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# Organophosphorus Compounds in 1,3-Dipolar Cycloaddition

N.G.Khusainova and A.N.Pudovik

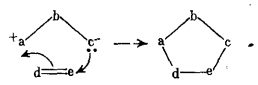
The cycloaddition of 1,3-dipoles to organophosphorus compounds containing a multiple bond is surveyed together with the reactions of phosphinylated 1,3-dipoles with various dipolarophiles, yielding five-membered heterocycles containing a phosphorus atom in either the ring or a side-chain. The Review covers also the "mixed dimerisation" of 1,3-dipoles with αβ-unsaturated compounds of tervalent phosphorus acting as 1,3-dipolar systems. A list of 146 references is included.

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## I. INTRODUCTION

1,3-Dipolar cycloaddition to unsaturated organophosphorus compounds forms an interesting and little studied branch of organophosphorus chemistry. The great structural variety both of 1,3-dipoles and of dipolarophiles makes this an important method for obtaining organophosphorus heterocycles that are difficult to prepare in other ways. Such addition can be defined as the interaction of a 1,3-dipole of general type $^{+}a-b-c^{-}$ with a multiple bond d=e accompanied by transfer of electrons within the cyclic transition state and by neutralisation of the formal charges[1]:



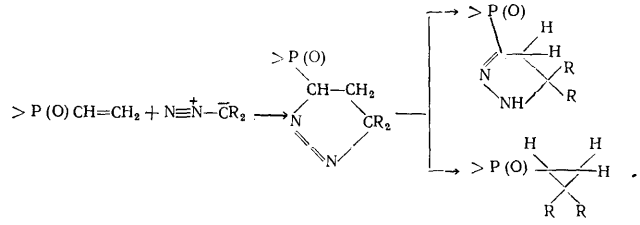
Despite the large number of investigations there is no generally accepted mechanism for 1,3-dipole cycloaddition. The majority of authors accept the single-stage mechanism first suggested by Huisgen[2,3], who regards such reactions as involving concerted but not necessarily simultaneous formation of two new σ bonds. This mechanism corresponds to a large negative entropy of activation and a moderate enthalpy of activation, a certain type of effect of substituents and solvent polarity, and *cis*-stereospecificity of addition[4,5]. Firestone[6-9] considers that a two-stage mechanism may also be possible, with intermediate formation of a diradical. A two-stage mechanism with an intermediate amphoteric compound has also been suggested[10]. In several papers the most important aspects of 1,3-dipolar cycloaddition, such as the effect of substituents, stereospecificity, regioselectivity, are discussed in terms of perturbation theory[11-14].

Considerable experimental information has now accumulated on 1,3-dipolar cycloaddition in the chemistry of organophosphorus compounds. The action of 1,3-dipoles on unsaturated compounds containing a four-coordinated phosphorus atom is a classical 3 + 2 → 5 cycloaddition. 1,3-Dipoles with phosphorus-containing substituents in a side-chain add to various dipolarophiles according to the same scheme. Reaction between αβ-unsaturated compounds containing tervalent phosphorus and 1,3-dipoles does not follow the usual scheme of 1,3-dipolar cycloaddition but a 3 + 3 → 6 scheme involving the phosphorus atom, with formation of six-membered heterocycles. This reaction can be regarded as mixed "dimerisation" of the 1,3-dipolar systems: under these conditions the phosphorus-containing component reacts similarly to other classical 1,3-dipoles. αβ-Unsaturated derivatives of three-coordinated phosphorus add to multiple bonds in various dipolarophiles according to a 3 + 2 → 5 scheme.

## II. 1,3-DIPOLAR CYCLOADDITION TO ORGANOPHOSPHORUS COMPOUNDS CONTAINING MULTIPLE BONDS

### 1. Phosphinylated Alkenes

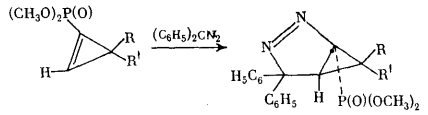
Results on the addition of diazomethane to vinyl- and allyl-phosphonic esters were first published by Pudovik and his coworkers in 1964.[15] The cycloaddition of diazomethane[15-19], diphenyldiazomethane[20-25], phenyldiazomethane[26], diazopropane[26], diazoacetic ester[27,28], and 9-diazofluorene[29] to such phosphonic esters involves intermediate formation of $\Delta^1$-pyrazolines, which either eliminate nitrogen and pass into cyclopropane derivatives or isomerise into thermodynamically stable $\Delta^2$-pyrazolines depending on the experimental conditions:



In contrast to other diazoalkanes, diazoacetic ester gives with vinylphosphonates mixtures of isomeric $\Delta^2$-pyrazolines differing in the positions of the phosphinyl and alkoxycarbonyl groups in the ring[27]. At higher temperatures the reactions of diazoalkanes with vinyl- and allylphosphonates yield cyclopropane derivatives.

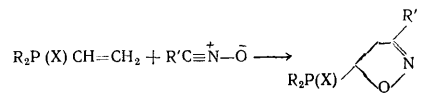
The kinetics of the cycloaddition of diphenyldiazomethane to vinylphosphonates and vinylphosphine oxides is consistent with a single-stage multicentre process with

cyclic electron transfer [25]. The cycloaddition of diphenyldiazomethane at the strained double bond in phosphinylcyclopropenes leads to the formation of substituted diazabicyclo[3,1,0]hexenes [30]:



(*a*) R = R' = $CH_3$; (*b*) R = $CH_3$, R' = $C_6H_5$.

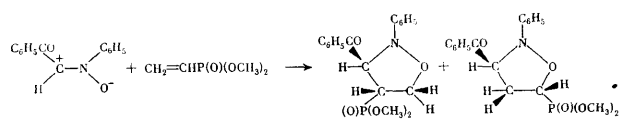
Nitrilimines, nitrile oxides, and nitrones also undergo 1,3-dipolar cycloaddition to vinylphosphonic esters and the tetramethyldiamide and to diphenylvinylphosphine oxide and sulphide [31]. Nitrilimines form 5-phosphinyl-$\Delta^2$-pyrazolines, whereas the *N*-oxides of aceto- and benzonitrile yield 5-phosphinyl-2-isoxazolines:



The rate of addition of diphenylnitrilimine to unsaturated organophosphorus compounds increases with the electrophilicity of the ethylenic double bond. Comparison of the relative addition rate constants indicates that in the case of benzonitrile *N*-oxide the sequence of dipolarophilic activity of unsaturated organophosphorus compounds does not coincide with their activity sequence on reaction with diphenylnitrilimine. This is attributed to differences in the way in which σ bonds are formed in the transition state in these reactions [32].

