Translated from *Uspekhi Khimii*, **49**, 1801-1828 (1980) U.D.C. 547.341

α,β-Unsaturated Heteroatomic Compounds in 1,3-Dipolar Addition Reactions

V.A.Galishev, V.N.Chistokletov, and A.A.Petrov

The reactions of α,β-unsaturated heteroatomic compounds with an unshared electron pair in the heteroatom, proceeding via the 1,3-dipolar addition mechanism, are examined. The ideas about 1,3-dipolar compounds developed by Huisgen are extended to compounds with elements in the Long Periods (phosphorus and sulphur).
The bibliography includes 231 references.

CONTENTS

I. Introduction 880
II. Oxygen- and nitrogen-containing π-systems 881
III. Phosphorus(III)-containing π-systems 882
IV. Sulphur-containing π-systems 886

I. INTRODUCTION

Among the methods for the synthesis of alicyclic and heterocyclic compounds, which play an exceptional role in modern organic chemistry and industry (mainly in the synthesis of polymers, dyes, pesticides, medicinal preparations, etc.), reactions in which ring formation involves the dissociation of π-bonds only, without the scission of any other fragments, occupy a notable place. Such processes include the reactions of carbenes with unsaturated compounds, the dimerisation of allenes, syntheses involving alkadienes (of the 4 + 1 = 5 type), the diene synthesis (4 + 2 = 6), and 1,3-dipolar cycloaddition (3 + 2 = 5 or 3 + 3 = 6).

The term 1,3-dipolar cycloaddition was proposed by Smith in 1938.[1] The complete classification of 1,3-dipolar systems (1,3-DS) was given by Huisgen[2,3]. According to Huisgen's definition, a 1,3-dipolar system can be any compound a–b–c, in which the atom a has an electron sextet and constitutes a positive centre, the atom c has a free electron pair and carries a negative charge, and the atom b has an unshared electron pair. According to Huisgen, six octet-stabilised 1,3-DS with a double bond and twelve octet-stabilised dipoles without a double bond can be constructed with elements in the Second Period. All the 1,3-DS with a double bond are known. Typical 1,3-DS are nitrile imines, nitrile ylids, nitrile *N*-oxides, diazo-compounds, and azides. Reactions involving addition to double bonds via a 3 + 2 = 5 mechanism and dimerisation reactions proceeding by both 3 + 2 = 5 and 3 + 3 = 6 mechanisms are most characteristic of 1,3-DS.

Huisgen's school investigated widely only the reactions of 1,3-DS incorporating the elements of the Second Period. The authors of the present review attempted to analyse on the basis of literature data the possibility of constructing 1,3-DS with participation of the elements of the Long Periods, in particular phosphorus and sulphur. Attention was turned to α,β-unsaturated compounds of the above elements, which correspond to Huisgen's limiting carbenoid structure of the 1,3-DS.

The reactivity of unsaturated compounds containing a heteroatom with an unshared electron pair ($\ddot{Z}$–X = Y, $\ddot{Z}$–X≡Y) in the α-position is determined by the degree of localisation of the unshared electron pair of the element $\ddot{Z}$ and the presence of vacant *d* orbitals in the latter. According to modern ideas, a heteroatom with an unshared electron pair exhibits as a rule an electron-donating effect in relation to the multiple bond: the unshared electron pair of the heteroatom is delocalised (p,π conjugation)[4]. The capacity of heteroatoms with an unshared electron pair for p,π conjugation is determined, according to Tsvetkov and Kabachnik[5], mainly by the nature of the hybridisation of this pair. Since the capacity of heteroatoms for p,π conjugation increases with increasing *p* character of the unshared electron pair, atoms can be arranged in the following sequence in terms of their capacity for p,π conjugation: N > O > S > P. The validity of this sequence has been confirmed by quantitative data for the ability of aromatic phosphines, sulphides, and amines to form polar complexes with strong acceptors (for example Group III metal halides).[6-10]

Whereas in the case of elements in the Second Period (O, N) the distribution of electron density in the ground state of the molecule gives rise only to a π-donor effect[11,12], for elements of the Third Period (S, P) the effect caused by the involvement in the conjugation of low-lying 3*d* orbitals (d–p) π-conjugation can also be manifested. The interaction of 3*d* orbitals with the electrons of the multiple bonds is responsible for the mesomeric electron-accepting properties of the heteroatoms of the elements of the Third Period: the electron density at the heteroatom increases and that in the multiple bond decreases. It has been shown[13] that the symmetry of the 3*d* orbitals permits overlap with a *p* orbital of the type of (p,p)π-bond. The possibility of (d–p)π-conjugation has also been confirmed for arylphosphines[14-16]. The degree of conjugation depends on the electronegativity of the substituents: a more electronegative substituent decreases the electron density at the phosphorus atom, promoting the contraction of the 3*d* orbitals and a stronger (d–p)π-interaction[13,17,18]. For example, in this connection, the degree of π-binding in acetylenic compounds of phosphorus(III) is greater than in the ethylenic compounds owing to the greater electronegativity of carbon in the *sp*-hybridised state that in the sp^2-state[19,20].

Thus in the Z–X=Y or Z–X≡Y systems, where X is a heteroatom with unshared electron pairs but without vacant *d* orbitals (Z = O or N), the electron density is markedly displaced from the heteroatom towards the multiple bond. By virtue of the delocalisation of the unshared electron pair, the nitrogen and oxygen atoms manifest π-donor properties[21].

If the heteroatom Z = S or P, then, apart from the electron pairs, low-lying vacant *d* orbitals can participate in the distribution of electron density. The negative inductive and weak π-donor effects of the sulphur atom as well as the involvement of the 3*d* orbitals in conjugation lead to the appearance of opposed shifts[21]. In the phosphorus atom the

effect due to p,π-conjugation is either absent or is overlapped by the $(d-p)\pi$-conjugation. As stated above, this is associated with the diminution of the p character of the unshared electron pair at the phosphorus atom and therefore, despite the presence of the electron pair, tervalent phosphorus in α,β-unsaturated compounds exhibits π-acceptor properties in relation to the multiple bonds.

The distribution of electron density in π-systems containing heteroatoms with unshared electron pairs has been studied by various physical methods: with the aid of NMR,[12,21-30] ultraviolet spectroscopy[31-36], infrared spectroscopy[37,38], and the determination of dipole moments[39]. The results of these studies indicate different roles of the effects of the p,π- and $(d-p)\pi$-conjugations in the distribution of electron density and hence a difference in the chemical properties of the compounds investigated.

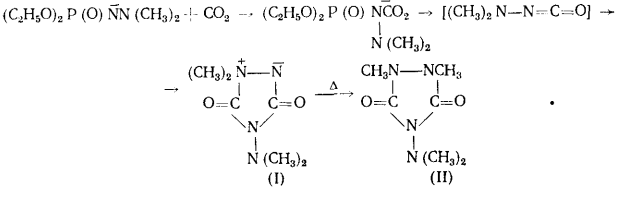
α,β-Unsaturated heteroatomic compounds can enter into 1,3-dipolar addition reactions in two ways. If the unshared electron pair is delocalised over the entire system, then the latter is a dipolarophile and interacts with the 1,3-DS via its multiple bond in accordance with the usual 3 + 2 = 5 cyclisation mechanism with formation of five-membered cyclic compounds. On the other hand, if conditions are created in the initial π-system for the localisation of the unshared electron pair of the heteroatom, two reaction centres are produced (the multiple bond and the heteroatom). Such α,β-unsaturated heteroatomic compounds can undergo cyclisation reactions with participation of the heteroatom both via 3 + 3 = 6 mechanism, i.e. via a mechanism involving the "mixed dimerisation" of the 1,3-DS, and via the 3 + 2 = 5 mechanism, behaving as a 1,3-DS. In the latter case only the electrophilic multiple bonds can behave as dipolarophiles.

II. OXYGEN- AND NITROGEN-CONTAINING π-SYSTEMS

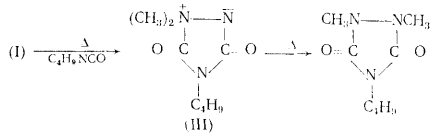
As a rule oxygen- and nitrogen-containing π-systems behave as dipolarophiles in 1,3-dipolar addition reactions. The mode of the reactions of such systems with 1,3-DS does not differ from that of the reactions of unsubstituted olefins and acetylenes: ynamines[40,41], enamines[42-50], and acetylenic [51-59] and vinyl ethers[60-62] form under these conditions five-membered cyclic compounds without the inclusion of the heteroatom in the ring.

The reactions of α,β-unsaturated oxygen-containing compounds, proceeding via a mechanism of the 1,3-dipolar addition type with inclusion of the oxygen atom in the reaction, have not so far been observed.

α,β-Unsaturated nitrogen-containing compounds can react via a 1,3-dipolar cyclisation mechanism with participation of the nitrogen atom only when the system is highly polarised. Thus it has been established[64] that the carboxylation of a phosphoramidate ion[63] (derivative of N,N-dimethylhydrazine) leads to the formation of a dimethylaminoisocyanate dimer (I), having the ylid structure. Its pyrolysis leads to the stable 1-dimethylamino-3,4-dimethyl-1,3,4-triazolidine-2,5-dione (II):

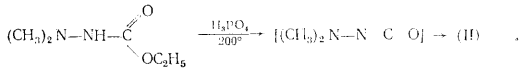


The interaction of the dimer (I) with an excess of butyl isocyanate leads to the formation of a new ylid (III), in which there is also a possibility of the migration of the methyl group:

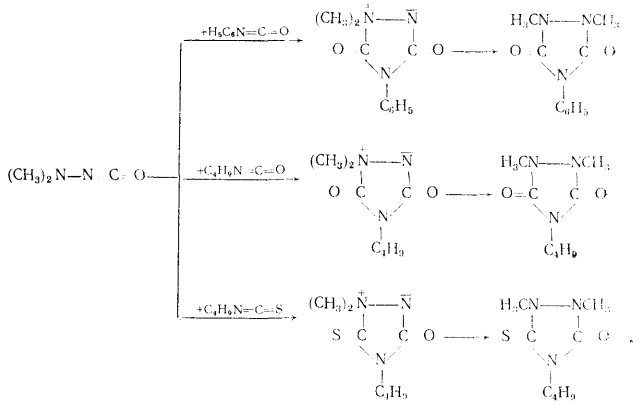


In the case of the t-octyl isocyanate, this type of reaction is reversible and at 90 °C the equilibrium is fully displaced towards the initial reactants, probably owing to steric hindrance.

