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# Reactions of phosphorus-containing compounds with diazo-compounds and carbenes

B A Khaskin, O D Molodova, N A Torgasheva
All-Union Institute of Chemical Plant Protecting Agents, Moscow

ABSTRACT. The reactions of various phosphorus-containing systems with diazo-compounds and carbenes are presented for the first time in a general form and a systematic account is given of literature data on the reactivities of phosphorus-containing acids, salts, esters, amides, sulphenamides, phosphorus acid sulphenyl halides, phosphorus halides, and derivatives of mono-, di-, and tri-coordinate phosphorus in reactions with diazo-compounds and carbenes.

The differences between the reactivities of diazo-compounds and carbenes in relation to the above groups of organophosphorus compounds are demonstrated.

The bibliography includes 244 references.

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## I. Introduction

The advances in the study of the reactivities of phosphorus-containing compounds in relation to diazo-compounds and carbenes are considered in the present review. These studies play an important role both in the synthetic and theoretical chemistry of organophosphorus compounds.

The beginning of studies on the reactions of diazo-compounds with phosphorus-containing systems dates back to the second decade of the present century. Systematic investigation of the reactions of phosphorus-containing compounds with carbenes developed in the last 30 years.

Extensive data have now accumulated on this problem and a number of special reviews have been published in both Russian and foreign literature on individual aspects of the interaction of certain phosphorus-containing compounds with diazo-compounds and carbenes, especially on the dual reactivity of phosphoromonothioic, phosphoromonoselenoic, and phosphoroselenothioic acids,[1] the reactions of phosphorus-containing polysulphides,[2] the 1,3-dipolar cycloaddition reactions,[3–5] and the reactions of α-ketophosphoryl compounds.[6]

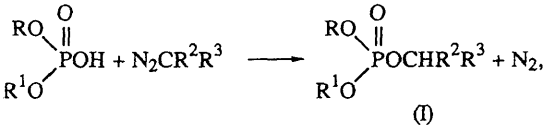
The reactions of different phosphorus-containing systems with diazo-compounds and carbenes are presented in the present review for the first time in a general form and a systematic account is given of literature data on the reactivities of phosphorus-containing acids, salts, esters, amides, sulphenamides, phosphorus acid sulphenyl halides, phosphorus halides, and derivatives of mono-, di-, and tri-coordinate phosphorus in reactions with diazo-compounds and carbenes. Studies concerned with the reactivities of phosphorus-containing diazo-compounds and carbenes are not considered in the review.

## II. Phosphorus-containing acids, salts, esters, amides, sulphenamides, phosphorus acid sulphenyl halides, phosphorus halides, and phosphorus-containing polysulphides in reactions with diazo-compounds and carbenes

### 1. Interaction of phosphoric, phosphonic, phosphinic, and phosphorous acids and their esters with diazo-compounds

The reactions of organophosphorus acids and their esters, containing P–O–H bonds, with diazo-compounds proceed as a rule with evolution of nitrogen and the insertion of a methylene or substituted methylene group in the O–H bond.

Thus in the reactions with diazo-compounds dialkylphosphoric acids form phosphates (I),[7–9] while hypophosphorous acid forms *O*-alkyl esters (II).[10] Even in the presence of a large excess of diazoalkane further reaction does not occur, i.e. there is no insertion in a P–H bond of the ester (II):



(I)

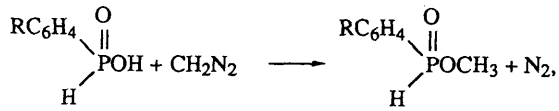
R = H, Alk($C_1$ — $C_4$), $CH_2C_6H_5$, $(CH_2)_{17}CH_3$;
$R^1$ = Alk($C_1$ — $C_4$), $(CH_2)_3Br$,
$(CH_2)_{18}CH_3$, $CH_2C_6H_5$; $R^2 = R^3 = C_6H_5$;
$R^3 = C_6H_5$, $R^3 = C(O)C_6H_5$; $R^2$ = H,
$R^3 = C(O)(CH_2)_{18}CH_3$,



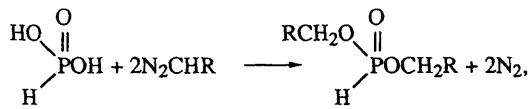
(II)

$R^1$ = H, $CH_3$.

Arylphosphinic acids[11] and phosphorous acid[12,13] react similarly:

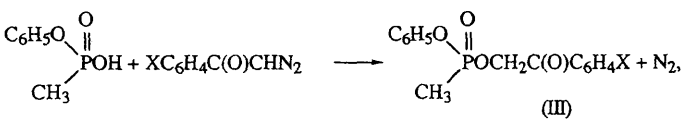


R = H, 3-Cl, 3-Br.



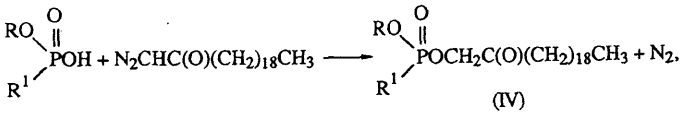
R = $CH_3$, $C(O)C_2H_5$.

The synthesis of the phosphonates (III) and (IV) by the reaction of phenoxymethylphosphonic acid with aromatic diazoketones and of alkyl(chloroalkyl)phosphonic acid esters with higher alkyl homologues of diazoacetone has been described:[9,14]



(III)

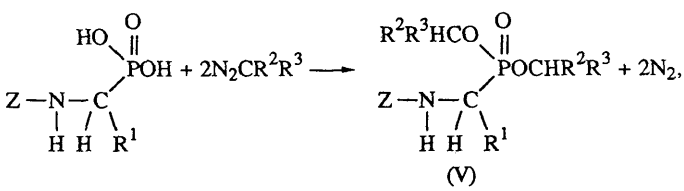
X = H, 4-Cl, 4-$CH_3O$, 4-$NO_2$, 4-$CH_3$, 2-$CH_3$, 3,5-$NO_2$,



(IV)

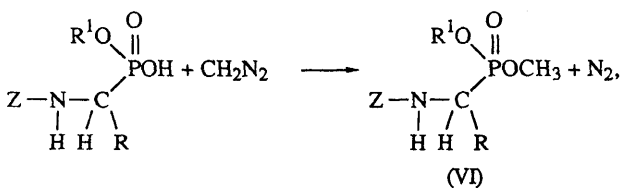
R = H, $(CH_2)_{17}CH_3$, $CH_2C_6H_5$; $R^1$ = $CH_3$, $CH_2CH_2Cl$, $CH_2Cl$.

The phosphonates (V) and (VI) have been obtained from *N*-acylated 1-aminoalkylphosphonic acid or its ester with diazomethane and diphenyldiazomethane:[15–17]



(V)

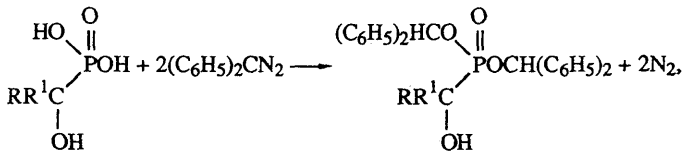
$R^1$ = H, Alk; $R^2$ = $R^3$ = H, $C_6H_5$,



(VI)

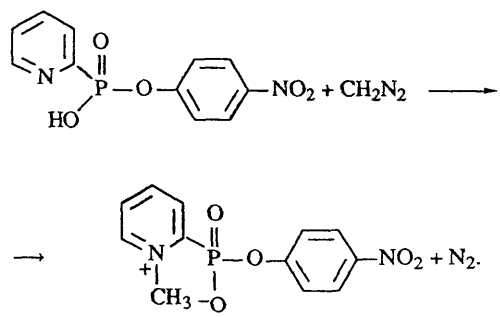
R = $R^1$ = H, Alk, $C_6H_5$; Z = $CH_3C(O)$, $C_6H_5CH(OH)C(O)$, $CH_3C_6H_4SO_2$, $(CH_3)_3COC(O)$, $C_6H_5CH_2OC(O)$.

The reactions of hydroxyalkylphosphonic acids with diphenyldiazomethane involve the insertion of the diphenylmethylene group only in the acid OH groups:[18]

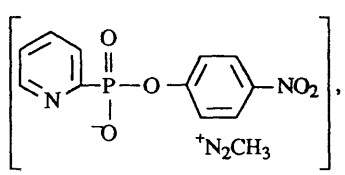


R = $R^1$ = Alk, $C_6H_5$.

In this connection, it is of interest to note a study[19] where it was shown that the interaction of 4-nitrophenyl-2-pyridylphosphonic acid with diazomethane proceeds selectively with formation of the *N*-methyl derivative:



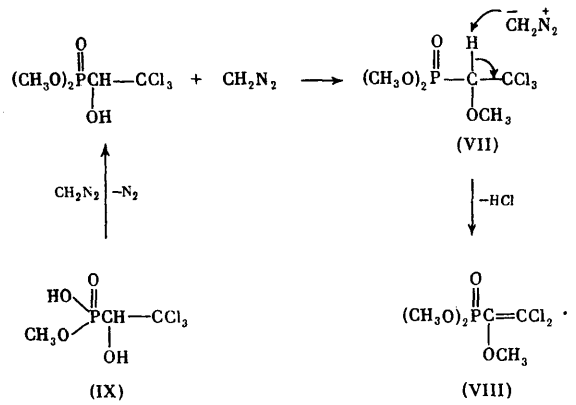
The authors attribute the formation of this product to alkylation by diazomethane at the nitrogen atom via the intermediate formation of the ion pair



where the phosphonate anion is a weaker nucleophile than the pyridinium nitrogen in relation to the methanediazonium cation.

The dimethyl ester of 2,2,2-trichloro-1-hydroxyethylphosphonic acid is methylated by diazomethane at the alcoholic OH group, which has been attributed to the strong electron-accepting influence of the trichloromethyl group, with formation of the dimethyl ester of 2,2,2-trichloro-1-methoxyethylphosphonic acid (VII), the excess diazomethane playing the role of a dehydrochlorinating agent, which leads to the formation of the ester (VIII). The latter has been

obtained also by treating methyl 2,2,2-trichloro-1-hydroxyethylphosphonate (IX) with an excess of diazomethane:[20]



(VII)

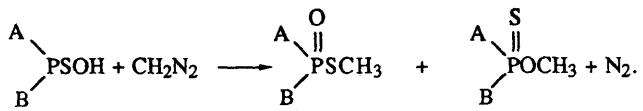
(IX)

(VIII)

## 2. Phosphoromonothioic, phosphoromonoselenoic, and phosphoroselenothioic acids in reactions involving alkylation by diazo-compounds

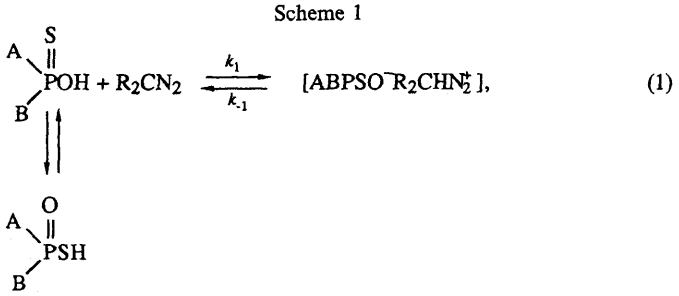
Phosphoromonothioic, phosphoromonoselenoic, and phosphoroselenothioic acids are typical substances involved in triad tautomerism and are therefore convenient objects for the study of the dual reactivities of ambident anions. Their reactions with diazocompounds have been studied by Mastryukova and Kabachnik[21–35] and have been described in detail in a review.[1] Here we shall confine ourselves to the considerations of general information about the results of such investigations.

The study of the reactions of phosphoromonothioic acids with diazomethane showed that alkylation proceeds with the preferential formation of *S*-methyl esters of phosphorothioic acids in 81–95% yield:[22]



The reaction mechanism is presented in Scheme 1 below:[1,21,22]

Scheme 1



$$[ABPSO^-R_2CHN_2^+] \xrightarrow{k_2} [ABPSO^-R_2CH^+] + N_2, \quad (2)$$

$$[ABPSO^-R_2CHN_2^+] \xrightarrow{k_3} ABP(O)SCHR_2 + N_2, \quad (3)$$

$$[ABPSO^-R_2CHN_2^+] \xrightarrow{k_3'} ABP(S)OCHR_2 + N_2, \quad (4)$$

$$[ABPSO^-R_2CH^+] \xrightarrow{k_4} ABP(S)OCHR_2, \quad (5)$$

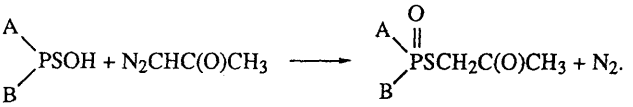
$$[ABPSO^-R_2CH^+] \xrightarrow{k_4'} ABP(O)SCHR_2. \quad (6)$$

In the reversible reaction of phosphorothioic acid with diazomethane [Eqn. (1)], the methanediazonium cation, behaving as the counterion in the ion pair formed, interacts as the attacking electrophile with the ambident anion via a reaction of the $S_N2$ type [reactions (3) and (4)] or a methyl cation is generated via a reaction of the $S_N1$ type [reaction (2)], recombining rapidly with the anion [reactions (5) and (6) in Scheme 1].

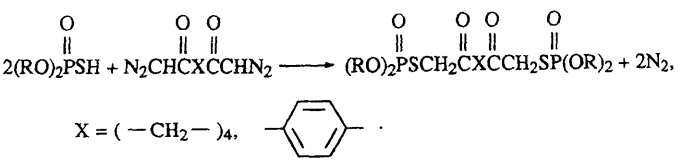
In conformity with the mechanism involving two types of reactions of phosphorothioic acids with diazomethane, it was postulated that the methanediazonium cation attacks only the sulphur atom as the most nucleophilic atom of the triad ($S_N2$), while the methyl cation attacks the oxygen atom in the same triad ($S_N1$). Evidently the yields of the *S*- and *O*-methyl derivatives depend on the nucleophilicity of the sulphur end of the triad, which is determined by the electron-accepting properties of the substituents at the phosphorus atom and by the relative rate of decomposition of the diazonium cation within the ion pair, which depends both on the polarity of the solvent and on the stability of the carbonium ion formed.[1,21,22]

The established features of the dual reactivity of phosphorothioic acids were confirmed and subsequently elaborated in reactions of phosphorothioic acids and cyclic phosphorothioic, phosphoroselenoic, and phosphoroselenothioic acids with other diazocompounds.[1,21,23–27]

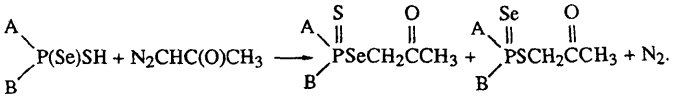
Thus primary diazoketones, in particular diazoacetone, give rise exclusively to the *S*-thiol ester in their reactions with phosphorothioic acids,[30,32] which has been attributed to the high reactivity of the diazonium cation:



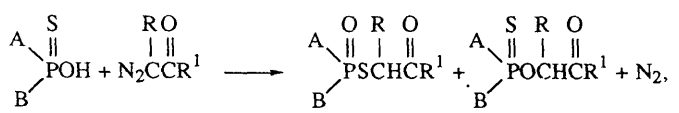
It has been shown recently that, similarly to their reactions with diazoacetone, phosphorothioic acids readily interact with bisdiazoketones: 1,8-bisdiazooctane-2,7-dione and 1,4-bis(diazoacetyl)benzene, affording thiol derivatives of bisphosphorylated products of insertion in the S–H bond of phosphorothioic acids:[39]



Phosphoroselenothioic acids react with diazoacetone to form both Se- and S-isomers, since both ends of the ambident triad are highly nucleophilic:[25]



Diazoacetic ester and a secondary diazoketone (α-phenylbenzoyldiazomethane) react with phosphorothioic acids to form both isomers. The presence of a large amount of the thionic esters (X) was attributed by the authors to some increase in the stability of the corresponding carbonium ions:[30,33]



R =H, $R^1 = OC_2H_5$; $R = R^1 = C_6H_5$.

The results of kinetic studies on the reactivities of five- and six-membered cyclic phosphorothioic acids in reactions with diphenyldiazomethane, obtained by Pudovik and co-workers,[36–38] are consistent with data for the reactions of phosphorothioic acids with diphenyldiazomethane.[26]

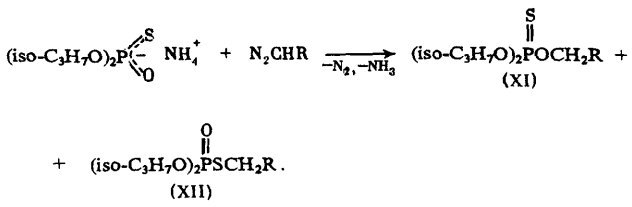
Thus the study of the alkylation of organophosphorus acids with diazo-compounds has made a major contribution to investigations of problems of the dual reactivities of both phosphorothioic and phosphoroselenoic acids themselves and the problem of dual reactivity as a whole.

### 3. Salts of phosphoromonothioic and phosphorodithioic acids in reactions with diazo-compounds and dihalocarbenes

Among different factors influencing the dual reactivity of ambident anions (polarisation, polarisability, the nature of the attacking agent, and the nature of the bond), the question of the influence of the metal and ammonium cations in ambident phosphorus systems has not so far been considered in the literature.

Khaskin et al.[40] was the first to investigate the dual reactivity of phosphorothioic salts in reactions involving alkylation and acylation by diazomethane, diazoacetone, and diazoacetophenone. It was established that alkali metal salts of phosphorothioic acids and a quaternary ammonium salt of phosphoric acid do not react with diazo-compounds in polar and non-polar solvents.

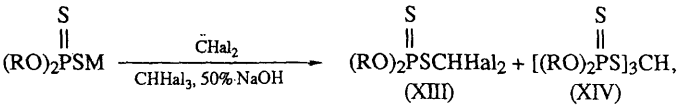
In contrast to this, the ammonium salts of phosphorothioic acids react with diazomethane to form a mixture of thione–thiol esters (XI) and (XII), the yield of the *O*-isomer (XI) increasing with increase in the dielectric constant of the solvent, while the reactions with diazoacetone and diazoacetophenone in both polar and weakly polar solvents afford exclusively the *S*-isomer (XII) with R = $C(O)CH_3$ or $C(O)C_6H_5$, since the formation of an acyl or an arylacyl carbonium ion is unfavourable because of energy factors:[30]



The reaction mechanism under discussion[40] agrees well with the mechanism proposed previously by Mastryukova and Kabachnik for phosphoromonothioic acids (see above).

