORUS INHIBITORS WITH ACETYLCHOLINESTERASE

AAVO AAVIKSAAR
Laboratory of Bioorganic Chemistry, Institute of Chemical Physics and Biophysics of the Estonian Academy of Sciences, Tallinn 200026, P.O.Box 670, USSR

Structure-activity relationships in inhibition of acetylcholinesterase by organophosphorus compounds  $\mathrm{(Y)(Z)P(=O)SX}$ have been analyzed using the equation $\log k_i = C + \rho\sigma + \phi\pi$ (1) with Taft σ^* for substituent electronegativity and Hansch π for hydrophobicity. The results show that the influence of the leaving group -SX is characterized by extremely high ρ values ($\rho^* > 4$), remarkable bulk tolerance and moderate ϕ values ($\phi = 0.6$–0.8) while the effect of positive charge in X does not appear in $\phi\pi$-term if the charged atom is separated from -S- by more than one $-CH_2-$ group. The influence of the phosphoryl part is characterized by ρ close to the values of alkaline hydrolysis of the compounds ($\rho^* \sim 2$) while the hydrophobic sensitivity coefficient ϕ is about two-fold of that for the leaving group. The direct applicability of eq. (1) for the phosphoryl part is, however, limited to substituents not exceeding the length of four $-CH_2-$ groups. The obtained relationships have been used in optimizing the structures of organophosphorus inhibitors for their maximum anticholinesterase activity.

4-14 COMPARATIVE STUDY OF NUCLEOPHILIC AND ENZYMIC REACTIONS OF 2-PROPYL METHYLPHOSPHONATE DERIVATIVES

Ildiko M. Kovach and Andrew J. Bennet
University of Kansas, Center for Biomedical Research,
2099 Constant Avenue, Lawrence, Kansas 66045 USA

Second-order rate constants and solvent isotope effects have been measured for the reactions of 4-nitrophenyl 2-propyl methylphosphonate (IMN) with acetylcholinesterase (AChE), chymotrypsin, imidazole base, hydroxide ion, phosphate dianion, and water. Second-order rate constants were also measured for the reactions of 2-propyl methyl phosphonofluoridate (sarin) with AChE and imidazole along with the solvent isotope effect for the former. The solvent isotope effects in this study are all very small (1.1 - 1.4), except for the reaction with hydroxide ion, indicative of nucleophilic attack on IMN by the nucleophiles and rate determining steps involving a diminished contribution of general base catalysis in the enzymic cases. The solvent isotope effect for the reaction of IMN with hydroxide ion was 0.94 ± 0.02 and the transition state fractionation factor of 0.5, based on an overall fractionation factor of 0.45-0.50 for hydroxide ion in the ground state, is consistent with a small loss of the solvent-shell around the hydroxide nucleophile from reactant to transition state. Removal of the 2-propyl group from 2-propyl methylphosphonyl AChE occurs with an isotope effect of 1.2 ± 0.06 indicative of preprotonation of the isopropyl group before water attack. The rate of dealkylation is very similar with chymotrypsin. A refinement of the X-ray crystallographic coordinates of trypsin-diisopropylphosphate (DIP) with molecular mechanics program YETI shows the dealkylation taking place from the "up" position. The organophosphorus compounds in this study have proven to be good probes of the active-site characteristics of serine hydrolase catalysis.[1]

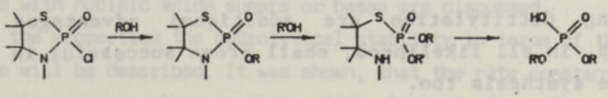
1. I.M.Kovach, J. Enzyme Inhib. 2, 199 (1988).

4-15 SYNTHESIS AND REACTIVITY OF FIVE-MEMBERED CYCLIC PHOSPHORYLATING REAGENTS AND OTHER AUXILIARIES FOR THE SYNTHESIS OF OLIGONUCLEOTIDES

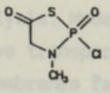
I. UGI, R. HERRMANN, P. JACOB, M. KLEIN, B. LANDGRAF, P. LEMMEN and W. RICHTER

Institute for Organic Chemistry of the
Technical University Munich
D-8046 Garching, FRG

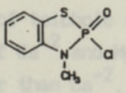
The five-membered cyclic phosphorylating reagents are up to 10^7 times more reactive than their acyclic analogs. For the synthesis of oligonucleotides such reagents of type 1 have some attractive features. The synthesis of 1a - c as representatives of the reagents 1 and their behaviour in phosphorylations according to 1 -> 2 -> 3 -> 4 is reported, including the relative rates of the individual reactions and the selective removal 3 -> 4 of the thiol protective group. Further, the use of oxaziridines 5 as (Tos = p-toluenesulfonyl, Ar = e.g. p-nitrophenyl) oxidizing agents for the P(III) intermediates of nucleotide syntheses by the phosphite method is described; the oxaziridines can also be used under anhydrous condition.



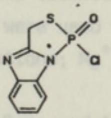
1 2 3 4



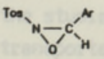
1a



1b



1c



5

4-16 (4-NITRO-α-PYRIDYL) METHYL PHOSPHORO-BIS-TRIAZOLIDE: A NEW PHOSPHATE PROTECTING GROUP IN OLIGONUCLEOTIDE SYNTHESIS

(Mrs) K.MISRA, (Mrs) G.WATAL, (Mrs) R.SRIVASTAVA

Nucleic Acids Laboratory, Chemistry Department,
Allahabad University, Allahabad 211 002, INDIA

(4-nitro α- pyridyl)-methyl phosphoro-bis-triazolide has been used successfully for phosphorylating all the four 5'-and N-protected deoxynucleosides at 3'-hydroxyl group. The phosphorylation is carried out in the presence of 1-methyl imidazole as catalyst and is quantitative in all the four cases. No symmetric dimers were detected. The resulting 3'-phosphorylated derivatives were obtained in the form of cyanoethyl derivatives or triethyl-ammonium salts, both being fairly stable. A dimer, T_pT, was prepared by condensing 5'-O-DMTr-T-3'-O-(4-nitro-α-pyridyl)-methyl phosphorotriazolide and thymidine-3'-O-acetate in the presence of triisopropylbenzenesulphonyl chloride (TPSCl) with and without the calalyst i.e. 1-methyl imidazole. The coupling yield above 95% with reduced coupling time (5-8 minutes) indicated the autocatalytic effect of the group. The easy removal of the group with 1,1,3,3-tetramethyl guanidinium syn-4-nitrobenzaldoximate (15 minutes) and no cleavage of the internucleotide bond or depurination/modification of base during detritylation are additional advantages. The group, in all likelihood, shall prove successful in solid phase synthesis too.

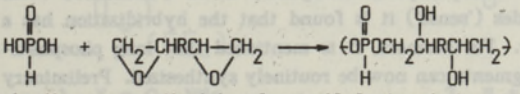
4-17 POLY(ALKYLENE PHOSPHATE)S RELATED TO NUCLEIC AND TEICHOIC ACIDS

PAWEŁ KŁOSIŃSKI and STANISŁAW PENCZEK

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

This paper consists of three parts. In the first one a short survey of these Authors' contribution to the syntheses of the bioanalogues polymers is given, summarizing the previously published reviews (1,2). Thus, ring-opening polymerization, polyaddition of diepoxides to the phosphorous and phosphoric acid or their silyl esters, as well as polycondensation methods are described. These methods, based on the known and new (addition of silyl phosphates to epoxides) reactions, allowed for the first time to prepare high molecular polyphosphates, with backbones similar to these in nucleic acids and teichoic acids.

