Translated from *Uspekhi Khimii*, **49**, 637-678 (1980) U.D.C. 547.46.052.3

Advances in the Chemistry of Pernitriles

N.S.Zefirov and D.I.Makhon'kov

The problems of a formal systematic treatment of nitrogen-carbon structures as well as the methods of synthesis, chemical properties, and applications of the most familiar representative of the class of nitrogen-carbon compounds, namely pernitriles, are examined.
The bibliography includes 298 references.

CONTENTS

I.	Introduction	337
II.	A formal systematic treatment of nitrogen-carbon structures	337
III.	Percyanoalkanes	338
IV.	Percyanoalkenes	339
V.	Percyanoalkynes	347
VI.	Percyanoarenes	349
VII.	Percyano-derivatives of nitrogen heterocycles	349
VIII.	Pernitriles with a nitrogen-carbon skeleton	350
IX.	Appendix	352

I. INTRODUCTION

Approximately 30 organic compounds, whose molecules consist solely of nitrogen and carbon atoms, and approximately the same number of anions of percyanohydrocarbon derivatives containing one or several acid C–H bonds—the so-called cyanocarbonic acids (see Appendix)—are now known. However, it is of interest that, although the majority of these acids form stable salts, for example dicyanamide, pentacyanocyclopentadiene etc., it has so far been impossible to synthesise compounds such as hexacyanocyclopentadiene, or tricyanamide, which are extremely interesting from both theoretical and possibly practical points of view.

Analysis of literature data shows that during the last 15 years the number of compounds of the "nitrogen–carbon" class synthesised has not only increased almost by a factor of nine[1], but every year there is an increase in the number of publications devoted to the investigation of the physicochemical and chemical properties of these compounds.

By virtue of advances in synthesis, the majority of representatives of this class have become relatively readily available and the intense development of quantum-chemical methods permitted a theoretical prediction of the existence of molecules of this type. This applies primarily to polycyano-compounds or pernitriles, which have recently become the objects of constant attention by investigators. The unusual properties of polynitriles are associated with the unique properties of the cyano-group, which combines powerful electron-accepting properties with a small bulk. Being linear and containing a cylindrical π-electron system, the cyano-group is capable of conjugation with a wide variety of π-electron systems, being favoured in this respect compared with other strong electron-accepting substituents such as the nitro- and sulphonyl groups.

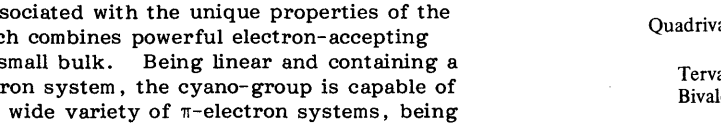
As an illustration, we may note that the electrical conductivities of salts of the tetracyanoquinodimethane radical-ion are virtually equal to the conductivity of graphite, pentacyanocyclopentadiene is a stronger acid than perchloric acid, tetracyanoquinone oxidises water, and tetracyano-oxiran adds to olefins and even to aromatic compounds, like ozone[2].

Despite the relative novelty of nitrogen–carbon compounds, certain representatives of this class of compounds have become quite familiar chemically. For example, the bibliography on the chemistry of tetracyanoethylene already numbers more than a thousand studies and there has been no slackening of the interest in this compound. Furthermore, each year new types of reactions of tetracyanoethylene are reported. On the other hand, the chemistry of many polynitriles has been studied very superficially, although it is of considerable theoretical and even practical interest.

The present review is devoted to advances in the chemistry of pernitriles and covers the literature up to 1976 inclusive. The section devoted to the systematic treatment of nitrogen–carbon molecules deals with an examination of literature data.

II. A FORMAL SYSTEMATIC TREATMENT OF NITROGEN–CARBON STRUCTURES

We shall consider a formal combinatorial approach to structures consisting of carbon and nitrogen atoms. Both these elements have coordination numbers ranging from unity to four depending on the oxidation state and are capable of forming double and triple bonds. On this basis, it is easy to deduce all possible monatomic fragments, which are illustrated below:



Any structure of a nitrogen–carbon compound can be obtained by scanning all possible combinations of these fragments, provided that the following requirements are fulfilled: all the valences are saturated and the molecule is electrically neutral overall. The role of the homologous modulus (cm^3)

† The list does not include bivalent carbon, because isonitriles can be described in terms of the fragment $-N\equiv C$.

can be fulfilled either by homogroups of the type $-C\equiv C-$ and $-N=N-$ (there is also a possibility of the formation of cumulene carbon chains) or by heterogroups such as, for example, $-N=C=N-$. Among these, only the azo-group has a geometry suitable for inclusion in a ring and for the formation of cyclic azaheterocycles. It is readily seen that the combination of the above atomic fragments permits a large variety of nitrogen–carbon skeletons, which can be divided into two types: (1) those with single free valences and (2) those with unused double bonds ("exo-double bonds").

The fundamental problem in the determination of molecular structures consists in finding the end group. Evidently, only two monatomic fragments, $Y\equiv$ and $Z=$, can play the role of an end group and neither is univalent. A bivalent end group can be derived from the diatomic fragment $=X=Z$; the diazo-group $=\overset{+}{N}=\overline{N}$ corresponds to such a fragment. In hydrocarbons the terminal valence is usually saturated by a univalent atom—hydrogen. Evidently, in a systematic treatment of nitrogen–carbon compounds it is essential to find univalent fragments capable of "covering" the unused valences; a nitrogen–carbon structure can then be derived by means of a systematic treatment of hydrocarbons involving the replacement of hydrogen atoms by the appropriate univalent nitrogen–carbon group. Among diatomic electrically neutral combinations, it is possible to obtain only one, $-X\equiv Y$, satisfying the requirement for a univalent state. The $-C\equiv N$ and $-\overset{+}{N}\equiv C^-$ functional groups, i.e. the nitrile and isonitrile groups, correspond to this combination. The azido-group $N\equiv\overset{+}{N}-\overline{N}- \leftrightarrow N=\overset{+}{N}=N-$ corresponds to the univalent triatomic fragments $Y\equiv X-Z-$ or $Z=X=Y-$. Thus the molecules of nitrogen–carbon compounds (with the exception of unsaturated cyclic structures consisting of azo- and acetylenic groups) should belong to the class of diazo-compounds, nitriles, isonitriles, and azides.

Molecules containing more than two isonitrile or diazo-groups are apparently unknown. On the other hand, pernitriles and perazides have been described in the literature. However, whereas there are only isolated publications on perazides[4–9], the literature on pernitriles is fairly extensive; the properties of pernitriles are the subject of the succeeding sections of the review.

III. PERCYANOALKANES

1. Tetracyanomethane

The only stable representative of the percyanoalkane series is tetracyanomethane (TCM). The first attempt to synthesise TCM from silver tricyanomethide and chlorocyanogen was undertaken by Schmidtmann[10] in 1896. Three years later Hantzch and Osswald[11] tried to obtain TCM by Schmidtmann's method having replaced chlorocyanogen by iodocyanogen. The attempts to synthesise TCM from bromotricyanomethane and potassium cyanide[12] and from the compounds $C(CH_2N{=}CHC_6H_5)_4$ and $C(CH_2NCl_2)_4$ were also unsuccessful[13].

It was not until 1969 that Mayer[14] succeeded in synthesising TCM in accordance with Schmidtmann's scheme:

$$AgC(CN)_3 + ClCN \xrightarrow{100^\circ} AgCl + C(CN)_4 \ . \qquad (1)$$

Mayer's product was a colourless crystalline compound, soluble in polar solvents, and decomposing fairly rapidly on storage with formation of an unidentified orange-yellow amorphous substance. Mayer described certain chemical properties of TCM, in particular its alkaline and acid hydrolysis:

$$C(CN)_4 + 2OH^- \rightarrow C(CN)_3^- + OCN^- + H_2O \ ,$$
$$C(CN)_4 + 2H_2O \rightarrow C(CN)_3^- + NH_4^+ + CO_2 \ .$$

Systematic study of the chemistry of TCM began as soon as it was shown[15] that the stability of this compound depends greatly on the conditions of its synthesis, particularly on the absence of traces of chlorine in chlorocyanogen and of traces of moisture in silver tricyanomethide (which catalyse the trimerisation of chlorocyanogen). The presence of an admixture of cyanuric chloride was in fact responsible for the instability of the first TCM specimens. The enthalpy of formation of TCM from the elements has been determined[16], its molecular geometry has been studied by electron diffraction[17] and X-ray diffraction[18], and its photoelectron[19], ^{13}C NMR[13,20], and infrared and Raman spectra[21] have been studied.

As was to be expected, TCM proved to be extremely reactive in relation to nucleophiles. Comparison of the thermochemical properties of TCM and polyhalogenomethanes showed that the accumulation of four cyano-groups at a saturated carbon atom leads to an appreciable destabilisation of the TCM molecule. The "bond separation" energy, the existence of which is reflected in a tendency towards reaction involving the formation of the nitrile cation and the tricyanomethyl anion, is 23.5 kcal mol^{-1}.[20]

Tetracyanomethane reacts readily with inorganic chlorides, for example:

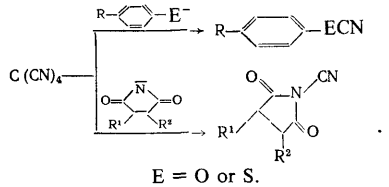
$$C(CN)_4 + LiCl \rightarrow LiC(CN)_3 + ClCN \ .$$

Formally, this reaction can be regarded as electrophilic substitution at a saturated carbon atom (the cyano-group is replaced by the lithium cation). However, the "cyanophilic" mechanism, involving attack by the nucleophile on the carbon atom of the cyano-group, is believed nowadays to hold for these reactions:

$$B^- + N\equiv C-C(CN)_3 \longrightarrow B-CN + C(CN)_3^- \ .$$

This mechanism is related to that of the so-called "halogenophilic" reactions of polyhalides[15,22,23].

The reaction of TCM with caesium fluoride has been used successfully as a method for the preparation of fluorocyanogen[24], but attempts to synthesise dicyanogen oxide by the analogous reaction with potassium and caesium cyanates led to the isolation of an unidentified polymer[25]. The reactions of TCM with the anions of dibasic acid imides[23] and phenoxide and thiophenoxide anions[22] take place under mild conditions (THF, 10–15 min) and lead respectively to *N*-cyanoimides, cyanates, and thiocyanates:



E = O or S.

Thus TCM behaves as a powerful cyanating agent in reactions with nucleophiles of this type.

The reactions of TCM with tertiary amines and phosphines, which in most cases lead to unidentified mixtures of products, proceed in a much more complex manner. It is believed[15] that in this case the primary reaction products are trisubstituted *N*-cyanoammonium or *P*-cyanophosphonium tricyanomethides [mechanism (2)]—extremely reactive compounds which undergo subsequent hydrolysis with elimination of the cyano-group from the cation or undergo intramolecular transformations involving attack on the cation by the ambident cyanoform anion:

$$R_3E + C(CN)_4 \rightarrow [R_3\overset{+}{E}CN]\,\bar{C}(CN)_3 \ ; \qquad (2)$$
$$E = N \text{ or } P \ .$$

The products of secondary reactions of the first type—tribenzylammonium and triphenylphosphonium tricyanomethides—have been isolated in yields of 90 and 20% respectively[15]. The reaction of TCM with triphenylphosphine complexes of transition metals have been reported[26] to proceed via the mechanism

$$Pt(Ph_3P)_4 + C(CN)_4 \rightarrow 2Ph_3P + Pt(Ph_3P)_2(CN)C(CN)_3 \quad .$$

However, in the light of later studies of the reactions of TCM with nucleophiles, the above reaction probably requires a more detailed investigation.

The ability of an electrophile such as TCM to react with compounds which are usually classified as electrophiles (hydrogen chloride and the halides of sulphur and phosphorus acid) was very much unexpected[15]:

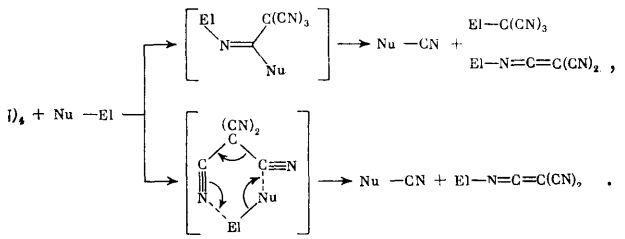
$$C(CN)_4 + HCl \rightarrow ClCN + HC(CN)_3 \xrightarrow{HCl} (NC)_2C{=}C\begin{matrix}NH_2\\Cl\end{matrix} \quad ,$$

$$C(CN)_4 + SO_2Cl_2 \rightarrow ClCN + ClC(CN)_3 + SO_2 \quad ,$$

$$C(CN)_4 + SOCl_2 \rightarrow ClCN + (NC)_2C{=}C\begin{matrix}N{=}S{=}O\\Cl\end{matrix} \quad ,$$

$$C(CN)_4 + PCl_5 \rightarrow ClCN + (NC)_2C{=}C\begin{matrix}N{=}PCl_3\\Cl\end{matrix} \quad .$$

Alternative mechanisms of the above reactions are presented below[15]:



us TCM is a unique compound in which a regular tetral structure and the consequent equivalence of all the ›-groups are combined with a high mobility of one of the ›-groups, since TCM reacts with equal ease with both nucleophiles and electroph'les.

Reactions of the first type are particularly useful when anions of different kinds are used as nucleophiles. The transfer of the cyano-group to an atom with a negative charge takes place under extremely mild conditions and leads to cyanation products in almost quantitative yields.

Reactions of the second type with compounds containing a mobile chlorine atom are also extremely convenient for the synthesis of compounds having four electron-accepting groups at a saturated carbon atom (for example, of chlorotricyanomethane) and derivatives of the keten imine form of the tricyanomethide anion such as thionylamino- and phosphazo-2,2-dicyanoethylenes.

2. Hexacyanoethane

In 1928 the first and unsuccessful attempt was made to obtain hexacyanoethane (HCE) by treating silver tricyanomethide with chlorine[27]. The synthesis of HCE was achieved in 1968 by the reaction of chlorocyanogen with pentacyanoethylsodium, obtained by treating tetracyanoethylene with sodium cyanide[28]. The yield of product was only 17%. The discoverers of this synthesis note that the success of the reaction depends on the absence of a solvent (apart from chlorocyanogen itself). The best results were obtained in the presence of aluminium chloride. Both in solutions and in crystalline state HCE decomposes rapidly (the process is catalysed by bases) with formation of tetracyanoethylene. As in many other reactions of pernitriles, dicyanogen, which theoretically should be formed in this reaction, could not be detected[28].

IV. PERCYANOALKENES

1. Tetracyanoethylene (TCE)

A number of reviews, both general[2,29] and concerned with certain specific questions, for example, the reactions of TCE with amines and aminoacids[30], the alkylation of TCE[31], transition metal complexes of pernitriles[32], the properties of polymeric compounds of metallic derivatives of TCE[33], and molecular complexes[34], have been devoted to the chemistry of tetracyanoethylene. The present review therefore deals solely with the most interesting studies carried out in the last eight years.

Vigorous investigation of the synthetic aspects of the chemistry of TCE led to the publication of new reports on the physicochemical properties of this compound. Thus the molecular constants[35] and molecular orbitals[36] of TCE have been calculated and studies have been made on the NMR[37] and NQR[38] spectra, mass spectra (of negative ions)[39], photoelectron spectra[40], and the relation between the ionisation potentials and electron affinities, on the one hand, and the reactivity of TCE, on the other[41].

(a) Molecular Complexes of TCE

The presence of four powerful electron-accepting groups is responsible for the extremely high tendency of TCE to form molecular complexes with a wide variety of classes of electron-donating molecules, among which complexes with aromatic compounds[34] and polymeric complexes of TCE have been most thoroughly investigated[42].