Dihalocarbenes, generated by the alkaline hydrolysis of haloforms, behave differently in relation to salts of phosphorothioic and phosphorodithioic acids.

Thus alkali metal salts of phosphorodithioic acids form *O,O*-dialkyl *S*-dihalomethyl phosphorodithioates (XIII) in 20–70% yield as the main product and tris(*O,O*-dialkylthiophosphoryl-thio)methanes (XIV) in 5–20% yields as the side product:[41,42]

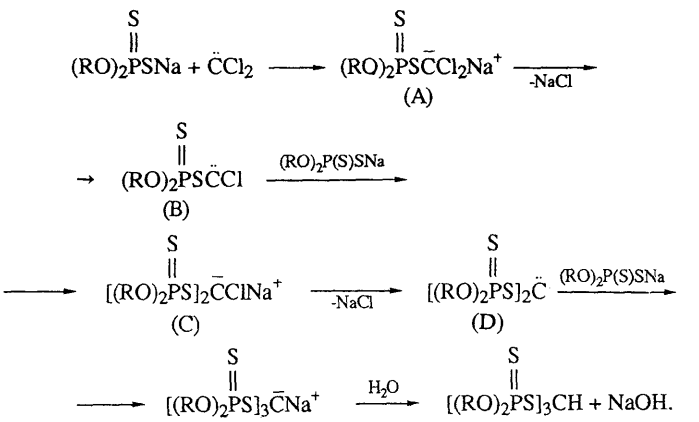


M = Na, K; Hal = Cl, Br.

The formation of compound (XIII) is represented as the result of the electrophilic attack by the dihalocarbene in the singlet state, formed at the interface,[43–46] on the sulphur atom in the molecule of phosphorodithioic acid to form an ion pair, which subsequently reacts with water:

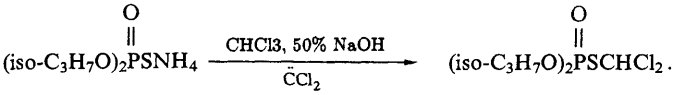


Since *O,O*-dialkyl *S*-dihalomethyl phosphorodithioates (XIII) do not react with the initial phosphorodithioic acid salts, the formation of compound (XIV) is represented as the result of the successive generation in the course of the reaction of unstable monothio- and dithio-derivatives of phosphorus-containing carbenes (B) and (D) via the intermediate formation of the ion pairs (A) and (C):



Similar products (XIII) and (XIV) were obtained from *O,O*-dialkylphosphorodithioic acids and bis(dialkoxythiophosphoryl) disulphides also under the conditions of the alkaline hydrolysis of haloforms, where a salt of the phosphorodithioic acid is formed initially.

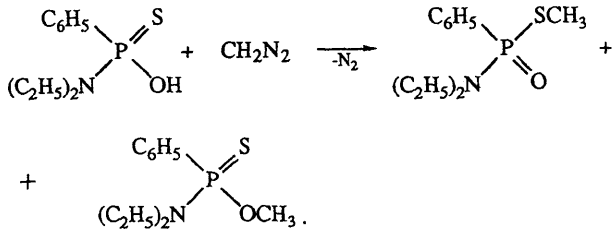
The attempt to extend this reaction to the salts of *O,O*-dialkylphosphorothioic acids and bis(dialkoxyphosphoryl) disulphides was unsuccessful. Only *O,O*-diisopropyl *S*-dichloromethyl phosphate was obtained by this procedure from the ammonium salt of *O,O*-diisopropylphosphorothioic acid in a yield of only about 2% as a consequence of the rapid hydrolysis of the final products:[42]



## 4. Reactions of the amides of phosphoric, phosphorothioic, phosphonothioic, and phosphinothioic acids and phosphoric acid sulphenamides with diazo-compounds

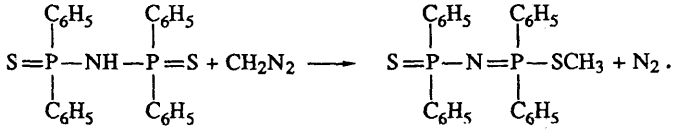
Dual reactivity is also manifested by the amides of phosphorus thio-acids when they are alkylated by diazo-compounds.[47–54]

The reaction of the diethylamide of phenylphosphonothioic acid with diazomethane involves the formation of both the *S*- and *O*-methyl esters of *N*,*N*-diethylphenylphosphonamidothioic acid:[47]

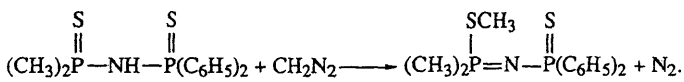


The dimethylamides of cyclohexylphosphonothioic and cyclohexylmorpholinophosphonothioic acids react similarly.[47]

In their study of the methylation of tetraphenyldiphosphinamidothioic acid, Schmidpeter and Groeger[48] established the exclusive formation of the product of alkylation at the sulphur atom — *S*-methyl tetraphenyldiphosphinimidothioate:



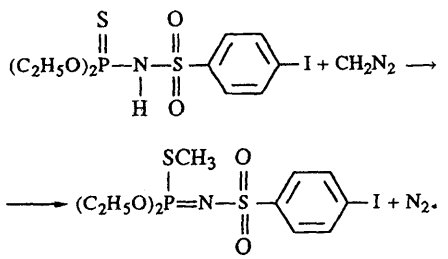
In the case of dimethyldiphenyldiphosphinamidodithioic acid, *S*-methylation with diazomethane takes place at the thiophosphoryl group linked to the methyl substituents:[49]



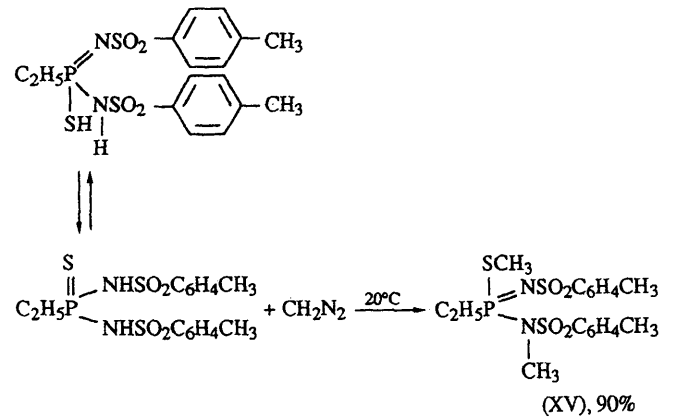
The formation of thiol imidoesters was detected similarly from the shift of the bond vibration band in the IR spectra in the reactions of phosphinothioic acid amides with diazomethane:[50]



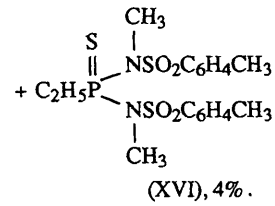
The *S*-methyl ester was also isolated as the main product in the methylation of *O*,*O*-diethyl *N*-(*p*-iodobenzenesulphonyl)phosphoramidothioate:[51]



In contrast to the reactions of phosphorus thio-acid amides presented above, the interaction of ethylphosphonothioic acid bis(*p*-methylbenzenesulphonamide) with diazomethane involves alkylation at both the sulphur and nitrogen atoms. The high yield of the *S*-methyl derivative (XV) together with the insignificant amount of the *N*-methyl derivative (XVI) are associated with the fact that the phosphonothioic acid diamide exists predominantly in the tautomeric imidothiol form:[52]

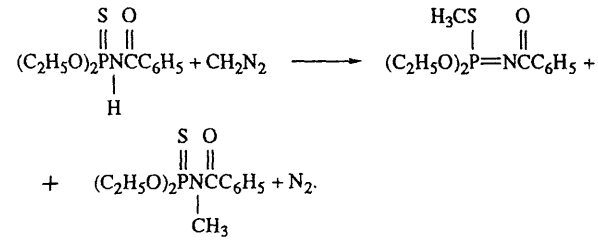


(XV), 90%

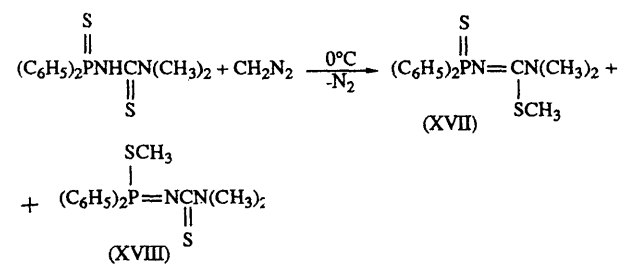


(XVI), 4%.

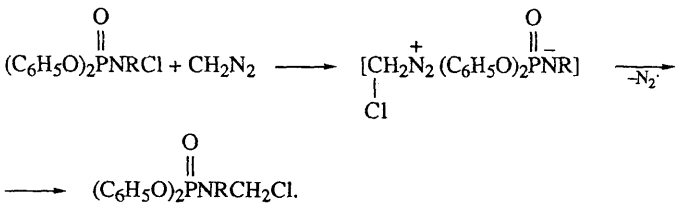
The reaction of *O*,*O*-diethyl *N*-benzoylphosphoramidothioate with diazomethane gives rise to yields of the *S*- and *N*-methyl derivatives in proportions of 5 : 1:[53]



The methylation with diazomethane of the *N*-dimethylthioureide of diphenylphosphinothioic acid takes place to the extent of 74% at the thiocarbonyl group with formation of *S*-methyl diphenylphosphinoisothioureidothioate (XVII) and to the extent of 26% at the thiophosphoryl group with formation of *S*-methyl diphenylphosphino(*N*-dimethylthiocarbamoylimido)thioate (XVIII):[54]

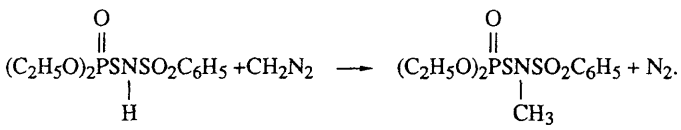


In contrast to the phosphorus thio-acid amides, the amides and sulphenamides of phosphoric acid are not methylated by diazomethane at the oxygen atom of the phosphoryl group. Thus *N*-chloromethylphosphoramidate was obtained from *N*-chlorophosphoramidate, its formation being represented as a result of the formal insertion of the methylene group in the N–Cl bond:[55]



R = Alk, $CH_2C_6H_5$.

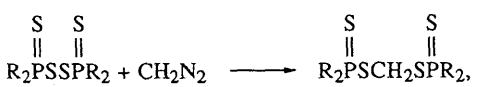
We are aware of only one study of the reactivity of the sulphenamides of phosphorus acids, described in the literature, in which it was shown that the aryl-substituted sulphenamide of diethylphosphoric acid affords the product of the methylation at the nitrogen atom on interaction with diazomethane:[56]



## 5. Interaction of phosphorus-containing polysulphides, sulphenyl halides of phosphorus acids, and phosphorus halides with diazo-compounds and carbenes

The interaction of phosphorus-containing polysulphides with diazo-compounds and carbenes has been studied only in recent years.[57–69] The review published previously[2] is supplemented here with new experimental data on the reactivities of phosphorus-containing polysulphides and sulphenyl halides of phosphorus acids.

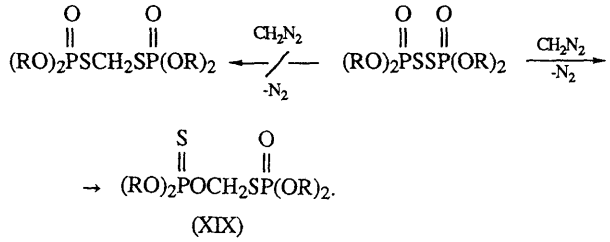
Thus symmetrical bis(dialkoxythiophosphoryl) and bis(diarylthiophosphoryl) disulphides react with diazomethane to form the products of the insertion of methylene in the S–S bond of the disulphides:[57,58]



R = AlkO, Ar.

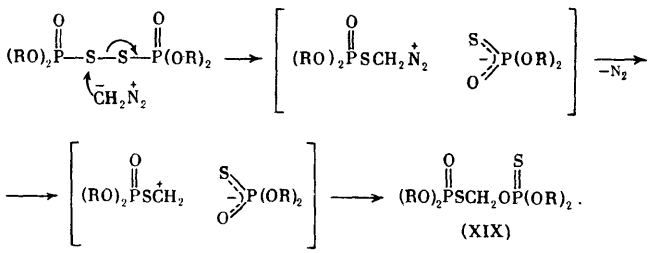
Similar products resulting from the insertion in the S–S bond are formed from aromatic disulphides by reaction with the Simmons-Smith reagent ($ICH_2ZnI$) and with carboxylic diazoacid esters.[70,71]

It is of interest that, in contrast to bis(dialkoxythiophosphoryl) and bis(diarylthiophosphoryl) disulphides, bis(dialkoxyphosphoryl) disulphides never form products of the insertion of the methylene group in the S–S bond on reaction with an excess of diazomethane in ethereal solution under various conditions (radiation with light from a mercury lamp, in daylight, or in the dark); this reaction leads to the formation, as a result of the phosphoryl–thiophosphoryl rearrangement, of products with an asymmetric structure, namely dialkoxythiophosphoryloxy(dialkoxyphosphorylthio)methanes (XIX):[59,60]

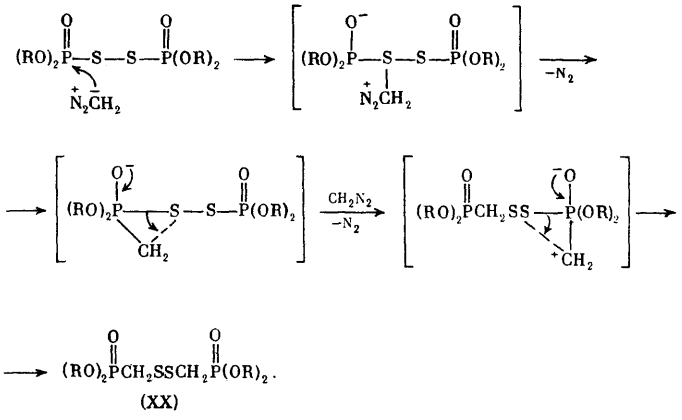


It has been suggested that, at least in the absence of illumination, bis(dialkoxyphosphoryl) disulphides interact with the undissociated diazomethane molecule. In the dark, the reaction is not restricted to the phosphoryl–thiophosphoryl rearrangement but is accompanied by the formation of the product of the insertion of two methylene groups in both P–S bonds of the disulphide with retention of the S–S bond and of the symmetry of the structure of compound (XX).[60] The formation of the products of the phosphoryl–thiophosphoryl rearrangement [compound (XIX)] and of insertion in the P–S bond [compound (XX)] is illustrated by Schemes 2 and 3 respectively:[59,60]

Scheme 2

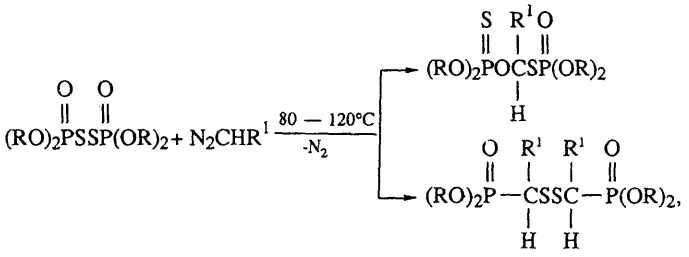


Scheme 3



The reactions of bis(dialkoxyphosphoryl) disulphides with diazoacetic ester and diazoacetone proceed similarly, with formation of the products of the phosphoryl–thiophosphoryl rearrangement

and of insertion in the P–S bond, under conditions which do not promote the formation of the corresponding carbenes:[60,61]

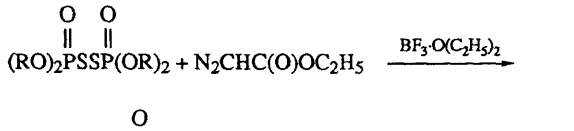


$R^1 = C(O)OC_2H_5$, $C(O)CH_3$.

The two competing reactions proceed at different rates, so that, depending on the reaction conditions, there is a possibility of the formation of one of the reaction products separately or of their mixtures in different proportions.

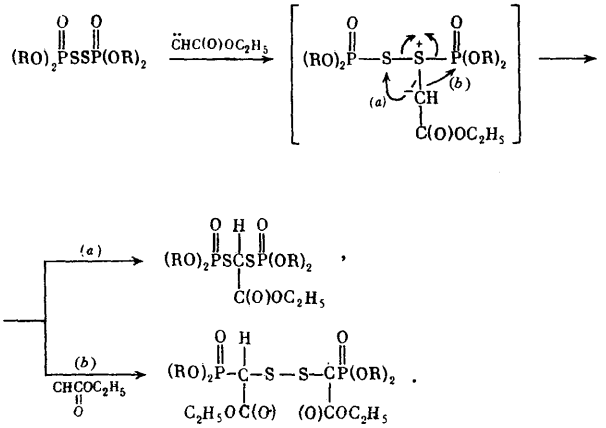
The reaction leads to different results under the conditions of the catalytic generation of ethoxycarbonylcarbene.