The ylid structure of compound (I) and its analogues has been demonstrated by the reaction with HCl in benzene and subsequent elimination of methyl chloride. The authors[64] used also another method for synthesising dimethylaminoisocyanate using N-dimethylaminourethane:

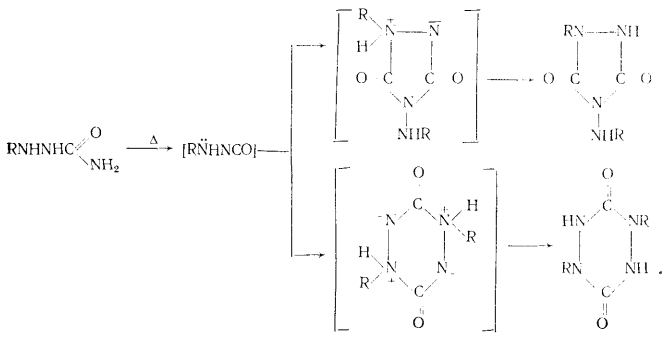


If the reaction is carried out in the presence of isocyanates or isothiocyanates, it is possible to "intercept" the intermediate monomeric dimethylaminoisocyanate:

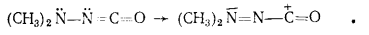


The stable triazolidine derivatives are formed as a result of the migration of the methyl groups. Pyrolysis of N-dimethylaminourethane in the presence of isocyanate or isothiocyanate constitutes a convenient method for the synthesis of various methyl-substituted triazolidines.

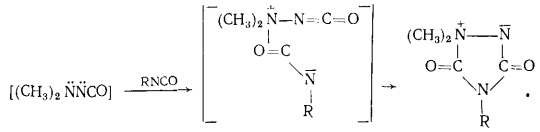
The pyrolysis of methylaminourea likewise leads to the formation of a triazolidinedione[65] and there is also a possibility of dimerisation via a 3 + 3 = 6 mechanism, leading to triazine derivatives:



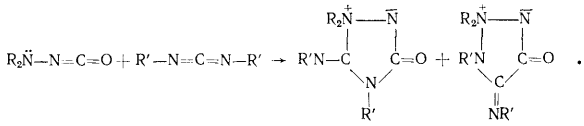
All the reactions described above may be regarded as 1,3-dipolar cycloadditions via the 3 + 2 = 5 mechanism. One molecule of dimethylaminoisocyanate behaves as a 1,3-DS, while another molecule of the same compound or a molecule of iso- or isothio-cyanate behaves as a dipolarophile. The stability of the product is determined by the stability of the ylid linkage. Dimethylaminoisocyanates can be classified as rare nitrogen-containing π-systems in which an electron pair is localised at the nitrogen atom adjoining the multiple bond. The localisation is probably caused by the presence of the adjacent nitrogen atom, which also has an unshared electron pair and this prevents the delocalisation of the charge over the system and enhances sharply the nucleophilic properties of the amino-nitrogen:



The extremely reactive 1,3-DS adds to the multiple bond of the initial molecule or alkyl isocyanate as a result of attack by the nucleophilic nitrogen atom of the dimethyl amino-group on the *sp*-hybridised carbon atom of the isocyanate group. Ring closure occurs when the nitrogen atom of the NCO group interacts with the carbon atom of the aminoisocyanate[64,66]:

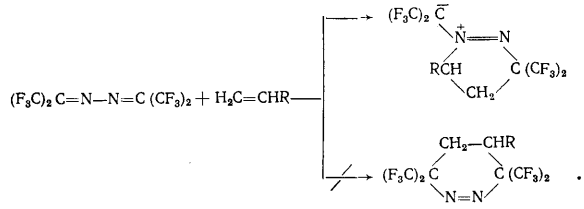


The reactions of dimethylaminoisocyanates with carbodiimides are also known. One of the two reaction products is a structural analogue of compound (I) and the other contains a bond between the amino-nitrogen of the dimethylaminoisocyanate and one of the nitrogen atoms (and not the *sp*-hybridised carbon atom) of the carbodi-imide:



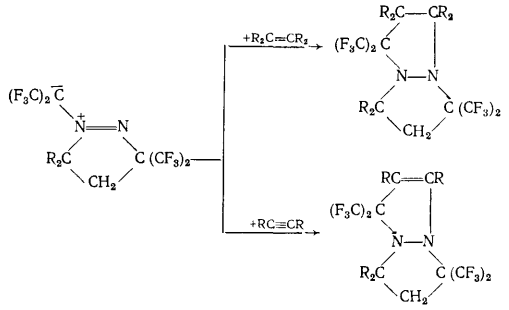
This probably involves nucleophilic attack on the carbodiimide nitrogen with transfer of the negative charge to the *sp*-hybridised carbon atom[67,68].

The interaction of hexafluoroacetone azine[69,70] with terminal olefins or dienes can also serve as an example of the 1,3-dipolar activity of a nitrogen-containing π-system[71-83]. The localisation of the unshared electron pair at the nitrogen atom converts such compounds into 1,3-DS. Hexafluoroacetone azine reacts with olefins of the type $H_2C{=}CHR$ and $H_2C{=}C(CH_3)R$ and with dienes to form, in the first stage, the product of 1,3-dipolar cycloaddition via the 3 + 2 = 5 mechanism and not via the mechanism of diene synthesis (4 + 2 = 6):[74]



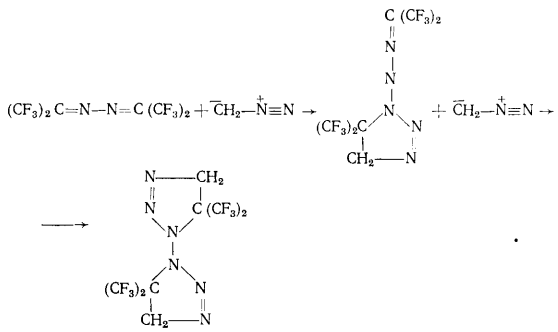
The product is a stable azomethine imine[2,76,81,83-88], If R is a bulky group, subsequent intramolecular deprotonation and reprotonation take place with formation of 3-pyrazolines[74-76,81,89].

The stable azomethine imine is capable of reacting further with systems containing multiple bonds via the usual 1,3-dipolar cycloaddition mechanism[74,75,80,81] to form a bicyclic heterocycle. This product can also be formed immediately if an excess of the olefin relative to the azine is taken:



Such mixed cycloaddition of two differently substituted systems with double bonds (or one system with a double bond and another system with a triple bond) in the 1,3 : 2,4-positions relative to hexafluoroacetone azine with intermediate formation of a stable azomethine imine leads to a new pathway to bicyclic heterocycles of the type of 1,5-diazobicyclo-octenes and 1,5-diazobicyclo-octanes and their heteroanalogues. One should note that the cycloaddition cross-reactions of azines with olefins had also been described earlier[92-97], but due importance had not been attached to them.

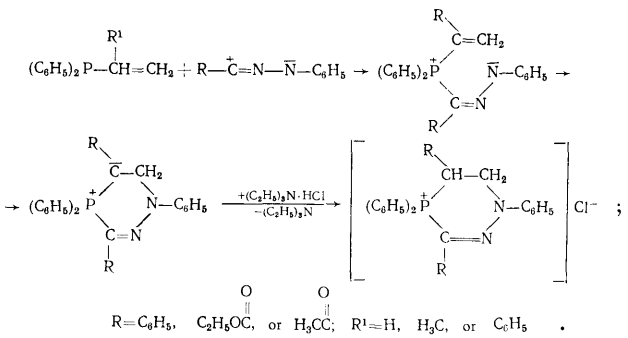
Hexafluoroacetone azine behaves as a dipolarophile in reactions with classical 1,3-DS. Thus the reaction with diazomethane involves one or both C=N bonds of the initial compound[98]:



III. PHOSPHORUS(III)-CONTAINING π-SYSTEMS

The interaction of α,β-unsaturated compounds of tervalent phosphorus and 1,3-DS can proceed via two reaction centres: the heteroatom and the multiple bond. In the general case phosphorus-containing π-systems can be regarded as reactive 1,3-DS with a negative charge on the phosphorus atom and a positive charge on the extreme carbon atom of the multiple bond. The first such reaction of α,β-unsaturated phosphorus(III) compounds with 1,3-DS via the mechanism involving mixed dimerisation of 1,3-DS (3 + 3 = 6) with participation of the phosphorus atom and the multiple bond in the reaction

and the formation of six-membered heterocycles has been described[99]. In this study the interaction of diphenylvinylphosphine with *C,N*-diphenylnitrile imine in the presence of triethylamine hydrochloride yielded a phosphonium salt—a derivative of 1,4,5,6-tetrahydrophosphoniapyridazine:

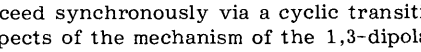


R=C_6H_5, C_2H_5OC, or H_3CC; R^1=H, H_3C, or C_6H_5 .

Alkenylphosphines having a substituent in the α-position relative to the multiple bond or one methyl group in the β-position react with nitrile imines in this way[100-103] regardless of their structure.

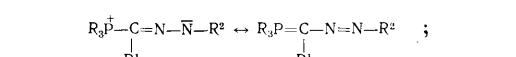
Nucleophilic attack by a tricoordinate phosphorus atom on the carbon atom of the nitrile imine leads apparently to the initial formation of a dipole ion, which, by virtue of the strong polarisation of the multiple bond and the influence of the tetracoordinate phosphorus atom, cyclises to a phosphorane. The cyclic phosphorane, being a stronger base than triethylamine, reacts with triethylamine hydrochloride to form a stable phosphonium salt. The stepwise course of the reaction can probably be regarded as a possible extreme case; one cannot rule out the possibility that such reactions can also proceed synchronously via a cyclic transition state. Different aspects of the mechanism of the 1,3-dipolar cycloaddition reaction are considered in reviews published previously[90,91].

When there are two methyl or phenyl groups in the β-position in alkenylphosphines, the reaction stops in some cases at the stage involving the formation of dipolar ions, the stabilisation of which is promoted by electron-accepting groups at the carbon atom of the nitrile amine. Account should also be taken of the steric hindrance caused by the substituents at the β-carbon atom of the multiple bond[101]:



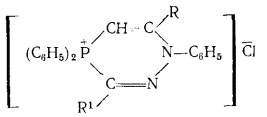
R=C_2H_5OCO, or H_3CCO .

The same azomethylenephosphoranes are formed when nitrile amines interact with various saturated derivatives of tervalent phosphorus[104-107] and with α,β-ethylenic compounds whose double bonds are involved in conjugation within the ring, for example, in pentaphenylphosphole[108]. The formation of these compounds confirms the proposed mechanism of the interaction of α,β-unsaturated derivatives of phosphorus(III) with nitrile amines:



R=Ar, $(Alk)_2N$, or AlkO; R^1=C_2H_5OCO, or H_3CCO; R^2=Ar .

