Tetrahedron Vol. 37, pp. 437 to 472
Pergamon Press Ltd., 1981. Printed in Great Britain

0040-4020/81/0201-0437 $05.00/0

TETRAHEDRON REPORT NUMBER 102

SIXTY YEARS OF STAUDINGER REACTION

YU. G. GOLOLOBOV,* I. N. ZHMUROVA and L. F. KASUKHIN
The Institute of Organic Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev 252660, USSR

(*Received* 14 *May* 1980)

CONTENTS

INTRODUCTION

In 1919 Staudinger and Meyer reported the first synthesis of phosphazo compounds by the reaction of tertiary phosphines with organic azides.[1]

$$R_3P + N_3X \longrightarrow \underset{\text{Phosphazide}}{R_3P{=}N{-}N{=}N{-}X} \xrightarrow[-N_2]{} R_3P{=}N{-}X \qquad (1)$$

This pioneering work was ahead of its time. In the following three-four decades only a few articles on the subject have appeared, and the number of known phosphazo compounds, up to 1950, did not exceed about a dozen. In 1950 Kirsanov discovered the phosphazo reaction, i.e. the imination of phosphorus pentachloride and its derivatives by compounds containing amino groups.[2,3]

$$\geqslant PCl_2 + H_2N{-}X \xrightarrow[-2HCl]{} \geqslant P{=}N{-}X \qquad (2)$$

This discovery initiated an extensive development of the chemistry of phosphazo compounds and renewed the interest to the Staudinger reaction.

Later, Kirsanov *et al.* found and examined a variety of new oxidative imination reactions of trivalent phosphorus compounds producing, as the Staudinger reaction does, the phosphazo derivatives.[4] A substantial contribution which extended the area of exploration and utilization of the Staudinger reaction was made by Kabachnik *et al.* They demonstrated that, besides the tertiary phosphines, the esters of phosphorous acids may also be used for the preparation of phosphazo compounds.[5] This fact revealed new possibilities of the Staudinger reaction and prompted its application to the solution of some fundamental theoretical problems in organophosphorus chemistry.

To date, some hundred articles and patents have been published which cover the synthesis of phosphazo compounds via the Staudinger reaction. Using this procedure one can prepare most of all conceivable phosphazo compounds having different substituents at the P and N atoms. The Staudinger and Kirsanov reactions complement each other and provide the main synthetic tool for preparation of compounds with the P=N bond.

The phosphazo reaction is generally used for the synthesis of P-halogenated products. The Staudinger reaction, on the other hand, is more convenient for the synthesis of P-alkoxylated, P-thioalkylated-, P-aroxylated and P-aminated phosphazo compounds. Either of the two methods can be applied to prepare the P-alkylated and P-arylated derivatives. In each case, the choice is conditioned by the availability of starting materials and by preparative considerations.

Some aspects of the Staudinger reaction have already been reviewed.[3,6a,7,8] The main object of this report is to provide a comprehensive survey of the preparative possibilities and mechanism of

the Staudinger reaction. A special section exemplifies the use of the reaction for analysis of some organic reactivity problems.

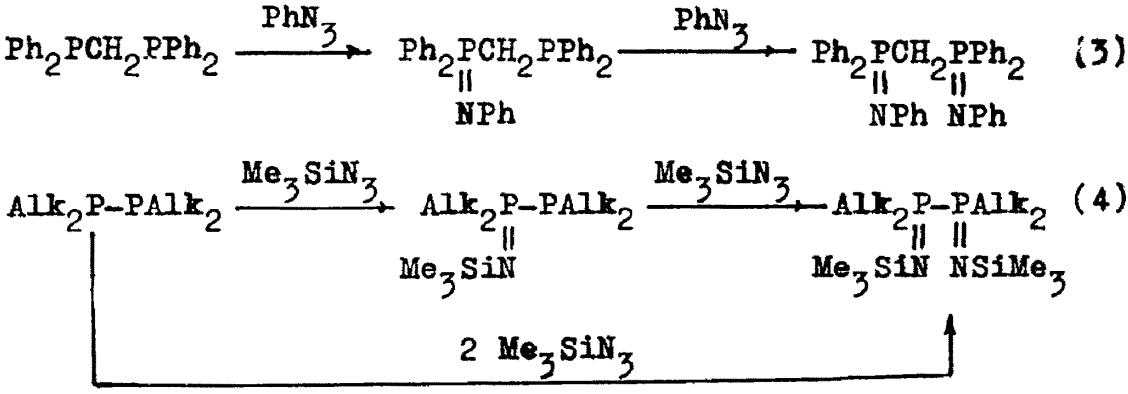
As a tribute to memory to the outstanding German scientist, H. Staudinger (1881 - 1965), we hope that this review will be helpful not only for those who work in the field of organophosphorus chemistry but also for other chemists.

1 SYNTHESIS OF PHOSPHAZO COMPOUNDS BY STAUDINGER REACTION

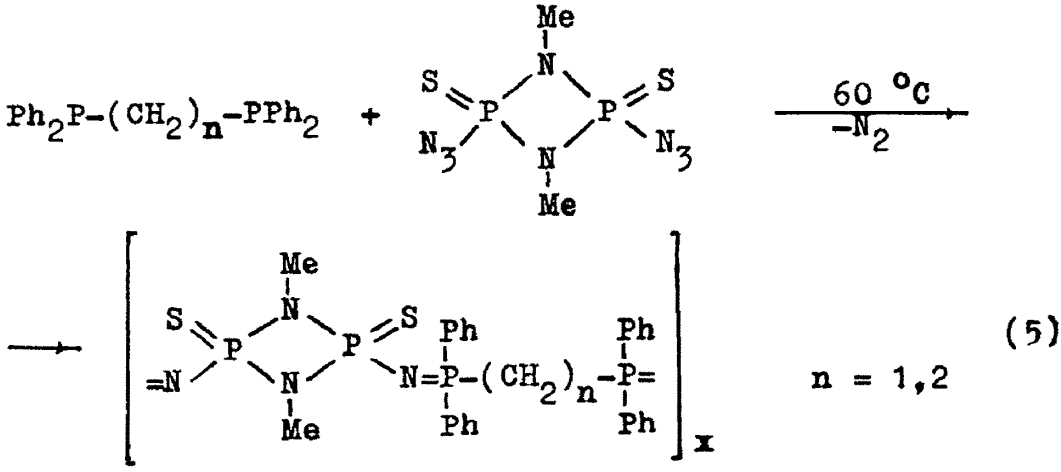
1.1 *Imination of tertiary phosphines.* Although the reaction with organic azides is typical for all tertiary phosphines—trialkyl and triaryl phosphines, mixed phosphines, unsaturated phosphines, diphosphines, etc. triphenyl phosphine which is easily accessible and convenient in operation is generally used. A variety of aliphatic and aromatic azides,[1,9-36] azides of carboxylic,[9,16,22,36-40] imidic[41] and carbamic[12,42-44] acids, guanyl azides,[45,46] cyanogen azide,[47] sulphur-,[12,16,22,31,36,37,48-52] phosphorus-[16,22,53-61] and metal-containing organic azides[62-77] can be employed for imination. Only azides of thiocarboxylic acids (*cf*[12,78]) and sulfinyl azides[79] fail to iminate tertiary phosphines. Alkyl and aryl azides are usually preferred.

Almost all known phosphazoalkanes and phosphazoarenes including those with active functional groups, phosphazobenzaldehydes,[24,25,80] phosphazoanilines,[21] phosphazobenzoic acids,[19] and phosphazophenols[20] were prepared by the Staudinger reaction. Many of them cannot be obtained by the phosphazo reaction or by any other method. The Staudinger reaction is very useful in the synthesis of phosphazo compounds having complex organic residues at N atom, phosphazoquinones,[81-83] phosphazocarbohydrates,[84,85] heterocyclic systems,[86-91] organic dyes containing auxochromic $Ar_3P{=}N$ groups,[17,25,30,92-94] and unsaturated phosphazo compounds.[36,95,96]

The imination of diphosphines yields bisphosphazo compounds[55,58,69-71,97,98] which are starting materials for the synthesis of heterocycles and polymers.[6b] This reaction can also be carried out in a stepwise manner.[71,98]



The treatment of diphosphines with diazides yields phosphorus–nitrogen polymers:[99]



The imination of tertiary phosphines by organometallic azides is one of the most important methods for the preparation of trialkyl- and triarylphosphazo derivatives of silicon.[63-71] germanium,[67,74,77] tin[67,72-74] and antimony.[75]

The Staudinger reaction is also unique in the synthesis of phosphazo compounds from tertiary phosphines of complex structure, in particular, those containing active functional groups or multiple bonds.[22,26,33,52,100]

Table 1 lists the most typical and interesting examples of triphenyl phosphine condensation with organic azides. Table 2 illustrates the Staudinger reaction for tertiary phosphines of complex structure.

The imination of trialkyl and triaryl phosphines with hydrazoic acid is a very important method for the synthesis of phosphazohydrides.[9,102-104]

$$R_3P \xrightarrow[-N_2]{HN_3} [R_3P{=}NH] \xrightarrow{HN_3} [R_3PNH_2]N_3 \xrightarrow{Base} R_3P{=}NH \qquad (6)$$

The free phosphazohydrides are obtained by treatment of their hydrazoic salts with such strong bases as sodium amide[104] and metallic sodium[102,103] or with triphenyl phosphine.[105]

$$[Ph_3PNH_2]N_3 + Ph_3P \xrightarrow[-N_2]{\Delta} 2\ Ph_3P{=}NH \qquad (7)$$

Table 1. Imination of triphenyl phosphine with organic azides

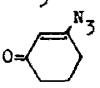
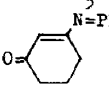
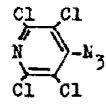
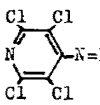
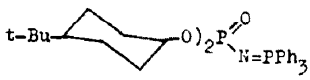
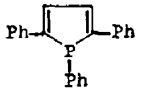
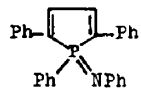
Azide	Phosphazo Product	References
PhN_3	$PhN{=}PPh_3$	1
$PhC(O)N_3$	$PhC(O)N{=}PPh_3$	9
$PhSO_2N_3$	$PhSO_2N{=}PPh_3$	12,48
$Me(EtO)P(O)N_3$	$Me(EtO)P(O)N{=}PPh_3$	101
Ph_3SiN_3	$Ph_3SiN{=}PPh_3$	63
NCN_3	$NCN{=}PPh_3$	47
		96
$PhCH{=}C(Ph)N_3$	$PhCH{=}C(Ph)N{=}PPh_3$	36
$PhOCH_2C(O)N_3$	$PhOCH_2C(O)N{=}PPh_3$	40
		91
$FcCH_2N_3$	$FcCH_2N{=}PPh_3$	35
$(EtO)_2P(O)NHC(O)N_3$	$(EtO)_2P(O)NHC(O)N{=}PPh_3$	43
		61
$O{=}P(N_3)_3$	$O{=}P(N{=}PPh_3)_3$	56
$(C_6F_5)_2PN_3$	$(C_6F_5)_2PN{=}PPh_3$	60
$Mes_2Si(N_3)_2$	$Mes_2Si(N_3)N{=}PPh_3$	68
Ph_3GeN_3	$Ph_3GeN{=}PPh_3$	62

Table 2. Imination of tertiary phosphines with phenyl azide and tosyl azide

Phosphine	Azide	Phosphazo Product	References
$Ph_2PC_6H_4CHO\text{-}p$	PhN_3	$Ph_2P(NPh)C_6H_4CHO\text{-}p$	32
$Ph_2PC{\equiv}CPh$	PhN_3	$Ph_2P(NPh)C{\equiv}CPh$	26,34
$Ph_2PC{\equiv}CNEt_2$	$TosN_3$	$Ph_2P(NTos)C{\equiv}CNEt_2$	52
$Ph_2PC(C(O)NEt_2)=C=CPh_2$	$TosN_3$	$Ph_2P(NTos)C(C(O)NEt_2)=C=CPh_2$	100
$[Ph_3P{-}C(Me_2P){-}PPh_3]^+Cl^-$	PhN_3	$[Ph_3P{-}C(Me_2P{=}NPh){-}PPh_3]^+Cl^-$	33
$Et_2PCH(COOEt)_2$	$TosN_3$	$Et_2P(NTos)CH(COOEt)_2$	31
	PhN_3		22
$Ph_2PCH_2PPh_2$	$2\ PhN_3$	$Ph_2P(NPh)CH_2P(NPh)Ph_2$	98

Phosphazohydrides, especially triphenylphosphazohydride, are widely used for the synthesis of phosphazo compounds with different substituents at the N atom (Section 4).

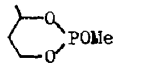
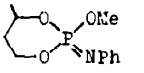
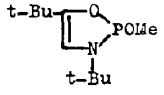
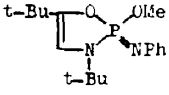
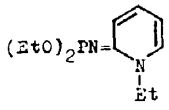
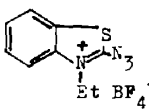
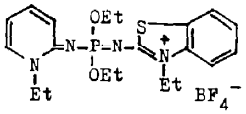
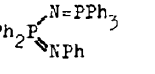
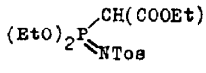
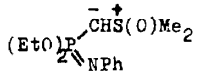
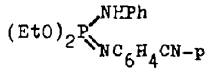
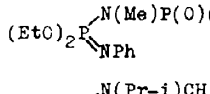
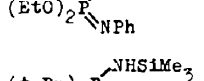
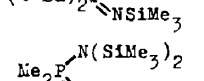
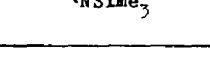
1.2 *Imination of esters, thioesters, and amides of phosphorus(III) acids.* The use of esters, thioesters, and amides of phosphorous,[5,16,38,43,55,56,59,73,83,88,101,106 142] phosphonous,[56,101,107,109,116,125,126,142 148] and phosphinous acids[55,108,109,116,117,126,142,145,149 155] in the Staudinger reaction considerably extended the limits of its application.

Table 3 lists several groups of phosphazo compounds prepared by imination of phosphorus(III) derivatives with organic and heteroorganic azides. Many are prone to various prototropic and elementotropic rearrangements. In some cases these processes are so facile that the expected phosphazo products cannot be isolated. Phosphazo compounds bearing methoxy or silyloxy groups at the P atom as well as those with a triad system $\diagdown N\text{-}P=N\diagup$, phosphamidines, are particularly labile.

These and some other unusual examples of oxidative imination, including the intramolecular variants of Staudinger reaction, and condensation of bisfunctional azides with phosphorus substrates, are discussed in Section 3.1.

1.3 *Imination of trivalent phosphorus compounds displaying low nucleophilic reactivity.* Halides, isocyanates, and anhydrides of phosphorus(III) acids are less reactive in imination than their esters and amides or tertiary phosphines. The ability of PCl_3, $PhPCl_2$ and Ph_2PCl to react with azides was revealed only in 1966, about 50 years after Staudinger's original study.[16,57,114,149] By that time, the corresponding phosphazo compounds had already been synthesized by the phosphazo reaction. To date, it is the most convenient method for the preparation of such chlorinated derivatives, while the Staudinger reaction is, in this case, mainly of theoretical interest. However, several phosphorus(III) compounds, such as isocyanates, mixed anhydrides, aminohaloidphosphites and phosphonites probably can be iminated only by the azide method (Table 4).

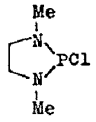
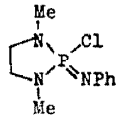
Table 3. Imination of derivatives of phosphorus(III) acids with organic and heteroorganic azides

Phosphorus Compound	Azide	Phosphazo Product	Refe-ren-ces
$(EtO)_3P$	PhN_3	$(EtO)_3P{=}NPh$	5
	$MeSO_2N_3$	$(EtO)_3P{=}NSO_2Me$	111
	$PhC(O)N_3$	$(EtO)_3P{=}NC(O)Ph$	114
	$(EtO)_2P(O)N_3$	$(EtO)_3P{=}NP(O)(OEt)_2$	110
	$Me_2P(S)N_3$	$(EtO)_3P{=}NP(S)Me_2$	127
	Me_3SiN_3	$(EtO)_3P{=}NSiMe_3$	137
$EtP(OEt)_2$	PhN_3	$Et(EtO)_2P{=}NPh$	144
	PhN_3		130
$(EtO)_2POSiMe_3$ [a]	$PhC(O)N_3$	$Me_3SiO(EtO)_2P{=}NC(O)Ph$	135
$(Me_2N)_3P$	PhN_3	$(Me_2N)_3P{=}NPh$	113
	$PhC(O)N_3$		120
$(Et_2N)_3P$	Me_3SiN_3	$(Et_2N)_3P{=}NSiMe_3$	137
	PhN_3		141
			115
$PhP(OEt)_2$	$(EtO)_2P(O)N_3$	$Ph(EtO)_2P{=}NP(O)(OEt)_2$	116
Et_2POEt		$Et_2(EtO)P{=}NP(O)(OEt)_2$	116
Et_2PNEt_2		$Et_2(Et_2N)P{=}NP(O)(OEt)_2$	116
$Ph_2PN{=}PPh_3$	PhN_3		156
$(EtO)_2PCH(COOEt)_2$ [b]	$TosN_3$		147
$(EtO)_2\overset{-}{P}\overset{+}{C}HS(O)Me_2$	PhN_3		148
$(EtO)_2PNHPh$	$p\text{-}NCC_6H_4N_3$		117
$(EtO)_2PNP(O)(OEt)_2$ (Me)	PhN_3		139
$(EtO)_2PNCH_2COOEt$ (i-Pr)	PhN_3		138
$(t\text{-}Bu)_2PNHSiMe_3$	Me_3SiN_3		150
$Me_2PN(SiMe_3)_2$	Me_3SiN_3		151

[a] For the reaction of O-silylated phosphites with phenyl azide see Section 3.1.

[b] For the reaction with phenyl azide see Section 3.1.

Table 4 Imination of weakly nucleophilic trivalent phosphorus compounds

Phosphorus Compound	Azide	Phosphazo Product	References
PCl_3	PhN_3	$PhN{=}PCl_3$ [a]	149
$PhPCl_2$	PhN_3	$PhN{=}PCl_2Ph$ [a]	149
Ph_2PCl	$TosN_3$	$TosN{=}PPh_2Cl$	57
$(Me_2N)_2PCl$	PhN_3	$(Me_2N)_2P(Cl)=NPh$	158
	PhN_3		159
$(EtO)_2PNCO$	$PhC(O)N_3$ [b]	$(EtO)_2P(NCO)=NC(O)Ph$	160
$(EtO)_2P{-}OP(O)(OEt)_2$ [c]	$(EtO)_2P(O)N_3$	$(EtO)_2P(OP(O)(OEt)_2)=NP(O)(OEt)_2$	162
$(EtO)_2PF$	CF_3N_3	$CF_3N{=}P(OEt)_2F$	125
$Me(EtO)PF$	CF_3N_3	$CF_3N{=}P(OEt)FMe$	125
$F_2P{-}N(t\text{-}Bu){-}CH_2COOMe$ [d]	PhN_3	$F_2P(N(Bu\text{-}t)CH_2COOMe)=NPh$	163

[a] Dimerizes to an aminophosphorane during the reaction[157].

[b] No imination with $P(NCO)_3$[161].

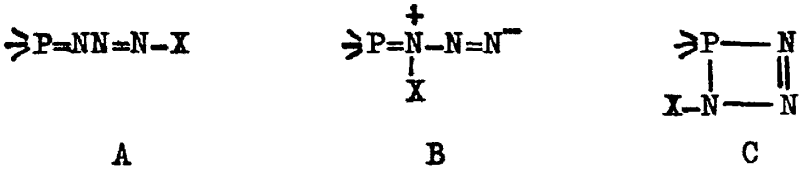
[c] For imination of $(EtO)_2P{-}OP(S)(OEt)_2$ see Section 3.1.

[d] For imination of $F_2P{-}N(Me)CH_2COOEt$ see Section 3.1.

1.4 *Phosphazides.* The primary imination products, phosphazides $R_3P{=}NN{=}NX$, as a rule, decompose during the reaction with loss of nitrogen. The intermediate formation of the phosphazides was first observed by Staudinger[9] in special runs carried out at low temperature, *ca* −80 °. However, in some cases, phosphazides are quite stable under the usual conditions of the Staudinger reaction, i.e. in organic solvents at 0-20 °, but evolve nitrogen on heating at 50-150 °.[12,13,16,18,37,44-46,48,51,54,87,164-168] Some phosphazides melt without decomposition, and lose nitrogen on heating above the m.p. The latter process is often accompanied by gum formation or even by explosions, but in organic solvents the conversion of phosphazides to the corresponding phosphazo compounds proceeds smoothly with practically quantitative yields.