Thus the reaction of bis(dialkoxyphosphoryl) disulphides with diazoacetic ester in the presence of catalytic amounts of boron trifluoride etherate results in the formation, even at −20–8 °C, of bis(dialkoxyphosphoryl)ethoxycarbonylmethanes — the products of the insertion of ethoxycarbonylcarbene in the S–S bond:[62]



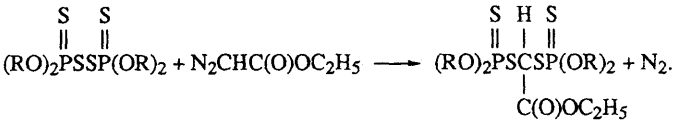
Under the conditions of the catalytic generation of ethoxycarbonylcarbene in the presence of copper powder at 80 °C in benzene or at 80–120 °C without a solvent, the reaction involving insertion in both P–S bonds competes with that leading to the formation of the products of the insertion of ethoxycarbonylcarbene in the S–S bond of the disulphide (Scheme 4):[62]

Scheme 4



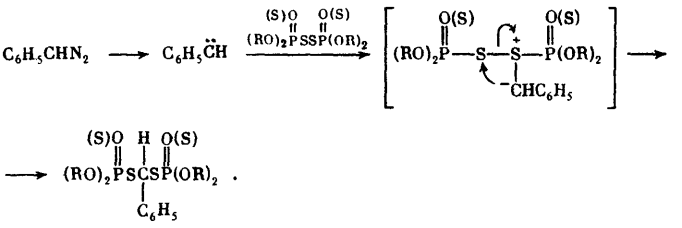
In contrast to diazoacetic ester, diazoacetone reacts with bis(dialkoxyphosphoryl) disulphides at 55–60 °C in the presence of metallic copper to form only the products of the insertion of acetylmethylene in the P–S bonds.[61]

The interaction of bis(dialkoxythiophosphoryl) disulphides with diazoacetic ester both via a non-catalytic reaction (80 °C, benzene) and under the conditions of the thermocatalytic decomposition of diazoacetic ester (Cu, 80 °C) proceeds selectively with formation of bis(dialkoxythiophosphorylthio)ethoxycarbonylmethanes only:[58]

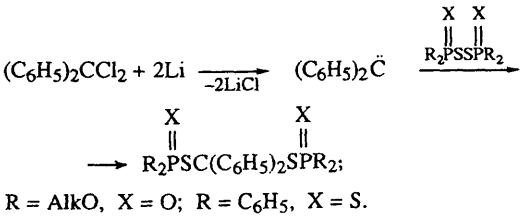


The reaction of bis(dialkoxythiophosphoryl) disulphides with diazoacetone under the conditions involving the generation of acetylcarbene (Cu, 55–60 °C) takes place with formation of the products of insertion in both S–S and P–S bonds,[61] while the reaction with benzoylcarbene afforded only the products of insertion in the S–S bond alone.[63]

It is of interest that the interaction of phenyldiazomethane with bis(dialkoxyphosphoryl) and bis(dialkoxythiophosphoryl) disulphides occurs even at room temperature and involves only the insertion of phenylmethylene in the S–S bond of the disulphide. The authors suggest that the reaction has a carbene mechanism and proceeds via an intermediate sulphonium ylid, whose conversion into the reaction products can occur as a concerted process as a result of a 1,2-sigmatropic rearrangement:[63]



In contrast to phenyldiazomethane, diphenyldiazomethane does not react with phosphorus-containing disulphides either on heating to 90 °C or under the conditions of the photolytic generation of diphenylcarbene. The interaction of bis(dialkoxyphosphoryl) and diphenylthiophosphoryl disulphides with diphenylcarbene, generated by treating dichlorodiphenylmethane with metallic lithium at 20 °C, was achieved. It afforded the products of the insertion of diphenylcarbene in the S–S bond of the disulphide:[63]



R = AlkO, X = O; R = $C_6H_5$, X = S.

Methylphenylcarbene, obtained from dichloro(methylphenyl)-ethane and metallic lithium, reacts with bis(diethoxythiophosphoryl) disulphide similarly to diphenylcarbene.[63]

The reaction of phosphorus-containing trisulphides and tetrasulphides with diazomethane affords the products of the phosphoryl–thiophosphoryl rearrangement:[64]

$$(RO)_2PS_nP(OR)_2 \xrightarrow[-N_2]{CH_2N_2} (RO)_2POCH_2S_{n-1}P(OR)_2 + (RO)_2POCH_2S_{n-2}CH_2OP(OR)_2;$$

$n = 3,4.$

In the reaction with diazoacetic ester, the rearrangement does not occur, but the products of the insertion of the ethoxycarbonylmethylene group in one of the P–S bonds of the polysulphide are formed in a high yield:[65]

$$(RO)_2PS_nP(OR)_2 + N_2CHC(O)OC_2H_5 \longrightarrow (RO)_2PCH(C(O)OC_2H_5)S_nP(OR)_2 + N_2;$$

$n = 3, 4.$

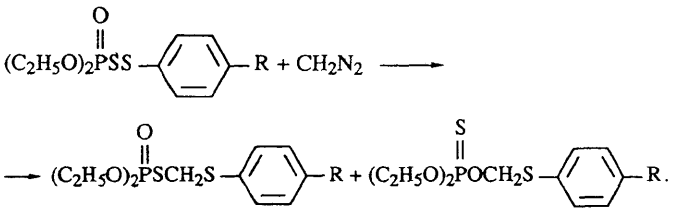
In the presence of an excess of diazoacetic ester, two ethoxycarbonylmethylene groups are inserted in the P–S bonds of polysulphides with partial desulphurisation:[65]

$$(RO)_2PS_nP(OR)_2 + N_2CHC(O)OC_2H_5 \longrightarrow \rightarrow [(RO)_2PC(H)(C(O)OC_2H_5)S]_2 + N_2 + (n-2)S;$$

$n = 3, 4.$

Reactions analogous to those described above have also been considered in relation to thiophosphoryl-substituted trisulphides and tetrasulphides.[66] The products of the insertion of the ethylene group both in one and in two disulphide bonds closest to the phosphorus atom were obtained.

In the case of phosphorus-containing disulphides with an asymmetric structure, namely aryl diethoxyphosphoryl disulphides, the insertion of the methylene group in the S–S bond has been reported, while the products of the phosphoryl-thiophosphoryl rearrangement have been obtained in an insignificant yield:[72–74]



The authors of the above studies suggest that the phosphoryl–thiophosphoryl rearrangement involves interaction with an undissociated molecule of the diazo-compound, while the insertion in the S–S bond is a reaction of the carbene type. As regards the insertion in the P–S bond, the reaction can apparently have both carbene and non-carbene mechanisms.

Thus the reactions of phosphorus-containing polysulphides with diazo-compounds make it possible to obtain organophosphorus compounds which are otherwise difficult to synthesise or were previously unknown, and lead to interesting possibilities for the investigation of carbene reactions in the chemistry of organophosphorus compounds.

Dithio- and monothio-phosphoryl groups

$$-(RO_2)PS(O)-$$

in phosphorus-containing polysulphides behave in many reactions as a pseudo-halogen.[75,76] This is confirmed by the analogous behaviour of thiophosphorylsulphenyl halides and disulphides in reactions with diazo-compounds and carbenes.

The first reports concerning the reactivity of sulphenyl halides derived from phosphorus acids in relation to diazoalkanes appeared in the 1960s. The interaction of diethoxy(thio)phosphorylsulphenyl chlorides with diazomethane and diazoethane has been described.[77,78] α-Chloro-substituted esters of phosphoromonothioic and phosphorodithioic acids were obtained:

$$(C_2H_5O)_2P(X)SCl + N_2CHR^1 \longrightarrow (C_2H_5O)_2P(X)SCH(R^1)Cl + N_2;$$

X = O, R = H; X = S, R = $CH_3$.

Later, other investigators[79–81] studied the interaction of dialkoxy(thio)phosphorylsulphenyl halides with various diazo-compounds: diazomethane, aryl- and diaryl-diazoalkanes, diazoacetic ester, and mono- and bis-diazoketones. It was shown that the reactions of dialkoxy(thio)phosphorylsulphenyl halides with the above diazo-compounds proceed similarly to those described above, with formation of the products of the insertion of the methylene or substituted methylene group in the S–halogen bond in the sulphenyl halides:

$$(RO)_2PS(O)Hal + N_2CR^1R^2 \longrightarrow (RO)_2PS(O)CR^1R^2Hal + N_2;$$

Hal = Cl; $R^1$ = H, $R^2$ = $C(O)OC_2H_5$, $C_6H_5$, $C(O)(CH_2)_4C(O)CHN_2$, $C(O)CH_3$, $C(O)C_6H_5$; $R^1 = R^2 = C_6H_5$; Hal = Br; R = Alk; $R^1$ = H; $R^2$ = $C(O)OC_2H_5$, $C_6H_5$; $R^1 = R^2$ = H, $C_6H_5$.

However, in the reaction of dialkoxyphosphorylsulphenyl bromides with diazoacetone and diazoacetic ester, a mixture of phosphorothiolic and phosphorothionic acid esters is formed, i.e., together with the insertion of the acetyl- and ethoxycarbonylmethylene group in the S–Br bond of the sulphenyl

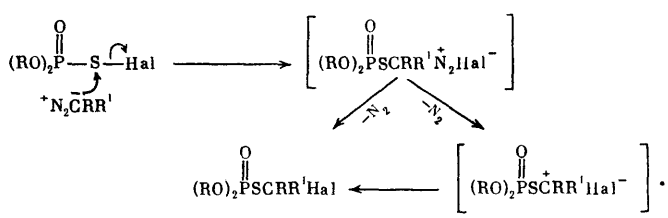
bromide, the products of the phosphoryl–thiophosphoryl rearrangement are formed:

$$(RO)_2P(O)SBr + N_2CHR^1 \longrightarrow (RO)_2P(O)SCHR^1Br + (RO)_2P(S)OCHR^1Br + N_2;$$

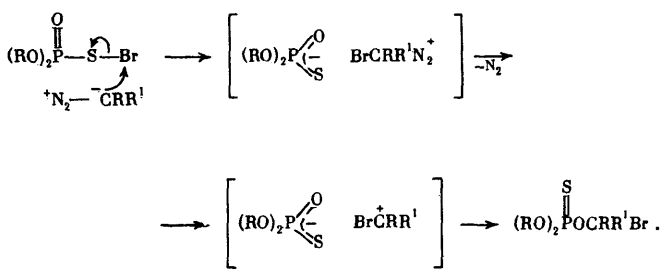
$R^1 = C(O)CH_3, C(O)OC_2H_5$.

The experimental conditions ($t = -50$ to $-20$ °C, absence of the catalyst or UV irradiation) enabled the authors of the above studies to reject the carbene reaction mechanism and to regard the interaction of dialkoxy(thio)phosphorylsulphenyl halides with an undissociated molecule of a diazo-compound via the intermediate formation of the diazonium cation as a result of nucleophilic attack either on the sulphur atom (Scheme 5) or on the halogen atom (Scheme 6):

Scheme 5



Scheme 6



The exclusive formation of the products of the insertion of the substituted methylene group in the S–halogen bond in the sulphenyl halides is evidence in support of Scheme 5. However, Scheme 6, involving nucleophilic attack on the bromine atom, operates in the reaction of diazoacetone and diazoacetic ester with dialkoxyphosphorylsulphenyl bromides.

As can be seen from the foregoing, the interaction of phosphoryl- and thiophosphoryl-sulphenyl halides with diazo-compounds involves mainly the insertion of the methylene or a substituted methylene group in the S–halogen bond. It is therefore of interest to examine the reactivities of phosphorus halides in relation to diazo-compounds, since this entails the insertion of the methylene group in the P–halogen bond.

Thus Yakubovich and Ginzburg[82] showed in 1952 that, under certain conditions ($t = -60$ °C), the interaction of phosphorus trichloride or tribromide with diazoalkanes proceeds smoothly with formation of haloalkyldihalophosphines:

$$PHal_3 + RCHN_2 \longrightarrow HalCHRPHal + N_2;$$

Hal = Cl, Br; R = H, $CH_3$.

Phosphorus pentachloride reacts with diazomethane to form tris(chloromethyl)dichlorophosphine, which is converted subsequently into tris(chloromethyl)phosphine oxide in the presence of traces of moisture:[82]

$$PCl_5 + 3CH_2N_2 \longrightarrow (ClCH_2)_3PCl_2 \xrightarrow{H_2O} (ClCH_2)_3P{=}O.$$

Phenylphosphorus tetrachloride behaves similarly:[83]

$$C_6H_5PCl_4 + 3CH_2N_2 \xrightarrow[-40°C]{} [C_6H_5P(CH_2Cl)_2Cl_2] \xrightarrow{H_2O}$$

$$\rightarrow C_6H_5P(O)(CH_2Cl)_2.$$

Phosphorus oxide chloride and phosphorus oxide bromide do not react with diazoalkanes even under the conditions involving the generation of the corresponding carbenes.[82]

## III. Phosphines and phosphites in reactions with diazo-compounds and carbenes

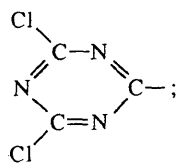
### 1. Reactions of acyclic trialkyl- and triaryl-phosphines and tertiary cyclic phosphines and their oxides with diazo-compounds

The reactions of trivalent phosphorus derivatives with diazo-compounds were first achieved by Staudinger and co-workers in 1919–1922 for acyclic tertiary phosphines.[84] Later, other workers greatly expanded the range of applications of this reaction.[85–91]

It has been shown in relation to acyclic tertiary phosphines that trialkyl- and triaryl-phosphines react with different acyclic diazo-compounds to form phosphazines:

$$R^1R^2R^3P + N_2CR^4R^5 \longrightarrow R^1R^2R^3P{=}N{-}N{=}CR^4R^5,$$

$R^1 = R^2 = R^3 = C_6H_5, C_2H_5, C_6H_5C_6H_4$; $R^4$ = H, $C_6H_5$, $C_6H_5C(O)$, $CH_3C(O)$, $CH_3C(O)O$, $C_2H_5OC(O)$, $CH_3OC(O)$, $C_6H_5SO$,

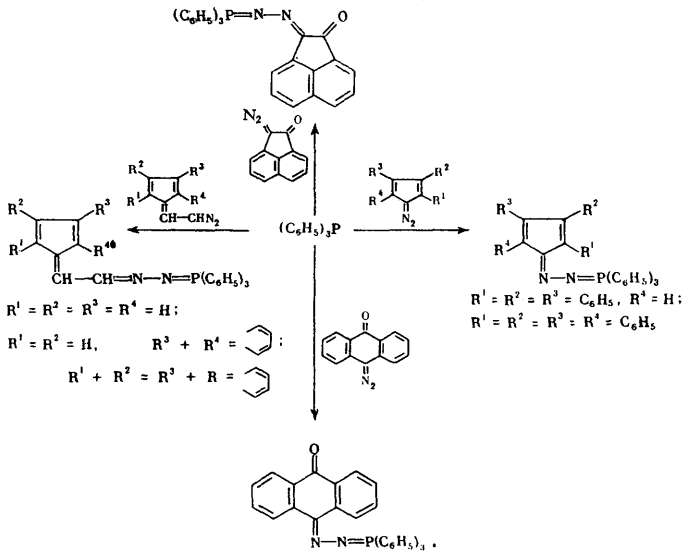


$R^5 = C_6H_5, C_2H_5OC(O), C_6H_5C(O), CH_3C(O), CH_3OC(O)$,

$C_6H_5CH{=}CHC(O)$, $C_6H_5S(O)O$.

The reactions of triphenylphosphine with cyclic diazo-compounds, namely diazoacenaphthene,[92] diazoanthrone,[93] diazoethylidene derivatives of cyclopentadiene, indene, and fluorene,[94] and

diazocyclopentadiene and its phenyl derivatives,[95,96] proceed similarly to form cyclic phosphazenes:



A kinetic study[97,98] confirmed the second order and irreversibility of the reactions of triphenylphosphines and aromatic ring-substituted triphenylphosphines with diazoalkanes and 9-diazofluorene.

It is of interest that the nature of the final product of the reactions of acyclic phosphines with diazo-compounds is influenced by the nature of the substituents at the phosphorus atom. In the presence of a mobile hydrogen atom in the phosphine molecule, phosphazines are not formed. Thus dibutoxyphosphine reacts with diphenyldiazomethane to form a mixture of the isomeric adducts (XXI) and (XXII), while the reactions with diazoacetone and diazoacetic esters afford only one adduct—the hydrazone (XXI):[99]

$$(C_4H_9O)_2PH + N_2CRR^1 \longrightarrow \underset{\text{(XXI)}}{(C_4H_9O)_2PNHN{=}CRR^1} +$$

$$+ \underset{\text{(XXII)}}{(C_4H_9O)_2PN{=}NCHRR^1};$$

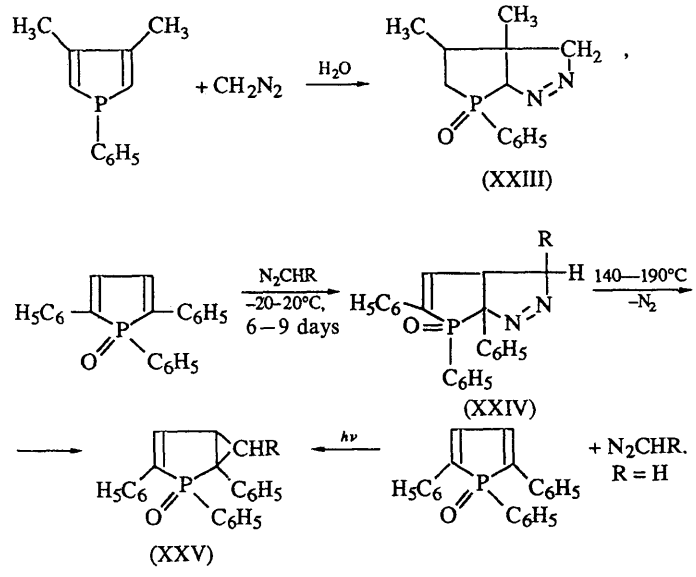
$$R = R^1 = C_6H_5;\ R = H,\ R^1 = C(O)CH_3,\ C(O)OC_2H_5.$$

In contrast to the reactions of acyclic phosphines, the reaction of an acyclic tertiary phosphine, having a mobile hydrogen atom in the α-position, with diazomethane takes place via the phosphoryl group to form a phosphorane:[100]

$$(C_6H_5)_2P(O)CH(SO_2C_6H_5)_2 + CH_2N_2 \longrightarrow (C_6H_5)_2P(OCH_3){=}C(SO_2C_6H_5)_2 + N_2.$$

The reactions of unsaturated tertiary cyclic phosphines and their oxides proceed quite differently.

