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α-Nitronitriles

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ABSTRACT. **The methods of synthesis and chemical reactions of nitrocyano-compounds, in which the nitro- and cyano-groups are joined by a common carbon atom, are examined.**

The bibliography includes 134 references.

Contents

I. Introduction 470
II. Methods of synthesis 470
III. Properties 471
IV. Applications of α-nitronitriles 475

I. Introduction

This review is devoted to the consideration of the methods of synthesis and chemical properties of nitrocyano-compounds in which the nitro- and cyano-groups are linked to a common carbon atom. Compounds of this type have found application as biologically active substances,[1-3] as initiators of chain polymerisation reactions,[4] as inhibitors of the thermooxidative ageing of polymers,[5] as components of energy absorbing compositions,[6-8] and also as intermediates for their preparation.[9-12]

α-Nitrocyano-compounds are widely used in organic synthesis. The presence in their molecules of several reaction centres makes it possible to involve these compounds in numerous reactions leading to a wide assortment of polyfunctional aliphatic and heterocyclic products. Many reactions proceed in a non-trivial manner under these conditions, which is associated with the specific features of the mutual influence of the functional groups and the ability of the reaction intermediates to enter into secondary intramolecular processes.

α-Nitronitriles have been used to investigate the inductive and resonance effects of substituents[13-18] and the electronic and steric structures of carbanions.[19-24]

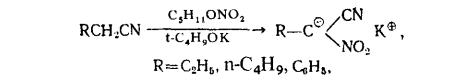
The chemical properties of nitriles and nitro-compounds have been described in detail in monographs and reviews,[25-28] while the methods of synthesis and chemical reactions of α-nitronitriles have been described in a fragmentary manner in only one book.[27]

II. Methods of synthesis

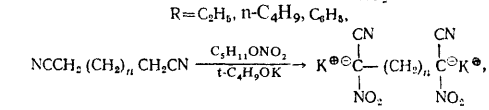
1. Methods of synthesis of α-nitrocyanoalkanes

The first member of the series—nitroacetonitrile—has been synthesised by the dehydration of metazonic acid.[29-35] Its homologues have been obtained by the oxidation[36,37] and photolysis[39] of α-nitrosocyanoalkanes, by the oxidation of α-hydroxyaminocyanoalkanes,[38] by the pyrolysis of 1,1-azobis-1,1-dicyanoalkanes,[40] and by the reaction of α-bromocyanoalkanes with $NaNO_2$.[41,42]

The methods of synthesis of α-nitrocyanoalkanes involving the nitration of nitriles or the cyanation of salts of nitroso-compounds are general in character. The nitration of nitriles by acid nitrating agents cannot be stopped, with rare exceptions,[43] at the stage involving the formation of mononitrocyanoalkanes. One nitro-group can be introduced by carrying out the reaction under alkaline conditions:[44,45]

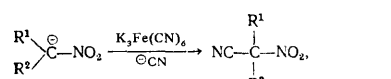


$R = C_2H_5$, n-C_4H_9, C_6H_5,



$n = 2-4, 6.$

α-Nitrocyanoalkanes have been synthesised in 60–80% yields by the oxidative cyanation of salts of secondary nitroalkanes and nitrocycloalkanes.[46,47] A one-electron redox mechanism has been proposed:[47]

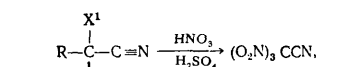


$R^1 = CH_3$, $R^2 = CH_3$, C_2H_5, n-C_5H_{11}; $R^1R^2 = -(CH_2)_n-$.

The preparation of functional derivatives of nitroacetonitrile containing aminocarbonyl,[48-51] alkoxycarbonyl,[51] and acyl[52] groups has been described.

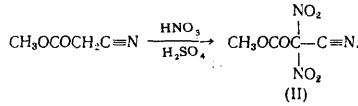
2. Methods of synthesis of α-polynitrocyanoalkanes

The interaction of cyanoacetic acid and its derivatives (amide, esters, nitrile, as well as their mono- and di-nitro-derivatives) with the nitrating mixture leads to the formation of trinitroacetonitrile (I).[53,54] However, the nitration of methyl cyanoacetate affords methyl dinitrocyanoacetate (II):[55]



(I)

X^1, $X^2 = H$, NO_2,
$R = COOH$, $CONH_2$, $C\equiv N$.