The formation of complexes of TCE with π-donors precedes as a rule the cycloaddition, tricyanovinylation, and cyanation reactions. Thus the interaction of TCE with ferrocene is not limited to the formation of a π-complex, which was believed for a long time, but leads to a mixture of cyanoferrocene (40%) and tricyanovinylferrocene (16%) (150 °C, sulpholane or acetonitrile as solvents)[43]. The analogous reaction with ferrocenylmercury chloride yields mainly tricyanovinylferrocene and the absence of the directing effect in the reaction with ethylferrocene indicates a radical mechanism of this reaction[43].

In the presence of bases TCE reacts with 2,4,6-trinitroanisole and 1,3,5-trinitrobenzene to form anionic σ-complexes, whose structure has been confirmed by NMR[44]. It has been shown recently that TCE forms molecular complexes also with saturated compounds of Group IVB metals (permethylpolysilanes[45], polygermanes[46], hexa-alkyldistannanes[46], and tetraalkyl derivatives of germanium, tin, and lead[47]) and even with saturated hydrocarbons—hexamethylethane, cyclohexane, bicyclohexyl, decalin, adamantane, and 1,1-biadamantyl[48].

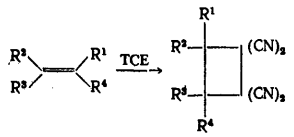
(b) Reactions Involving Addition to the C=C Bond of TCE

The vast majority of reactions of TCE (probably with the sole exception of reactions involving the cyano-group and the cracking reaction) include the stage in which the substrate adds to the C=C bond of TCE, leading as a rule to a zwitterionic intermediate, which then cyclises intramolecularly or undergoes intermolecular reactions, frequently accompanied by fragmentation processes of different types. In particular, this factor is responsible for the wide variety and complexity of the chemistry of TCE.

Another type of addition reaction (in the presence of a mobile hydrogen atom in the substrate molecule) involves the formation of substituted tetracyanoethanes, which are in many instances the final products, but which usually decompose with elimination of an HCN molecule, malononitrile, or tetracyanoethane.

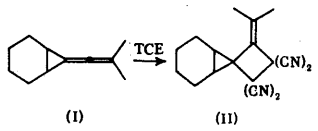
The reactions of TCE with olefins, the principal pathway of which in the case of monoalkenes involves the formation of cyclic 1,2-adducts, have apparently been most thoroughly investigated. When the molecule contains a large number of double bonds (particularly conjugated double bonds or bonds with a suitable steric arrangement), the reaction products are 1,*n*-adducts. In the simplest case of conjugated donors $n = 4$ (the Diels–Alder reaction), but in more complex systems there is a possibility of the formation of adducts with $n = 3$, 5, 6, 8, and higher values, the reactions being usually accompanied by different kinds of rearrangements and leading as a rule to mixtures of isomers. The study of reactions of this type is extremely interesting for the investigation of problems of reactivity.

1,2-Cycloaddition reactions. The activation of the double bond by steric strain or by electron-donating substituents entails addition to TCE with formation of cyclobutane derivatives. Vinyl sulphides, *N*-vinylamides, *N*-vinylsulphonamides[29], vinyl ethers, and vinylcyclopropanes react via the general mechanism



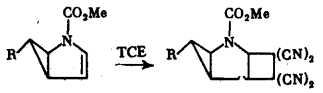
(3)

In the last case, however, the reaction is complicated by the ability of TCE to react with cyclopropane via the $[2\pi + 2\sigma]$ mechanism (see below). Nevertheless, the reaction with allene (I) yields both isomers of the spiro-compound (II):[49]



(I) (II)

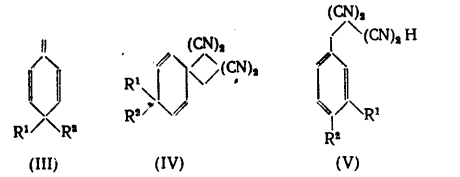
Nor is the three-membered ring involved in reactions of derivatives of 2-azabicyclo[3,1,0]hex-3-ene[50]:



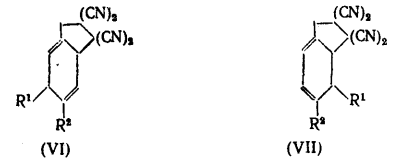
Aryl-substituted olefins, namely styrenes[51], acenaphthylene[52,53], 1-vinylpyrene[53], as well as indene and vinylferrocene react with TCE in accordance with the $[2\pi + 2\pi]$ mechanism[53,54]. However, in many cases the reaction involves the aromatic system and leads to 1,4-addition products (see below).

1,3-Dienes incapable of undergoing the Diels–Alder reaction (for example, cyclic olefins with an exomethylene group and polymethylated butadienes) also form 1,2-adducts as a rule. Reactions of this kind have been reviewed[55].

The reaction of TCE with 6,6-disubstituted 3-methylenecyclohexa-1,4-dienes greatly depends on the structure of the triene. Whereas the dimethyl derivative (IIIa) forms adducts (IV) and (V) [adduct (IV) rearranges to adduct (V) in polar solvents], the corresponding aryl derivatives (IIIb) and (IIIc) give rise to adduct (V) and a further two adducts (VI) and (VII), the relative amounts of which depend on the polarity of the solvent[56]:



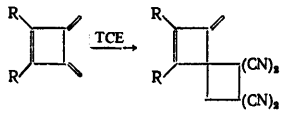
(III) (IV) (V)



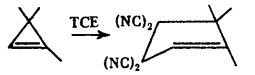
(VI) (VII)

(a) $R^1 = R^2 = CH_3$; (b) $R^1 = Ph$, $R^2 = CH_3$; (c) $R^1 = R^2 = Ph$.

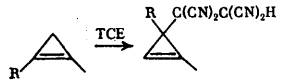
The reactions of diphenyl- and dimethyl-dimethylenecyclobutenes take place via the 1,2-cycloaddition mechanism[29]:



The reaction of TCE with cyclopropenes depends on the presence or absence of an allylic hydrogen atom. In the latter case ring opening occurs (via the stage involving the addition of TCE to the double bond), while in the former case a substituted tetracyanoethane is produced[57]:

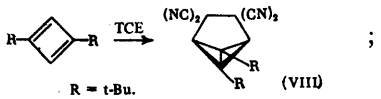


;



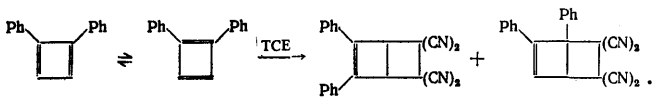
.

1,3-Di-(t-butyl)cyclobutadiene reacts with TCE to form derivative of dihydrobenzvalene (VIII) in a high yield[58]:



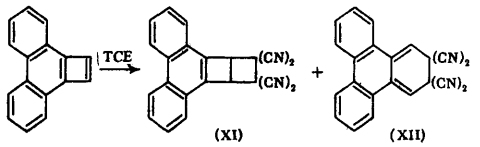
;

On the other hand, the existence of *o*-diphenylcyclobutadiene as an equilibrium mixture of two isomers was confirmed by the formation of adducts (IX) and (X) in proportions of 1 : 7:[59]



(IX) (X)

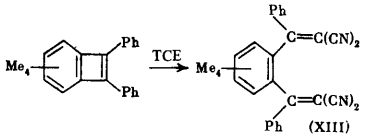
The reaction of phenanthro[*l*]cyclobutadiene with TCE leads to a mixture of adducts (XI) and (XII), the former being unstable and rearranging to the latter on heating[60]:



(XI) (XII)

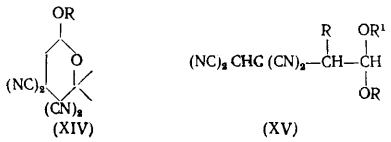
The reaction of benzocyclobutenes proceeds differently[61,62]. The addition of one equivalent of TCE leads to the formation

of adducts with structure (XIII)[62]:



(XIII)

The cycloaddition of TCE to vinyl ethers proceeds via the stage of a 1,4-dipolar intermediate, which has been convincingly demonstrated by Schug and Huisgen[63], who isolated compound (XIV) after the reaction of ethoxyethylene with TCE in acetone[63]. Tetrahydropyridines and piperidines respectively are formed analogously in the presence of nitriles and amines[63]. The products (XV) of the reaction of the zwitter-ionic intermediate with alcohols have also been isolated and conformational and kinetic studies on this process have been carried out[64,65]:



(XIV) (XV)

The cyclobutanes obtained by the reaction of TCE with ring-substituted phenyl vinyl ethers decompose slowly with loss of HCN and the formation of 4-aryloxy-1,1,2-tricyanobuta-1,3-dienes[66]. Metalloalkylolefins (XVI), containing Group IV elements, behave analogously to vinyl ethers[67]:

$$CH_2{=}CH{-}CH_2{-}MR_3 \ (M = Si,\ Ge,\ or\ Sn;\ R = Me\ or\ Ph)\ .$$

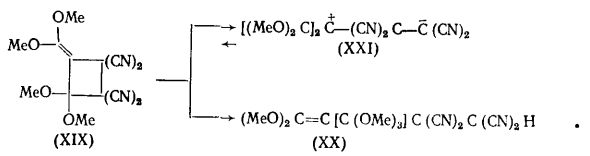
(XVI)

The coordination of an olefin to transition metals (Fe, Co, ', Mo)[68] leads, as in the case of polyenes (see below), to a ange in the reaction pathway and to the formation (for yl and allenyl derivatives) of rearranged products of types VII) and (XVIII):



(XVII) (XVIII)

.'he reaction of TCE with tetramethoxyethylene leads to the normal [2 + 2]-adduct[69], while the analogous reaction with tetramethoxyallene gives an equilibrium mixture of compound (XIX) [which gives rise to compound (XX) on treatment with methanol] and the betaine (XXI)—the principal component at room temperature[70]:

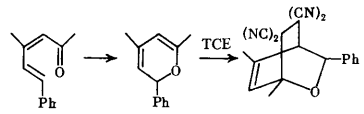


(XXI)

(XIX) (XX)

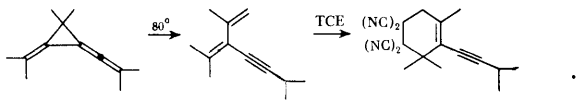
Conjugated dienes and polyenes. After it had been found that TCE is such a powerful dienophile that it can be used for the quantitative determination of dienes[71], the formation of the corresponding adducts became a virtually permanent feature of studies on the synthesis of compounds containing a diene or heterodiene fragment. This led to the publication of a whole series of reports dealing with the study of the mechanism, kinetics, and thermochemistry of the Diels–Alder reaction with TCE[72–77].

TCE proved to be extremely useful for the trapping of various kinds of intermediates containing a diene system [for example, the pyran (XXII), formed in the isomerisation of 4-methyl-6-phenylhexa-3,5-dien-2-one, was identified in this way[78] (scheme (IV)] and also for the investigation of problems of electrocyclic tautomerism (particularly for the quantitative estimation of the content of isomers):

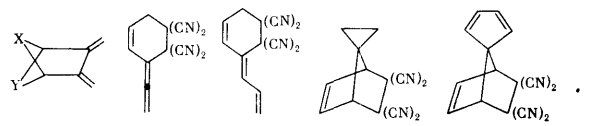


(XXII) (4)

As an example, mention may be made of studies by Huisgen and coworkers on the cycloaddition of TCE to substituted cyclo-octatetraenes[79–81]. TCE has found extensive applications for the identification of unstable dienes formed in thermal, photochemical, or catalytic isomerisation reactions. An interesting example of this kind is provided by the thermal isomerisation of 1-dimethylvinylidene-2-isopropylidene-3,3-dimethylcyclopropane[82]:



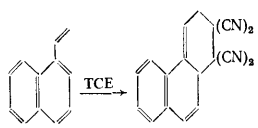
Among the dienes introduced into the Diels–Alder reaction with TCE, a wide variety of systems have been investigated: phenafulvenes to which TCE adds in the 8- and 10-positions[83], dimethylene derivatives of bi- and tri-cyclic hydrocarbons having the general formula (XXIII)[84–86], thioacetals[87], phencyclone[73,88], *N*-methylisoquinolinone[89], dialkyl butadien-2-yl phosphates[90], biscyclopentadienylmercury[91], as well as divinylallene[92], 1,2,3,5-hexatetraene[93], spiro[2,4]heptatriene[94], and spiro[4,4]nonatriene[95], which combine with only one equivalent of TCE [adducts (XXIV)–(XXVII)]:



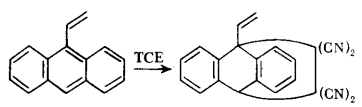
(XXIII) (XXIV) (XXV) (XXVI) (XXVII)

The diene and ene synthesis reactions involving polyene systems have also been studied in relation to derivatives of vitamin A_1 and steroid alkenes[96,97].

Aryl-substituted olefins give rise as a rule to [2 + 2]-adducts (see above). On the other hand, 1-vinyl- and 2-vinyl-naphthalenes react via the Diels–Alder mechanism[29,53], for example:

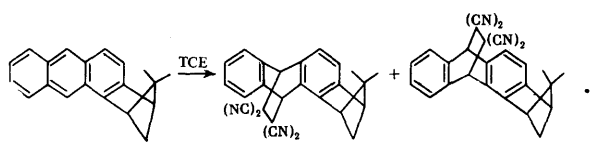


while 9-vinylanthracene[53] reacts like anthracene itself[98], combining with TCE in the 9- and 10-positions, i.e. the vinyl group is not involved in the reaction. Adduct (XXVIII) dissociates readily in solution:



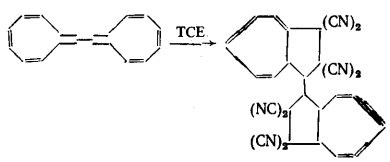
(XXVIII)

The reaction of TCE with apopinanthracene reacts anomalously—the addition to the sterically hindered part of the molecule takes place preferentially [(XXIX) : (XXX) = 1.5][99]:

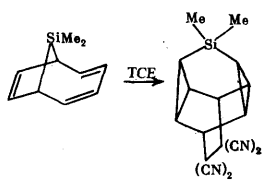


(XXIX) (XXX)

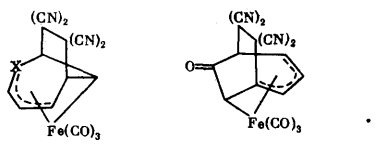
The reaction of 8,8-biheptafulvenyl with TCE leads to a mixture of adducts, which has not been separated, believed to contain, on the basis of spectroscopic data, the products of [8 + 2]-cycloaddition[100]:



Among unusual reactions of TCE, mention may also be made of the reaction with 9,9-dimethyl-9-silabicyclo[4,2,1]nona-2,4,7-triene[101]:



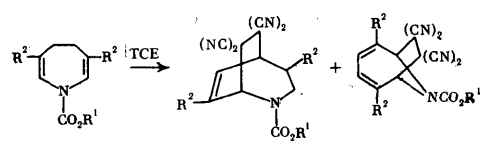
The reactions of TCE with polyene systems are also of special interest for the study of the influence of transition metals on the reactivity of coordinated olefins. Investigations[102–104] have shown that tricarbonyliron complexes of cycloheptatriene and cyclooctatetraene readily undergo 1,3-exo-cycloaddition with formation of the σ,π-complexes (XXXI) and (XXXII) respectively:



(XXXI), X = CH_2; (XXXII), X = —CH=CH— (XXXIII)

while the reaction of troponetricarbonyliron with TCE gives the 1,5-cycloaddition product (XXXIII).