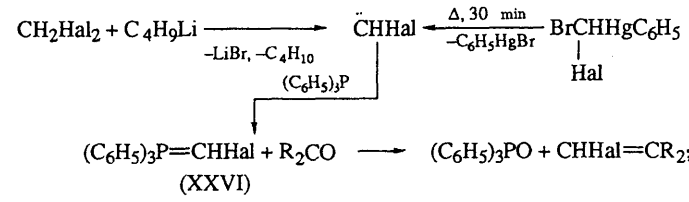
Thus the reactions of 3,4-dimethyl-1-phenylphosphole with diazomethane in the presence of water[101] and of 1,2,5-triphenylphosphole oxide with diazomethane and diazoacetic acid esters[102] proceed as 1,3-dipolar cycloaddition to one of the multiple bonds of the ring with formation of the pyrazoline derivatives (XXIII) and (XXIV) respectively. The cyclopropane derivatives (XXV) were obtained by the thermal decomposition of compound (XXIV). They are formed as a result of the photochemical reaction of 1,2,5-triphenylphosphole oxide with diazomethane:



## 2. Reactions of trialkyl- and triaryl-phosphines with carbenes

The reactivity of phosphines in relation to carbenes has been studied in fair detail and it has been found that trialkyl- and triaryl-phosphines are mild carbene trapping agents and that this reaction serves as one of the methods for the synthesis of phosphorus ylids which are used in synthetic organic chemistry for the synthesis of olefins by the Wittig reaction.[93,103–116]

Halomethylenephosphoranes (XXVI) are formed in the reaction of triphenylphosphine with chlorocarbene, generated from methylene chloride by treatment with butyllithium[103–105] or by the thermolysis of phenyl(bromohalomethyl)mercury:[106]



Hal = Cl, Br.

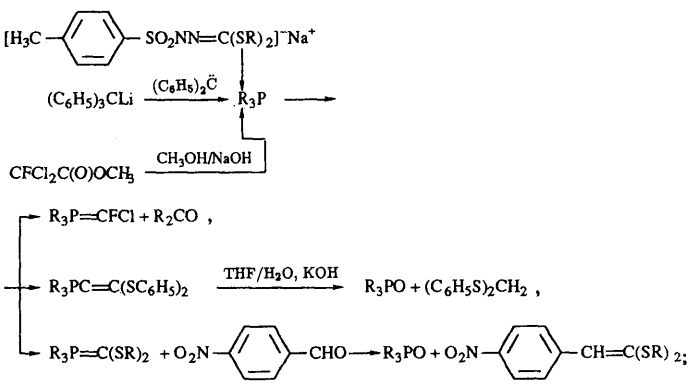
Dihalomethylenephosphoranes (XXVII, Hal = F, Cl, Br) have been obtained from trialkyl- and triaryl-phosphines and dihalocarbenes, generated from haloform by the treatment with potassium t-butoxide,[107–109] by the thermolysis of phenyl(bromodichloromethyl)mercury[110] or the sodium salt of chlorodifluoroacetic

acid,[111] or from dibromodifluoromethane by treatment with lithium butoxide:[112]

$$R_3P + \ddot{C}HHal_2 \longrightarrow \underset{(XXVII)}{R_3P{=}CHHal_2} + R_2CO \longrightarrow R_3PO + Hal_2C{=}CR_2;$$

R = Alk, Ar; Hal = Cl, Br, F.

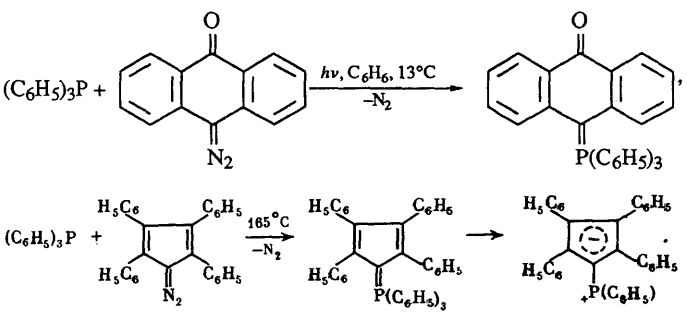
Chlorofluoromethylene, obtained from methyl dichlorofluoroacetate and sodium hydride,[109,113] bis(phenylthio)carbene, generated from tris(phenylthiomethyllithium)[114] and bis(alkylthio)carbene, generated by the thermal decomposition of the sodium salt of tosylhydrazone[115] enter into similar reactions with phosphines:



R = $CH_3$, $C_2H_5$.

Phosphorus ylids are formed when the carbene precursor is a diazo-compound, for example, in the reaction with triphenylphosphine under the conditions of catalytic, photolytic, or thermal decomposition of the corresponding diazo-compound:[93,95,96,116]

$$(C_6H_5)_3P + CH_2N_2 \xrightarrow[-N_2]{CuCl} (C_6H_5)_3P{=}CH_2,$$



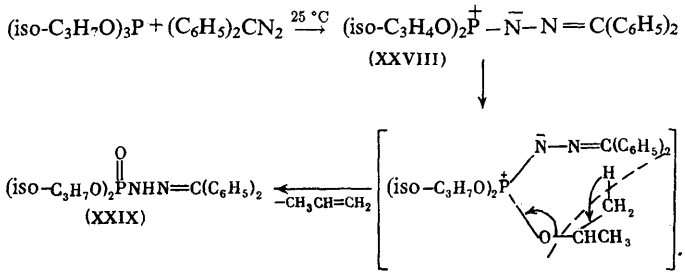
### 3. Phosphites in reactions with diazo-compounds and carbenes

Kabachnik and Arbuzov[13,117–119] showed that trialkyl phosphites behave similarly to phosphines in reactions with diazomethane and diazoacetic acid esters, forming trialkyl phosphate *N*-methylene- and *N*-ethoxycarbonyl-azines respectively in yields of at least 60%:

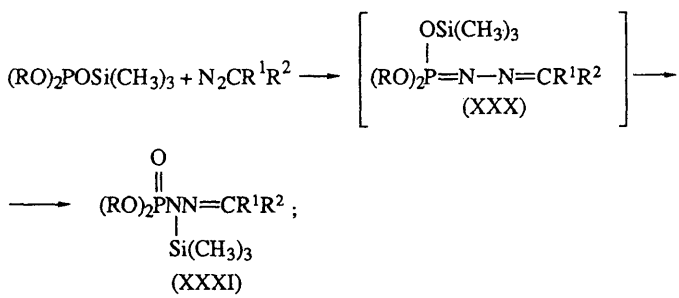
$$(RO)_3P + N_2CHR^1 \longrightarrow (RO)_3P{=}N{-}N{=}CHR^1;$$

$R^1$ = H, $C(O)CH_3$, $C(O)OC_2H_5$.

It has been observed[120] that the reaction of triisopropyl phosphite with diphenyldiazomethane does not stop at the stage involving the formation of benzophenone triisopropylphosphorazine (XXVIII). Instead, a compound with the hydrazone structure, namely diisopropyl *N*-(diphenylmethylene)phosphorohydrazidate (XXIX), is formed in 75% yield, provided that the reaction is carried out under severe conditions:



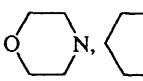
In the case of dialkyl trimethylsilyl phosphites, the intermediate phosphorazines (XXX) almost wholly isomerise already under experimental conditions with migration of the trimethylsilyl group to the phosphimine nitrogen atom and the quantitative formation of dialkyl *N*-trimethylsilylphosphorohydrazidates (XXXI):[121,122]



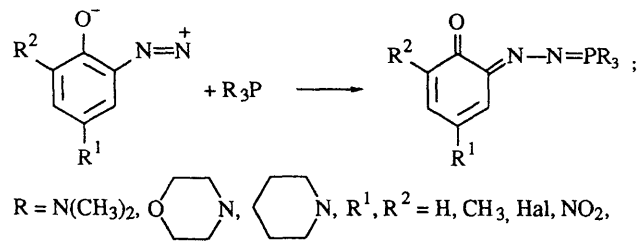
$R^1 = R^2$ = H, $C_6H_5$; $R^1$ = H, $R^2$ = $C(O)CH_3$, $C(O)OCH_3$, $C(O)OC_2H_5$.

Phosphorous triamides react vigorously with various acyclic and cyclic diazo-compounds similarly to trialkyl phosphites. About 60 compounds of the class of tris(dimethylamino)phosphorazines were obtained:[123–125]

$$R_3P + N_2CR^1R^2 \longrightarrow R_3P{=}N{-}N{=}CR^1R^2,$$

R = , $(CH_3)_2N$, $(C_2H_5)_2N$; $R^1 = R^2$ = H, $C(O)OCH_3$, $C(O)OC_2H_5$, $C_6H_5$, $R^1$ = H, $R^2$ = $C(O)OC_2H_5$, $C(O)OCH_3$; $R^1$ = $C(O)CH_3$, $R^2$ = $C(O)C_6H_5$; $R^1 + R^2$ = $(CH_3)_3C(CH_2)_2CO_2$, *o*-$C_6H_4(CO)_2$.

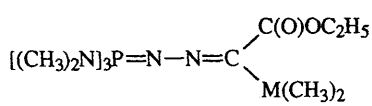
The reaction with *O*-diazoquinone and its various derivatives 4,6-disubstituted in the aromatic ring proceeds similarly:[126]



$R = N(CH_3)_2$, O, N, N, $R^1, R^2 = H, CH_3$, Hal, $NO_2$, $C(O)CH_3$, $C(O)OCH_3$.

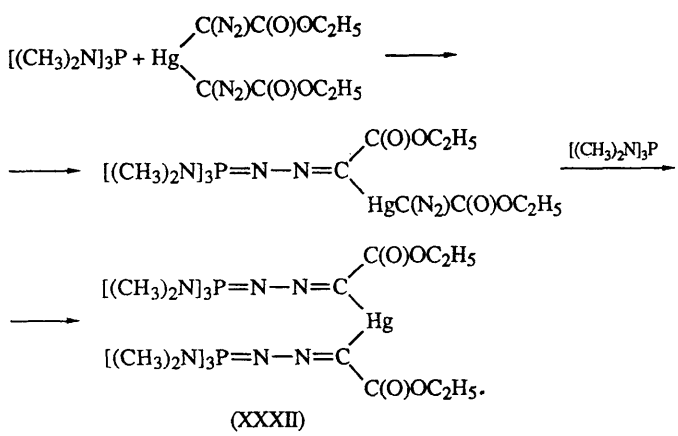
Towards the end of the 1970s, Krommes and Lorberth[124,127] investigated the reactions of phosphorous tris(dimethylamides) with a whole series of organoelement derivatives of diazomethane: $(CH_3)_nMCN_2$ [M = Si, Ge, Sn, Pb, As, Sb, Bi: $n$ = 2, 3; R = H, $C(O)OC_2H_5$].

From the available literature data on the chemistry of organoelement diazoalkanes,[128] it was postulated that the introduction of any element into the molecule of the diazo-compound does not alter the chemical behaviour of organoelement derivatives or diazomethane in their reactions with phosphorous tris(dimethylamides). Indeed, the tris(dimethylamino)phosphorazines



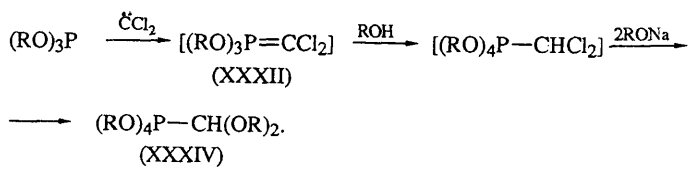
were obtained for M = As or Sb. When R = H, M = Si, Ge, or As, and $n$ = 2 or 3, a mixture of the *cis*- and *trans*-isomers of tris(dimethylamino)phosphorazines is formed.

The interaction of phosphorous tris(dimethylamide) with bis(ethyl diazoacetate)mercury to form the tris(dimethylamino)phosphorazine (XXXII) can proceed in stages:



(XXXII)

As regards the interaction of trialkyl phosphites with carbenes, it was found that, in contrast to phosphines, trialkyl phosphites, in the presence of which dichlorocarbene is generated from chloroform and sodium alkoxide, give rise to the adducts (XXXIII), which undergo further changes and are converted into tetraalkoxy(dialkoxy-methylene)phosphoranes (XXXIV):[129]

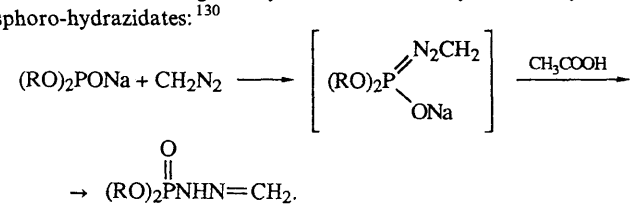


(XXXII) (XXXIV)

Thus a common feature of the reactions of phosphines and phosphites with diazo-compounds is the formation of a new phosphorus–nitrogen bond. Evidently, these reactions are based on addition to the lone pair of the phosphorus atom, probably as a result of the electrophilic attack by the terminal nitrogen atom and the conversion of the trivalent phosphorus derivative into the corresponding pentavalent phosphorus derivative.

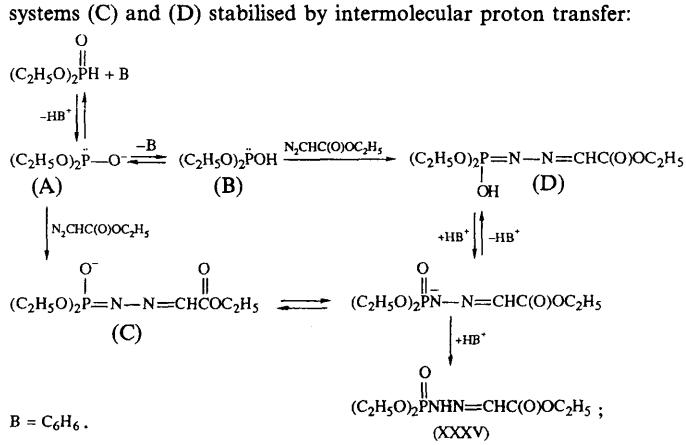
## 4. Dialkyl phosphites in reactions with diazo-compounds

In contrast to trialkyl- and triaryl-phosphines, trialkyl phosphites, and phosphorous triamides, dialkyl phosphites do not react with aliphatic diazo-compounds under the usual conditions. Only their sodium salts react vigorously to form dialkyl *N*-methylene-phosphoro-hydrazidates:[130]



The inability of dialkyl phosphites to react with diazoalkanes has been attributed to the low acidity of dialkyl phosphites, because their tautomeric equilibrium is strongly displaced towards the form with pentavalent phosphorus[131] and the insertion of the methylene group in the P–H bond, specially investigated in relation to hypo-phosphorous acid esters, was not observed.[10]

However, the use of benzene as the solvent, which promotes the shift of the tautomeric equilibrium of diethyl phosphite towards the formation of the trivalent form (B) according to the authors,[119] leads to the interaction between the diethyl phosphite and diazoacetic ester with formation of diethyl *N*-ethoxycarbonylmethylene-phosphorohydrazidate (XXXV). A mechanism is proposed for the formation of the reaction product via the intermediate phosphazine systems (C) and (D) stabilised by intermolecular proton transfer:



B = $C_6H_6$.

(XXXV)

Diphenyl phosphite, which has more acid properties than diethyl phosphite, reacts with diazomethane to form methyl diphenyl phosphite due to the presence of the tautomeric equilibrium between the pentavalent and trivalent forms:[132]

$$(C_6H_5O)_2\overset{O}{\overset{\|}{P}}H \rightleftharpoons (C_6H_5O)_2\ddot{P}OH + CH_2N_2 \longrightarrow$$

$$\rightarrow (C_6H_5O)_2POCH_3 + N_2.$$

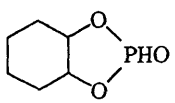
The unusual behaviour of diazoacetone in the reaction with diethyl phosphite and the formation of diethyl isopropenyl phosphate have been noted:[87,133]

$$(C_2H_5O)_2\overset{O}{\overset{\|}{P}}H \longrightarrow (C_2H_5O)_2\ddot{P}OH + N_2CHC(O)CH_3 \longrightarrow$$

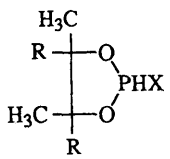
$$\longrightarrow (C_2H_5O)_2\overset{O}{\overset{\|}{P}}-\underset{CHN_2}{\overset{OH}{\overset{|}{\underset{|}{C}}}}CH_3 \xrightarrow{-N_2} \left[(C_2H_5O)_2\overset{O}{\overset{\|}{P}}-\underset{{}^{+}CH_2}{\overset{O^-}{\overset{|}{\underset{|}{C}}}}CH_3\right] \longrightarrow$$

$$\longrightarrow (C_2H_5O)_2\overset{O}{\overset{\|}{P}}OC(CH_3)=CH_2.$$

In contrast to acyclic dialkyl phosphites, the high reactivity of cyclic phosphorous acids and their sulphur and nitrogen analogues (XXXVI)–(XXXIX) in reactions with diazomethane indicates a greater shift of the tautomeric equilibrium of the acid towards the trivalent form, which is the reason for their acid properties:[134,135]

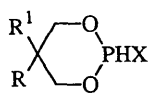


(XXXVI)



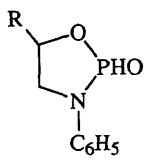
(XXXVII)

R = H, $CH_3$, X = O, S



(XXXVIII)

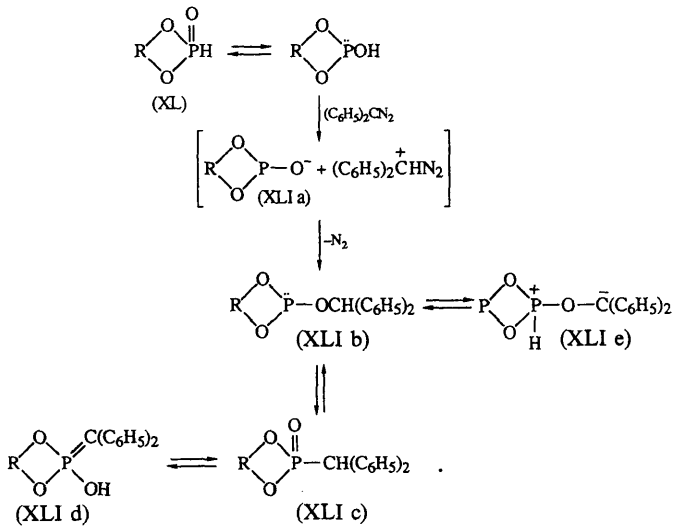
R = $CH_3$, $R^1$ = H, X = O;
R = H, $R^1$ = $CH_3$, X = S



(XXXIX)

R = H, $CH_3$.

