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1,3-Dipolar Cycloaddition—A General Method of Synthesis of Five-membered Nitrogen-containing Heterocycles with Organoelemental Substituents

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The review deals with the possibilities and advances in the application of the method of 1,3-dipolar cycloaddition to the synthesis of five-membered nitrogen-containing heterocycles with organoelemental substituents.
The bibliography includes 203 references.

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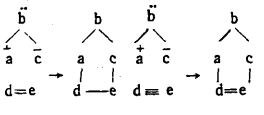
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I. INTRODUCTION

Heterocyclic compounds with organoelemental substituents play a significant role in modern chemistry: they serve as monomers for the synthesis of heterochain metal-containing oligomers and polymers,[1-5] as ligands for complex formation,[1,2,6,7] and as models for the solution of important theoretical problems, for example in the study of elementotropic processes in the series of five-membered nitrogen-containing heterocycles.[8-14] They are of interest as biologically active compounds[15-19] and are also used for other purposes.[15]

The most widely used methods of synthesis of heterocycles with organoelements substituents are based on the introduction of organometallic fragements into complete heterocyclic systems by direct[20-26] or covalent[27-29] metallation, as a result of the exchange of a halogen for the metal,[21,23,25,26] by the interaction of organometallic derivatives of heterocycles with metal salts,[30-33] via the reaction of the carbonylmetallate anion with halogeno-derivatives of heterocycles,[34-39] etc.

At the same time it is known that heterocycles can be synthesised by constructing the ring from simpler starting materials.[40-44] Methods such as different types of condensations and cyclisations[42-48] or recyclisation[49-51] are therefore applicable also to the synthesis of heterocycles with organoelemental substituents. Such procedures include also the 1,3-dipole addition (1,3-DCA),[52-66] which takes place on addition of two addends: a 1,3-dipole and a dipolarophile. The organoelemental groups can enter into the composition of 1,3-dipoles (diazoalkanes, azides, nitrile oxides, nitrones, nitrile imines, etc.) and dipolarophiles (olefins, acetylenes, nitriles, isonitriles, and heterocumulenes).[56,57,63-66] The general principle governing the construction of five-membered heterocycles by the 1,3-DCA method can be represented as follows on the basis of Huigen's ideas:[52-55]



Thus the type of heterocycle formed in the 1,3-DCA reaction is determined mainly by the nature of the 1,3-dipole ($\overset{+}{a}-\ddot{b}-\bar{c}$), while the dipolarophile (d = e or d ≡ e) determines the degree of saturation of the heterocyclic system. This is why we thought it useful to arrange the description of the data relevant to the present review by taking into account primarily the character of the 1,3-dipole. At the same time one should bear in mind that, when dipolarophiles with heteroatoms are used, the latter can enter into the composition of the heterocycle and hence can alter its type.[56,57,64]

1,3-DCA makes it possible to obtain a wide variety of heterocyclic systems containing the N and O heteroatoms and organoelemental substituents. Since the latter can enter into the composition of the molecules of 1,3-dipole and dipolarophiles, wide prospects arise for the synthesis of N- and C-substituted heterocycles. Whereas the syntheses of heterocycles with organoelemental substituents at the nitrogen atom from complete heterocyclic systems are comparatively easy processes (see, for example, Refs.1, 2, 21, 23, 25, 26), the syntheses of the analogous C-substituted heterocycles give rise to serious difficulties.[67,68] This is why 1,3-DCA is especially useful for the preparation of C-organoelemental derivatives of heterocycles and also of a series of heterocyclic systems with organoelemental substituents in exocyclic fragments which are difficult to obtain.

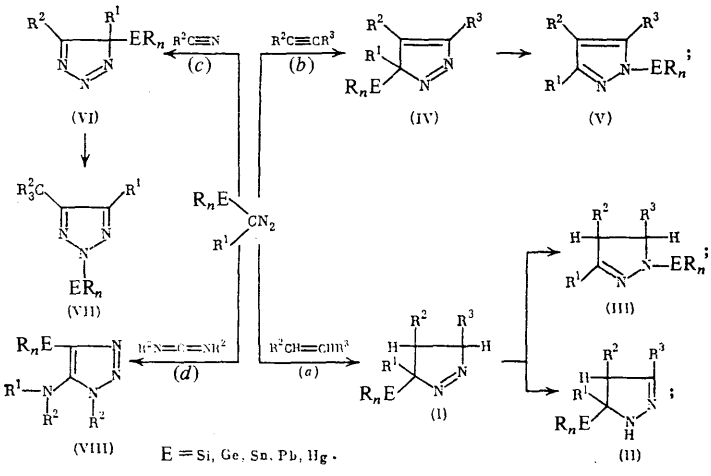
II. SYNTHESES WITH PARTICIPATION OF DIAZOALKANES

1. Synthesis of Heterocycles from Diazoalkanes with Organoelemental Substituents

In order to obtain five-membered nitrogen-containing heterocycles, diazoalkanes with organoelemental substituents are widely used[54-56,63,69,70] (Scheme 1). These make it possible to obtain R_nEN- and R_n-EC-substituted pyrazolines (on interaction with olefins—pathway a), pyrazolenines and

pyrazoles (in reactions with acetylene—pathway *b*), and triazoles (in reactions with participation of nitriles—pathway *c*, or when nitrogen-containing heterocumulenes, for example carbodiimide, are used as the dipolarophile—pathway *d*).

Scheme 1



(a) Pyrazolines

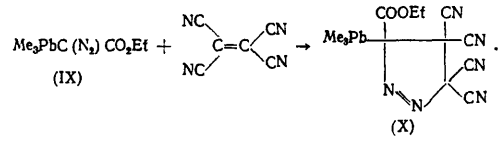
The 1,3-DCA of α-silyldiazoalkanes to acrylonitrile, methyl acrylate, ethyl fumarate, and other dipolarophiles with an activated ethylenic bond has been studied systematically.[63,71–76] The 1,3-DCA reactions considered proceed via intermediate products detected in a whole series of instances. Thus it has been shown from ^{1}H NMR spectra[74,76] that the primary products in Scheme 1 (pathway *a*) are 3-organosilyl-Δ^1-pyrazolines (I). Since the majority of Δ^1-pyrazolines readily isomerise to Δ^2-pyrazolines,[77] the isomerisation of the heterocycles (I) leads to compounds (II), if the process is accompanied by the 1,3-transfer of a proton, or to compounds (III) as a result of the 1,3-migration of R_3Si. A rearrangement of the first type is characteristic of diazoalkanes $R_3SiC(N_2)R^1$ for R^1 = H or Me and one of the second types occurs when R^1 = Ph or COOEt.[73,74,76] It has been established for diethyl fumarate[76] that the relative rate of cycloaddition of a diazoalkane diminishes in the sequence

$$\underset{1}{Me_3SiC(N_2)Me} > \underset{2\cdot10^{-2}}{Me_2SiC(N_2)Ph} > \underset{2,5\cdot10^{-3}}{Ph_2SiC(N_2)Me} > \underset{2,5\cdot10^{-4}}{Ph_2SiC(N_2)Ph} > \underset{2,5\cdot10^{-7}}{Me_3SiC(N_2)COOEt}$$

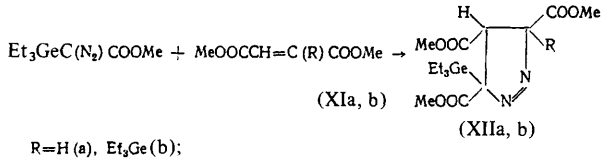
It is believed that the rate of such reactions depends on the degree of p_π, d_π conjugation of the silicon atoms and the diazo-group in silyl diazoalkanes and on steric factors in the transition state of the cycloaddition reaction.[76]

It has also been shown[74,76] that (1) the 1,3-migration of a hydrogen atom [(I)–(II)] is accelerated by electron-accepting groups R^3 and is catalysed by traces of water or amines and (2) that the rate of isomerisation reaction (I) → (II) diminishes as the electron-accepting character of the substituent R^1 becomes more pronounced: Me ≥ Ph > COOEt.

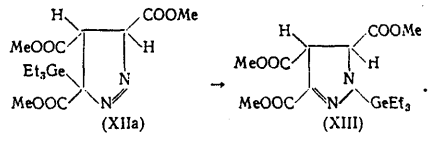
The 1,3-DCA of ethyl trimethylplumbyldiazoacetate (IX) to a wide variety of alkenedipolarophiles, namely acrylonitrile, acetylenedicarboxylic acid, dimethyl maleate, and tetracyanoethylene takes place in accordance with Scheme 1 (pathway *a*).[78] For example, the 1,3-DCA involving tetracyanoethylene (in ether at −20 °C) results in the formation of a derivative of tetracyanotrimethylplumbylpyrazoline (X) in 52% yield:



The 1,3-DCA of methyl triethylgermyldiazoacetate to dimethyl fumarate and 1-triethylgermyl-1,2-ethylenedicarboxylic acids (XIa, c) leads to the Δ^1-pyrazolines (XIIa, b).[79] Among them, the monogermylated adduct (XIIa) isomerises to the Δ^2-pyrazoline (XIII) as a result of the 1,3-migration of the Et_3Ge group. It has been noted that the ester (XIb) is a mixture of the *Z*- and *E*-isomers and that the adduct (XIIb) is therefore also a mixture of isomeric Δ^2-pyrazolines:



R=H (a), Et_3Ge (b);

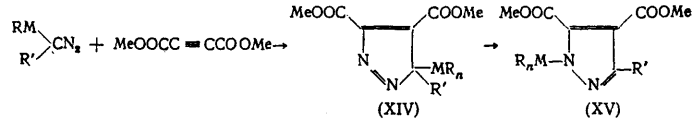


Previously the same authors[80] had obtained bis(triethylgermyl)pyrazolines by the joint thermolysis of ethyl triethylgermyldiazoacetate and ethyl diazoacetate.

(b) Pyrazolenines and Pyrazoles

Organoelemental diazomethanes reacting as 1,3-dipoles in interactions involving dipolarophiles containing the acetylenic bond can give rise in the first stage to a pyrazolenine (IV) (Scheme 1, pathway *b*), which is converted into the pyrazole (V) in the course of the sigmatropic rearrangement.

Progress in the development of the methods of synthesis of a wide variety of organometallic diazoalkanes (derivatives of tin,[81] germanium, lead, Group IIB elements,[82] mercury,[83] Group VB elements,[84] thallium,[85] etc.[63,70]) made it possible to introduce them into the 1,3-DCA reaction. For example, the reactions of metallated diazoalkanes $R_nMC(N_2)R'$ with dimethyl acetylenedicarboxylate have been investigated:



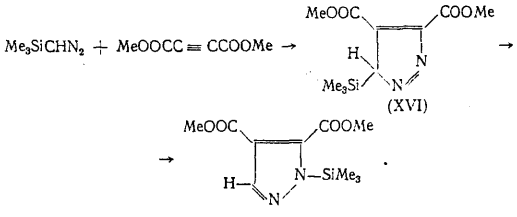
R_nM=Me_2Sn, Me_3Pb, Me_2Sb, Me_2Bi, MeHg, HgC(N_2)COOEt, HgC(N_2)COMe; R′=R_nM, COOEt, COMe, COPh.

The pyrazolenine (XIV), which readily isomerises to the pyrazole (XV) with 1,3-migration of the R_nM fragments, is formed in the course of the reaction.