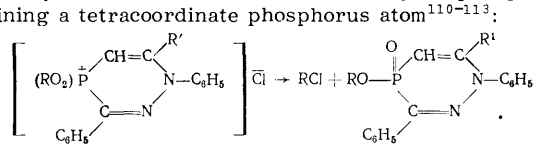
In contrast to alkenylphosphines, alkynylphosphines react with nitrile imines to form cyclic quasi-phosphonium compounds regardless of the degree of substitution at the β-carbon atom of the multiple bond[103,109,110], which indicates a lower sensitivity of acetylenic derivatives of phosphorus(III) to steric hindrance than that of the ethylenic derivatives:



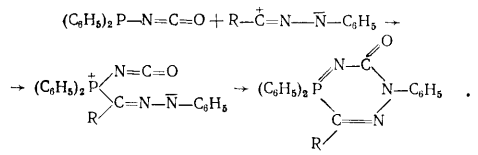
R=H, CH_3, $C(CH_3)_3$, or C_6H_5 .

The degree of conjugation of the 3*d* orbitals of the phosphorus atom with a triple bond is greater than with a double bond[19,20], so that the β-carbon atom should be more activated in the former case. Account should also be taken of the fact that the *sp*-hybridised carbon atom is more reactive in reactions with nucleophiles.

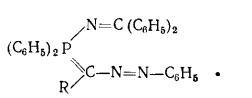
α,β-Unsaturated ethylenic and acetylenic phosphonites react with nitrile amines regardless of the nature of the substitution in the β-position of the multiple bond via the 1,3-DS mixed dimerisation mechanism. The quasi-phosphonium salts obtained undergo the Arbuzov rearrangement with elimination of the alkyl halide and the formation of a cyclic phosphinate containing a tetracoordinate phosphorus atom[110-113]:



The amides of alkenyl- and alkynyl-phosphonous acids form cyclic compounds only with nitrile amines without electron-accepting substituents at the carbon atom. In all the remaining cases the reaction stops at the stage involving the formation of open-chain azomethylenephosphoranes[101,114]. Heteroatomic α,β-unsaturated compounds of tervalent phosphorus such isocyanates of phosphorus acids and methyleneaminophosphines can also enter into Huisgen's 1,3-dipolar addition reactions with 1,3-DS. The reaction with diphenylphosphinyl isocyanate also proceeds via the 1,3-DS "mixed dimerisation" mechanism and stops at the stage involving the formation of a cyclic ketoiminophosphorane[115,116]. The isolation of this product can be regarded as confirmation of the possibility of the formation of cyclic methylenephosphoranes as intermediates also in the other cases described above:



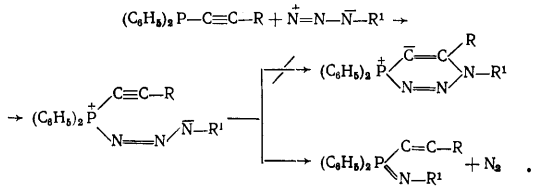
Acyclic azomethylenephosphoranes are products of the interaction of diphenylmethyleneaminophosphines with nitrile imines:



Cyclisation does not take place, apparently owing to the steric hindrance in ring closure caused by the phenyl groups[117].

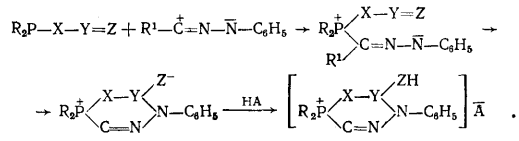
The choice of a 1,3-DS for reactions with α,β-unsaturated phosphorus(III) compounds is limited by the high reducing capacity of the latter. This factor rules out the possibility of using oxygen-containing 1,3-DS such as nitrile oxides, nitrones, etc. Together with nitrile imines, organic azides can serve as 1,3-DS. The interaction of α,β-unsaturated acetylenic phosphines with organic azides does not lead to cyclic products. The initial dipolar ion (phosphatriazene) is unstable and decomposes with liberation of nitrogen and the formation of a phosphine imine with an unsaturated group at

the phosphorus atom[118]:

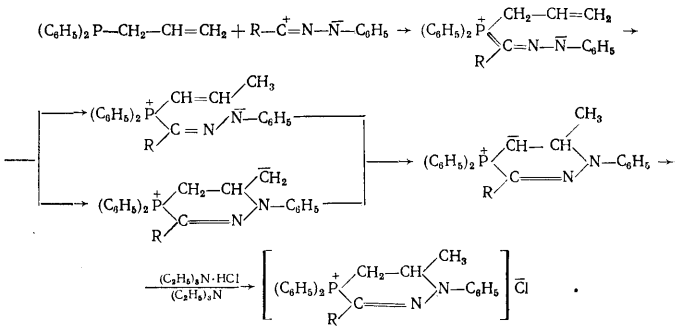


The nucleophilic mechanism of the reaction of unsaturated phosphorus(III) compounds with nitrile imines is also indicated by the relative rate constants for the reactions of different phosphorus-containing compounds with diphenylnitrile imine. For example, $(k_2)_{rel} = 0.56$, 1.00, and 2.72 for $(C_2H_5O)_2P{-}C{\equiv}C{-}C_6H_5$, $(C_6H_5)_2P{-}C{\equiv}CH$, and $[(CH_3)_2N]_2P{-}C{\equiv}C{-}C(CH_3)_3$ respectively[114]. The study of the dipole moments and ^1H NMR spectra of unsaturated phosphorus(III) derivatives is also important for the understanding of the mechanism of this reaction[119,120].

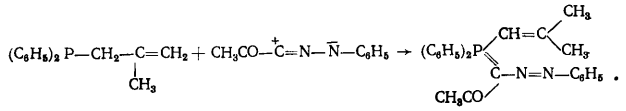
In the case of β,γ-unsaturated phosphorus(III) compounds the manifestation of 1,3-dipolar activity may be expected when an active electrophile is present in the β-position:



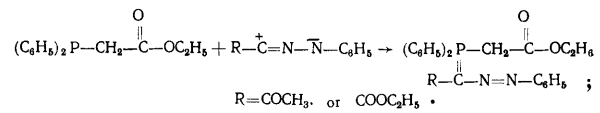
β,γ-Unsaturated phosphines (studied in relation to allyldiphenylphosphine)[102] isomerise in the reaction and the resulting phosphoniapyridazine is identical with the products of the reaction of diphenylpropenylphosphine (an α,β-unsaturated compound of tervalent phosphorus) with nitrile imines:



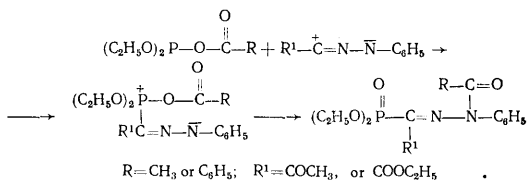
The isomerisation can occur either in the stage involving the formation of the intermediate dipolar ion or in the intermediate formed as a result of the attack by the nitrogen atom on the β-position of the multiple bond; this is followed by the transfer of a proton from the methylene group. The first pathway is apparently preferred, since the positively charged phosphorus atom facilitates the isomerisation of the allyl group[121]. In addition, it has been established that methylallyldiphenylphosphine reacts with *C*-acetyl-*N*-phenylnitrile imine to form azomethylenephosphorane as the product of the isomerisation of the phosphorane formed in the first stage[102]:



When nitrile imines react with ethoxycarbonylmethyldiphenylphosphine, the ethoxycarbonyl group is not involved in the reaction. Evidently the abstraction of a methylene proton and the substitution of the ethoxy-group, without which a stable product cannot be formed, is impossible in this case. The reaction stops at the stage involving the formation of azomethylenephosphorane[122]:

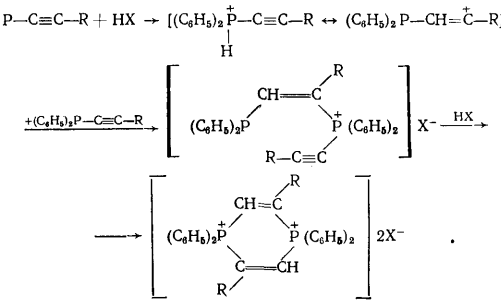


Only mixed anhydrides of dialkylphosphorus and carboxylic acids (diethyl acetyl phosphite and diethyl benzoyl phosphite) react with nitrile imines, where the carbon atom of the carbonyl group is involved in the reaction in addition to the phosphorus atom. As a result of the rearrangement, the final reaction products are acyclic phosphonates



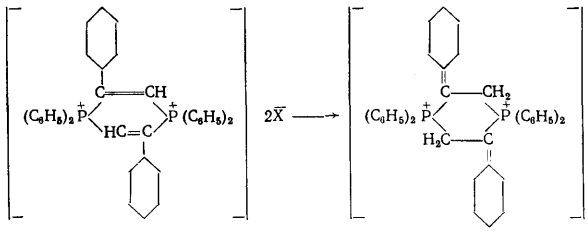
Mixed anhydrides of dialkylphosphorous and carboxylic acids react via a similar mechanism with methyl iodide[123], aldehydes, and ketones[124-126].

α,β-Acetylenic phosphines can also participate in simple dimerisation reactions via the 3 + 3 = 6 mechanism. Derivatives of 1,1,4,4-tetraphenyl-1,4-diphosphiniacyclohexa-2,5-diene are formed from alkynyldiphenylphosphines in glacial acetic acid in the presence of HBr.[127,129] According to the authors, the initial phosphine is protonated at the phosphorus atom in the first stage of the reaction, as a result of which the β-carbon atom of the multiple bond becomes more electrophilic owing to the strong conjugation of the 3*d* orbitals of phosphorus with the π-electrons of the triple bond. A second phosphine molecule with a localised unshared electron pair attacks the β-carbon atom of the first phosphine molecule with subsequent cyclisation and formation of a diphosphonium salt[130,131]:



The mode of this reaction, which proceeds in a protic solvent, can depend on the nature of the halide involved in it. The strongest nucleophile (the iodide ion) prevents cyclisation and the competing reaction involving the formation of β-iodovinylphosphine takes place; in the presence of the bromide ion, which is less nucleophilic than the iodide ion, cyclisation proceeds more readily. It is facilitated still further in the presence of the chloride ion. If the substituents in the β-position of the multiple bond are alkyl, cyclopentyl,

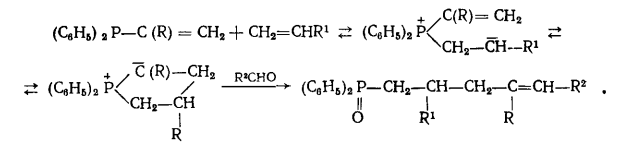
or cyclohexyl, then heating of the cyclic salts can lead to irreversible isomerisation, showing that the degree of stabilisation of the system as a result of the π-electronic interaction with the phosphorus atom is low[129,131]. For example, with R = cyclohexyl, the isomerisation proceeds as follows:



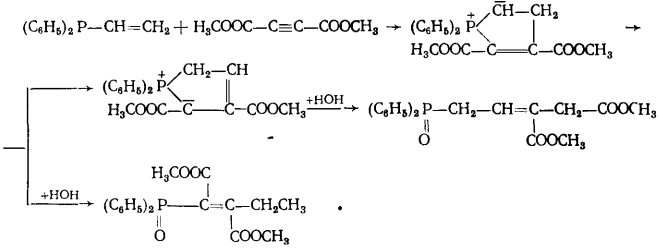
It is noteworthy that the study of the electrochemistry of derivatives of 1,4-diphosphophoniacyclohexa-2,5-diene led to the discovery of a new class of radical-cations[132,133].