The stability of a phosphazide molecule is determined by the electronic (a conjugative delocalization of the cationic charge on phosphorus) and steric factors (screening of the P atom by bulky substituents). Some examples of stable phosphazides are given in Table 5.

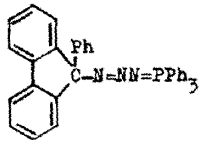
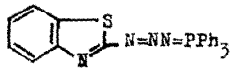
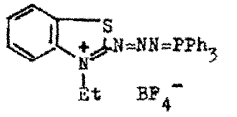
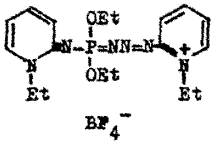
Besides the linear formula **A**,[11,82] the branched **B**[12,66] and cyclic **C**[132] structures were also proposed for phosphazides.



A **B** **C**

But in view of the available chemical,[82] spectroscopic,[50,51,132] and kinetic data (Section 2) the presence of a linear skeletal P=NN=N framework in these compounds appears more acceptable.

Table 5. Stable phosphazides

Phosphazide	Preparative Conditions	M. p. °C	Notes	References
$PhN{=}NN{=}P(C_5H_{11})_3$	In ether on cooling	57–58	Decomposes on standing, some times with explosion	9
$PhN{=}NN{=}P(Ph)Et_2$	In ether, −80 °C	51–52 (dec.)	Explodes on melting big samples	9
$p\text{-}O_2NC_6H_4N{=}NP(Et)C_6H_4Cl\text{-}p$	In ether, 10 °C	57–58 (dec.)	Yields the corresponding phosphazo compound on gentle warming in vacuum	18
$Ph_3CN{=}NN{=}PPh_3$	In ether	104–105	In cold benzene converts to the phosphazo compound[36]	164
$n\text{-}BuN{=}NN{=}PPh_3$	In ether, 0 °C	106–108 (dec.)		12
	In boiling ether	73–74		44
$2,4,6\text{-}(O_2N)_3C_6H_2N{=}NN{=}PPh_3$	In ether, 0 °C	131 (dec.)		13
	In chloroform	75 (dec.)		87
	In acetone, 0 °C	164–167 (dec.)		168
$TosN{=}NN{=}PPh_3$	In cold benzene	101		51
$MeN{=}NN{=}P(NMe_2)_3$	In ether, 5 °C	–	Decomposes at room temperature	132
$Me_2N{-}N{=}NN{=}PPh_3$	In ether	161–163		54
$[(H_2N)_2CN{=}NN{=}PPh_3]^+ Cl^-$	In dichloromethane, −78 °C	110 (dec.)	Slowly decomposes on standing	46
$(Ph_3P{-}N{=}NN{=}PPh_3)^+ SbCl_4^-$	In benzene, 20 °C	90 (dec.)		167
	In dichloroethane, 20 °C	100–110 (dec.)		169

2 MECHANISM OF STAUDINGER REACTION

The stability of the intermediate phosphazide (I) determines the kinetic order of the products formation in the Staudinger reaction.

$$R_3P + N_3R' \underset{}{\overset{k_1}{\rightleftharpoons}} \underset{\mathbf{I}}{R_3PN_3R'} \xrightarrow{k_2} R_3P{=}NR' + N_2 \qquad (8)$$

It can be either the first or the second, depending on whether the unimolecular decomposition or bimolecular formation of the phosphazide is the rate-determining step.[37]

Phosphazides of Ar_3PN_3Ar type were found to dissociate into the starting reagents.[11] The dissociation is slowed up by acceptor or donor substituents in azides or phosphorus components, respectively. The formation of the phosphazides $(Me_2N)_3PN_3R$ (R = Me, Ph)[132] and Ph_3PN_3Tos[170] is practically irreversible. The equilibrium (8) for the imination of phosphites with aryl azides is also considerably shifted to the right.[171,172]

In general outline, the mechanism of the Staudinger reaction is known. It seems to proceed without either free radicals[a] or nitrene participation[11,132] and, possibly, with retention of phosphorus stereoconfiguration.[14] Using ^{15}N labelling technique, the N-R' bond in a phosphazide was found to transfer to a phosphazo product without splitting.[50,51]

$$\left.\begin{array}{l} Ph_3P{=}{}^{15}NN{=}NTos \\ Ph_3P{=}N{}^{15}N{=}NTos \end{array}\right\} \xrightarrow{\Delta} Ph_3P{=}NTos + {}^{15}NN \qquad (9)$$

The primary electrophilic attack of an azide molecule on phosphorus, i.e. the first step in Scheme (8), is accelerated by acceptor groups in the azide[11,12,37] and donor radicals in the trivalent phosphorus compound.[11,173] This fact expressed in terms of the Hammett correlation parameters ρ is illustrated in Table 6.

The phosphazide decomposes to give the corresponding phosphazo compound by the intramolecular mechanism via the 4-membered ring transition state (II).[11,50]

$$R_3P{=}NN{=}NR' \longrightarrow \underset{\mathbf{II}}{\left[\begin{array}{c} R_3P\text{-----}N\text{-}R' \\ \diagdown \quad \diagup \\ N{\equiv}N \end{array}\right]^{\neq}} \longrightarrow R_3P{=}NR' + N_2 \qquad (10)$$

The effect of radicals at phosphorus upon the rate of formation and decomposition of the phosphazide is inverse[11,175] as the nucleophilic function of the phosphorus centre changes into an electrophilic one along the reaction co-ordinate. The sign of the Hammett parameter ρ for the second step of the Staudinger reaction alters on varying the azide component (Table 6). It is probably due to a nonconcerted character of the bond redistribution at the transition state (II).[140]

σ,ρ-Analysis of substituent effects upon the imination rate in terms of inductive, mesomeric and steric increments has revealed some unexpected features of the Staudinger reaction.[176] This study was mainly performed with phenyl azide. The first imination step is controlled only by the inductive properties of the radicals attached to phosphorus and the corresponding log k_1 values are linearly related to the sums of σ_I parameters of the substituents (Fig. 1).

---

[a] A charge transfer in the transition state and the intermediate ion-radicals formation in the Staudinger reaction have been discussed[35,80] as a mechanistic possibility.

Table 6. ρ-Values of Hammett correlations in Staudinger reaction (THF)

Phosphorus Reagent	Azide	ρ-Values 1-st Step	ρ-Values 2-d Step	References
$(EtO)_3P$	$XC_6H_4N_3$	1.53	0.67	171
$(EtO)_2PNMe_2$	$XC_6H_4N_3$	0.85	0.67	140
$(EtO)_2PCH(COOEt)_2$	$XC_6H_4N_3$	1.28	0.93	146
$(EtO)_2\overset{-}{P}\overset{+}{C}HS(O)Me_2$	$XC_6H_4N_3$	0.76	0.61	174
Ph_3P (xylene)	$XC_6H_4N_3$	1.36	-	12
Ph_3P (benzene)	$XC_6H_4N_3$	1.25	-0.19	11
$(EtO)_2PCH(COOEt)_2$	$XC_6H_4SO_2N_3$	0.46	-0.16	146
$(EtO)_2\overset{-}{P}\overset{+}{C}HS(O)Me_2$	$XC_6H_4SO_2N_3$	-	-0.12	174
Ph_3P (benzene)	$XC_6H_4C(O)N_3$	0.78	-	37
$(XC_6H_4)_3P$ (benzene)	PhN_3	-1.07	0.43	11

The reactivity of the compounds with amino, haloid, alkoxyl, aryl, and alkyl radicals, distinctly differing in their ability to conjugate with phosphorus, is described by the same linear equation (11):

$$\log k_1 = 2.274 - 5.656\ \Sigma\sigma_1 \qquad (11)$$
$$r = 0.996,\ s = 0.08$$

A complete levelling of steric properties of the radicals in the phosphorus environment and an unhindered mode of the attack by phenyl azide on P^{III} centre become evident on surveying the data listed in Table 7. The replacement of a MeO- or EtO-group in phosphites by a bulky 1-adamantoxyl radical (1-AdO) does not affect significantly the rate constant k_1 of the reaction with phenyl azide.[177]

This effect is probably due to the fact that an electron pair of the P^{III} trigonal-pyramidal atom is easily accessible to a small electrophile, PhN_3. The conjugation with phosphorus is completely suppressed which is an unusual phenomenon and may probably be attributed to some structural peculiarities of the transition state (II).

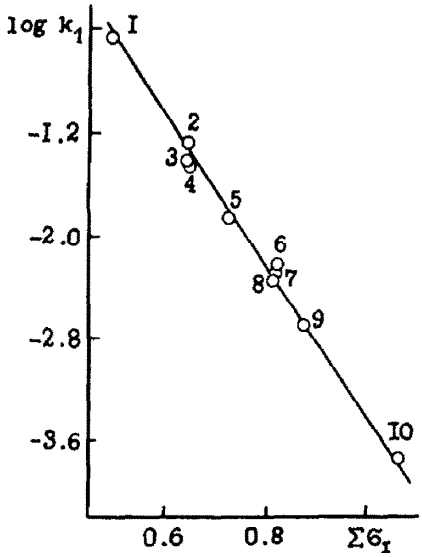


Fig. 1. Plot of log k_1 versus $\Sigma\sigma_1$-parameters of the radicals R^1, R^2, and R^3 for the first step of the reaction between $R^1R^2R^3P$ and phenyl azide in THF at 20°. 1. $(EtO)_2PMe$; 2. $(EtO)_2PNMe_2$; 3. $(EtO)_2PNEt_2$; 4. $(EtO)_2PPh$; 5. $(Me_2N)_2PF$; 6. $(EtO)_2POPr\text{-}i$; 7. $(EtO)_2POC_6H_{11}\text{-}c$; 8. $(EtO)_3P$; 9. $(MeO)_3P$; 10. $(EtO)_2PF$.

Table 7. The rates of the first step of phosphites imination with phenyl azide (THF, 20)

Phosphite	$k_1 \cdot 10^3$ $M^{-1}s^{-1}$
$(MeO)_3P$	1.97
$(EtO)_3P$	4.48
$(EtO)_2POPr\text{-}i$	5.58
$(MeO)_2POAd\text{-}1$	1.73
$(EtO)_2POAd\text{-}1$	2.93

The unique inductive control of the first step in the Staudinger reaction has been used to evaluate the polar properties of various radicals R at phosphorus, following eqn (11) with known experimental constants k_1 for the imination of model compounds, $(EtO)_2PR$, by phenyl azide under standard conditions (THF, 20) (Table 8).

The dependence of the phosphazide decomposition rate on the properties of substituents at phosphorus is more complicated. Their inductive, mesomeric and steric characteristics commensurably contribute to the reactivity of a phosphorus reagent as it follows from the three-parameter representation of $\log k_2$.[176] The total donative character of electronic effects (inductive and mesomeric) stabilizes the phosphazide and reduces its decomposition rate. The introduction of donor groups to phosphorus results in a shift of the limiting act from the first to the second step and a change in the kinetic order of the reaction. For instance, in the series of 1-cyclohexenyl phosphites $(EtO)_2POC_6H_9$, $EtO(Me_2N)POC_6H_9$ and $(Me_2N)_2POC_6H_9$ where the EtO-radicals are successively substituted by more donor Me_2N-groups, the kinetic order of nitrogen evolution is 2, 2 and 1, respectively.[178] The steric screening of phosphorus causes the analogous stabilization of phosphazides. The steric requirements in the transition state (II) are much more rigorous than in the transition state of the primary electrophilic addition of azide.

As mentioned above, the bulky adamantoxyl radical does not affect the rate of the first step (Table 7), but at the second step the retardation effect can amount to two powers of ten (Table 9).[177]

The constancy of contribution of structural and electronic factors to the reactivity of phosphorus(III) compounds in the imination with phenyl azide is confirmed by isokinetic relationships found for the both reaction steps by the Exner method.[179] The isokinetic character of the Staudinger reaction is expressed in terms of the linear correlations between $\log k_1$ or $\log k_2$ values at two fixed temperatures, 10 and 30 .[176,180]

The primary addition of phenyl azide to trivalent phosphorus compounds displays the specific features of an isoenthalpic process.[176,180] The variations of k_1 within the range of three orders of magnitude are mainly governed by the change of entropy factor from -15 to -46 e.u. at nearly constant activation enthalpy, 12.3 ± 0.4 kcal/mole (for 45 compounds). The electronic factors at the transition state of the first step seem to affect the rate by the influence on a phosphorus centre solvation. In the phosphazide decomposition step the energetic factors control the observed change in $\Delta F^{\neq}$ with distinct compensation relationship between $\Delta H^{\neq}$ and $\Delta S^{\neq}$.[176,180] The analogous correlations of activation parameters were also found for the decomposition of phosphazides formed by tosyl azide.[140]

3. STAUDINGER REACTION AND SOME ASPECTS OF HETEROORGANIC AND ORGANIC CHEMISTRY

3.1 *Rearrangements and tautomeric conversions accompanying the Staudinger reaction.* The Staudinger reaction of P^{III} compounds possessing at least one alkoxyl group is often accompanied by the alkyl fragment migration to phosphazyl nitrogen.

$$\text{AlkO}\!\!>\!\!\text{P} + \text{N}_3\text{X} \longrightarrow \text{AlkO}\!\!>\!\!\text{P=NX} \longrightarrow \!\!>\!\!\overset{\overset{\text{O}}{\|}}{\text{P}}\!\!-\!\!\underset{\text{Alk}}{\overset{|}{\text{N}}}\!\!-\!\!\text{X} \qquad (12)$$

$$\text{X} = \text{Alk, Ar, COOR, SO}_2\text{R, SiMe}_3$$

Table 8. Rate constants for the first step of the reaction between $(EtO)_2PR$ and phenyl azide (THF, 20) and σ_1 parameters of radicals R [176]

Radicals	$k_1 \cdot 10^3$ $M^{-1}s^{-1}$	σ_I [a]
-OC(Bu-t)=CHN(Bu-t)- [b]	0.16	0.78
-OCH(Bu-t)CH_2N(Bu-t)- [c]	356.0	0.53
-OC(CN)=CHMe	0.25	0.50
-OC(Me)=CHAc	0.28	0.49
-OC(Me)=CHCl	0.43	0.46
	0.60	0.43
	1.28	0.37
-OC_6H_4CN-p	0.25	0.50
-OAd-1	2.93	0.31
-OAd-2	5.11	0.27
-OC_6H_{11}-c.	5.68	0.26
-OP(S)$(OEt)_2$	0.21	0.51
-OP(O)$(OEt)_2$	0.26	0.50
-OP$(OEt)_2$ [d]	2.54	0.34
-N(Ph)N=CMe_2	2.50	0.32
-N(Me)P(S)$(OEt)_2$	0.30	0.48
-N(Me)P(O)$(OEt)_2$	0.47	0.45
-N(Me)P(=NPh)$(OEt)_2$	0.96	0.39
-N(Me)P$(OEt)_2$ [d]	6.65	0.30
-N(Pr-i)CH_2P(S)$(OEt)_2$	11.3	0.21
-N(Pr-i)CH_2P(O)$(OEt)_2$	12.3	0.20
-N(Pr-i)CH_2COOEt	28.8	0.14
-CH_2P(S)$(OEt)_2$	6.66	0.25
-CH_2P(=NPh)$(OEt)_2$	11.8	0.20
-CH_2P$(OEt)_2$ [d]	94.5	0.10
-CH$(COOEt)_2$	1.59	0.36
-CH_2COOEt	11.1	0.21
-CHS(O)Me_2	253.0	-0.03

[a] Calculated from the equation $\Sigma\sigma_I = 0.405 - 0.176 \log k_1$.

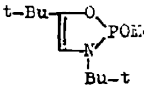
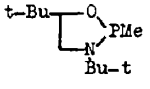
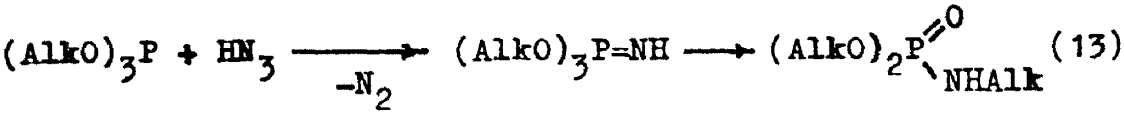
[b] In the compound  [c] In the compound  [d] The value of k_1 /? was used for σ_I calculation to take into account the statistic factor of acceleration of the reaction when a molecule includes two equivalent reactive centres.

Table 9. Rate constants for the second step of the reaction of phosphites and phosphonites with phenyl azide (THF, 20 °C)

Phosphorus Reagent	$k_2 \cdot 10^3$ s^{-1}
$(MeO)_3P$	87.0
$(EtO)_3P$	53.3
$PhP(OEt)_2$	154.0
$(MeO)_2POAd\text{-}1$	28.1
$(EtO)_2POAd\text{-}1$	14.4
$EtOP(OAd\text{-}1)_2$	0.24
$PhP(OAd\text{-}1)_2$	1.05

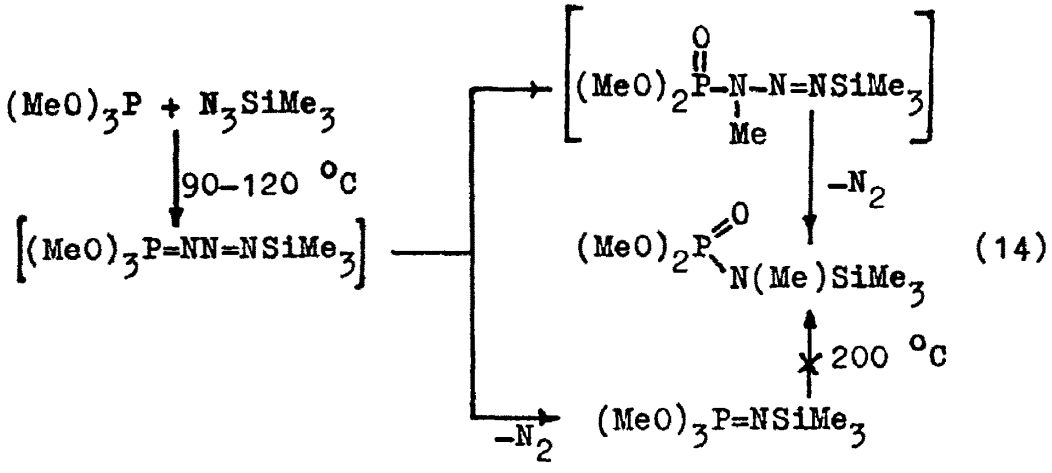
P-Methoxylated phosphazo compounds rearrange easily, while the lengthening or branching the alkyl radicals results in reduction of their migration aptitude.[118,121-123,181,182] The imination of trialkyl phosphites with hydrazoic acid produces, besides other products, N-alkyl phosphoramidates formed during the rearrangement of unstable intermediate trialkoxyphosphazohydrides.[183]



$$(AlkO)_3P + HN_3 \xrightarrow[-N_2]{} (AlkO)_3P{=}NH \longrightarrow (AlkO)_2P(=O)NHAlk \qquad (13)$$

The isomerization of N-silylated trialkoxyphosphazo compounds is rather slow. Approximately half trimethoxyphosphazotrimethylsilane rearranges under relatively rigid experimental conditions (above 100°),[133] while triethoxy-, tripropoxy- and tributoxy-derivatives remain unchanged.[137]