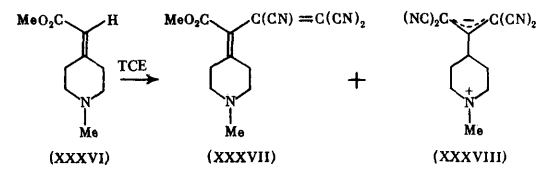
The addition of TCE to azepines[105–107] proceeds via mechanism (5), the formation of the 1,6-adducts (XXXV) being observed only for 3,6-di(isopropyl or t-butyl)azepines; it has been shown[107] that it is a kinetically controlled process, the 1,4-adducts (XXXIV) being thermodynamically more stable:



(5)

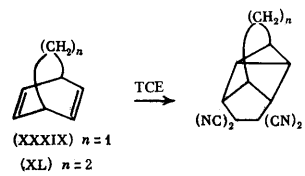
(XXXIV) (XXXV)

It is of interest that the formation of cyclic adducts is not observed at all in the reaction with dihydropyridine (XXXVI). The principal reaction products are compounds (XXXVII) and (XXXVIII)[108]. The mechanism of this reaction has not been studied:



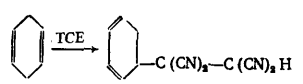
(XXXVI) (XXXVII) (XXXVIII)

Homodiene structures. The study of the interaction of homoconjugated dienes with TCE showed that the reactivity of bicyclo[2,2,*n*]alkadienes ($n = 1,2,3$, or 4) decreases with increasing *n* and that, whereas compounds (XXXIX) and (XL) react with TCE via the [2*s* + 2*s* + 2*s*] mechanism [Eqn.(6)], cyclohexa-1,4-diene forms adduct (XLI), which readily loses a molecule of tetracyanoethane to form benzene[109] [mechanism (7)]:



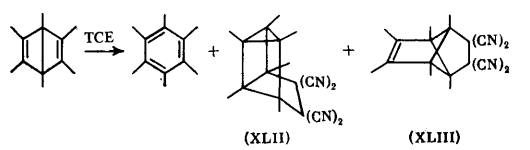
(XXXIX) *n* = 1
(XL) *n* = 2

(6)



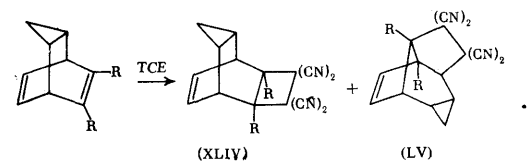
(7)

The reaction with hexamethylbicyclo[2,2,0]hexadiene gives a mixture of hexamethylbenzene (12–15%) and adducts (XLII) and (XLIII) in proportions of 10 : 1:[110]



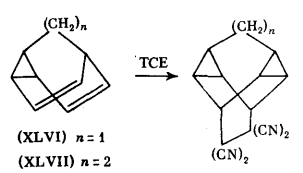
(XLII) (XLIII)

The photoaddition of TCE to tricyclo[3,2,2,$0^{2,4}$]nonadiene derivatives leads to a mixture of adducts (XLIV) and (XLV)[111]:



(XLIV) (LV)

Bridged homotropylidenes combine with TCE via the mechanism of the Diels–Alder reaction. Thus barbaralane (XLVI) and dihydrobullvalene (XLVII) react with TCE via the following mechanism[112]:

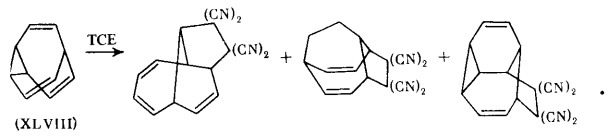


(XLVI) *n* = 1
(XLVII) *n* = 2

The photochemical reaction with barbaralone proceeds analogously[113].

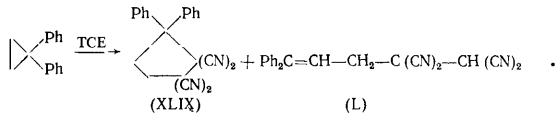
The reaction of bullvalene (XLVIII) with TCE leads to the formation of products whose relative amounts depend on the

polarity of the solvent#:



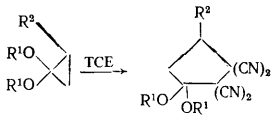
(XLVIII)

Reactions with strained hydrocarbons. Whereas cyclopropane itself does not react with TCE, the reaction with 1,1-diphenylcyclopropane leads to a mixture of products (XLIX) and (L) in proportions of 1 : 1.3[114]:

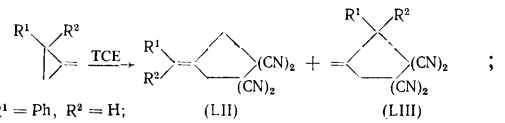


(XLIX) (L)

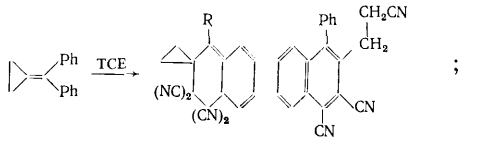
The cycloaddition of cyclopropanone and phenylcyclopropanone acetals proceeds via the $[2\sigma + 2\pi]$ mechanism[115]:



Methylenecyclopropanes (LIa) and (LIb) react with TCE to form the 1 : 1 adducts (LII) and (LIII); the introduction of aromatic substituents into the methylene component of the molecule of (LIV) leads (via a zwitter-ionic intermediate) to adduct (LV)[116]:



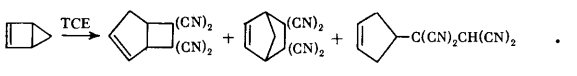
(LI) (a) $R^1 = Ph$, $R^2 = H$; (LII) (LIII)
(b) $R^1 = R^2 = Ph$.



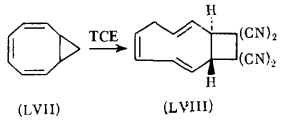
(LIV) (a) R = H; (LV) (LVI)
(b) R = Ph .

It has been shown[117] that compound (LVb) is then aromatised with the opening of the three-membered ring and the loss of HCN; the final product has the structure (LVI).

The reaction of TCE with bicyclo[2,1,0]pent-2-ene in THF leads to a mixture of products via the following mechanism[118]:

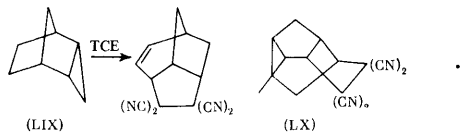


The electrophilic addition of TCE to *cis*-bicyclo[6,1,0]nonatriene (LVII) also proceeds with the simultaneous expansion of both rings[119]. Kinetic measurements have shown that compound (LVII) does not react directly with TCE; the latter adds to the valence isomer of this compound—1-*cis*, 3-*trans*, 5-*cis*, 7-*cis*-cyclononatetraene, with formation of adduct (LVIII)[120]:



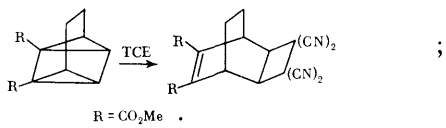
(LVII) (LVIII)

The non-concerted polar cycloaddition of TCE to *endo*-tricyclo[3,2,1,$0^{2,4}$]oct-6-ene (LIX) proceeds with the opening of the three-membered ring[121]. It is of interest that the introduction of a methyl group in the 2-position of compound (LIX) results in the formation of an adduct having the structure (LX)[122]:



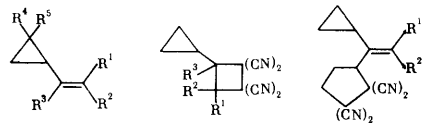
(LIX) (LX)

The reaction of TCE with tetracyclo[4,2,$0^{2,8}$,$0^{5,7}$]octane-1,6-dicarboxylate[123] leads to the stereospecific addition to the bis(homocyclobutane) system:

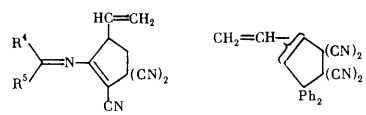


The reaction with quadricyclane proceeds in the same way[124]. On the other hand, the structure of the adduct with hexamethylprismane[125] has not so far been established.

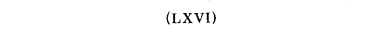
Cyclopropylalkenes. The mode of reaction of TCE with cyclopropylethylenes has been found to depend markedly on the structural characteristics of the latter. Whereas the reaction with cyclopropylethylene (LXIa) and 1,1-dicyclopropylethylenes (LXI, b and c) leads exclusively to the products of [2 + 2]-cycloaddition (LXII), the replacement of the methyl groups by phenyl groups or cyclopropyl groups [compounds (LXI, d and e)] gives rise to adducts having the structure (LXIII). The reaction of compound (LXIf) leads to a 7 : 1 mixture of compounds (LXIV) and (LXV), while the reaction of compound (LXIg) yields, apart from adduct (LXIV), also compound (LXVI) [the reaction with compound (LXIh) proceeds analogously].



(LXI) (LXII) (LXIII)



(LXIV) (LXV)



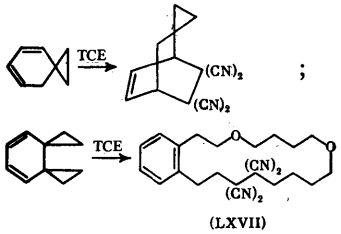
(LXVI)

(a) R = H; (b) R = H, R^3 = cyclopropyl; (c) R = H, $R^1 = R^2$ = Me,
R^3 = cyclopropyl; (d) R = H, $R^1 = R^2 = R^3$ = cyclopropyl;
(e) R = H, $R^1 = R^2$ = Ph, R^3 = cyclopropyl; (f) R = H, $R^4 = R^5$ = Ph;
(g) R = H, $R^4 = R^5$ = *o*-biphenylene; (h) R = H, R^3 = Me, R^4, R^5 = *o*-biphenylene.

The latter finding suggests that cycloadditions of this type take place with formation of a zwitter-ionic intermediate[126-128]. However, the formation of a TCE radical-anion in reactions with cyclopropylethylenes has been confirmed spectroscopically in a number of instances[127].

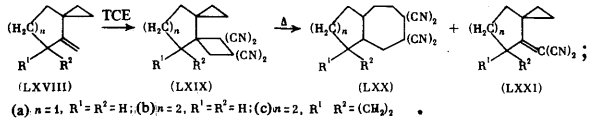
See P.Cernuschi, C.De Micheli, and R.Gandolfi, Tetrahedron Letters, 3667 (1977).

The reaction of spiro[2,5]octa-4,6-diene with TCE[129] led to the normal [4+2]-adduct, while the reaction of dispiro-[2,0,2,4]deca-7,9-diene in THF is accompanied by the opening not only of both three-membered rings but also of two solvent molecules, so that structure (LXVII) has been assigned to the final product[130]:



(LXVII)

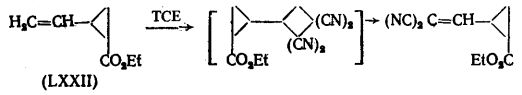
Vinylcyclopropanes (LXVIII, a–c) react with TCE to form the [2+2]-adducts (LXIX) whose thermal rearrangement results in a mixture of compounds (LXX) and (LXXI), the relative amounts of which depend strongly on the nature of the solvent[131,132]:



(LXVIII) (LXIX) (LXX) (LXXI)

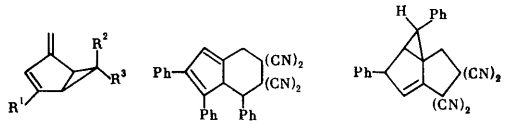
(a) $n=1$, $R^1=R^2=H$; (b) $n=2$, $R^1=R^2=H$; (c) $n=2$, $R^1R^2=(CH_2)_2$.

A metathetical reaction, analogous to the conversion of (LXVIII) into (LXXI), also takes place in the case of cyclopropylethylene (LXXII)[133]:



(LXXII)

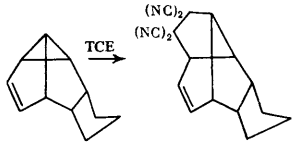
The mode of reaction of TCE with homofulvenes depends markedly on the structure. Whereas compound (LXXIIIa) gives rise to adduct (LXXIV), the reaction with compound (LXXIIIb) leads to adduct (LXXV)[134]:



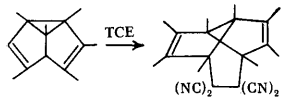
(LXXIII) (LXXIV) (LXXV)

(a) $R^1=R^3=Ph$, $R^2=H$; (b) $R^1=R^3=H$, $R^2=Ph$.

The cycloaddition of TCE to 3,7-*endo*-1-methoxytetracyclo-[6,3,0,$0^{2,11}$,$0^{3,7}$]undec-9-ene proceeds via the [$\pi^2_\sigma+\sigma^2_s+\pi^2_s$] mechanism[135]:

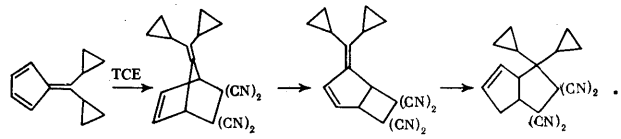


The reaction of octamethylsemibulvalene with TCE leads to adduct (LXXVI)[136]:



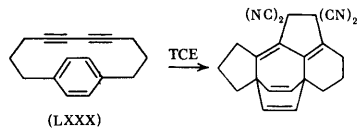
(LXXVI)

The study of the competitive reactivities of diene, ene, and cyclopropyl systems in relation to the reactions of TCE with dicyclopropylfulvene led to the discovery of the phenomenon of the "reaction cascade": the product of the [4+2] diene synthesis (LXXVII) rearranges to the more stable [2+2]-adduct (LXXVIII), which then isomerises quantitatively to the [2+6]-adduct (LXXIX)[137]:



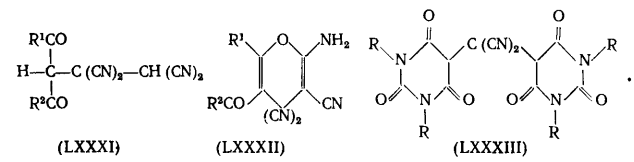
(LXXVII) (LXXVIII) (LXXIX)

Reactions with alkynes. The only example of a reaction of TCE with conjugated diynes is the reaction with compounds of type (LXXX) via the [$\pi 1s+\pi 2s+\pi 2s+\pi 2a$] mechanism[138]:



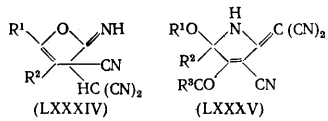
(LXXX)

Reactions with carbonyl compounds and their analogues. The reactions of TCE with active methylene compounds lead to the formation in the first stage of non-cyclic Michael adducts (LXXXI), which then undergo at least four different types of reactions. Reactions with cyclic β-diketones (4-hydroxycoumarin, 4-hydroxycarbostyril[139], dimedone, and cyclohexane-1,3-dione)[140] lead to derivatives of the 4*H*-pyran (LXXXII). The analogous reaction with barbituric acid derivatives leads to the simultaneous formation of the bipyrimidyl derivative (LXXXIII), whose content increases with increasing reaction temperature, although adduct (LXXXII) is not converted into (LXXXIII) on heating[141]:



(LXXXI) (LXXXII) (LXXXIII)

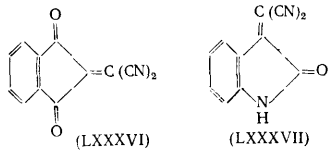
The reactions with 1,3-disubstituted 5-pyrazolones[141] and 2-indanone[142] also involve the formation of disubstituted malononitriles of type (LXXXIII). The reaction of TCE with acetylacetone yields adduct (LXXXI) in ethanol, but in acetonitrile the product is adduct (LXXXII)[143]. On the other hand, when the reaction was carried out in benzene, the only product proved to be the dihydrofuran (LXXXIV), which rearranges to dihydropyrrole (LXXXV) on heating[144]:



(LXXXIV) (LXXXV)

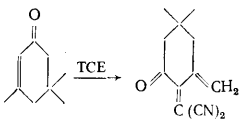
It has been shown[144] that the reactions of other acyclic β-diketones with TCE also lead to dihydropyrroles (LXXXV) via the stage involving the formation of dihydropyrans (LXXXIV), which cannot be isolated in most instances owing to their instability.