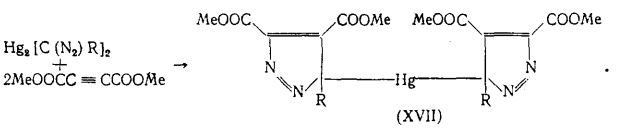
However, it has been found that not all the organometallic diazoalkanes described enter into the 1,3-DCA reaction with acetylenic dipolarophiles: the amount of ionic character of the bond and the bulk of the substituents in the 1,3-dipoles play a significant role in these reactions. Thus, whereas the organoelemental diazoalkanes of the type $R_nEC(N_2)R^1$, where E = Si,[63,70,71,75,86] Sn,[63,87] Pb,[78] Hg,[87] etc.,[63] react with alkynes, the analogous arsenic derivatives do not enter into the 1,3-DCA reaction due to steric hindrance[63] and the

thallium derivative, namely bis(dimethylthallium)diazomethane, does not react because it has an ionic structure.[85]

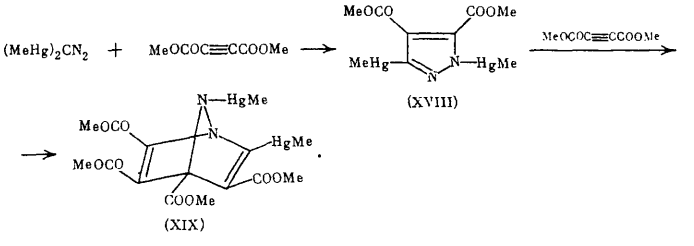
It has also been shown that sigmatropic rearrangements of the type (IV) → (V) are observed also for the 1,3-DCA of $(Me_3Sn)_2CN_2$ and $Me_3SiC(N_2)R$ to MeOOCC≡CCOOMe and are characterised by a decrease of the capacity of the group R for migration in the sequence Me_3Sn > Me_3Si > H > COOEt. For example, the isomerisation of the pyrazolenine (XVI) is accompanied by the migration of Me_3Si and not of a hydrogen atom as had been suggested earlier:[75]



When organoelemental bisdiazoalkanes were involved in the reactions considered above bisheterocyclic systems were isolated. For example, the mercuribisdiazoalkane $Hg[C(N_2)R]_2$, in which R = COOEt or COMe, reacts with dimethyl acetylenedicarboxylate to form the dipyrazoleninemercury derivatives (XVII):[87]



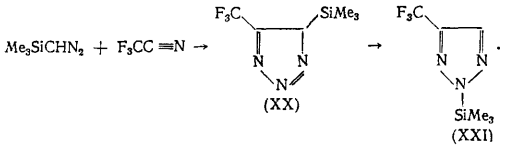
In an analogous reaction bis(methylmercuri)diazomethane is converted into the 1,3-bis(methylmercuri)pyrazole (XVIII), which gives rise to the *CN*-bis(methylmercuri)-derivative of diazanorbornadiene (XIX) on interaction with a second molecule of MeOCOC≡CCOOMe:[87]



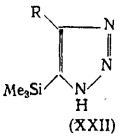
α-Metallated diazoalkanes hardly react with phenylacetylene, diphenylacetylene, sodium acetylenedicarboxylate and bis(trimethylstannyl)acetylene.[63] The causes of such behaviour of the above dipolarophiles are obscure.

(c) Triazoles

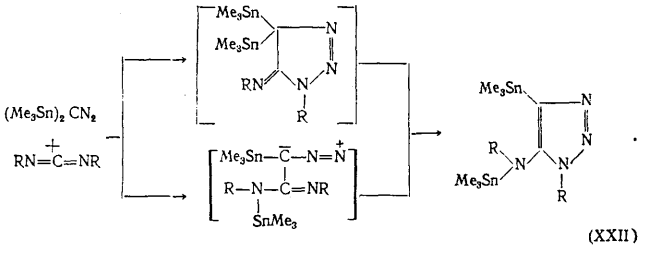
The 1,3-DCA of organoelemental diazoalkanes to nitriles (Scheme 1, pathway *c*) and carbodiimide (Scheme 1, pathway *d*) results in the formation of the triazoles (VI)–(VIII). In particular, it has been established[88] that the interaction of trimethylsilyldiazomethane with trifluoroacetonitrile produces the adduct (XX) which is readily converted into 5-trifluoromethyl-2-trimethylsilyl-1,2,3-triazole (XXI):



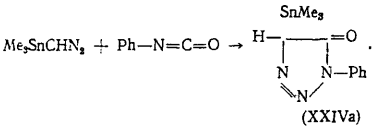
In contrast to the *N*-trimethylsilyltriazoles (XXI) indicated above, the C-substituted triazoles (XXII) with R = Pr, t-Bu, Ph, $PhCH_2$, 1-naphthyl, 2-pyridyl, 1-isoquinolinyl, EtS, and PhO have been obtained via the 1,3-DCA reaction from the lithium salts of trimethylsilyldiazomethane and nitriles.[89–91]



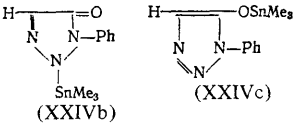
Thus the data presented show that 1,3-DCA can be used for the specific synthesis of *C*- and *N*-organoelemental derivatives of triazoles. Triazole systems with organoelemental substituents are also formed on interaction of organoelemental derivatives of diazomethane with heterocumulene dipolarophiles (Scheme 1, pathway *d*). Thus the dimetallated triazole (XXIII) is formed in the reaction of bis(trimethylstannyl)diazomethane with carbodiimide:[70]



1,3-DCA apparently proceeds analogously in the case of trimethylstannyldiazomethane and phenyl isocyanate.[81] The authors[81] believe that the reaction leads to the formation of the triazolone (XXIVa):



However, a further two isomeric structures, (XXIVb) and (XXIVc), may be proposed for the reaction product taking into account the data presented above, and of these we believe that (XXIVb) is the most probable:



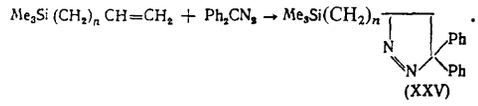
The elucidation of the mechanism of 1,3-DCA with participation of heterocumulene dipolarophiles and of the structure of the products formed therefore requires additional investigation.

2. The Synthesis of Heterocycles from Diazoalkanes and Organoelemental Dipolarophiles

Pyrazolines, pyrazolenines, and pyrazoles with organoelemental substituents are formed from diazoalkanes and organoelemental dipolarophiles in the course of 1,3-DCA reactions.[56,57,92–111]

(a) Pyrazolines

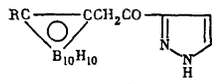
Silylolefins react with diphenyldiazomethane (in proportions of 3 : 1 at +5 °C) to form trimethylsilylpyrazolines (XXV):[92]



(XXV)

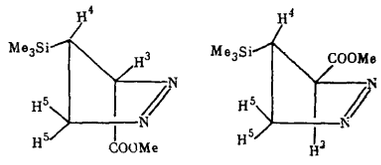
In particular, 3,3-diphenyl-5-trimethylsilyl-Δ^1-pyrazoline (XXV, $n = 0$) has been synthesised in this way. We may note that the same reaction in the presence of copper sulphate as the catalyst leads to silyl derivatives of cyclopropane.

The interaction of carbaboranylmethyl β-chlorovinyl ketones with diazomethane affords the pyrazoles (XXVI).[93]



(XXVI)

The 1,3-DCA of diazoalkanes to alkenes with organoelemental substituents has been studied in detail in relation to the methyl esters of 3-methylsilylpropenoic acid.[94] The *cis*- and *trans*-isomers of $Me_3Si-CH=CHCOOMe$ (XXVIIa, b). obtained by the reduction of $Me_3SiC\equiv CCOOMe$, give rise to high yields of the isomeric *cis*- and *trans*-3-methoxycarbonyl-4-methylsilyl-1-pyrazolines (XXVIIIa, b) on 1,3-DCA to diazomethane (in ether and a nitrogen atmosphere):

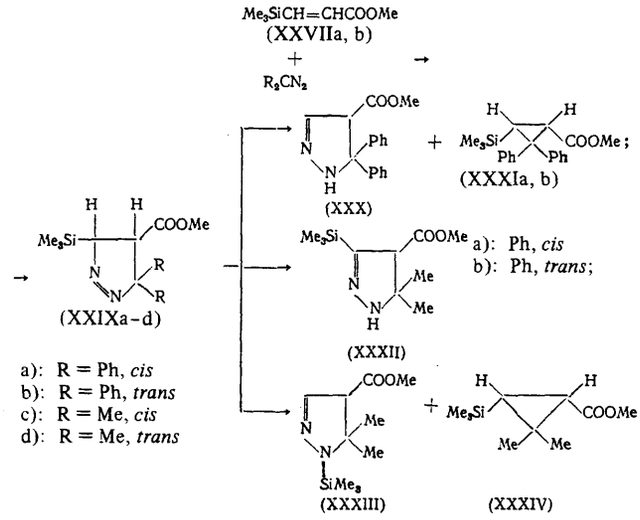


(XXVIIIa) (XXVIIIb)

The pyrazolines (XXVIIIa, b) whose structure has been demonstrated by ^1H NMR, subsequently rearrange with elimination of a nitrogen molecule, the migration of the Me_3Si substituent from the C(4) to the C(5) atom of the pyrazoline ring, and the formation of a series of *cis*(*trans*)-isomeric silicon-containing ethylene derivative. The reaction involving monosubstituted diazomethanes proceeds analogously.[94]

The cycloaddition of diphenyldiazomethane to the *cis*-isomer of the methyl ester (XXVIIa) gives rise to *cis*-4-methoxycarbonyl-3,3-diphenyl-5-trimethylsilylpyrazoline (XXIXa) in 71% yield, while its addition to the *trans*-isomer of the methyl ester (XXVIIb) results in the formation of *trans*-4-methoxycarbonyl-3,3-diphenyl-5-trimethylsilyl-1-pyrazoline (XXIXb). Heating of the pyrazoline (XXIXa) in protic solvents leads to disilylation and the formation of compound (XXX), while prolonged thermolysis in boiling hexane produces *cis*- and *trans*-2,2-diphenyl-3-trimethylsilylcyclopropanecarboxylates (XXXIa, b) in proportions of 2 : 3. The thermal stability of the pyrazoline (XXIXa) is higher than that of compound (XXIXb), but it eliminates nitrogen in boiling octane, forming the *cis*- and *trans*-carboxylates (XXXIa, b) in proportions of 1 : 4.

The reaction of the *cis*-isomer of the methyl ester (XXVIIa) with 2-diazopropane leads to the formation of 4-methoxycarbonyl-5,5-dimethyl-3-trimethylsilyl-2-pyrazoline (XXXII) in 75% yield, which has been demonstrated by the ^1H NMR spectrum of the reaction mixture before its further treatment. Other results have been obtained for the reaction of 2-diazopropane with the *trans*-isomer of the methyl ester (XXVIIb). In this case analysis by the GLC method demonstrated the presence in the reaction mixture of 4-methoxycarbonyl-5,5-dimethyl-1-trimethylsilyl-2-pyrazoline (XXIII) and the *trans*-cyclopropanecarboxylate (XXXIV) in proportions of 1 : 1. However, the signals which could be assigned to compounds (XXXIII) and (XXXIV) are absent from the ^1H NMR spectrum of the above mixture, but signals due to the pyrazoline (XXIXd) are present. The authors point out that, under the GLC conditions, compound (XXIXd) is the starting material in the formation of compounds (XXXIII) and (XXXIV). The dimethylpyrazoline (XXIXd) is sensitive to the action of water, like the diphenylpyrazoline (XXIXa), and when moist 2-diazopropane is employed in this case, the desilylated 4-methoxycarbonyl-5,5-dimethyl-2-pyrazoline is formed in a high yield:



(XXIXa-d)

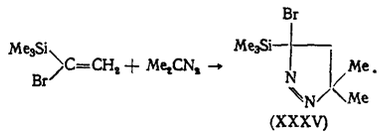
a): R = Ph, *cis*
b): R = Ph, *trans*
c): R = Me, *cis*
d): R = Me, *trans*

(XXX) (XXXIa, b) (XXXII) (XXXIII) (XXXIV)

a): Ph, *cis*
b): Ph, *trans*;

It was then shown that the 1,3-DCA is stereospecific and is sensitive to the nature of the 1,3-dipole, namely to the character of the substituents R, and makes it possible to synthesise specifically the isomeric forms of pyrazolines.

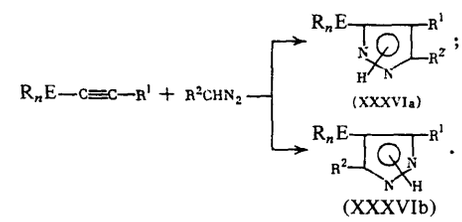
Treatment of an ethereal solution of dimethyldiazomethane with α-bromovinylsilane at 0 °C leads to the formation of 3-bromo-5,5-dimethyl-3-trimethylsilylpyrazoline (XXXV) in 63% yield:[95]



(XXXV)

(b) Pyrazoles

The addition of diazoalkanes to acetylenes with organoelemental substituents has been studied fairly completely.[56,57] It proceeds in accordance with the 1,3-DCA principle and leads to the formation of two isomeric pyrazoles (XXXVIa, b):

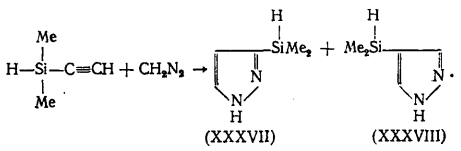


(XXXVIa)

(XXXVIb)

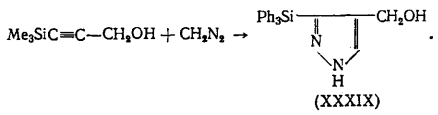
E usually represents Group IV elements (Si, Ge, Sn, and Pb), although similar syntheses of pyrazoles with other organoelemental substituents are known.[56,57] R, R^1, and R^2 are usually aliphatic or aromatic substituents, R^1 representing not only hydrocarbon groups but also a wide variety of functional groups (CH_2OH, $-C(=O)P$, etc.). Thus the interaction of diazomethane (R^2 = H) and its monosubstituted derivatives (R^2 = alkyl or aryl) with trialkyl derivatives of silicon[96,97] or tin[98,99] leads to the formation of pyrazoles containing the substituents R_3E (E = Si or Sn) in the 3- or 5-position.