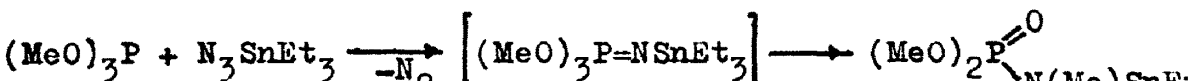
It is noteworthy that pure trimethoxyphosphazotrimethylsilane is not liable to rearrange upon prolonged heating up to 200 . The isomerization is suggested to occur in the intermediate phosphazide.[133]



$$(MeO)_3P + N_3SiMe_3 \xrightarrow{90\text{–}120\ ^\circ C} [(MeO)_3P{=}NN{=}NSiMe_3] \longrightarrow \begin{cases} [(MeO)_2P(=O)N(Me)N{=}NSiMe_3] \xrightarrow{-N_2} (MeO)_2P(=O)N(Me)SiMe_3 \\ (MeO)_3P{=}NSiMe_3 \xrightarrow{-N_2} \end{cases} \qquad (14)$$

$$(MeO)_3P{=}NSiMe_3 \xrightarrow{200\ ^\circ C} (MeO)_2P(=O)N(Me)SiMe_3$$

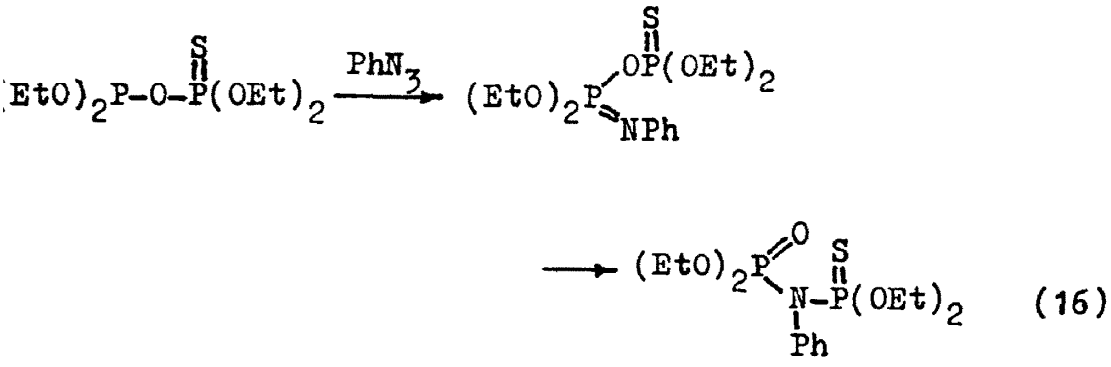
Tris-(1,1,1-trifluorethoxy)phosphazotrimethylsilane, on the other hand, polymerizes at 200 .[184] Trimethoxyphosphazotriethyltin rearranges in the course of preparation.[73]



$$(MeO)_3P + N_3SnEt_3 \xrightarrow[-N_2]{} [(MeO)_3P{=}NSnEt_3] \longrightarrow (MeO)_2P(=O)N(Me)SnE$$

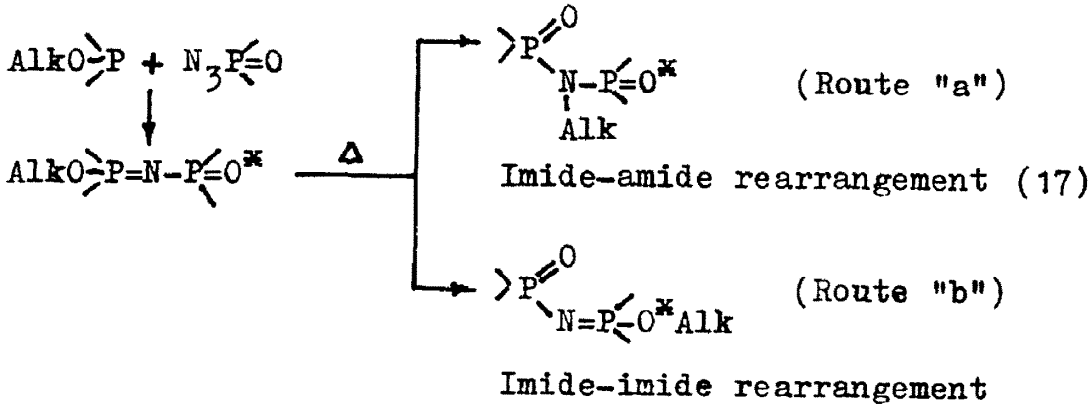
(1

The imination of a mixed anhydride of phosphorous and thiophosphoric acids by phenyl azide is accompanied by migration of a thiophosphoryl group.[185]



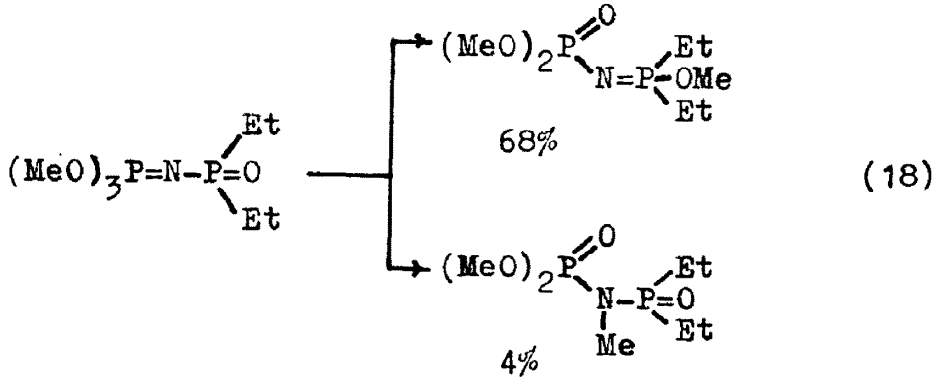
(16)

When a P=O fragment is attached to the N atom of a P-alkoxylated phosphazo compound the rearrangement may occur either within a triad O-P=N (route "a") or a pentad system O-P=N-P=O (route "b").



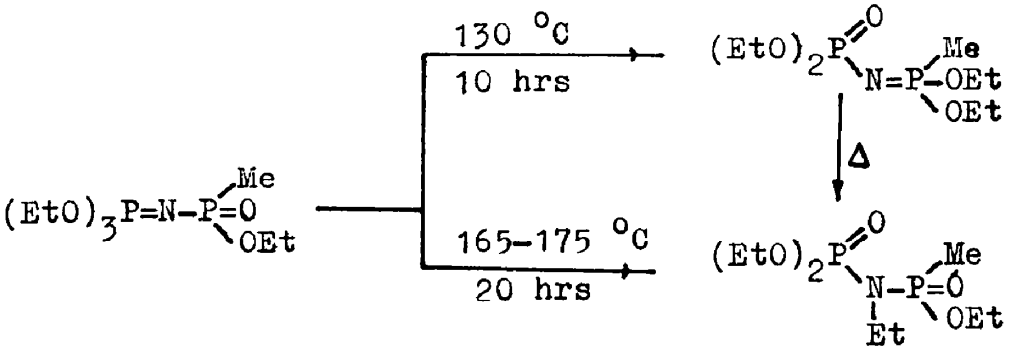
(17)

The rearrangement proceeds, as a rule, via the route "b"[101,119,186,187] but sometimes the reaction products contain small amounts of N-alkylated derivatives from the route "a".[186]



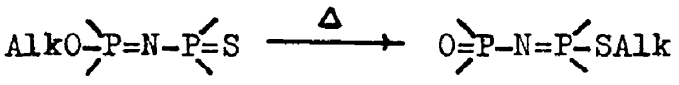
(18)

In some cases the direction of the reaction can be governed: under relatively mild conditions the rearrangement proceeds via the route "b", while under more rigid ones it yields the product corresponding to the route "a" as shown below.[101]



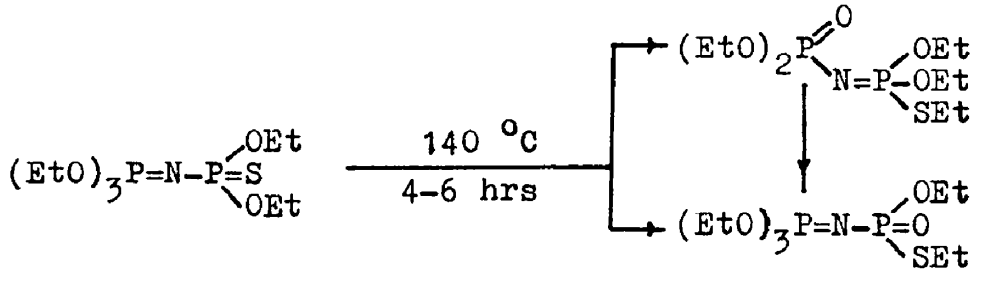
(19)

Phosphazo compounds containing a P=S group at the N atom rearrange according to eqn (17b).[136]



(20)

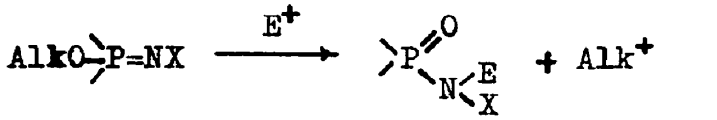
The resulting thiolphosphate can further rearrange to yield an isomeric thiolphosphate.[188]



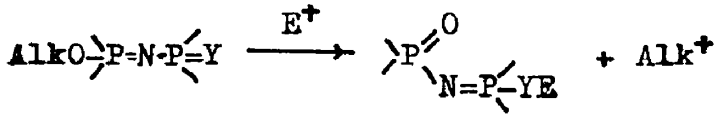
(21)

It should be noted that the isomerization of phosphazo compounds in the course of their preparation seldom occurs but often proceeds spontaneously on distillation or storage of the products (Table 10). Nevertheless, even labile P-methoxylated derivatives can be obtained if some precautions are taken (low temperatures, rapid distillation of small samples or chromatographic separation).

The thermal rearrangement via the pathway "a" or "b" in eqn (17) is only a special case of the reactions of P-alkoxylated phosphazo compounds with electrophiles covered by eqn (22),[189] where E^+ is a positively charged fragment of an electrophile, Y being O or S.



(22a)



(22b)

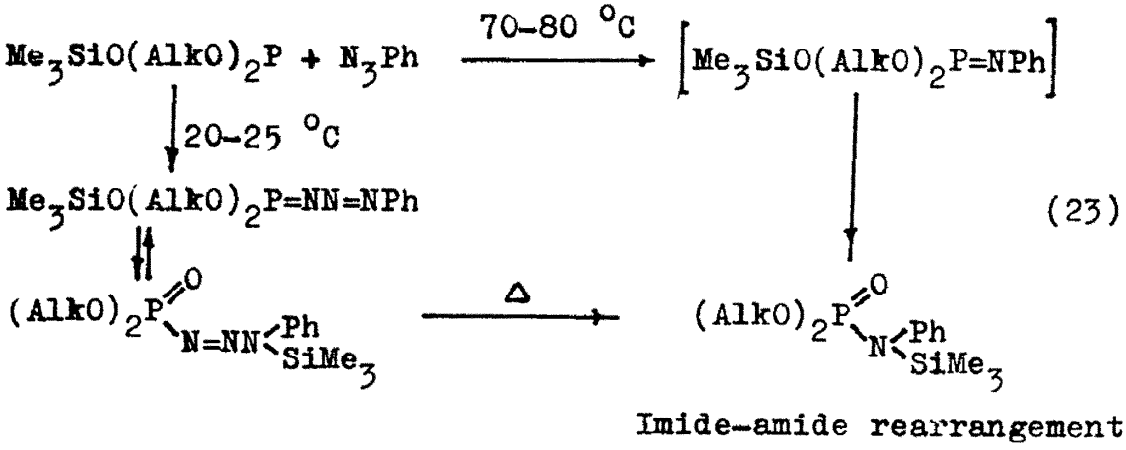
The Staudinger reaction with silylphosphites is usually followed by the imide-amide or imide-imide rearrangement with a trialkylsilyl group participation. Whereas alkyl groups shift only

Table 10 Imination of trialkyl phosphites and thermal stability of P-alkoxylated phosphazo products

Phosphorus Substrate	Azide	Reaction Products	Attitude to Heating	References
$(MeO)_3P$	PhN_3	$(MeO)_3P{=}NPh$	Can be distilled in vacuum at 80–85 °C without rearrengement.	118
$(EtO)_3P$	PhN_3	$(EtO)_3P{=}NPh$	50% isomerization in solution at 100 °C for 30 days.	181
$(MeO)_3P$	$MeOOCN_3$	$[(MeO)_3P{=}NCOOMe] \rightarrow (MeO)_2P(=O)N(Me)COOMe$	Isomerizes in boiling ether in the course of preparation.	123
$(EtO)_3P$	$MeOOCN_3$	$(EtO)_3P{=}NCOOMe$	No isomerization on distillation.	123
$(MeO)_3P$	$Et_2P(O)N_3$	$(MeO)_3P{=}N{-}P(=O)(Et)Et$	Partial isomerization during preparation, distillation and storage.	186
$(EtO)_3P$	$Me(EtO)P(O)N_3$	$(EtO)_3P{=}N{-}P(Me)(=O)OEt$	No isomerization on distillation.	101
$(EtO)_3P$	$Ph(EtO)P(O)N_3$	$[(EtO)_3P{=}N{-}P(Ph)(=O)OEt] \rightarrow (EtO)_2P(=O)N{=}P(Ph)(OEt)OEt$	Isomerizes in the course of preparation.	186
$(EtO)_3P$	$(Me_2N)_2P(S)N_3$	$(EtO)_3P{=}N{-}P(NMe_2)(=S)NMe_2$	No isomerization on distillation.	134

irreversibly, for Alk_3Si residues some cases of reversible migration within the O-P=N or O-P=N -P=O framework are known.

During the imination of silylphosphites with phenyl azide the resulting phosphazo compounds undergo the imide-amide rearrangement.[135,190,191] The reversible migration of a trimethylsilyl group between oxygen and nitrogen was also detected in the intermediate phosphazides.[190]



(23)

For the rearranged N-silylated phosphoramidates the inverse shift of the trimethylsilyl group from nitrogen to oxygen is not characteristic.[190] However, the possibility of such migration, in

Table 11. Staudinger reaction of heteroorganic phosphorus(III) compounds and accompanying conversions

Phosphorus Substrate	Azide	Reaction Products	Type of Rearrangement	References
$Me_3SiO(EtO)_2P$	PhN_3	$[Me_3SiO(EtO)_2P{=}NPh] \rightarrow (EtO)_2P(O)N(Ph)SiMe_3$	Imide-amidic	190
$Me_3SiO(EtO)_2P$	$PhC(O)N_3$	$Me_3SiO(EtO)_2P{=}NC(O)Ph$	-	135
$Me_2(Me_3SiO)P$	Me_3SiN_3	$Me_2(Me_3SiO)P{=}NSiMe_3$	-	154
$Me_3SiO(EtO)_2P$	$(Me_2N)_2P(O)N_3$	$[Me_3SiO(EtO)_2P{=}N{-}P(O)(NMe_2)_2] \rightarrow (EtO)_2P(O){-}N{=}P(OSiMe_3)(NMe_2)_2$	Imide-imidic	135
$Me_3SiO(EtO)_2P$	$Et_2P(O)N_3$	$[Me_3SiO(EtO)_2P{=}N{-}P(O)Et_2] \rightarrow (EtO)_2P(O){-}N{=}P(OSiMe_3)Et_2$	Imide-imidic	135
$Me_3SiO(EtO)_2P$	$(i\text{-}BuO)_2P(O)N_3$	$Me_3SiO(EtO)_2P{=}N{-}P(O)(OBu\text{-}i)_2 \rightleftharpoons (EtO)_2P(O){-}N{=}P(OSiMe_3)(OBu\text{-}i)_2$	Imide-imide elementotropy	135
$Me_3SiO(MeO)_2P$	$(MeO)_2P(O)N_3$	$Me_3SiO(MeO)_2P{=}N{-}P(O)(OMe)_2 \rightleftharpoons (MeO)_2P(O){-}N{=}P(OSiMe_3)(OMe)_2$	Degenerated imide-imide elementotropy	135
$Me_2P{-}N(Me)SiMe_3$	Me_3SiN_3	$Me_2P(N(Me)SiMe_3)(NSiMe_3)$	-	142
$Me_2P{-}N(Bu\text{-}t)SiMe_3$	Me_3SiN_3	$[Me_2P(N(Bu\text{-}t)SiMe_3)(NSiMe_3)] \rightarrow Me_2P(NBu\text{-}t)N(SiMe_3)_2$	Imide-imidic	142
$Me_2P{-}N(Me)SiMe_2(Bu\text{-}t)$	Me_3SiN_3	$[Me_2P(N(Me)Si(Bu\text{-}t)Me_2)(NSiMe_3)] \rightarrow Me_2P(NSi(Bu\text{-}t)Me_2)(NMeSiMe_3)$	Imide-imidic	142
$Me_2P{-}N(SiMe_3)_2$	Me_3SiN_3	$Me_2P(NSiMe_3)N(SiMe_3)_2 \rightleftharpoons Me_2P(N(SiMe_3)_2)NSiMe_3$	Degenerated imide-imide elementotropy	151
$t\text{-}Bu(Me)P{-}N(Me)SiMe_3$	MeN_3	$t\text{-}Bu(Me)P(N(Me)SiMe_3)(NMe) \rightleftharpoons t\text{-}Bu(Me)P(NMe)(NMeSiMe_3)$	Degenerated imide-imide elementotropy	151
$Me_2P{-}N(Me)GeMe_3$	MeN_3	$Me_2P(N(Me)GeMe_3)(NMe) \rightleftharpoons Me_2P(NMe)(NMeGeMe_3)$	Degenerated imide-imide elementotropy	193

principle, was demonstrated in the case of N-trimethylsilyl-N-phenyl-O,O-diphenylphosphoramidate which exists as an equilibrium mixture of O- and N-silylated tautomers.[192]

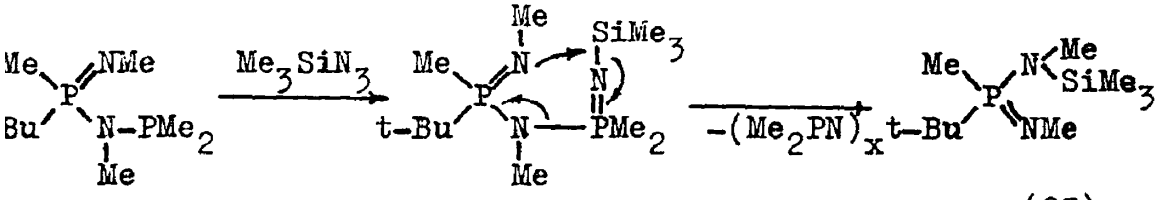
$$(PhO)_2P(O)N(Ph)SiMe_3 \rightleftharpoons (PhO)_2P(OSiMe_3)NPh \qquad (24)$$

89% 11%

O-Silylated phosphazo compounds, having weakly nucleophilic N atoms, do not rearrange even at temperatures higher than 100 [154] (Table 11).

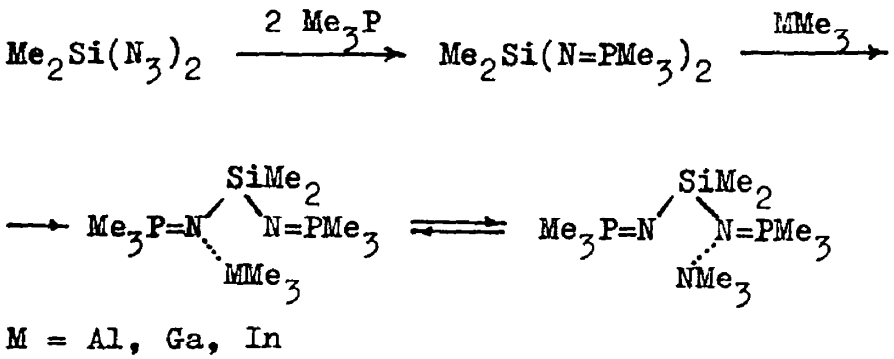
The condensation of O-silylated esters of phosphorus(III) acids with phosphoric acid azides is accompanied by reversible and irreversible shifts of a trimethylsilyl residue from one P atom to another[135] (Table 11).

The oxidative imination yielding heteroorganic phosphamidines is also followed by reversible and irreversible migrations of heteroorganic fragments.[124,142,150-152,193,194] By its nature, the migration of these ligands within N-P-N triad is closely related to the prototropic rearrangements which are so typical for phosphamidines. An example of Me_3Si migration between two separated phosphazo groups has been recently reported.[195]



(25)

The elementotropic shifts are also characteristic for bisphosphazosilane complexes with aluminium, gallium and indium methylates.[196]



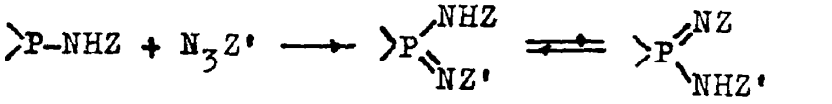
(26)

M = Al, Ga, In

The facility of the imide-amide or imide-imide rearrangements and the direction of organic or heteroorganic radical migration are mainly determined by the relative nucleophilicity of the terminus atoms in the O-P-N or N-P-N triad and O-P-N-P-O pentad systems. When the pair of O or N terminus atoms display similar nucleophilic properties, the migration of the heteroorganic residue becomes reversible (Table 11).