On the other hand, the reactions of TCE with indan-1,3-dione and oxindole[145,146] gives rise to the dicyanomethylene derivatives (LXXXVI) and (LXXXVII):

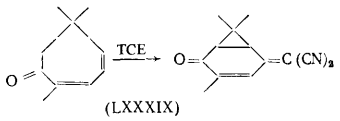


(LXXXVI) (LXXXVII)

The product of the reaction with anthrone in acetonitrile is the normal Michael adduct, but the latter is converted under the influence of a base into 10,10'-bianthrone, which is also formed directly when anthrone is acted upon by TCE in a neutral medium (ethanol–chloroform)[143]. The causes of the differences between these reactions of TCE have still not been completely elucidated. Cyclic α,β-unsaturated ketones do not give rise to bicyclic adducts despite the possibility of enolisation to a planar diene. The reactions of TCE with isophorone[147] and eucarvone[148] proceeds in an acid medium and lead to the formation of the dicyanomethylene derivatives (LXXXVIII) and (LXXXIX), the reaction in the latter case being accompanied by the formation of a three-membered ring:



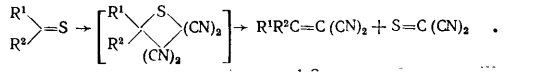
(LXXXVIII)



(LXXXIX)

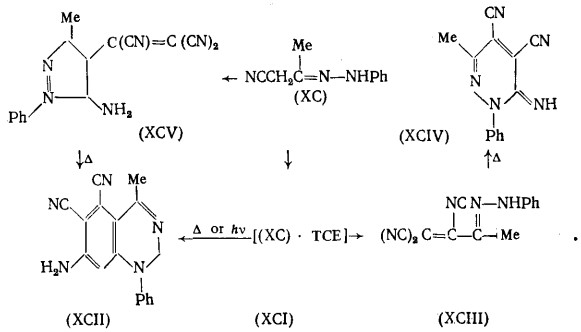
On the other hand, 5-substituted cyclohexa-2,4-dienones do not react with TCE, which is believed to be due to steric factors[149].

Thioketones react with TCE via a cycloaddition–cyclofragmentation mechanism with formation of dicyanomethylene derivatives:



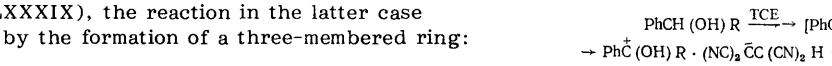
Reactions of this type have been described for 5-aryl-1,2-dimercapto-3-thiones[150], tropothione[151], and thioacetals of thioacylketens[152].

The mode of reaction of TCE with cyanoacetone hydrazones depends markedly on the nature of the solvent and the reaction temperature. Thus the corresponding phenylhydrazone (XC) gives rise in benzene to a 1 : 1 complex (XCI), which is converted into pyrazolopyridine (XCII), either thermally or under irradiation, whereas in ethanol or acetonitrile (at 20 °C) it loses a malonitrile molecule to form the hydrazone (XCIII), which cyclises to compound (XCIV) on heating. On the other hand, the reaction in boiling ethanol leads directly to compound (XCII)—it is believed to proceed via adduct (XCV), undergoing thermal cyclisation to compound (XCII), and not via a stage involving the formation of the complex (XCI)[153]:



(XCV) (XC) (XCIV) (XCII) (XCI) (XCIII)

Dehydrogenation reactions. The reactions of TCE with alkylarylmethanols, tetrahydroquinoline, and 2,5-dihydrofuran lead to the formation of tetracyanoethane and the corresponding dehydrogenated compound, in many instances in almost quantitative yield (the yield of furan is 95%)[154]. It has been shown that the reaction with alcohols proceeds via the mechanism[154]



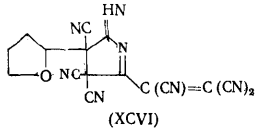
The dehydrogenation reactions of 1,4-dihydrobenzene[109] [see Scheme (7) above] and 9(11)-dihydroergosteryl acetate[155] belong to the same type.

Other addition reactions. The use of TCE as an inhibitor of the radical polymerisation of olefins is based on its ability to combine with free radicals, for example, via the mechanism



(8)

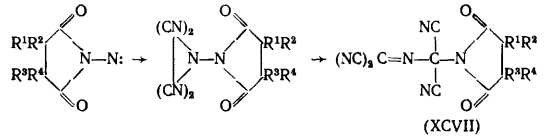
It is believed that the photoaddition of tetrahydrofuran to TCE takes place via a radical mechanism; the structure



(XCVI)

has been assigned to the final product[156].

Carbenes[2,157] and imidonitrenes[158] readily add to TCE to form respectively cyclopropanes and unstable aziridines, which rearrange quantitatively to imines of type (XCVII):

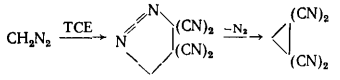


(XCVII)

TCE is hydrogenated to tetracyanoethane[159] and is oxidised by hydrogen peroxide in acetonitrile[160] to tetracyano-oxiran. Tetracyano-oxiran can also be obtained from TCE and primary ozonides[161]. This also results in the formation of the corresponding aldehydes and ketones and in higher yields than in the standard ozonisation procedure, which makes the above reaction particularly useful in structural studies with the aid of ozonolysis.

The addition of chlorine[162] is catalysed by chloride ions, which confirms the electrophilic nature of the bond in TCE. The reaction of TCE with diazomethane[163], leading to pyrazoline which loses a nitrogen molecule on heating, is of interest from the standpoint of the synthesis of nitrogen–carbon

compounds:

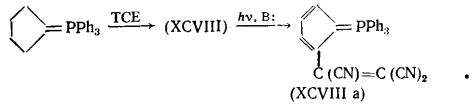


Sulphuric acid and bisulphites add reversibly to TCE even in water[159]. The reactions of alkali metal cyanides leads to the formation of the corresponding pentacyanopropanides[2].

(c) Reactions Involving the Substitution of a Cyano-Group in TCE

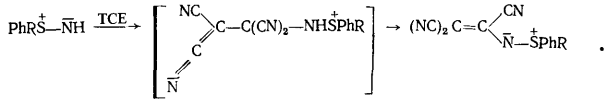
Treatment of TCE with alcohols and primary and secondary aliphatic amines can lead to the successive elimination of one or two HCN molecules and the formation of tricyanovinyl or dicyanomethylene derivatives[2]. However, in the majority of cases the reactions of TCE involving the elimination of a cyano-group stop at the first stage and lead to tricyanovinylation products. Such reactions take place with ammonia and hydrazine, *o*-alkylphenols, pyrrole, phenanthrene, phenylhydrazones, 2-methylfuran, and azulenes[2].

The reaction of TCE with cyclopentadienylphosphorane in the presence of bases leads to tricyanovinylation in the sterically hindered 2-position[164]. In the absence of bases the reaction yields the unstable product (XCVIII), which is converted photochemically or under the influence of bases into compound (XCVIIIa). It has not so far been possible to determine the structure of compound (XCVIII)[164].

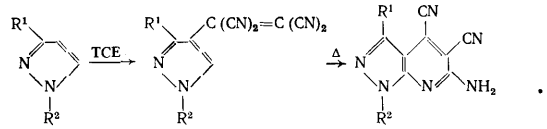


(XCVIII a)

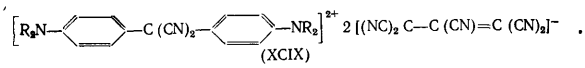
The interaction of TCE with *N*-unsubstituted arylsulphilimines proceeds via an addition–elimination mechanism[165]:



The reaction of 3-aminopyrazoles with TCE also leads to the elimination of HCN and the formation of tricyanovinylpyrazoles, which cyclise on heating to pyrazolo[3,4-*b*]pyridines[141]:



Whereas treatment of aniline with TCE leads to *N*-tricyanovinylaniline (it is believed to proceed via a stage involving the formation of a π-complex, which then reacts with one or two aniline molecules[166]), the product of the reaction with *N,N*-dimethylaniline (DMA) is *N,N*-dimethyl-4-(tricyanovinyl)-aniline, while *N,N'*-dialkylanilines with a higher molecular weight react with TCE to form complex mixtures containing bispentacyanopropenides of substituted malononitriles of type (XCIX) as the main components[167]:

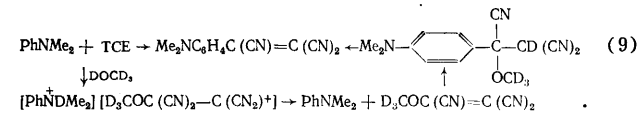


(XCIX)

Compounds of this kind have also been detected as admixtures in TCE–DMA reaction mixtures[167].

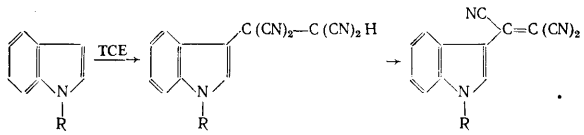
EPR data indicate the formation of the TCE radical-anion in reactions with *N,N*-disubstituted anilines and its virtually complete absence in the case of aniline[166].

The study of the reaction of TCE with DMA in deuteromethanol[168] led to the detection of the intermediates indicated below:



(9)

On the other hand it has been shown synthetically and spectroscopically that the intermediate in the reaction of TCE with DMA is not a zwitterion, as was believed previously, but a neutral substituted tetracyanoethane[169]. The same intermediate is formed in the tricyanovinylation of indoles[170]:

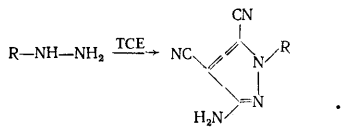


The detailed mechanism of these reactions is still the subject of controversy[171].

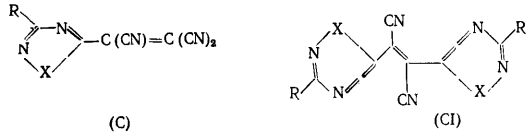
(d) Reactions Involving Addition to a Cyano-Group of TCE

Only a small number of reactions involving addition to a cyano-group of TCE are known. At first sight, this appears unexpected, because a cyano-group in TCE is formally linked to the strongly electron-accepting tricyanovinyl group and should therefore be more reactive than, for example, in dicyanogen. However, the even greater reactivity of the double bond in TCE is responsible for the preferential occurrence of reactions involving this bond.

The reaction of TCE with monosubstituted hydrazines leads to the formation of 3-amino-4,5-dicyanopyrazoles[172,173] and not 5-amino-3,4-dicyanopyrazoles as reported previously[2]:



Nitrile sulphides and nitrile oxides undergo 1,3-dipolar addition to a cyano-group of TCE with formation of mono- and bis-thiadiazoles and mono- and bis-oxadiazoles [(C) and (CI)][157]:



(C) (CI)

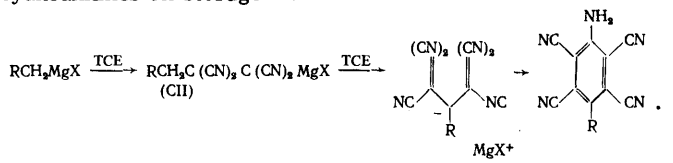
X = O or S.

It is believed that these reactions proceed via a concerted mechanism[174].

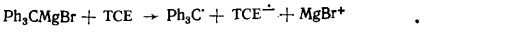
(e) Mixed Reactions

Reactions with Grignard reagents. Treatment of Grignard reagents with one equivalent of TCE leads to adduct (CII), whose treatment with trifluoroacetic acid results in the formation of a high yield of substituted tetracyanoethanes, while

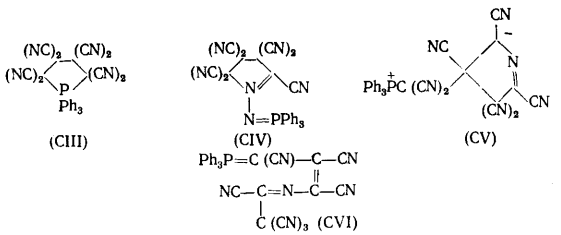
interaction with a second equivalent of TCE gives rise to 3-substituted hexacyanopentadienides, which rearrange to tetracyanoanilines on storage[175]:



The reaction of TCE with phenyl-, isopropyl-, and t-butylmagnesium halides proceeds analogously in the first stage but reaction of adducts (CII) with a second TCE molecule leads to complex mixtures containing, apart from the TCE radical-anion, tricyanovinylbenzene in the case of phenylmagnesium bromide and 3-amino-6,6-dimethylhexacyanocyclohexene in the case of isopropylmagnesium bromide. An electron transfer stage has been discovered in the reaction of TCE with tritylmagnesium bromide[176]:



Reactions with aromatic phosphines. The reactions of TCE with triarylphosphines lead to the formation of 2 : 1 adducts, which hydrolyse to tetracyanoethane and racemic phosphine oxides (in the case of optically active phosphines)[177]. It has been suggested that the hydrolysis involves a stage in which a phosphinium radical-cation is formed[177]. The structure of the adduct of TCE with triphenylphosphine still remains unknown. Instead of the phosphole structure (CIII) proposed initially, which is inconsistent with ^{31}P NMR data[178], the aminoylid structure (CIV) and the betaine structures (CV) and (CVI) are nowadays considered as the most likely[177]:



(f) Polymerisation of TCE

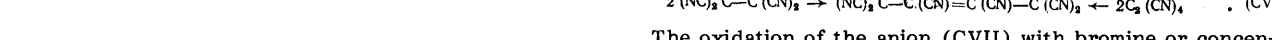
Compared with acrylonitrile and vinylidene cyanide, TCE polymerises with much more difficulty. However, when TCE is heated to a sufficiently high temperature in the presence of metals, metal complexes, alcohols, phenols, amines, and amides, it undergoes degradation with formation of dark-coloured polymeric materials with semiconducting and catalytic properties[2].

A careful study of this type of polymerisation has been carried out[179] for a series of salts of polycyanohydrocarbons, which on heating also undergo spontaneous rearrangements with rupture of the $-C\equiv N$ triple bond and the formation of black powders with a crystalline lustre. Studies by differential thermal analysis showed that the first stage probably involves the formation of radical-ions which then undergo thermal rearrangements.

The polymerisation of TCE in the presence of organotin catalysts takes place with formation in the first stage of addition products having Sn—N bonds and subsequent chain growth as a result of the reaction of these bonds with the cyano-groups[180]. TCE itself can also serve as a catalyst of the polymerisation reaction; thus tricyanoethanol containing TCE initiates the polymerisation of alkyl vinyl ethers[181] [while pure TCE reacts to form cyanobutanes (see above)]. TCE is added in the synthesis of thermostable polyoxymethylenes[182] and in the cationic copolymerisation of olefins (to increase the reactivity of the less reactive component[183]), and also in order to inhibit anionic polymerisation processes[184].

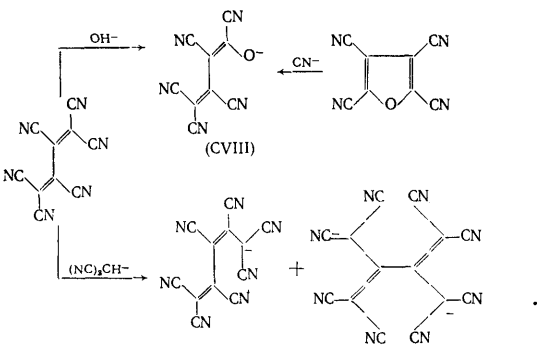
2. Hexacyanobutadiene

The condensation, catalysed by the addition of tetracyanoethane and tricyanoethylene, of the tetracyanoethanedi-ide anion, formed when TCE is treated with sodium hydride in acetonitrile, gives rise to the hexacyanobutenedi-ide anion (CVII), which can also be readily obtained by heating salts of the TCE radical-anion in solution[185]:



The oxidation of the anion (CVII) with bromine or concentrated nitric acid leads to the formation of hexacyanobutadiene (HCBD)—the only known example of the series of percyanoalkadienes.

Being a strong π-acid, HCBD undergoes the diene synthesis reaction as a dienolphile[185] and forms readily complexes with aromatic compounds as well as an unusual complex with tetrathiafulvalene (TTF), in which TTF exists in two oxidation states (0 and +1) and which exhibits a high electrical conductivity at room temperature (its resistivity is $10^{-3}\ \Omega$ cm)[186]. The HCBD radical-ion is formed readily even in the presence of mild agents such as sodium bromide and metallic mercury[185]. Treatment of HCBD with aqueous sodium bicarbonate leads to substitution of one of the terminal cyano-groups by a hydroxy-group. It is of interest that product (CVIII) is also formed when tetracyanofuran reacts with the cyanide ion[185]:



On the other hand, the reaction of HCBD with the malononitrile anion yields products of the substitution of the cyano-groups in both 1- and 2-positions[2,185].