The second part describes the newly elaborated methods, mostly polyaddition of H_3PO_3 to diepoxides, not applied till now for the polymer synthesis:



$$\mathrm{HO\overset{O}{\underset{H}{P}}OH} + \mathrm{\underbrace{CH_2\text{-}CH}_{O}R\underbrace{CH\text{-}CH_2}_{O}} \longrightarrow \mathrm{(O\overset{O}{\underset{H}{P}}OCH_2\overset{OH}{C}HR\underset{OH}{C}HCH_2)}$$

Another new method involves silyl phosphates.

In the final part, transformations of these polymers, and some of their properties and applications are described. Particularly transformation of polyphosphites into polyphosphates by oxidation, synthesis of the polyphosphate - polypeptide conjugates, as well as polyphosphates with nucleic acids sugars or bases are discussed.

Among the properties the hydrolytical stability in terms of the pH profile will be described. It was shown, that the rate constants of hydrolysis are very close to these of the low mol.wt. analogues, although, the rate constants are functions (decrease) of the extent of hydrolysis. Models of teichoic acids were used for the studies of the active transport of Ca^{+2} and Mg^{+2} cations; Mg^{+2} is transported in liquid membranes faster than Ca^{+2}.

(1) S.Penczek, G.Łapienis, P.Kłosiński, Pure and Appl.Chem., 56,1309 (1984).
(2) S.Penczek, G.Łapienis, P.Kłosiński, Phosphorus and Sulphur, 27, 153(1986).

4-18 PHOSPHATE-METHYLATED DNA FRAGMENTS INVOLVED IN PARALLEL AND ANTIPARALLEL DUPLEX FORMATION. NOVEL ASPECTS OF STRUCTURE, STABILITY AND BIOLOGICAL ACTIVITY

H.M. BUCK, M.H.P. VAN GENDEREN, H.M. MOODY and L.H. KOOLE

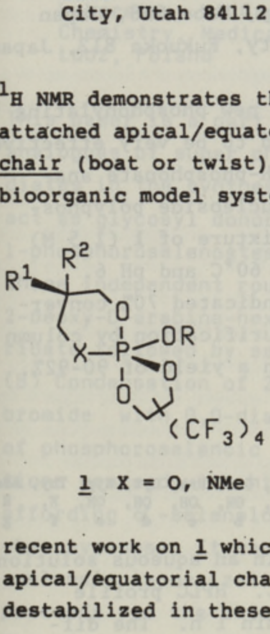
Department of Organic Chemistry, Eindhoven University of Technology. P.O. Box 513, 5600 MB Eindhoven, The Netherlands.

A parallel duplex of the phosphate-methylated DNA dimer d(CpC) is described. This duplex is formed exclusively for the S_P configuration, since inward location of the methyl group (R_P) encounters severe steric interactions in the groove. It is found that complexation with polylysine (side chains $-(CH_2)_4-NH_3^+$) results in a parallel duplex for natural $d(T_{10})$ and also for natural $d(C_{10})$. Polyornithine (shorter side chains $-(CH_2)_3-NH_3^+$) also induces a parallel duplex for $d(T_{10})$, but not for $d(C_{10})$. It is concluded that C-C base pairing can occur only upon complexation of the protein in such a way that exclusively pro-S oxygens of the DNA phosphates are used. For antiparallel duplexes of phosphate-methylated DNA ('antisense') with natural polynucleotides ('sense') it is found that the hybridization has a cooperative character. Furthermore, it is mentioned that long phosphate-methylated DNA fragments can now be routinely synthesized. Preliminary experiments revealed that these systems specifically inhibit DNA replication in vitro. Thus, phosphate-methylated DNAs are potentially useful as a new class of antisense antiviral or cytostatic agents.

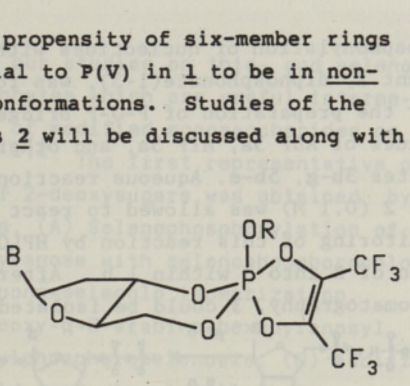
4-19 CONFORMATIONS OF BIOORGANIC P(V) CYCLIC NUCLEOTIDE MODEL COMPOUNDS

W. G. BENTRUDE, J. H. YU, and A. E. SOPCHIK
Department of Chemistry, University of Utah, Salt
Lake
City, Utah 84112, USA

^{1}H NMR demonstrates the propensity of six-member rings attached apical/equatorial to P(V) in 1 to be in non-chair (boat or twist) conformations. Studies of the bioorganic model systems 2 will be discussed along with recent work on 1 which suggests that the apical/equatorial chair conformation is intrinsically destabilized in these structures.



1 X = O, NMe

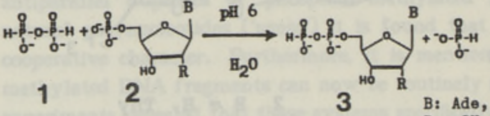


2 B = H, Thy

4-20 A NEW AND VERSATILE APPROACH TO THE PREPARATION OF H-PHOSPHONATE ANALOGUES FOR ADP AND ATP

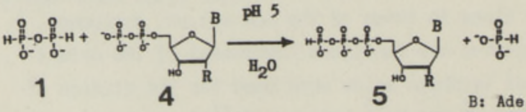
<u>Y. BABA</u>, M. TSUHAKO[a], and N. YOZA[b]
Chemical Laboratory, Faculty of Education, Oita University, Dannoharu, Oita 870-11, Japan
[a]Kobe Women's College of Pharmacy, Kobe 658, Japan
[b]Dept. of Chem., Kyushu University, Fukuoka 812, Japan

Phosphonylation of nucleotides with a new phosphonylating agent **1**, diphosphonate(1-3), was found to be very effective for the preparation of P-O-P bridged H-phosphonate analogues of ADP **3a**, ATP **5a**, and other nucleoside polyphosphates **3b-g**, **5b-e**. Aqueous reaction mixture of **1** (1.5 M) and **2** (0.1 M) was allowed to react at 60°C and pH 6. Monitoring of this reaction by HPLC indicated 70% conversion of **2** into **3** within 1 h. After purification by column chromatography, **3** could be isolated in a yield of 90-92%.



B:	Ade,	Gua,	Ura,	Cyt,	Hyp,	Thy,	Ade
R:	OH,	OH,	OH,	OH,	OH,	H,	H
	a	b	c	d	e	f	g

Reaction of **1** (1.8 M) with **4** (0.1 M) in an aqueous solution at 60°C and pH 5 was monitored by HPLC. HPLC profile showed 56% conversion of **4** into **5** within 1 h. The difference in yield between **3** and **5** is attributable to the different charges on **2** and **4**, because more negatively charged **4** is slowed by charge repulsion in attacking **1**.



B:	Ade,	Gua,	Ura,	Cyt,	Thy
R:	OH,	OH,	OH,	OH,	H
	a	b	c	d	e

(1)Y. Baba et al., <u>Nucl. Acids Res.Symp.Ser.</u>, <u>17</u>, 69(1986).
(2)Y. Baba et al., <u>Chem. Lett.</u>, <u>1987</u>, 1389.
(3)Y. Yamamoto et al., <u>Bull.Chem.Soc.Jpn.</u>, <u>61</u>, 3217(1988).

4-21 SELENONO-SELENOLO ISOMERISATION OF 2-DEOXYGLYCOSYLPHOSPHOROSELENOATE. SYNTHETIC AND MECHANISTIC ASPECTS.