In the course of its 1,3-DCA to diazomethane in absolute ether at 0–5 °C (three weeks), ethynyldimethylsilane gives rise to a mixture of approximately equal amounts of 3- and 4-dimethylsilylpyrazoles (XXXVII) and (XXXVIII):[100]



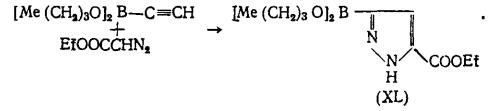
(XXXVII) (XXXVIII)

Triphenylsilylpropargyl alcohols enter into the 1,3-DCA reaction,[99,101] producing mainly compound (XXXIX):



(XXXIX)

Reaction specificity has been observed also in the addition of diazoacetic ester to dibutyl ethynylboronate[102] with formation of a boron-substituted pyrazole (XL):



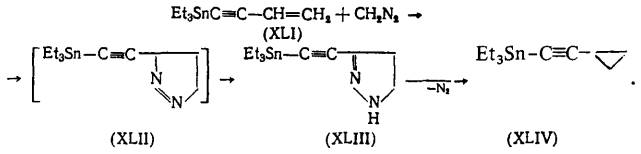
(XL)

Ethyl diazoacetate enters into an analogous reaction with dibutyl ethynylboronate.

The 1,3-DCA reaction with participation of bi- and polyfunctional dipolarophiles is of considerable interest; heterocycles not only with organoelemental but also with active functional groups have been obtained in the course of this process. Polyheterocyclic systems with organoelemental substituents are frequently formed as a result of this type of 1,3-DCA.

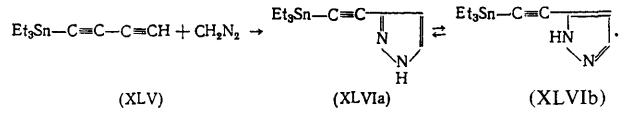
Systematic studies of the competitive reactivities of difunctional dipolarophiles[64,103] have shown that, in the presence of two reaction centres, αβ-unsaturated heteroatomic compounds can react in two ways: with participation of the multiple bond, i.e. [3 + 2]-cycloaddition, or via the heteroatom. Furthermore, it has been established in studies by the same authors that, in the presence of two multiple bonds in the dipolarophile molecule, the most electrophilic of these enters into the 1,3-DCA reaction.[104,105] The data presented above clearly illustrate this behaviour.

Metallated vinylacetylenes combine with diazo-compounds at the more electrophilic double bond with formation of the corresponding pyrazolines. In particular, triethylstannylfinylacetylene (XLI) reacts in this way with diazomethane to form the Δ^1-pyrazoline (XLII), which readily isomerises to Δ^2-pyrazoline (XLIII). On heating to 120 °C, the latter is fully converted into cyclopropyltriethylstannylacetylene (XLIV) with evolution of a nitrogen molecule:



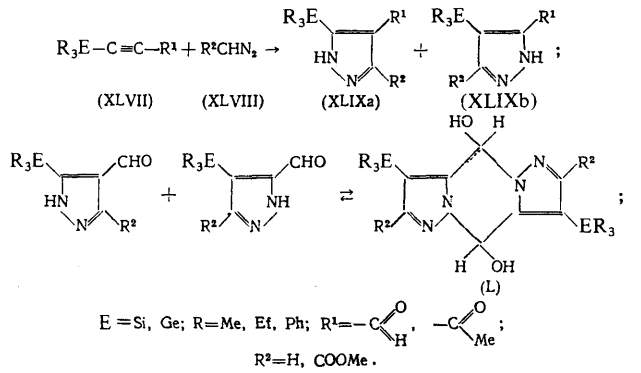
(XLII) (XLIII) (XLIV)

1,3-DCA takes place analogously at the more electrophilic carbon atom of the terminal acetylenic bond in the case of triethylstannyldiacetylene (XLV) with formation of 3(5)-(triethylstannylethynyl)pyrazoles (XLVIa, b):



(XLV) (XLVIa) (XLVIb)

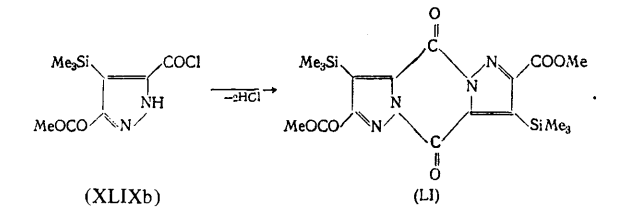
The reactions of triorganylgermanium- or triorganylsilicon-containing carbonyl derivatives (XLVII) with diazoalkanes[106] or with methyl esters of diazoacetic acid (XLVIII)[107–112] lead to the formation of the isomeric pyrazoles (XLIXa, b) and also of the tricyclic hemiaminal (L, R^1 = CHO):



(XLVII) (XLVIII) (XLIXa) (XLIXb) (L)

E = Si, Ge; R = Me, Et, Ph; R^1 = –C(=O)H, –C(=O)Me; R^2 = H, COOMe.

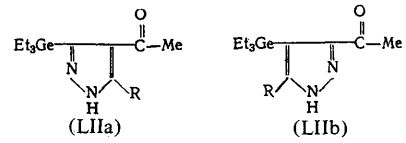
The interaction of trimethylsilylpropiolic acid chloride (XLVII, E = Si, R = Me, R' = COCl) and methyl diazoacetate (XLVIII, R^2 = COOMe)[112] proceeds analogously. However, the dioxopiperazine (LI) and not a heminal of type (L) is then formed from the pyrazole (XLIXb) on dehydrohalogenation:



(XLIXb) (LI)

The 1,3-DCA reaction described above proceeds under mild conditions at room temperature or on cooling in absolute ether, albeit over a long period (from 1 to 60 days). The character of the adducts formed, whose structure has been demonstrated on the basis of IR and ^{1}H NMR spectra, and the ratio of the isomeric pyrazoles depend on the substituent R^2 in the diazoalkane and on the nature of the solvent.

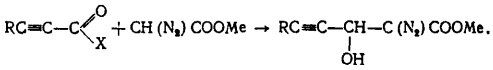
It has been shown[105] that only a mixture of the isomeric pyrazoles (LIIa, b) is formed from methyl triethylgermylethynyl ketone.



(LIIa) (LIIb)

The ratio of the isomers depends on the composition of the 1,3-dipole: an equilibrium mixture of the isomers (LIIa, b) is obtained from diazomethane, in the reaction involving diazoacetic ester the isomer (LIIb) greatly predominates, and in the reaction of diazoacetone the isomer (LIIa) is obtained preferentially.

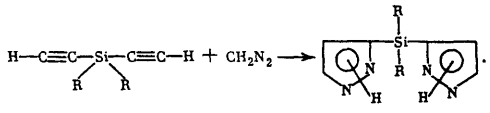
The 1,3-DCA reaction with participation of organoelemental propynals as 1,3-dipoles leads to the formation, apart from pyrazoles, of cyclic hemiaminals (L)[106–110] and also of element-containing diazoesters (LIII) as a result of addition to the aldehyde group:[108]



(LIII)

The nature of the solvent has a significant effect on the content of the dimeric form (L) and the monomeric form (XLIX): according to ^{1}H NMR data, the equilibrium in weakly polar solvents (THF, $CHCl_3$, and dioxan) is displaced towards the dimer, while in more polar solvents [MeOH and dimethyl sulphoxide (DMSO)] it is shifted towards the monomeric formylpyrazole.[108,109]

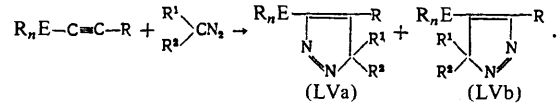
Here we may also note that the 1,3-DCA of diazomethane to bisacetylenic derivatives with equally electrophilic dipolarophile groups, for example, $R_2Si(C{\equiv}CH)_2$, is accompanied by the reaction involving both triple bonds and leads to silylenebispyrazole systems (LIV):[56]



(LIV)

(c) Pyrazolenines

The 1,3-DCA method makes it possible to obtain pyrazole isomers which are otherwise difficult to synthesis—the pyrazolenines,[113] their formation being promoted by the use of disubstituted diazo-compounds and disubstituted acetylenes. Thus pyrazolenines have been obtained in the form of two isomers (LVa, b) by the reaction of metallated acetylenes with disubstituted diazoalkanes:[101]



(LVa) (LVb)

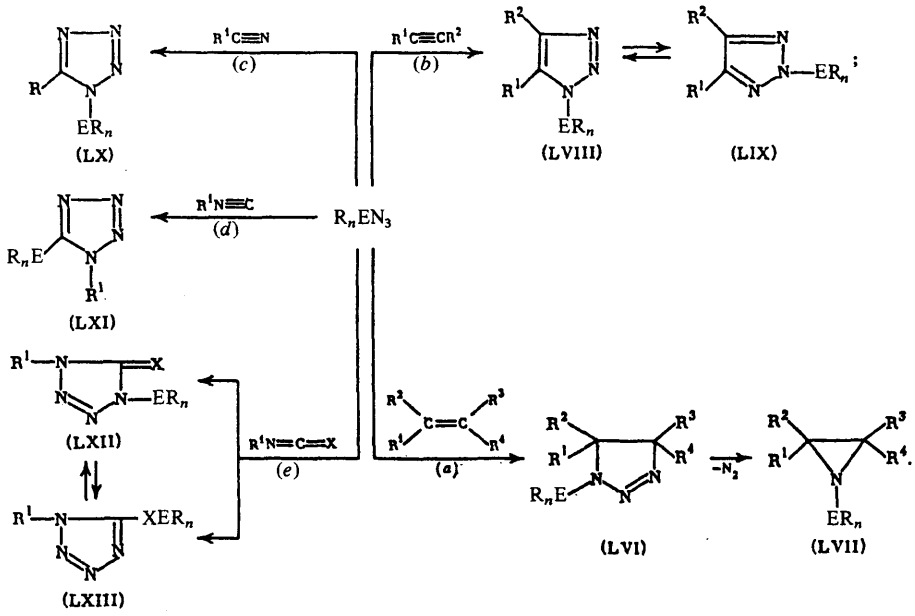
The data presented in Section II suggests the conclusion that 1,3-DCA makes it possible not only to obtain a wide variety of *C*- and *N*-derivatives of pyrazolines, pyrazoles, pyrazolenines, triazoles, and complex polycyclic systems but also to direct the reaction towards the preferential formation of specific isomers.

III. SYNTHESES WITH PARTICIPATION OF AZIDES

1. Syntheses of Heterocycles Based on Organoelemental Azides

The common instances of syntheses based on organoelemental azides are presented in Scheme 2:

Scheme 2

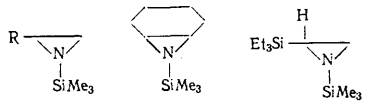


(LXII), (LXIII) X = O, S; E = Cu, Au, Hg, Si, Sn, Pb, Pt, Pd, Ru

(a) Triazolines and Azirdines

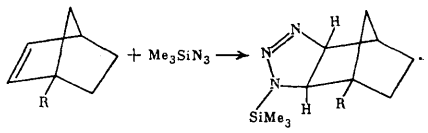
The interaction of organoelemental azides with alkenes (Scheme 2, pathway *a*) leads to the unstable triazolines (LVI), which are converted, as a result of the elimination of a nitrogen molecule, into the N-substituted aziridines (LVII) which are comparatively difficult to obtain.

Thus the interaction of trialkylsilyl azide with the corresponding olefin, which takes place after the reactants have been allowed to stand for a long time (up to 85 days), makes it possible to obtain a series of aziridines (LXIV)–(LXVI),[114] including the formation of the bistrialkylsilyl derivatives (LXVI) from a silylated olefin:



(LXIV) (LXV) (LXVI)

A fairly stable triazoline (LXVII) can be isolated after the interaction of trimethylsilyl azide with a bridge bicyclic olefin:[115]

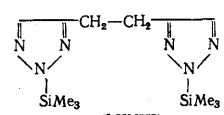


(LXVII)

(b) Triazoles

1,3-DCA with participation of organoelemental azides and acetylenic dipolarophiles (Scheme 2, pathway *b*) was first used to obtain organoelemental derivatives of 1,2,3-triazoles by Birkofer and co-workers:[116–120] after prolonged heating of mixtures of trimethylsilyl azide and substituted acetylenes, high yields of *N*-trimethylsilyl-1,2,3-triazoles were obtained. It was established by the method of dipole moments that the R_3Si-substituted 1,2,3-triazoles exist in the form of isomers and it has been suggested that the R_3Si substituent migrates rapidly between the N(1) and N(2) atoms of the triazole ring. This was evidently the first case of elementotropism among heterocyclic compounds, which was later demonstrated convincingly in a whole series of tautomeric systems,[7–13] including pyrazole[8,10] and triazole[11,13] derivatives containing organoelemental substituents.