A number of physicochemical properties of HCBD and its radical-anion have been reviewed[2].

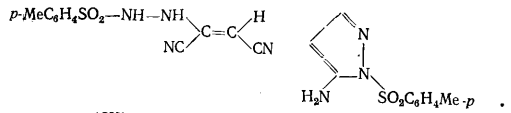
V. PERCYANOALKYNES

The chemistry of dicyanoacetylene (DCA) and dicyanodiacetylene (DCDA), synthesised before all other percyanohydrocarbons (1908), has been developing most vigorously only in the last 15 years. The sharply increased interest in these compounds can be explained not only by the great variety of their chemical properties and of their synthetic possibilities but also by their ability to generate ultrahigh temperatures on combustion in oxygen or ozone. The latter

factor stimulated a detailed investigation of the reactions of DCA not only with oxygen[187–189] but also with active nitrogen[190].

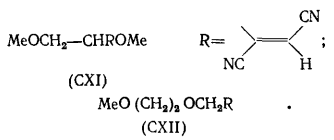
The review of cyanoacetylenes[191] published in 1977 gives a virtually exhaustive description of studies on the physical chemistry and chemistry of DCA and DCDA, so that the list of the main types of reactions of percyanoalkynes can only be supplemented by certain data not considered in the above review and new results.

It has been shown recently that DCA is capable of adding not only to alcohols, thiols, and aromatic amines[191] but also to tosylhydrazine[192]. The adduct has the structure (CIX), while the analogous reaction with cyanoacetylene yields mainly the cyclic adduct (CX)[191]:



(CIX) (CX)

Ethers, normally employed as solvents (tetrahydrofuran, diethyl ether, and monoglyme) also add to DCA. For example, the reaction with monoglyme leads to a 1:1 mixture of compounds (CXI) and (CXII)[193]:



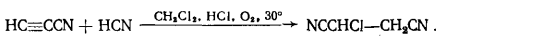
(CXI)

(CXII)

It is believed that the reaction is preceded by the formation of a charge-transfer complex.

The reactions of cyanoacetylenes with hydrogen halides and halogens are more unexpected. The addition of HX (X = Cl or Br) to the acetylenic bond takes place even at room temperature with formation of a mixture of isomers of dicyanohalogenoethylene[194,195]. The addition of bromine to DCA also takes place at room temperature with formation of dibromofumaronitrile[196]. The addition of iodine is much slower even in the presence of iron iodide[196]. The mechanism of this reaction is obscure; it has been suggested[2] that it is more likely to proceed via a radical than an ionic mechanism.

The attempt to obtain DCA from HCN and cyanoacetylene also led to the formal addition of HCl and HCN to cyanoacetylene:



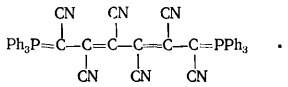
The mechanism of this reaction has still not been elucidated[197]. Bearing in mind the known electrophilic properties of the molecule, the ready formation of a 1:1 complex of DCA with aluminium bromide is fairly unexpected[198]. Although the structure of the complex is unknown, by analogy with many complexes of nitriles with Lewis acids[2] the complex is believed to involve the coordination of aluminium bromide to the cyano-group. The complex is extremely sensitive to moisture and readily reacts with dienes, giving rise to Diels–Alder products.

The study of the ultraviolet spectra of colourless solutions of DCA in aromatic hydrocarbons demonstrated the absence of charge-transfer complexes even for hexamethylbenzene, which forms intensely coloured complexes with tetracyanoethylene[2].

On the other hand, it has been reported[199] that solutions of DCDA in benzene are blue. However, since toluene, being a stronger π-base, gives rise to a blue solution much more slowly, it is believed that the colour of the benzene solution is caused by some other factors, for example, the presence of impurities[2].

DCA reacts vigorously with metal compounds: it is reduced by tributylstannane in methanol, is inserted in the C–Au bond in the reaction with the ferrocenylgold–triphenylphosphine complex, combines with mercury(II) chloride in aqueous solution (in proportions of 2:1), and forms compounds containing C–Co bonds with pentacyanocobalt and octacarbonyldicobalt[191].

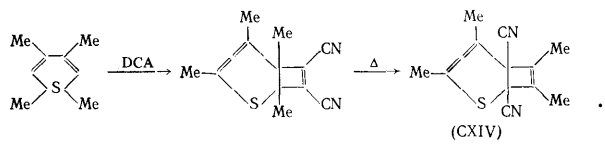
The 3:2 adduct of DCA with triphenylphosphine, formed at room temperature, is believed to have structure (CXIII)[2]:



(CXIII)

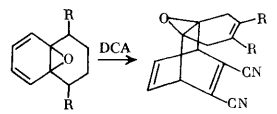
The 1,4-cycloaddition of DCA to dienes has been studied most extensively at the present time and is frequently used to synthesise a wide variety of polycyclic compounds[2,191]. Apart from aliphatic dienes and cyclodienes, DCA reacts with aromatic compounds (benzene, naphthalene, and anthracene) and with heterocycles (derivatives of furan and pyridine). Thiophens are an exception; the structures of thiepins and [2+2]-adducts have been attributed to the products of their reactions with DCA[200].

The latest studies have shown that the adduct of DCA with tetramethylthiophen undergoes the Cope thermal rearrangement, so that the final product has structure (CXIV)[200]:



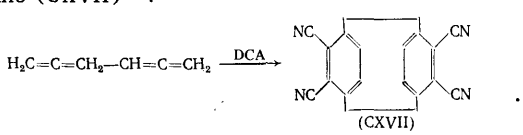
(CXIV)

Arene oxides of type (CXV) react with DCA to form the tricyclic adducts (CXVI)[201]:



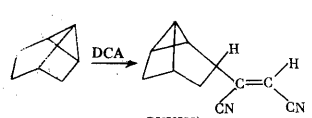
(CXV) (CXVI)

The reaction with hexa-1,2,4,5-tetraene leads to [2,2]paracyclophane (CXVII)[202]:



(CXVII)

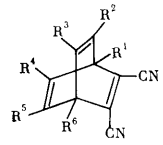
Like TCE, DCA is capable of transannular addition to norbornadiene and barrelene and of reactions, involving ring opening, with strained alicyclic systems of the type of bicyclo[2,1,0]pentane[191]. However, the reaction with tricyclo[4,1,0,$0^{3,7}$]heptane leads to a substituted maleonitrile (CXVIII) and not to a cyclic adduct[203]:



(CXVIII)

A study of the ultraviolet spectra of adducts of DCA with aromatic hydrocarbons (CXIX) revealed the presence of absorption bands corresponding to the formation of intramolecular charge-transfer complexes, where the dicyanoethylene bridge functions as the acceptor and the remaining two double

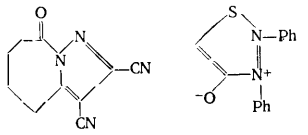
bonds are donors[29]:



(CXIX)

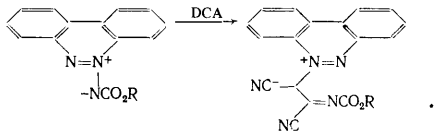
Being an active dipolarophile, DCA undergoes 1,3-cycloaddition reactions with diazomethane, diazocyclopentadienes, ethyl diazoacetate, benzonitrile oxide, and isoquinolinium ylids; it also reacts with 1,4-dipoles—for example, with 2-hydroxy-1,6,8-trimethyl-4-oxopyrimido[1,2-*a*]pyrimidinium[191].

The reaction of DCA with 2-diazocyclohexanone, which proceeds via a 1,3-dipolar addition stage, includes a sigmatropic (1,5)-acyl shift and leads to 1,10-diazabicyclo[5,3,0]deca-7,9-dien-2-one (CXX)[204]:



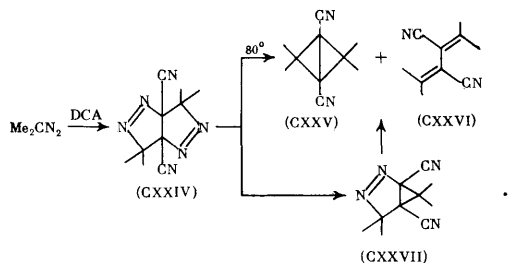
(CXX) (CXXI)

Phosphoryldiazo-compounds[205], anhydro-4-hydroxythiazolium hydroxide (CXXI)[206], and azimines [for example, compound (CXXII)] have also been made to react with DCA as 1,3-dipoles. In the last instance the resulting [1,3]-adduct undergoes a spontaneous electrocyclic opening of the triazoline ring and is converted into the azomethine (CXXIII)[207]:



(CXXII) (CXXIII)

Treatment of DCA with an excess of dimethyldiazomethane gives rise to pyrazoline (CXXIV) and the latter loses on heating two nitrogen molecules with formation of a mixture of products whose main components are the dicyclobutane (CXXV) and the diene (CXXVI):



(CXXIV) (CXXV) (CXXVI) (CXXVII)

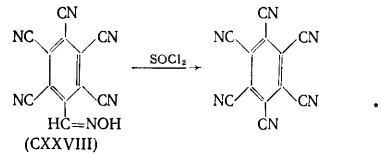
The latter is formed quantitatively when compound (CXXIV) is irradiated and particularly in the thermolysis of compound (CXXV). When the bisadduct (CXXIV) was heated cautiously, it was possible to obtain also cyclopropanopyrazoline (CXXVII), whose thermolysis also gives rise to a mixture of compounds (CXXV) and (CXXVI) but with a higher content of the diene[208].

Cyanoacetylenes have attracted particular attention as potential monomers for semiconducting polymers. Thus DCA–olefin copolymers[209] have semiconducting properties and are thermally stable, which permits their use in the manufacture of transistors, thermoelectric devices, and as casings for rocket engines.

Furthermore, DCA polymers proved to be convenient objects for the study of the electrophoretic behaviour of polyconjugated systems[210].

VI. PERCYANOARENES

The only example of aromatic percyanohydrocarbons is hexacyanobenzene (HCB), which was synthesised for the first time in 1963 by the dehydration of the oxime (CXXVIII) in accordance with the reaction[211]:



(CXXVIII)

The synthesis of HCB from 1,3,5-tricyano-2,4,6-trifluorobenzene and calcium cyanide in dimethylformamide in a yield of approximately 50% was described later[212].

Treatment of 2,4,6-trichloro-1,3,5-tricyanobenzene with sodium methoxide or ethoxide (at −20 °C) followed by treatment with sodium cyanide (at −5 °C) and refluxing in a $POCl_3$–pyridine mixture gives rise to a mixture of HCB and chloropentacyanobenzene (in proportions of 1 : 9 in the former case and 1 : 3 in the latter)[213].

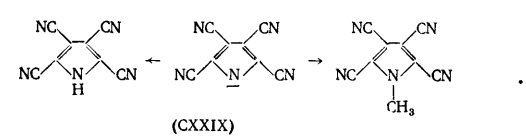
The molecular orbitals of HCB were calculated by Shwarts[214]. HCB readily forms coloured complexes with aromatic hydrocarbons[211] and a black 1 : 2 complex with pyrene[215].

Spectroscopic studies on complexes of this composition with aromatic methoxy- and methylthio-compounds led to the establishment of the following series based on the strength of "electron-accepting" properties: tetracyanoquinodimethane > TCE > HCB > tetracyanobenzene[216]. The hydrolysis of HCB leads to the formation of pentacyanophenol—a very strong acid whose methylation with diazomethane yields pentacyanoanisole and whose halogenation gives rise to the corresponding halogenopentacyanobenzenes[217]. The reactions of HCB with alcohols and amines take place even at room temperature[218,219]. In the former case there is slow formation of alkoxypentacyanobenzenes, which react with the excess alcohol even following a moderate temperature rise, forming the corresponding ether and pentacyanophenol[218]. The reactions of HCB with ammonia and dimethylamine also proceed under exceptionally mild conditions and lead to products of mono- and 1,3-di-substitution in the aromatic ring. However, the analogous reaction with aniline and o-diaminobenzene requires heating to 80 °C.[219]

As regards condensed aromatic percyano-systems, there have been no reports of compounds containing more than two cyano-groups, with the exception of tricyanoperylene[220].

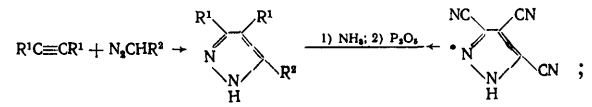
VII. PERCYANO-DERIVATIVES OF NITROGEN HETEROCYCLES

Although salts of tetracyanopyrrole (CXXIX) can be obtained by treating tetracyano-1,4-dithiine with azide ions[221] and can be converted into the corresponding pyrrole (on ion exchange resins) and *N*-methylpyrrole, the percyano-compound has not so far been synthesised:



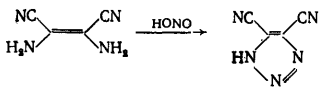
(CXXIX)

Tetracyanopyrazole and tricyanotriazole have not been synthesised either, although 3,4,5-tricyanopyrazole has been prepared in two ways[222]:



(a) $R^1=CN$, $R^2=CO_2Et$;
(b) $R^1=CO_2Et$, $R^2=CN$.

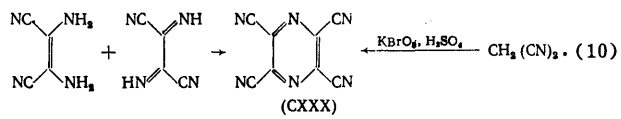
It is of interest that it is not impossible to carry out the direct synthesis (for $R=R^1=CN$)[222]. 4,5-Dicyanotriazole can be obtained by treating diaminomaleonitrile with nitrous acid[223–227]:



Both compounds are strong acids and readily form stable salts.

The reports of the synthesis of pentacyanopyridine have not so far been confirmed by the description of the relevant experiment, although the pentacyanopyridine radical-anion was studied by EPR in 1966.[228]

Tetracyanopyrazine (CXXX) can be obtained by the condensation of diaminomaleonitrile and diiminosuccinonitrile[229] or by the direct oxidation of malononitrile[230] via reaction (10). In both cases 1-aminotricyanopyrazine and 1,2-diaminodicyanopyrazine are formed simultaneously:

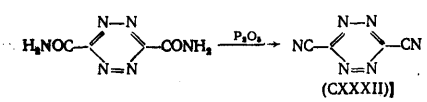


(CXXX)

Tetracyanopyrazine itself is used as a regulator of plant growth[231] and derivatives of 3,5-diamino-2,4-dicyanopyrazine, obtained by treating compound (CXXX) with ammonia and primary and secondary amines, are used to synthesise fluorescent materials, dyes, and "ladder" polymers[232,233]. The reaction of compound (CXXX) with *N,N*-disubstituted anilines leads to the corresponding 2-(4-aminophenyl)-3,5,6-tricyanopyrazines, which are used as dyes[234]. The mass spectra of polycyanopyrazines have been investigated[235].

The most thoroughly investigated six-membered heterocyclic pernitrile, which has been known for a long time, is tricyano-1,3,5-triazine[131]. In contrast to the usual method for the synthesis of *sym*-triazines, compound (CXXXI) cannot be obtained by the trimerisation of dicyanogen. It was synthesised in a very low yield in 1919 via the triamide of cyanuric acid[236]. Pyrolysis of compound (CXXXI) gives rise to dicyanogen[236,237] and treatment with alcohols leads to the successive substitution of cyano-groups by alkoxy-groups and the formation of the corresponding cyanurates[236,238]. Reduction with alkali metals or irradiation of a mixture of compound (CXXXI) and hexamethylmelamine results in a stable blue radical-ion[239,240].