Thus, when equimolar amounts of 2,3-butylene-, *o*-phenylene, and neopentylene-phosphorous acids (XL) are mixed with diphenyldiazomethane at 20–25 °C, an equilibrium mixture of products (XLIb–e) is formed:



(XL) (XLI a) (XLI b) (XLI e) (XLI d) (XLI c)

From the entire set of experimental data and the results of kinetic studies of the reactions of cyclic phosphorous acids with diphenyldiazomethane, it was established that the reaction proceeds via a two-stage mechanism. In the first stage, diphenyldiazomethane is protonated with formation of the ion pair (XLIa), while in the second stage the ion pair is converted into the final reaction products (XLIb–e).

Thus the kinetic studies indicate the existence of common mechanisms in the reactions of phosphorous acids and cyclic phosphoromonothioic and phosphorodithioic acids[36,37] as well as acyclic phosphorus monothio acids[22,26] with diazo-compounds.

## 5. Reactions of dialkyl phosphites and dialkyl phosphorothioites with carbenes

Until the beginning of the 1960s, there was no information in the literature about the reactions of organophosphorus compounds containing a P–H bond in the molecule with diazo-compounds under carbene generation conditions.

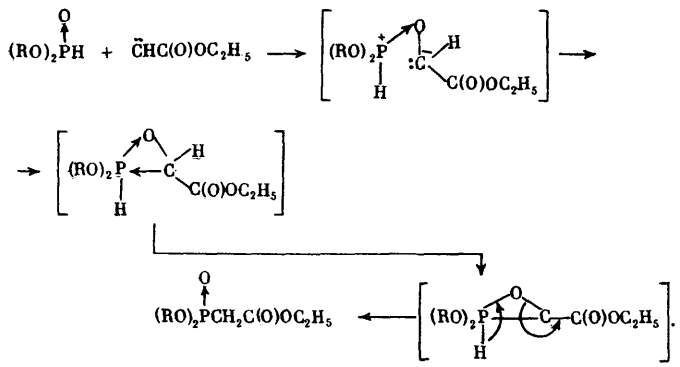
The formation of dialkyl phosphonoacetate esters (XLII) and small amounts (5–6%) of dialkyl *N*-ethoxycarbonylmethylene-phosphorohydrazidates (XLIII, R = $CH_3$, $C_3H_7$) was achieved for the first time[12,13] in the $CuSO_4$-catalysed decomposition of diazoacetic ester in the corresponding dialkyl phosphites. The authors represent the formation of the phosphorohydrazidates as a result of the interaction of dialkyl phosphites with still undecomposed diazoacetic ester:

$$(RO)_2\overset{O}{\overset{\|}{P}}H + N_2CHC(O)OC_2H_5 \xrightarrow[\ddot{C}HC(O)OC_2H_5]{CuSO_4,\ 60—90°C}$$

$$\longrightarrow \underset{(XLII)}{(RO)_2\overset{O}{\overset{\|}{P}}CH_2C(O)OC_2H_5} + \underset{(XLIII)}{(RO)_2\overset{O}{\overset{\|}{P}}NHN{=}CHC(O)OC_2H_5};$$

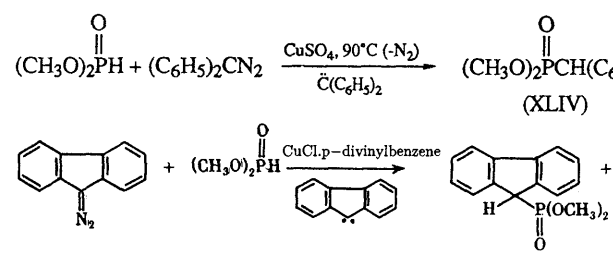
R = $CH_3$, $C_2H_5$, $C_3H_7$.

The mechanism proposed for the formation of compounds (XLII) includes electrophilic attack by the ethoxycarbonylcarbene on the oxygen of the dialkyl phosphite with subsequent redistribution of bonds in the intermediate complex formed:[13]

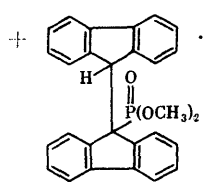


According to the authors, the hypothesis of the possible direct insertion of the ethoxycarbonylcarbene in the P–H bond is no less likely.

The product of insertion in the P–H bond, namely dimethyl diphenylmethylphosphonate (XXIV) [136] and, in the case of diazofluorene, the adducts (XLV) and (XLVI),[137] were obtained similarly in the thermocatalytic decomposition of diphenyldiazomethane in dimethyl phosphite:



(XLV)



(XLVI)

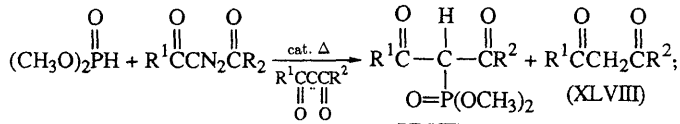
The reactions with diazoindene and 7-diazo-8-naphthene are likewise similar.[137]

As regards diazodicarbonyl compounds, especially diazodiketones which are known to be capable of the specific Wolff rearrangement in the decomposition process,[138] by suppressing this process or by creating conditions promoting the occurrence of the Wolff rearrangement, it is possible to alter the mode of the reactions of diazoketones with organophosphorus compounds.

It has been established that, under conditions promoting the Wolff rearrangement, phosphorus-containing products cannot be isolated. The only reaction product was alkyl 2-oxo-1,2-diphenylpropionate.[139]

In order to suppress the Wolff rearrangement and to make it possible to synthesise the products of insertion in the P–H bond, a study has been made[139–146] of the thermocatalytic decomposition,[139–142], direct photolysis,[142] and photosensitised decomposition[142,144–146] of a whole series of 2-diazo-1,3-diketones in dialkyl phosphites and phosphorothioites.

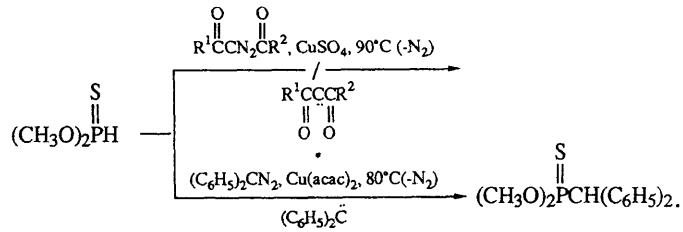
The thermocatalytic decomposition of 2-diazo-1,3-diketones ($CuSO_4$ or copper acetylacetonate; 80–90 °C) in dimethyl phosphite led to the isolation in 16.5–46% yield of 2-phosphono-1,3-diketones (XLVII) — the products of the insertion of the corresponding diketocarbene in the P–H bond of dimethyl phosphite and the products of the reduction of the diketocarbenes (XLVIII). The reaction constitutes a general method for the *C*-phosphorylation of 1,3-dicarbonyl compounds:



(XLVII)

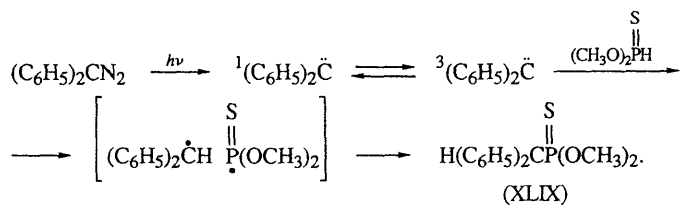
$R^1 = R^2 = CH_3$, $OCH_3$, $C_6H_5$; $R^1 + R^2 = (CH_3)_2C(CH_2)_2$.

In the case of dialkyl phosphorothioites, the insertion of diketocarbenes, obtained under similar conditions, in the P–H bond could not be achieved,[142] in contrast to diphenylcarbene:[136]



Until recently, there was no information in the literature about the insertion of photochemically generated carbenes in the P–H bond.

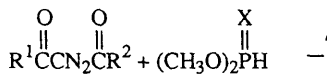
It was not until 1989[136] that the product of the insertion of diphenylcarbene in the P–H bond, namely dimethyl diphenylmethylphosphonothioate (XLIX), was obtained by the direct photolysis of diphenyldiazomethane in dimethyl phosphorothioite. The formation of compound (XLIX) was represented as a reaction proceeding via the mechanism involved in the recombination of the radical pairs generated from the triplet form of diphenylcarbene:[147]



(XLIX)

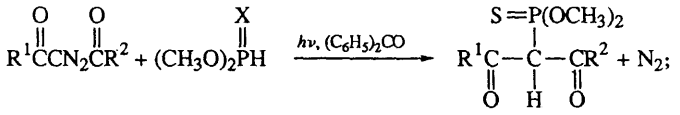
There are no literature data indicating that the diketocarbenes obtained by the direct photolysis of diazodicarbonyl compounds exist predominantly in the triplet form. This is apparently the

reason why the attempt in 1986 to obtain the products of insertion in the P–H bond was unsuccessful:[142]



$R^1 = CH_3$, $R^2 = OCH_3$, $CH_3$; $R^1 + R^2 = (CH_3)_2(CH_2)_2$; X = O, S.

However, 2-(thio)phosphono-1,3-dicarbonyl compounds — the products of insertion in the P–H bond — were obtained in 6.5–3.9% yields by the photosensitised decomposition of 2-diazo-1,3-dicarbonyl compounds in dimethyl phosphite (phosphorothioite) in the presence of benzophenone:[142,144,145]



$R^1 = R^2 = OCH_3$, X = S; $R^1 = CH_3$, $R^2 = OCH_3$, X = S;

$R^1 = R^2 = CH_3$; X = O, S;

$R^1 + R^2 = (CH_3)_2C(CH_2)_2$, X = S.

Thus the results obtained for the reactions of the photochemically generated diketocarbenes in dialkyl phosphites (phosphorothioites) led the investigators[142,144] to put forward the hypothesis that a triplet carbene is the main intermediate in the insertion in the P–H bond, which was confirmed by a study, using the chemically induced dynamic nuclear polarisation method ($^{31}P$ CIDNP), of the mechanism of the insertion of carbenes in the P–H bond.[145,146]

Thus it is evident from the literature data on the reactions of organophosphorus compounds with a P–H bond in the molecule that the formation of the products of insertion in this bond in the reactions of dialkyl phosphites (phosphorothioites) with diazo-compounds occurs in two cases: (a) under the conditions of the thermocatalytic generation of carbenes and (b) in the photosensitised decomposition of diazodicarbonyl compounds. In the reactions with diphenyldiazomethane, such products are formed under the conditions of direct photolysis owing to the specific properties of the diphenylcarbene generated.

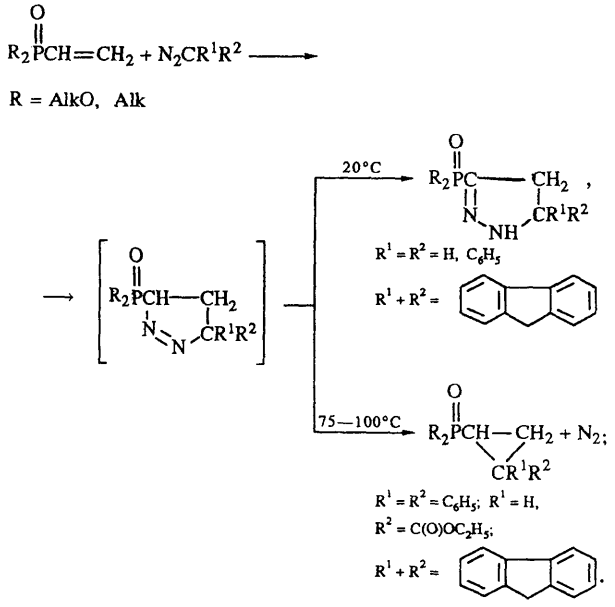
## IV. Reactions of diazo-compounds and carbenes with phosphorus-containing systems having multiple bonds

### 1. Reactions involving the 1,3-dipolar cycloaddition of diazo-compounds and the cycloaddition of alkoxycarbonylcarbenes to phosphorus-containing systems with multiple bonds

A series of studies devoted to the comprehensive investigation of the reactions of aliphatic diazo-compounds and carbenes with unsaturated organophosphorus compounds has been carried out since the beginning of the 1960s by the Kazan School of organophosphorus chemists[148–157,159–161,169–180] and have been described in a review.[3] There exist also communications and reviews by foreign authors.[4,5,158,162–168,181–193]

The study of the 1,3-dipolar cycloaddition reactions of diazo-compounds is of considerable interest not only for the elucidation of the reactivity of unsaturated organophosphorus compounds with which the mode of the reactions and the nature of the products formed are associated, but also as a possible way of synthesising five-membered heterocycles.

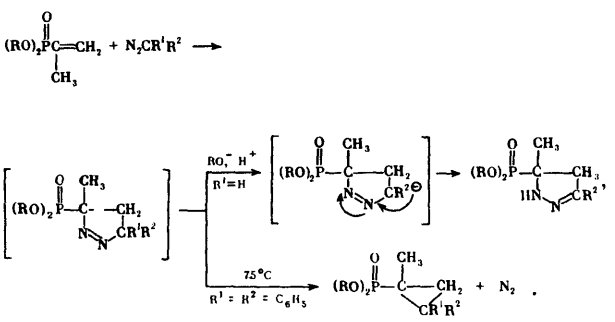
It has been shown that the 1,3-dipolar cycloaddition of diazomethane, diazoacetic ester, diphenyldiazomethane, and diazofluorene to dialkyl vinylphosphonates[148–153] and of diphenyldiazomethane to tertiary vinylphosphine oxides[154] proceeds via the intermediate formation of phosphorylated 3-$\Delta^1$-pyrazolines, which, depending on the experimental conditions, either isomerise to phosphorylated 3-$\Delta^2$-pyrazolines, or eliminate nitrogen and are converted into cyclopropane derivatives:



R = AlkO, Alk

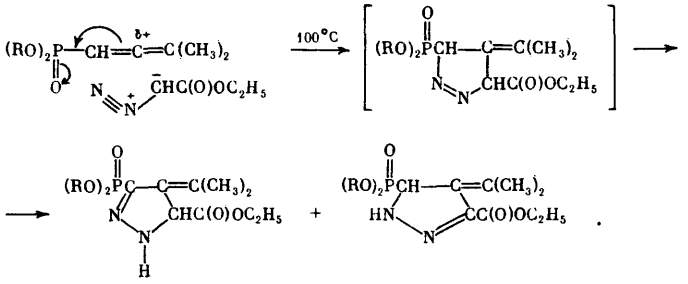
The reactions of diethyl allylphosphonate and diethylallylphosphine oxide with diazomethane and diphenyldiazomethane proceed similarly via the 1,3-dipolar cycloaddition mechanism.[148,154]

As a result of the 1,3-dipolar cycloaddition of diazo-compounds, dialkyl isopropenylphosphonates give rise to either phosphorylated 5-$\Delta^2$-pyrazolines or to cyclopropane derivatives, depending on the experimental conditions:[155–157]



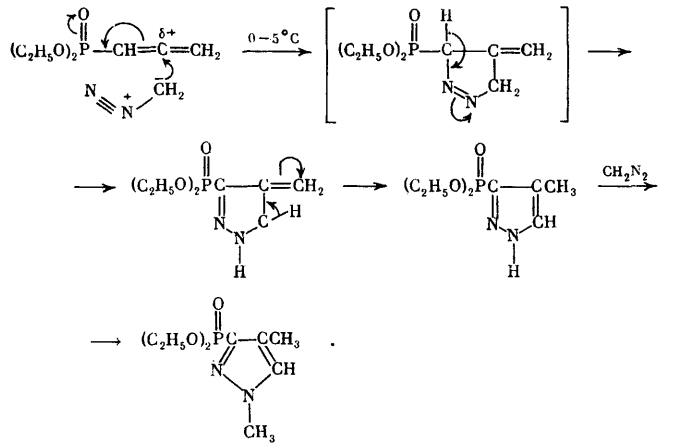
The addition of diazomethane to α-cyanovinylphosphonates takes place similarly with formation of phosphorylated 5-$\Delta^2$-pyrazolines.[158]

The interaction of diazoalkanes with organophosphorus compounds containing cumulated or conjugated double bonds also proceeds via the mechanism involving 1,3-dipolar cycloaddition to the α,β-double bond. The reaction of γ,γ-dimethylallenylphosphonate with diazoacetic ester affords under these conditions a mixture of phosphorylated 3(5)-$\Delta^2$-pyrazolines with exocyclic isopropenyl groups:[159]

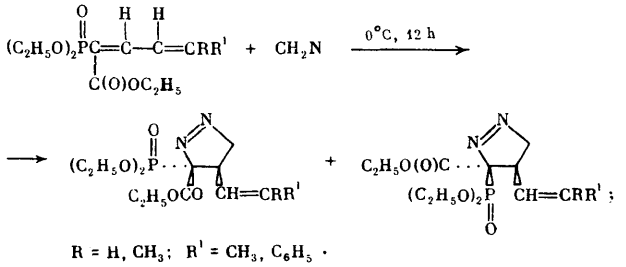


The cycloaddition of diphenyldiazomethane to allenylphosphonate takes place regiospecifically with the exclusive formation of 3-$\Delta^2$-phosphorylated pyrazoline containing an exocyclic methylene group.[160]

In the case of the reaction with diazomethane, the analogous product, namely phosphorylated 3-$\Delta^2$-pyrazoline, fully isomerises during distillation to 3-diethoxyphosphono-4-methylpyrazole. After *N*-methylation with diazomethane, 3-diethoxyphosphono-1,4-dimethylpyrazole was isolated:[161]

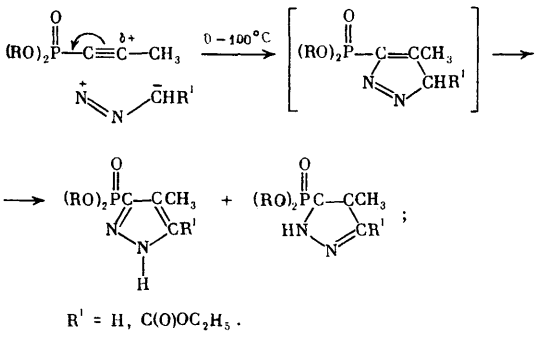


The cycloaddition of diazomethane to diethyl buta-1,3-dienylphosphonates proceeds with formation of a mixture of isomeric phosphorylated 3-$\Delta^2$-pyrazolines, which are stable under the reaction conditions:[162]



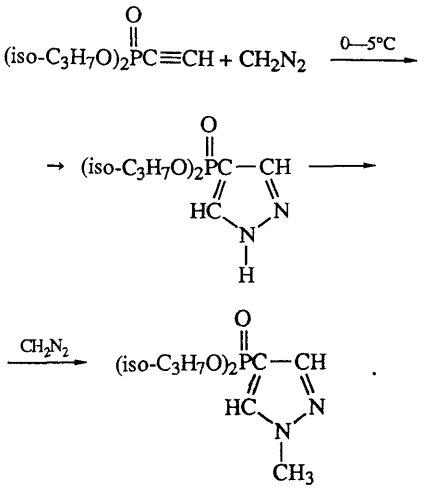
R = H, $CH_3$; R' = $CH_3$, $C_6H_5$.