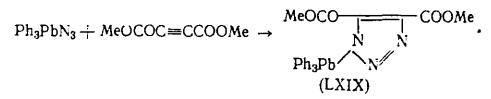
The bisheterocyclic systems (LXVIII) was also synthesised by means of the reactions indicated above; the reaction was carried out in an autoclave at 120–150 °C and the yield of the product was 80%.[119]



(LXVIII)

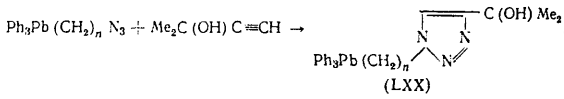
The interaction of trimethylsilyl azide with substituted acetylene RC≡CR′ leads to the formation of 1-trimethylsilylmethyl-4-R-5-R′-1,2,3-triazoles.[121]

Triphenylplumbyl azide,[122–125] was made to react with a large number of olefinic and acetylenic compounds.[126] However, the reaction does not take place with maleic anhydride, dimethyl maleate, ethyl vinyl ether, morpholinocyclopentene, diphenylacetylene, phenylacetylene, propargyl alcohol or 2-methylbut-2-en-2-ol. 4,5-Dimethoxycarbonyl-1-triphenylplumbyl-1,2,3-ditrazole (LXIX) is formed only in the reaction with dimethylacetylenedicarboxylate, which is a very powerful dipolarophile:



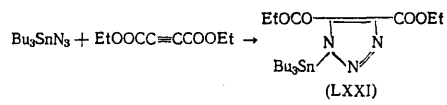
(LXIX)

In contrast to triphenylplumbyl azide, triphenylplumbylalkyl azides readily enter into 1,3-DCA even with weak dipolarophiles such as 2-methylbut-3-en-2-ol, forming the corresponding triazoles (LXX):



(LXX)

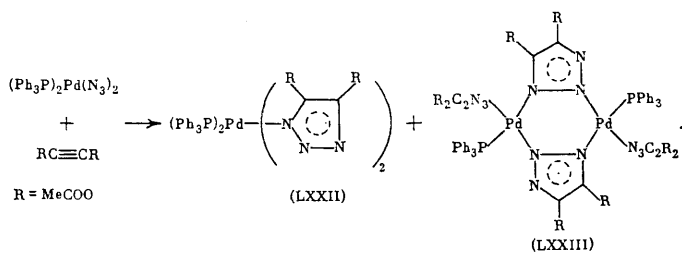
Heterocycles with a N–Sn bond [compounds (LXXI)] can be synthesised from organotin azides and substituted acetylenes as described, for example, by Leijten and van der Kerk:[127]



(LXXI)

We may note that the structures of compounds (LXIX)–(LXXI) quoted in the studies considered above are open to doubt: they have not been demonstrated and, when account is taken of the possibility of the metallotropic N(1)–N(2) migrations of the organoelemental groups, structures of type (LIX) appear to be more probable.

Unusual products are obtained on 1,3-DCA of palladium-substituted organophosphorus azides to dimethyl acetylenedicarboxylate: apart from N-palladium derivatives of the bispyrazoles (LXXII), the highly symmetric dimers (LXXIII) are produced:[128]



(LXXII) (LXXIII)

(c) Tetrazoles, Tetrazolones, and Their Thio-analogues

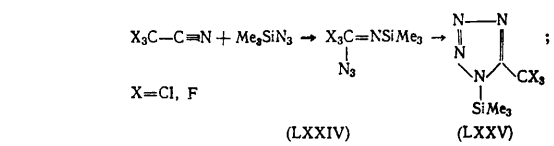
Organoelemental derivatives of the tetrazoles (LX) and (LXI) are formed as a result of the 1,3-DCA of organoelemental azides to nitriles (Scheme 2, pathway *c*) and isonitriles (Scheme 2, pathway *d*).[129–147] The reactions of these azides with heterocumulenes lead to the tetrazolones (LXII) (Scheme 2, pathway *e*) and their thio-analogues.[128,133,135]

Using Scheme 2 (pathways *c*, *d*, and *e*), it is possible to synthesise specifically *N*-substituted [compounds (LX) and (LXII)] or *C*-substituted [compounds (LXI) and (LXIII)] derivatives respectively.

The addition of trimethysilyl azide to benzonitrile takes place in the presence of catalytic amounts of $AlCl_3$ or other Lewis acids.[135]

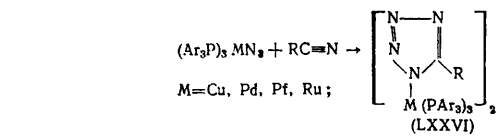
It has been found[136] that trimethylsilyl azide adds to the C≡N bond also in the presence of catalytic amounts of triethylamine. Thus the interaction of Me_3SiN_3 with trichloro- or trifluoroacetonitrile with participation of the

above catalyst leads to trihalogenomethyl-1-trimethylsilyltetrazoles (LXXV). It has been shown that aluminium chloride is ineffective in this reaction, since it induces the polymerisation of the nitriles. The 1,3-DCA proceeds in this case via the stage involving the formation of 1-azido-2,2,2-trihalogeno-1-(trimethyl-silylimino)ethanes (LXXIV):



(LXXIV) (LXXV)

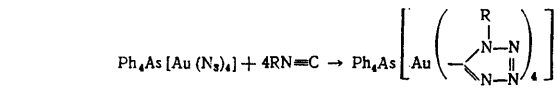
Bistetra-azotriarylphosphine complexes of copper, palladium, platinum, and ruthenium (LXXVI) have been obtained [75,131,138,141,147]† by the interaction of metal azides with nitriles:



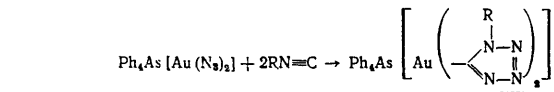
(LXXVI)

The 1,3-DCA involving azidotriphenylphosphinoisonitrile complex on platinum, leading to Pt–N-derivatives of tetrazoles, proceeds analogously.[141]

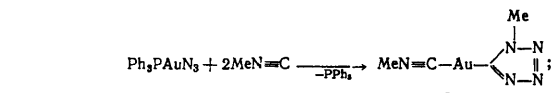
The azide-containing complexes $Ph_4As[Au(N_3)_4]$, $Ph_4As.[Au(N_3)_2]$, Ph_3PAuN_3, and $(Ph_3P)_2M(N_3)_2$ (M = Pd, Pt, or Hg) react with isonitriles under very mild conditions, forming tetrazolate complexes[132,140] in which the organometallic substituents are bound to a carbon atom of the tetrazole ring [compounds LXXVII)–LXXXIII)]:



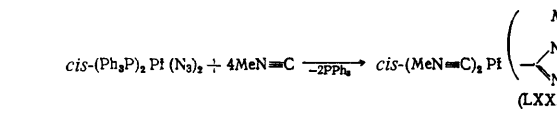
(LXXVII)



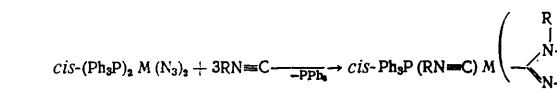
(LXXVIII)



(LXXIX)

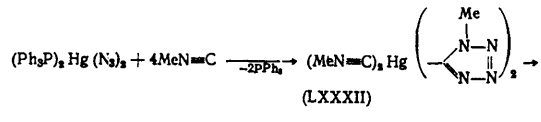


(LXXX)

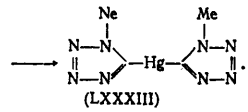


(LXXXI) M=Hg, Pd, Pt

† A whole series of communications[128,144–147] concerning the 1,3-DCA of organoelemental azides to nitriles, isonitriles, and other dipolarophiles, leading to N- and C-substituted tetrazoles, have been published. The examination of all these studies is outside the framework of the present review. In most cases the above investigations were concerned with the reactions of the azides of various metals and provided no fundamental information. We therefore considered the most important and latest studies of this series.



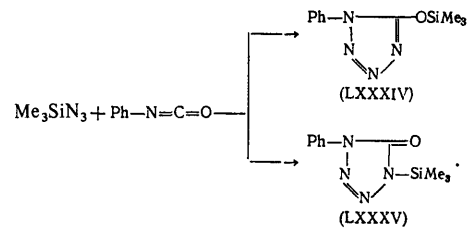
(LXXXII)



(LXXXIII)

Other methods, which are difficult to apply, have been suggested for the synthesis of the complexes (LXXXII)–(LXXXIII).

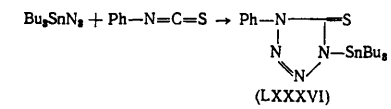
The synthesis of the tetrazolones (LXII, X = O)[128,135] and their thio-analogues (LXII, X = S)[128,131] in accordance with Scheme 2 (pathway *e* usually take place under fairly severe conditions in the presence of catalysts. Thus the 1,3-DCA of trimethylsilyl azide to phenyl isocyanate, which takes place on heating to 140 °C for 12 h in the presence of $AlCl_3$, leads to the silyloxytetrazole (LXXIV) and the *N*-silyltetrazole (LXXXV):[135]



(LXXXIV)

(LXXXV)

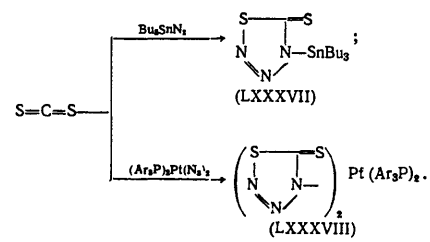
A reaction involving tributylstannyl azide and phenyl isothiocyanate has also been described,[131] although the authors postulate only one structure for the 1,3-DCA product—that of the thionotetrazole (LXXXVI):



(LXXXVI)

The 1,3-DCA reactions of platinum- and palladium-substituted bistriphenylphosphine azides proceed in accordance with analogous mechanisms.[128]

Carbon disulphide has also been used as the heterocumulene dipolarophile:[128,131–133] the 1,3-DCA leads to extremely unusual heterocycles—the thionotriatriazoles (LXXXVII) and (LXXXVIII), the possibility of the synthesis of which by other methods is obscure:[40–43]



(LXXXVII)

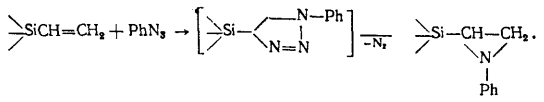
(LXXXVIII)

2. The Syntheses of Heterocycles Based on Azides and Organoelemental Dipolarophiles

(a) Triazolines and Aziridines

C-Organosilicon derivatives of aziridine have been obtained[148–150] by the interaction of vinylsilanes with phenyl azide at room temperature[149–150] or of alkenylmethylsiloxanes

with benzoyl azide at 60–80 °C.[148] The first stage of this reaction is apparently the addition of the azide to the vinyl group with formation of a five-membered ring, which eliminates a nitrogen molecule and is converted into the *N*-phenylaziridine derivatives (LXXXIX):



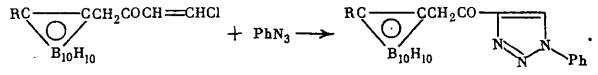
(LXXXIX)

The yields of *C*-aziridinyl derivatives after a 40-day reaction of vinylheptamethylcyclotetrasilane or 3-vinylheptamethyltrisiloxane with phenyl azide did not exceed 11%. The reaction of allylsilanes with PhN_3, is even more difficult,[150] while phenyl azide adds somewhat more readily to 3-vinylheptamethyltrisilane;[150] the yield of the reaction product in petroleum ether after ten days at 30–40 °C reaches 40.5%.[148]

When the alkenylsilanes RCH=CHSiR′ are used in the reaction with *p*-bromophenyl azide, 1-*p*-bromophenyl-2-trimethylsilyl-3-R-aziridines are formed.[151] On heating $PhCH=CHSiMe_3$ with $p\text{-}BrC_6H_4N_3$ in CCl_4 for 24 h, it is possible to isolate 1-*p*-bromophenyl-5-phenyl-4-trimethylsilyl-Δ^2-1,2,3-triazoline in 10% yield. On further heating in the course of 4 days, the triazoline is converted into an aziridine and a 1 : 1 mixture of Me_3SiCHN_2 and $PhCH=NC_6H_4.Br\text{-}p$.