M. MICHALSKA, J. BOROWIECKA, P. LIPKA and T. ROKITA-TRYGUBOWICZ

Laboratory of Organic Chemistry, Institute of
Chemistry, Medical Academy, Muszyńskiego 1, 90-151
Łódź, Poland

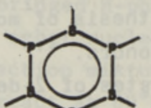
This paper is a part of our studies on thio- and seleno analogues of sugar phosphates which are useful intermediates in the synthesis of modified monosaccharides or act as glycosyl donors. [1,2] The first representative of 1-phosphoroselenoates of 2-deoxysugars was obtained by three independent routes. (A) Selenophosphorylation of 2-deoxy-D-arabino-hexopyranose with selenophosphorochloridate followed by selenono-selenolo isomerization. (B) Condensation of 2-deoxy-α-D-arabino-hexopyranosyl bromide with O,O-dialkylphosphoroselenoate. (C) Addition of phosphoroselenoic acid to D-glucal. All these reactions proceed with high yield and full stereoselectivity affording α-selenolophosphate of 2-deoxy-D-arabino-hexopyranose. It was demonstrated that the selenono-selenolo isomerization which takes place in route (A) proceeds via the intermediate 2-deoxyglycosyl chloride. This finding confirms the mechanism proposed by Chabrier et al. [3,4] for selenono-selenolo phosphates isomerization catalysed by ammonium halides.

(1) W. Kudelská, M. Michalska, Tetrahedron 42, 629 (1986).
(2) J. Borowiecka, P. Lipka, M. Michalska, Tetrahedron 44, 2067 (1988).
(3) N.P. Nguyen, N.T. Thuong, P. Chabrier, C.R. Acad. Sci., Ser. C 272, 1145 (1971).
(4) N.P. Nguyen, N.T. Thuong, P. Chabrier, C.R. Acad. Sci., Ser. C 272, 1588 (1971).

5-1 SYNTHESIS AND REACTIONS OF BORON-PHOSPHORUS RING COMPOUNDS

H.V.R. DIAS and P.P. POWER
Department of Chemistry, University of California, Davis, California 95616, U.S.A.

Treatment of an organoborondihalide RBX_2 with two equivalents of a lithium salt of a primary phosphide, LiPHR', has resulted in the isolation and characterization of boron-phosphorus analogues of borazine (1) as illustrated

$2LiPHR' + RBX_2 \longrightarrow 1/3$  $+ H_2PR' + 2LiX$

A range of these 6-membered rings involving various R and R' groups has been isolated. Various spectroscopic, structural and reactivity studies show that they probably possess considerable aromatic character. In addition, the use of larger R and R' substituents has permitted isolation of the anti-aromatic 4-membered ring species. The physical and chemical properties of the ring species as well as the possible mechanism of formation and the structures of intermediates will be discussed.

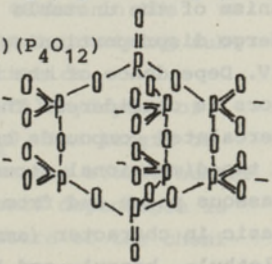
(1) H.V.R. Dias, P.P. Power. Angew. Chem. Int. Ed. Engl. 26, 1270 (1986).

5-2 MAIN TYPES OF CONDENSED PHOSPHATES OF ALCALINE AND TRIVALENT METALS OBTAINED FROM POLYPHOSPHORIC ACID MELTS

H.Grunze, N.N.Chudinova*, and I.Grunze
Central Institute of Inorganic Chemistry of the GDR
Academy of Sciences, Rudower chausee 5, Berlin 1199, GDR
*N.S.Kurnakov Institute of General and Inorganic Chemistry,
Academy of Sciences of the USSR, Leninsky pr. 31, Moscow
117907, USSR

Some characteristics of reactions between polyphosphoric acid melts (PAM) and metal oxides are considered. These reactions result in production of different condensed phosphate types having chain as well as ring and branch anions. Recently the number of condensed phosphate types has increased sharply due to the synthesis of double phosphates. For example, a lot of ring phosphates containing anions with up to twelve phosphorus atoms were obtained. Anion-mixed phosphates were synthesized. Until now no double ultraphosphates were known. In this paper the synthesis and structure of double sodium and trivalent metal ultraphosphates $Na_3M^{III}P_8O_{23}$, which contain anions formed by three hexaphosphate rings with two common vertexes (figure), are reported. All known types of double condensed phosphates of alcaline and trivalent metals obtained from PAM are classified.

Diphosphates: $M^IM^{II}(H_2P_2O_7)_2$, $M^IM^{III}H_3(P_2O_7)_2$, $M^IM^{III}P_2O_7$
Triphosphates: $M^IM^{III}HP_3O_{10}$
Anion-mixed compounds: $M^IM_2^{III}(H_2P_3O_{10})(P_4O_{12})$
Polyphosphates: $M^IM^{III}(PO_3)_4$
Cyclotetraphosphates: $M^IM^{III}P_4O_{12}$
Cyclohexaphosphates: $M_3^IM_3^{III}(P_6O_{18})_2$
Cyclooctyphosphates: $M_2^IM_2^{III}P_8O_{24}$
Cyclododecaphosphates: $M_3^IM_3^{III}P_{12}O_{36}$
Ultraphosphates: $M_3^IM^{III}P_8O_{23}$



Conditions of synthesis, structures, and thermal transformations of above mentioned compounds are discussed. Possible fields of application are reported briefly.

5-3 ION EXCHANGE AND SORPTION PROCESSES AS METHODS OF SYNTHESIS OF DOUBLE PHOSPHATES AND INTERCALATED COMPOUNDS

V.LUTSKO

Scientific Research Institute for Physicochemical Problems,
Byelorussian State University, Leningradskaya Str. 14,
Minsk 220080, USSR

Anhydrous acid phosphates of polyvalent metals with a three-dimensional structure are known to demonstrate no ion-exchange properties in the solution. The analysis of the available data as well as our investigations permit to draw the conclusion that the display of the ion-exchange properties by these salts can be provoked by increasing their proton mobility. We have studied the interaction of the following acid phosphates with the melts of alkaline metals: $MHPO_4$(I), $MH_2P_2O_7$(II), M=Mg,Ca,Sr,Ba; $PbHPO_4$(III), $Ca_2HP_3O_{10}$(IV); $BaH(PO_3)_3$(V); β-$FeHP_2O_7$(VI), α-,β-,γ-$MnHP_2O_7$(VII), $MNH_4HP_3O_{10}$(VIII), M=Al,Cr; $H_2MP_3O_{10}\cdot 2H_2O$(IX), M=Al,Ga,V,Cr,Mn,Fe; $GeHP_3O_{10}$(X). The medium of the melts has provided both the necessary heating of the systems and the possibility to realize the exchange processes. The studies were carried out by thermoanalytical methods: DTA, TGA, DTGA and DSC. The reaction products were studied by chemical analysis, chromotography, X-ray powder diffraction, IR- and Raman spectroscopy. It was shown that the exchange reactions occur with the formation of double phosphates in the systems with I-IV, VI-X. The formation mechanism of the unstable substituted compounds which then undergo disproportioning takes place in the system with II, IV. Dependence of the reaction mechanism on different factors is considered. The possibility of preparation of intercalated compounds on the basis of the acid salts with a two-dimensional structure IX by means of sorption from gaseous phase and from solutions of the products which are basic in character (ammonia, methyl-, ethyl-, dimethyl-, diethyl-, benzyl- and hydroxylamine, hydrazine, ethyl-, phenylhydrazine) has also been investigated.