The 1,3-dipolar cycloaddition of diazoacetic ester and diazomethane to the triple bond of dialkyl propynylphosphonates has been described.[159,161] A mixture of isomeric 3(5)-dialkoxyphosphono-5(3)-ethoxycarbonyl-4-methylpyrazoles was obtained as a result of the reaction:

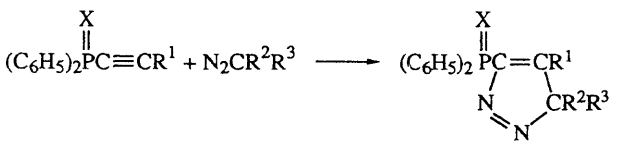


R' = H, $C(O)OC_2H_5$.

Diisopropyl ethynylphosphonate reacts with an excess of diazomethane to form diisopropyl 1-methylpyrazol-5-ylphosphonate only:[163]



The reactions involving the 1,3-dipolar cycloaddition of diazomethane, diazopropane, diphenyldiazomethane, and methylphenyldiazomethane to alkynyldiphenylphosphine oxides (sulphides) and alkynylbis(diphenylphosphine) oxides (sulphides) involve only the triple bond with formation of diphenyl [3*H*]-pyrazol-5-ylphosphonates and diphenyl [3*H*]-pyrazol-5-ylthiophosphonates:[4,164]

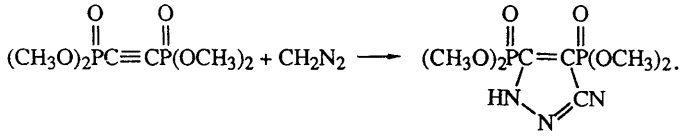


$R^1$ = H, $CH_3$, $C_6H_5$, $P(C_6H_5)_2$; $R^2$ = $R^3$ = H, $CH_3$, $C_6H_5$;

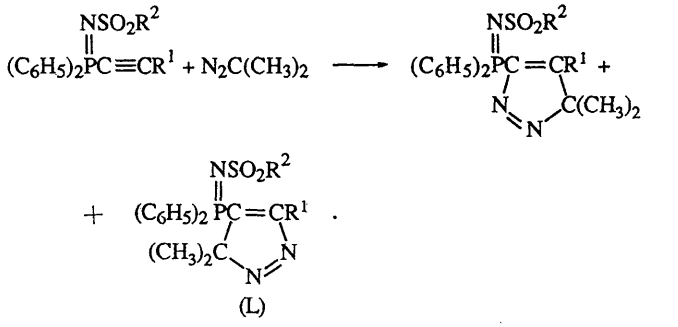
$R^2$ = $CH_3$, $R^3$ = $C_6H_5$;

X = O, S.

The reaction of tetramethyl acetylenebisphosphonate with diazomethane proceeds similarly:[165]

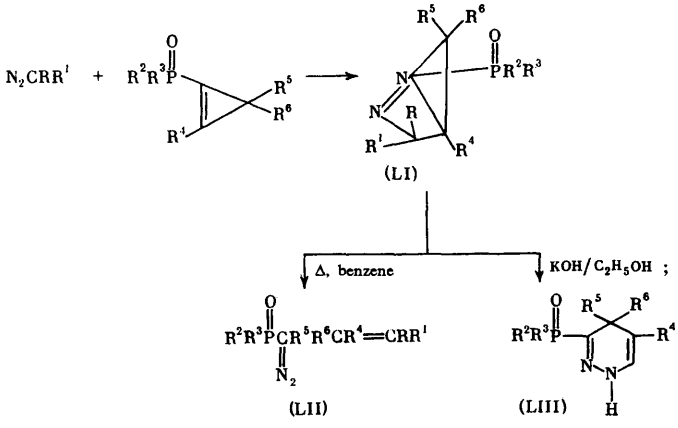


The reaction of *N*-[alkynyl(diphenyl)phosphorandiyl]sulphonamide with diazopropane either affords a mixture of isomeric 3*H*-pyrazoles (if $R^1$ = $C_6H_5$ and $R^2$ = $CH_3$, $C_6H_5$, *p*-$CH_3C_6H_4$, *p*-$ClC_6H_4$, or *p*-$NO_2C_6H_4$) or the cycloaddition takes place regiospecifically with the exclusive formation of the cyclic adduct (L) (if $R^1$ = H or $CH_3$ and $R^2$ = $CH_3$, $C_6H_5$, *p*-$ClC_6H_4$, *p*-$FC_6H_4$, or *p*-$CH_3C_6H_4$ [164]). The phosphimine bond remains unreactive:



(L)

Regitz and co-workers[166,167] investigated the reactions involving the 1,3-dipolar cycloaddition of diazo-compounds to phosphorylated cyclopropenylphosphonates and cyclopropenylphosphine oxides. It was shown that the reactions proceed regiospecifically with formation of homopyrazolylphosphonates (LI), the cyclic adduct formed isomerising on heating either to allylphosphoryldiazomethane (LII) or to 3-phosphorylated 1,4-dihydropyridazine (LIII) in the presence of a strong base as the catalyst:



(LI)

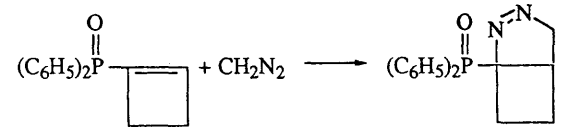
(LII) (LIII)

R = R' = H, $CH_3$, $C_6H_5$; R = H, R' = $C(O)OC_2H_5$, $C_6H_5$;

R + R' = ; $R^2$ = $R^3$ = $CH_3O$, $C_6H_5$;

$R^4$ = H, $CH_3$, $C_6H_5$, $P(O)(C_6H_5)_2$; $R^5$ = H, $CH_3$, $C_6H_5$;
$R^6$ = $CH_3$, $C(CH_3)_3$.

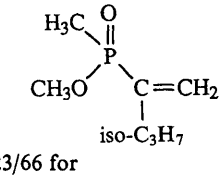
1-Cyclobutenyldiphenylphosphine oxide reacts with diazomethane to form $\Delta^1$-pyrazolinylphosphine oxide:[168]



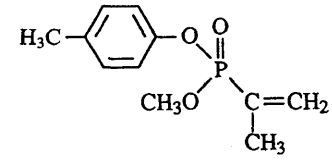
The 1,3-dipolar cycloaddition mechanism is a single-stage many-centre process with cyclic electron transfer as was confirmed in a study of the kinetics of the cycloaddition of diazoacetic ester to allenylphosphonates and allenylphosphine oxides[169] and of diphenyldiazomethane to vinylphosphonates and vinylphosphine oxides.[170,171]

The mutual orientation of the 1,3-dipole and of the dipolarophile in the transition state constitutes an important condition for reactions involving the 1,3-dipolar cycloaddition of diazoalkanes to phosphorus-containing dipolarophiles with a chiral phosphorus atom, which proceeds via a many-centre synchronous mechanism. The stereochemistry of such reactions has been investigated in relation to vinylphosphonates and vinylphosphinates and their α,β-substituted derivatives,[172–176] as well as allenyl- and ethynylphosphonates.[177]

It was shown that the stereospecificity of the reactions, determined by the diastereoisomeric composition of the isomers of 3-phosphorylated $\Delta^1$-pyrazolines (the *threo*/*erythro* percentage ratio) depends both on the immediate steric environment of the chiral centre and on the effective volume of the substituents at the double bond. The approach of the diazoalkane molecule from the less hindered side determines the preferential formation of the *threo*-diastereoisomer, while its approach from the opposite side gives rise to the preferential formation of the *erythro*-diastereoisomer. For example, the ratio of the *threo*- and *erythro*-diastereoisomers varies from 90/10 for

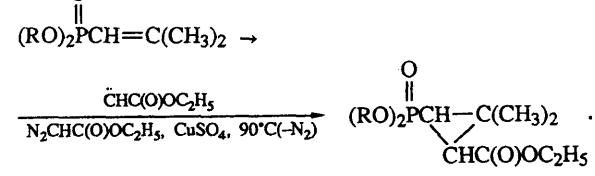


to 23/66 for



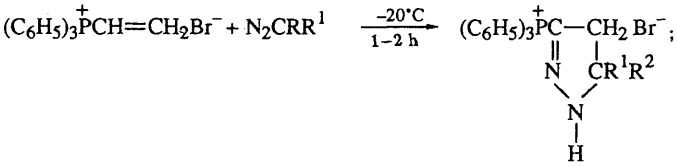
Ref. 172.

The reactions involving the cycloaddition of alkoxycarbonylcarbenes to vinyl- and allyl-phosphonic and vinylphosphoric esters proceed via the carbene mechanism with formation of cyclopropane derivatives. The direct dependence of the reactivity on the nucleophilicity of the double bond has been established:[148,151,178,179,180]



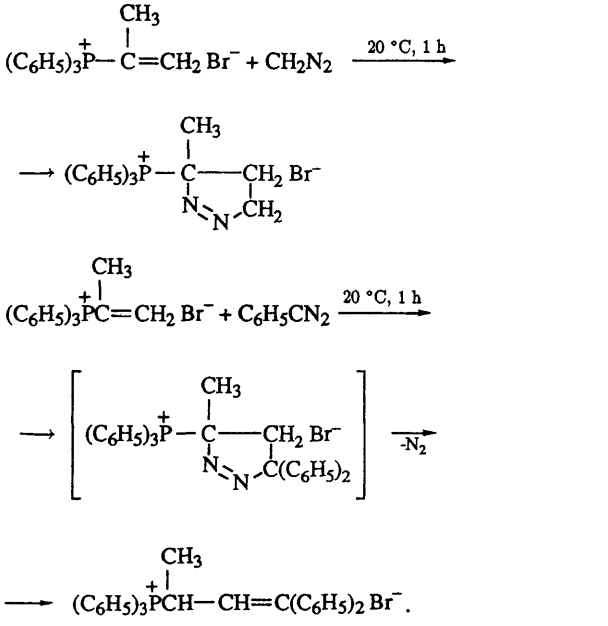
The reactions of phosphonium salts containing multiple bonds with diazo-compounds also involve 1,3-dipolar cycloaddition. It has been shown[5,168,181–183] that the final result of the reaction depends on the structure of the phosphonium salt and the diazo-compound.

Triphenylvinylphosphonium bromide gives rise to triphenyl-3-$\Delta^2$-pyrazolinylphosphonium bromide:[181,182]



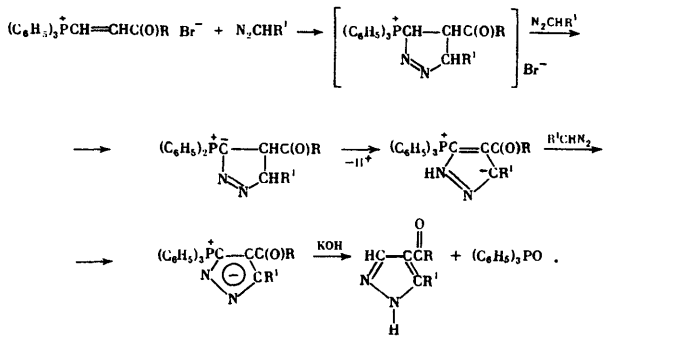
$R = R^1 = H,\ CH_3,\ C_6H_5;\ R = H,\ R^1 = CH_3,\ C_6H_5.$

Isopropenyltriphenylphosphonium bromide reacts with diazomethane to form triphenyl-5-$\Delta^1$-pyrazolinylphosphonium bromide, while in the reaction with diphenyldiazomethane under the same conditions the analogous reaction products proved to be unstable, substituted allyltriphenylphosphonium bromide being formed after the evolution of nitrogen:[182]

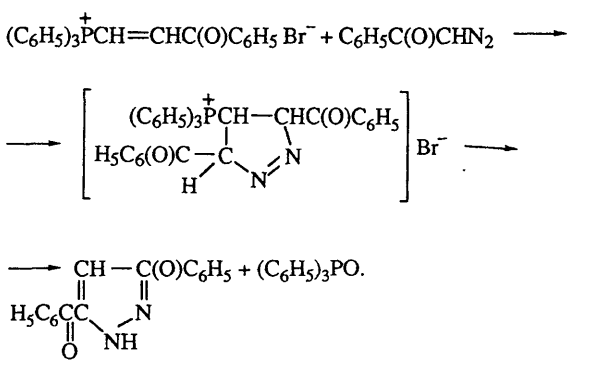


It is of interest that β-substituted triphenylvinylphosphonium and allyltriphenylphosphonium bromides do not react with diazoalkanes.[182] On the other hand, the introduction of an acyl group into the triphenylvinylphosphonium bromide alters its reactivity.

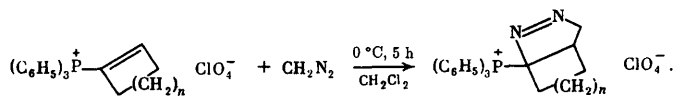
Although the cycloaddition of diazomethane and diazoacetic ester to β-acylvinyltriphenylphosphonium bromide does in fact proceed via the stage involving the formation of the intermediate triphenyl-5-$\Delta^1$-pyrazolinylphosphonium salt, the reaction product isolated was the phosphorus-containing ylide (LIV), which is converted into 4-acylpyrazole on alkaline hydrolysis:[183]



After the reaction of β-acylvinyltriphenylphosphonium bromide with diazoacetophenone, 3,5-diacylpyrazole was isolated:[183]



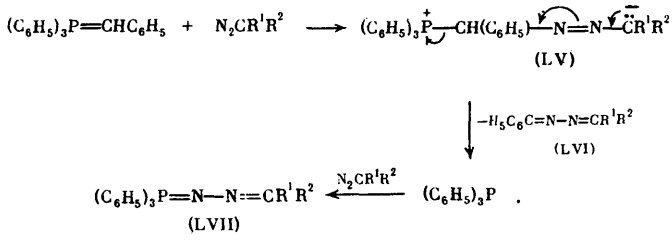
The 1,3-dipolar cycloaddition of diazomethane to 1-cycloalkenylphosphonium salts takes place with formation of bicyclic adducts:[168]



## 2. Phosphorus-containing ylids in reactions with diazo-compounds and carbenes

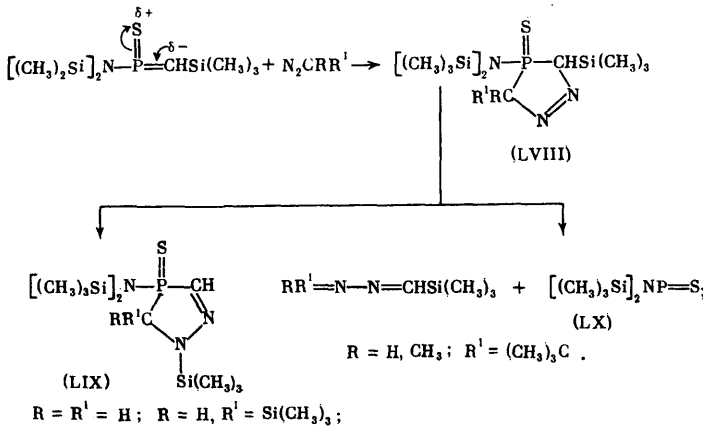
Phosphorus-containing ylids react unambiguously with diazo-compounds depending on the structure of the ylid and the reaction conditions. It has been shown[185,185] that the reaction of benzylidenetriphenylphosphorane with diazoacetophenone and phenyldiazomethane proceeds readily at room temperature with formation of a mixture of the azine (LVI) and triphenylphosphazine (LVII). It is assumed that the reaction proceeds via the intermediate formation of the betaine (LV), its decomposition to the

azine (LVI) and triphenylphosphine, and subsequent interaction of triphenylphosphine with the diazo-compound:

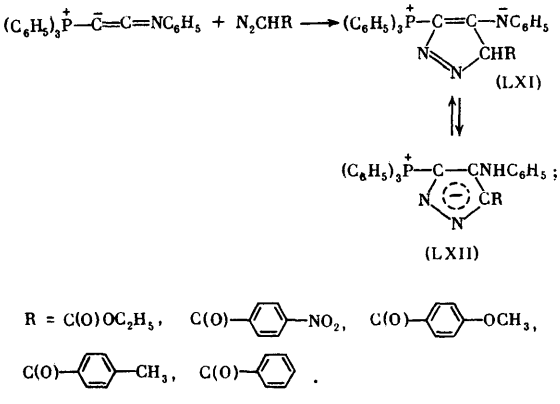


A much more complex reaction occurs between benzoylmethylenetriphenylphosphorane and diazoacetophenone; it leads to 4-benzylidene-2,6-diphenylpyran.[186,187]

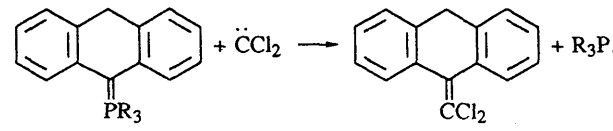
Silylated aminothionophosphorane reacts differently with diazoalkanes. The 1,3-dipolar cycloaddition to the P=C double bond lead to the formation of 3-trimethylsilysl-$\Delta^1$-diazophospholene (LVIII), which either isomerises to 1-trimethylsilyl-$\Delta^2$-diazaphospholene (LIX) as a result of the migration of the trimethylsilyl group or it decomposes to an azine and bis(trimethylsilyl)aminothionophosphorane (LX):[188]