The synthesis of 3,6-dicyano-1,2,4,5-tetrazine (CXXXII) was achieved in 1961[241] via the reaction



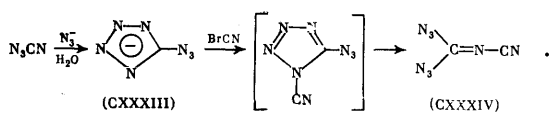
(CXXXII)]

Compound (CXXXII) was obtained in an amount of 0.15 g and a yield of 12–18%; being extremely unstable, it decomposed fully after several days even in an atmosphere of argon and in the absence of moisture[241]. The latest studies are limited to a description of the mass-spectrum[242] and the calculation of the molecular orbitals of the radical-anion (CXXXII)[243].

VIII. PERNITRILES WITH A NITROGEN–CARBON SKELETON

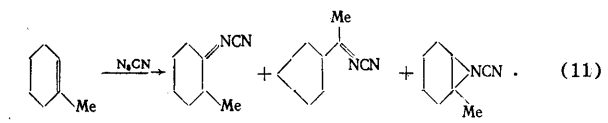
The simplest pernitrile of this series—tricyanamide—has not so far been synthesised. The attempt to obtain it from silver dicyanamide and chlorocyanogen was unsuccessful[244], while reports of the synthesis of this compound by the pyrolysis of mercury thiocyanate[245] and mercury dicyanamide[246] are apparently erroneous.

One of the most thoroughly investigated "azapernitriles", namely, cyanogen azide, is a colourless oily liquid which detonates on mechanical, electrical, and thermal shock and can be obtained in virtually quantitative yield when sodium azide is treated with chlorocyanogen in an anhydrous medium[247]. When cyanogen azide, obtained by the analogous reaction with bromocyanogen in an aqueous medium, is acted upon by the azide ion, the anion of 5-azidotetrazole (CXXXIII) is formed and reacts in its turn with bromocyanogen to form the *gem*-diazide (CXXXIV)—the product of the rearrangement of an unstable cyanazidotetrazole. Treatment of cyanogen azide with aqueous alkali at room temperature can also lead to the formation of the salt (CXXXIII). Hydrogen sulphide readily reduces cyanogen azide to cyanamide[247]:



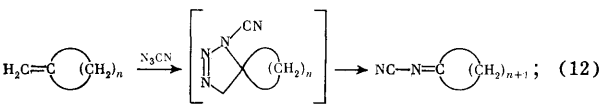
(CXXXIII) (CXXXIV)

Below 60 °C, cyanogen azide reacts as a powerful electrophilic azide, adding to olefins with formation of unstable triazolines, which decompose to alkylidenecyanamides and (or) *N*-cyanoaziridines, whose proportions can be varied within wide limits depending on the type of olefin and the solvent employed[248]:

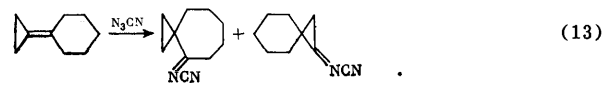


(11)

Cycloalkenes can also undergo ring contraction[248,249] [for example, via reaction (11)]; on the other hand, the reactions of methylenecycloalkanes are accompanied as a rule by ring expansion[243] [reaction (12)]. Alkylidenecycloalkanes give rise to a mixture of isomers [for example, via reaction (13)]:



(12)

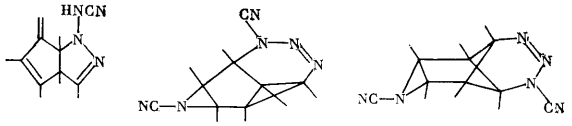


(13)

We may note that the attempt to catalyse these reactions by the introduction of silver ions did not lead to an increase of the rate of reaction, but altered (in many cases considerably) the proportions of the isomers formed[249]. Alkylidenecyanamides hydrolyse extremely readily to the corresponding ketones, which makes these reactions the basis of a valuable synthetic method.

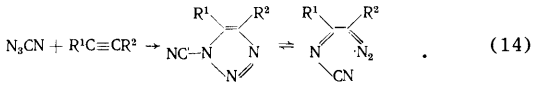
The time and temperature variation of the reaction of cyanogen azide with hexamethylbicyclo[2,2,0]hexadiene is of interest; the reaction gives rise to adduct (CXXXV) after 10 h at 20 °C, to compound (CXXXVI) at 0 °C over the same

period, and to compound (CXXXVII) at 0 °C after 20 min[250]:



(CXXXV) (CXXXVI) (CXXXVII)

The reaction of cyanogen azide with acetylenes leads to the formation of an equilibrium mixture of triazoles and diazoamines via the reaction[251]



(14)

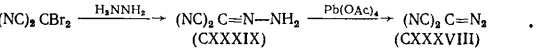
The photolysis and thermolysis of cyanogen azide above 50 °C[248,252,253] give rise to cyanonitrene, which is a convenient intermediate in processes involving the modification of polymers[254] and in the synthesis of aziridines, alkylidenecyanamides, and azepines from olefins and aliphatic and aromatic hydrocarbons respectively[248,255].

Cyanogen azide reacts with tertiary phosphines to form *N*-cyanophosphinimides which are effective repellents, insecticides and hematocides[256]. The reactions with aromatic arsines and phosphites proceeds similarly[257,258]. The method for the synthesis of *N*-alkoxyalkylcyanamides is based on the reaction of cyanogen azide with ethers and polyethers[259].

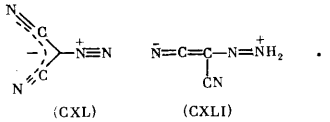
The molecular[260] and electronic[261,262] structures, ionisation potentials[263], and microwave[264,265], infrared[266,267], and Raman[267] spectra of cyanogen azide have also been calculated and investigated.

The pyrolysis of cyanogen azide in the gas phase at 200 °C leads to the formation (apparently as a result of the reaction of cyanonitrene with the unreacted cyanogen azide) of azodinitrile NC–N=N–CN[268]—a red-orange volatile explosive compound, which was subsequently synthesised from hydrazine and chlorocyanogen in the presence of sodium azide[269]. The study of the infrared and Raman spectra of this compound showed that it exists exclusively in the *trans*-form (it has been shown by calculation to be more stable than the *cis*-form by 20 kcal mol^{-1}[270–272]). Azodinitrile is a powerful dienophile, which reacts instantaneously (even at room temperature) with cyclopentadiene, 2,3-dimethylbutadiene, and even (albeit slowly) anthracene[268].

Dicyanodiazomethane (CXXXVIII) was first synthesised from dibromomalononitrile via the hydrazone (CXXXIX)[73]:

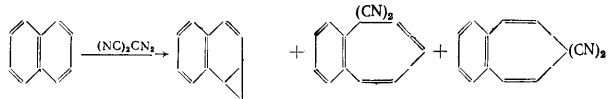


Here one should note the unusual stability of the hydrazone (CXXXIX). The high dipole moments of compounds (CXXXVIII) and (CXXXIX) (5.82 and 3.8 D respectively) together with NMR and ultraviolet spectroscopic data confirmed the contribution of the betaine structures (CXL) and (CXLI).



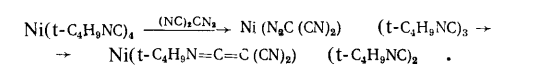
(CXL) (CXLI)

In contrast to other diazo-compounds, dicyanodiazomethane oxidises primary and secondary amines even at 20 °C, being itself reduced to the hydrazone (CXXXIX). While it is resistant to the action of even 2 *N* sulphuric acid, it readily reacts with nucleophiles such as triphenylphosphine and Grignard reagents[2]. The thermolysis and photolysis[2] of compound (CXXXVIII) yield dicyanocarbene, which makes it possible, for example, to obtain cyclopropanes by reaction with olefins[274] and norcaradiene derivatives from benzene and xylene[275]. However, it is of interest that the thermolysis of dicyanodiazomethane in naphthalene yields in addition products (CXLII) and (CXLIII)[275]:

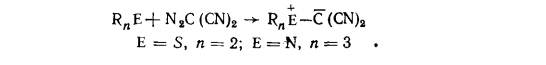


(CXLII) (CXLIII)

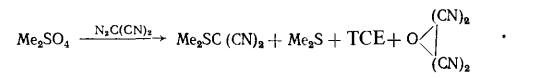
The reaction of compound (CXXXVIII) with isonitrile complexes proceeds via a substitution stage and leads to the formation of keten imines[276]:



A method for the synthesis of sulphonium and ammonium dicyanomethylides is based on the interaction of compound (CXXXVIII) with sulphides and amines[277,278]:



The reaction of compound (CXXXVIII) with dimethyl sulphoxide proceeds via the mechanism[277]



The infrared spectra of compound (CXXXVIII) and of the free radical $C(CN)_2$ have also been studied[279].

Treatment of TCE with sodium hydride in acetonitrile yields the hexacyanobutenediide anion (CVII), which cyclises in aqueous solutions to the aminotetracyanocyclopentadienide anion via 1-amino-2,3,4,5,5-pentacyanocyclopentadiene. The diazotisation of the cyclopentadienide anion yields diazotetracyanocyclopentadiene[280]—the initial compound for the synthesis of various salts of substituted tetracyanocyclopentadienes which are used as propellants, weed killers and pesticides, sensitisers and, dyes[281]—in particular the salts of pentacyanocyclopentadiene and cyanodiazotetracyanocyclopentadiene as well as the salts of azobis(tetracyanocyclopentadiene), which are used in the syntheses of organic conductors[282].

---o0o---

Thus analysis of the literature data shows that the chemistry of polycyano-compounds has been the subject of increasing attention by investigators for more than half a century and that approximately four-fifths of the total number of publications dealing with these compounds have appeared in the last fifteen years.

The range of reactions in which pernitriles can be involved is extremely wide. They can be reduced and oxidised, can undergo various kinds of fragmentation, are capable of undergoing reactions involving addition to double bonds (when these are present) and to cyano-groups, which can participate in their turn in substitution reactions. The majority of pernitriles are extremely sensitive to nucleophilic attack and readily give rise to radical-anions.

The stability of these compounds varies within very wide limits, ranging from that of tetracyanoethylene, which can be isolated from solution in fuming nitric acid, to compounds of the type of cyanogen azide or azodinitrile, which decompose explosively. The reactions of pernitriles proceed in most cases at room temperature, but the identification of certain products of these reactions is sometimes extremely difficult because of their instability or their tendency to polymerise.

Thus not a single instance of the identification of dicyanogen, formed in reactions of polynitriles, has been described hitherto and the products of the reactions of percyano-anions are frequently unidentified coloured amorphous substances which probably have a polymeric structure.

There is no doubt that further development of the chemistry of pernitriles may prove to be extremely fruitful for the synthesis of compounds with valuable properties (for example, organic conductors, ingredients of fuel mixtures, thermostable polymers, etc.), and for the development of new synthetic methods and methods for the investigation of problems in theoretical and physical organic chemistry.

IX. APPENDIX

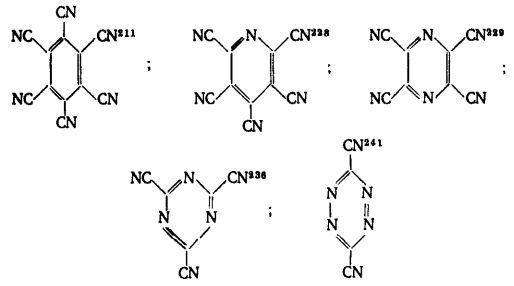
1. NITROGEN–CARBON COMPOUNDS§

I. Pernitriles:

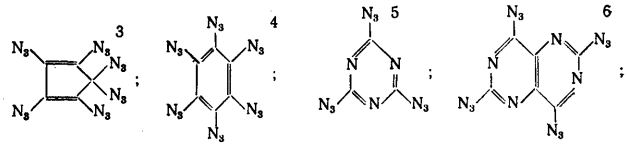
$(CN)_2^{263}$; $C(CN)_4^{14}$; $C_2(CN)_6^{28}$; $(NC)_2C{=}C(CN)_2^{284}$;

$(NC)_2C{=}C(CN){-}C(CN){=}C(CN)_2^{285}$;

$NCC{\equiv}CCN^{286}$; $NCC{\equiv}C{-}C{\equiv}CCN^{285}$; $NCN{=}C{=}NCN^{286}$; $NCN{=}NCN^{246}$;

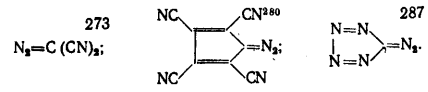


II. Perazides:

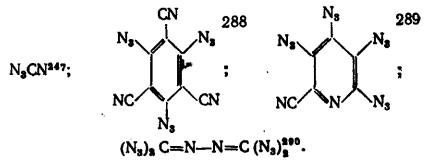


$(N_3)_2C{=}N{-}N{=}C(N_3)_2^7$.

III. Diazo-Compounds



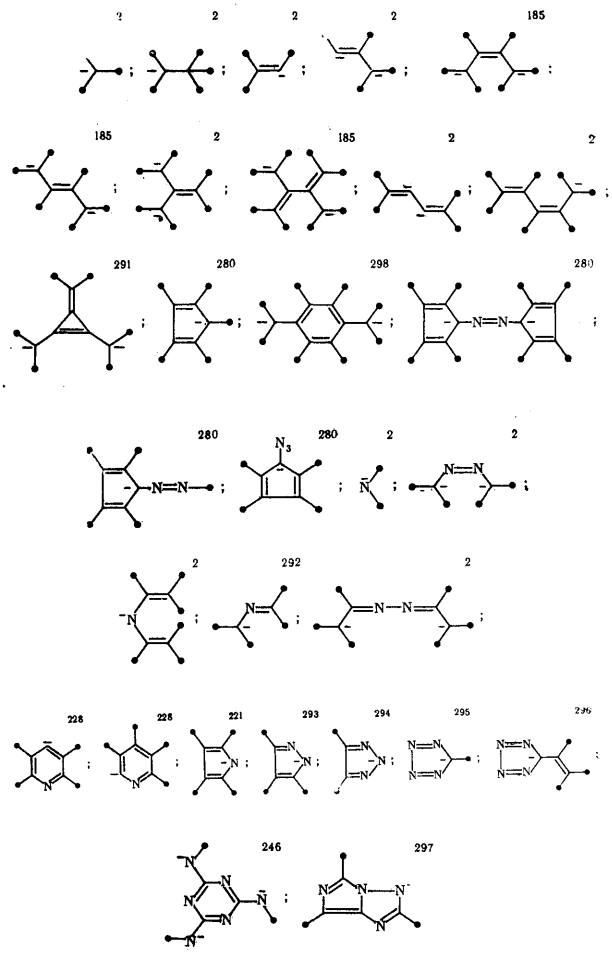
IV. Mixed Nitrogen–Carbon Compounds:



$(N_3)_2C{=}N{-}N{=}C(N_3)_2^{290}$.

§ The literature references are to publications in which the synthesis was described for the first time.

2. NITROGEN–CARBON PERCYANO-ANIONS¶



¶ The symbol ⇀ always designates the $-C{\equiv}N$ group.

REFERENCES

1. O.Griszkiewicz-Trochimowski, Bull.Soc.chim.France, 1437 (1961).
2. E.Ciganek, W.J.Linn, and O.W.Webster, in "The Chemistry of the Cyano Group" (Edited by Z.Rappoport), Intersci.Publ.London, 1970, p.427.
3. J.Senior, J.Org.Chem., **3**, 1 (1938).
4. US P.3217017 (1966); Chem.Abs., **64**, 1896 (1966).
5. J.G.Morse and L.P.Kuhn, US Clearing House Fed. Sci.Techn.Inform., No.713665 (1970); Chem.Abs., **75**, 19826 (1970).
6. "Beilsteins Handbuch der Organischen Chemie", Bd. 26, II. Springer-Verlag, Berlin, 1954, Vol.26, II, p.16.
7. N.B.Smirnova and I.Ya.Postovskii, Biol.Akt.Soed., 102 (1965).
8. US P.2990412 (1961); Chem.Abs., **55**, 25256 (1961).
9. E.W.Hughes, J.Chem.Phys., **3**, 1 (1935).
10. A.Schmidtmann, Chem.Ber., **29**, 1174 (1896).
11. A.Hantzch and G.Osswald, Chem.Ber., **32**, 641 (1899).