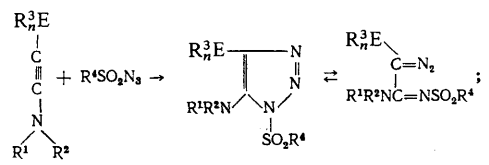
(b) Triazoles

4-(*o*-Carbaboranylacetyl)-1-phenyltriazoles (XC) are formed after prolonged heating of carbaboranylmethyl β-chlorovinyl ketone with phenyl azide in benzene solution:[152]



(XC)

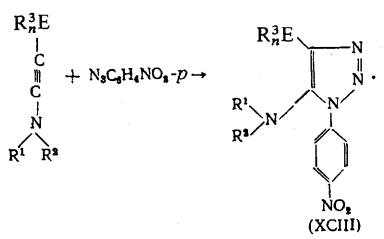
The reactions of sulphonyl azides with organometallic ynamines are regiospecific[153,154] and lead to 5-amino-1,2,3-triazoles (XCI), which, depending on the nature of the substituents R^1, R^2, R^3, and R^4, either isomerise wholly to the α-metallated diazoacetamidines (XCII) or are involved in a tautomeric equilibrium with the latter:



(XCI) (XCII)

R^1, R^2, R^4=alkyl, aryl; $R_n^3E = R_2^1As$, R_2^1Sb, R_3^1Si, R_3^1Ge, R_3^1Sn, $Ph_2P(O)-$, $Ph_2P(S)-$.

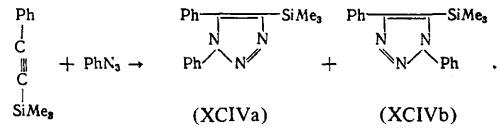
The analogous triazoles (XCIII) with *N*-*p*-nitrophenyl substituents instead of the sulpho-group are more stable:[155]



(XCIII)

We may note that tolyl azide does not react with phenylacetylene itself but does react with its sodium salt.[153] There are also data indicating the condensation of various lithium and magnesium acetylides with azides.[156,157]

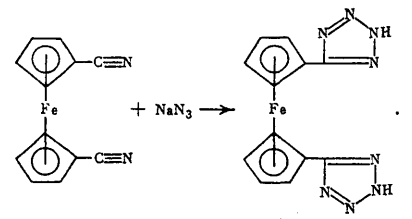
In contrast to the 1,3-DCA with participation of diazoalkanes, which exhibits an appreciable structural specificity in reactions with alkynes, in the case of azides, such specificity is not always marked. However, an appreciable selectivity of the addition reaction, leading to the preferential formation of one isomer, for example (XCIVa), has been sometimes noted; the second isomer (XCIVb) has been obtained in a yield of only 3%:[117,120]



(XCIVa) (XCIVb)

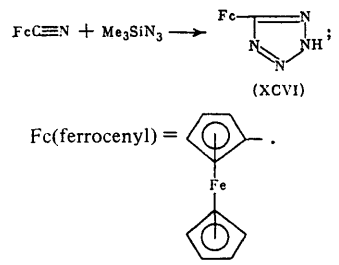
(c) Tetrazoles

The interaction of 1,1′-dicyanoferrocene with NaN_3 in THF in the presence of $AlCl_3$ leads to the formation of 1,1-di(5-tetrazolyl)ferrocene (XCV):[158]



(XCV)

The *C*-ferrocenyltetrazole (XCVI) is formed in the reaction of 1-cyanoferrocene and trimethylsilyl azide in *o*-dichlorobenzene in the presence of $AlCl_3$:[159]



(XCVI)

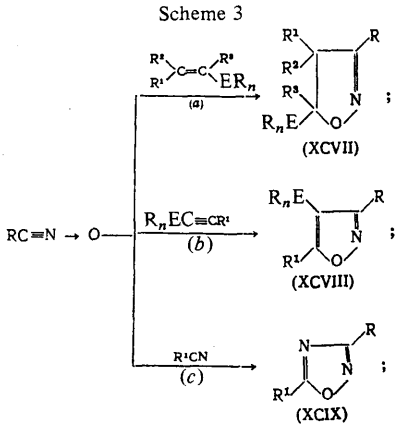
We must emphasise that, so far as we are aware, organoelemental derivatives of heterocumulenes have not been introduced into this type of 1,3-DCA, although the dipolarophiles have been fairly thoroughly investigated (see, for example, Refs.160–162).

IV. SYNTHESES WITH PARTICIPATION OF NITRILE *N*-OXIDES

1,3-DCA with participation of nitrile *N*-oxides as dipolarophiles, which arise in the course of the reaction and react *in situ*, have been used fairly widely in the synthesis of heterocycles with organoelemental substituents.[95,163–173] The reactions lead to the formation of *NO*-heterocyclic systems—isoxazolines (XCVII), isoxazoles (XCVIII), and oxadiazoles

(XCIX), the methods of synthesis of which are illustrated in Scheme 3:

Scheme 3



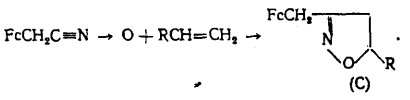
(XCVII) (XCVIII) (XCIX)

a) and *b*) R_nE = carbaborane- and ferrocene-containing groups, R = Ar, and R^1, R^2, R^3 = alkyl or aryl; *c*) R = $FcCH_2$ and R = Me.

1. The Syntheses of Heterocycles from Organoelemental Nitrile *N*-oxides

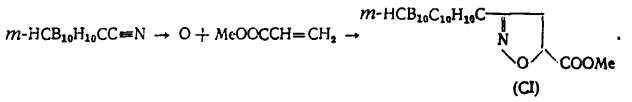
(a) Isoxazolines

Ferrocenylacetonitrile *N*-oxide, formed from ferrocenylnitroethane, reacts *in situ* with a series of olefinic dipolarophiles—hept-1-ene, styrene, acrylonitrile, or trimethylsilylethylene, forming isoxazolines (C):[163]



(C)

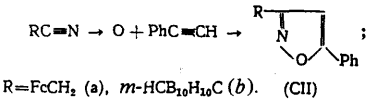
m-Carbaboranylnitrile *N*-oxide has been synthesised.[164] Its reaction *in situ* with methyl acrylate leads to an isoxazoline having a *m*-carbaboranyl substituent (CI):



(CI)

(b) Isoxazoles

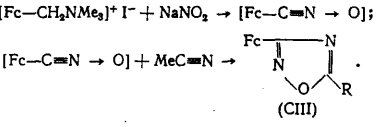
The interaction of phenylacetylene with ferrocenylacetonitrile *N*-oxide or with *m*-carbaboranylnitrile *N*-oxide, obtained *in situ*, results in the formation of the corresponding isoxazoles (CII):[163,164]



R=$FcCH_2$ (a), *m*-$HCB_{10}H_{10}C$ (*b*). (CII)

(c) Oxadiazoles

The reaction of ferrocenylmethyltrimethylammonium iodide with sodium nitrite and acetonitrile, which entails the formation of ferrocenyloxadiazole (CIII),[165] probably involves a stage in which ferrocenylacetonitrile *N*-oxide is formed *in situ*:

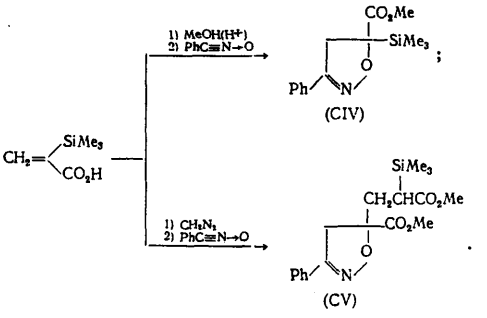


(CIII)

2. The Synthesis of Heterocycles from Nitrile *N*-oxides and Organoelemental Dipolarophiles

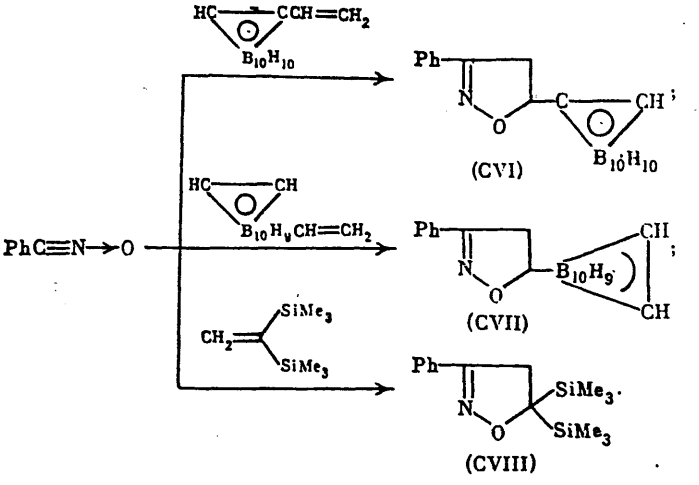
(a) Isoxazolines

Isoxazolines (XCVII) are formed in the course of 1,3-DCA of nitrile *N*-oxides to dipolarophiles containing a double bond (Scheme 3, pathway *a*). Thus treatment of benzonitrile with methyl α-trimethylsilylacrylate affords the isoisoxazoline (CIV). The interaction of 2-trimethylsilylacrylic acid with benzonitrile oxide leads mainly to the product (CV):[95,166]



(CIV) (CV)

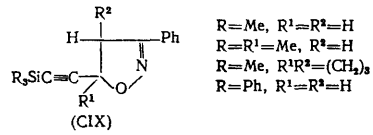
The 1,3-DCA of benzonitrile oxide to unsaturated *o*-carbaborane derivatives gives rise to the isoxazolines (CVI) and (CVII) with a *o*-carboboranyl substituent, while the interaction of 1,1-bis(trimethylsilyl)ethylene results in the formation of the disilylated isoxazoline (CVIII):[164,166]



(CVI) (CVII) (CVIII)

The study of the competitive reactions of benzonitrile *N*-oxide with dipolarophiles containing double and triple bonds established that the 1,3-DCA is exclusive to the new reaction centre and leads to isoxazolines with silylethynyl substituents.[167,168] Thus the interaction of 1,3-enyne silylhydrocarbons (1-trimethylsilylbut-3-en-1-yne, 1-trimethylsilyl-3-methylbut-3-en-1-yne, 1-trimethylsilylethynylcyclopentene, and 1-triphenylsilylbut-3-en-1-yne) with

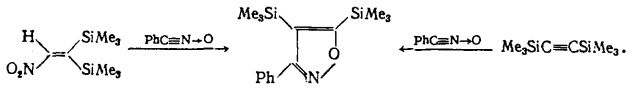
benzonitrile oxide results in the formation of compound (CIX) in satisfactory yields:[168]



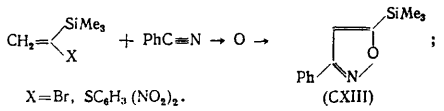
(CIX)

(b) Isoxazoles

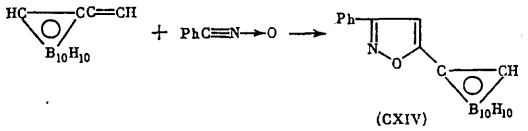
Disilylated isoxazoles of the type of compound (CXI) are obtained instead of the expected isoxazolines (Scheme 3, pathway *a*) in the interaction of nitrovinylidenebistrimethylsilane (CX) with benzonitrile oxide.[95,166] There is in general no doubt about the structure of the isoxazole (CXI), since it has been obtained by specific synthesis from bis(trimethylsilylacetylene). The isoxazole (CXI) had been obtained earlier from benzonitrile oxide and bis(trimethylsilyl)acetylene:[169]


(CX) (CXI) (CXII)

The isoxazole (CXIII) is formed analogously instead of isoxazolines on interaction of α-bromovinyltrimethylsilane or α-(2,4-dinitriphenylthio)vinyltrimethylsilane with benzonitrile oxide:[166]

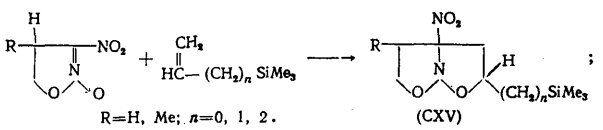

X=Br, $SC_6H_3(NO_2)_2$. (CXIII)

The 1,3-DCA of 1-ethynyl-*o*-carbaborane to benzonitrile oxide leads to the formation, as was to be expected, of the *o*-carbaboranylisoxazole (CXIV):[164]


(CXIV)

(c) Isoxazolidines

3-Nitroisoxazoline *N*-oxides react with silylolefins to form the bicyclic isoxazolidines (CXV):[170]