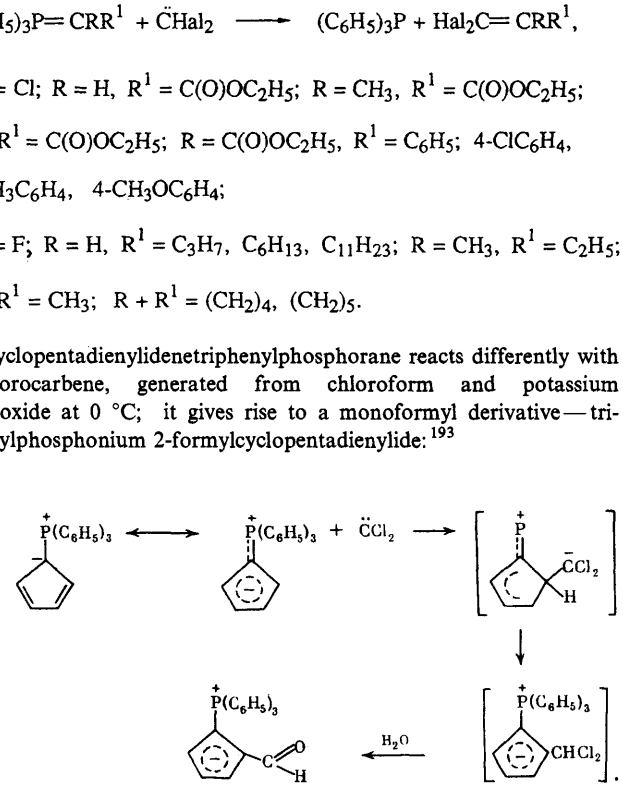
The reaction of *N*-phenylaminoketenylidenetriphenylphosphorane with diazocarbonyl compounds proceeds as 1,3-dipolar cycloaddition with formation of a phosphorylated pyrazoline derivative (LXI), which is involved in a tautomeric equilibrium with the phosphorylated imidopyrazole (LXII):[189]



The interaction of phosphorus-containing ylids with dihalocarbenes proceeds in most cases with formation of the corresponding olefins and phosphines and is believed to occur as a result of the electrophilic attack by the dihalocarbene on the negatively charged carbon atom of the phosphorus ylid.[190–192] The reactions of fluorenylidenetriphenyl(butyl)phosphorane and phosphorus-containing ylids having different electron-accepting groups proceed via the same mechanism:[190–192]



$R = C_6H_5$, $C_4H_9$;



Cyclopentadienylidenetriphenylphosphorane reacts differently with dichlorocarbene, generated from chloroform and potassium t-butoxide at 0 °C; it gives rise to a monoformyl derivative — triphenylphosphonium 2-formylcyclopentadienylide:[193]

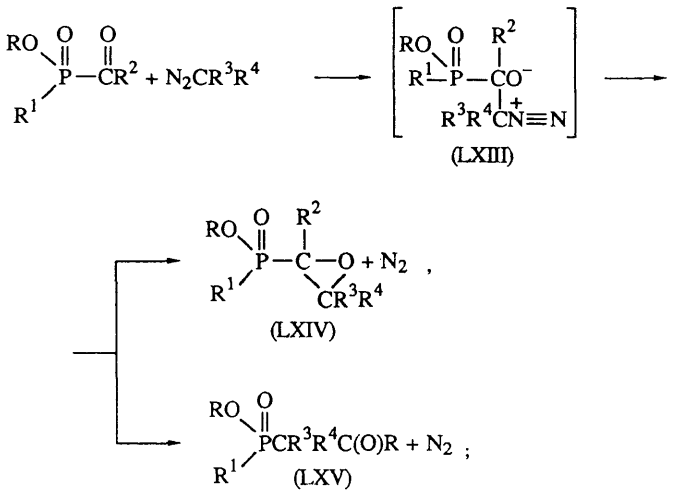


## 3. Reactions of diazoalkanes with ketophosphoryl compounds and phosphoryl isothiocyanates

The available literature data on the reactivities of organophosphorus compounds containing a carbonyl group with aliphatic diazo-compounds are restricted mainly to those obtained in the studies by Pudovik and co-workers.[194,197–199,202–204] Since the results of these studies have been described in detail in a review[6] and in a review report,[200] we shall confine ourselves to their brief consideration only.

The authors showed that, depending on the nature of the substituent at the carbonyl group and of the diazo-compound, the interaction of α-ketophosphonates and α-ketophosphinates with diazo-compounds proceeds with formation of either phosphorylated

oxiran derivatives (LXIV) or β-ketophosphonates and β-ketophosphinates—the products of insertion in the P—C bond of the initial organophosphorus compound (LXV):[194–200]

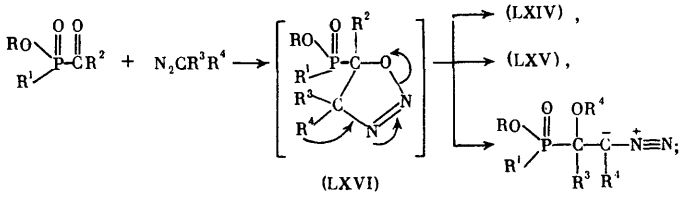


R = Alk; $R^1$ = AlkO, Alk, $C_6H_5$; $R^2$ = $CH_3$, $C_6H_5$, X = $C_6H_4$;

$R^3$ = $R^4$ = H, $C_6H_5$; $R^3$ = H, $R^4$ = $CH_3$.

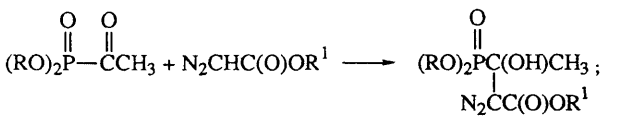
The formation of the reaction products (LXIV) and (LXV) is explained, in conformity with the generally accepted mechanism of the reactions of diazoalkanes with carbonyl compounds,[201] by the stabilisation of the intermediate dipolar ion (LXIII).

However, Pudovik et al.[194] do not exclude also the 1,3-dipolar cycloaddition mechanism with formation of the intermediate 1,2,3-oxadiazoline derivative (LXVI), which, depending on the substitution at the C(4) ring atom, either decomposes with evolution of nitrogen and the formation of the products (LXIV) and (LXV) or isomerises with formation of the phosphorus-containing diazo-compound (LXVII):



R = Alk; $R^1$ = AlkO, Alk, $C_6H_5$;
$R^2$ = $CH_3$, $C_6H_5$, X-$C_6H_4$;
$R^3$ = $R^4$ = H, $C_6H_5$; $R^3$ = H, $R^4$ = $CH_3$.

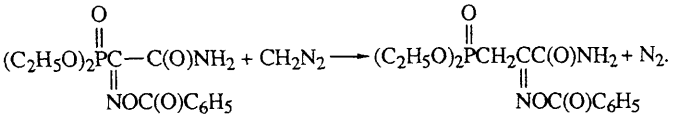
It is of interest that an adduct, similar to compound (LXVII), was obtained by the reaction of diazoacetic esters with acetylphosphonates:



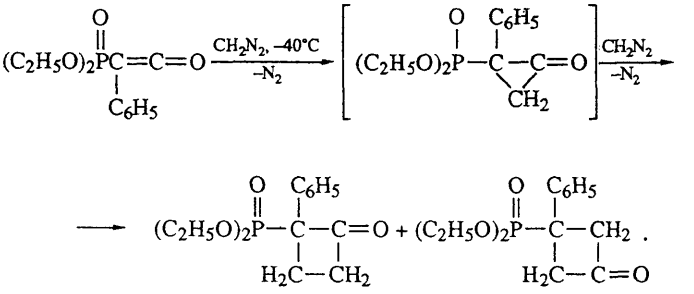
R = $R^1$ = $CH_3$, $C_2H_5$.

Neither the product with the oxiran structure (LXIV) nor the product (LXV) of insertion in the P—C bond were detected in the reaction mixture.[202–204]

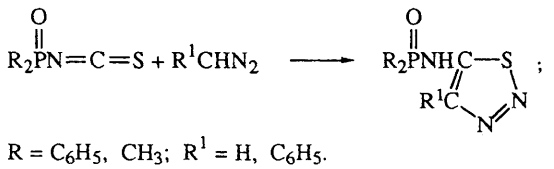
Similarly to the reaction with α-ketophosphoryl compounds, the reaction of acyloxyiminoalkylphosphonate with diazomethane leads to the product of the insertion of the methylene group in the P—C bond:[205]



The interaction of diethylphosphonophenylketene, which is an extremely reactive compound, with an excess of diazomethane involves not the carbonyl group but the C=C double bond and proceeds via the formation of the reactive phosphorylated cyclopropanone and leads to a mixture of isomeric phosphorylated cyclobutanes:[206]



One study is described in the literature,[207] where it was shown that phosphorylated isothiocyanates enter into reactions involving the 1,3-dipolar cycloaddition of diazomethane and phenyldiazomethane with formation of the corresponding 5-phosphinamido-1,2,3-thiadiazoles:



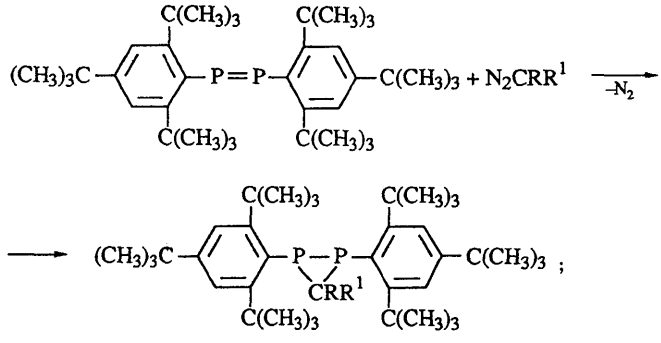
R = $C_6H_5$, $CH_3$; $R^1$ = H, $C_6H_5$.

## V. Derivatives of di- and mono-coordinate phosphorus in reactions with diazo-compounds and carbenes

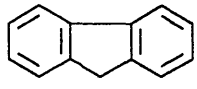
### 1. Reactions of diazo-compounds and carbenes with acyclic derivatives of dicoordinate and monocoordinate phosphorus

Acyclic derivatives of dicoordinate phosphorus containing the —P=P—, —P=C—, and —P=N— bonds have been investigated in reactions with diazo-compounds and carbenes.

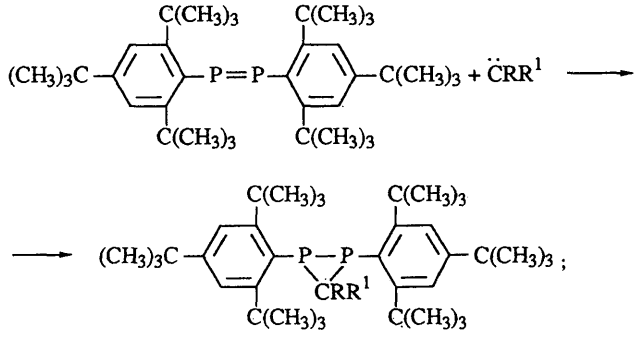
The stable diphosphirans (LXVIII) have been obtained by cyclising a diphosphene, a derivative of dicoordinate phosphorus, with diazomethane at 0 °C [208] and with diphenyldiazomethane and diazofluorene on heating and UV irradiation:[209]



(LXVIII)

$R = R^1 = H,\ C_6H_5;\ R + R^1 =$ 

The hypothesis of the carbene mechanism of the formation of compound (LXVIII) under the conditions involving the generation of diphenyl- and fluorenylidene-carbenes (UV irradiation) was confirmed by the fact that the diphosphirans (LXIX) are formed from the diphosphene and dichloro-, dibromo-, and phenylbromocarbenes:[209]

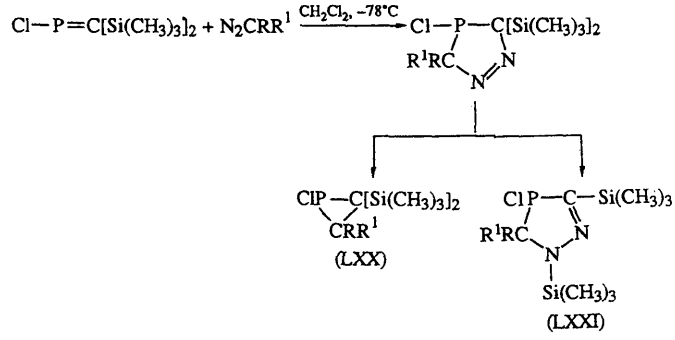


(LXIX)

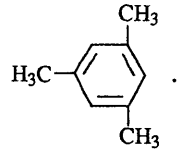
$R = R^1 = Cl,\ Br;\ R = Br,\ R^1 = C_6H_5.$

The interaction of *P*-chlorophosphaalkenes with diazocompounds, except organometallic derivatives of diazomethane, proceeds as 1,3-dipolar cycloaddition to the P=C double bond of the *P*-chlorophosphaalkene.[210–212] It was shown that the nature of the reaction product formed depends on the structure of the diazocompound and the *P*-chlorophosphaalkene.

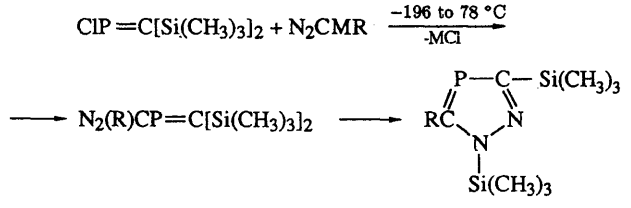
Thus the reaction of 1-chloro-2-bis(trimethylsilyl)-1-phosphaalkenes with both mono- and di-substituted derivatives of diazomethane occurs even at a very low temperature with formation of unstable 3*H*-1,2,4-diazaphospholenes at room temperature, which either decompose with elimination of nitrogen and the formation of 1-chlorophosphirans (LXX) or are converted into 4,5-dihydro-1,2,4-diazaphospholenes (LXXI) as a result of the migration of the trimethylsilyl group:[212]



$R = H,\ CH_3;\ R^1 = t\text{-}C_4H_9;\ R = H,\ R^1 = Si(CH_3)_3.$

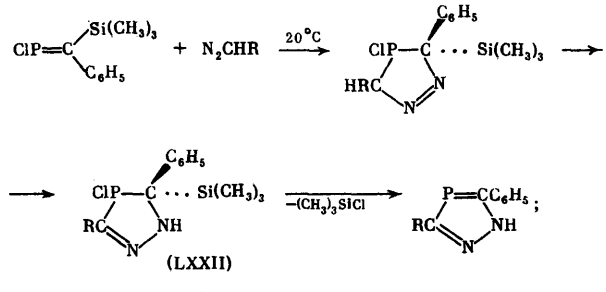


Organometallic derivatives of diazomethane react quite differently. The reaction proceeds with retention of the P=C bond of the initial 1-chloro-2-bis(trimethylsilyl)-1-phosphaalkene and the formation of phosphavinyldiazoalkane which cyclises to 1,2,4-diazaphosphole on subsequent heating:[213]



M = Li, $HgC(N_2)OC(O)C(CH_3)_3$; R = $Si(CH_3)_3$, 2, 4, 6-$(CH_3)_3C_6H_2$, $CH_3C(O)O$.

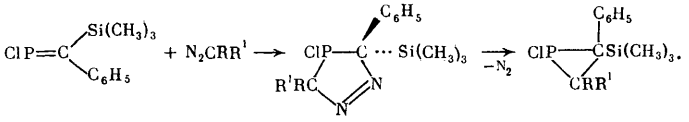
Monosubstituted derivatives of diazomethane react with 1-chloro-2-phenyl-2-trimethylsilyl-1-phosphaalkene at room temperature to form 1*H*-1,2,4-diazaphospholes via the intermediate cyclic adduct (LXXII) and subsequent elimination of chlorotrimethylsilane:[210]



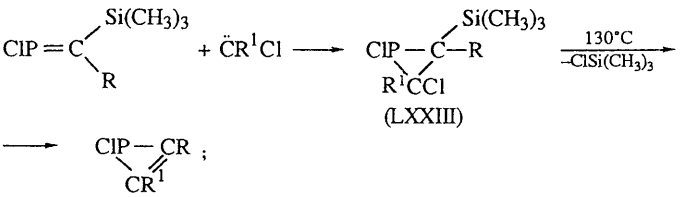
(LXXII)

R = H, $C_6H_5$, $C(O)OC_2H_5$, $C(O)C_6H_5$.

However, the reaction with disubstituted derivatives of diazomethane proceeds with the exclusive formation of 1-chlorophosphirans:[211]

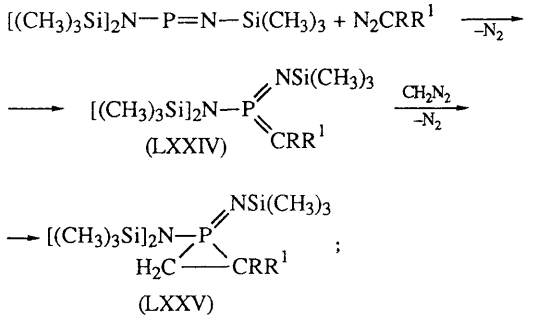


The reaction of *P*-chlorophosphaalkenes with chloro(phenyl)- and chloro(phenoxy)-carbenes has been described recently.[214] The analogous 1-chlorophosphirans (LXXIII) were obtained, their thermal decomposition resulting in the elimination of chlorotrimethylsilane and the formation of 1-chloro-1*H*-phosphirenes:



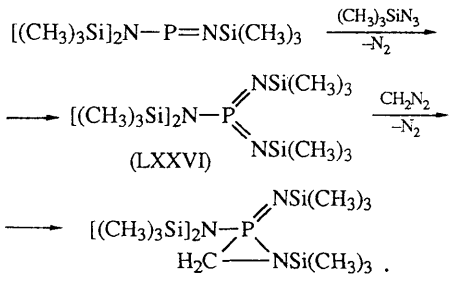
R = $C_6H_5$, $Si(CH_3)_3$; $R^1$ = $C_6H_5$, $C_6H_5O$.

In contrast to *P*-chlorophosphaalkenes, silylated amino-iminophosphanes react with diazo-compounds not via the 1,3-dipolar cycloaddition mechanism but with retention of the P=N bond and the formation of stable diylide structures. Thus the interaction of bis(trimethylsilyl)aminotrimethylsilyliminophosphane with diazoalkanes leads to the formation of bis(trimethylsilyl)aminotrimethylsilyliminophosphoranes (LXXIV), the subsequent reaction of which with diazomethane, proceeding as 1,2-cycloaddition, results in the formation of bis(trimethylsilyl)trimethylsilylimino-$\lambda^5$-phosphirans (LXXV):[215–217]

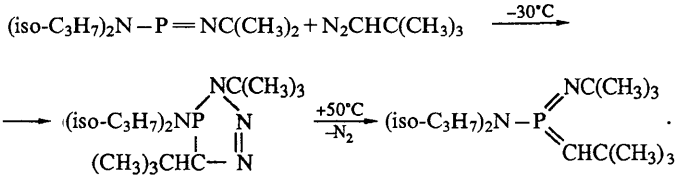


R = $CH_3$, H; $R^1$ = $CH_3$, $C_2H_5$, $CH(CH_3)_2$, $C(CH_3)_3$.