In the cycloaddition of benzaldehyde *N*-phenyloxime to dimethyl vinylphosphonate the phosphinyl group occupies position 4 in the isoxazolidine ring according to Arbuzov et al. [33], in contrast to Kolokol'tseva et al. [31] Stereochemical investigation has established the *trans*-configuration for substituents in the isoxazolidine rings formed on the addition of this nitrone to vinylphosphonic and β-cyanovinylphosphonic esters, as well as to methyl β-diethoxyphosphinylacrylate [33,34].

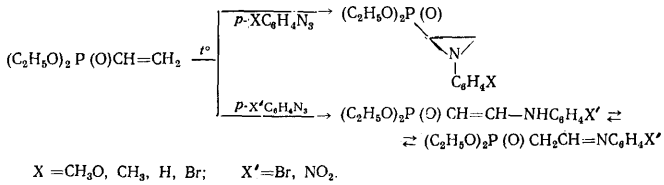
Phenylglyoxal *N*-phenylmonoxime adds to dimethyl vinylphosphonate at 20°C to form isomeric isoxazolidines corresponding to different orientations of dipole and dipolarophile [35]:



In boiling benzene only the first isomer is obtained. Cycloaddition of the nitrone to diethyl vinylphosphonate also yields only 4-diethoxyphosphinylisoxazolidine. Dimethyl allylphosphonate adds nitrones to form isoxazolodines containing a 5-phosphinyl group [35]. Potassium diethyl β-hydroxyvinylphosphonate reacts with toluene-*p*-sulphonyl azide to give a diazophosphonic ester and a potassium salt of formyltoluene-*p*-sulphonamide [36], with possible intermediate formation of a phosphorus-containing triazoline.

Aryl azides react with vinylphosphonates at room temperature [37,38] to form $\Delta^2$-triazolines containing a phosphinyl group at position 4. To prove the orientation of addition of the azide use was made of the ability of the triazoline ring to cleave into a linear diazo-derivative in the presence of a base. Cycloaddition of *p*-nitrophenyl azide to a β-diethylaminovinylphosphonate yields a 4-phosphinyl-1,2,3-triazole as a consequence of elimination of diethylamine from the triazoline formed initially [38].

When heated (75–80°C) aryl azides react with β-cyanovinyl-, propenyl-, and vinyl-phosphonates to form aziridines [37–39]. It is interesting that, when the azide contains donor substituents, cycloaddition leads only to phosphinylaziridines, but in the presence of acceptor substituents an enamine is also formed:



X = $CH_3O$, $CH_3$, H, Br; X' = Br, $NO_2$.

Differential thermal analysis with quantitative measurement of gas evolution has shown that thermal reactions between phenyl azide and vinylphosphonates involve intermediate formation of $\Delta^2$-triazolines, which under the experimental conditions break down with evolution of nitrogen and formation of aziridines.

Table 1. Rate constants ($10^3k_2$, $M^{-1}$ $min^{-1}$) for the reactions of azides *p*-$XC_6H_4N_3$ with vinylphosphonates $(C_2H_5O)_2$.PO.CH : CHY in xylene at 115°C.

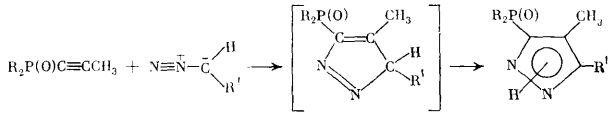
| X | Y = $PO(OC_2H_5)_2$ | | Y = H | | Y = N($C_2H_5$)$_2$ |
|---|---|---|---|---|---|
| | $10^3k_2$ | $10^3k_2$ | $E^{\neq}$, kcal mole$^{-1}$ | $\Delta S^{\neq}$, e.u. | $10^3k_2$ |
| $NO_2$ | 5.60 | 16.5 | 18.0 | −31.1 | 55.5 |
| Br | 6.80 | 13.7 | — | — | 6.08 |
| H | 6.55 | 12.6 | 17.2 | −33.5 | 1.40 |
| $CH_3$ | 7.65 | 12.1 | — | — | 0.93 |
| $CH_3O$ | 8.70 | 18.0 | 15.7 | −36.3 | 0.89 |

Kinetic investigation of the cycloaddition of aryl azides to phosphinylated ethylenes [38] has shown (Table 1) that the reactions of a diphosphinylethylene with azides are of the "dipolarophile–acceptor, 1,3-dipole–donor" type (reactions controlled by highest occupied orbital [13,14]), whereas the reactions of azides with a β-diethylaminovinylphosphonate are of the "dipolarophile–donor, 1,3-dipole-acceptor" type. Both donor and acceptor substituents accelerate the reaction of phenyl azides with diethyl vinylphosphonate. Donor–acceptor interaction of "neutral" type probably operates in this case (reactions controlled by highest occupied and lowest unoccupied orbitals). Reactivity of the aryl azide–vinylphosphonate system is determined mainly by intermolecular donor–acceptor interactions, which stabilise the transition state and depend on the donor–acceptor properties of the reactants.

## 2. Phosphinylated Alkynes

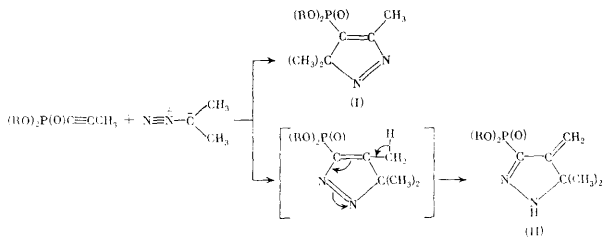
In 1963 Saunders and Simpson obtained an *N*-methylated phosphinylpyrazole by the action of diazomethane on di-isopropyl ethynylphosphonate [40]. A little later the cycloaddition of diazomethane to a diphosphinylacetylene to form a diphosphinylpyrazole was accomplished [41]. With

propynylphosphonates and propynylphosphine oxides diazoalkanes also form the corresponding 3(5)-phosphinylated pyrazoles[42,43]:



R = AlkO, Alk, Ar; R' = H, $CO_2C_2H_5$.