5-4 CRYSTAL CHEMISTRY OF CONDENSED PHOSPHATES OF TRIVALENT METALS

K.K.PALKINA
Kurnakov Institute of General and Inorganic Chemistry of the USSR Academy of Sciences, 31 Leninsky pr., Moscow 117907, USSR

X-ray diffraction studies of binary condensed phosphates with trivalent and alkali metals of the $M^{I}M^{III}(PO_3)_4$ type were carried out. On the basis of the obtained data a quantitative criterion was established for evaluating the probability of the formation of anions in the form of simple chains, complex chains and cyclic structures.

On the basis of an analysis of the atomic structure of binary phosphates of rare-earth elements and alkali metals, the characteristic structural peculiarities were established. Thus, polyhedrons LnO_n are completely isolated from one another, while the shortest distances between the cations Ln-In are sufficiently large to account for the increase in the probability of emission transition of Nd^{3+} ions from a metastable state.

The ultraphosphate of iron and sodium, $Na_3FeP_8O_{23}$, is of special interest. The anion has an unusual structure being in the form of three linked hexacycles of mutually isolated oligomers. Because of the large Fe-Fe distances (7.29 Å) and the absence of a symmetry center in the crystal, one can regard this compound as a promising substance to be used in quantum microelectronics.

In the new type of compounds, crystalohydrytes of rare-earth hypophosphates, in $HP_2O_6 \cdot nH_2O$, the length of the P-P bond is found to be dependent on the atomic number of the lanthanide. Elucidation of the said dependence is of basic importance for studying the nature of the chemical bond in the $(P_2O_6)^{4}$-anion.

5-5 ON THE MECHANISMS OF REACTIONS OF Me(II)-PHOSPHATES IN THE SOLID STATE

K.-H.JOST, M.SCHNEIDER, and H.WORZALA
Zentralinstitut für anorganische Chemie der Akademie der Wissenschaften der DDR, DDR-1199 Berlin Rudower Chaussee 5

The aim of this contribution is to report on the results of investigations of topotactic reactions in the systems $PbO-P_2O_5-H_2O$ and $CaO-P_2O_5-H_2O$ and cautiously to draw conclusion on the mechanisms of the respective reactions on an atomic scale.

In both the systems starting from the 4-Hydrate of the cyclotetraphosphates the polyphosphates are formed in a series of crystallographically oriented steps. While the starting compounds for Pb and Ca have different crystal structures the final products are isotypic. Similar series of reactions are originating from the dihydrogenmonophosphates.

Progress of the reactions was pursued by high-temperature Guinier-photographs and TG, anion constitution of the intermediate products by paper chromatography, orientation relations between respective educt and product crystals by single crystal X-ray methods. Conclusions on reaction mechanisms were drawn from comparison of the structures.

Results: The crystallographically oriented course of the reactions rests on taking over layer- and chain-like structural units of $Me(II)O_x$-polyhedra from the educt into the product structure. Moreover it was shown that orientation relations can be transfered via an "amorphous" intermediate phase. Large atoms are staying on their positions during reaction if possible. In order to follow this principle these atoms partly have to change their chemical function, e. g. oxygen, originally bonded to phosphorus becomes water oxygen and vice versa.

5-6 CRYSTAL CHEMISTRY OF CYCLOPHOSPHATES

A. DURIF

Laboratoire de Cristallographie, associé à l'Université J. Fourier, C.N.R.S.,
166 X, 38042 Grenoble Cédex, France.

The chemistry of cyclophosphates has been very long to develop for two main reasons : the lack for a long time of appropriate starting materials authorizing the elaboration of general methods of preparation and the necessity of a proper structural characterization to verify the true nature of the condensed anion. For this second reason one can observe that the development of this chemistry is parallel to the evolution of the X-ray techniques of crystal structure determination. Examining successively the main types of cyclophosphates presently well investigated we present a survey of this field insisting on the main steps of its development and its possibilities for the future. In such a short summary it is not possible to review all types of cyclophosphates ; let us briefly examine as a typical exemple the evolution of the cyclohexaphosphates chemistry. The first structural evidence for the existence of the P_6O_{18} ring anion was given by Jost [1] in 1965 and the same year was reported by Griffith and Buxton [2] a process authorizing the production of a convenient starting material, $Li_6P_6O_{18}$. In spite of this opportunity only three cyclohexaphosphates have been clearly characterized during the following twenty years and in addition all of them have been discovered by indirect methods : study of phase equilibrium diagram as $Cu_2Li_2P_6O_{18}$, systematic studies of various sytems by flux method... In 1985 Shulke and Kayser [3] reported an important improvement of the Griffith–Buxton process. Then Averbuch–Pouchot [4] described the chemical preparation and a complete structural characterization of the silver salt, $Ag_6P_6O_{18}.H_2O$, opening so the way for the preparation of water soluble cyclohexaphosphates by a process of metathesis deriving of the Boulle method. Since this date more than twenty new cyclohexaphosphates both organic and inorganic have been prepared and clearly characterized within a period of time of less than a year. Finally we examine some possibilities to avoid in the future such delays between the publication of a fundamental process and its use for systematic investigations.

[1] JOST K.H.
Acta Cryst., (1965), **19**, 555–560.

[2] GRIFFITH E.G. and BUXTON R.L.
Inorg. Chem., (1965), **4**, 549–551.

[3] SHULKE U. and KAYSER R.
Z. anorg. allg. Chem., (1985), **531**, 167–176.

[4] AVERBUCH–POUCHOT M.T.
Z. Kristallogr. (in Press).

5-7 TOPOCHEMISTRY OF CONDENSED PHOSPHATES

E.A. PRODAN
Institute of General and Inorganic Chemistry of the Belorussian Academy of Sciences, Surganova Str. 9, Minsk
220606, USSR

The structure and reactivity of condensed phosphates, kinetics and reaction mechanisms of phosphates with chain-type and ring-type anion structure is studied. Dehydration of crystal hydrates and hydration of anhydrous salts, deammoniation of ammonium salts and ammoniation of acid salts, disproportionation of acid salts, anion degradation, and anion condensation is compared in solid state and in aqueous solutions, in low viscous and high viscous oily phases, in amorphous and crystalline phases, on the surface and in the bulk of crystals, and on different crystal faces of a single crystal. For chain triphosphates the following sequence, in which the anion degradation rate raises and the stability of linear anion goes down, is established: crystalline phase, aqueous solution, amorphous phase, high viscous oily phase. On the basis of the obtained results it is possible to synthesize some crystalline double salts that previously have been obtained only in amorphous state, for example the crystalline double salt $NH_4Mg_2P_3O_{10}\cdot6H_2O$ and its amorphous analogue $NH_4Mg_2P_3O_{10}\cdot7H_2O$, the crystalline $NH_4Mn_2P_3O_{10}\cdot5H_2O$ and the amorphous $NH_4Mn_2P_3O_{10}\cdot6H_2O$. Synthesis conditions for a new class of crystalline chain trihydrogentriphosphates, for $Na_5P_3O_{10}\cdot6D_2O$ crystals, and for epitaxially grown $(NH_4)_5P_3O_{10}\cdot2H_2O$ crystals are discussed. The data on interaction kinetics of neutral and acid chain triphosphates of sodium or potassium with water vapour and gaseous ammonia can be used to obtain granular sodium salts and crystalline salts of potassium-ammonium.