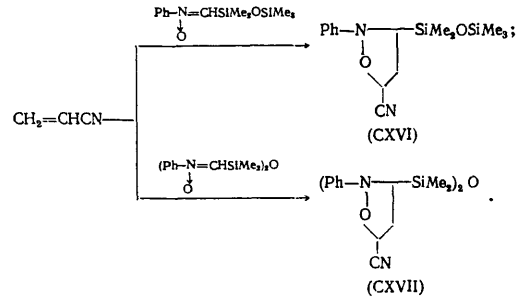

R=H, Me; *n*=0, 1, 2. (CXV)

V. SYNTHESES WITH PARTICIPATION OF NITRONES

1. The Synthesis of Heterocycles from Organoelemental Nitrones

(a) Isoxazolidines

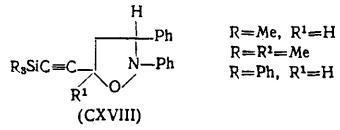
The 1,3-DCA of organosilicon nitrones to compounds containing a double bond results in the formation of derivatives of fully saturated *NO*-heterocycles—isoxazolidines. However, these 1,3-dipoles exhibit a weak affinity for olefins—the cycloaddition products (CXVI) and (CXVII) are obtained in low yields only after the reactants have been allowed to stand for a long time:[171]


(CXVI) (CXVII)

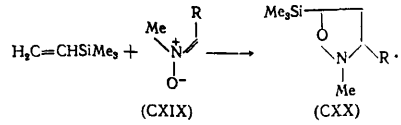
2. The Synthesis of Heterocycles from Nitrones and Organoelemental Dipolarophiles

(a) Isoxazolidines

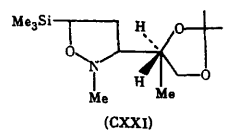
The addition of α*N*-diphenylnitrone to silylethynylalkenes (1-trimethylsilylbut-3-en-1-yne, 1-trimethylsilyl-3-methylbut-3-en-1-yne, and 1-triphenylsilylbut-3-en-1-yne) takes place at the double bond with formation of 5-organylsilylethynyl-2,3-diphenyloxazolidines (CXVIII):[168]


(CXVIII)

The reaction of trimethylvinylsilane with the nitrone (CXIX) affords 5-trimethylsilylisoxazolidine (CXX):[172,173]


(CXIX) (CXX)

The demonstration of the possibility of this reaction enabled the authors[173] to employ the principle in the synthesis of two stereoisomeric isoxazolidines (CXXI) which are deoxysugar derivatives:


(CXXI)

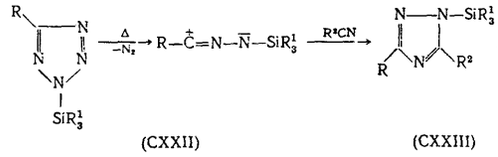
VI. SYNTHESES WITH PARTICIPATION OF NITRILE IMINES

Nitrile imines are 1,3-dipoles which react exclusively *in situ*. Their 1,3-DCA reactions lead to the formation of pyrazolines (in reactions with olefins)[168,174] or 1,3,4-triazoles (in reactions with nitriles as dipolarophiles).[114]

1. The Synthesis of Heterocycles from Organoelemental Nitrile Imines

(a) Triazoles

Silylated nitrile imines (CXXII) are formed when *N*-silyltetrazoles are heated, the 1,3-DCA to the nitrile resulting in the formation of 2-trimethylsilyl-1,2,4-triazoles (CXXIII):[114]

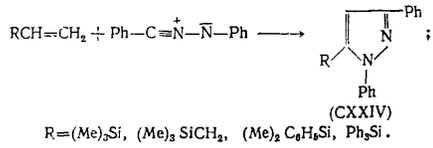


(CXXII) (CXXIII)

2. The Synthesis of Heterocycles from Nitrile Imines and Organoelemental Dipolarophiles

(a) Pyrazolines

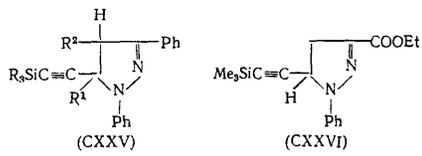
The reactions of dimethylvinylsilane, trimethylvinylsilane, and triphenylvinylsilane with diphenylnitrile imine give satisfactory yields of derivatives of 1,3-diphenyl-2-pyrazoline with organosilicon substituents in the 5-position of the heterocycle as in compound (CXXIV).[174] The dipolarophile activity of the double bond in allyltrimethylsilane is much lower and the 2-pyrazolines are formed in lower yields:



(CXXIV)

R=$(Me)_3Si$, $(Me)_3SiCH_2$, $(Me)_2C_6H_5Si$, Ph_3Si.

2,3-Enyne silylhydrocarbons (1-trimethylsilylbut-3-en-1-yne, 1-trimethylsilyl-3-methylbut-3-en-1-yne, 1-trimethylsilylethynylcyclopentene, and 1-triphenylsilylbut-3-en-1-yne) also react with diphenyl nitrile imine as the double bond with formation of 2-pyrazolidines (CXXV).[168] *C*-ethoxycarbonyl-*N*-phenylnitrile imine adds to 1-trimethylsilylbut-3-en-1-yne to form 3-ethoxycarbonyl-1-phenyl-5-trimethylsilylethynyl-2-pyrazoline (CXXVI):[168]



(CXXV) (CXXVI)

VII. CONCLUSION

The data presented in this review clearly indicate the extensive possibilities for the use of 1,3-DCA in the synthesis of heterocycles with organoelemental substituents. This aspect is important for the chemistry of heterocyclic compounds, since it enables one to avoid the use of complete heterocycles, whose preparation frequently involves multistage syntheses or the application of initial reactants which are difficult to obtain.[40-43]

This review was devoted to 1,3-DCA, but it is already clear[42,66] that other types of cycloaddition used to construct heterocyclic systems can also be regarded as universal methods of synthesis of heterocycles with organoelemental substituents: "2 + 1 = 3", "2 + 2 = 4", and "4 + 2 = 6" additions in the syntheses of three-membered, four-membered, and six-membered heterocycles. Examples of such reactions are available in the literature for organoelemental reagents. Thus the [2 + 2]-cycloaddition of heterocumulenes to a cobalt complex led to the synthesis of metallocyclic compounds.[175,176]

The [2 + 2]-cycloaddition of triphenylstibazosulphonylarenes to diethyl acetylenedicarboxylate gives rise to a four-membered stiba-azaheterocycle.[177]

In addition, one should bear in mind that five-membered heterocyclic systems with organoelemental substituents can be obtained, by analogy with the data quoted by Paquette,[42] Grimmett,[44] and Grüning and Lorberth,[178] as a result of [4 + 1]-cycloaddition, while condensed heterocycles can be produced by intramolecular 1,3-cycloaddition.[66]

In connection with the above, it appears useful to modify both 1,3-dipoles and dipolarophiles by introducing organoelemental substituents and also to employ other types of cycloaddition in order to extend the number of types of heterocycles with organoelemental fragments. The development of new methods of synthesis of organoelemental dipoles and dipolarophiles is also useful in this connection (see, for example, Refs. 179–186).

In our view, the study of the physicochemical properties, structure, and reactivity of heterocycles with organoelemental substituents may be of considerable interest; this field of the chemistry of heterocyclic and organoelemental compounds has been little studied and this is why some of the data presented above concerning the structures of heterocycles with organoelemental substituents are open to doubt. In particular, such heterocycles with organometallic substituents contain simultaneously electron-donating (the N, O, and S heteroatoms) and electron-accepting (M = Ge, Sn, Pb, etc.) centres. Most of them should therefore[1,2] have oligomeric or polymeric structures. This question so far remains open, since in the studies examined above the molecular weights of the heterocycles synthesised were frequently not measured and no mass-spectrometric investigations were made. In this connection, we may note that the dimers (L) described in a series of studies,[107-111] especially the dimers of germylpyrazoles, can also have a different structure (with involvement of the Ge and N atoms of the pyrazole ring), which is extremely characteristic of boron, aluminium, and other organoelemental derivatives of azoles.[1,2,6]

The extensive possibilities for the synthesis of heterocycles with organoelemental substituents with the aid of 1,3-DCA and other types of cycloaddition and the investigation of the nature of this process can be considered also in terms of another aspect, associated with the study of the mechanisms of the reactions of organometallic compounds,[187] including also a wide variety of different types of elementotropic processes.[7-13] The influence of the nature of elements entering into the composition of the fragments of 1,3-dipoles and dipolarophiles considered in this review on the 1,3-DCA mechanism therefore appears to have been inadequately investigated.[61,65,188,189]

Finally, both for a deeper investigation of 1,3-DCA and from the standpoint of the synthesis of heterocycles incorporating different elements in the ring, the study of

the corresponding silyl[190–196] and other organoelemental reagents[175–177,197–201] is of interest. Definite advances in this little investigated field have been made. The first examples of the synthesis of heterocycles by 1,3-DCA with participation of a dipolarophile having a silicon atom in the reaction centre has been described,[190] namely the reaction of 1,1-dimethyl-2,2-bis(trimethylsilyl)-1-silaethylene and trimethylsilyl azide. However, the formation of a silatriazole ring requires more rigorous proof, as has been done in the synthesis of cobalt-containing[175] and arsenic-containing[177] heterocycles.

After the synthesis of silylenes,[191–196] it was natural to attempt to introduce them as dipolarophiles into the 1,3-DCA reaction (see, for example, Masuune et al.).[194] However, it was shown that the cycloaddition product formed in this reaction is unstable; disilacyclopropane was formed as a result.[194]

We believe that the aspects indicated above are promising and can assist in the progess of both theoretical chemistry and the chemistry of heterocyclic and organoelemental compounds.

We emphasise that monographs thematically related to the present review have been published recently.[202,203] However, the aspects of the 1,3-DCA as a general method of synthesis of heterocyclic compounds which we examined are not adequately dealt with in these publications.