Formation of an intermediate phosphinylpyrazolenine in the 1,3-dipolar cycloaddition of diazoalkanes to phosphinylacetylenes is confirmed in the reactions of disubstituted diazo-compounds with a triple bond. The cycloaddition of 2-diazopropane to propynylphosphonates[44] yields a mixture of a 4-dialkoxyphosphinyl-3,5,5-trimethylpyrazolenine (I) and a 3-dialkoxyphosphinyl-5,5-dimethyl-4-methylene-$\Delta^2$-pyrazoline (II) (in the proportions 60 : 40):



The first stage produces a mixture of pyrazolenines differing in the position of the phosphinyl group in the ring. The 3-dialkoxyphosphinylpyrazolenine undergoes prototropic isomerisation into the phosphinyl-$\Delta^2$-pyrazoline. Prototropic isomerisation of a 4-phosphinylpyrazolenine is impossible.

Study of the cycloaddition of diazoacetic ester to propynylphosphonates and propynylphosphine oxides by differential thermal analysis enables[43] $P$-substituents to be ranged in the sequence

$$C_6H_5 \simeq C_2H_5 > C_2H_5O \sim C_3H_7O \sim C_4H_9O > Cl$$

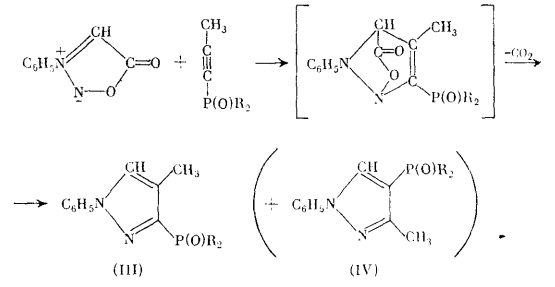
according to their effect in raising the temperature at which the exothermic effect begins. The dipolarophilic activity of the triple bond in the above compounds obviously increases in the same sequence, owing to the diminution in the electron-accepting properties of the phosphinyl group.

Table 2. Rate constants ($10^3k_2$, $M^{-1}$ $min^{-1}$ for the cycloaddition of azides $p$-$XC_6H_4N_3$ to diethyl ethynylphosphonates $(C_2H_5O)_2PO.C \vdots CY$ in $m$-xylene at 115 °C.

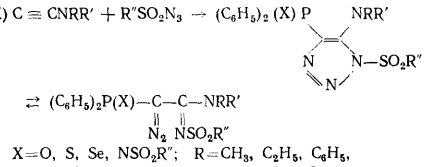
| Y | X=$NO_2$ | X-Br | X=H | | | X=$CH_3$ | X=$OCH_3$ |
|---|---|---|---|---|---|---|---|
| | $10^3k_2$ | $10^3k_2$ | $10^3k_2$ | $E^{\neq}$, kcal mole$^{-1}$ | $\Delta S^{\neq}$, e.u. | $10^3k_2$ | $10^3k_2$ |
| $(C_2H_5O)_2P(O)$ | 22.1 | 32.1 | 33.1 | 16.6 | −32.9 | 36.2 | 43.2 |
| Cl | 4.40 | 6.28 | 7.50 | 17.9 | −32.7 | 8.53 | 9.82 |
| $CH_3$ | 3.47 | 2.20 | 3.10 | 18.7 | −32.5 | 3.80 | 4.66 |
| $N(C_2H_5)_2$ | 2.11 | 44.0 | 15.4 | 16.8 | −34.2 | 11.6 | 8 56 |

Pyrazoles containing a phosphinyl group at the 3-position are formed by the addition of diazomethane to ethynyldiphenylphosphine and its oxide[45]. Methyl $\beta$-diphenylphosphinopropiolate forms with diazomethane a mixture of two isomeric pyrazoles corresponding to different orientations of the dipole relative to the dipolarophile[45].

The cycloaddition of $N$-phenylsydnone to propynylphosphonates, propynylphosphonothioates, and propynyldiphenylphosphine oxide[46] involves fixation of a dipole nitrogen atom mainly on the dipolarophile $\alpha$-carbon atom [proportions of isomers (III) : (IV) = 85 : 15]:



The addition of organic azides to phosphinylethynylamines yields triazoles contaminated with diazo-compounds[47], the quantity of which depends on the nature of the substituents:

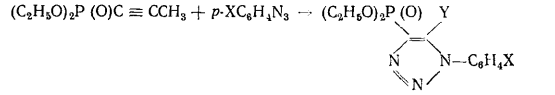


X=O, S, Se, $NSO_2R''$; R=$CH_3$, $C_2H_5$, $C_6H_5$, $p$-$CH_3C_6H_4$; R'=$C_2H_5$, $C_6H_5$; R''=$C_6H_5$, $p$-$CH_3C_6H_4$, $(CH_3)_3C_6H_2$, $p$-$NO_2C_6H_4$.

Thus, when the substituents R and R' have a high $-M$ effect, the tautomeric triazole form is absent.

The cycloaddition of aryl azides to propynylphosphonates and propynylphosphine oxides is regioselective and leads to the formation of triazoles having the phosphinyl group in the 4-position[48-51]. The structure of the adducts has been established by infrared spectroscopy, $^1H$ and $^1H-\{^{31}P\}$ nuclear magnetic resonance spectroscopy, and the nuclear Overhauser effect.

The reactivity of phosphinylacetylenes towards azides is increased both by donor and by acceptor substituents Y in the $\beta$ position of the dipolarophile[52,53] (Table 2):



X=$OCH_3$, $CH_3$, H, Br, $NO_2$; Y=$N(C_2H_5)_2$, $CH_3$,Cl,P (O) $(OC_2H_5)_2$.