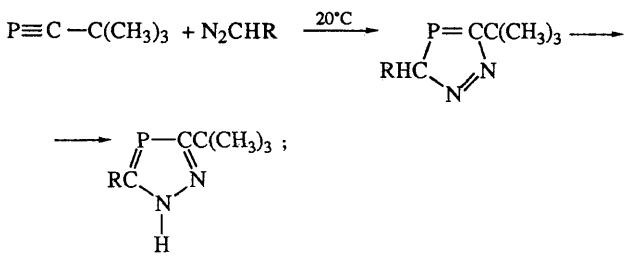
The 1,2-cycloaddition of diazomethane to one of the P=N bonds of aminodiiminophosphorane (LXXVI) leads to the formation of 1,2-$\lambda^5$-azaphosphoridine:[215]



An aminoiminophosphorane is also formed on interaction of t-butyliminodiisopropylaminophosphane with t-butyldiazopropane. It is suggested that the reaction proceeds as 1,3-dipolar cycloaddition to the P=N bond with formation of cyclic adducts and subsequent elimination of nitrogen on raising the temperature:[218]



The interaction of diazo-compounds with derivatives of monocoordinate phosphorus has been reported.[219] 1,3-Dipolar cycloaddition to a phosphaalkyne results in the formation of 1*H*-1,2,4-diazaphospholes:



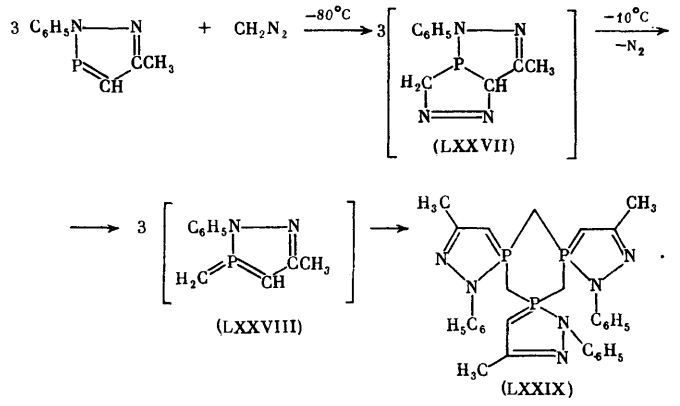
R = H, $CH_3$, t-$C_4H_9$, $C(O)C_6H_5$, $C(O)OCH_3$.

## 2. Reactions of diazo-compounds and carbenes with cyclic derivatives of dicoordinate phosphorus

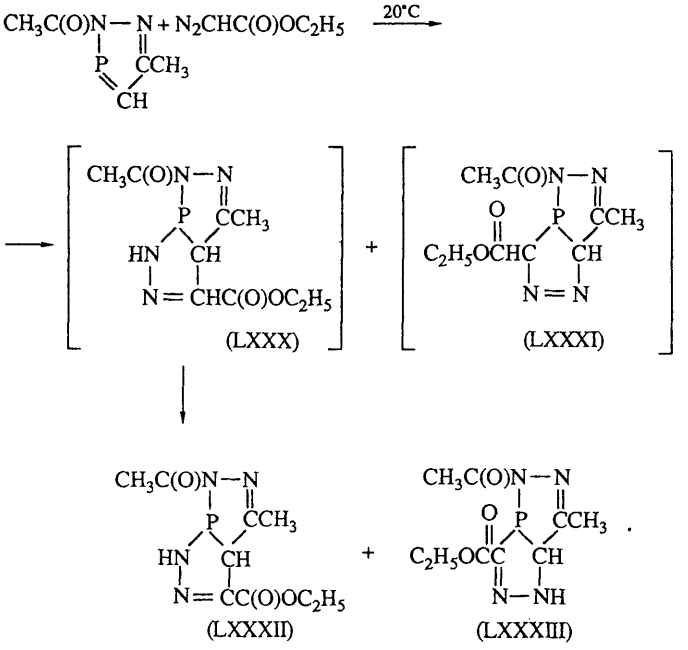
The reactions of five-membered cyclic derivatives of dicoordinate phosphorus with diazo-compounds have been investigated by Arbuzov and co-workers in relation to substituted 1,2,3-diazaphospholes. It was shown that the final reaction product depends to a considerable extent on the structures of both initial reactants and on the experimental conditions.[220–241]

Thus diazomethane readily reacts at room temperature with 5-methyl-2-phenyldiazaphosphole with evolution of nitrogen and the formation of an adduct having the structure of the trimer (LXXIX).[220]

It was later established[221] that this reaction proceeds via the formation of the unstable cyclic [2 + 3]adduct (LXXVII), having the pyrazoline structure, with subsequent elimination of nitrogen, the formation of the reactive phosphorus diylid (LXXVIII), and its subsequent trimerisation:

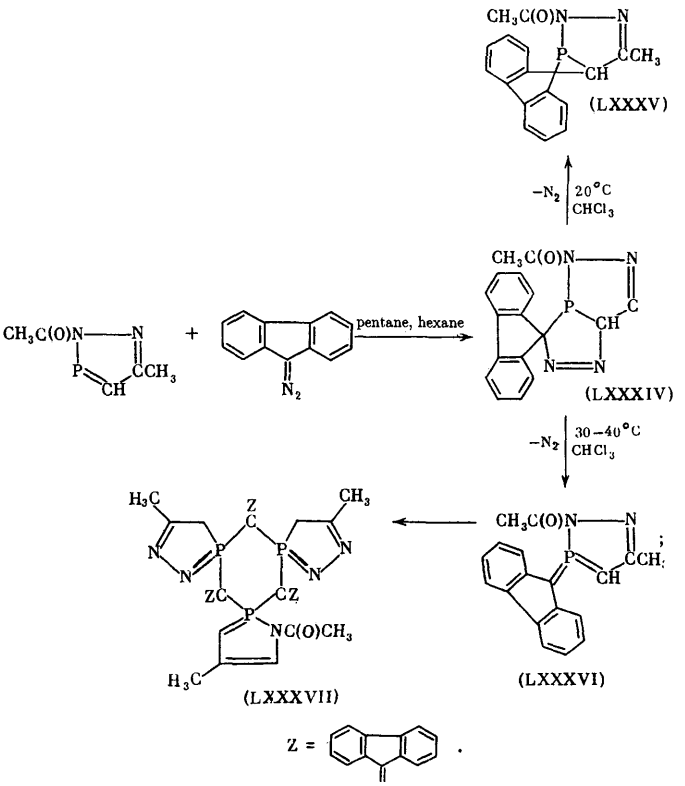


In contrast to the reaction with diazomethane, the reaction of 2-acetyl-5-methyl-1,2,3-diazaphosphole with diazoacetic ester proceeds via the 1,3-dipolar cycloaddition mechanism without the evolution of nitrogen, a mixture of compounds (LXXX) and (LXXXI) being formed, regardless of the nature of the solvent, and isomerising to the $\Delta^2$-phosphapyrazoline derivatives (LXXXII) and (LXXXIII) respectively:[222]



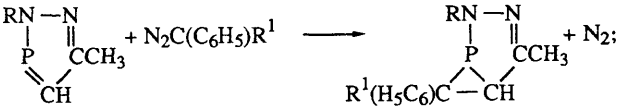
2-Acetyl-5-methyl-1,2,3-diazaphosphole reacts differently with diazoacetone depending on the experimental temperature.[221] At room temperature, the reaction proceeds with evolution of nitrogen and the formation of a trimer, whose structure is similar to that of compound (LXXIX). At 10 °C, the reaction takes place without the evolution of nitrogen and, as in the reaction with diazoacetic ester, a mixture of isomeric derivatives of $\Delta^2$-phosphapyrazoline is formed.

The reactions of 2-acetyl-5-methyldiazaphosphole with 9-diazofluorene, proceeding via the 1,3-dipolar cycloaddition mechanism, proved to be of interest.[220,223] Thus at room temperature in pentane and hexane, the product is the $\Delta^1$-phosphapyrazoline derivative (LXXXIV), which is converted in chloroform at room temperature into the bicyclic phosphiran (LXXXV), while at 30–40 °C it is converted into the trimer of the diazaphosphole ylid (LXXXVII) via a stage involving the formation of the diylid structure (LXXXVI):



The trimer (LXXXVII) is formed without the isolation of the bicyclic compound (LXXXIV) when the reaction is carried out in benzene, methylene chloride, and carbon tetrachloride. In diethyl ether, the reaction proceeds with formation of a mixture of the products (LXXXIV) and (LXXXVII).[220]

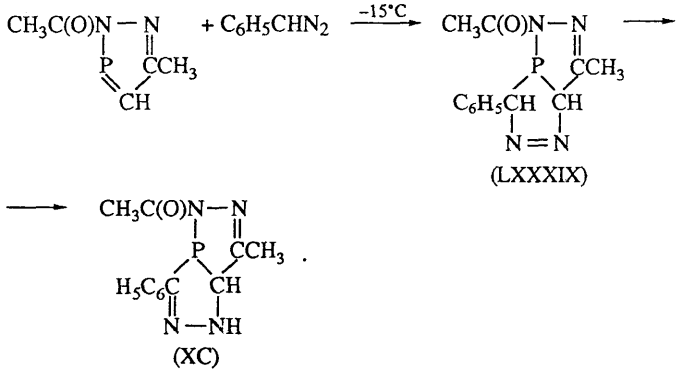
The possibility of cycloaddition to the P=C bond involving a dicoordinate phosphorus atom with formation of stable bicyclic phosphirans (LXXXVIII) was first demonstrated in relation to the reactions of *N*-substituted diazaphospholes with diphenyldiazomethane in different solvents[224–227] and later with methylphenyldiazomethane.[228] The structure of the bicyclic phosphirans was established by X-ray diffraction.[229–232]



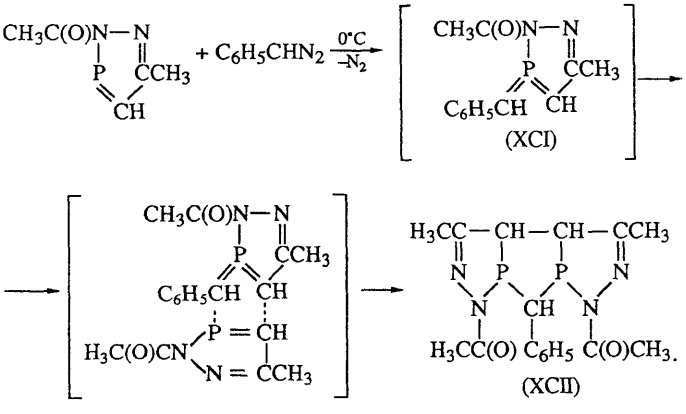
R = $C_6H_5$, $CH_3C(O)$; $R^1$ = $C_6H_5$, $CH_3$.

In the study of the mechanism of the reaction of 5-methyl-2-phenyl(acetyl)diazaphospholes with diphenyldiazomethane, it was shown that the reaction is of the non-carbene type and proceeds via the 1,3-dipolar cycloaddition mechanism.[233]

In contrast to diphenyldiazomethane, phenyldiazomethane does not give rise to a bicyclic phosphiran in its reaction with 2-acetyl-5-methyl-1,2,3-diazaphosphole. In hexane at −15 °C, the reaction product is the $\Delta^1$-phosphapyrazoline derivative (LXXXIX), which isomerises to the $\Delta^2$-phosphapyrazoline derivative (XC):[234]

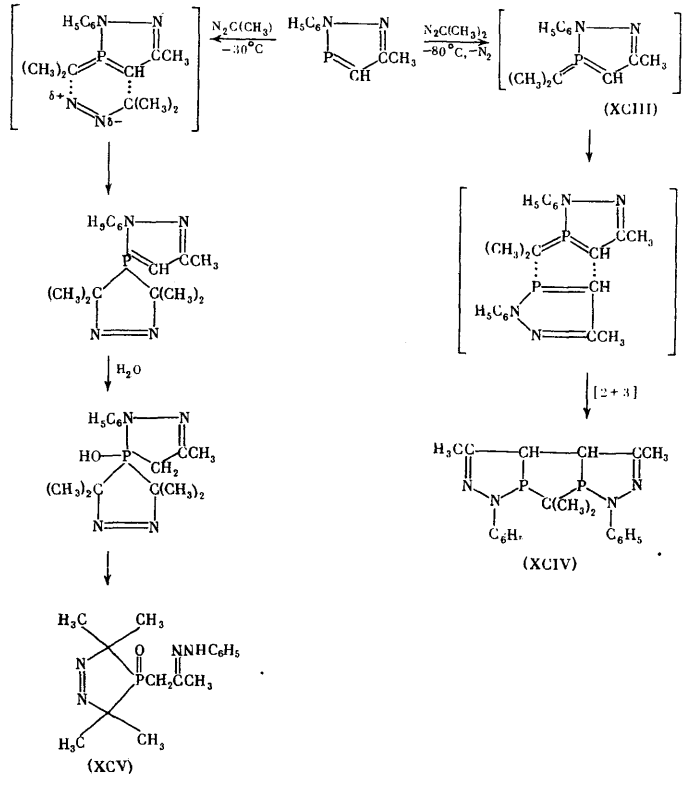



When the temperature is raised to 0 °C and the reactants are added in the opposite order, nitrogen is evolved and the tricyclic compound (XCII) is formed. It is the product of the cyclic [2 + 3]addition of the intermediate diylid (XCI) to the initial diazaphosphole:[234]




The reaction of 5-methyl-2-phenyl-1,2,3-diazaphosphole with diazopropane proceeds, in contrast to the reaction with diphenyldiazomethane, in a much more complex manner with formation of products of different structure as the experimental conditions are varied.[235–239] As in the reaction with phenyldiazomethane, bicyclic phosphirans were not obtained in any of the experiments.

It was established by X-ray diffraction that the reaction of 5-methyl-2-phenyl-1,2,3-diazaphosphole with diazopropane, which proceeds with evolution of nitrogen on intensive cooling, results in the formation of the diphosphorus tricyclic compound (XCIV), whose structure is similar to that of compound (XCII).[235–238] Compound (XCIV) is evidently formed as a result of the 1,3-dipolar cycloaddition of the intermediate reactive phosphorus diylid (XCIII), which behaves as the dipole:

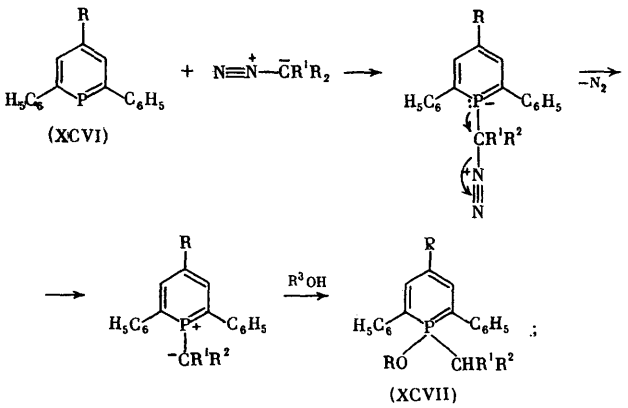



The reaction of 5-methyl-2-phenyl-1,2,3-diazaphosphole with an excess of diazopropane at −30 °C takes place differently and leads to the formation of the phosphorylated phenylhydrazone derivative (XCV), evidently as a result of the 1,3-dipolar cycloaddition of the intermediate phosphorus diylid, acting as the dipolarophile, to the diazopropane molecule.[237]

5-Methyl-2-phenyl-1,2,3-diazaphosphole reacts with 1-diazo-2-methylpropane and 1-diazo-2,2-dimethylpropane to form only a tricyclic diphosphorus compound, whose structure is analogous to that of compound (XCIV).[240]

The reaction of diazo-compounds and carbenes with a six-membered cyclic derivative of dicoordinate phosphorus, such as the trisubstituted phosphabenzene (XCVI), have also been investigated.[242–244] Thus treatment of 2,4,6-trisubstituted $\lambda^3$-phosphorins with alcoholic or phenolic solutions of diazo-compounds afforded 39 different derivatives of the $\lambda^5$-phosphorins (XCVII).[242,243] It is assumed that compounds (XCVII) are formed as a result of the nucleophilic attack by the diazo-compound on the phosphorus atom of the phosphabenzene with subsequent elimination of nitrogen and

the formation of a dipolar ion, which then reacts with the alcohol or the phenol:

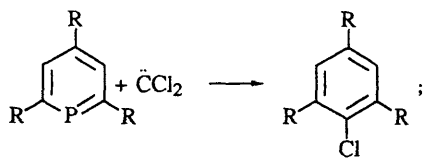


(XCVI) (XCVII)

R = $C_6H_5$, $C_6H_5CH_2$; $R^1 = R^2 = H$, $C_6H_5$; $R^1 = H$, $R^2 = C(O)OC_2H_5$;

$R^3 = CH_3$, $C_2H_5$, $CH(CH_3)_2$, $C_6H_5$, $C_6H_5CH_2$, $CH_2{=}CH{=}CH_2$, $CH_2CH_2Cl$, $CH_2CCl_3$.

The reactions of trisubstituted phosphabenzenes — 2,4,6-triphenyl- and 2,4,6-tributyl-phosphabenzenes — with dichlorocarbene, generated by the thermolysis of $Cl_3CC(O)ONa$ and $C_6H_5HgCCl_2Br$ or obtained from $CH_2Cl_2$ and $CHCl_3$ in the presence of t-$C_4H_9OK$, proceed in an unusual way. They result in the formation of trisubstituted benzenes:



R = $C_6H_5$, t-$C_4H_9$.

The reaction with chloro(phenyl)carbene, generated from dichloro(phenyl)methane and potassium t-butoxide, takes place similarly. The reaction mechanism has been discussed.[244]

Thus the study of the reactivities of various phosphorus-containing systems in relation to diazo-compounds and carbenes has led to interesting possibilities both for the synthetic organic chemistry of phosphorus and for the development of theoretical ideas in the chemistry of organophosphorus compounds and carbenes.

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