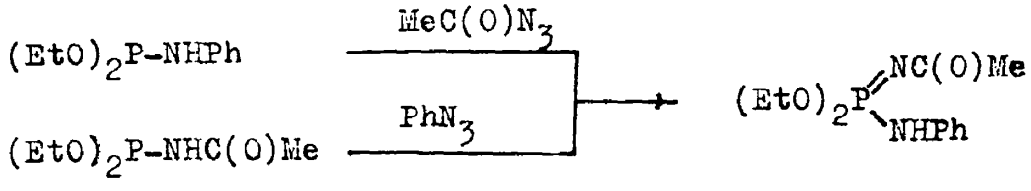
The electrophilicity of a migrating group is also important but in some cases its steric effect becomes a decisive factor. In sterically hindered phosphamidines heteroorganic radicals migrate in such a way that the most bulky group locates at the less hindered imide nitrogen.

Phosphazo compounds are known to be rather strong bases. Therefore, when a molecule of the phosphorus(III) compound or that of the azide contains HO-, HN- or HC-acidic proton the Staudinger reaction is often accompanied by the prototropic rearrangements. Such convertions in the N-P-N triad are well known for the Staudinger reaction with N-monosubstituted amides of P^{III} acids.[112,197]

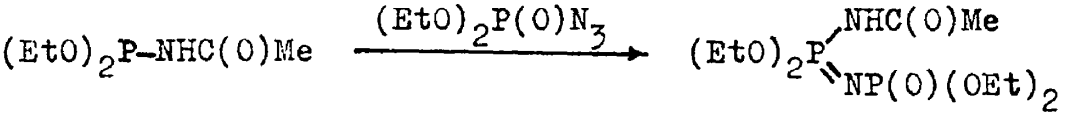


(27)

Irrespective of a preparative route, the tautomeric form ($Z \neq Z'$) being a weaker acid is predominantly or exclusively formed according to the theory of tautomeric equilibrium.[198] Some examples are presented below.[112]

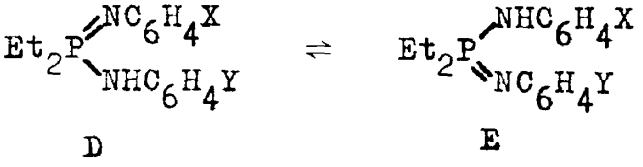


(28)



(29)

The tautomeric equilibrium of N,N'-diaryl phosphamidines is very sensitive to the nature of X and Y substituents. For example, the equilibrium constant, $K_T = [E]/[D]$, for the following set of substituents changes in the range of several orders of magnitude:[197]

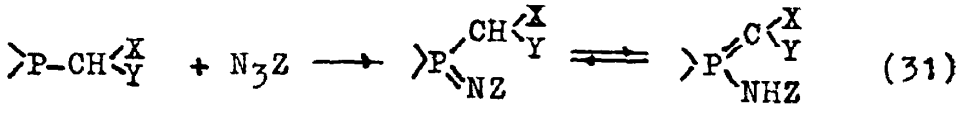


(30)

X	Y	K_T
p-Me_2N	H	38.41
p-MeO	H	3.25
H	H	1.00
p-Cl	H	0.28
p-NO_2	H	0.01

The relatively high value of ρ constant in the correlation equation, $pK_T = 1.793(\sigma_p^X - \sigma_p^Y)$, is indicative of a high flexibility of the tautomeric interconversion.[197]

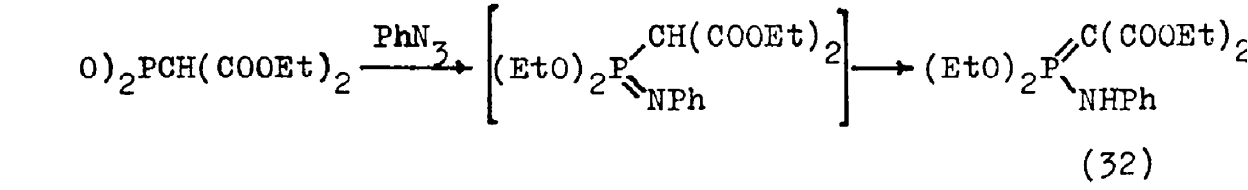
Recently, the carbon analogs of phosphamidines, containing the C-P-N triad system, have been obtained by the Staudinger reaction.[31,146,147]



(31)

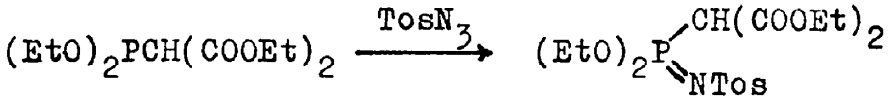
The carbon centre in such structures is known to be more basic than the nitrogen site. However, when X and Y are sufficiently electronegative the basicity of the nitrogen may exceed that of the C atom, and this inevitably results in the migration of a CH-acidic proton and ylid formation as shown in eqn (31).

The phosphazo-ylid isomerization was first discovered in 1974 in the imination of C-phosphorylated malonic esters by phenyl azide.[199]



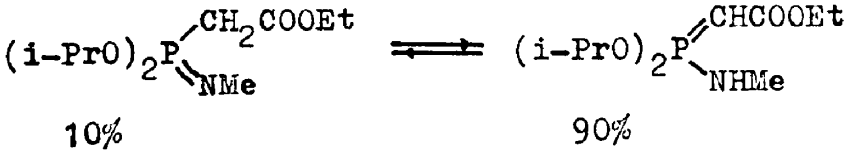
(32)

The prototropic shift in the reaction with tosyl azide does not occur because the basicity of the N atom in the phosphazo compound formed is markedly reduced.[31]

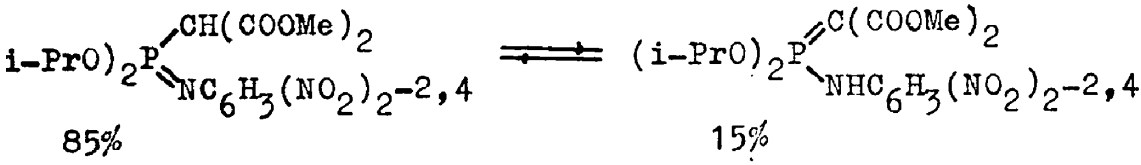


(33)

When CH- and NH-acidity are comparable the proton migration becomes reversible.[200]

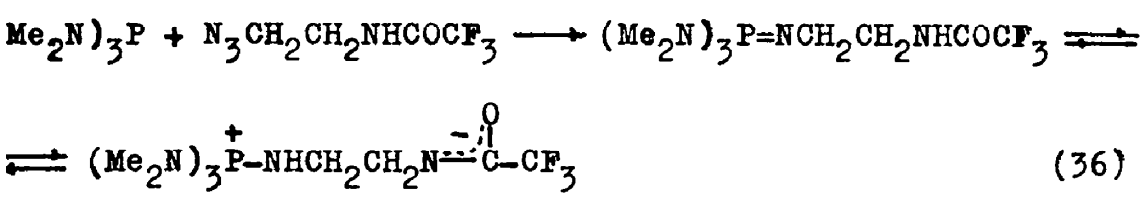


(34)



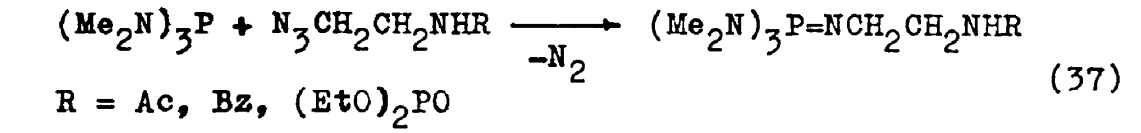
(35)

Some interesting cases of prototropic rearrangements have been revealed in the condensation of phosphorus(III) compounds with acylamino- and carboxy-substituted alkyl azides. The phosphazo compounds thus formed undergo an intramolecular protonation of the P=N bond to give zwitterions which are stable in the solid state but convert into the neutral form in solution.[201,202]



(36)

As NH-acidity decreases the phosphazo-betaine isomerization becomes slower and finally ceases,[201] e.g.



(37)

In the imination of triethyl phosphite by azidoacetic acid the intermediate zwitterion undergoes an intramolecular alkylation.[202]

$$(EtO)_3P + N_3CH_2COOH \xrightarrow[-N_2]{} \left[(EtO)_3\overset{+}{P}-NHCH_2COO^-\right] \longrightarrow (EtO)_2P(=O)NHCH_2COOEt \quad (38)$$

The prototropic rearrangement also accompanies some reactions of azides with secondary phosphines. It proceeds with a proton migration from phosphorus to nitrogen to yield, finally, phosphamidines.[114,203-206] Some examples are given in eqns (39).[203] (40)[204] and (41).[205]

$$Et_2PH \xrightarrow{PhN_3} Et_2P(H)=NPh \longrightarrow Et_2P-NHPh \xrightarrow{PhN_3} Et_2P(=NPh)NHPh \quad (39)$$

$$Ph_2PH \xrightarrow{Ph_2P(O)N_3} Ph_2P(=O)-NHPPh_2 \xrightarrow{Ph_2P(O)N_3} Ph_2P(NHP(O)Ph_2)=NP(O)Ph_2 \quad (40)$$

$$Ph_2PH \xrightarrow{Me_3SiN_3} Ph_2P-NHSiMe_3 \xrightarrow{Me_3SiN_3} Ph_2P(=NSiMe_3)NHSiMe_3 \quad (41)$$

In the case of tetraethyldiamino phosphine and phenyl azide the reaction is completed at the stage of secondary phosphazide formation.[206]

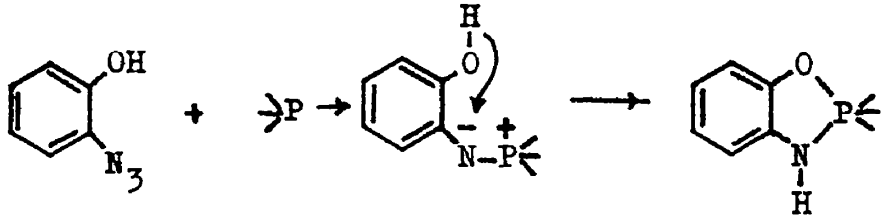
$$(Et_2N)_2PH \xrightarrow[-N_2]{PhN_3} (Et_2N)_2P-NHPh \xrightarrow{PhN_3} (Et_2N)_2P(NHPh)=N-N=NPh \quad (42)$$

Heteroorganic phosphines react with azides similarly,[153,193,207] as shown in eqn (43)[153] and (44).[193]

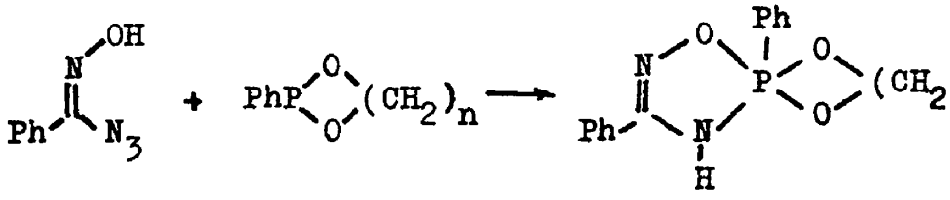
$$Me_2PSiMe_3 \xrightarrow{Me_3SiN_3} Me_2P-N(SiMe_3)_2 \xrightarrow{Me_3SiN_3} Me_2P(N(SiMe_3)_2)=NSiMe_3 \quad (43)$$

$$Me_2PGeMe_3 \xrightarrow{MeN_3} Me_2P-N(Me)GeMe_3 \xrightarrow{MeN_3} Me_2P(N(Me)GeMe_3)=NMe \quad (44)$$

The Staudinger reaction with azides containing either an hydroxyl or amino functional group is followed by an intramolecular nucleophilic attack of the O or N atom on phosphorus and subsequent proton migration to the N atom of the P=N bond and pentaco-ordinate phosphorane formation.[208,209]

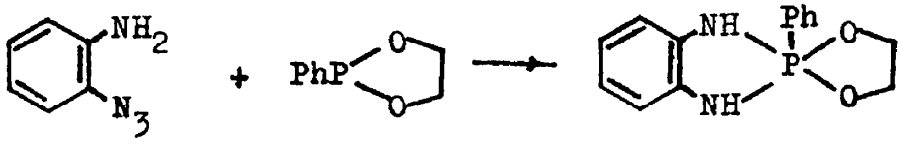


(45)



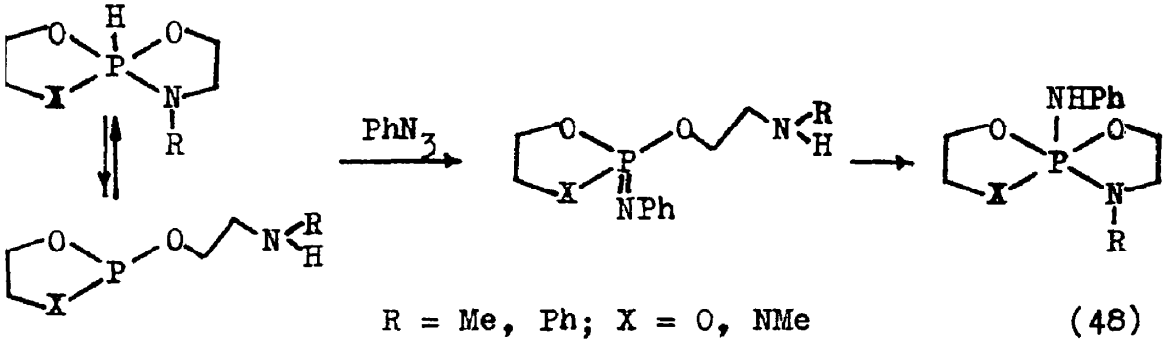
(46)

n = 1–3

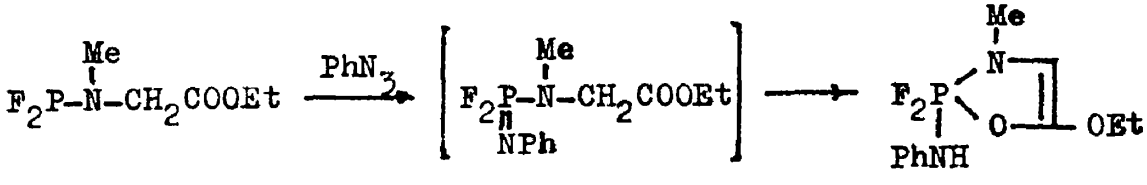


(47)

Analogous results were obtained in the condensation of azides with bisfunctional organophosphorus(III) derivatives as depicted in eqns (48)[210] and (49).[163]

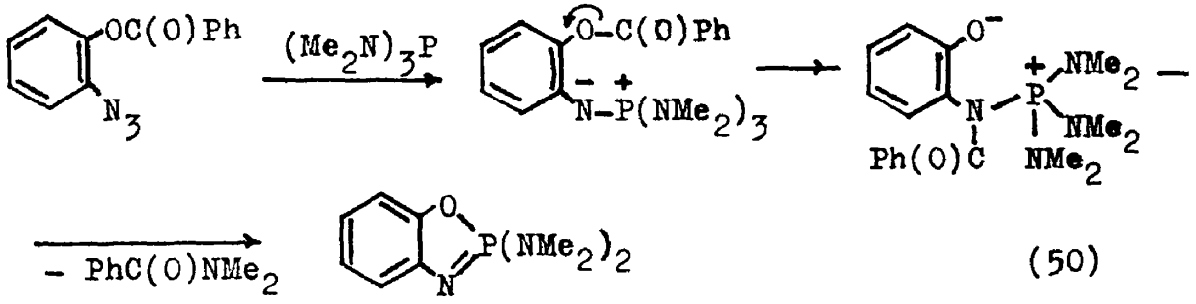


R = Me, Ph; X = O, NMe (48)



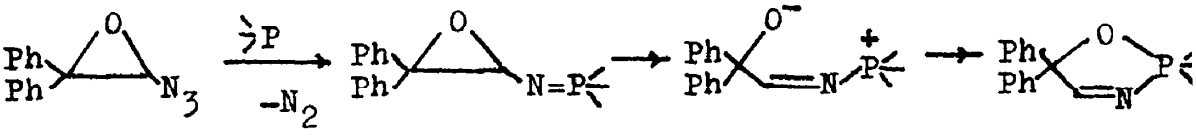
(49)

A benzoyl fragment can also act as an electrophilic migrating group.[208]



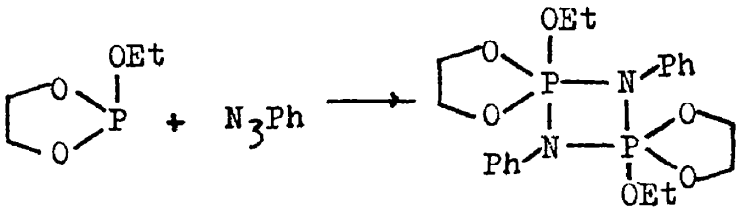
(50)

The Staudinger reaction with 2-azido-oxiranes proceeds with C–O–C bond cleavage and formation of 5-membered cyclic phosphoranes.[211]



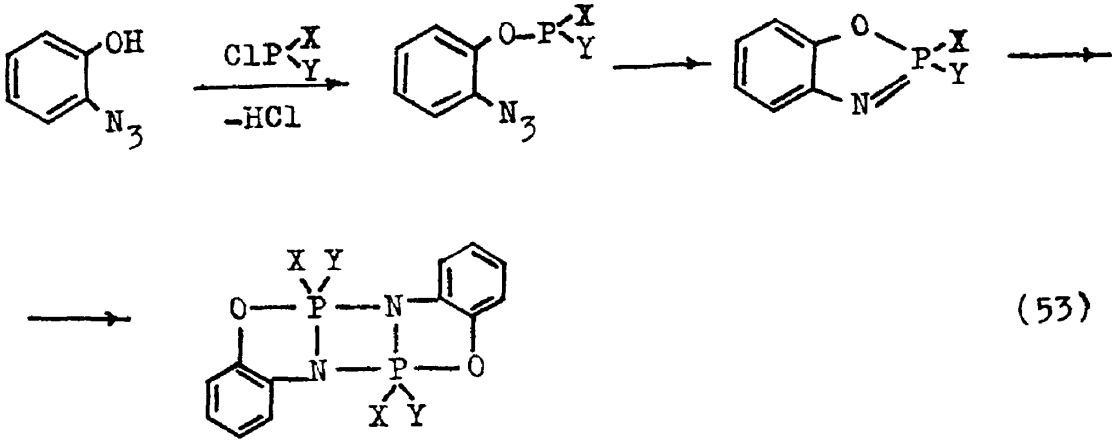
(51)

Some phosphazo compounds with highly electrophilic phosphorus and a sufficiently nucleophilic N atom are known to dimerize to 4-membered aminophosphoranes with alternating P–N bonds. For their preparation the phosphazo reaction is usually used, while the Staudinger procedure is chosen occasionally,[212] e.g.



(52)

Recently, the interesting intramolecular Staudinger reaction yielding dimeric 2-phosphabenzoxazoles has been reported.[213]



(53)

3.2 *Electronic nature of phosphazo group.* The electrodonative character of the $R_3P{=}N$ group with respect to the organic residue, Z, attached to the N atom is due to a polar nature of P=N bond. It was confirmed by many known physical and chemical properties of phosphazo compounds.

$$R_3P{=}N\text{-}Z$$

If Z is an aromatic system one can determine the position of a $R_3P{=}N$ group in a series of known electron-releasing substituents using $\sigma\rho$-analysis. The Staudinger reaction is the best method for the preparation of the phosphazo compounds required for this purpose.

As will be shown, the influence of the phosphazo group upon the remaining part of a molecule is negligibly affected by the kind of substituents on phosphorus. Therefore, in order to assess the electron nature of all or most of $R_3P{=}N$ groups it is sufficient to characterize one of them. The triphenylphosphazo group, $Ph_3P{=}N$, may be chosen as a "standard" because the corresponding phosphazo compounds are easily accessible and convenient in operation.

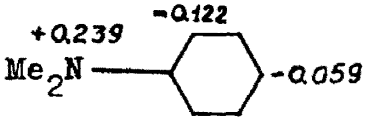
In the aromatic ring, the electron-releasing effect of triphenylphosphazo group approaches that of dimethylamino radical,[19,24,214,215] the main qualitative difference being the reverse sign of Taft σ^* and the inductive component of Hammett σ constants. As a substituent on tetrahedral phosphorus, the triphenylphosphazo group is the most effective of the known donors, twice as strong as the dimethylamino group (Kabachnik σ^φ constants[216]).