The reactions of tetraethyl ethynylenediphosphonate and of diethyl chloroethynylphosphonate must be regarded as belonging to the "dipolarophile–acceptor, 1,3-dipole–donor" type, in which interaction between the highest occupied orbital of the dipole and the lowest unoccupied orbital of the dipolarophile predominates. Those of diethyl diethylaminoethynylphosphonate with azides are of the "dipole–acceptor, dipolarophile–donor" type. Kinetic study of the reactions of diethyl propynylphosphonate with aryl azides has shown that neither electron-donor nor electron-acceptor substituents in the azide accelerate the reaction significantly.

In a series of *para*-substituted phenyl azides the sensitivity of the reactivity to the activating influence of donor substituents in the phosphinylacetylenes diminishes and

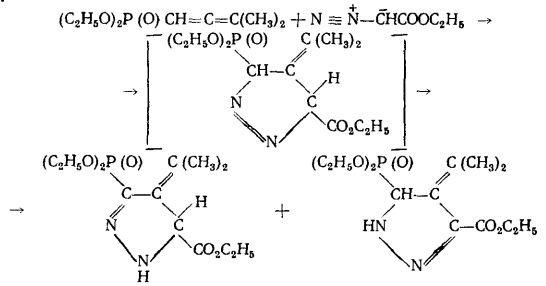
the sensitivity to acceptor substituents increases. This involves inversion from the "dipole–acceptor, dipolarophile–donor" type of reaction through the region of "neutral" cycloaddition to the "dipole–donor, dipolarophile–acceptor" type. Comparison of the logarithms of the rate constants for propynylphosphine oxides (measured at 115 °C) with the Kabachnik $\sigma^f$ constants has shown that the dipolarophilic activity of the triple bond intensifies as substituents attached to the phosphorus atom ($\rho = 0.24$, $r = 0.993$) become more electronegative. Propynylphosphonates do not conform to this correlation. The factors governing the reactivity of these dipolarophiles towards azides are evidently not described by specific phosphorus constants. The variation in the relative reactivity of these systems may be significantly influenced not only by changes in the donor–acceptor properties of the ligands but also by changes in their localisation energies.

These results taken together suggest that the reactivity of 1,3-dipoles and dipolarophiles is a consequence mainly of the highest occupied orbital–lowest unoccupied orbital model, and is consistent with a concerted reaction mechanism. The large negative entropies of activation, indicating a high degree of order in the transition state, and the moderate energies of activation agree with a single-stage multicentre mechanism. The observed slight dependence of rate of addition on solvent polarity is inconsistent with a two-stage mechanism involving an intermediate zwitterion. The weak sensitivity of the reactivity to interchange of substituents in the ligands is also evidence of the insignificant polarity of the transition state.

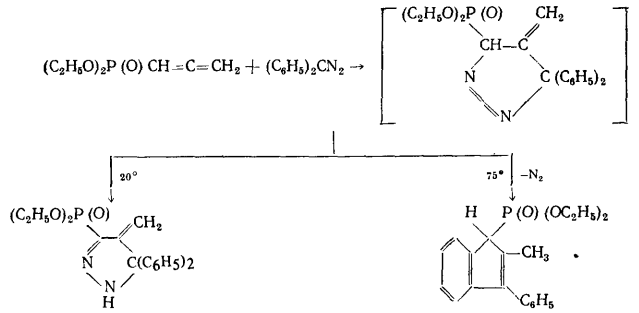
### 3. Phosphinylated Allenes

The cycloaddition of unsubstituted and monosubstituted diazoalkanes to phosphinylalenes yields phosphinylated pyrazoles [42]. The activating influence of the electron-accepting phosphinyl group is responsible for the dipolarophilic activity of the $\alpha\beta$-double bond of the allene system, and the carbon atom of the diazoalkane becomes attached to the $\beta$-carbon atom of the cumulene.

Kinetic investigation of the cycloaddition of diazoacetic ester to allenylphosphonates and allenylphosphine oxides has shown that the activation parameters are consistent with a single-stage simultaneous mechanism [55]. The dipolarophilic activity of the allene system increases with the electronegativity of the *P*-substituents, which suggests that the reactions are of the "dipole–donor, dipolarophile–acceptor" type. A 3-methylbuta-1,2-dienylphosphonate adds diazoacetic ester at the $\alpha\beta$-double bond with formation of an isomeric mixture of phosphinyl-$\Delta^2$-pyrazolines differing in the position of the phosphinyl group in the ring [43]:



Depending on the temperature the thermodynamically unstable $\Delta^1$-pyrazoline formed on the cycloaddition of diphenyldiazomethane to diethyl allenylphosphonate [54] may either isomerise into the $\Delta^2$-pyrazoline or decompose with the evolution of nitrogen and the formation of a phosphinylated indene:

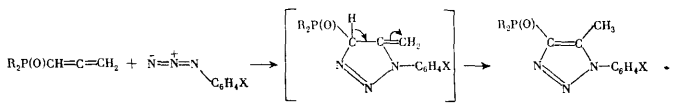


A 1-phenylpropa-1,2-dienylphosphonate with diphenyldiazomethane forms a methylenecyclopropane derivative. 2-Diazopropane reacts with allenylphosphonates at room temperature to give dialkyl 5,5-dimethyl-4-methylene-$\Delta^2$-pyrazol-3-ylphosphonates [44]. The cycloaddition of *N*-phenylsydnone to allenylphosphonates and allenylphosphine oxides [56,57] produces a mixture of isomeric pyrazoles having different orientations of the dipole with respect to the dipolarophile.