Phosphorus-containing π-systems, like the classical 1,3-DS, can react with compounds containing activated multiple bonds (dipolarophiles) via the 3 + 2 = 5 mechanism. The five-membered heterocycles formed in these reactions are unstable. in some cases. For this reason, the products of their interaction with other substances have been isolated.

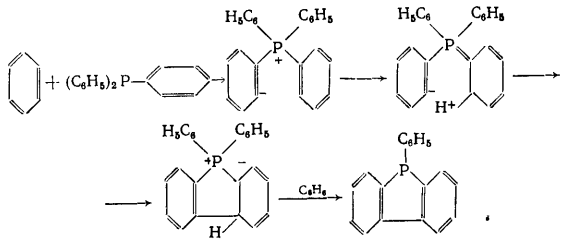
The interaction of vinylphosphines with activated olefins leads to the formation of five-membered ylids, apparently with the intermediate formation of dipolar ions[134]. When the reaction is carried out in the presence of aldehydes, the five-membered ylid undergoes the Wittig reaction with formation of the corresponding phosphine oxide[135]:



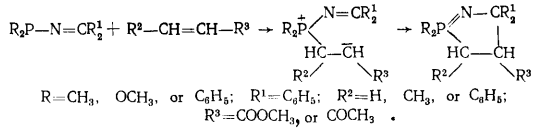
Diphenylphosphine reacts with the dimethyl ester of acetylenedicarboxylic acid to form a cyclic compound which can rearrange to a tautomer having the ylid structure: on interaction with water, both ylids decompose with formation of phosphine oxides[136]:



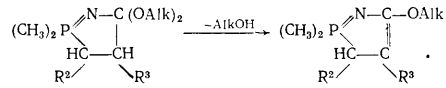
When triphenylphosphine interacts with dehydrobenzene, biphenylenephenylphosphine is formed as one of the products. A betaine is apparently formed as an intermediate with subsequent cyclisation and elimination of benzene[137]:



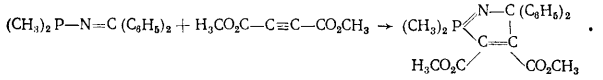
Phosphorus-containing dipolar π-systems with multiple heterobonds can also undergo the 3 + 2 = 5 cycloaddition reactions. Methyleneaminophosphines[138] react with derivatives of acrylic, crotonic, and cinnamic acids and α,β-unsaturated ketones to form five-membered addition products via the 2 + 3 = 5 mechanism[139,140] and the intermediate formation of the betaine is also postulated:



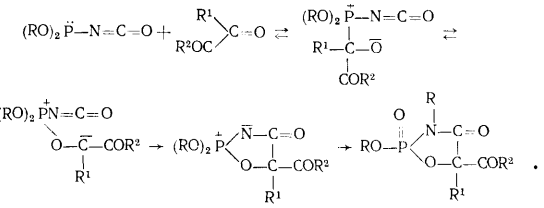
If R^1 = OAlk, then the cyclic product is converted with elimination of the alcohol, forming a more stable product[140]:



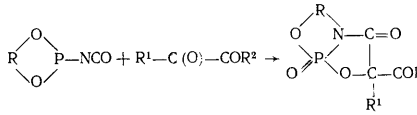
The dimethyl ester of acetylenedicarboxylic acid reacts with methyleneaminophosphines to form a cyclic iminophosphorane:



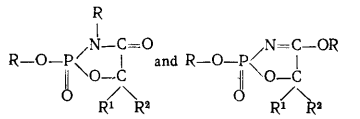
Dialkyl and alkylene phosphoromonoisocyanatidites also react via the 3 + 2 = 5 1,3-dipolar cycloaddition mechanism with carbonyl compounds activated by electron-accepting substituents α,β-unsaturated phosphorus(III) compounds with an unshared electron pair at the phosphorus atom functioning as the 1,3-DS. In cases where the dipolarophiles are the esters of α-ketocarboxylic acids and α,β-diketocarboxylic acids or α-diketones, the reaction begins with nucleophilic attack by the phosphorus atom on the carbon atom of the carbonyl group with formation of a dipolar ion, which rapidly isomerises to the thermodynamically more stable ion with P–O–C bonds. The latter is stabilised with formation of a five-membered ring as a result of the attack by the carbanion on the carbon atom of the isocyanate group. The final reaction product is obtained after subsequent *N*-alkylation[141-143]:



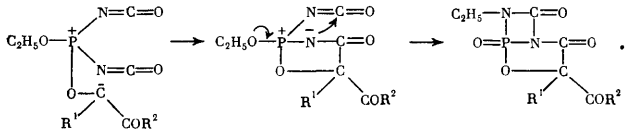
Alkylene phosphoroisocyanatidites form bicyclic addition products[143,144]:



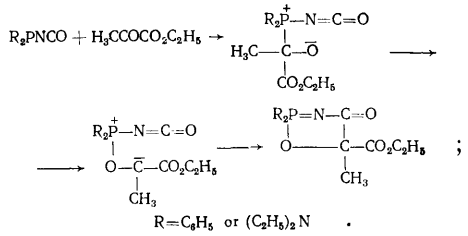
If the dipolarophiles are the nitriles of α-ketocarboxylic acids, the final stage of the reaction is not only *N*-alkylation, but also *O*-alkylation and a mixture of two products is formed[145,146]:



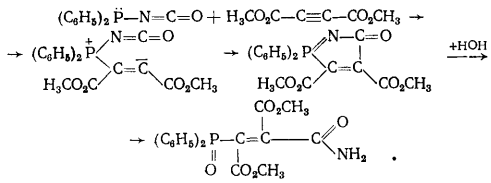
The ethyl ester of a phosphorodi-isocyanatidic acid reacts with carbonyl-containing compounds via a mechanism common to such reactions, but the second isocyanate group also participates in the stabilisation process[147]:



The intermediate dipolar ions can be stabilised not only via transalkylation but also via a pathway involving the formation of cyclic phosphine imines. The reaction between diethyl phosphoroisocyanatidite and aldehydes[148] and between isocyanatodiphenylphosphine and the bis-(*N*,*N*-diethylamide)-of phosphoroisocyanatidic acid, on the one hand, and ethyl pyruvate, on the other, also proceeds via this pathway[149]:



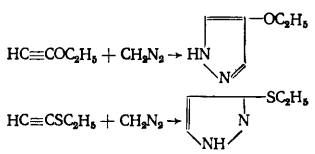
Isocyanatodiphenylphosphine reacts as a 1,3-DS with a dipolarophile such as dimethyl acetylenedicarboxylate with formation of a five-membered heterocycle, which being unstable, decomposes with formation of phosphine oxide. The reaction apparently proceeds via a stage involving the formation of a dipolar ion[150]:



The data presented show that formally α,β-unsaturated compounds of phosphorus(III) do not differ in type of reactivity from classical 1,3-DS.

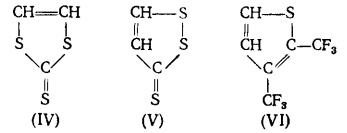
IV. SULPHUR-CONTAINING π-SYSTEMS

In many cases ethylenic and acetylenic compounds of sulphur and its analogues (selenium and tellurium) combine with 1,3-DS as dipolarophiles via the multiple bond[151], although the presence of vacant 3*d* orbitals in the sulphur atom influences the mode of the 1,3-dipolar cycloaddition[59]. For example, the interaction of diazomethane with ethoxyacetylene and ethylthioacetylene leads to products of different structure, which makes it possible to postulate the possibility of the stabilisation of the carbanion formed initially by (*d*-*p*) π-conjugation, which determines the mode of addition in the case of a sulphur-containing compound:

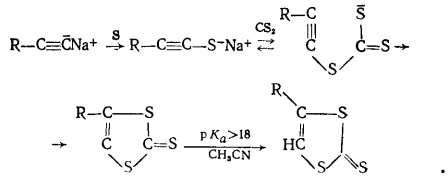


However, the multiple bond nevertheless remains the reaction centre.

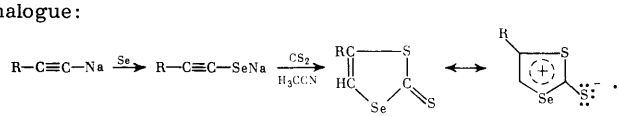
The reactions of compounds containing sulphur next to a multiple bond, which proceed via the 1,3-dipolar addition mechanism, have been described in recent years. The reaction of acetylene with sulphur and carbon disulphides, yields, together with other compounds, the isomeric 1,3-dithiole-2-thione (IV) and 1,2-dithiole-3-thione (V).[152] The analogous reaction in the presence of perfluoro-2-yne yields 1,3-bis-(trifluoromethyl)thiophen (VI):[153,154]



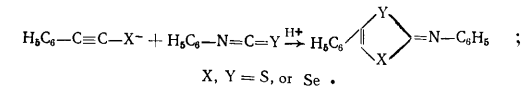
The reaction apparently proceeds with formation of a primary thiolation product. The interaction of acetylenes with sulphur and carbon disulphide in polar solvents probably proceeds via the same mechanism with formation of 1,3-dithiole-2-thiones[155-157]. If one begins with sodium acetylide, sulphur, and carbon disulphide, then derivatives of 1,3-dithiole-2-thiones are formed in the presence of a proton-donating solvent even at room temperature[156-158]. The formation of the product of the thiolation of sodium acetylide is most probably an intermediate stage[159]:



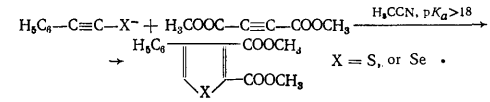
Products of analogous structure are formed also by selenium and tellurium which are sulphur analogues[160-162]. In the presence of carbon disulphide in a proton-donating solvent, when the product obtained by treating sodium acetylide with selenium is acted upon by carbon disulphide in a proton-donating solvent, 1-thia-3-selenole-2-thione is formed[163] and is stabilised by resonance, like its sulphur analogue:



The use of phenyl isothiocyanate and phenyl isoselenocyanate as heterocumulenes in this type of reaction does not alter its mechanism[164]:

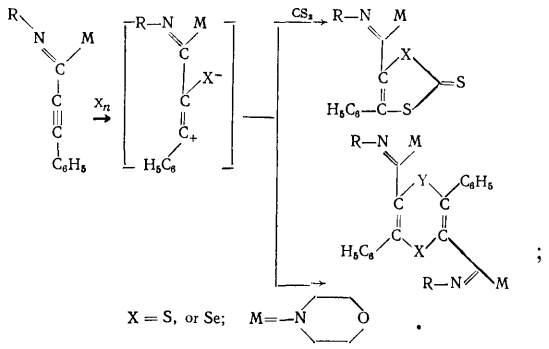


Acetylenic thiolates and selenolates also react with dimethylacetylenedicarboxylate via the 1,3-dipolar cycloaddition mechanism with formation of derivatives of thiophen- or selenophen-dicarboxylic acids[165-166]:



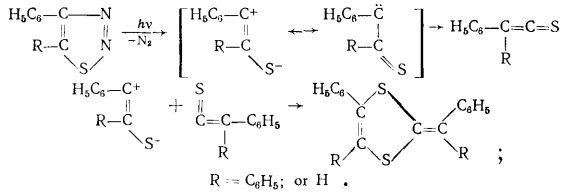
1,3-Dithiole-2-thiones have been obtained not only from terminal acetylenes with intermediate formation of thiolates but also from compounds having a doubly substituted triple bond. When the amidines of phenylpropiolic acid interact with sulphur or selenium in the presence of a tertiary amine, derivatives of 1,3-dithiole-2-thiones are produced[167]. A

sulphur-containing 1,3-DS is apparently formed in the first stage and then reacts with the dipolarophile (carbon disulphide):

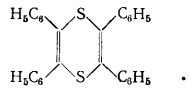


If phenyl isocyanate or phenyl isothiocyanate is introduced into the reaction mixture instead of carbon disulphide, the sulphur-containing 1,3-DS dimerises, apparently owing to the lower reactivity of the multiple bond of the heterocumulene.