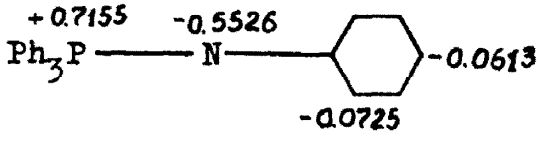
	$Ph_3P{=}N$	Me_2N
σ_m	−0.33*)[214,215]	−0.21
σ_p	−0.77[214,215]	−0.83
σ_m^o	−0.33[19]	−0.15
σ_p^o	−0.40[19]	−0.44
σ_R	−0.66[215]	−0.93
σ_R^o	−0.39[215]	−0.54
σ_I	−0.11[215]	+0.10
σ^+	−1.66[24]	−1.70
σ^*	−0.68[156]	+0.65
σ^φ	−2.72 (in $MeNO_2$)[156]	−1.22**)

*All σ values are presented for ethanolic solutions.

**The values of σ^φ are taken from the compilation[216] if otherwise mentioned.

Though the electron effects of Me_2N and $Ph_3P{=}N$ groups on a carbon reactive centre are comparable, it does, by no means, predict a close analogy in the chemical behaviour of dimethylanilines and triphenylphosphazobenzenes. Due to strong polarization of P=N bond, the N atom in triphenylphosphazobenzene is much more electron-rich than that in dimethylaniline.[217]





Such a different distribution of electron density results in markedly different properties. Triphenylphosphazobenzenes are far more basic than anilines and dimethylanilines.[15,19,215,218,219]

Compound	$PhNH_2$	$PhNMe_2$	$Ph_3P{=}NPh$
pK_a (in $MeNO_2$)	9.07[220]	11.00[221]	16.74[19]

Phosphazo compounds having two basic sites, triphenylphosphazoanilines, triphenylphosphazobenzylidenanilines, and even triphenylphosphazoazobenzenes, are protonated exclusively or mainly at phosphazyl nitrogen.[23,222] Whereas triphenylphosphazo compounds are readily protonated, they, in contrast to dimethylanilines, reveal no electrophilic substitution in weakly acidic media. Meanwhile, only one example of such reactions, i.e. tricyanovinylation, proceeding, however, in pyridine solution is known.[17]

The substitution of a phenyl fragment, attached to phosphorus, by any other radical has a weak influence on the electron-releasing character of a phosphazyl group. For ten phosphazobenzenes of the type $R^1R^2R^3P{=}NC_6H_4X$ (III) with a set of substituents, R^1, R^2, R^3, displaying different influences on phosphorus ($\Sigma\sigma^\varphi$), the σ_p values for $R^1R^2R^3P{=}N$ groups are almost the same,[126] e.g.

	$(MeO)_3P{=}N$	$Et(EtO)_2P{=}N$	$Et_2N(EtO)_2P{=}N$
σ_p	−0.51	−0.55	−0.58
$\Sigma\sigma^\varphi$	−0.36	−1.52	−1.96

An analogous situation was observed in the series of substituted phosphazobenzenes, $(R^1C_6H_4)(R^2C_6H_4)(R^3C_6H_4)P{=}NC_6H_4X$ (IV), where σ parameters of triarylphosphazo groups show little dependence on variable substituents X,[94,223,224] and $\Sigma\sigma^\varphi$ values of three aryl groups at phosphorus.[24,29,94,223] Their σ_p constants range in the same short interval as for Et_2N, Me_2N and H_2N.

	$(p\text{-}Me_2NC_6H_4)_3P{=}N$	$Ph_3P{=}N$	$(p\text{-}F_3CC_6H_4)_3P{=}N$
σ_p	−0.87[223]	−0.79[223]	−0.72[223]
σ_I	−0.24[29]	−0.16[29]	−0.01[29]
σ^+	−1.80[223]	−1.66[24]	−1.52[24]
$\Sigma\sigma^\varphi$	−3.51	−1.77	−0.22[93]

For systems III and IV the linear relationships between electron donor effect of phosphazo groups and $\Sigma\sigma^\varphi$ values of three substituents attached to phosphorus have been found.[29,126] The extremely low values of ρ constants in the corresponding correlation equations (54) give more evidence for the relative constancy of the electron effect of $\geqslant P{=}N$ radicals bearing various substituents at phosphorus.

$$\sigma_p = -0.485 + 0.05\Sigma\sigma^\varphi \quad \text{(for III)}^{126} \quad (54a)$$

$$\sigma_p = -0.71 + 0.048\Sigma\sigma^\varphi \quad \text{(for IV)}^{29} \quad (54b)$$

$$\sigma_p^0 = -0.43 + 0.090\Sigma\sigma^\varphi \quad \text{(for IV)}^{29} \quad (54c)$$

$$\sigma^+ = -1.48 + 0.097\Sigma\sigma^\varphi \quad \text{(for IV)}^{29} \quad (54d)$$

In contrast, the basicity and nucleophilic properties of phosphazo compounds are fairly sensitive to variation in the electronic nature of the phosphorus substituents.[15,27,219,225] For compounds III[219] and IV[27] pK_a values in nitromethane range within four and seven units, respectively, while ρ constants for the modified Hammett correlation of the type $pK_a - \Sigma\sigma^\varphi$ are −1.8 and *ca* −2.0.

Compounds of the type III[219]	pK_a (in $MeNO_2$)	$\Sigma\sigma^\varphi$
$Et_2(EtO)P{=}NPh$	17.81	−2.41
$(MeO)_3P{=}NPh$	13.81	−0.36
Compounds of the type IV[27]		
$(p\text{-}Me_2NC_6H_4)_3P{=}NPh$	20.77	−3.51
$Ph_3P{=}NPh$	16.74	−1.77
$(p\text{-}F_3CC_6H_4)_3P{=}NPh$	13.78	−0.22

Phosphazo compounds are useful models to study the conductivity of electronic effects through the bridge fragments including a tetrahedral P atom. For instance, comparing the influence of the substituents X and R^i upon basicity of the phosphazobenzenes (IV) is is possible to describe quantitatively the attenuation effect of the P atom. Its measure will be the ratio of ρ constants in the correlation equations $pK_a - \Sigma\sigma_p^{R^i}$ and $pK_a - \sigma_p^x$, ρ_2/ρ_1, which equals 0.49 (for nitromethane solvent).[28]

ρ_2 ρ_1

$$(R^1C_6H_4)(R^2C_6H_4)(R^3C_6H_4)P{=}NC_6H_4X \qquad \text{(IV)}$$

$$pK_a = 16.42 - 3.47\sigma_p^x \quad (R^1 = R^2 = R^3 = H) \qquad (55a)$$

$$pK_a = 16.75 - 1.69\Sigma\sigma_p^{R^i} \quad (X = H) \qquad (55b)$$

The similar attenuation of electronic effects by the P atom was obtained in protonation and methylation reactions of phosphamidines (V) and their anions (VI).

Substrate		Reaction	ρ_2/ρ_1 (Solvent)
$(\rho_2)\ (\rho_1)$ $RC_6H_4(Me)N-P(Et)(Et)=NC_6H_4X$	(V)	Methylation with MeI	0.40 (THF)[226]
		Protonation	0.40 ($MeNO_2$)[226]
$(\rho_2)\ (\rho_1)$ $[RC_6H_4N=P(EtO)(OEt)=NC_6H_4X]^-$	Na^+ (VI)	Methylation with MeI	0.59 (THF)[225] 0.646 (THF)[227]

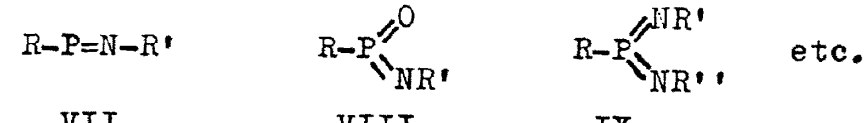
For each of the three series, IV, V and VI, the ρ_2/ρ_1 ratio is *ca* 0.5, i.e. the P atom reduces the effect of the substituents R' approximately by a factor of two.

The compounds IV contain one more bridge system which links the removed reactive centres, with the P atom being in the middle of a conjugation chain. The quantitative measure of the transmission ability of a fragment -N=P-C_6H_4- may be the ratio ρ'_2/ρ'_1 taken from the correlation equations describing a dependence of any measurable property of the groups X or C_6H_4X on variable radicals R in properly substituted phosphazobenzenes and benzenes.

Measurable Property	Number of Series	ρ'_2/ρ'_1
ν_{max} in electronic spectra of the C_6H_4X fragment	5	0.045–0.097 [28]
δ_p^F (X = F)	1	0.053 [29]

As one can see, the ratios ρ'_2/ρ'_1 are extremely low, *ca* 0.05. For the carbon analogs of phosphazo compounds, phosphinomethylenes $Ph_2(RC_6H_4)P=CHC_6H_4X$, the value of ρ'_2/ρ'_1 characterizing the transmission effect of the -CH=P-C_6H_4- fragment is of the same order, i.e. 0.021–0.039.[228]

3.3 *Staudinger reaction and evidences for existence of compounds containing tri-coordinate quinquevalent phosphorus.* The existence of bi-coordinate phosphorus(III) and tri-coordinate phosphorus(V) compounds has been a controversial question since Michaelis' investigations. This nearly centennial discussion was closely connected with the more general problem of similarities and differences in the chemical behaviour of nitrogen and phosphorus compounds. At the end of the XIXth and the beginning of the XXth century the existence of any phosphorus analogs of nitrogen compounds was thought to be a matter of course, and Michaelis, by analogy, assigned to some phosphorus derivatives the following structures



VII VIII IX

Later on, Michaelis and others found that many substances of the type VII-IX were dimeric or polymeric, though the possible occurrence of the monomers was not rejected. In the years between 1940 and 1950 an opposite point of view emerged. Such structures were postulated to be impossible because of already known fundamental differences in properties of nitrogen and phosphorus. However, in 1964 the first representatives of bi-coordinate phosphorus(III) were synthesized and in 1973 the compounds VII possessing bulky radicals, R and R', were prepared. In 1974 the first derivative of tri-coordinate phosphorus(V), [bis(trimethylsilyl)-amino]bis(trimethylsilylimino) phosphorane (IXa), was obtained by the Staudinger procedure.[229,230]

$$(Me_3Si)_2N\text{-}P{=}NSiMe_3 + 2\ Me_3SiN_3 \longrightarrow (Me_3Si)_2N\text{-}P(=NSiMe_3)(=NSiMe_3)\cdot Me_3SiN_3 \xrightarrow{\Delta} (Me_3Si)_2N\text{-}P(=NSiMe_3)(=NSiMe_3) \quad (56)$$

IXa

The monomeric nature of the compound IXa was unambiguously proved by chemical[231] and physical methods[229] including X-ray data.[232] A molecule of the phosphorane IXa is flat, with both P=N bonds being considerably shortened, presumably because of their π-character.

The synthesis of compound IXa provides more evidence in favour of a definite, though limited, analogy between nitrogen and phosphorus chemistry.

4. PHOSPHAZO COMPOUNDS AS STARTING MATERIALS IN SYNTHESIS

Many phosphazo compounds obtained by the Staudinger reaction may be converted to other phosphazo products by the substitution or modification of the radicals on nitrogen. For this purpose, phosphazosilanes are mainly used, as shown in eqns (57)[233-241] and (58).[236]

$\geqslant P{=}NSiMe_3$ →

$Me_{4-n}SiF_n$	$\geqslant P{=}NSiMe_{3-n}F_n$	Ref. 233
C_6F_6	$\geqslant P{=}NC_6F_5$	Ref. 234
ClCN	$\geqslant P{=}NCN$	Ref. 235
SO_3	$\geqslant P{=}NSO_2OSiMe_3 \xrightarrow{H_2O} \geqslant P{=}NSO_3H$	Ref.2
Cl_3CCHO	$\geqslant P{=}NCH(CCl_3)\text{-}OSiMe_3$	Ref. 237
AlkNCO	$\geqslant P{=}NC(O)N(Alk)SiMe_3$	Ref. 238
Alk_2NCCl_3	$\geqslant P{=}NCCl_2NAlk_2$	Ref. 239
$P(OR)_3$	$\geqslant P{=}NP(OR)_2$	Ref. 240
R_2BHal	$\geqslant P{=}NBR_2$	Ref. 241

$$Ph_2P(=N\text{-}SiMe_3)\text{-}CH_2\text{-}PPh_2(=N\text{-}SiMe_3) \xrightarrow[-(Me_3SiO)_2SO_2]{SO_3} Ph_2P(=N)\text{-}CH_2\text{-}PPh_2(=N)\text{-}SO_2 \quad (58)$$

The alcoholysis of trialkyl-,[65] triaryl-,[242] triamido-[131,137] and other P-substituted phosphazosilanes[152,243] is one of the most convenient methods for synthesis of phosphazohydrides.

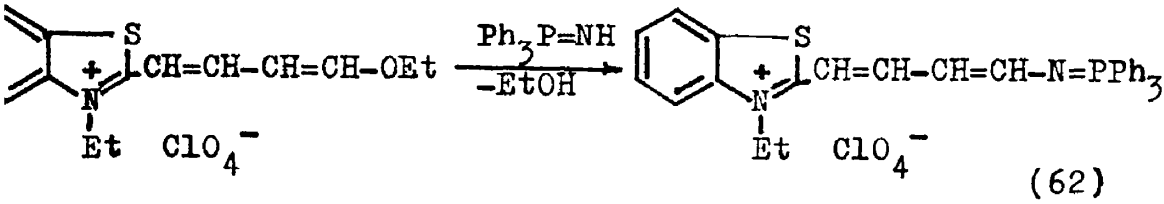
$$\geqslant P{=}NSiMe_3 \xrightarrow{ROH} \geqslant P{=}NH \qquad (59)$$

The hydrolytic cleavage of the silanes by HCl yields the hydrochloric salts of the corresponding phosphazohydrides.[244]

$$\geqslant P{=}NSiMe_3 \xrightarrow{HCl} \left[\geqslant P{-}NH_2\right]^+ Cl^- \qquad (60)$$

The phosphazohydrides, in turn, are widely used for preparation of phosphazo compounds with various substituents on nitrogen. For some this synthetic route is the only or the preferred one. Some examples are shown in eqns (61),[245-248] (62),[249] (63),[73] (64)[250] and (65).[131]

$$Ph_3P{=}NH \xrightarrow{\begin{array}{l}RSOCl\\ SO_2Cl_2\\ RNCO\\ Cl_3CCN\end{array}} \begin{array}{l}Ph_3P{=}NSOR\\ Ph_3P{=}NSO_2Cl\\ Ph_3P{=}NC(O)NHR\\ Ph_3P{=}NC(NH)CCl_3\end{array} \qquad (61)$$



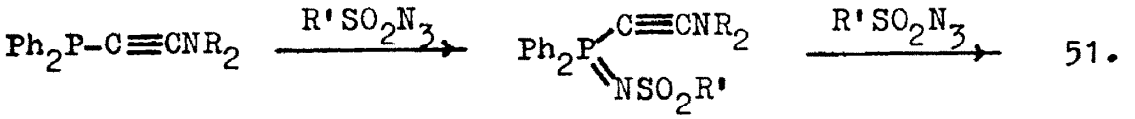
(62)

$$Et_3Sn{-}NEt_2 \xrightarrow[-Et_2NH]{Ph_3P{=}NH} Et_3Sn{-}N{=}PPh_3 \qquad (63)$$

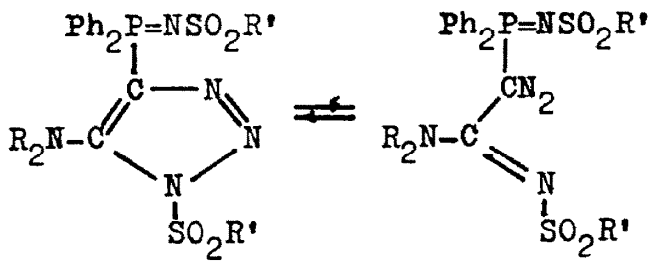
$$(Me_2N)_3P \xrightarrow[-\ 3\ Me_2NH]{Ph_3P{=}NH} P(N{=}PPh_3)_3 \qquad (64)$$

$$MeHg{-}N(SiMe_3)_2 \xrightarrow{(Me_2N)_3P{=}NH} MeHg{-}N{=}P(NMe_2)_3 \qquad (65)$$

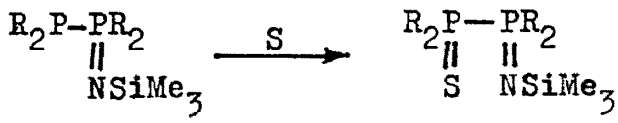
There are several cases when the products of the Staudinger reaction are converted to the new phosphazo compounds by the modification of substituents on the P atom.



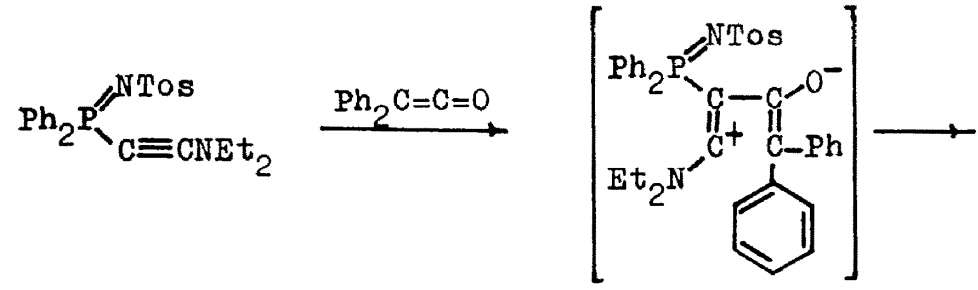
51.

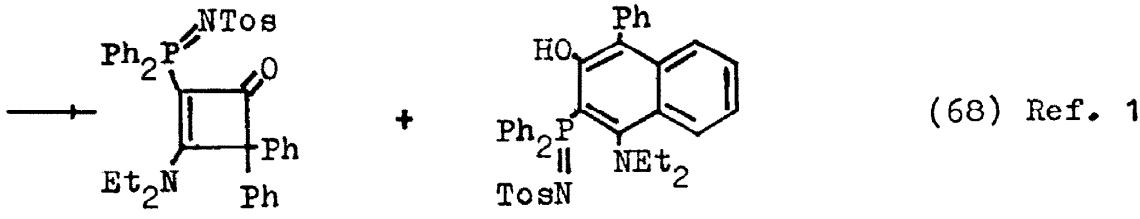


(66) Ref. 5



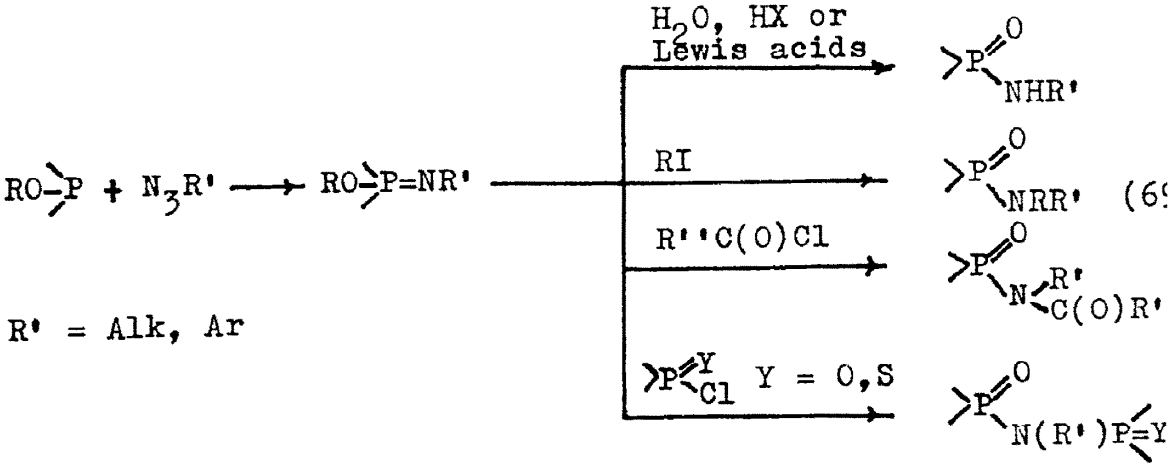
(67) Ref. 7



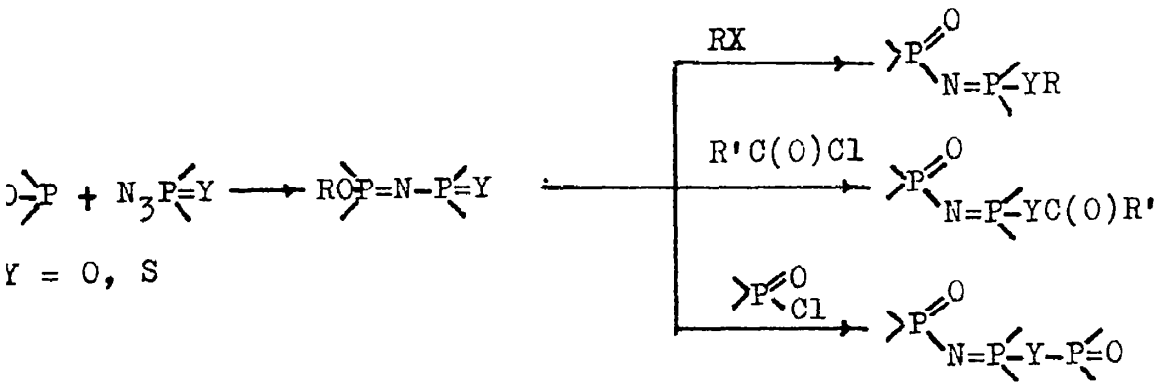


(68) Ref. 1

The reaction of P-alkoxylated phosphazo compounds with electrophiles are often used to prepare N-mono- and N,N-disubstituted amidophosphates, N-phosphorylated imidophosphates, imidopyrophosphates, imides of carboxylic acids, etc according to eqns (69) – (71).[189]