Table 3. Rate constants ($10^3 k_2$, $M^{-1}$ $min^{-1}$) for the reactions of aryl azides *p*-$XC_6H_4N_3$ with phosphinylated allenes $R_2PO.CH:C:CH_2$.

| R | X | | | | |
|---|---|---|---|---|---|
| | $NO_2$ | Br | H | $CH_3$ | $CH_3O$ |
| Cl | 1.25 | 5.88 | 9.30 | 15.1 | 19.9 |
| $C_2H_5O$ | 1.30 | 1.15 | 1.04 | 1.50 | 1.99 |
| $N(CH_3)_2$ | 113.4 | 16.0 | 6.03 | 4.00 | 3.30 |

The $\Delta^1$-triazolines having an exocyclic methylene group that are formed by the cycloaddition of aryl azides to phosphinylated cumulenes are very unstable, and are stabilised by prototropic isomerisation into triazoles [38]:

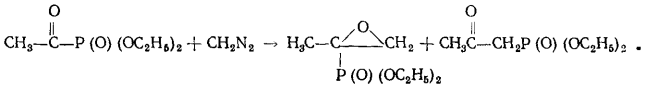


A kinetic study has been made [38] of the reactions of *para*-substituted aryl azides with phosphinylated allenes containing electron-accepting (chloro) and weakly and strongly electron-donor (ethoxy and dimethylamino) substituents attached to the phosphorus atom [38]. The reaction of allenylphosphonic dichloride is accelerated by donor and retarded by acceptor substituents in the aryl azide. Comparison of the logarithms of the reaction rate constants (Table 3) with the Hammett $\sigma$ constants reveals a good linear dependence ($\rho = -0.85$, $r = 0.996$); the reaction belongs to the "dipolarophile–acceptor, 1,3-dipole–donor" type. The action of aryl azides on allenylphosphonic bisdimethylamide must be regarded as the "dipolarophile–donor, dipole–acceptor" type. Donor–acceptor interaction of "neutral" type occurs in the reactions of diethyl allenylphosphonate with aryl azides, as in those of diethyl propynylphosphonate and vinylphosphonate. The reactivity

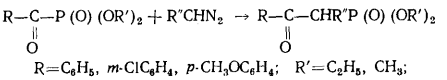
of the ligands is obviously determined by the electronic effects of the $P$-substituents, and the phosphorus atom iself participates in transmitting the effects of the substituents to the reactive centre [38].

## 4. $\alpha$-Oxo-phosphonates

In 1963 Arbuzov et al.[58] studied the reaction of diazomethane with diethyl acetylphosphonate, from which diethyl 2-methyloxiran-2-ylphosphonate and a small quantity of diethyl acetonylphosphonate were obtained:

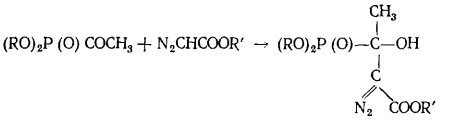


The action of diazomethane on diethyl benzoylphosphonate gives only the benzoylmethylphosphonic ester. Pudovik et al.[59] have shown that the action of diphenyldiazomethane on derivatives of acetyl- and benzoyl-phosphonic acids at high temperatures yields products of oxiran structure. The latter was confirmed by infrared spectral data and by the catalytic and thermal isomerisation of the products with rupture of a cyclic carbon–oxygen bond and formation of a phosphinyl ketone. More recently $\beta$-keto-phosphonates have been obtained[60] by the action of diazomethane and phenyldiazomethane on benzoylphosphonates under similar conditions:

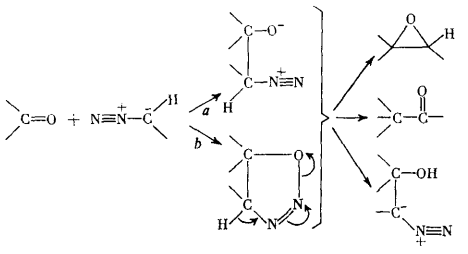


It is assumed[60] that such reactions involve migration of the phosphinyl group to form the thermodynamically stable $\beta$-keto-phosphonates. The action of diazoethane on $\alpha$-oxo-phosphinyl compounds yields exclusively the corresponding $\beta$-keto-phosphinyl derivatives[61,62].

Diazoacetic esters form adducts of "aldol" type—alkyl $\beta$-dialkoxyphosphinyl-$\alpha$-diazo-$\beta$-hydroxybutyrates[63,64]:



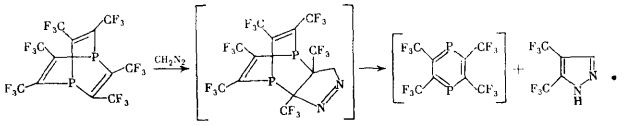
The mechanism of the reactions of diazoalkanes with $\alpha$-oxo-phosphonates is represented by the general scheme[64]



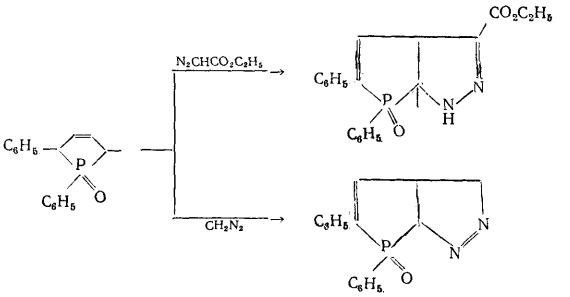
Reaction path (*a*) presupposes formation of a zwitterion in the first stage; path (*b*) involves 1,3-dipole cycloaddition, with formation of a 1,2,3-oxadiazoline derivative in the first stage. The products may be oxirans, $\beta$-keto-phosphonates, and diazohydroxyalkylphosphonates. The direction of the reaction of $\alpha$-oxo-phosphonates with diazoalkanes is significantly influenced by the nature of the substituents both adjacent to the carbonyl group[58,59] and attached to the carbon atom of the diazo-component[59,61,63,64].

## 5. Tertiary Cyclic Phosphines and their Oxides

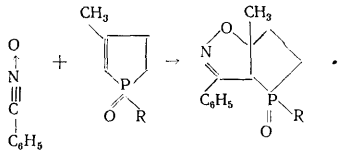
A substituted diphosphabarrelene behaves as a dipolarophile, undergoing addition at the multiple bond in diazomethane and phenyl azide[65]. However, the adducts formed by cycloaddition are unstable:



The 1,3-dipolar cycloaddition of diazoalkanes to 1,2,5-triphenylphosphole oxide yields adducts of dihydropyrazole structure[66,67]:



$\Delta^2$-Phospholens form with oxides of aromatic nitriles derivatives of oxazaphosphabicyclo[3,3,0]octene[68]:

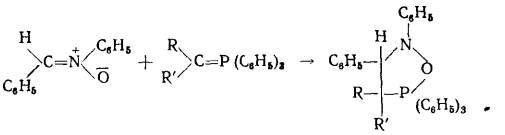


In the case of $\Delta^3$-phospholen the sequence in which the nitrile oxide is added has no significance, because of the symmetry of the former molecule.