12. L.Birckenbach and K.Huttner, Chem.Ber., **62**, 160 (1929).
13. E.Griszkiewicz-Trochimowski and O.Griszkiewicz-Trochimowski, Mem.Poudres, **40**, 109 (1958).
14. E.Mayer, Monatsh., **100**, 462 (1969).
15. D.I.Makhon'kov, Candidate's Thesis, Moscow State University, 1977.
16. D.S.Barnes, C.T.Mortimer, and E.Mayer, J.Chem. Termodyn., **5**, 481 (1973).
17. H.Oberhammer, Z.Naturforsch., **26a**, 2042 (1971).
18. D.Britton, Acta Cryst., **30b**, 1818 (1974).
19. H.Bock, E.Haselbach, E.Mayer, and H.Stafast, Helv.Chim.Acta, **59**, 1035 (1976).
20. N.S.Zefirov, N.M.Sergeev, D.I.Makhon'kov, and L.Ya.D'yachkova, Zhur.Org.Khim., **13**, 3 (1977).
21. R.E.Hester, K.M.Lee, and E.Mayer, J.Phys.Chem., **74**, 3373 (1970).
22. N.S.Zefirov, N.K.Chapovskaya, and D.I.Makhon'kov, Zhur.Org.Khim., **12**, 617 (1976).
23. D.I.Makhon'kov, N.S.Zefirov, and L.Ya.D'yachkova, Zhur.Org.Khim., **13**, 968 (1977).
24. E.Mayer, Angew.Chem., **81**, 627 (1969).
25. E.Mayer, Monatsh., **101**, 846 (1970).
26. W.Beck, K.Schopp, C.Oetker, and R.Schlödder, Chem.Ber., **106**, 2145 (1973).
27. L.Birkenbach and K.Huttner, Chem.Ber., **62b**, 153 (1929).
28. S.Trofimenko and B.C.McKusick, J.Amer.Chem.Soc., **84**, 3677 (1962).
29. D.N.Dhar, Chem.Rev., **67**, 611 (1967).
30. R.Foster, Mol.Complexes, **2**, 251 (1974).
31. D.N.Dhar, Chem.Techn.Rep., **2** (1966).
32. W.H.Baddley, Inorg.Chim.Acta, **2**, 7 (1968).
33. A.A.Berlin and A.J.Sherle, Inorg.Macromol.Rev., **1**, 235 (1971).
34. K.Koyama and M.Nishimura, Kagaku To Kogyo, **45**, 243 (1971); Chem.Abs., **75**, 109890 (1971).
35. K.Venkaterswarlu and M.K.Warrier, Bull.Soc.Roy. Sci.Liege, **38**, 766 (1969).
36. H.Stafast and H.Bock, Tetrahedron, **32**, 855 (1976).
37. O.A.Ganson, A.R.Burke, R.B.King, and M.S.Saran, Inorg.Nuclear Chem.Letters, **10**, 291 (1974).
38. I.Murgich and S.Pissanetzky, J.Chem.Phys., **62**, 92 (1975).
39. C.E.Brion and L.A.R.Olsen, Int.J.Mass Spectrom. Ion Phys., **9**, 413 (1972).
40. I.Ikemoto, K.Samizo, T.Fujikawa, K.Ishii, T.Ohta, and H.Kuroda, Chem.Letters, 785 (1974).
41. K.N.Houk and L.L.Munchausen, J.Amer.Chem.Soc., **98**, 937 (1976).
42. M.Rougee and C.Andre, J.Polymer Sci., **16c**, 3167 (1968).
43. V.P.Nefedov, B.P.Bespalov, and V.V.Titov, Zhur.Org.Khim., **10**, 1553 (1974).
44. S.M.Shein, T.V.Leshina, N.A.Geraseva, A.D.Khmelinskaya, and L.V.Bryukhovetskaya, Zhur.Org.Khim., **11**, 2538 (1975).
45. H.Sakurai and M.Kira, J.Amer.Chem.Soc., **95**, 6826 (1973).
46. V.F.Traven' and R.West, Zhur.Obshch.Khim., **44**, 1837 (1974).
47. H.A.Gardner and J.K.Kochi, J.Amer.Chem.Soc., **97**, 5026 (1975).
48. V.F.Traven', V.F.Donyagina, N.S.Fedotov, G.V.Everst, and B.I.Stepanov, Zhur.Obshch.Khim., **46**, 2761 (1976).
49. R.Gompper and D.Lash, Tetrahedron Letters, 2687 (1973).
50. S.R.Tanny and F.W.Fowler, J.Org.Chem., **39**, 2715 (1974).
51. S.Nishida and I.Moritani, J.Org.Chem., **38**, 1878 (1973).
52. Y.Shirota, I.Nagata, and H.Mikawa, Chem.Letters, 49 (1972).
53. Y.Shirota, I.Nagata, H.Mikawa, Y.Nakata, and T.Nogami, J.Chem.Soc., Perkin Trans.I, 14 (1977).
54. K.R.Berger, E.R.Bichl, and P.C.Reeves, J.Org. Chem., **39**, 477 (1974).
55. P.D.Barlett, Quart.Rev., **24**, 473 (1970).
56. N.K.Hamer and M.E.Stubbs, J.Chem.Soc., Perkin Trans.I, 2971 (1972).
57. O.A.Nesmeyanova, S.V.Zotova, and E.I.Vostokova, Izv.Akad.Nauk SSSR, Ser.Khim., **11**, 2639 (1976).
58. P.Reeves, J.Henery, and R.Pettit, J.Amer.Chem. Soc., **91**, 5889 (1969).
59. P.Reeves, T.Devon, and R.Pettit, J.Amer.Chem. Soc., **91**, 5890 (1969).
60. T.Miyamoto and Y.Odaira, Tetrahedron Letters, 43 (1973).
61. A.Huth, H.Straub, and E.Muller, Tetrahedron Letters, 2845 (1973).
62. F.Toda and N.Dan, Chem.Comm., 30 (1976).
63. R.Schug and R.Huisgen, Chem.Comm., 60 (1975).
64. R.Huisgen, R.Schug, and G.Steiner, Angew.Chem., **86**, 47 (1974).
65. I.Karle, J.Flippen, R.Huisgen, and R.Schug, J.Amer.Chem.Soc., **97**, 5285 (1975).
66. I.R.Dombroski, M.L.Hallensleben, and W.Regel, Tetrahedron Letters, 3881 (1971).
67. G.D.Hartman and T.G.Traylor, Tetrahedron Letters, 939 (1975).
68. A.Culter, D.Ehntholt, W.P.Giering, P.Lennon, S.Raghu, A.Rosan, M.Rosenblum, J.Tancrede, and D.Wells, J.Amer.Chem.Soc., **98**, 3495 (1976).
69. R.W.Hoffmann, U.Bressel, J.Gehlhaus, and H.Häuser, Chem.Ber., **104**, 873 (1971).
70. R.W.Hoffmann and W.Schaeffer, Angew.Chem.Int. Ed., **9**, 733 (1970).
71. M.Ozolins and G.H.Schenk, Anal.Chem., **33**, 1035 (1961).
72. F.E.Rogers, J.Phys.Chem., **76**, 106 (1972).
73. A.I.Konovalov, Ya.D.Samuilov, and Z.A.Khairullin, Zhur.Org.Khim., 8, 229 (1972).
74. A.I.Konovalov, Zhur.Org.Khim., **5**, 1713 (1969).
75. T.Kojima and T.Inukai, J.Org.Chem., **35**, 1342 (1970).
76. C.C.Thompson and D.D.Holder, J.Chem.Soc., Perkin Trans.II, 257 (1972).
77. A.I.Konovalov, V.N.Solomonov, and A.N.Ustyugov, Dokl.Akad.Nauk SSSR, **211**, 102 (1973).
78. P.Scheiss, Helv.Chim.Acta, **55**, 2365 (1972).
79. I.Gasteiger and R.Huisgen, Angew.Chem., Int.Ed., **11**, 716 (1972).
80. L.A.Paquette, W.Kitching, W.E.Heyd, and R.H.Meisinger, J.Amer.Chem.Soc., **96**, 7371 (1974).
81. R.Huisgen, W.E.Konz, and G.A.Gream, J.Amer. Chem.Soc., **92**, 4105 (1970).
82. G.Köbrich and B.Rösner, Tetrahedron Letters, 2031 (1973).
83. N.Morita and T.Asao, Chem.Letters, 71 (1975).
84. D.N.Butler and R.A.Snow, Canad.J.Chem., **53**, 256 (1975).
85. H.Hogeveen and P.W.Kwant, Tetrahedron Letters, 3747 (1973).
86. G.Capozzi and H.Hogeveen, J.Amer.Chem.Soc., **97**, 1479 (1975).

87. F.A.Carey and A.S.Court, J.Org.Chem., **37**, 4474 (1972).
88. T.Sasaki, K.Kanematzu, and K.Jizuka, J.Org. Chem., 41, 1105 (1976).
89. N.J.Mruk and H.Tieckelmann, Tetrahedron Letters, 1209 (1970).
90. US P.3978171 (1976); Chem.Abs., **85**, 192180 (1976).
91. A.R.Bursies, P.Laszlo, M.Murray, F.Stone, and A.Gordon, J.Organomet.Chem., **111**, 31 (1976).
92. U.Moedlhammer and H.Hopf, Angew.Chem., **87**, 492 (1975).
93. H.Maurer and H.Hopf, Angew.Chem., **88**, 687 (1976).
94. H.Duerr, B.Ruge, and B.Weiss, Annalen, 1150 (1974).
95. M.F.Semmelhack, J.S.Foos, and S.Katz, J.Amer. Chem.Soc., **94**, 8637 (1972).
96. K.H.Pfoertner, Helv.Chim.Acta, **58**, 833 (1975).
97. A.M.Andrews, Diss.Abs., Int.B, **32**, 6286 (1972).
98. A.I.Konovalov, V.D.Kiselev, A.N.Ustyugov, and N.G.Gess, Zhur.Org.Khim., **12**, 2541 (1976).
99. G.J.Miller, A.Singermann, and L.Friedman, J.Amer. Chem.Soc., **93**, 7109 (1971).
100. S.Kuroda, M.Oda, and Y.Kitahara, Angew.Chem., **85**, 93 (1973).
101. J.T.Barton and M.Juvet, Tetrahedron Letters, 2561 (1975).
102. M.Green, S.Heathcock, and D.S.Wood, J.Chem. Soc., Dalton Trans., 1564 (1973).
103. L.A.Paquette, S.V.Ley, S.Maiorana, D.F.Schneider, M.J.Broadhurst, and R.A.Boggs, J.Amer.Chem.Soc., **97**, 4658 (1975).
104. Z.Goldschmidt and Y.Bakal, Tetrahedron Letters, 1229 (1976).
105. J.M.Photis, J.Heterocycl.Chem., **7**, 1249 (1970).
106. R.A.Abramovitch, S.R.Challand, and E.F.V.Seriven, J.Amer.Chem.Soc., **94**, 1374 (1972).
107. J.M.Photis, J.Heterocycl.Chem., 8, 729 (1971).
108. R.M.Acheson and J.Woollard, J.Chem.Soc., Perkin Trans.I, 744 (1975).
109. E.Haselbach and M.Rossi, Helv.Chim.Acta, **59**, 2635 (1976).
110. H.Iwamura, Y.Tanabe, and H.Kobayashi, Tetrahedron Letters, 1987 (1976).
111. H.Prinzbach, H.Fritz, H.Hagemann, D.Hunkler, S.Kagabu, and G.Philippossian, Chem.Ber., **107**, 1971 (1974).
112. H.P.Loeffler, T.Martini, H.Musso, and G.Schroeder, Chem.Ber., **103**, 2109 (1970).
113. K.Kurabayashi and T.Mukai, Chem.Comm., 1016 (1972).
114. T.Martini and J.A.Kampmeier, Angew.Chem., Int. Ed., **9**, 236 (1970).
115. A.A.P.Noordstand, H.Steinberg, and T.I.DeBoer, Tetrahedron Letters, 2611 (1975).
116. R.Noyori, N.Hayashi, and M.Kato, J.Amer.Chem. Soc., **93**, 4948 (1971).
117. J.E.Baldwin and E.R.Peavy, J.Org.Chem., **36**, 1441 (1971).
118. J.E.Baldwin and R.K.Pinschmidt, Tetrahedron Letters, 935 (1971).
119. L.Paquette, M.J.Broadhurst, L.K.Read, and J.Clardy, J.Amer.Chem.Soc., **95**, 4639 (1973).
120. G.Boche, H.Weber, and J.Benz, Angew.Chem., **86**, 238 (1974).
121. M.E.Battiste, J.M.Coxon, G.P.Posey, W.R.King, M.Mathew, and G.J.Palenic, J.Amer.Chem.Soc., **97**, **947 (1975).**
122. J.Coxon, M.De Bruin, and C.K.Lau, Tetrahedron Letters, 337 (1975).
123. H.Prinzbach, G.Philippossian, and U.Scheidegger, Helv.Chim.Acta, **53**, 857 (1970).
124. D.M.Lemal and J.P.Lokemsgard, J.Amer.Chem.Soc., **88**, 593 (1966).
125. C.D.Smith, J.Amer.Chem.Soc., **88**, 4273 (1966).
126. N.Shimizu, S.Ishizuka, T.Takashi, and S.Nishida, Chem.Letters, 751 (1975).
127. S.Nishida, J.Moritani, and T.Teraji, J.Chem.Soc., D, 36 (1971).
128. F.Effenberger and O.Gerlach, Chem.Ber., **107**, 278 (1974).
129. A.De Meijere, Chem.Ber., **107**, 1702 (1974).
130. D.Kaufmann, A.De Meijere, B.Hingerty, and W.Saender, Angew.Chem., **87**, 842 (1975).
131. S.Sarel, A.Felzenstein, and J.Yovell, Chem.Comm., 859 (1973).
132. S.Sarel, A.Felzenstein, and J.Yovell, Chem.Comm., 753 (1974).
133. A.Felzenstein, S.Sarel, and J.Yovell, Chem.Comm., 918 (1975).
134. R.Askani and J.P.Chesick, Chem.Ber., **106**, 8 (1973).
135. G.Subrahmanyam, Indian J.Chem., **14b**, 365 (1976).
136. R.Askani and M.Wieduwilt, Chem.Ber., **109**, 1887 (1976).
137. A.Cornelis and P.Laszlo, J.Amer.Chem.Soc., **97**, 244 (1975).
138. T.Kaneda, T.Ogawa, and S.Misumi, Tetrahedron Letters, 3373 (1973).
139. H.Junek, Monatsh., **96**, 1421 (1965).
140. H.Junek and H.Aigner, Z.Naturforsch., **25b**, 1423 (1970).
141. H.Junek and H.Aigner, Chem.Ber., **106**, 914 (1973).
142. O.S.Wolfbeis, G.Zacharias, and H.Junek, Monatsh., **106**, 1207 (1975).
143. Z.Rappoport and D.Ladkani, J.Chem.Soc., Perkin Trans.I, 2595 (1974).
144. J.W.Ducker and H.J.Gunter, Austral.J.Chem., **26**, 1551 (1973).
145. H.Junek and H.Sterk, Tetrahedron Letters, 4309 (1968).
146. H.Junek and H.Aigner, Monatsh., **102**, 622 (1971).
147. A.Cornelis, P.Laszlo, and C.Pasquet, Tetrahedron Letters, 4335 (1973).
148. M.Acar, A.Cornelis, and P.Laszlo, Tetrahedron Letters, 3625 (1972).
149. G.Anderson, Acta Chem.Scand., **30b**, 403 (1976).
150. A.Rouessac and J.Vialle, Bull.Soc.chim.France, 2054 (1968).
151. T.Machiguchi, K.Okuma, M.Hoshino, and Y.Kitahara, Tetrahedron Letters, 2011 (1973).
152. R.Okazaki, A.Kitamura, and N.Inamoto, Chem. Comm., 257 (1975).
153. H.Junek, A.Hermetter, H.Fischer-Colbrie, M.Wittmer-Metz, and A.M.Braun, Chem.Ber., **109**, 1787 (1976).
154. T.Nishigushi, H.Sakakibara, and K.Fukuzumi, Chem.Letters, 649 (1976).
155. A.J.Andrews, R.C.Fort, and P.W.L.Quesne, J.Org.Chem., **36**, 83 (1971).
156. J.Dickmann and C.J.Pedersen, J.Org.Chem., **28**, 2879 (1963).
157. I.E.Franz, R.K.Hose, and H.K.Pearl, J.Org.Chem., **41**, 620 (1976).
158. H.Person, A.Foucaud, K.Luauglath, and C.Fayat, J.Org.Chem., **41**, 2141 (1976).
159. W.J.Middleton, R.E.Heckert, and E.L.Little, J.Amer. Chem.Soc., **80**, 2783 (1958).