(69)



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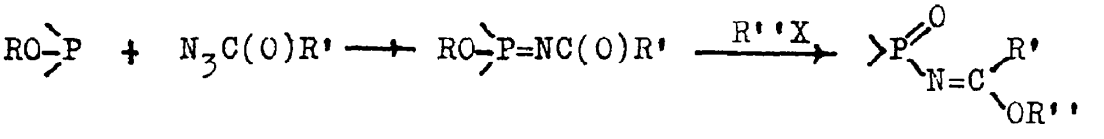
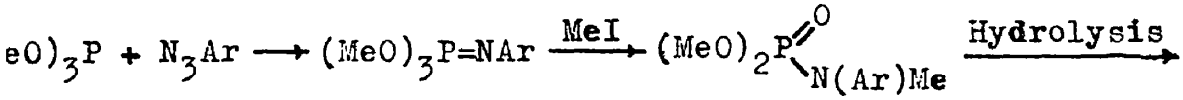


(71)

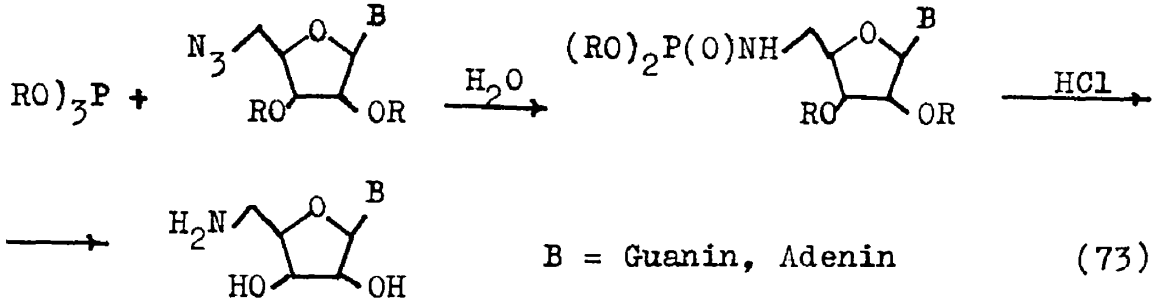
Some of these compounds cannot be obtained by any other method. The thermal rearrangements of phosphazo compounds are used for preparative purposes only occasionally (Section 3.1).

Sometimes, the phosphorus-containing fragments introduced into a molecule by the Staudinger reaction act as easily removable protective groups. The reaction of trimethyl phosphite with aromatic azides can, for example, be used for preparation of monomethylanilines of high purity.[118]



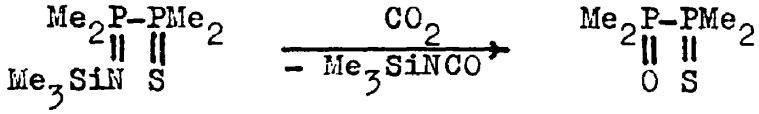
(72)

The phosphite-azide coupling method is utilized to introduce free or phosphorylated amino groups into synthetic analogs of natural substances,[85,251,252] for example[252]



(73)

The well-known reactions of phosphazo compounds with carbon dioxide, carbon disulphide, carbonyl compounds, ketenes, isocyanates, etc are of limited preparative value.[253] Some typical examples of their use are shown below.



(74) Ref.254

$$RC_6H_4C(O)CF_3 + Ph_3P{=}NC_6H_4R' \xrightarrow[-\,Ph_3PO]{} RC_6H_4C(NC_6H_4R')CF_3 \quad (75)\ \text{Ref.25}$$

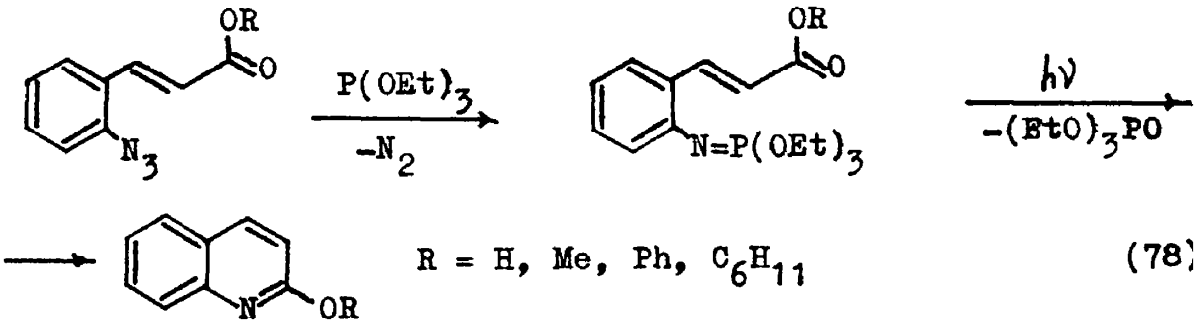
$$RCHO + FcCH_2N{=}PPh_3 \xrightarrow[-\,Ph_3PO]{} FcCH_2N{=}CHR \quad (76)\ \text{Ref. 3}$$

This type of conversion includes also the fairly convenient method for synthesis of primary enamines under acidic catalysis.[256]

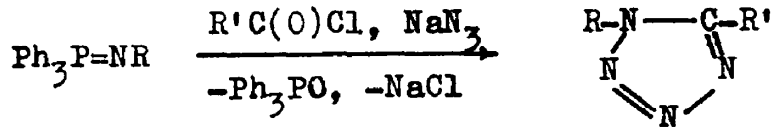
$$Me_3SiN{=}PPh_3 + \text{(1,3-dicarbonyl)}X \xrightarrow[-Ph_3PO,\ -Me_3SiOPr\text{-}i]{i\text{-}PrOH,\ TosOH} \text{(3-amino-2-en-1-one)}X$$

X = R, RO (77)

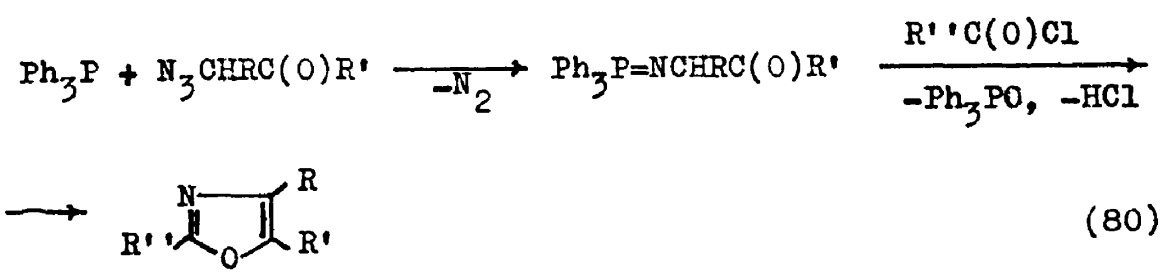
Some chemical and photochemical reactions of phosphazo compounds yield quinolines,[257] tetrazoles,[258] oxazoles[259] and pyrazines.[260]



R = H, Me, Ph, C_6H_{11} (78)



(79)



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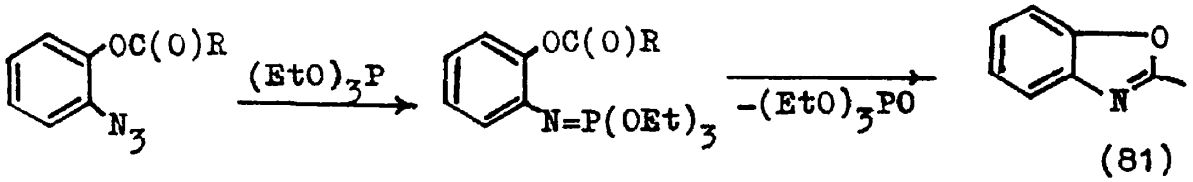
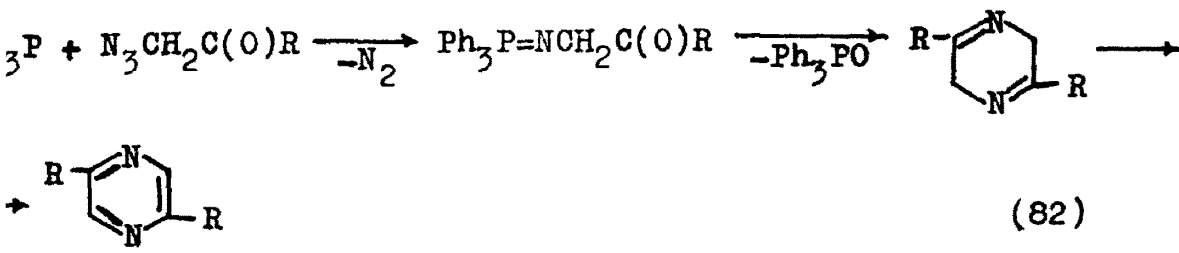


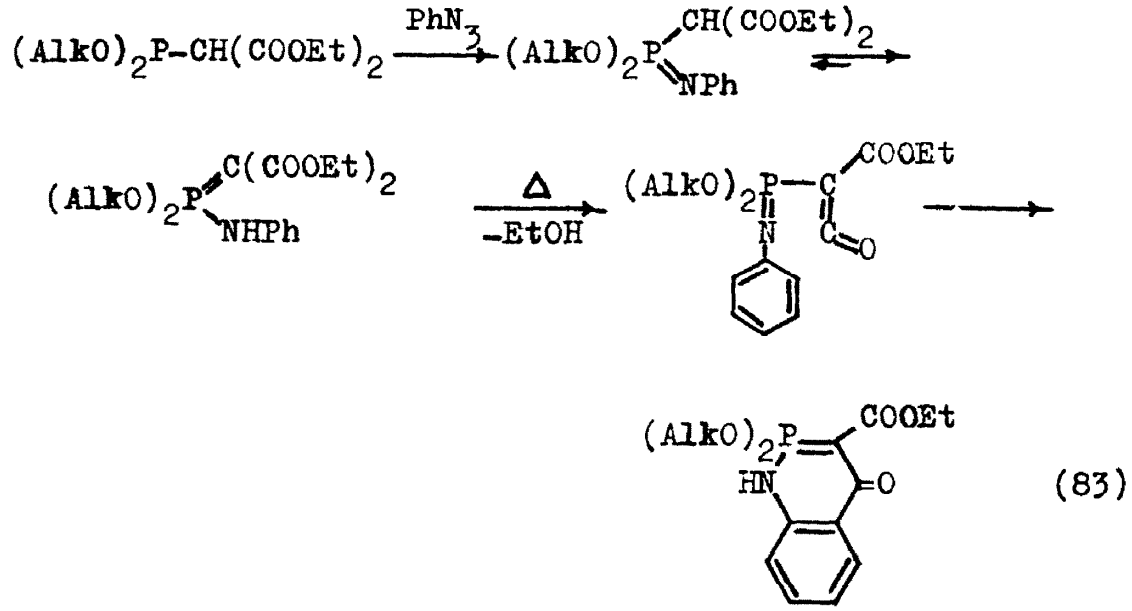
(81)



(82)

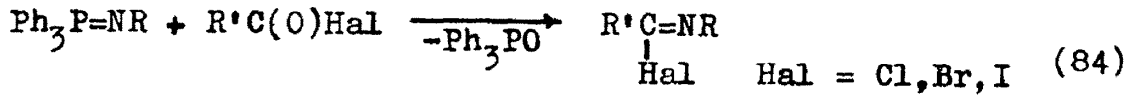
For the quinolines and tetrazoles this method has some advantages over the conventional procedures.

The imination of phosphorylated malonic esters by phenyl azide is accompanied by the elimination of ethyl alcohol and leads to the phosphorus-containing heterocyles, 2-phospha-4-quinolones.[261]



(83)

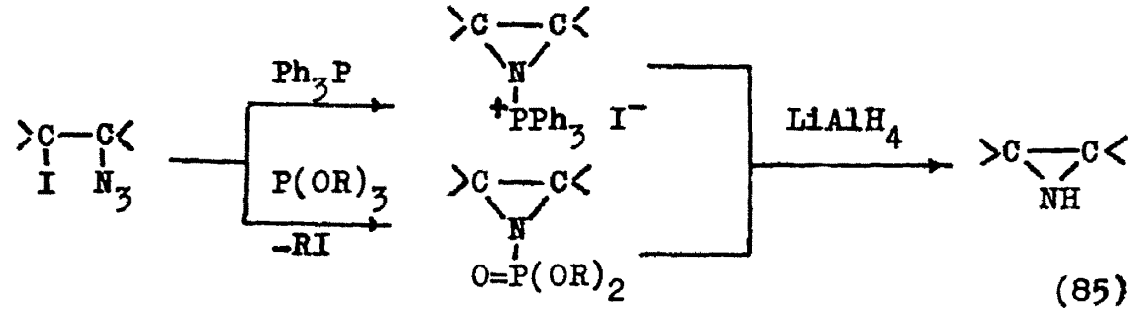
Phosphazo compounds react with acyl halides to give imidoyl halides.[262]



(84)

The reaction is unique in the preparation of imidoyl bromides and iodides, but fails in the case of imidoyl fluorides.

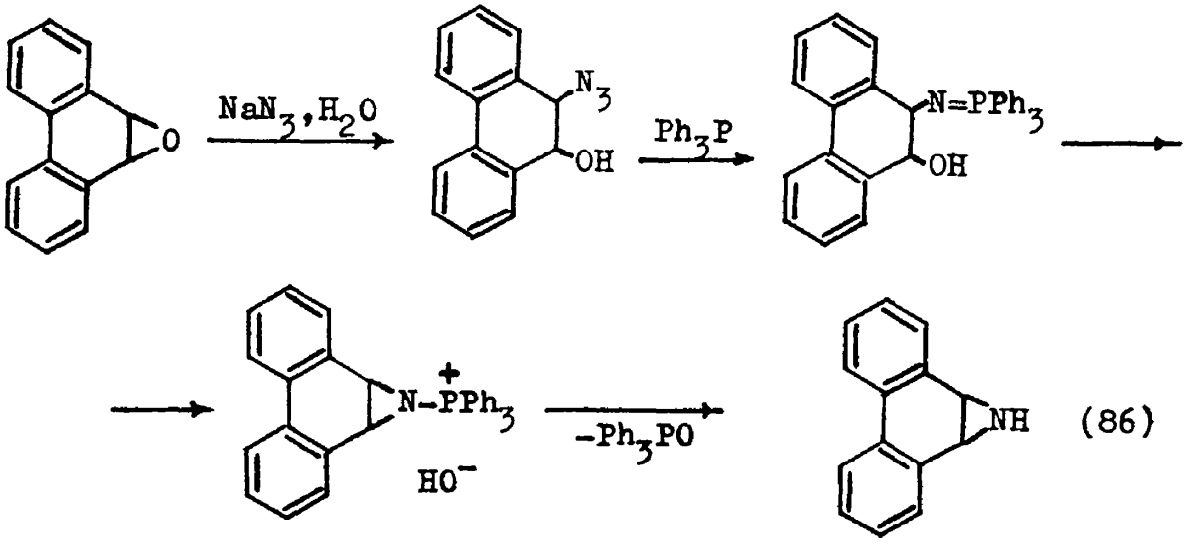
The reaction of 2-iodoalkyl azides with trivalent phosphorus nucleophiles was shown to be a valuable method for aziridine synthesis.[263]



(85)

The phosphorus-containing fragments are readily removed by lithium aluminium hydride.

The Staudinger procedure can also be applied to prepare unsubstituted on nitrogen aziridines from oxiranes.[264] This approach is particularly useful when the oxiranes are accessible, while the corresponding aziridines are impossible or difficult to prepare by the conventional methods.



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REFERENCES

[1] H. Staudinger and J. Meyer, *Helv. Chim. Acta* **2**, 635 (1919).

[2] A. V. Kirsanov, *Izv. Akad. Nauk SSSR. Otd. Khim. Nauk* 426 (1950)

[3] G. I. Derkach, I. N. Zhmurova, A. V. Kirsanov, V. I. Shevchenko and A. S. Shtepanek, *Phosphazo Compounds*. Naukova Dumka, Kiev (1965).

[4] G. I. Derkach, E. S. Gubnitskaya, V. A. Shokol and A. V. Kirsanov, *Zh. Obshch. Khim.* **32**, 1201, 1874 (1962); G. I. Derkach, L. I. Samarai, A. S. Shtepanek and A. V. Kirsanov, *Ibid* **32**, 3759 (1962); G. I. Derkach, E. S. Gubnitskaya, L. I. Samarai and V. A. Shokol, *Ibid.* **33**, 557 (1963).

[5] M. I. Kabachnik, V. A. Gilyarov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* 790 (1956).

[6a] H. R. Allcock, *Phosphorus-Nitrogen Compounds*, Chap. 4. Academic Press, New York (1972); [b] *Ibid.* Chaps. 15 and 16.

[7] G. Singh and H. Zimmer, *Organomet. Chem. Revs* **2**, 279 (1967)

[8] G. L'abbe, *Ind. Chim. Belge* **34**, 519 (1969).

[9] H. Staudinger and E. Hauser, *Helv. Chim. Acta* **4**, 861 (1921).

[10] H. Hellmann, F. Lingens and E. Folz, *Chem. Ber.* **89**, 2433 (1956); A. P. Claydon, P. A. Fowell and C. T. Mortimer, *J. Chem. Soc.* 3284 (1960); G. Wittig and E. Kochendoerfer, *Chem. Ber.* **97**, 741 (1964); I. N. Zhmurova and A. V. Kirsanov, *Zh. Obshch. Khim* **36**, 1248 (1966); B. I. Stepanov, T. G. Edel'man and I. M. Kolbasova, *Ibid.* **37**, 1883 (1967); S. P. Makarov, A. Ya. Yakubovich, A. S. Filatov, M. A. Englin and T. Ya. Nikiforova, *Ibid.* **38**, 709 (1968); H. Goetz and D. Probst, *Liebigs Ann.* **715**, 1 (1968); T. G. Edel'man and B. I. Stepanov, *Zh. Obshch. Khim.* **39**, 712 (1969); B. I. Stepanov and T. G. Edel'man, *Ibid.* **39**, 1549 (1969); B. S. Drach, A. D. Sinitsa and A. V. Kirsanov, *Ibid.* **39**, 2192 (1969); I. N. Zhmurova, A. A. Tukhar and A. V. Kirsanov, *Ibid.* **40**, 986, 2154 (1970); T. G. Edel'man and B. I. Stepanov, *Ibid.* **42**, 1477 (1972); I. N. Zhmurova, V. G. Yurchenko, A. P. Martynyuk and A. V. Kirsanov, *Ibid.* **42**, 1948 (1972); R. E. Banks and A. Prakash, *Tetrahedron Letters* 99 (1973); R. E. Banks and A. Prakash, *J. Chem. Soc.* Perkin I, 1365 (1974); N. A. Orlov, L. L. Dmitrieva, T. N. Gerasimova and E. P. Fokin, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk* No. 3, 114 (1976); R. I. Yurchenko and V. P. Malitskaya, *Zh. Org. Khim.* **13**, 1980 (1977).

[11] J. E. Leffler and R. D. Temple, *J. Am. Chem. Soc.* **89**, 5235 (1967).

[12] L. Horner and A. Gross, *Liebigs Ann.* **591**, 117 (1955).

[13] G. Wittig and K. Schwarzenbach, *Ibid.* **650**, 1 (1961).

[14] L. Horner and H. Winkler, *Tetrahedron Letters* 175 (1964).

[15] A. W. Johnson and S. C. K. Wong, *Can. J. Chem.* **44**, 2793 (1966).

[16] W. Wiegrabe and H. Bock, *Chem. Ber.* **101**, 1414 (1968).

[17] I. N. Zhmurova and R. I. Yurchenko, *Zh. Obshch. Khim.* **38**, 613 (1968).