Extremely reactive compounds are formed on decomposition of 1,2,3-thiadiazoles. Photolysis of derivatives of 1,2,3-thiadiazoles proceeds with evolution of nitrogen and the formation of dithiafulvenes[168]. It has been suggested[169] that, when a nitrogen molecule is split off, a thioketocarbene is formed as an intermediate and can then be converted into a thioketen as a result of a rearrangement analogous to the Wolff rearrangement. The reaction probably proceeds subsequently via the 1,3-dipolar cycloaddition mechanism: the thioketocarbene (1,3-DS) reacts with the thioketen (dipolarophile) via the 3 + 2 = 5 mechanism:

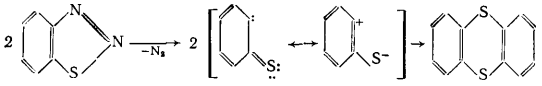


If R = C_6H_5, the competing dimerisation reaction of the 1,3-DS (thioketocarbene) can proceed via the 3 + 3 = 6 mechanism with formation of dithiacyclohexadiene[168]:

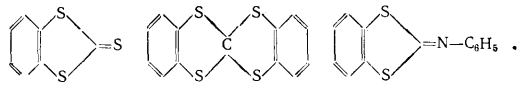


It is noteworthy that the products of cycloaddition via the 3 + 2 = 5 mechanism (the dithiafulvenes) are also obtained from acetylenic thiolates and selenolates[157,165,166] and the lower the pK_a of the solvent the higher the yield of the dithiafulvenes.

The aromatic thioketocarbenes formed on thermolysis of benzothiazoles dimerise with formation of thianthrene[170]:

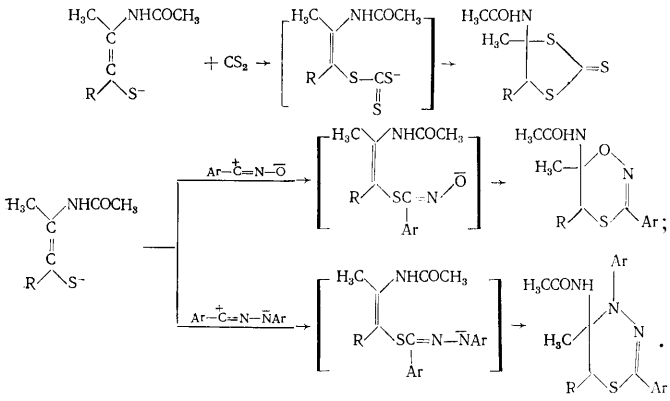


Thioketocarbenes dimerise so readily that, even when the reaction is carried out in dipolarophiles (used as solvents) such as diethyl fumarate, α-naphthyl isocyanate, or benzonitrile, the products of addition via the 2 + 3 = 5 mechanism are not obtained; the product of the 3 + 3 = 6 reaction is formed exclusively[2,171]. Only certain compounds containing the C=S double bond combine with thioketocarbene relatively smoothly. Carbon disulphide reacts via both one and two multiple bonds, while phenyl isothiocyanate forms 2-phenylimino-1,3-benzodithiole[171]:

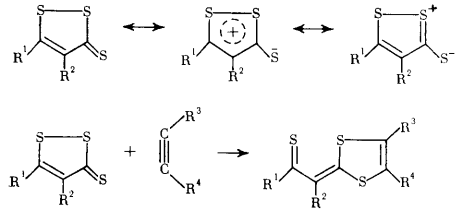


The decomposition of unsubstituted 1,2,3-thiadiazole in carbon disulphide at 200 °C yields only 0.2% of 1,3-dithiole-2-thione[171], while the reaction with perfluorobut-2-yne leads to the formation of 2,3-bis(trifluoromethyl)thiophen; the reaction involving 5-methyl-1,2,3-thiadiazole proceeds analogously[153].

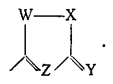
It has been shown recently that alkenethiolates[172,173] are also capable of behaving as 1,3-DS and of reacting with dipolarophiles (carbon disulphide) via the 3 + 2 = 5 cyclisation mechanism[174] and with other 1,3-DS (nitrile oxides, nitrile imines) via the 3 + 3 = 6 cyclisation mechanism[175]:



Numerous studies published recently have been devoted to yet another form of sulphur-containing π-systems capable of undergoing 1,3-dipolar cycloaddition reactions. It has been shown[176,177] that 1,2-dithiole-3-thiones react with activated acetylenes via the 3 + 2 = 5 cyclisation mechanism[176,177]. The nucleophilic properties of the exocyclic sulphur atom in such compounds are based on the stability of the quasi-aromatic dithiole ring system, by virtue of which the unshared electron pair is localised at the thione sulphur atom and the system as a whole is a kind of 1,3-DS:



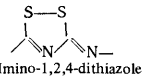
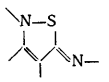
Apart from 1,2-dithiole-3-thiones, their isoelectronic analogues can enter into similar reactions and all these compounds can be represented by the general formula



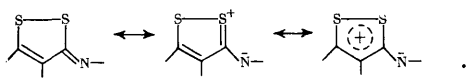
The examples investigated are summarised in Table 1.

Table 1 shows that the ring system can include both sulphur and nitrogen and in the latter case the electron density in the ring increases, which enhances the nucleophilic properties of the exocyclic atom and hence the 1,3-dipolar activity. 1,2,4-Dithiazole-3-thiones react more vigorously with activated acetylenes than 1,2-dithiole-3-thiones.

Table 1. Sulphur-containing 1,3-DS.

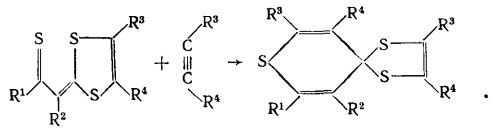
Compound	References	Compound	References
 1,2-Diothiole-3-thione	176—200	 3-Imino-1,2-dithiole	184, 189
 1,2,4-Dithiazole-3-thione	180; 184—186, 189, 195, 199, 201—205	 3-Imino-1,2,4-dithiazole	180, 209
 Isothiazole-5-thione	206—208	 5-Iminoisothiazole	206
 Isothiazole-3-thione	208		

The reaction proceeds in some cases with dissociation of the S–S bond and in others with rupture of the S–N bond, which, incidentally, does not alter its essential features. Instead of the exocyclic sulphur atom, the system may contain an exocyclic nitrogen atom; such a system is also a 1,3-DS and a partly ionised structure can be formulated for it as well:



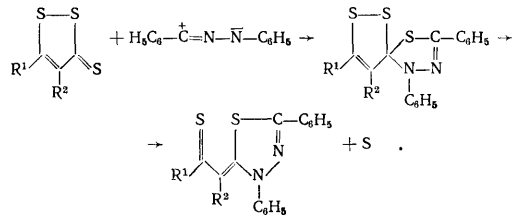
Such systems could be considered in the section devoted to nitrogen-containing π-systems, but, relative to the thiolethione systems, the 1,3-dipolar activity of iminothioles is particularly clear-cut.

The initial 1 : 1 product of the 1,3-dipolar cycloaddition can react in many instances with yet another molecule of the dipolarophile with formation of spirans (1,4-addition):



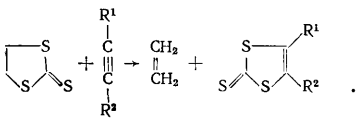
Such spirans can be obtained with almost all the systems investigated[177,184,185,187,191,204], but in some cases the 1,3-dipolar cycloaddition products could not be isolated, since the subsequent reaction was rapid[184,208].

1,2-Dithiole-3-thiones and their analogues participate only via their C=S double bond in reactions with classical 1,3-DS (benzonitrile oxide and diphenylnitrile imines); in other words, sulphur-containing heterocycles behave in this reaction as dipolarophiles[203,210–213]. The products formed initially react subsequently in a way which depends on the nature of the initial substances. For example, the reaction involving 1,2-dithiole-3-thione and diphenylnitrile imine proceeds via the following mechanism[212,213]:



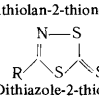
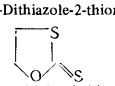
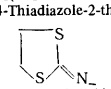
Sometimes the reaction involving addition to the C=S bond (1,2-addition) takes place also with substituted acetylenes[178–181,204], tetracyanoethylene[214], and diphenylketen[215]; likewise one should note that, under the influence of certain reagents, the 1,3-cycloaddition products can rearrange to 1,2-addition products[178,193,220].

Apart from 1,2-dithiole-3-thiones and their analogues, 1,3-dithiolan-2-thione systems and other compounds isoelectronic with them can undergo reactions via the 1,3-dipolar cycloaddition mechanism. During the reaction, ethylenic hydrocarbons or other unsaturated compounds are split off. For example, the reaction of 1,3-dithiolan-2-thiones proceeds as follows:

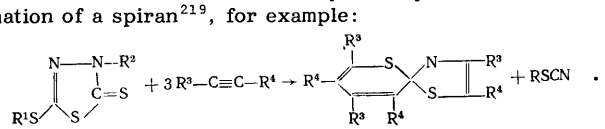


The compounds investigated are listed in Table 2.

Table 2. Nitrogen- and sulphur-containing 1,3-DS.