REFERENCES

1. A.D.Garnovskii, Doctoral Thesis, in Chemical Sciences, Izd.Rostov.Univ., Rostov-on-Don, 1972.
2. A.D.Garnovskii, O.A.Osipov, L.I.Kuznetsova, and N.N.Bogdashev, Uspekhi Khim., 1973, **42**, 177 [Russ. Chem.Rev., 1972(2)].
3. P.C.Poller, "The Chemistry of Organtotin Compounds", Logos Press, London, 1970, p.94.
4. A.N.Nesmeyanov, D.N.Kravtsov, A.P.Zhukov, P.M.Kochergin, and G.K.Semin, Dokl.Akad.Nauk SSSR, 1968, **179**, 102.
5. V.V.Korshak, V.A.Zamyatina, and N.I.Bekasova, "Bororganicheskie Polimery" (Organoboron Polymers), Izd.Nauka, Moscow, 1975, p.61.
6. S.Trofimenko, Uspekhi Khim., 1972, **41**, 1669 [Russ. Chem.Rev., 1972(9)].
7. E.Fraendorfer and J.Puca, J.Organomet.Chem., 1984, **265**, 157.
8. D.H.O'Brien and C.P.Hrung, J.Organomet.Chem., 1971, **27**, 185.
9. F.A.Cotton, in "Dynamic NMR Spectroscopy" (Edited by E.Jackman and F.A.Cotton), Acad.Press, New York–London, 1975, p.377.
10. V.I.Minkin, L.P.Olekhnovich, and Yu.A.Zhdanov, "Molekulyarnyi Dizain Tautomernykh Sistem" (Molecular Design of Tautomeric Systems), Izd.Rostov.Univ., Rostov-on-Don, 1977, p.60.
11. V.N.Torocheshnikov, N.M.Sergeyev, N.A.Victorov, G.S.Goldin, V.G.Poddubny, and A.N.Koltsova, J.Organomet.Chem., 1974, **70**, 347.
12. L.A.Fedorov, D.N.Kravtsov, and A.S.Peregudov, Uspekhi Khim., 1981, **50**, 1304 [Russ.Chem.Rev., 1981(7)].
13. N.M.Sergeev, Doctoral Thesis in Chemical Sciences, Institute of Organoelemental Compounds, USSR Academy of Sciences, Moscow, 1981, p.98.
14. V.A.Bren', V.A.Chernoivanov, N.I.Borisenko, L.G.Konstantinovskii, Zh.I.Bren', and V.I.Minkin, Dokl.Akad.Nauk SSSR, 1980, **255**, 107.
15. E.Lukevics and A.E.Pestunovich, Uspekhi Khim., 1972, **41**, 1994 [Russ.Chem.Rev., 1972(11)].
16. A.N.Nesmeyanov and N.S.Kochetkova, Uspekhi Khim., 1974, **43**, 1513 [Russ.Chem.Rev., 1974(9)].
17. N.Oda, T.Osaki, S.Nagai, and T.Ito, Chem.Pharm. Bull.(Tokyo), 1978, **26**, 359.
18. B.E.Maryanoff, S.L.Keeley, and F.Persico, J.Med. Chem., 1983, **26**, 226.
19. E.Lukevics, A.Kimenis, M.Veveris, Z.Atare, and E.N.Popova, Khim.-Farm.Zhur., 1982, **16**, 1201.
20. S.Gronowitz, in "Advances in Heterocyclic Chemistry" (Edited by A.R.Katritzky), Acad.Press, New York, 1963, p.75.
21. S.T.Ioffe and A.N.Nesmeyanov, "Metody Elementoorganicheskoi Khimii. Magnii, Berillii, Kal'tsii, Strontsii, Barii" (Methods of Organoelemental Chemistry. Magnesium, Beryllium, Calcium, Strontium, and Barium), Izd.Akad.Nauk SSSR, Moscow, 1963.
22. K.A.Andrianov, "Metody Elementoorganicheskoi Khimii. Kremnii" (Methods of Organoelemental Chemistry. Silicon), Izd.Nauka, Moscow, 1971.
23. T.V.Talalaev and K.A.Kocheshkov, "Metody Elementoorganicheskoi Khimii. Litii, Natrii, Kalii, Rubidii, Tsezii" (Methods of Organoelemental Chemistry. Lithium, Sodium, Potassium, Rubidium, and Caesium), Izd.Nauka, Moscow, 1971.
24. A.D.Garnovskii, Yu.I.Ryabukhin, and A.S.Kuzharov, Koord.Khim., 1984, **10**, 1011.
25. Ya.L.Gol'dfarb and L.I.Belen'kii (Editors), "Novye Napravleniya Khimii Tiofena" (New Trends in the Chemistry of Thiophen), Izd.Nauka, Moscow, 1976, p.96.
26. A.M.Simonov, Khim.Geterotsikl.Soed., 1982, 1589.
27. P.J.Fraser, W.R.Roper, and F.G.A.Stone, J.Organomet.Chem., 1973, **50**, C54.
28. E.W.Abel and G.Towers, J.Chem.Soc., Dalton Trans., 1979, 814.
29. R.Gompper and E.Gottmair, Tetrahedron Letters, 1981, **22**, 2685.
30. E.Krause and G.Renwanz, Chem.Ber., 1932, **65**, 777.
31. M.D.Rausch, T.R.Criswell, and A.K.Igantowitz, J.Organomet.Chem., 1968, **13**, 419.
32. L.L.Garber and C.H.Brubaker, Jr., J.Amer.Chem. Soc., 1968, **90**, 309.
33. C.Ullenius, Acta Chem.Scand., 1972, **26**, 3383.
34. L.G.Makarova and A.N.Nesmeyanov, "Metody Elementoorganicheskoi Khimii. Rtut'" (Methods of Organoelemental Chemistry. Mercury), Izd.Nauka, Moscow, 1965, p.94.
35. E.M.Panov and K.A.Kocheshkov, Dokl.Akad.Nauk SSSR, 1958, **123**, 295.
36. P.L.Pauson, "Organometallic Chemistry" (Translated into Russian), Izd.Mir, Moscow, 1970, pp.52, 53.
37. B.L.Booth, R.N.Haszeldine, and M.B.Taylor, J.Organomet.Chem., 1966, **6**, 570.
38. J.Cook, M.Green, and F.G.A.Stone, J.Chem.Soc.A, 1968, 173.
39. P.J.Fraser, W.R.Roper, and F.G.A.Stone, J.Chem. Soc., Dalton Trans., 1974, 102.

40. R.M.Elderfield (Editor), "Heterocyclic Compounds" (Translated into Russian), Inostr.Lit., Moscow, 1961.
41. R.M.Elderfield (Editor), "Heterocyclic Compounds" (Translated into Russian), Izd.Mir, Moscow, 1965 and 1969, Vols.7 and 8.
42. L.A.Paquette, "Principles of Modern Heterocyclic Chemistry" (Translated into Russian), Izd.Mir, Moscow, 1971.
43. V.I.Ivanskii, "Khimiya Geterotsiklicheskikh Soedinenii" (The Chemistry of Heterocyclic Compounds), Izd. Vys.Shkola, Moscow, 1978.
44. M.R.Grimmett, "Comprehensive Organic Chemistry", Vol.8 (Edited by D.Barton and W.D.Ollis), Izd. Khimiya, Moscow, 1985, p.429.
45. L.L.Shchukovskaya, L.D.Budakova, and R.I.Pal'chik, Zhur.Obshcch.Khim., 1972, **43**, 1989.
46. Ya.M.Paushkin, A.M.Shevchik, and D.V.Romanovskaya, Dokl.Akad.Nauk SSSR, 1974, **214**, 114.
47. E.W.Neuse and L.Bednarik, Synthesis, 1977, 481.
48. B.V.Polyakov, V.P.Tverdokhlebov, I.V.Tselinskii, N.M.Bakstova, and G.M.Frolova, Zhur.Obshch. Khim., 1983, **53**, 2046.
49. O.V.Drygina and A.D.Garnovskii, Khim.Geterotsikl. Soed., 1983, 579.
50. O.V.Drygina, Candidate's Thesis in Chemical Sciences, Izd.Rostov.Univ., Rostov-on-Don, 1981.
51. V.V.Krasnikov and G.N.Dorofeenko, Khim.Geterotsikl. Soed., 1979, 21.
52. R.Huisgen, Angew.Chem., 1963, **75**, 604.
53. R.Huisgen, Uspekhi Khim., 1966, **35**, 150 [Russ.Chem. Rev., 1966(1)].
54. R.Huisgen, R.Grashey, and J.Sauer, in "The Chemistry of Alkenes" (Edited by S.L.Patai) (Translated into Russian), Izd.Khimiya, Leningrad, 1969, p.444.
55. R.Fuks and H.G.Viehe, in "Chemistry of Acetylenes" (Edited by H.G.Viehe) (Translated into Russian), Izd. Khimiya, Moscow, 1973, p.266.
56. H.Ulrich, "Cycloaddition Reactions of Heterocumulenes" Acad.Press, New York, 1967.
57. J.Bastide, J.Hamlin, F.Texier, and V.Vo Quant, Bull.Soc.chim.France, 1973, 2555, 2871.
58. T.Kaufmann, Angew.Chem., 1974, **86**, 715.
59. D.St.C.Black, R.F.Grozier, and V.C.Davis, Synthesis, 1975, 205.
60. R.Huisgen, Pure Appl.Chem., 1981, **53**, 171.
61. A.A.Tartakovskii and I.E.Chlenov, Zhur.Vses.Khim. Obshch.Mendeleeva, 1977, **22**, 252.
62. N.G.Khusainov and A.N.Pudovik, Uspekhi Khim., 1978, **47**, 1507 [Russ.Chem.Rev., 1978(9)].
63. O.A.Kruglaya and N.S.Vyazankin, Uspekhi Khim., 1980, **49**, 679 [Russ.Chem.Rev., 1980(4)].
64. V.A.Galishchev, V.N.Chistokletov, and A.A.Petrov, Uspekhi Khim., 1980, **49**, 1801 [Russ.Chem.Rev., 1980(9)].
65. A.D.Samoilov and A.I.Konovalov, Uspekhi Khim., 1984, **53**, 566 [Russ.Chem.Rev., 1984(4)].
66. S.F.Karaev, Sh.V.Garaeva, and A.M.Sladkov, 1984, **53**, 853 [Russ.Chem.Rev., 1984(5)].
67. V.A.Tertov, Doctoral Thesis in Chemical Sciences, Izd.Rostov.Univ., Rostov-on-Don, 1975.
68. B.Iddon and B.L.Lim, J.Chem.Soc., Perkin Trans., 1983, Part 1, 271.
69. M.F.Lappert and J.S.Poland, in "Advances in Organometallic Chemistry" (Edited by C.F.G.A.Stone and R.West), Acad.Press, New York, 1970, Vol.9, p.397.
70. M.F.Lappert and J.S.Poland, J.Chem.Soc.C, 1971, 3910.
71. U.Schöllkopf, D.Hoppe, N.Rieber, and V.Jakobi, Annalen, 1969, **730**, 1.
72. D.Seyferth, A.W.Dow, H.Menzel, and T.C.Flood, J.Amer.Chem.Soc., 1968, **90**, 1080.
73. D.Seyferth, H.Menzel, A.W.Dow, and T.C.Flood, J.Organomet.Chem., 1972, **44**, 279.
74. A.G.Brook and P.F.Jones, Canad.J.Chem., 1971, **49**, 1841.
75. M.F.Lappert and J.S.Poland, Chem.Comm., 1969, 156.
76. A.R.Bassindale and A.G.Brook, Canad.J.Chem., 1974, **52**, 3474.
77. G.W.Cowell and A.Ledwith, Quart.Rev., 1970, **24**, 113.
78. R.Grüning and J.Lorberth, J.Organomet.Chem., 1974, **69**, 213.
79. O.A.Kruglaya, I.B.Fedot'eva, V.V.Fedot'ev, I.D.Kalikhman, and N.S.Vyazankin, Zhur.Obshch. Khim., 1978, **48**, 1431.
80. O.A.Kruglaya, I.B.Fedot'eva, B.V.Fedot'ev, N.S.Vyazankin, and I.D.Kalikhman, Izv.Akad.Nauk SSSR, Ser.Khim., 1975, 2790.
81. M.F.Lappert and J.Lorberth, J.Chem.Comm., 1967, 836.
82. I.Lorberth, J.Organomet.Chem., 1971, 27, 303.
83. I.Lorberth, F.Schmock, and G.Zange, J.Organomet. Chem., 1973, **54**, 23.
84. P.Krommes and I.Lorberth, J.Organomet.Chem., 1975, **93**, 339.
85. P.Krommes and I.Lorberth, J.Organomet.Chem., 1976, **120**, 131.
86. D.Seyferth and T.C.Flood, J.Organomet.Chem., 1971, **29**, C25.
87. R.Grüning and I.Lorberth, J.Organomet.Chem., 1977, **129**, 55.
88. I.M.Crossman, R.N.Haszeldine, and A.E.Tipping, J.Chem.Soc., Dalton Trans., 1973, 483.
89. T.Aoyama, K.Sudo, and T.Shioiri, Chem.Farm. Bull.(Tokyo), 1982, **30**, 3849.
90. T.Aoyama and T.Sioiri, Chem.Farm.Bull.(Tokyo), 1982, **30**, 3450.
91. T.Aoyama and K.Sudo, Heterocycles, 1983, **20**, 163.
92. I.A.D'yakonov, I.B.Rebinskaya, and G.V.Golodnikov, Zhur.Org.Khim., 1966, **2**, 2256.
93. L.I.Zakharkin, A.V.Grebennikov, and L.A.Savina, Izv.Akad.Nauk SSSR, Ser.Khim., 1968, 1130.
94. R.F.Cunico and H.M.Leen, J.Amer.Chem.Soc., 1977, **99**, 7613.
95. A.Padwa and J.C.McDonald, J.Org.Chem., 1983, **48**, 3189.
96. L.Birkofer and M.Franz, Chem.Ber., 1967, **100**, 2681.
97. L.Birkofer and M.Franz, Chem.Ber., 1971, **104**, 3062.
98. L.G.Sharanina, V.S.Zavogorodnii, and A.A.Petrov, Zhur.Obshch.Khim., 1968, **38**, 1146.
99. G.Guillerm and M.Leguan, Compt.rend., 1969, **269 C**, 853.
100. V.D.Sheludyakov, N.A.Kiktorov, A.S.Tkachev, and V.F.Mironov, Zhur.Obshch.Khim., 1974, **47**, 90.
101. G.Guillerm, A.L'Honore, L.Veniard, G.Pourcelot, and J.Beniam, Bull.Soc.chim.France, 1973, 2739.
102. D.S.Matesson, J.Org.Chem., 1962, **27**, 4293.
103. V.N.Chistokletov and A.A.Petrov, Zhur.Obshch. Khim., 1972, **42**, 1865.
104. V.S.Zavgorodnii and A.A.Petrov, Zhur.Obshch. Khim., 1964, **34**, 1931.
105. V.S.Zavgorodnii, A.I.Maleeva, and A.A.Petrov, Zhur.Obshch.Khim., 1971, **41**, 2231.
106. M.M.Demina, A.S.Medvedeva, N.I.Protsuk, I.D.Kalikhman, and N.S.Vyazankin, Zhur.Obshch. Khim., 1979, **49**, 1331.