[18] T. G. Edel'man and B. I. Stepanov, *Ibid.* **39**, 714 (1969).

[19] V. P. Kukhar, A. A. Petrashenko, I. N. Zhmurova, A. A. Tukhar and S. N. Solodushenkov, *Ibid.* **40**, 1696 (1970).

[20] I. N. Zhmurova, A. P. Martynyuk and A. V. Kirsanov, *Ibid.* **41**, 782 (1971).

[21] I. N. Zhmurova, A. A. Tukhar and A. V. Kirsanov, *Ibid.* **41**, 785 (1971).

[22] J. I. G. Cadogan, R. Gee and R. J. Scott, *J. Chem. Soc.* Chem. Comm. 1242 (1972); J. I. G. Cadogan, R. J. Scott, R. D. Gee and I. Gosney, *Ibid.* Perkin I. 1694 (1974)

[23] V. P. Kukhar, I. N. Zhmurova, L. A. Zolotareva and A. A. Tukhar, *Zh. Org. Khim.* **8**, 756 (1972).

[24] I. N. Zhmurova, R. I. Yurchenko, V. G. Yurchenko, A. A. Tukhar and A. V. Kirsanov, *Zh. Obshch. Khim.* **42**, 779 (1972).

[25] I. N. Zhmurova and V. G. Yurchenko, *Ibid.* **43**, 86 (1973).

[26] V. A. Galishev, V. N. Chistokletov, A. A. Petrov and L. A. Tamm, *Ibid.* **43**, 1470 (1973).

[27] I. N. Zhmurova, V. G. Yurchenko, V. P. Kukhar and L. A. Zolotareva, *Ibid.* **42**, 2656 (1972).

[28]I. N. Zhmurova, V. G. Yurchenko, V. P. Kukhar and L. A. Zolotareva, *Ibid.* **44**, 74 (1974).
[29]I. N. Zhmurova, V. G. Yurchenko, R. I. Yurchenko, E. V. Konovalov and Yu. P. Egorov, *Ibid.* **44**, 2414 (1974).
[30]I. N. Zhmurova and V. G. Yurchenko, *Ibid.* **45**, 1958 (1975).
[31]L. A. Repina, R. A. Loktionova and Yu. G. Gololobov, *Ibid* **46**, 2683 (1976).
[32]I. N. Zhmurova, V. G. Yurchenko, R. I. Yurchenko and T. V. Savenko, *Ibid.* **47**, 2207 (1977).
[33]T. A. Mastryukova, I. M. Aladzheva, I. V. Leont'eva, V. A. Svoren, P. V. Petrovski and M. I. Kabachnik, *Ibid.* **47**, 2449 (1977).
[34]I. N. Zhmurova and V. G. Yurchenko, *Ibid.* **48**, 88 (1978).
[35]V. I. Boiev, *Ibid.* **48**, 1594 (1978).
[36]A. S. Yim, M. H. Akhtar, A. M. Unrau and A. C. Oehlschlager, *Can. J. Chem.* **56**, 289 (1978).
[37]J. E. Leffler and Y. Tsuno, *J. Org. Chem.* **28**, 902 (1963).
[38]V. A. Shokol, V. V. Doroshenko and G. I. Derkach, *Zh. Obshch. Khim.* **45**, 1713 (1975).
[39]C. D. Weis, *J. Org. Chem* **27**, 3514 (1962); H. Neunhoeffer, G. Cuny and W. K. Franke, *Liebigs Ann.* **713**, 96 (1968); H. R. Kricheldorf, *Synthesis* 695 (1972); V. A. Shokol, V. F. Gamaleya and L. I. Molyavko, *Zh. Obshch. Khim.* **44**, 90 (1974).
[40]Y. S. Lo and J. C. Sheehan, *J. Org. Chem.* **40**, 191 (1975).
[41]R. Neidlein and W. Haussmann, *Tetrahedron Letters* 5401 (1966), M. O. Lozinskii, S. N. Kukota, T. N. Kudrya, E. S. Gubnitskaya and P. S. Pel'kis, *Zh Org. Khim.* **5**, 1432 (1969).
[42]R. Neidlein, *Arch. Pharm.* **299**, 1003 (1966); R. Neidlein, *Angew. Chem.* **78**, 333 (1966); E. S. Gubnitskaya, N. S. Tishchishina and A. V. Kirsanov, *Zh. Obshch. Khim.* **43**, 739 (1973); R. Neidlein and W. Friedrich, *Arch. Pharm.* **310**, 614 (1977).
[43]L. I. Samarai, O. I. Kolodyazhnyi, O. V. Vishnevskii and G. I. Derkach, *Zh. Obshch. Khim.* **40**, 750 (1970).
[44]J. E. Leffler, U. Honsberg, Y. Tsuno and I. Forsblad, *J. Org. Chem.* **26**, 4810 (1961).
[45]W. P. Norris and R. A. Henry, *Ibid.* **29**, 650 (1964).
[46]W. Buder and A. Schmidt, *Z. Naturforsch.* **30b**, 503 (1975).
[47]F. D. Marsh and M. E. Hermes, *J. Am. Chem. Soc.* **86**, 4506 (1964); F. D. Marsh, *J. Org. Chem.* **37**, 2966 (1972).
[48]J. E. Franz and C. Osuch, *Tetrahedron Letters* 841 (1963).
[49]V. I. Shevchenko, A. M. Pinchuk and A. V. Kirsanov, *Zh. Obshch. Khim.* **35**, 1488 (1965); E. S. Kozlov and A. I. Sedlov, *Ibid.* **44**, 1029 (1974); C. R. Hall and D. J. H. Smith, *Tetrahedron Letters* 1693 (1974); H. R. Kricheldorf and E. Leppert, *Synthesis* 49 (1975); G. E. Chivers, R. J. W. Cremlyn, Th. N. Cronje and R. A. Martin, *Austral. J. Chem.* **29**, 1573 (1976); Masatomo Nojima, *J. Chem. Soc.* Perkin I, 1811 (1979).
[50]H. Bock and M. Schnöller, *Angew. Chem.* **80**, 667 (1968).
[51]H. Bock and M. Schnöller, *Chem. Ber.* **102**, 38 (1969).
[52]G. Himbert and M. Regitz, *Ibid.* **107**, 2513 (1974).
[53]R. A. Baldwin and R. M. Washburn, *J. Am. Chem. Soc.* **83**, 4466 (1961); R. A. Baldwin, *J. Org. Chem.* **30**, 3866 (1965); R. A. Baldwin, Ch. O. Wilson and R. I. Wagner, *Ibid.* **32**, 2172 (1967); H. W. Roesky and D. Bormann, *Chem. Ber.* **101**, 630 (1968); A. D. Bliss and R. F. W. Raetz, *US Pat.* 3,358,004; U. Felcht and M. Regitz, *Liebigs Ann.* 1309 (1977).
[54]H. Bock and K.-L. Kompa, *Z. Anorg. Allg. Chem* **332**, 238 (1964).
[55]R. A. Baldwin and R. M. Washburn, *J. Org. Chem.* **30**, 3860 (1965).
[56]R. M. Washburn and R. A. Baldwin, *US Pat.* 3,189,564.
[57]H. Bock and W. Wiegräbe, *Chem. Ber.* **99**, 1068 (1966).
[58]R. A. Baldwin and M. T. Cheng, *J. Org. Chem.* **32**, 2636 (1967).
[59]V. A. Shokol, G. A. Golik and G. I. Derkach, *Zh. Obshch. Khim.* **41**, 545 (1971).
[60]H.-G. Horn, M. Gersemann and U. Niemann, *Chem. Ztg.* **100**, 197 (1976).
[61]R. J. W. Cremlyn, R. M. Ellam and N. Akhtar, *Phosphor Sulfur* **5**, 1 (1978).
[62]W. T. Reichle, *Inorg. Chem.* **3**, 402 (1964).
[63]N. Wiberg, F. Raschig and R. Sustmann, *Angew. Chem.* **74**, 388, 716 (1962).
[64]H. Schmidbaur and W. Wolfsberger, *Chem. Ber.* **100**, 1000 (1967); H. Schmidbaur, W. Wolfsberger and K. Schwirten, *Ibid* **102**, 556 (1969); S. S. Washburne and W. R. Peterson, *J. Organomet. Chem.* **33**, 153 (1971); W. Wolfsberger, *Z. Naturforsch.* **30b**, 907 (1975); W. Wolfsberger, *Ibid.* **32b**, 961 (1977).
[65]L. Birkofer and Sung Man Kim, *Chem. Ber.* **97**, 2100 (1964).
[66]J. S. Thayer and R. West, *Inorg. Chem.* **3**, 406 (1964).
[67]R. M. Washburn and R. A. Baldwin, *U.S. Pat.* 3,112,331.
[68]N. Wiberg and B. Neruda, *Chem. Ber.* **99**, 740 (1966).
[69]K. L. Paciorek and R. H. Kratzer, *J. Org. Chem.* **31**, 2426 (1966).
[70]R. Appel and I. Ruppert, *Z. Anorg. Allg. Chem* **406**, 131 (1974).
[71]R. Appel and R. Milker, *Chem. Ber.* **107**, 2658 (1974).
[72]W. L. Lehn, *Inorg. Chem.* **6**, 1061 (1967).
[73]J. Lorberth, H. Krapf and H. Nöth, *Chem. Ber.* **100**, 3511 (1967).
[74]H. Schmidbaur and W. Wolfsberger, *Ibid.* **101**, 1664 (1968).
[75]W. T. Reichle, *J. Organomet. Chem.* **13**, 529 (1968).
[76]S. Yolles and J. H. R. Woodland, *Ibid.* **54**, 95 (1973).
[77]W. Wolfsberger, *Z. Naturforsch.* **32b**, 152 (1977).
[78]Hiroshi Yoshida, Tsuyoshi Ogata and Saburo Inokawa, *Bull. Chem. Soc. Japan* **52**, 1541 (1979).
[79]T. J. Maricich and V. L. Hoffman, *J. Am. Chem. Soc.* **96**, 7770 (1974).
[80]I. N. Zhmurova, A. A. Tukhar and R. I. Yurchenko, *Zh. Obshch. Khim.* **39**, 2201 (1969).
[81]K. Brass and F. Albrecht, *Ber. Deut. Chem. Ges.* **61**, 983 (1928).
[82]W. L. Mosby and M. L. Silva, *J. Chem. Soc.* 1003 (1965).
[83]W. L. Mosby and M. L. Silva, *U.S. Pat.* 3,387,004.
[84]H. Paulsen, Z. Györgydeak and M. Friedmann, *Chem. Ber.* **107**, 1590 (1974).
[85]R. Rauganathan and D. Larwood, *Tetrahedron Letters* 4341 (1978).
[86]I. N. Zhmurova, A. P. Martynyuk and A. V. Kirsanov, *Zh. Obshch. Khim.* **39**, 1223 (1969), A. Messmer, Gy. Hajós, P. Benko and L. Pallos, *J. Heterocycl. Chem.* **10**, 575 (1973); Kenji Fujinuma, Joji Hashida and Kahji Matsui, *Bull. Chem. Soc. Japan* **51**, 2394 (1978).
[87]J. A. Van Allan and C. A. Reynolds, *J. Heterocycl. Chem.* **5**, 471 (1968).
[88]M. I. Bukovskii, S. N. Solodushenkov, A. I. Mosiichuk and V. P. Kukhar, *Zh. Obshch. Khim.* **40**, 782 (1970); V. P. Kukhar, M. I. Bukovskii, T. N. Kasheva, V. S. Paliichuk, A. A. Petrashenko and S. N. Solodushenkov, *Ibid.* **40**, 1226 (1970).

[89]T. Sasaki, K. Kanematsu and M. Murata, *Tetrahedron* **27**, 5359 (1971).
[90]T. Sasaki, K. Kanematsu and M. Murata, *Ibid.* **28**, 2383 (1972).
[91]I. R. A. Bernard, G. E. Chivers, R. J. W. Cremyln and K. G. Mootoosamy, *Austral. J. Chem.* **27**, 171 (1974).
[92]I. N. Zhmurova, R. I. Yurchenko and A. V. Kirsanov, *Zh. Obshch. Khim.* **40**, 982 (1970); I. N. Zhmurova, A. I. Tolmachev, R. I. Yurchenko and Yu. L. Slominskii, *Ibid.* **40**, 2553 (1970); I. N. Zhmurova, R. I. Yurchenko and A. V. Kirsanov, *Ibid.* **41**, 778 (1971).
[93]I. N. Zhmurova, V. G. Yurchenko and A. V. Kirsanov, *Ibid.* **42**, 1944 (1972).
[94]I. N. Zhmurova, V. G. Yurchenko and R. I. Yurchenko, *Ibid.* **43**, 2190 (1973).
[95]G. R. Harvey and K. W. Ratts, *J. Org. Chem.* **31**, 3907 (1966); G. L'abbé and A. Hassner, *Ibid.* **36**, 258 (1971).
[96]Yasumitsu Tamura, Tomohisa Miyamoto, Jiro Eiho, Hiroshi Taniguchi, Tadashi Nishimura and Yasuyuki Kita, *J. Chem. Soc.* Perkin I, 105 (1974).
[97]D. L. Herring, *J. Org. Chem.* **26**, 3998 (1961); A. M. Aguiar and J. Beisler, *Ibid.* **29**, 1660 (1964); V. Yu. Kovtun, V. A. Gilyarov and M. I. Kabachnik, *Izv. Akad. Nauk SSSR, Ser. Khim.* 2612 (1972).
[98]V. A. Gilyarov, V. Yu. Kovtun and M. I. Kabachnik, *Ibid.* 1159 (1967).
[99]H. G. Horn, *Makromol. Chem.* **138**, 163 (1970).
[100]G. Himbert, *Liebigs Ann.* 829 (1979).
[101]V. A. Shokol, G. A. Golik, V. T. Tsyba, Yu. P. Egorov and G. I. Derkach, *Zh. Obshch. Khim.* **40**, 1680 (1970).
[102]H. Schmidbaur and G. Jonas, *Angew. Chem.* **79**, 413 (1967), H. Schmidbaur and G. Jonas, *Chem. Ber.* **100**, 1120 (1967).
[103]H. Schmidbaur and G. Jonas, *Ibid.* **101**, 1271 (1968).
[104]A. S. Shtepanek, E. N. Tkachenko and A. V. Kirsanov, *Zh. Obshch. Khim.* **40**, 1677 (1970).
[105]R. Appel, G. Köhnlein and R. Schöllhorn, *Chem. Ber.* **98**, 1355 (1965).
[106]I. N. Zhmurova and A. V. Kirsanov, *Zh. Obshch. Khim* **29**, 1687 (1959); H. J. Vetter, *Z. Naturforsch.* **19b**, 168 (1964); W. L. Mosby and M. L. Silva, *J. Chem. Soc.* 2727 (1965); M. I. Kabachnik, V. A. Gilyarov and R. V. Kudryavtsev, *Zh. Obshch. Khim.* **35**, 1476 (1965); I. V. Kazimirchik, G. F. Bebikh, F. S. Denisov and M. I. Kabachnik, *Ibid.* **36**, 1226 (1966); V. A. Shokol, N. K. Mikhailyuchenko and G. I. Derkach, *Khim. Org. Soedin. Fosfora, Akad. Nauk SSSR, Otd. Obshch. Tech. Khim.* 78 (1967); K. Pilgram, F. Gorgen and C. Pollard, *J. Heterocycl. Chem.* **8**, 951 (1971); V. A. Gilyarov and M. I. Kabachnik, *Zh. Obshch. Khim.* **42**, 2148 (1972); A. A. Khodak, V. A. Gilyarov and M. I. Kabachnik, *Ibid.* **44**, 27 (1974); M. Bergmann and J. R. Van Wazer, *Inorg. Chem.* **13**, 737 (1974); R. D. Kroshefsky and J. G. Verkade, *Ibid.* **14**, 3090 (1975); O. A. Radchenko, V. P. Nazaretyan and L. M. Yagupol'skii, *Zh. Obshch. Khim.* **46**, 565 (1976); J. A. Goldstein, *J. Org. Chem.* **42**, 2466 (1977); E. A. Suvalova, Zh. M. Ivanova, L. F. Kasukhin, M. P. Ponomarchuk and Yu. G. Gololobov, *Zh. Obshch. Khim.* **48**, 1281 (1978); L. F. Kasukhin, T. I. Klepa, M. P. Ponomarchuk and Yu. G. Gololobov, *Ibid.* **48**, 1715 (1978); R. S. Hay, B. P. Roberts, K. Singh and J. P. T. Wilkinson, *J. Chem. Soc.* Perkin II, 756 (1979).
[107]M. I. Kabachnik, V. A. Gilyarov and E. N. Tsvetkov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* 2135 (1959); H. Goldwhite, P. Gysegem, St. Schow and Ch. Swyke, *J. Chem. Soc.* Dalton Trans. 12 (1975).
[108]M. I. Kabachnik, V. A. Gilyarov, Cheng-Te Chang and E. I. Matrosov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* 1589 (1962); V. A. Gilyarov, E. N. Tsvetkov and M. I. Kabachnik, *Zh. Obshch. Khim.* **36**, 274 (1966); A. M. Maksudov, V. A. Gilyarov and M. I. Kabachnik, *Izv. Akad. Nauk SSSR, Ser. Khim.* 871 (1969).
[109]I. N. Zhmurova, R. I. Yurchenko and A. V. Kirsanov, *Zh. Obshch. Khim.* **38**, 2078 (1968); G. K. Genkina, V. A. Gilyarov and M. I. Kabachnik, *Ibid.* **38**, 2513 (1968); R. I. Yurchenko, I. N. Zhmurova and A. I. Sedlov, *Ibid.* **45**, 1740 (1975).
[110]M. I. Kabachnik and V. A. Gilyarov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* 819 (1961).
[111]J. Goerdeler and H. Ullmann, *Chem. Ber.* **94**, 1067 (1961).
[112]M. I. Kabachnik, V. A. Gilyarov and E. M. Popov, *Zh. Obshch. Khim.* **32**, 1598 (1962).
[113]H.-J. Vetter and H. Nöth, *Chem. Ber.* **96**, 1308 (1963).
[114]G. I. Derkach and E. S. Gubnitskaya, *Zh. Obshch. Khim.* **34**, 604 (1964).
[115]M. I. Kabachnik, V. A. Gilyarov and M. M. Yusupov, *Dokl. Akad. Nauk SSSR* **160**, 1079 (1965).
[116]N. I. Shvetsov, I. V. Lebedeva and I. M. Filatova, *Zh. Neorg. Khim.* **10**, 993 (1965).
[117]V. A. Gilyarov and M. I. Kabachnik, *Zh. Obshch. Khim.* **36**, 282 (1966).
[118]V. A. Gilyarov, R. V. Kudryavtsev and M. I. Kabachnik, *Ibid.* **36**, 708 (1966).
[119]I. M. Filatova, E. L. Zaitseva and A. Ya. Yakubovich, *Ibid.* **36**, 1861 (1966).
[120]G. I. Derkach and S. K. Mikhailik, *Khim. Org. Soedin. Fosfora, Akad. Nauk SSSR, Otd. Obshch. Khim.* 59 (1967).
[121]A. N. Pudovik, I. M. Aladzheva and V. G. Kotova, *Zh. Obshch. Khim.* **37**, 1173 (1967).
[122]I. T. Kay and B. K. Snell, *Tetrahedron Letters* 2251 (1967).
[123]V. A. Shokol, N. K. Mikhailyuchenko and G. I. Derkach, *Zh. Obshch. Khim.* **38**, 337 (1968).
[124]O. J. Scherer and J. Wokulat, *Z. Anorg. Allg. Chem.* **361**, 296 (1968).
[125]V. N. Kulakova, Yu. M. Zinov'ev, S. P. Makarov, V. A. Shpanskii and L. Z. Soborovskii, *Zh. Obshch. Khim.* **39**, 385 (1969).
[126]G. K. Genkina, V. A. Gilyarov and M. I. Kabachnik, *Dokl. Akad. Nauk SSSR* **188**, 1288 (1969).
[127]S. Z. Ivin, I. D. Shelakova and V. K. Promonenkov, *Zh. Obshch. Khim.* **40**, 561 (1970).
[128]V. A. Shokol, L. I. Molyavko and G. I. Derkach, *Ibid.* **41**, 2379 (1971).
[129]O. J. Scherer and R. Thalacker, *Z. Naturforsch.* **27b**, 1429 (1972).
[130]W. Stec and A. Lopusinski, *Tetrahedron* **29**, 547 (1973).
[131]J. Lorberth, *J. Organomet. Chem.* **71**, 159 (1974).
[132]H. Goldwhite, P. Gysegem, St. Schow and Ch. Swyke, *J. Chem. Soc.* Dalton Trans. 16 (1975).
[133]O. Schlak, W. Stadelmann, O. Stelzer and R. Schmutzler, *Z. Anorg. Allg. Chem.* **419**, 275 (1976).
[134]N. N. Zaslavskaya, V. A. Gilyarov and M. I. Kabachnik, *Izv. Akad. Nauk SSSR, Ser. Khim.* 931 (1976).
[135]M. I. Kabachnik, N. N. Zaslavskaya, V. A. Gilyarov, P. V. Petrovskii and V. A. Svoreń, *Dokl. Akad. Nauk SSSR* **228**, 849 (1976).
[136]A. A. Khodak, V. A. Gilyarov, T. M. Shcherbina and M. I. Kabachnik, *Zh. Obshch. Khim.* **46**, 2482 (1976).
[137]E.-P. Flindt, H. Rose and H. C. Marsmann, *Z. Anorg. Allg. Chem.* **430**, 155 (1977).
[138]L. I. Nesterova, L. F. Kasukhin, M. P. Ponomarchuk and Yu. G. Gololobov, *Zh. Obshch. Khim.* **48**, 1061 (1978).
[139]T. I. Klepa, L. F. Kasukhin, M. P. Ponomarchuk and Yu. G. Gololobov, *Ibid.* **48**, 1065 (1978).
[140]M. P. Ponomarchuk, L. F. Kasukhin, I. Yu. Budilova and Yu. G. Gololobov, *Ibid.* **48**, 1504 (1978).
[141]Yu. V. Balitskii, L. F. Kasukhin, M. P. Ponomarchuk and Yu. G. Gololobov, *Ibid.* **49**, 42 (1979).
[142]J. C. Wilburn, P. Wisian-Neilson and P. H. Neilson, *Inorg. Chem.* **18**, 1429 (1979).