Compound	Compounds split off	References
 1,3-Dithiolan-2-thione		177, 180, 191, 201, 217, 218
 1,3,4-Dithiazole-2-thione		181, 201, 203
 1,3-Oxathiolan-2-thione		217
 1,3,4-Thiadiazole-2-thione		199, 219
 2-Imino-1,3-dithiolan		199, 219

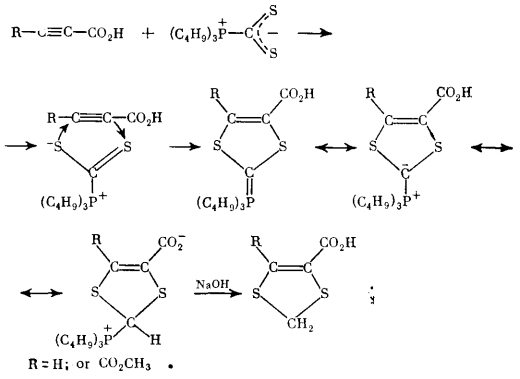
In some cases the product formed initially can combine with a further two molecules of the acetylenic hydrocarbon with formation of a spiran[219], for example:



There exist also other examples of the 1,3-dipolar activity of sulphur-contaning π-systems. Complexes of phosphines with carbon disulphide, which have been known for a very long time, can react with acetylenic hydrocarbons via a mechanism which can be regarded as 1,3-dipolar cycloaddition.

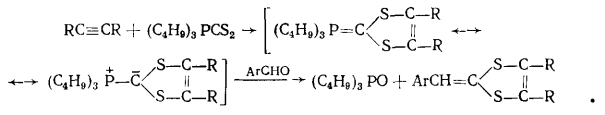
Propiolic and acetylenedicarboxylic acids react with the complex $(C_4H_9)_3 \rightarrow CS_2$ to form a dipolar ion[221,222]. The authors suggest that the reaction proceeds via a concerted single-stage addition and that a dipolar complex with a positive charge on the phosphorus atom and a negative charge on the CS_2 group can be regarded as the 1,3-DS in the given reaction; in the limiting case one can postulate the presence of the C=S double bond and a negative charge on the second sulphur atom.

The reaction between $(C_4H_9)_3P \rightarrow CS_2$ and substituted acetylenes in the presence of aldehydes[223,224], leading to the formation of dithiafulvene derivatives, proceeds via an analogous mechanism:

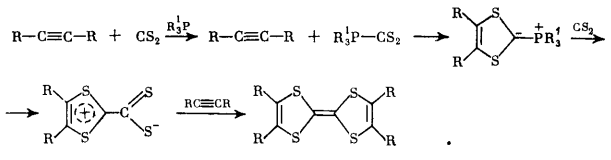


R = H; or CO_2CH_3 .

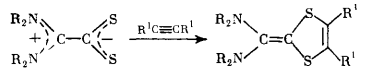
The authors suggest that the intermediate reacts with the aldehyde to form the product of the Wittig reaction:



It is known that acetylenic hydrocarbons react with carbon disulphide to form tetrathiafulvenes[222,223,225-230]. As a rule, this type of reaction takes place in the presence of tertiary phosphines. The formation of fulvenes can be accounted for if one postulates the existence of an intermediate phosphorane, which reacts with carbon disulphide to form a 1,3-dipolar compound[228,229]. The subsequent interaction with a second acetylene molecule gives rise to the final product:



The following reaction probably proceeds via a similar mechanism[193,220]:



The study of reactions in which unsaturated systems containing a heteroatom with an unshared electron pair in the α-position, which are capable of reacting as 1,3-DS, made it possible to formulate new principles for the structure of 1,3-DS.[231] Apparently any system $\ddot{Z}-X=Y$ and $\ddot{Z}-X\equiv Y$, where $\ddot{Z}$ is an element having an unshared electron pair and X and Y are elements capable of forming π-bonds, can behave as a 1,3-DS.[231] The 1,3-dipolar activity of compounds of this type is determined in each individual case by the nature of the elements Z, X, and Y.

Anions of the type $\bar{Z}-X=Y$ or $\bar{Z}-X\equiv Y$ should be more active 1,3-DS, although it is then necessary to add a proton donor to the reaction mass in order to stabilise the anion formed as a result of cyclisation.

The proposed principle for the construction of 1,3-DS can be extended also to the usual Huisgen 1,3-DS. The analogy is particularly clear when the formulae of these 1,3-DS are written as those of carbenoid structures[231].

REFERENCES

1. L.J.Smith, Chem.Rev., **23**, 193 (1938).
2. R.Huisgen, Angew.Chem., **75**, 604 (1963).
3. R.Huisgen, R.Greschy, and J.Sawyer, in "The Chemistry of Alkenes" (Translated into Russian), Izd. Khimiya, Leningrad, 1969, p.181.
4. C.K.Ingold, "Theoretical Principles of Organic Chemistry" ["Structure and Mechanism in Organic Chemistry?"] (Translated into Russian), Izd.Mir, Moscow, 1973.
5. E.N.Tsvetkov and M.I.Kabachnik, Uspekhi Khim., **40**, 177 (1971) [Russ.Chem.Rev., No.1 (1971)].
6. I.P.Romm, E.N.Guryanova, and K.A.Kocheshkov, Tetrahedron, **25**, 2455 (1969).
7. I.P.Romm and E.I.Gur'yanova, Zhur.Obshch.Khim., **38**, 1927 (1968).
8. I.P.Romm, E.M.Sadykova, E.I.Gur'yanova, I.D.Kolme, and K.A.Kocheshkov, Dokl.Akad.Nauk SSSR, **195**, 372 (1970).
9. I.P.Romm, V.V.Kopylov, and E.I.Gur'yanova, Zhur. Strukt.Khim., **11**, 672 (1970).
10. I.P.Gol'dshtein, E.N.Kharlamova, and E.I.Gur'yanova, Zhur.Obshch.Khim., **38**, 1984 (1968).
11. T.Yonezawa, J.Synth.Org.Chem.Japan, **28**, 1197 (1970).
12. D.Rosenberg, J.W.De Haan, and W.Drenth, Rec.Trav. chim., **87**, 1387 (1968).
13. D.P.Craig, A.Maccol, R.S.Nyholm, L.E.Orgel, and L.E.Sutton, J.Chem.Soc., 332 (1954).
14. M.I.Kabachnik, Dokl.Akad.Nauk SSSR, **110**, 395 (1956).
15. M.J.Kabachnik, T.A.Mastrjukowa, T.A.Melentyewa, and A.E.Shipow, Tetrahedron, **9**, 10 (1960).
16. M.I.Kabachnik, T.A.Melentyewa, and T.A.Mastrjukowa, Tetrahedron, **17**, 239 (1962).
17. B.I.Ionin, Doctoral Thesis, Lensovet Leningrad Technological Institute, 1970.
18. R.F.Hudson, "Structure and Mechanism in Organophosphorus Chemistry" (Academic Press, New York, 1965) (Translated into Russian), Izd.Mir, Moscow, 1967.
19. G.V.Bykov, "Elektronnye Zaryady Svyazei v Organicheskikh Soedineniyakh" (The Electronic Bond Charges in Organic Compounds), Izd.Akad.Nauk SSSR, Moscow, 1960.
20. S.S.Batsanov, "Elektrootritsatel'nost' Elementov i Khimicheskaya Svyaz'" (The Electronegativities of Elements and the Chemical Bond), Izd.Sibir.Otd.Akad. Nauk SSSR, 1962.