5-8 PROTONIC CONDUCTION AND O-H BONDING STATE IN PHOSPHATE GLASSES

Y. ABE, H. HOSONO, and T. KAMAE,

Department of Materials Science and Engineering,
Nagoya Institute of Technology, Showa-ku, Nagoya 466,
Japan

Protonic conduction in glasses has attracted much attention as the search for developing fast proton conductive glasses. It was found that protons in alkaline-earth phosphate glasses give extremely high proton mobility than those in silicate glasses. This is caused by the difference in O-H bonding state; the protons in P-O-H form a strong hydrogen bonding, resulting in formation of weak O-H bond. The electrical conductivity at 417 K($10^3/T=2.4$)(σ)and the activation energy (E)in alkaline-earth phosphate glasses were found to be expressed by the following equations (1) and (2), respectively.

$$\sigma = A_0 [H^+]^2 \quad ....(1)$$

$$E = E_0 + E_1 \quad ....(2)$$

where, $[H^+]$ is proton concentration(in mol/l), E_0 is activation energy at $[H^+]=1$, and E_1 is an activation energy depending on proton concentration. The constant A_0 was found to decrease with V_{OH} as in eq.(3).

$$\log A_0 = -0.00937\ V_{OH} + 17.1 \quad ....(3)$$

where V_{OH} is peak wavenumber of IR absorption band due to O-H stretching vibration mode(around 2600~3000 cm^{-1} for phosphate glasses depending on the O-H bonding strength). The reason why protons are more mobile rather than alkali or Ag+ ions in phosphate glasses is clarified in this work.

5-9 BINARY CYCLO-TETRAPHOSPHATES AS A NEW SPECIAL PIGMENTS

M.TROJAN, D.BRANDOVÁ and P.MAZAN

Institute of Chemical Technology, Lenin sqr. 565,
Pardubice, 532 10 Czechoslovakia

A number of new compounds of binary cyclo-tetraphosphates of the type of $Me^{II}_{2-x}M^{II}_{x}P_4O_{12}$ have been prepared in our laboratories, especially such as cyclo-tetraphosphates of bivalent metals (Me^{II} is e.g. Zn, Mn, Co), where a part of Me ion is replaced by more inexpensive calcium or magnesium (M^{II} ions). First the products are synthetized as pure substances, which is based on the preparation of glass semiproducts of binary higher linear phosphate type. These products are thermally recrystallized to the cyclo-tetraphosphates. After evaluation of the products by analytical and physico-chemical methods, experiments were carried out with the aim of their possible synthesis by more frasible low-temperature processes, based on dehydration of a suitable starting mixture. It seems that in the case of binary cyclo-tetraphosphates containing calcium it is possible to prepare the requested product only with in a closed range of x (where $x \in (0; 1 >)$ where as binary products with magnesium exist in the whole range x, i.e. $x \in (0; 2)$. The products have been tested as special inorganic pigments and especially as new anticorrosive pigments, luminiscent and pearlescent pigments, and colour pigments for high-temperature purposes.

5-10 DYNAMIC CRYSTALLOCHEMISTRY OF APATITE

R.G.Knubovets
Institute for Mined Raw Materials, Oktjabrskii 259,
Moscow-Lyubertsy 140000, USSR

Apatite $(Ca_{10}(PO_4)_6)Fe_2$ is situated on the border between organic and inorganic materials, this being one of the main reasons of the exceptional dynamics of the mineral's structure. Every atom in natural apatite is characterized by at least two crystallochemical positions. Hydroxyl groups form hydrogen bonds with other anions located on hexagonal axis. Partial condensation of orthophosphate groups to pyrophosphates also takes place in natural apatites. The fluorine content plays the main role in the regulation of orthophosphate condensation in the apatite: integral intensity of bridge bonds P-O-P vibrational bands depend in the extreme fashion on the fluorine concentration. Carbonate ions are always found in mineralogical apatites where they are located in the positions of orthophosphate groups and on the hexagonal axis. The distribution of atoms between various sites in the structure depends on the crystallization conditions and the "history" of the mineral. The intrinsic mobility of anions from one crystallochemical position into another in the structure takes place during thermal treatment of apatite. The quantity of fluorine on the hexagonal axis has a decisive influence on this mobility, adjacent medium also produces a marked effect. Physical and physico-chemical properties of apatites depend on different distribution of atoms between various crystallochemical positions. Technological properties of phosphate rocks are markedly determined by structural peculiarities and dynamics of the apatite lattice.

5-11 THERMAL TRANSFORMATIONS IN SYSTEMS BASED ON NATURAL APATITES

M.Veiderma, T.Kaljuvee, R.Knubovets*, M.Põldme, K.Tõnsuaadu

Tallinn Technical University, ESSR

*Research Institute for Mined Raw Materials, Moscow, USSR

Calcination is widely used in benefication and processing of phosphate rock. In order to control these processes efficiently, the mechanism of the reactions involved and the phase transformations should be carefully studied and the existing experimental data generelized.

The present study deals with thermal transformations in systems based on the main types of natural apatites, fluorapatite, fluorcarbonateapatite and fluorhydroxyapatite, under the conditions of solid state processes of thermal benefication of phosphorites as well as of manufacturing thermal feed and fertilizer phosphates. The systems contained both natural impurity minerals (quartz, carbonates, silicates, pyrites, etc.) and specially introduced additives (H_3PO_4, Na_2CO_3, etc.). Experiments were carried out in the medium of air and inert gases as well as in a mixture of gases. The methods used included chemical, thermal, IR-spectroscopic and x-ray analyses, electronmicroscopy, paper chromatography, etc.

The results of the experiments revealed thermal structural transformations in apatite, the character of competitive reactions, and the conditions of decomposition and interaction of the components of the systems. Intermediate and endproducts were indentified and the quality of the products determined. Dependence (sometimes also the possibility of realization) of the processes on the existence and quantity of impurity minerals in the rock and on the composition of the gas phase has been shown, as well as the necessity to observe carefully the proposed optimum parameters of the processes.

5-12 CALCIUM PHOSPHATE COATING OF TITANIUM PLATE

T.UMEGAKI, S.YAMADA, Y.HISANO, K.YAMASHITA and T. KANAZAWA

Department of Industrial Chemistry, Faculty of Technology,
Tokyo Metropolitan University, 2-1-1, Fukasawa, Setagaya,
Tokyo, 158 Japan

Calcium phosphate films were prepared on Ti plate by electrophoretic deposition and radiofrequency sputtering. The composition and structure of the films so obtained were studied by means of X-ray diffraction, IR and XPS. Hydroxyapatite films (10-50mg/cm^2) were formed on Ti plate when the voltage gradient of 60-100 v/cm was applied to the suspension of the apatite powder(5-10g/l) in alcohols and amides. The mixtures of alcohols and amides were the most appropriate dispersive solvents for electrophoresis. After heat treat of electrophoretically deposited films under reduced pressure, phosphorus atoms diffused into Ti plate and the surface of the apatite layer lack of phosphate appeared. Thin calcium phosphate films containing condensed phosphates were obtained on Ti plate and some other substrates by sputtering when the calcium phosphate glass was used as a target. The ratios of Ca/P of the sputtered layers were about 1.5-1.6, which were larger than that of the calcium phosphate glass target(about 0.5). Phosphorus-rich layers were found at the top surfaces of the calcium phosphate films obtained after the sputtering(0.5-30 hr). The chemical shifts of O 1s and Ti 2p spectra for the sputtered films were observed, which indicated the films consisted of compounds with various oxidation states of Ti.

5-13 DIRECTIONAL SOLIDIFICATION OF THE CaO-P_2O_5 BIOCERAMIC-GLASSES

Jaw-Chay Perng and Chin-Wang Huang
Department of Chemistry, Chung-Yuan Christian University, Chung-Li, Taiwan, R.O.C.

Calcium phosphate glass-ceramics were prepared by reheating the glass rods between 675° and 750°C under a temperature gradient of ~100°C/cm. Floating zone method and silicon carbide furnace was made use to crystallizing the glass. The crystalline phases occured as long fibers aligned parallel to the growth direction of the specimen. The spacings between the fibrous phases were smaller than 1 μm and very uniform.

Microstructure of the crystalized phases was examined by scanning electron microscope. Crystalline phases and crystallography were checked by X-ray diffraction.