[143]A. S. Shtepanek, E. N. Tkachenko and A. V. Kirsanov, *Zh. Obshch. Khim.* **37**, 2092 (1967); V. A. Shokol, L. I. Molyavko and G. I. Derkach, *Ibid.* **40**, 998 (1970); E. E. Nifant'ev, I. V. Komlev, I. P. Konyaeva, A. I. Zavalishina and V. M. Tul'chinskii, *Ibid.* **43**, 2368 (1973); H. H. Falius, K. P. Giesen and U. Wannagat, *Z. Anorg. Allg. Chem.* **402**, 139 (1973); U. Wannagat, K.-P. Giesen and H.-H. Falius, *Monatsch. Chem.* **104**, 1444 (1973); D. M. Malenko, L. F. Kasukhin, M. P. Ponomarchuk and Yu. G. Gololobov, *Zh. Obshch. Khim.* **48**, 1722 (1978).
[144]M. I. Kabachnik and V. A. Gilyarov, *Dokl. Akad. Nauk SSSR* **96**, 991 (1954).
[145]V. A. Shokol, L. I. Molyavko, N. K. Mikhailyuchenko and G. I. Derkach, *Zh. Obshch. Khim.* **41**, 318 (1971).
[146]L. F. Kasukhin, M. P. Ponomarchuk, L. A. Repina and Yu. G. Gololobov, *Dokl. Akad. Nauk SSSR* **224**, 95 (1975).
[147]L. A. Repina, R. A. Loktionova and Yu. G. Gololobov, *Zh. Obshch. Khim.* **45**, 2341 (1975).
[148]V. P. Lysenko, I. E. Boldeskul, R. A. Loktionova and Yu. G. Gololobov, *Ibid.* **48**, 978 (1978).
[149]R. K. Bunting and C. D. Schmulbach, *Inorg. Chem.* **5**, 533 (1966).
[150]O. J. Scherer and G. Schieder, *Chem. Ber.* **101**, 4184 (1968).
[151]O. J. Scherer and P. Klusmann, *Z. Anorg. Allg. Chem* **370**, 171 (1969).
[152]O. J. Scherer and G. Schieder, *J. Organomet. Chem.* **19**, 315 (1969).
[153]J. C. Wilburn and R. H. Neilson, *Inorg. Chem.* **16**, 2519 (1977).
[154]M. Volkholz, O. Stelzer and R. Schmutzler, *Chem. Ber.* **111**, 890 (1978).
[155]A. N. Degtyarev, N. N. Godovikov, V. I. Bregadze, E. I. Matrosov, T. M. Shcherbina and M. I. Kabachnik, *Izv. Akad. Nauk SSSR, Ser. Khim.* 2099 (1978).
[156]I. N. Zhmurova, A. P. Martynyuk, A. S. Shtepanek, V. A. Zasorina and V. P. Kukhar, *Zh. Obshch. Khim.* **44**, 79 (1974).
[157]I. N. Zhmurova and A. V. Kirsanov, *Ibid.* **30**, 3044 (1960).
[158]V. A. Gilyarov, R. V. Kudryavtsev and M. I. Kabachnik, *Ibid.* **38**, 352 (1968).
[159]K. Utvary, V. Gutmann and Ch. Kemenater, *Inorg. Nucl. Chem. Letters* **1**, 75 (1965).
[160]E. S. Gubnitskaya, A. G. Matyusha and G. I. Derkach, *Zh. Obshch. Khim.* **40**, 1205 (1970).
[161]E. S. Gubnitskaya and G. I. Derkach, *Ibid.* **42**, 296 (1972).
[162]N. N. Zaslavskaya, V. A. Gilyarov and M. I. Kabachnik, *Khim. Elementoorg. Soedin.*, "*Nauka*", 84 (1976).
[163]L. I. Nesterova and Yu. G. Gololobov, *Zh. Obshch. Khim.* **49**, 2625 (1979).
[164]E. Bergmann and H. A. Wolff, *Ber. Deut. Chem. Ges.* **63**, 1176 (1930).
[165]H. Malz, *Ger. Pat.* 1,104,958.
[166]H. Bock and W. Wiegräbe, *Angew. Chem.* **75**, 789 (1963).
[167]N. Wiberg and K. H. Schmid, *Ibid.* **79**, 938 (1967).
[168]H. Balli, *Helv. Chim. Acta* **57**, 1912 (1974).
[169]M. I. Kabachnik, V. A. Gilyarov and M. M. Yusupov, *Dokl. Akad. Nauk SSSR* **164**, 812 (1965).
[170]T. A. Albright, W. J. Freeman and E. E. Schweizer, *J. Org. Chem.* **41**, 2716 (1976).
[171]L. F. Kasukhin, M. P. Ponomarchuk, T. I. Klepa, V. P. Lysenko and Yu. G. Gololobov, *Zh. Obshch. Khim.* **47**, 2188 (1977).
[172]L. F. Kasukhin and M. P. Ponomarchuk, *Zh. Vses. Khim. O-va* **22**, 108 (1977).
[173]R. D. Temple and J. E. Leffler, *Tetrahedron Letters* 1893 (1968).
[174]L. F. Kasukhin, M. P. Ponomarchuk, V. P. Lysenko and Yu. G. Gololobov, *Ukr. Khim. Zh.* **44**, 519 (1978).
[175]L. F. Kasukhin, M. P. Ponomarchuk, T. I. Klepa, V. P. Lysenko, L. A. Repina and Yu. G. Gololobov, *Dokl. Akad. Nauk SSSR* **228**, 1380 (1976).
[176]Yu. G. Gololobov and L. F. Kasukhin, *Zh. Obshch. Khim.* **49**, 961 (1979).
[177]Yu. G. Gololobov, L. Kasukhin, M. Ponomarchuk, T. Klepa and R. Yurchenko, in press.
[178]L. F. Kasukhin, M. P. Ponomarchuk, T. V. Kim, Zh. M. Ivanova and Yu. G. Gololobov, *Zh. Obshch. Khim.* **48**, 354 (1978).
[179]O. Exner, *Coll. Czech. Chem. Comm.* **29**, 1094 (1964).
[180]L. F. Kasukhin, M. P. Ponomarchuk and Yu. G. Gololobov, *Teor. Eksp. Khim.* **14**, 652 (1978).
[181]B. C. Challis, J. A. Challis and J. N. Iley, *J. Chem. Soc.* Perkin II, 813 (1978).
[182]V. I. Shevchenko, V. P. Tkach and A. V. Kirsanov, *Zh. Obshch. Khim.* **35**, 1224 (1965).
[183]M. I. Kabachnik and V. A. Gilyarov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* 816 (1961).
[184]E.-P. Flindt and H. Rose, *Z. Anorg. Allg. Chem.* **428**, 204 (1977).
[185]Yu. G. Gololobov, T. N. Dudchenko and S. K. Tupchienko, *Zh. Obshch. Khim.* **49**, 2624 (1979).
[186]I. M. Filatova, E. L. Zaitseva, A. P. Simonov and A. Ya. Yakubovich, *Ibid.* **38**, 1304 (1968).
[187]N. N. Zaslavskaya, V. A. Gilyarov and M. I. Kabachnik, *Izv. Akad. Nauk, Ser. Khim.* 675 (1976).
[188]A. A. Khodak, V. A. Gilyarov and M. I. Kabachnik, *Zh. Obshch. Khim.* **44**, 256 (1974).
[189]V. A. Gilyarov, *Usp. Khim.* **47**, 1628 (1978).
[190]R. D. Gareév, *Zh. Obshch. Khim* **46**, 2662 (1976).
[191]Don E. Gibbs, *Tetrahedron Letters* 679 (1977); L. V. Nesterov, N. E. Krepysheva, R. A. Sabirova and G. N. Lipkina, *Zh. Obshch. Khim.* **48**, 790 (1978).
[192]P. K. G. Hodgson, R. Katz and G. Zon, *J. Organomet. Chem.* **117**, C63 (1976).
[193]J. Escudié, C. Couret and J. Satgé, *C. R. Acad. Sci.* **280**, 783 (1975).
[194]O. J. Scherer, *Angew. Chem.* **81**, 871 (1969).
[195]O. J. Scherer, G. Schnabl and Th. Lenhard, *Z. Anorg. Allg. Chem.* **449**, 167 (1979).
[196]H. Schmidbaur and W. Wolfsberger, *Angew. Chem.* **79**, 411 (1967); W. Wolfsberger and H. Schmidbaur, *J. Organomet. Chem.* **122**, 5 (1976).
[197]M. I. Kabachnik, V. A. Gilyarov, B. A. Korolev and T. A. Raevskaya, *Izv. Akad. Nauk SSSR, Ser. Khim.* 772 (1970).
[198]M. I. Kabachnik, *Khim. i Primenenie Fosfororg. Soedin., Akad. Nauk SSSR, Trudy I Konf.* 18 (1957).
[199]O. I. Kolodyazhnyi, L. A. Repina and Yu. G. Gololobov, *Zh. Obshch. Khim.* **44**, 1275 (1974).
[200]O. I. Kolodyazhnyi and V. P. Kukhar, *Ibid.* **49**, 1992 (1979).
[201]N. I. Gusar, M. P. Chaus and Yu. G. Gololobov, *Ibid* **49**, 1782 (1979).
[202]N. I. Gusar, M. P. Chaus and Yu. G. Gololobov, *Ibid* **48**, 2376 (1978).
[203]V. A. Gilyarov, *Khim. i Primenenie Fosfororg. Soedin., Akad. Nauk SSSR, Trudy II Konf.* 75 (1962).
[204]R. H. Kratzer and K. L. Paciorek, *J. Org. Chem.* **32**, 853 (1967).
[205]H. Schmidbaur, K. Schwirten and H.-H. Pickel, *Chem. Ber.* **102**, 564 (1969).
[206]V. S. Sergeev and Yu. G. Gololobov, *Zh. Obshch. Khim.* **47**, 952 (1977).
[207]H. Schumann and A. Roth, *J. Organomet. Chem.* **11**, 125 (1968).

[208]J. I. G. Cadogan, N. J. Stewart and N. J. Tweddle, *J. Chem. Soc.* Chem. Comm. 182 (1978).
[209]J. I. G. Cadogan, I. Gosney, E. Henry, Th. Naisby, B. Nay, N. J. Stewart and N. J. Tweddle, *Ibid.* 189 (1979).
[210]M. Sanchez, J.-F. Brazier, D. Houalla, A. Munoz and R. Wolf, *Ibid.* 730 (1976).
[211]E. P. Kyba and D. C. Alexander, *Ibid.* 934 (1977).
[212]V. A. Gilyarov, N. A. Tikhonina, V. G. Andrianov, Yu. T. Struchkov and M. I. Kabachnik, *Zh. Obshch. Khim.* **48**, 732 (1978).
[213]N. A. Tikhonina, G. I. Timofeeva, E. I. Matrosov, V. A. Gilyarov and M. I. Kabachnik, *Ibid.* **45**, 2414 (1975); N. A. Tikhonina, V. A. Gilyarov and M. I. Kabachnik, *Ibid.* **48**, 44 (1978).
[214]V. P. Kukhar, I. N. Zhmurova and R. I. Yurchenko, *Ibid.* **42**, 279 (1972).
[215]I. N. Zhmurova, V. P. Kukhar, A. A. Tukhar and L. A. Zolotareva, *Ibid.* **43**, 82 (1973).
[216]T. A. Mastryukova and M. I. Kabachnik, *Usp. Khim.* **38**, 1751 (1969).
[217]H. Labhart and G. Wagniere, *Helv. Chim. Acta* **46**, 1314 (1963); P. Schuster, *Monatsch. Chem.* **98**, 1310 (1967).
[218]M. I. Kabachnik, *Phosphorus* **1**, 117 (1971); T. G. Edel'man and B. I. Stepanov, *Zh. Obshch. Khim.* **37**, 963 (1967).
[219]G. K. Genkina, B. A. Korolev, V. A. Gilyarov and M. I. Kabachnik, *Ibid.* **41**, 80 (1971).
[220]B. A. Korolev, N. A. Rozanel'skaya and B. I. Stepanov, *Ibid.* **39**, 1161 (1969).
[221]L. I. Chekunina, A. I. Bokanov and B. I. Stepanov, *Ibid.* **42**, 110 (1972).
[222]I. N. Zhmurova, R. I. Yurchenko, V. P. Kukhar, A. A. Petrashenko and A. V. Kirsanov, *Zh. Org. Khim.* **7**, 1027 (1971); I. N. Zhmurova, R. I. Yurchenko, V. P. Kukhar, L. A. Zolotareva and A. V. Kirsanov, *Zh. Obshch. Khim.* **42**, 1954 (1972).
[223]I. N. Zhmurova, R. I. Yurchenko, V. G. Yurchenko and A. A. Tukhar, *Ibid.* **43**, 1036 (1973).
[224]I. N. Zhmurova, V. G. Yurchenko, R. I. Yurchenko and T. I. Pavelko, *Ibid.* **43**, 1789 (1973).
[225]M. I. Kabachnik and V. A. Gilyarov, *Izv. Akad. Nauk SSSR, Ser. Khim.* 2036 (1968).
[226]V. A. Gilyarov, A. M. Maksudov, B. A. Korolev, B. I. Stepanov and M. I. Kabachnik, *Ibid.* 2019 (1968).
[227]V. A. Gilyarov and R. V. Kudryavtsev, *Khim. i Primenenie Fosfororg. Soedin., Akad. Nauk SSSR, Trudy III Konf.* 174 (1972).
[228]R. I. Yurchenko, O. M. Voitsekhovskaya, I. N. Zhmurova and N. N. Lysova, *Zh. Obshch. Khim.* **45**, 1735 (1975).
[229]E. Niecke and W. Flick, *Angew. Chem.* **86**, 128 (1974).
[230]O. J. Scherer and N. Kuhn, *Chem. Ber.* **107**, 2123 (1974).
[231]E. Niecke, R. Kröher and S. Pohl, *Angew. Chem.* **89**, 902 (1977); R. Appel, M. Halstenberg and F. Knoll, *Z. Naturforsch.* **32b**, 1030 (1977); M. Halstenberg and R. Appel, *Chem. Ber.* **111**, 1815 (1978).
[232]S. Pohl, E. Niecke and B. Krebs, *Angew. Chem.* **87**, 284 (1975); S. Pohl and B. Krebs, *Chem. Ber.* **110**, 3183 (1977).
[233]W. Wolfsberger, *J. Fluor. Chem.* **11**, 159 (1978).
[234]D. Dahmann and H. Rose, *Chem. Ztg.* **101**, 401 (1977).
[235]I. Ruppert and R. Appel, *Chem. Ber.* **111**, 751 (1978).
[236]R. Appel, I. Ruppert and M. Montenarh, *Ibid.* **109**, 71 (1976).
[237]L. V. Nesterov and N. E. Krepysheva, *Izv. Akad. Nauk SSSR, Ser. Khim.* 2846 (1975).
[238]Kenji Itoh, M. Okamura and J. Ishii, *J. Organomet. Chem.* **65**, 327 (1974).
[239]V. P. Kukhar, V. I. Pasternak, M. V. Shevchenko, A. S. Shtepanek and A. V. Kirsanov, *Zh. Obshch. Khim.* **46**, 249 (1976).
[240]E.-P. Flindt, *Z. Anorg. Allg. Chem.* **447**, 97 (1978).
[241]W. Maringgele, A. Meller, H. Nöth and R. Schroen, *Z. Naturforsch.* **33b**, 673 (1978).
[242]L. Birkofer, A. Ritter and Sung Man Kim, *Chem. Ber.* **96**, 3099 (1963).
[243]A. S. Shtepanek, L. M. Tochilkina and A. V. Kirsanov, *Zh. Obshch. Khim.* **45**, 2117 (1975).
[244]W. Wolfsberger, *Z. Anorg. Allg. Chem.* **438**, 206 (1978).
[245]I. N. Zhmurova and A. P. Martynyuk, *Zh. Obshch. Khim.* **37**, 2706 (1967); A. Senning and P. Kelly, *Naturwiss.* **55**, 543 (1968).
[246]A. S. Shtepanek, V. A. Zasorina and A. V. Kirsanov, *Zh. Obshch. Khim.* **43**, 25 (1973).
[247]A. S. Shtepanek, V. V. Doroshenko, V. A. Zasorina, L. M. Tochilkina and A. V. Kirsanov, *Ibid.* **44**, 2130 (1974).
[248]A. S. Shtepanek, E. N. Tkachenko and A. V. Kirsanov, *Ibid.* **39**, 1475 (1969).
[249]I. N. Zhmurova, Yu. L. Slominskii, A. I. Tolmachev and R. I. Yurchenko, *Ibid.* **39**, 1732 (1969).
[250]A. S. Shtepanek, V. A. Zasorina, I. N. Zhmurova and A. P. Martynyuk, *Ibid.* **45**, 1012 (1975).
[251]V. Kvita and G. Baschang, *Helv. Chim. Acta* **55**, 2683 (1972); R. L. Letsinger and G. A. Heavner, *Tetrahedron Letters* 147 (1975).
[252]W. Freist, K. Schattka, F. Cramer and B. Jastorff, *Chem. Ber.* **105**, 991 (1972).
[253]J. I. G. Cadogan and R. K. Mackie, *Chem. Soc. Revs.* **3**, 87 (1974).
[254]R. Appel and R. Milker, *Chem. Ber.* **110**, 3201 (1977).
[255]Yu. L. Yagupol'skii, N. V. Kondratenko and L. M. Yagupol'skii, *Zh. Org. Khim.* **8**, 1253 (1972).
[256]J. A. Klock and K. L. Leschinsky, *J. Org. Chem.* **43**, 1460 (1978).
[257]S. A. Foster, L. Y. Leyshon and D. G. Saunders, *J. Chem. Soc.* Chem. Comm. 29 (1973).
[258]E. Zbiral and J. Stroh, *Liebigs Ann.* **725**, 29 (1969).
[259]E. Zbiral, E. Bauer and J. Stroh, *Monatsch. Chem.* **102**, 168 (1971); L. J. Leyshon and D. G. Saunders, *J. Chem. Soc.* Chem. Comm. 1608 (1971).
[260]E. Zbiral and J. Stroh, *Liebigs Ann.* **727**, 231 (1969).
[261]O. I. Kolodyazhnyi, L. A. Repina, V. P. Kukhar and Yu. G. Gololobov, *Zh. Obshch. Khim.* **49**, 1004 (1979).
[262]E. Zbiral and E. Bauer, *Phosphorus* **2**, 35 (1972).
[263]A. Hassner and J. E. Galle, *J. Am. Chem. Soc.* **92**, 3733 (1970).
[264]Y. Ittah, Y. Sasson, I. Shahak, S. Tsaroom and J. Blum, *J. Org. Chem.* **43**, 4271 (1978).