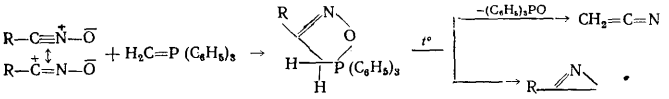
## 6. Alkylidenephosphoranes

The cycloaddition of 1,3-dipoles to alkylidenephosphoranes produces five-membered heterocycles containing the phosphorus atom either directly in the ring or in a side-chain. Methylene- and imino-phosphoranes have been subjected to reaction with nitrones[69–71], nitrile oxides[70,72–75], nitrilimines, and other 1,3-dipoles[70,76].

Reaction between benzaldehyde $N$-phenyloxime and an alkylidenetriphenylphosphorane yields a 1,2,5($P^V$)-oxazaphospholidine[71]:



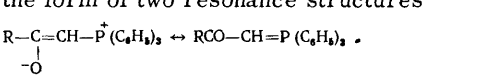
Benzonitrile oxide adds to methylenetriphenylphosphorane to form an oxazaphospholen, which breaks down at 140°C into a phosphine oxide, an $N$-arylketenimine, and a 2-arylazirine:



Huisgen and Wulff suggest[75] a multicentre single-stage addition for these reactions. The direction of cycloaddition is determined by the principle of maximum gain in energy of the σ bond, with consequent formation of an energetically favourable phosphorus–oxygen bond.

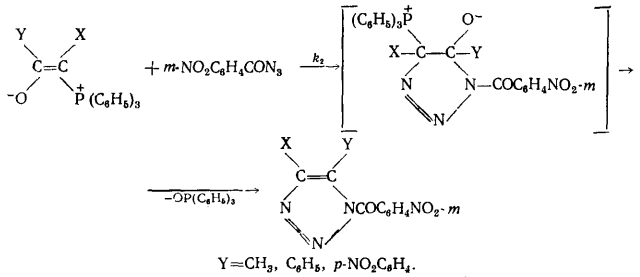
Iminophosphoranes are less active as dipolarophiles than are methylenephosphoranes. Cycloadducts of the latter with a nitrile oxide and a nitrone are quite stable and can be isolated, but with iminophosphoranes only decomposition products of the initial adducts are obtained. Thus the adduct of phenylglyoxal *N*-phenylmonoxime and phenyliminotriethylphosphorane eliminates a phosphine oxide to form $N^2$-benzoyl-$N^1N^1$-diphenylformamidine[70].

In contrast to methylene- and imino-phosphoranes, β-oxoalkylidenephosphoranes are able to react with 1,3-dipoles in the form of two resonance structures[77]



1,3-Dipolar cycloaddition of organic azides[77-81] to β-oxoalkylidenephosphoranes gives a mixture of products formed by incorporation into the phosphorane (*a*) at the C=C bond (triazoles and phosphine oxides) and (*b*) at the C=P bond (phosphoranes), one of which may predominate depending on the substituent in the initial phosphorane or on the conditions[77,82-84]. Benzonitrile oxides resemble azides in reacting with acylmethylenetriphenylphosphoranes to give a mixture of an isoxazole and a new phosphorane[82].

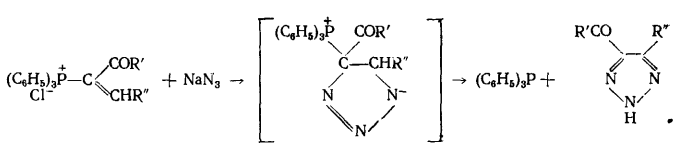
The mechanism of the reaction of azides with β-oxoalkylidenephosphoranes has been clarified by means of the kinetic investigations[77,80]



The activation parameters are consistent with 1,3-dipolar cycloaddition. It is considered[80] that concerted formation of σ bonds takes place, but at different rates.

### 7. Vinylphosphonium Salts

Cycloaddition of inorganic azides[85,86] or diazoalkanes[87-90] to vinylphosphonium salts takes place at the double bond by a 3 + 2 → 5 scheme with the formation of heterocycles containing the phosphorus atom in a side-chain. Cycloaddition of sodium azide to a vinylphosphonium salt produces an unstable adduct, which splits into triphenylphosphine and a triazole:



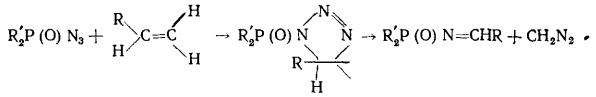
Stable 2-pyrazol-3-yltriphenylphosphonium bromides have been obtained[88] by the cycloaddition of diazoalkanes to unsubstituted vinylphosphonium salts. The action of diazo-compounds on β-acylvinylphosphonium salts gives pyrazoles and a phosphine oxide[89]. The direction of cycloaddition is controlled by the electronic and steric effects of the substituents and also by the reaction conditions.

## III. 1,3-DIPOLAR CYCLOADDITION OF PHOSPHINYLATED 1,3-DIPOLES

### 1. 1,3-Dipoles containing Phosphinyl Substituents in a Side-chain

The cycloaddition of diazoalkanephosphonates to various unsaturated compounds yields phosphinylated pyrazoles and pyrazolines[91-104]. The dependence of the vicinal spin–spin coupling constant of phosphorus-31 and hydrogen-1 nuclei on the dihedral angle found from the nuclear magnetic resonance spectra has been used to determine the configurations of the $\Delta^1$-pyrazolines formed by the cycloaddition of a diazoalkanephosphonate to norbornene and norbornadiene[102]. Electronic factors play an important part in the formation of configurational isomers epimeric with respect to the 3-carbon atom in the pyrazoline. The conformation has been determined for the $\Delta^1$-pyrazolines obtained by 1,3-dipolar cycloaddition of ethyl α-diazo-β-dimethoxyphosphinyl-β-hydroxybutyrate to methyl methacrylate[104]. Reaction of this butyrate with dimethyl acetylenedicarboxylate is accompanied by decomposition of the resulting diastereomeric pyrazolenines as a consequence of rupture of phosphorus–carbon and carbon–carbon bonds[105].