21. W.Drenth and A.Loewenstein, Rec.Trav.chim., **91**, 635 (1962).
22. W.Drenth and O.Rosenberg, Rec.Trav.chim., **86**, 27 (1967).
23. C.Charrier, W.Chodkiewicz, and P.Cadiot, Bull.Soc. chim.France, 1002 (1966).
24. M.P.Simonnin, Bull.Soc.chim.France, 1774 (1966).
25. M.P.Simonnin, J.Organomet.Chem., **5**, 155 (1966).
26. B.P.Dailey and J.N.Shooley, J.Amer.Chem.Soc., **77**, 3977 (1955).
27. J.R.Cavanaugh and B.P.Dailey, J.Chem.Phys., **34**, 1099 (1961).
28. J.Ficini and C.Barbara, Bull.Soc.chim.France, 871 (1964).
29. W.Drenth, Colloq.int.CNRS, No.182, 91 (1970); Ref.Zhur.Khim., 6B496 (1971).
30. A.Saika and C.P.Slichter, J.Chem.Phys., **22**, 26 (1954).
31. I.P.Gol'dshtein, E.N.Gur'yanova, and K.A.Kocheskov, Dokl.Akad.Nauk SSSR, **138**, 1099 (1961).
32. I.P.Romm and E.N.Gur'yanova, Dokl.Akad.Nauk SSSR, **171**, 877 (1966).
33. H.Saot, K.Hirota, and S.Nagatura, Bull.Chem.Soc. Japan, **38**, 962 (1965).
34. H.H.Jaffé and L.D.Freedman, J.Amer.Chem.Soc., **74**, 1069 (1952).
35. C.N.R.Rao, J.Ramachandran, S.Somasekhara, and T.V.Kajakumar, Nature, **183**, 1476 (1959).
36. G.Shaw, J.K.Becconsall, R.M.Canadine, and R.Murray, Chem.Comm., 425 (1966).
37. B.I.Ionin, A.A.Petrov, and G.M.Bogolyubov, Uspekhi Khim., **36**, 587 (1967).
38. M.I.Kabachnik, Tetrahedron, **20**, 655 (1964).
39. W.Drenth, G.L.Hekkert, and B.Z.Zwanenberg, Rec. Trav.chim., **81**, 313 (1962).
40. R.Fuks, R.Buijle, and H.G.Viehe, Angew.Chem., **78**, 594 (1966).
41. H.G.Viehe, R.Fuks, and M.Roinsteinn, Angew.Chem., **76**, 571 (1964).
42. R.Fusko, G.Bianchetti, and D.Pocar, Gazzetta, **91**, 1233 (1961).
43. M.E.Kuchne and S.J.Wegver, J.Org.Chem., **29**, 1582 (1964).
44. G.Bianchetti, D.Pocar, and D.C.Piero, Gazzetta, **93**, 1714 (1963).
45. G.Bianchetti, D.Pocar, and D.C.Piero, Gazzetta, **93**, 1726 (1963).
46. P.Caramella and P.Bianchessi, Tetrahedron, **26**, 5773 (1970).
47. N.Yujuro, F.Fumio, and T.Yoshita, Bull.Chem.Soc. Japan, **40**, 1740 (1967).
48. N.Yujuro, F.Fumio, and T.Yoshita, Bull.Chem.Soc. Japan, **43**, 3001 (1970).
49. O.Fsuje, M.Tashiro, and Y.Nishihara, Tetrahedron Letters, 3769 (1967).
50. D.F.Bettenetti, A.Codoli, and S.A.Omodoi, Ricerca Sci., **38**, 806 (1968).
51. R.Huisgen, R.Knorr, L.Mobius, and G.Sreimies, Chem.Ber., **98**, 4014 (1965).
52. P.Grünanger, P.V.Finzi, and E.Falbori, Gazzetta, **90**, 413 (1960).
53. P.V.Finzi, C.Skotti, and A.Quilico, Atti Accad.naz. Lincei Rend.Classe Sci.fis.mat.nat., **41**, 204 (1966).
54. P.Grünanger and M.P.Langella, Gazzetta, **89**, 1784 (1959).
55. P.Bravo, G.Gaudiano, A.Quilico, and A.Ricco, Gazzetta, **91**, 47 (1961).
56. G.Gaudiano, A.Ricco, and R.Merlin, Gazzetta, **89**, 2466 (1959).
57. P.Grünanger, Atti Accad.naz.Lincei Rend.Classe Sci. fis.mat.nat., **24**, 163 (1958).
58. P.Grünanger and P.V.Finzi, Atti Accad.naz.Lincei Rend.Classe Sci.fis.mat.nat., **31**, 128 (1961).
59. S.W.Groen and J.F.Arens, Rec.Trav.chim., **80**, 879 (1961).
60. P.Paul and S.Schiltchoff, Bull.Soc.chim.France, 4179 (1967).
61. R.Huisgen, R.Sustmann, G.Wallbillich, Chem.Ber., **100**, 1786 (1967).
62. R.Huisgen, R.Groshey, H.Seidl, and H.Hanck, Chem. Ber., **100**, 2559 (1967).
63. W.S.Wadsworth and W.D.Emmons, J.Amer.Chem.Soc., **84**, 1316 (1962).
64. W.S.Wadsworth and W.D.Emmons, J.Org.Chem., **32**, 1279 (1967).
65. M.Busch, Ber., **34**, 2311 (1901).
66. W.Lwowski, R.A.De Maurac, R.A.Murray, and L.Lunow, Tetrahedron Letters, 425 (1971).
67. R.Huisgen, H.Seidl, and J.Bruhning, Chem.Ber., **102**, 1102 (1969).
68. R.Huisgen, J.Org.Chem., **33**, 2291 (1968).
69. W.J.Middleton and C.G.Krespan, J.Org.Chem., **30**, 1398 (1965).
70. K.Burger, J.Fehn, and W.Thenn, Angew.Chem., **85**, 541 (1973).
71. T.P.Forshaw and A.E.Tipping, Chem.Comm., 816 (1969).
72. T.P.Forshaw and A.E.Tipping, J.Chem.Soc.C, 2404 (1971).
73. T.P.Forshaw and A.E.Tipping, J.Chem.Soc., Perkin Trans.I, 1059 (1972).
74. S.E.Armstrong and A.E.Tipping, J.Fluor.Chem., **3**, 119 (1973).
75. S.E.Armstrong and A.E.Tipping, J.Chem.Soc., Perkin Trans.I, 538 (1975).
76. S.E.Armstrong and A.E.Tipping, J.Chem.Soc., Perkin Trans.I, 1411 (1975).
77. K.Burger, W.Thenn, and A.Gieren, Angew.Chem., **86**, 481 (1974).
78. A.Gieren, P.Narayanan, K.Burger, and W.Thenn, Angew.Chem., **86**, 482 (1974).
79. K.Burger, W.Thenn, H.Schickaneder, and H.Peuker, Angew.Chem., **86**, 483 (1974).
80. K.Burger, W.Thenn, R.Rauch, and H.Schickaneder, Angew.Chem., **86**, 484 (1974).
81. K.Burger, W.Thenn, R.Rauch, H.Schickaneder, and A.Gieren, Chem.Ber., **108**, 1460 (1975).
82. K.Burger, H.Schickaneder, and W.Thenn, Tetrahedron Letters, 1125 (1975).
83. K.Burger and H.Schickaneder, Tetrahedron Letters, 2911 (1975).
84. K.Burger, W.Thenn, and H.Schickaneder, Chem.Ber., **108**, 1468 (1975).
85. K.Burger, H.Schickaneder, and M.Pinzel, Annalen, 30 (1976).
86. R.Huisgen, R.Fleischmann, and A.Eckell, Tetrahedron Letters, 1 (1960).
87. R.Huisgen and A.Eckel, Tetrahedron Letters, 5 (1960).
88. H.Dorn and A.Otto, Chem.Ber., **101**, 3287 (1968).
89. S.E.Armstrong, T.P.Forshaw, and A.E.Tipping, J.Chem.Soc., Perkin Trans.I, 1902 (1975).
90. K.Houk, Acc.Chem.Res., **8**, 361 (1975).
91. V.A.Tartakovskii and I.E.Chlenov, Zhur.Vses.Khim. Obshch.im.Mendeleeva, **22**, 252 (1977).
92. T.Wagner-Jauregg, Ber., **63**, 3219 (1930).
93. J.Van Alphen, Rec.Trav.chim., **61**, 892 (1942).

94. D.B.Dutt and P.C.Guha, J.Indian Chem.Soc., **27**, 151 (1950).
95. J.Kovacs, V.Bruckner, and J.Kandel, Acta Chim.Acad. Sci.Hung., **1**, 230 (1951).
96. M.Haring and T.Wagner-Jauregg, Helv.Chim.Acta, **40**, 852 (1957).
97. H.Günther and S.W.Tam, Helv.Chim.Acta, **52**, 1672 (1969).
98. K.Burger, S.Tremmel, and H.Schickaneder, J.Fluor. Chem., **7**, 471 (1976).
99. I.G.Kolokol'tseva, V.N.Chistokletov, and A.A.Petrov, Zhur.Obshch.Khim., **38**, 2819 (1968).
100. V.V.Kosovtsev, V.N.Chistokletov, and A.A.Petrov, Zhur.Obshch.Khim., **40**, 2570 (1970).
101. V.V.Kosovtsev, V.N.Chistokletov, and A.A.Petrov, Zhur.Obshch.Khim., **41**, 2463 (1971).
102. I.A.Stepanov, V.I.Zakharov, V.N.Chistokletov, and A.A.Petrov, Zhur.Obshch.Khim., **46**, 2463 (1976).
103. I.G.Kolokol'tseva, V.N.Chistokletov, and A.A.Petrov, Zhur.Obshch.Khim., **40**, 574 (1970).
104. V.V.Kosovtsev, V.N.Chistokletov, and A.A.Petrov, Zhur.Obshch.Khim., **40**, 2132 (1970).
105. S.P.Konotopova, V.N.Chistokletov, and A.A.Petrov, Zhur.Obshch.Khim., **41**, 235 (1971).
106. S.P.Konotopova, V.N.Chistokletov, and A.A.Petrov, Zhur.Obshch.Khim., **42**, 2412 (1971).
107. S.P.Konotopova, V.N.Chistokletov, and A.A.Petrov, Zhur.Obshch.Khim., **43**, 987 (1973).
108. N.P.Ivanova, V.N.Chistokletov, L.A.Tamm, and A.A.Petrov, Zhur.Obshch.Khim., **47**, 763 (1977).
109. L.A.Tamm, V.N.Chistokletov, and A.A.Petrov, Zhur.Obshch.Khim., **42**, 1926 (1972).
110. V.V.Kosovtsev, V.N.Chistokletov, and A.A.Petrov, Zhur.Obshch.Khim., **39**, 223 (1969).
111. V.V.Kosovtsev, V.N.Chistokletov, and A.A.Petrov, Zhur.Obshch.Khim., **41**, 2649 (1971).
112. L.A.Tamm, V.N.Chistokletov, and A.A.Petrov, Zhur. Obshch.Khim., **42**, 1864 (1972).
113. L.A.Tamm, V.N.Chistokletov, and A.A.Petrov, Zhur. Obshch.Khim., **43**, 2178 (1973).
114. L.A.Tamm, V.N.Chistokletov, E.S.Turbanova, and A.A.Petrov, Zhur.Obshch.Khim., **44**, 1468 (1974).
115. V.A.Galishev, V.N.Chistokletov, and A.A.Petrov, Zhur.Obshch.Khim., **42**, 1876 (1972).
116. V.A.Galishev, V.N.Chistokletov, and A.A.Petrov, Zhur.Obshch.Khim., **43**, 1473 (1973).
117. V.A.Galishev, V.N.Chistokletov, and A.A.Petrov, Zhur.Obshch.Khim., **45**, 1695 (1975).
118. V.A.Galishev, V.N.Chistokletov, A.A.Petrov, and L.A.Tamm, Zhur.Obshch.Khim., **43**, 1470 (1973).
119. K.S.Mingaleva, V.N.Chistokletov, V.V.Kosovtsev, and A.A.Petrov, Zhur.Obshch.Khim., **41**, 862 (1971).
120. V.V.Kosovtsev, T.N.Timofeeva, B.I.Ionin, and V.N.Chistokletov, Zhur.Obshch.Khim., **41**, 2638 (1971).
121. L.Horner, I.Ertel, H.D.Ruprecht, and O.Belovsky, Chem.Ber., **103**, 1582 (1970).
122. I.A.Stepanov, V.N.Chistokletov, and A.A.Petrov, Dokl.Akad.Nauk SSSR, **220**, 127 (1975).
123. A.N.Pudovik, T.Kh.Gazizov, and A.M.Pashinkin, Zhur.Obshch.Khim., Symposium, "Khimiya Organicheskikh Soedinenii Fosfora" (The Chemistry of Organic Phosphorus Compounds), 1967.
124. P.I.Alimov and L.V.Cheplanova, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 939 (1956).
125. A.N.Pudovik and T.Kh.Gazizov, Zhur.Obshch.Khim., **37**, 706 (1967).
126. L.V.Nesterov, R.A.Sabirova, and I.E.Krepysheva, Zhur.Obshch.Khim., **39**, 1943 (1969).
127. A.M.Aguiar, K.C.Hansen, and G.S.Reddy, J.Amer. Chem.Soc., **89**, 3067 (1967).
128. A.M.Aguiar and K.C.Hansen, J.Amer.Chem.Soc., **89**, 4235 (1967).
129. M.S.Chatta and A.M.Aguiar, J.Org.Chem., **38**, 1611 (1973).
130. A.M.Aguiar, J.R.S.Irelan, G.W.Prejean, J.P.John, and C.J.Morrow, J.Org.Chem., **34**, 2681 (1936).
131. A.M.Aguiar, G.W.Prejean, J.R.S.Irelan, and G.J.Morrow, J.Org.Chem., **34**, 4024 (1969).
132. R.D.Rieke, R.A.Copenhafer, A.M.Aguiar, M.S.Chatta, and J.C.Williams, Chem.Comm., 1130 (1972).
133. R.D.Rieke, R.A.Copenhafer, A.M.Aguiar, M.S.Chatta, and J.C.Williams, J.Electroanal.Chem., **42**, 309 (1973).
134. E.E.Schweizer and L.D.Smucker, J.Org.Chem., **31**, 3146 (1966).
135. M.E.Savage and S.Trippett, J.Chem.Soc.C, 591 (1968).
136. A.N.Hughes and M.Davies, Chem.Ind.(London), 138 (1969).
137. G.Witting and E.Benz, Chem.Ber., **92**, 1999 (1959).
138. A.Schmidpeter and W.Zeiss, Chem.Ber., **104**, 1199 (1971).
139. A.Schmidpeter and W.Zeiss, Angew.Chem., **83**, 397 (1971).
140. A.Schmidpeter, W.Zeiss, and H.Eckert, Z.Naturforsch., **B27**, 769 (1972).
141. A.N.Pudovik, I.V.Gur'yanova, and V.P.Kakurina, Zhur.Obshch.Khim., **41**, 1976 (1971).
142. A.N.Pudovik, I.V.Konovalova, V.P.Kakurina, L.A.Burnaeva, and T.A.Komissarova, Zhur.Obshch. Khim., **43**, 256 (1973).
143. I.V.Konovalova, L.A.Burnaeva, and A.N.Pudovik, Zhur.Obshch.Khim., **44**, 261 (1974).
144. A.N.Pudovik, I.V.Konovalova, V.P.Kakurina, and L.A.Burnaeva, Zhur.Obshch.Khim., **43**, 553 (1973).
145. I.V.Konovalova, L.A.Burnaeva, G.S.Temnikova, and A.N.Pudovik, Zhur.Obshch.Khim., **45**, 1003 (1975).
146. I.V.Konovalova, L.A.Burnaeva, L.S.Yuldasheva, and A.N.Pudovik, Zhur.Obshch.Khim., **44**, 2408 (1974).
147. I.V.Konovalova, L.A.Burnaeva, and A.N.Pudovik, Zhur.Obshch.Khim., **45**, 2558 (1975).
148. R.I.Tarasova, N.M.Kislitsina, and A.N.Pudovik, Zhur.Obshch.Khim., **41**, 1972 (1971).
149. I.V.Konovalova, L.A.Burnaeva, and A.N.Pudovik, Zhur.Obshch.Khim., **44**, 743 (1974).
150. L.S.Rodionova, V.A.Galishev, V.N.Chistokletov, and A.A.Petrov, Zhur.Obshch.Khim., **45**, 1652 (1975).
151. S.I.Radchenko, V.N.Chistokletov, and A.A.Petrov, Zhur.Org.Khim., **1**, 51 (1965).
152. F.Challenger, E.A.Mason, E.C.Holdsworth, and R.Emmett, J.Chem.Soc., 292 (1953).
153. O.P.Strausz, J.Fout, E.L.Dedio, P.Kebarle, and U.E.Gummig, J.Amer.Chem.Soc., **89**, 4805 (1967).
154. C.G.Krespan and D.C.England, J.Org.Chem., **33**, 1850 (1968).
155. R.Mayer and K.Gewald, Angew.Chem., **79**, 298 (1967).
156. R.Mayer, B.Gebhardt, J.Fabian, and A.K.Müller, Angew.Chem., **76**, 143 (1964).
157. R.Mayer, B.Hunger, R.Prousa, and A.K.Müller, J.prakt.Chem., **35**, 294 (1967).
158. R.Mayer and B.Gebhardt, Chem.Ber., **97**, **1298** (1964).
159. M.Schmidt and V.Potschka, Naturwiss., **50**, 302 (1963).
160. L.Brandsma, H.Wijers, and J.E.Arens, Rec.Trav. chim., **81**, 583 (1962).
161. L.Brandsma, H.Wijers, and C.Jonker, Rec.Trav.chim., **83**, 208 (1964).
162. L.Bransma, Rec.Trav.chim., **83**, 307 (1964).