5-14 ON THE NUCLEOPHILIC DEGRADATION OF PHOSPHORUS CHALCOGENIDES WITH ADAMANTANE-LIKE STRUCTURE BY FLUORIDES

M. MEISEL

Zentralinstitut für anorganische Chemie der Akademie
der Wissenschaften der DDR, Rudower Chaussee 5,
Berlin 1199, DDR

There are two possibilities of the course of degradation reaction of the adamantane-like structures of phosphorus chalcogenides:

- reorganization which causes change of constitution and structure of compounds in the reaction system without change of the gross composition
- directed degradation yielding only some definite reaction products according to a clear mechanism

Which of these two reaction types will be realized strongly depends on influences like temperature, reaction medium, physical and chemical properties of the primary formed products.
A typical reorganization process is the melting or solid state reaction of alkali or ammonium fluoride with P_4O_{10} forming mixtures of oligomeric fluorophosphates.

The reaction behaviour of $P_4O_6S_4$ is quite different. Thus, it is impossible to obtain only fluoro monothiophosphates via a melting process, because as a result of sulfur-oxygen exchange in addition to the monothio derivatives sulfur-free and dithiophosphates are formed. But, in glacial acetic acid as reaction medium $P_4O_6S_4$ reacts with NH_4F to difluoro monothiophosphate and trithio cyclotriphosphate whereas with KF the predominant formation of monofluoro monothiophosphate is observed.

P_4S_{10} reacts with fluorides or hydrogenfluorides in solution depending on the cation and the molar ratio F:P either to difluoro pentathiodiphosphate, $P_2S_5F_2^{2-}$, or to difluoro dithiophosphate, $PS_2F_2^-$. The latter can be obtained in a very easy way by melting KHF_2 or NH_4HF_2 with P_4S_{10} in the corresponding molar ratio.

In generalization of the results some reaction mechanisms of nucleophilic degradation of the phosphorus chalcogenides under different conditions are discussed.

5-15 SYNTHESES OF NITROSONIUM AND NITRONIUM SALTS BY THE REACTION OF OXIDES OF NITROGEN WITH PHOSPHORUS TRIFLUORIDE AND THIOPHOSPHORYL FLUORIDE

R.G. KALBANDKERI and D.K. PADMA

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

The oxides of nitrogen (N_2O_3, N_2O_4 and N_2O_5) are found to react with phosphorus trifluoride and thiophosphoryl fluoride at room temperature or slightly below room temperature to form nitrosonium and nitronium salts ($NOPF_6$, $NOPO_2F_2$, $NO_2PO_2F_2$, NO_2PF_6, $NOPS_2F_2$, $NOPSOF_2$, $NO_2PS_2F_2$, NO_2PSOF_2). These salts are stable in an inert atmosphere and decompose on exposure to moisture. They have been characterised by their infrared spectral data and their capacity to nitrate benzene at room temperature.

5-16 CRYSTALLINE NITRIDOPHOSPHATES OBTAINED BY THERMAL REACTIONS

W. Feldmann
Akademie der Wissenschaften der DDR, Zentralinstitut für Anorganische Chemie, DDR-1199

We have found two new types of polymeric crystalline nitridophosphates:

$[Na_nP_nO_{3n-3}N_2]_x$ and $[M^I{}_3M^{III}P_3O_9N]_x$ and
$[M^I{}_2M^{II}{}_2P_3O_9N]_x$

<u>A</u> <u>B</u>

with n = 4; 5; 6, M^I = Na; K, M^{III} = Al; Ga; Fe; Cr;Mn, M^{II} = Mg; Co,

which can be obtained by thermal reactions using phosphates or phosphorus-nitrogen-compounds $[Na_3P_3O_6(NH_3)_3 \cdot H_2O$; $(PON)_x]$ as sources of phosphorus and besides these P-N-compounds as sources of nitrogen a great deal of nitrogen compounds with N having the oxidation number -3, e.g. urea, cyanuric acid, aluminium nitride. The salts of type <u>A</u> are sparingly soluble in water, whereas the compounds of type <u>B</u> with the formula $[M^I{}_3M^{III}P_3O_9N]_x$ are insoluble even in boiling solutions of concentrated acids and alkali hydroxides with the exception of boiling sulphuric acid. $[Na_2Mg_2P_3O_9N]_x$ is soluble in concentrated hydrochbric acid with decomposition.

5-17 NON-ENZYMATIC PHOSPHATE CONDENSATION IN DILUTE AQUEOUS MEDIA--THE EFFECT OF ALKYL SUBSTITUENTS ON SULFAMIDE

DAVID R. GARD

Detergents and Phosphates Division
Monsanto Chemical Company
St. Louis, Missouri, USA 63167

Sodium triphosphate undergoes intramolecular cyclocondensation to trimetaphosphate in mildly alkaline solutions of sulfamide. This reaction is the first known example of non-enzymatic, net formation of a P-O-P linkage in dilute aqueous solution. The reactions of alkyl substituted sulfamides with sodium triphosphate and diphosphate are examined to determine the reaction requirements concerning the relative location of amino-hydrogen atoms on the sulfamide molecule. N-Butylsulfamide and N,N-dimethylsulfamide react with sodium triphosphate to yield sulfamate and dimethylsulfamate, respectively, along with trimetaphosphate. With sodium diphosphate, N-butylsulfamide reacts to yield $BuNH-P_2O_6^{3-}$ and sulfamate. N,N-Dimethylsulfamide reacts with sodium diphosphate to give $H_2N-P_2O_6^{3-}$ and dimethylsulfamate. The N,N'-dimethylsulfamide exhibits no reaction with either the triphosphate or the diphosphate, indicating one unsubstituted $-NH_2$ group on the sulfamide is required for reaction. The reactions are proposed to proceed via an unstable intermediate containing a $-SO_2-N-PO_2-$ linkage which decomposes to a sulfamate and an amidophosphate. Amidotriphosphates cyclize to the more readily observed trimetaphosphate. The unusual substitution pattern of the sulfamates vs. the starting sulfamides is explained by a facile irreversible intramolecular rearrangement.

5-18 REACTIONS OF AMINO ACIDS WITH COMPLEX TRIMETAPHOSPHATES - A ROUTE TO PEPTIDE SYNTHESIS

C.K.Oza
Chemical Laboratories, University of Rajasthan, Jaipur,
India 302 004

The present investigations describes the reactions of glycine and dl-alanine with metal trimetaphosphates.

The reactions of glycine and dl-alanine with metal trimetaphosphates (in 1:1 molar ratios) were carried out at pH 12. The various peptide and N-polyphosphate derivatives were separated and identified by thin-layer chromatographic technique. The peptide-N-phosphate and dipeptide-N-phosphate derivatives were obtained in maximum yield after 48 hours. The yields of dipeptides (dialanine and diglycine) increases steadily and attains constancy after 7 days. On the other hand the concentration of dipeptide--N-tripolyphosphate, which is obtained in higher yields in the initial period of the reaction, decreases and attains constancy after the same period. The effects of metal ions, on the formation of peptides have also been investigated. It has been found that the yields of various peptide derivatives formed follow the order

$$Ni^{+2} > Cu^{+2} > Na^{+}$$

and it has been ascribed to their datalytic activity order. The metal ions catalyse the hydrolysis of the cyclic acyl phosphoramidate as well as-N-phosphates. The chelation by metal ions must result in an increased nucleophilicity of phosphorus atoms and consequent attack by CH^{-} ions and hence it can be suggested that cation catalyse the peptide formation due to their chelation with triphosphate moiety. This explains the higher yields of dipeptide in presence of Ni^{+2} ions. Probable mechanism of the reaction has also been discussed.