160. W.J.Linn, O.W.Webster, and R.E.Benson, J.Amer. Chem.Soc., **85**, 2032 (1963).
161. R.Criegee and P.Gunther, Chem.Ber., **96**, 1564 (1963).
162. C.L.Dickinson and B.C.McKusick, J.Org.Chem., **29**, 3087 (1964).
163. J.Bastus and J.Castells, Proc.Chem.Soc., 216 (1962).
164. C.W.Rigby, E.Lord, M.P.Naan, and C.D.Hall, J.Chem.Soc., **B**, 1192 (1971).
165. Y.Tamura, K.Sumoto, H.Matsushima, H.Tanigushi, and M.Ikeda, J.Org.Chem., **38**, 4324 (1973).
166. P.N.Ngo, Diss.Abs, Int.B, 4209 (1974).
167. P.Farrell and R.K.Wojtowski, J.Chem.Soc., C, 1394 (1970).
168. M.J.T.Robinson and S.M.Rosenfeld, Tetrahedron Letters, 1431 (1975).
169. P.Farrell and R.K.Wojtowski, J.Chem.Soc., (C), 1390 (1970).
170. S.Kusabayashi and H.Mikawa, Bull.Chem.Soc. Japan, **45**, 836 (1972).
171. T.Nogami, T.Hasegawa, Y.Shirota, and H.Mikawa, Bull.Chem.Soc.Japan, **48**, 3048 (1975).
172. D.D.Traficante, M.Sundaralingam, P.Prusiner, T.Ito, and T.Sakurai, J.Org.Chem., **40**, 1815 (1975).
173. R.A.Earl, R.J.Pugmire, R.R.Ganopatti, and L.B.Townsend, J.Org.Chem., **40**, 1822 (1975).
174. Y.M.Chang, J.Sims, and K.N.Honk, Tetrahedron Letters, 4445 (1975).
175. H.C.Gardner and J.K.Kochi, J.Amer.Chem.Soc., **98**, 558 (1976).
176. M.N.Ponomarchuk, L.F.Kasukhin, and V.D.Pokhodenko, Zhur.Obshch.Khim., **41**, 43 (1971).
177. C.D.Hall, M.P.Naan, and R.L.Powel, J.Chem.Soc., (B), 1683 (1971).
178. M.A.Shaw, J.C.Tebby, R.S.Ward, and D.H.Williams, J.Chem.Soc.(C), 1609 (1968).
179. C.E.Looney and J.R.Downing, J.Amer.Chem.Soc., **80**, 2840 (1958).
180. S.Freireich, D.Gertner, and A.Zilkna, Europ. Polymer J., **9**, 411 (1973).
181. R.F.Tarvin, S.Aoki, and J.K.Stille, Macromolecules, **5**, 663 (1972).
182. US P.3963676 (1978); Chem.Abs., **85**, 124681 (1976).
183. G.Heublein, O.Barth, and W.Roemer, Adv.Ionic Polymer Proc.Int.Symp., 175 (1972).
184. A.A.Berlin, A.I.Kadantseva, A.A.Ivanov, G.K.Goryacheva, and N.I.Vorob'eva, Dokl.Akad. Nauk SSSR, **228**, 1364 (1976).
185. O.W.Webster, J.Amer.Chem.Soc., 86, 2898 (1964).
186. F.Wudl and W.E.Southwick, Chem.Comm., 254 (1974).
187. J.A.Meyer and D.W.Setser, J.Phys.Chem., **74**, 3452 (1970).
188. W.C.Hand and M.R.Richard, J.Phys.Chem., **80**, 557 (1976).
189. W.C.Hand and H.R.Obenauf, J.Phys.Chem., **76**, 269 (1972).
190. R.H.Obenauf, Diss.Abstr.Int.**B**, **33**, 1075 (1972).
191. A.N.Volkov and A.N.Nikol'skaya, Uspekhi Khim., **46**, 712 (1977) [Russ.Chem.Rev., No.4 (1977)].
192. M.Franck-Neumann and G.Leclerc, Bull.Soc.chim. France, 247 (1975).
193. R.J.Bushby, J.Chem.Soc., Perkin Trans.I, 274 (1974).
194. C.Moureu and J.C.Bongrand, Ann.Chim., **14**, 5 (1920).
195. C.Moureu and J.C.Bongrand, Compt.rend., **170**, 1025 (1920).
196. E.Kloster-Jensen, Acta Chem.Scand., **17**, 1866 (1963).
197. S.Murahashi, T.Takizawa, and S.Kurioka, Nippon Kagaku Zasshi, **77**, 1689 (1956); Chem.Abs., **53**, 5163 (1959).
198. E.Ciganek, Tetrahedron Letters, 3321 (1967).
199. US P.2200689 (1940); Chem.Abs., **34**, 6455 (1940).
200. D.N.Reinhoudt and C.G.Kowenhoven, Tetrahedron, **30**, 2093 (1974).
201. F.G.Klaerner and E.Vogel, Angew.Chem., **85**, 864 (1973).
202. H.Hopf and E.T.Lenich, Chem.Ber., **107**, 1891 (1974).
203. P.G.Gassman and G.D.Richmond, J.Amer.Chem. Soc., **92**, 2093 (1970).
204. M.Martin and M.Regitz, Annalen, 1702 (1974).
205. A.Hartmann and M.Regitz, Phosphorus, **5**, 21 (1974).
206. K.T.Potts, E.Houghton, and U.P.Singh, J.Org. Chem., **39**, 3627 (1974).
207. S.R.Challand, S.F.Gait, M.J.Ranee, W.C.Rees, and R.C.Storr, J.Chem.Soc., Perkin Trans.I, 26 (1975).
208. M.Franck-Neumann and D.Martina, Tetrahedron Letters, 1767 (1975).
209. US P.3419537 (1968); Chem.Abs., **70**, 48028 (1969).
210. E.Machowska, Coll.Czech.Chem.Comm., 4395 (1968).
211. K.Wallenfels and K.Friedrich, Tetrahedron Letters, 1223 (1963).
212. K.Friedrich and S.Oeckl, Chem.Ber., **103**, 3951 (1970).
213. BRD P.2205226 (1973); Chem.Abs., **79**, 115334 (1973).
214. V.N.Shwarts, "Obshchaya i Prikladnaya Khimiya, Respublikanskii Mezhvedomstvennyi Sbornik" (General and Applied Chemistry. All-Republic Interdepartmental Collection), 1972, No.4, p.59.
215. BRD P.1183900 (1965); Chem.Abs., **62**, 9074 (1965).
216. A.Sucharda-Sobczyk and L.Syper, Roczniki Chem., **49**, 479 (1975).
217. K.Friedrich and S.Oeckl, Chem.Ber., **106**, 2361 (1973).
218. K.Friedrich and S.Oeckl, Chem.Ber., **106**, 3796 (1973).
219. K.Friedrich and S.Oeckl, Chem.Ber., **106**, 3803 (1973).
220. A.Zinke, A.Dadieu, and A.Pongratz, Monatsh. **50**, 77 (1928).
221. R.D.West and H.E.Simmons, US P.3221113 (1965); Chem.Abs., **64**, 8359 (1966).
222. C.D.Weis, J.Org.Chem., **27**, 3695 (1962).
223. L.E.Hinkel and G.O.Richards, J.Chem.Soc., 1432 (1937).
224. H.Bredereck and G.Schmotzer, Annalen, **600**, 95 (1956).
225. E.Griszkiewicz-Trochimowski, Roczniki Chem., **1**, 468 (1921).
226. E.Griszkiewicz-Trochimowski, Zhur.Russ.Fiz.Khim. Obshch., **55**, 548 (1924).
227. E.Griszkiewicz-Trochimowski, Zhur.Russ.Fiz.Khim. Obshch., **55**, 551 (1924).
228. P.Neumann, Dissertation, University of Freiburg, 1967.
229. R.W.Begland, D.R.Hartter, and D.S.Donald, J.Org.Chem., **39**, 1235 (1974).
230. BRD P.2425928 (1974); Chem.Abs., **83**, 10144 (1975).
231. BRD P.2134946 (1972); Chem.Abs., **76**, 140884 (1972).

232. US P.3808209 (1974); Chem.Abs., **83**, 81219 (1975).
233. US P.3928351 (1975); Chem.Abs., **84**, 122557 (1976).
234. US P.3963715 (1976); Chem.Abs., **85**, 178975 (1976).
235. G.Holzmann, H.W.Rothkopf, R.Mueller, and D.Woehlire, Org.Mass Spectrom., **10**, 97 (1975).
236. E.Ott, Chem.Ber., **52**, 656 (1919).
237. I.B.Johns, E.A.McElhill, and J.O.Smith, J.Chem. Eng.Data, **7**, 277 (1962).
238. A.S.Bayley, B.R.Henn, and J.M.Langdom, Tetrahedron, **19**, 161 (1963).
239. A.Carrington, H.C.Longuet-Higgins, and P.F.Todd, Mol.Phys., **9**, 211 (1965).
240. M.T.Jones, J.Amer.Chem.Soc., **88**, 5060 (1966).
241. E.Griszkiewicz-Trochimowski and M.Bousquet, Compt.rend., **258**, 2992 (1961).
242. S.J.Weininger and E.R.Thornton, J.Amer.Chem. Soc., **89**, 2950 (1967).
243. J.A.Pople, D.Beveridge, and P.A.Dobosh, J.Amer. Chem.Soc., **90**, 4201 (1968).
244. C.Mauguin and L.J.Simon, Compt.rend., **170**, 993 (1920).
245. E.S.Franklin, J.Amer.Chem.Soc., **44**, 486 (1922).
246. W.L.Burdick, J.Amer.Chem.Soc., **47**, 1485 (1925).
247. F.D.Marsh, J.Org.Chem., 37, 2966 (1972).
248. M.E.Hermes and F.D.Marsh, J.Org.Chem., **37**, 2969 (1972).
249. J.E.McMurry and A.F.Coppolino, J.Org.Chem., (**38**), 2881 (1973).
250. A.Anastssiou and S.W.Eachus, J.Chem.Soc., D, 429 (1970).
251. M.E.Hermes and F.D.Marsh, J.Amer.Chem.Soc., **89**, 4760 (1967).
252. H.Okabe and A.Mele, J.Chem.Phys., **51**, 2100 (1969).
253. H.W.Kroto, T.F.Morgan, and H.H.Sheena, Trans. Faraday Soc., **66**, 2237 (1976).
254. US Appl.620292 (1968); Chem.Abs., **71**, 22556 (1969).
255. A.G.Anastassiou, J.Amer.Chem.Soc., **87**, 5512 (1965).
256. US P.3896188 (1975); Chem.Abs., **83**, 164373 (1975).
257. US P.3776950 (1973); Chem.Abs., **81**, 63769 (1974).
258. J.I.G.Cadogan and I.Gosney, J.Chem.Soc., Perkin Trans.I, 460 (1974).
259. US P.3427323 (1969); Chem.Abs., **71**, 70149 (1969).
260. A.Almenningen, B.Bak, J.Peter, and T.G.Strand, Acta Chem.Scand., **27**, 1538 (1973).
261. K.Bolton, R.D.Brown, and F.R.Burden, Chem. Phys.Letters, **15**, 79 (1972).
262. V.V.Mel'nikov, S.A.Zacheslavskii, L.F.Baeva, and B.V.Gidaspov, Zhur.Org.Khim., **8**, 1805 (1972).
263. B.Bak, P.Jansen, and H.Stafst, Chem.Phys.Letters, **35**, 247 (1975).
264. G.L.Blackman, K.Bolton, R.D.Brown, F.R.Burden, and A.Mishra, J.Mol.Spectrosc., **47**, 457 (1973).
265. C.C.Costain and H.W.Kroto, Canad.J.Phys., **50**, 1453 (1972).
266. H.F.Shurvell and D.W.Hyslop, J.Chem.Phys., **52**, 881 (1970).
267. B.Bak, O.Bang, F.Nicolaisen, and O.Rump, Spectrochim.Acta, **27a**, 1865 (1971).
268. F.D.Marsh and M.E.Hermes, J.Amer.Chem.Soc., **87**, 1819 (1965).
269. B.Bak, R.Eskildsen, and P.Jansen, Acta Chem. Scand., **25**, 3181 (1971).
270. B.Bak, R.Eskildsen, and P.Jansen, J.Mol.Struct., **11**, 25 (1972).
271. B.Bak and P.Jansen, J.Mol.Struct., 12, 167 (1973).
272. B.Bak, Dansk.Kem., 53, 81 (1972).
273. E.Ciganek, J.Org.Chem., **30**, 4198 (1965).
274. Y.Tatsuno, A.Konishi, A.Nakamura, and S.Otsuka, Chem.Comm., 558 (1974).
275. E.Ciganek, J.Amer.Chem.Soc., 89, 1454 (1967).
276. D.J.Yarrow, J.A.Ibers, and Y.Tatsuno, J.Amer. Chem.Soc., **95**, 8590 (1973).
277. J.Rieser and K.Friedrich, Annalen, 641 (1976).
278. J.Rieser and K.Friedrich, Annalen, 669 (1976).
279. W.H.Smith and G.E.Leroi, Spectrochim.Acta, **25a**, 1917 (1969).
280. O.W.Webster, J.Amer.Chem.Soc., **88**, 4055 (1966).
281. US P.3536694 (1970); Chem.Abs., **74**, 65559 (1971).
282. R.C.Wheland and J.L.Gillson, J.Amer.Chem.Soc., **98**, 3916 (1976).
283. V.Migridichian, "The Chemistry of Organic Cyanogen Compounds", New York, 1947.
284. T.L.Cairns, R.A.Carboni, D.D.Coffman, R.E.Heckert, E.L.Little, B.C.McKusick, R.M.Scribner, and H.L.Winberg, J.Amer.Chem.Soc., **80**, 2775 (1958).
285. C.Moureu and J.C.Bongrand, Bull.Soc.chim.France 846 (1909).
286. D.R.Williams and R.Damrauer, Theoret.Chim.Acta, 23, 195 (1971).
287. R.Kuhn and H.Kainer, Angew.Chem., 65, 442 (195
288. E.Wassermann, K.Schueller, and W.Yager, Chem.Phys.Letters, 259 (1968).
289. C.Pannel, US P.3773774 (1973); Chem.Abs., 80, 59869 (1974).
290. C.V.Hart, J.Amer.Chem.Soc., **50**, 1922 (1928).
291. T.Fukunaga, J.Amer.Chem.Soc., **98**, 610 (1976).
292. L.Bucsis and K.Friedrich, Chem.Ber., **109**, 2469 (1976).
293. K.Friedrich and W.Ertel, Tetrahedron Letters, 4771 (1972).
294. C.D.Weis, J.Org.Chem., **27**, 3695 (1962).
295. L.E.Hinkel and G.O.Richards, J.Chem.Soc., 1432 (1937).
296. P.Scheiner, Tetrahedron Letters, 4489 (1971).
297. M.Brown, US P.3338915; Chem.Abs., **68**, 87299 (1970).
298. O.W.Webster, D.R.Hartter, R.W.Begland, W.A.Sheppard, and A.Cairncross, J.Org.Chem., **37**, 4134 (1972).

Faculty of Chemistry,
Lomonosov Moscow State University