163. R.Mayer and A.K.Muller, Z.Chem., **4**, 384 (1964).
164. H.Spies, K.Gewald, and R.Mayer, J.prakt.Chem., **313**, 804 (1971).
165. M.L.Petrov, V.N.Chistokletov, and A.A.Petrov, Zhur. Org.Khim., **12**, 2035 (1976).
166. M.L.Petrov, L.S.Rodionova, and A.A.Petrov, Zhur. Org.Khim., **13**, 1564 (1977).
167. W.Ried and M.Wegwitz, Annalen, 89 (1975).
168. O.Kirmse and L.Horner, Annalen, **614**, 4 (1958).
169. V.Franzen, Annalen, **602**, 199 (1957).
170. P.Jacobson and H.Janssen, Annalen, **277**, 209 (1893).
171. R.Huisgen and V.Weberndorfer, Experientia, **17**, 566 (1961).
172. S.Hoff, A.P.Blok, and E.Zwanenberg, Rec.Trav.chim., **92**, 879 (1973).
173. S.Hoff, A.P.Blok, and E.Zwanenberg, Rec.Trav.chim., **92**, 890 (1973).
174. S.Hoff and A.P.Blok, Rec.Trav.chim., **93**, 75 (1974).
175. S.Hoff and E.Zwanenberg, Rec.Trav.chim., **92**, 929 (1973).
176. H.Behringer and R.Wiedenmann, Tetrahedron Letters, 3705 (1965).
177. D.B.J.Easton and D.Leaver, Chem.Comm., 585 (1965).
178. H.Davy, M.Demuynck, D.Paquer, A.Rouessag, and J.Vialle, Bull.Soc.chim.France, 1150 (1966).
179. C.Portail and J.Vialle, Bull.Soc.chim.France, 3187 (1966).
180. H.Behringer, D.Bender, J.Falkenberg, and R.Wiedenmann, Chem.Ber., **101**, 1428 (1968).
181. H.Davy, M.Demyunck, D.Paquer, A.Rouessag, and J.Vialle, Bull.Soc.chim.France, 2057 (1968).
182. M.Stavaux and N.Lozac'h, Bull.Soc.chim.France, 4273 (1968).
183. M.Stavaux and N.Lozac'h, Bull.Soc.chim.France, 4184 (1969).
184. J.M.Buchshriber, D.M.McKinnon, and M.Ahmed, Canad. J.Chem., **47**, 2039 (1969).
185. M.Ahmed, J.M.Buchshriber, and D.M.McKinnon, Canad. J.Chem., **48**, 1991 (1970).
186. N.Lozac'h, Adv.Heterocycl.Chem., **13**, 161 (1971).
187. D.M.McKinnon and J.M.Buchshriber, Canad.J.Chem., **49**, 3299 (1971).
188. G.Hervien, P.Rioult, and J.Vialle, Bull.Soc.chim. France, 4375 (1971).
189. G.Hervien, P.Rioult, and J.Vialle, Bull.Soc.chim. France, 4380 (1971).
190. M.Stavaux, Bull.Soc.chim.France, 4426 (1971).
191. D.B.J.Easton, D.Leaver, and T.J.Rawlings, J.Chem. Soc., Perkin Trans.I, 41 (1972).
192. K.T.Pedersen, N.L.Huaman, and J.Moeller, Acta Chem.Scand., **26**, 565 (1972).
193. H.Davy and J.Vialle, Compt.rend., **C**, **275**, 625 (1972).
194. C.T.Pedersen, Acta Chem.Scand., **B28**, 367 (1974).
195. J.-M.Decrouen, D.Paquer, and R.Pou, Compt.rend., **C**, **279**, 259 (1974).
196. K.T.Pedersen, H.Davy, J.Moeller, and J.Vialle, Acta Chem.Scand., **B28**, 964 (1974).
197. H.Davy and J.Vialle, Bull.Soc.chim.France, 1435 (1975).
198. H.Davy and J.-M.Decrouen, Bull.Soc.chim.France, 115 (1976).
199. D.Paquer and R.Pou, Bull.Soc.chim.France, 120 (1976).
200. K.T.Pedersen, H.Davy, E.Wolff-Jensen, J.Moeller, and J.Vialle, Acta Chem.Scand., **B30**, 471 (1976).
201. H.Behringer and D.Deichmann, Tetrahedron Letters, 1013 (1967).
202. A.Grandin and J.Vialle, Bull.Soc.chim.France, 1851 (1967).
203. D.Noel and J.Vialle, Bull.Soc.chim.France, 2239 (1967).
204. G.Long and J.Vialle, Bull.Soc.chim.France, 2865 (1967).
205. J.W.McDonald and D.M.McKinnon, Canad.J.Chem., **45**, 1225 (1967).
206. H.Behringer, J.Kilger, and R.Wiedenmann, Tetrahedron Letters, 1185 (1968).
207. G.F.Bachers, D.M.McKinna, and J.M.Buchshriber, Canad.J.Chem., **50**, 2568 (1972).
208. N.S.Chauhan, M.E.Hassan, and D.M.McKinnon, Canad. J.Chem., **52**, 1738 (1974).
209. H.Behringer and D.Weber, Chem.Ber., **97**, 2567 (1964).
210. F.Boberg and J.Knoop, Annalen, **708**, 148 (1967).
211. G.Le Coustumer and J.Moeller, Compt.rend., **C**, **270**, 433 (1970).
212. J.Poirier, Bull.Soc.chim.France, 1203 (1968).
213. M.Maquet, J.Poirier, and J.Teste, Bull.Soc.chim. France, 1503 (1970).
214. A.Rouessac and J.Vialle, Bull.Soc.chim.France, 2054 (1968).
215. P.Rioult and J.Vialle, Bull.Soc.chim.France, 2883 (1967).
216. S.Davidson and D.Leaver, Chem.Comm., 540 (1972).
217. B.R.O'Connor and F.N.Jones, J.Org.Chem., **35**, 2002 (1970).
218. C.M.Pittman, M.Narita, and J.E.Liang, J.Org.Chem., **41**, 2855 (1976).
219. C.Gueden and J.Vialle, Bull.Soc.chim.France, 270 (1973).
220. H.Behringer and J.Falkenberg, Tetrahedron Letters, 1865 (1967).
221. C.U.Pittman and M.Narita, Chem.Comm., 960 (1975).
222. C.U.Pittman and M.Narita, Bull.Chem.Soc.Japan, **49**, 1996 (1976).
223. H.D.Hartzler, J.Amer.Chem.Soc., **93**, 4961 (1971).
224. H.D.Hartzler, US P.3 781 281 (1973); Chem.Abs., **80**, 70 796 (1974).
225. H.D.Hartzler, J.Amer.Chem.Soc., **92**, 1412 (1970).
226. H.D.Hartzler, J.Amer.Chem.Soc., **92**, 1413 (1970).
227. A.Krebs and H.Kimling, Angew.Chem., Int.Ed., **10**, 509 (1971).
228. H.D.Hartzler, J.Amer.Chem.Soc., **95**, 4379 (1973).
229. L.R.Melby, H.D.Hartzler, and W.A.Sheppard, J.Org. Chem., **39**, 2456 (1974).
230. H.D.Hartzler, US P.3 876 662 (1974); Chem.Abs., **83**, 58 890 (1975).
231. V.N.Chistokletov and A.A.Petrov, Zhur.Obshch.Khim., **42**, 1865 (1972).

Lensovet Leningrad
Technological Institute

Leningrad Technological Institute
of the Cellulose and Paper Industry