5-19 CHEMISTRY OF DOUBLE AND INDIVIDUAL PHOSPHATES AND POLYPHOSPHATES OF DIVALENT METALS

L.SHCHEGROV, N.Antrapatseva, and V.Kopilevich
Ukrainian Agricultural Academy, Geroev Oborony Str. 15,
Kiev 252041, USSR

The problems of formation of double and individual hydrated divalent metal phosphates of different protonization level are discussed. The results of the systematic experimental research done with the purpose of determining the possibility, production conditions and nature the double hydrated phosphates Mg - M^{II} (M^{II} = Mn, Co, Cu, Zn) are reviewed. The production conditions and the performance of double dihydrophosphates of composition $Mg_{1-x}Mn_x(H_2PO_4)_2 \cdot 2H_2O$, $Mg_{1-x}Co_x(H_2PO_4)_2 \cdot 2H_2O$ and $Mg_{1-x}Zn_x(H_2PO_4)_2 \cdot 2H_2O$ ($0 < x < 1{,}00$) are presented. The composition of synthesized double hydrophosphates is described in the formulas $Mg_{1-x}Mn_xHPO_4 \cdot 3H_2O$ ($0 < x < 1{,}00$), $Mg_{1-x}Co_xHPO_4 \cdot 3H_2O$, $Mg_{1-x}Zn_xHPO_4 \cdot 3H_2O$. The hydrophosphates of magnesium-manganese form a continuous range of solid substitution solutions. The solid solution composition boundary line of hydrophosphates of magnesium-cobalt and magnesium-zinc is determined. Is is shown that the double average phosphates Mg - M^{II} (M^{II} = Co, Zn) form the limited series of solid substitution solutions. With the use of a complex of modern physical and chemical methods investigations of the individuality of all produced double phosphates is shown, their composition and the sphere of exsistence are determined, the main characteristics are defined. Formation conditions of some hydrated copper phosphates ($Cu_2OHPO_4 \cdot 0{,}2H_2O$, $CuHPO_4 \cdot H_2O$, $Cu_3(PO_4)_2 \cdot 2H_2O$ and $Cu(H_2PO_4)_2 \cdot 2H_2O$) are described. They are obtained on the basis of phosphoric acid and copper hydroxocarbonate.

5-20 THE COMBUSTION OF PHOSPHORUS - ON THE FORMATION MECHANISM OF THE MOLECULAR PHOSPHORUS OXIDES

D. HEINZ

Sektion Chemie, Humboldt-Universität zu Berlin
Hessische Str. 1-2 , Berlin 1040 , GDR

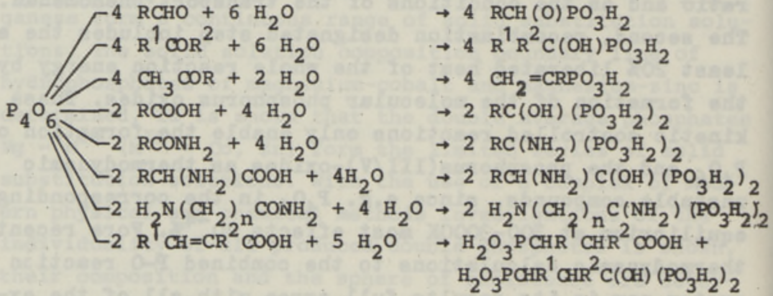
Experimental results and theoretical studies show the combustion of phosphorus as a hot flame process to be suitable for the formation of the molecular phosphorus oxides as P_4O_6, P_4O_7, P_4O_8, P_4O_9, P_4O_{10}, optional only depending on the O_2/P_4 ratio. The combustion process is characterized by a two step reactionflow essentially. The first step at temperatures of 2000-2600 K is founded on the formation of an emitting ensemble of $(PO)_2^*$, PO_2^* and hypothetical PO_3^* as a very fast reaction, followed by the combination to P_2O_3, P_2O_4 or P_2O_5 in dependence on the O_2/P_4 ratio and on the conditions of the transport phenomenon. The second, recombination designated step includes the at least 20% liberated heat of the whole reaction energy by the formation of the molecular phosphorus oxides. These kinetic controlled reactions only enable the formation of P_4O_6 and the phosphorus(III/V)-oxides as thermodynamic unstable compounds, since e.g. P_4O_6 in the corresponding equilibrium at 300-3000K most effects 10^{-4}%. Fore recent thermodynamic calculations to the combined P-O reaction system, now in its results full agree with all of the experimental results.

The phosphorus(III/V)-oxides and P_4O_6 in solid states undergo polymerization to form glasslike substances by thermal energy exposure, along with reorganization, variation of the composition and decreasing the vapor pressure of the resulting polymers. The energy of activation e.g. of the decomposition of P_4O_6 was found near 70 kJ/mol.

5-21 PHOSPHONYLATION BY TETRAPHOSPHORUS HEXOXIDE

U. SCHÜLKE
Central Institute of Inorganic Chemistry of the Academy of Sciences, Rudower Chaussee 5, Berlin 1199, GDR

Tetraphosphorus hexoxide, P_4O_6, is a colourless, hygroscopic substance (m.p. 28,8°C, b.p. 175,4°C), soluble in most inert organic solvents. Above 400°C it is quickly decomposed to phosphorus(III/V)-oxides, P_4O_{7-9}, phosphorus suboxide, P_4O, and phosphorus. Nucleophiles, as water, alcohols or amines, react with P_4O_6 to phosphorous acid, polymeric phosphorous acids, trivalent phosphorus esters and -amides, respectively. Electrophiles, as carbonyl compounds, yield C-P compounds. The general usefulness of P_4O_6 as phosphonylation agent for the preparation of phosphonic acids is demonstrated in the following equations:



$$
\begin{array}{lll}
 & 4\ RCHO + 6\ H_2O & \rightarrow 4\ RCH(O)PO_3H_2 \\
 & 4\ R^1COR^2 + 6\ H_2O & \rightarrow 4\ R^1R^2C(OH)PO_3H_2 \\
 & 4\ CH_3COR + 2\ H_2O & \rightarrow 4\ CH_2{=}CRPO_3H_2 \\
P_4O_6 & 2\ RCOOH + 4\ H_2O & \rightarrow 2\ RC(OH)(PO_3H_2)_2 \\
 & 2\ RCONH_2 + 4\ H_2O & \rightarrow 2\ RC(NH_2)(PO_3H_2)_2 \\
 & 2\ RCH(NH_2)COOH + 4H_2O & \rightarrow 2\ RCH(NH_2)C(OH)(PO_3H_2)_2 \\
 & 2\ H_2N(CH_2)_nCONH_2 + 4\ H_2O & \rightarrow 2\ H_2N(CH_2)_nC(NH_2)(PO_3H_2)_2 \\
 & 2\ R^1CH{=}CR^2COOH + 5\ H_2O & \rightarrow H_2O_3PCHR^1CHR^2COOH + \\
 & & \quad H_2O_3PCHR^1CHR^2C(OH)(PO_3H_2)_2
\end{array}
$$

R = organyl

The reaction conditions and mechanisms of the phosphonylation of some carbonyl compounds by P_4O_6 are discussed.