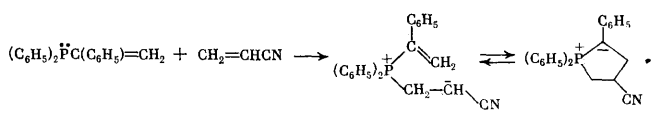
Phosphinyl azides add at multiple bonds in unsaturated compounds:



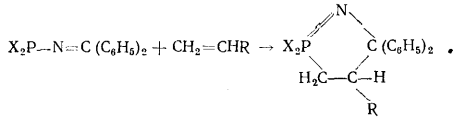
The reaction products are in one case stable triazolines[106-108], and in another *N*-phosphinylated imines and diazomethane both formed on decomposition of unstable initial adducts[109]. Diphenyl phosphorazidate reacts with enamines of cyclic ketones to form unstable triazolines, which evolve nitrogen and give products of ring contradiction[110].

### 2. αβ-Unsaturated Phosphines and Phosphinites

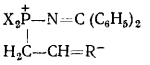
αβ-Unsaturated compounds containing a three-coordinated phosphorus atom react with such dipolarophiles as acrylates, acetylenedicarboxylic esters, and derivatives of α-keto-carboxylic acids by adding to C=C, C≡C, and C=O multiple bonds according to the classic 3 + 2 → 5 scheme. Thus 1,3-dipolar cycloaddition of diphenyl-1-phenylvinylphosphine (dipole of type $=\dot{P}-C=C$) to acrylonitrile yields a cyclic adduct[111]:



A substituted methyleneaminophosphine adds to acrylonitrile or methyl acrylate to form a $\Delta^1$-1,2-aza-(PV)-phospholine, the first cyclic phosphazen containing fewer than six atoms in the ring[112,113]:

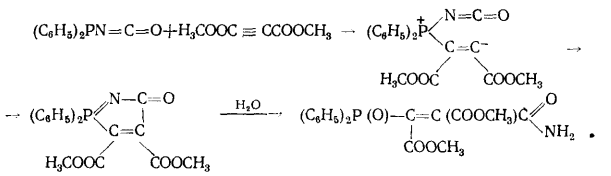


A betaine structure



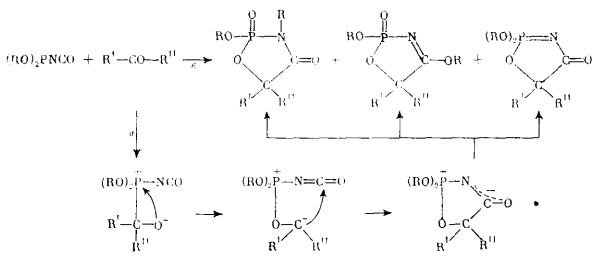
may well be formed as an intermediate stage[112,113]. Cycloaddition of diethoxymethyleneaminophosphines to acrylic esters gives derivatives of dihydroazaphospholopyridine[114].

The reaction of isocyanatodiphenylphosphine with dimethyl acetylenedicarboxylate is regarded[115] as involving an intermediate zwitterion, which cyclises into an unstable five-membered heterocycle readily hydrolysed to a phosphine oxide:

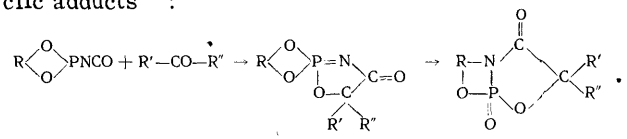


Diethyl phosphoramidinate reacts readily with acetylenedicarboxylic and maleic esters[116] to form azaphospholes and azaphospholines.

The carbonyl group also exhibits dipolarophilic activity towards phosphorisocyanatidites and methyleneaminophosphines. These esters react with esters[117,118,125,126,128] and nitriles[119,128] of $\alpha$-oxo-carboxylic acids, with $\alpha$-dicarbonyl compounds[120,121], and with $\alpha$-oxo-phosphonates[126,127], forming mixtures of structurally isomeric substituted oxazaphospholidinones, oxazaphospholines, and oxazaphospholinones. Reaction is assumed[128] to follow path (*a*):

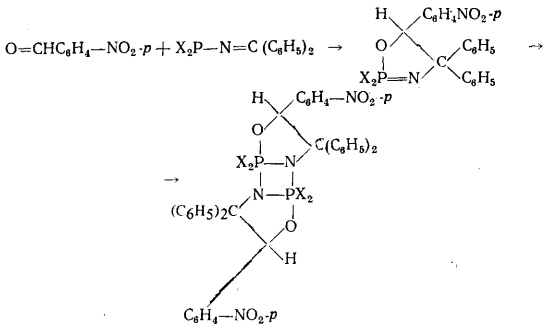


The reactions of isocyanatodiphenylphosphine and of phosphorisocyanatidous tetraethyldiamide with ethyl pyruvate go in the same direction, forming substituted oxazaphospholines, which contain a phosphimide bond[122]. Alkylene glycol esters of isocyanates of phosphorous acid form with $\alpha$-oxo-carboxylic esters and phenylglyoxal 1 : 1 bicyclic adducts[123]:



Substituted bicycloheptanes are obtained by the action of carbonyl compounds on ethyl phosphorodi-isocyanatidite[124].