107. A.S.Medvedeva, M.M.Demina, N.I.Protsuk, I.D.Kalikhman, E.I.Brodskaya, G.A.Kalabin, and N.S.Vyazankin, Zhur.Obshch.Khim., 1980, **50**, 1775.
108. A.S.Medvedeva, M.M.Demina, J.D.Kalikhman, and N.S.Vyazankin, "III Intern.Conf.Organomet.and Coord.Chem.Germanium.Tin and Lead. Dortmund" 1980, p.66.
109. A.S.Medvedeva, M.M.Demina, A.I.Borisova, I.D.Kalikhman, and N.S.Vyazankin, Zhur.Obshch. Khim., 1981, **51**, 1324.
110. A.S.Medvedeva, M.M.Demina, A.I.Borisova, O.M.Mardorskaja, J.D.Kalikhman, E.I.Brodskaja, and N.S.Vyazankin, J.Organomet.Chem., 1982, **231**, 109.
111. A.S.Medvedeva, O.I.Mirgorodskaya, M.M.Demina, I.D.Kalikhman, and N.S.Vyazankin, Zhur.Obshch. Khim., 1983, **53**, 2247.
112. A.S.Medvedeva, M.M.Demina, L.P.Safronova, I.D.Kalikhman, V.Yu.Vitkovskii, and N.S.Vyazankin, Zhur.Obshch.Khim., 1983, **53**, 2251.
113. R.R.Bekmukhametov, Symposium, "Sovremennye Problemy Organicheskoi Khimii" (Modern Problems of Organic Chemistry), Izd.Leningrad.Gos.Univ., Leningrad, 1976, p.105.
114. E.Ettenhuber and K.Rühlmann, Chem.Ber., 1968, **101**, 743.
115. W.R.Peterson, B.Arkles, and S.S.Washburne, J.Organomet.Chem., 1976, **121**, 285.
116. L.Birkofer and P.Ritter, Chem.Ber., 1963, **96**, 2750.
117. L.Birkofer and P.Wegner, Chem.Ber., 1966, **99**, 2512.
118. L.Birkofer and W.Kaiser, Annalen, 1975, 266.
119. L.Birkofer, M.Franz, and G.Schmidtberg, Org.Mass Spectrom., 1974, **8**, 347.
120. L.Birkofer, A.Ritter, and K.Uhlenbrank, Chem.Ber., 1963, **96**, 3280.
121. O.Tsuge, S.Kanomasa, and K.Matsuda, Chem.Letters, 1983, 1131.
122. E.Lieber and F.M.Kleane, Chem.Ind., 1961, 747.
123. E.Lieber, C.N.R.Rao, and F.M.Klane, J.Inorg. Nucl.Chem., 1963, **25**, 631.
124. W.T.Reichle, Inorg.Chem., 1964, **3**, 402.
125. J.S.Thayer and R.West, Inorg.Chem., 1964, **3**, 406.
126. H.Gorth and M.C.Henry, J.Organomet.Chem., 1967, **9**, 117.
127. J.G.A.Leijten and G.J.M.van der Kerk, Rec.trav. Chim., 1964, **83**, 295.
128. P.Kreutzer, C.Weis, H.Boehme, T.Kemmerich, W.Beck, C.Spencer, and R.Mason, Z.Naturforsch., 1972, **276**, 745.
129. T.A.George and M.F.Lappert, J.Organomet.Chem., 1968, **14**, 327.
130. K.Sisiolo, K.Nabika, T.Isida, and S.Kozima, J.Organomet.Chem., 1971, **33**, 337.
131. P.Dunn and D.Oldfield, Austral.J.Chem., 1971, **24**, 645.
132. W.Beck and W.P.Fehlhammer, Angew.Chem., 1967, **79**, 146; Inter.Ed., 1967, **6**, 169.
133. H.Bock and M.Bauder, Chem.Ber., 1969, **102**, 3637.
134. A.G.Davis and P.G.Harrison, J.Organomet.Chem., 1967, **8**, 19.
135. A.D.Sinitsa, N.A.Parkhomenko, and L.N.Markovskii, Zhur.Obshch.Khim., 1977, **47**, 232.
136. L.A.Lazukina and V.P.Kukhar', Zhur.Org.Khim., 1979, **15**, 2216.
137. C.C.Addison and D.Sutton, Progress Inorg.Chem., 1967, **3**, 105.
138. W.Beck and W.P.Fehlhammer, Chem.Ber., 1969, **102**, 3637.
139. W.P.Fehlhammer and L.F.Dahl, J.Amer.Chem.Soc., 1972, **94**, 3370, 3377.
140. W.Beck, K.Burger, and W.P.Fehlhammer, Chem.Ber., 1971, **104**, 1816.
141. W.Beck and K.Schorpp, Chem.Ber., 1975, **108**, 3317.
142. W.P.Fehlhammer, K.Bartel, and W.Patel, J.Organomet.Chem., 1975, **87**, C34.
143. W.P.Fehlhammer, T.Kemmerich, and W.Beck, Chem. Ber., 1979, **112**, 468.
144. W.P.Fehlhammer, K.Bartel, A.Völke, and D.Achatz, Z.Naturforsch., 1982, **37b**, 1044.
145. W.P.Fehlhammer and W.Beck, Z.Naturforsch., 1983, **39b**, 546.
146. J.Erbe and W.Beck, Chem.Ber., 1983, **116**, 3867.
147. P.H.Kreutzer, J.C.Weis, H.Bock, J.Erbe, and W.M.Beck, Chem.Ber., 1983, **116**, 2691.
148. K.A.Andrianov, V.I.Sidorov, and L.M.Khananashvili, Dokl.Akad.Nauk SSSR, 1964, **158**, 868.
149. K.A.Andrianov, V.I.Sidorov, and L.M.Khananashvili, J.Organomet.Chem., 1965, **4**, 360.
150. K.A.Andrianov, V.I.Sidorov, and L.M.Khananashvili, Zhur.Obshch.Khim., 1968, **36**, 168.
151. A.R.Bassindale, A.G.Brook, O.F.Jones, and J.A.G.Stewart, J.Organomet.Chem., 1978, **152**, 25C.
152. L.I.Zakharkin and A.V.Grebennikov, Zhur.Obshch. Khim., 1969, **39**, 575.
153. G.Himbert, D.Frank, and M.Regitz, Chem.Ber., 1976, **109**, 370.
154. D.Frank, G.Himbert, and M.Regitz, Chem.Ber., 1978, **111**, 183.
155. J.H.Boyer, C.H.Mack, N.Goebel, and L.R.Morgan, J.Org.Chem., 1958, **23**, 1051.
156. G.S.Akimova, V.N.Chistokletov, and A.A.Petrov, Zhur.Org.Khim., 1967, **3**, 968.
157. G.S.Akimova, V.N.Chistokletov, and A.A.Petrov. Zhur.Org.Khim., 1968, **4**, 389.
158. H.-J.Lorkowski and R.Pannier, J.prakt.Chem., 1969, **311**, 958.
159. S.S.Washburne and W.R.Peterson, J.Organomet. Chem., 1970, **21**, 427.
160. L.V.Vilkov, V.S.Mastryukova, and N.I.Sadatova, "Opredelenie Geometricheskogo Stroeniya Svobodnykh Molekul" (Determination of the Geometrical Structure of Free Molecules), Izd.Khimiya, Moscow, 1978, p.155.
161. I.V.Zhakova, Candidate's Thesis in Chemical Sciences, Izd.Rostov.Univ., Rostov-on-Don, 1983.
162. Yu.V.Kolodyazhnyi, I.V.Zhakova, S.B.Bulgarevich, A.P.Sadimenko, and A.D.Garnovskii, Zhur.Obshch. Khim., 1983, **53**, 2266.
163. G.A.Shvekhgeimer, V.I.Evolinskii, K.I.Kobrakov, and A.M.Krapivin, Dokl.Akad.Nauk SSSR, 1980, **252**, 636.
164. V.N.Kalinin, A.V.Astakhin, A.V.Kazantsev, and L.I.Zakharkin, Zhur.Obshch.Khim., 1982, **52**, 1932.
165. T.Kondo, K.Yamamoto, H.Danda, and M.Kumada, J.Organomet.Chem., 1973, **61**, 361.
166. A.Padwa and J.G.MacDonald, Tetrahedron Letters, 1982, **23**, 3219.
167. M.D.Stadnichuk, Candidate's Thesis in Chemical Sciences, Lensovet Leningrad Technological Institute, Leningrad, 1969.
168. I.G.Kolokol'tseva, V.N.Chistokletov, M.D.Stadnichuk, and A.A.Petrov, Zhur.Obshch.Khim., 1968, **38**, 1820.
169. L.Berkofer and R.Stilke, Chem.Ber., 1974, **107**, 3717.
170. G.A.Shvekhgeimer, E.V.Arslanov, and A.Baranski, Roczn.Chem., 1972, **46**, 1249.
171. Yu.V.Svetkin and Yu.R.Kolesnik, Zhur.Obshch.Khim., 1982, **52**, 907.

172. P.DeShong and J.M.Leginus, J.Org.Chem., 1984, **49**, 3421.
173. P.DeShong and J.M.Leginus, Tetrahedron Letters, 1984, **25**, 5355.
174. I.G.Kolokol'tseva, V.N.Chistokletov, and A.A.Petrov, Zhur.Obshch.Khim., 1970, **40**, 2612.
175. H.Werner, B.Heisler, and A.Burschka, Chem.Ber., 1982, **115**, 3069.
176. H.Werner, J.Wolf, and H.Schubert, Chem.Ber., 1983, 1116, 2848.
177. Z.I.Kuplesnik, Zh.N.Belaya, and A.M.Pinchuk, Zhur.Obshch.Khim., 1984, **54**, 462.
178. D.Barton and W.D.Ollis (Editors), "Comprehensive Organic Chemistry" (Translated into Russian), Izd. Khimiya, Moscow, 1982, pp.518, 612, 613, 644, 709.
179. V.I.Boev and A.V.Dombrovskii, Zhur.Obshch.Khim., 1984, **54**, 1192.
180. I.V.Efimov, M.A.Kazankova, and I.F.Lutsenko, Zhur.Obshch.Khim., 1982, **52**, 2375.
181. I.V.Efimov, B.E.Kalganov, M.A.Kazankova, and I.F.Lutsenko, Zhur.Obshch.Khim., 1982, **52**, 459.
182. R.J.P.Corriu, V.Huynh, and J.J.E.Moreau, J.Organomet.Chem., 1983, **259**, 283.
183. S.Rajagopalan and G.Zweifel, Synthesis, 1984, 111.
184. J.G.Smith, N.P.Quinn, and M.Viswamthan, Synth. Comm., 1983, **13**, 773.
185. N.Plavac and M.Bersohn, Synth.Comm., 1983, **13**, 867.
186. J.Hibino, S.Matsubara, J.Morizawa, K.Oshima, and H.Nozaki, Tetrahedron Letters, 1984, **25**, 2151.
187. O.A.Reutov, I.P.Beletskaya, and V.I.Sokolov, "Mezkhanizmy Reaktsii Metalloorganicheskikh Soedinenii" (The Mechanisms of the Reactions of Organometallic Compounds), Izd.Khimiya, Moscow, 1972.
188. S.Huisgen, J.Org.Chem., 1968, **33**, 2291.
189. E.Stephan, Tetrahedron, 1975, **31**, 1623.
190. N.Wiberg and G.Pfeiner, Angew.Chem., 1977, **89**, 343.
191. R.West, M.Fink, and J.Michl, Science, 1981, **214**, 1343.
192. S.Masamune, H.Yuji, M.Shu, B.Thomas, and J.F.Blount, J.Amer.Chem.Soc., 1982, **104**, 1150.
193. M.Weittenbruch, A.Schäfer, and K.L.Thom, Z.Naturforsch., 1983, **B38**, 1695.
194. S.Masamune, S.H.Murakami, I.T.Snow, and H.Tohita, Organometallics, 1984, **3**, 333.
195. S.Masamune, S.Murakami, and D.J.Williams, J.Amer.Chem.Soc., 1983, **105**, 7776.
196. S.Murakami, S.Collins, and S.Masamune, Tetrahedron Letters, 1984, **25**, 2131.
197. H.Lavayaaiere, G.Douss, I.Satge, I.Barrau, and M.Traore, Angew.Chem., 1982, **97**, 455.
198. I.Satge, Pure and Appl.Chem., 1984, **56**, 137.
199. J.A.Walker, C.B.Knobler, and M.Hawthorne, J.Amer. Chem.Soc., 1983, **105**, 3370.
200. J.L.D'Errico, L.Messerle, and M.D.Curtis, Inorg. Chem., 1983, **22**, 849.
201. A.H.Cowley, Polyhedron, 1984, **3**, 389.
202. A.Padwa (Editor), "1,3-Dipolar Cycloaddition in Chemistry", J.Wiley Intersci., New York, 1984, Vols.1–2.
203. A.R.Katritsky and C.W.Rees (Editors), "Comprehensive Heterocyclic Chemistry", Pergamon Press, New York, 1984, Vol.5.

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