5-22 ELECTRICAL PROPERTIES OF SILVER PHOTODOPED AMORPHOUS RED PHOSPHORUS

K.KAWASHIMA, J.Z.DING, H.HOSONO and Y.ABE

Department of Materials Science and Engineering,
Nagoya Institute of Technology,
Gokiso-cho, Showa-ku, Nagoya 466, Japan

Effects of photodoping and thermal doping of silver into sputtered amorphous red phosphorus films (a-P_{red}) on the electrical properties are studied. The specimen films were prepared by evaporating and depositing silver on the a-P_{red} film. When the specimen film is illuminated by Xe-light, increase in the optical transmission of the specimen is observed with the illumination time. SIMS measurement of the depth profile of silver in the photodoped film used in this experiment gives no concentration gradient of silver. The d.c. electrical conductivity of the photodoped a-P_{red} at room temperature is about 1×10^{-5} S cm^{-1} which is a very high value comparing with that of the undoped a-P_{red} (1×10^{-14} S cm^{-1}). The activation energy for the conduction of the photodoped a-P_{red} is lower than that of the a-P_{red}. In contrast, the activation energy of the thermally doped a-P_{red} is essentially the same as that of the undoped a-P_{red}. EDX results show that colloidal silver was deposited in the thermally doped a-P_{red} but not in the photodoped a-P_{red}. It seems that the photodoping involves the ionization process of silver by illumination, i.e., $Ag^0 \xrightarrow{h\nu} Ag^+ + e^-$. The photodoping rate increased with increasing oxygen partial pressure in the atmosphere. Oxygen plays a role as the electron acceptor in this process.

5-23 SYNTHESIS AND REACTIVITY OF NEW PHOSPHORUS-NITROGEN AND PHOSPHORUS-NITROGEN-BORON CONDENSATION MONOMERS

Charles E. Davis, Rahim Hani, David L. Jinkerson, Purnendu Mukherjee, Gary M. Scheide, Christopher E. Wood, and Robert H. Neilson

Department of Chemistry, Texas Christian University, Fort Worth, TX 76129, USA

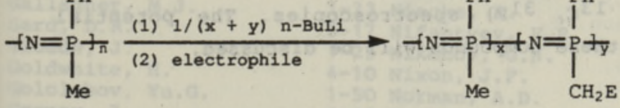
The synthesis of cyclic and polymeric phosphazenes that are fully substituted with P-alkyl/aryl side groups can be readily accomplished via the thermal decomposition of P-functional N-silylphosphoranimines, $Me_3SiN{=}P(X)R_2$. Some of our recent studies of this condensation polymerization reaction, the phosphoranimine precursors, and the phosphazene products are reported, including: (1) the effect of the leaving group (X) on the polymerization/cyclization process, (2) the synthesis and characterization of several new poly(dialkylphosphazenes), $[R_2PN]_n$ and $[(Me)RPN]_n$ (e.g., R = n-Pr, n-Bu, n-Hex), and some of the related cyclic analogues, (3) the synthesis (via Peterson olefination reactions) and polymerization of several vinyl-substituted precursors, and (4) the solubility, acid/base, and thermal properties of these types of phosphazenes. As part of a related study of potential synthetic routes to tractable, linear B-N and/or P-N-B-N polymers, we have prepared a series of new phosphorus-(III) and -(V) derivatives of the 1,3,2-diazaboracyclohexane ring system. The synthesis and structural characterization of several of these P-N-B-N compounds are reported.

5-24 NEW POLYMERS DERIVED FROM POLY(METHYLPHENYLPHOSPHAZENE)

P. Wisian-Neilson, R. R. Ford, S. Ganapathiappan, M. S. Islam, K. S. Raguveer, M. A. Schaefer, and T. Wang

Department of Chemistry, Southern Methodist
University, Dallas, TX 75725, USA

Poly(alkyl/arylphosphazenes) are a relatively new class of phosphazenes that have all substituents attached to the phosphazene backbone by direct P-C linkages. Unlike most polyphosphazenes, in which the polymer backbone is formed through a ring opening process, these alkyl and aryl substituted polymers are accessible only through a condensation polymerization process. In order to extend the range of properties of the poly(alkyl/arylphosphazenes), we have been studying the derivatization reactions of these preformed polymers. For example, poly(methylphenylphospha-zene), $[Me(Ph)P{=}N]_n$ is easily derivatized by deprotonation/substitution reactions that involve sequential treatment of the polymer with *n*-BuLi and electrophiles such as substituted chlorosilanes, aldehydes and ketones, and carbon dioxide. Graft copolymers have also been prepared by using the anionic polymer intermediate to initiate anionic addition polymerization of styrene, $CH_2{=}C(Ph)H$, and ring opening polymerization of hexamethylcyclotrisiloxane, $[Me_2SiO]_3$. The synthesis, characterization, and properties of these new polyphosphazenes will be discussed.



$$-\!\!\left[N{=}\underset{Me}{\overset{Ph}{P}}\right]_n \xrightarrow[\text{(2) electrophile}]{\text{(1) } 1/(x+y) \text{ n-BuLi}} -\!\!\left[N{=}\underset{Me}{\overset{Ph}{P}}\right]_x\!\left[N{=}\underset{CH_2E}{\overset{Ph}{P}}\right]_y$$

$E = SiMe_2R$; $R = Me, H, CH{=}CH_2, (CH_2)_3CN$
$E = C(OH)RR'$; $R = H, Me$; $R' = Me, Ph$, ferrocenyl, thiophenyl
$E = COOH, COOCH_2C_6H_4NO_2$
$E = [CH_2C(Ph)H]_zH, [Me_2SiO]_zSiMe_3$

5-25 ORGANO PHOSPHAZENES: PREPARATION AND STRUCTURE DETERMINATION OF SOME REACTIVE DIFUNCTIONS-TERMINATED TETRA(PHENOXY)CYCLOTRIPHOSPHAZENES

Y. W. Chen-Yang, S. Fan and B. D. Tsai

Department of Chemistry, Chung Yuan Christian University
Chung-Li, Taiwan 32023, R. O. C.

In order to incorporate the phosphazene ring system onto a traditional organic polymer, it is valuable to prepare some difunctions-terminated cyclotriphosphazene compounds as potential precursors for this purpose. In this study, the reactions of $N_3P_3Cl_6$, (I), with $NaOC_6H_5$ and the salt of proper functional alcohol were carried out successively. And with proper mole ratio and reaction order the nongeminal difunctions-terminated tetra(phenoxy)cyclotriphosphazenes, $N_3P_3(OC_6H_5)(OY)_2$, where OY = OC_6H_4CHO, $OC_6H_4CH_2OH$, and $OCH_2C{\equiv}CH$, were obtained as major product with good yields. Hence the aldehyde-terminated phosphazene, $N_3P_3(OC_6H_5)_4(OC_6H_4CHO)_2$, (II), was prepared by reaction of (I) with $NaOC_6H_5$ and followed by reaction with $NaOC_6H_4CHO$. Compound II was then reduced to the hydroxy-terminated phosphazene compound III, $N_3P_3(OC_6H_5)_4(OC_6H_4CH_2OH)_2$. On the other hand, the terminal acetylene phosphazene compound IV, $N_3P_3(OC_6H_5)_4(OCH_2C{\equiv}CH)_2$, was synthesized by reaction of (I) with $NaOCH_2C{\equiv}CH$ first and followed by reaction with $NaOC_6H_5$. The structures of compounds II, III and IV were determinated by the combination of Mass spectroscopy, Elemental Analysis, IR and NMR(^1H, ^{13}C, ^{31}P) spectroscopies. The potential applications of these compounds will be discussed.

LECTURES

Академия наук Эстонской ССР, Институт химической и биологической физики. XI Международная конференция химии фосфора. Тезисы докладов. На английском языке.
Toimetaja M.Pank. Trükkida antud 11.05.89 MB-04436. Paber 60x84/16. Trükipoognaid 9,50. Tingtrükipoognaid 8,83. Arvestuspoognaid 6,59. Trükiarv 750. Tellimuse nr. 131. Hind 1.30. ENSV TA rotaprint, 200001 Tallinn, Estonia pst. 7.