Cycloaddition of a substituted methyleneaminophosphine to *p*-nitrobenzaldehyde gives a dimeric 1 : 1 adduct[129]:



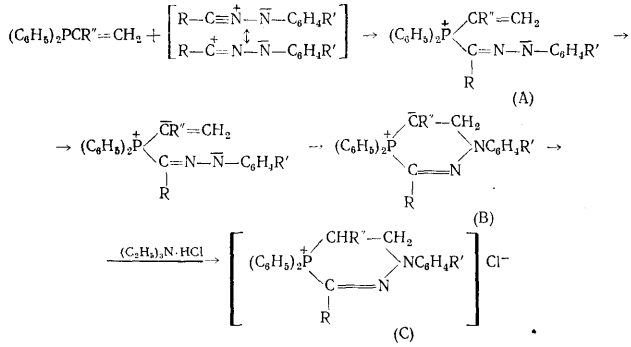
The ability of $\alpha\beta$-unsaturated compounds containing tervalent phosphorus to react as 1,3-dipolar systems is attributed[130,131] to the behaviour of the phosphorus atom as a nucleophile in virtue of its lone pair of electrons. On becoming quaternised, the phosphorus atom develops $\pi$-acceptor properties as a consequence of $d\pi - p\pi$ conjugation, activating the $\beta$ position of the multiple bond. It is considered[130,131] that any system of the type $\ddot{Z}-X=Y$ can react as a 1,3-dipole, where $\ddot{Z}$ is an element having a lone pair of electrons, while X and Y are elements capable of forming $\pi$ bonds.

## IV. MIXED "DIMERISATION" of 1,3-DIPOLES AND $\alpha\beta$-UNSATURATED PHOSPHINES AND PHOSPHONITES

### 1. Ethylenic and Acetylenic Phosphines and Phosphonites

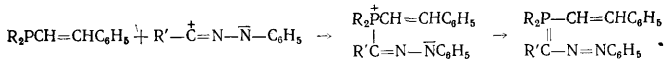
As well as reactions in which $\alpha\beta$-unsaturated compounds containing three-coordinated phosphorus behave as 1,3-dipolar systems, these substances also undergo mixed "dimerisation" with classic 1,3-dipoles.

Vinyl-, isopropenyl-, allyl, and alkynyl-phosphines react with substituted nitrilimines according to a 3 + 3 → 6 scheme involving the phosphorus atom to form (in the presence of triethylamine hydrochloride) six-membered cyclic phosphonium salts[132-134,137,138,146]:



Nucleophilic attack by the three-coordinated phosphorus atom on the positively charged carbon atom of the nitrilimine leads initially to formation of a betaine (A). As a consequence of the strong polarisation of the double bond due to the positively charged phosphorus atom, the betaine cyclises into a phosphorine (B), which is then converted into a phosphonium salt (C). The reaction of $\alpha\beta$-unsaturated ethylenic and acetylenic phosphonites with nitrilimines proceeds similarly, but the concluding stage is accompanied by an Arbuzov rearrangement[135,136,139,140].

Alkynylphosphonous tetra-alkyldiamides react with diphenylnitrilimine to form cyclic phosphonium salts, derivatives of 1,4-dihydro-4-phosphapyridazine [141]. Reaction between nitrilimines having electron-accepting groups attached to the carbon atom and $\beta$-substituted ethylenic and acetylenic dialkyl-, diamino-, and diphenylphosphines gives azomethylenephosphoranes [134,141]:



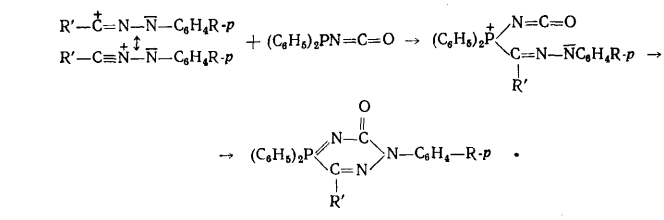
The nature (saturated or aromatic) of substituents attached to the phosphorus atom has no effect on the course of the reaction. With $\alpha\beta$-ethylenic phosphines and phosphonites this is determined mainly by two factors—steric hindrance by $\beta$-substituents in the unsaturated group and the nature of the substituents attached to the carbon atom of the nitrilimine. The reactions of acetylenic derivatives of tervalent phosphorus with nitrilimines, in contrast to those of ethylenic compounds, are less sensitive to steric hindrance at the $\beta$-carbon atom of the ethynyl group and to the nature of substituents attached to the nitrilimine carbon atom [137]. This difference in behaviour is attributed [137] to greater activity of the *sp*-hybridised carbon atom in reactions with nucleophilic reagents.

Kinetic investigation by the method of competing reactions has shown [141] that the reactivity of unsaturated derivatives of three-coordinated phosphorus towards nitrilimines is determined primarily by the inductive effects of the substituents and to a less extent by the $d\pi-p\pi$ conjugation. Comparison of the relative rate constants for reactions of a series of $\alpha\beta$-unsaturated compounds of tervalent phosphorus with diphenylnitrilimine suggests [141] a two-stage nucleophilic mechanism. The rate-determining stage is nucleophilic attack by the phosphorus atom on the electron-deficient carbon atom of the nitrilimine. Thus the rules of mixed "dimerisation" differ from those of classic 1,3-dipolar cycloaddition.

Study of the reactions of organic azides with $\alpha\beta$-unsaturated phosphines has shown [142] that the multiple bond is not involved, and as a result previously unknown unsaturated phosphinimines are formed.

## 2. Isocyanatophosphines and Methyleneaminophosphines

Three-coordinated phosphorus compounds containing an $\alpha\beta$-N=C bond react as 1,3-dipoles with nitrilimines, according to a 3 + 3 → 6 scheme similarly to alkenyl- and alkynyl-phosphines. Reaction between isocyanatodiphenylphosphine and a nitrilimine yields a cyclic ketoiminophosphorane independently of the nature of the substituents in the nitrilimine [143,144]:



The course of the reaction supports the above two-stage nucleophilic mechanism of interaction between $\alpha\beta$-unsaturated compounds of tervalent phosphorus and 1,3-dipolar systems [141]. Diphenylmethyleneaminodiphenylphosphine, in contrast to the isocyanate, reacts with *C*-ethoxycarbonyl- and *C*-acetyl-*N*-arylnitrilimines to form open-chain azomethylenephosphoranes [145].

Thus 1,3-dipolar cycloaddition of organophosphorus compounds provides a convenient method for synthesising phosphorus-containing heterocycles, which find widespread use in many branches of the national economy—as medicinals, as insecticides in agriculture, and as polymerisation initiators in chemical industry. Investigation of such reactions broadens our ideas on the influence of substituents in ligands on the dipolarophilic activity of a multiple bond, the factors determining the reactivity of dipole–dipolarophile systems, and the mechanism of cycloaddition reactions.

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