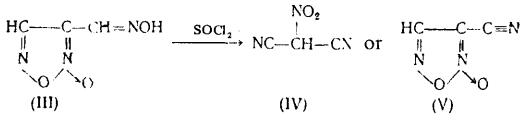


(II)

The nitration of α-hydroxyiminonitriles is a more general method of synthesis of αα-dinitrocyanoalkanes.[4,55-57] The cyanation of the silver salt of trinitromethane by iodocyanogen, leading to trinitroacetonitrile, can serve as an example of another approach to the synthesis of α-polynitrocyanoalkanes.[58]

3. Methods of synthesis of α-polycyanonitroalkanes

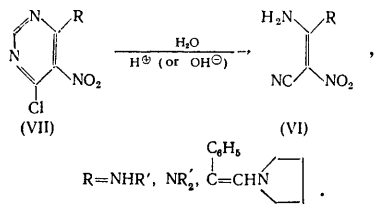
The dehydration of furoxanealdoxime (III), to which the structure of nitrocyanoacetaldoxime was erroneously attributed previously,[59] gives rise to dicyanonitromethane (IV) or to the cyanofuroxane (V).[51] The ammonium, potassium, and silver salts of compound (IV) have been obtained:[59,60]



(III) (IV) (V)

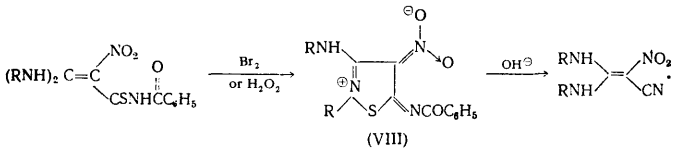
4. Methods of synthesis of α-nitronitriles whose functional groups are linked to an sp^2-hybridised carbon atom

The simplest representative of α-nitrocyanoalkenes, namely α-nitroacrylonitrile, is unstable,[61] but many of its β-substituted derivatives are stable. 1-Amino- and 1,1-diamino-2-nitro-2-cyanoalkenes (VI) are formed in the degradative hydrolysis of chloronitropyrimidines (VII) under acid[62–64] or alkaline[65] conditions:



(VII) (VI)

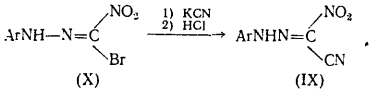
The alkaline hydrolysis of derivatives of isothiazoline (VIII), obtained by oxidising nitroketen aminals, also leads to 1,1-diamino-2-nitro-2-cyanoethylenes:[66]



(VIII)

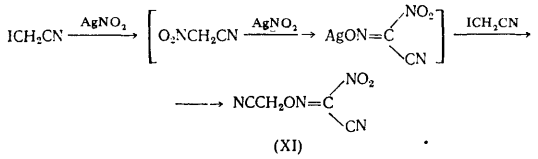
Methods have been developed for the preparation of 1-amino-2-nitro-2-cyanoethylenes by the interaction of 3-chloro-4-nitroisothiazole[67] and 5-methyl-4-nitroisooxazole[68] with amines.

The cyanation of the arylhydrazones of bromonitroformaldehyde (X) constitutes a general method of synthesis of the arylhydraxones of cyanonitroformaldehyde (IX):[2,69]



(X) (IX)

The interaction of iodoacetonitrile with $AgNO_2$ leads to a derivative of cyanonitroformaldoxime (XI):[70]



(XI)

III. Properties

1. The structure and acid–base properties of α-nitrocyanoalkanes

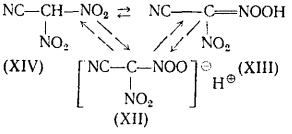
α-Nitronitriles containing hydrogen atoms in the α-position relative to the nitro- and cyano-groups are strong CH acids and are able to form salts with metals or organic bases. The thermodynamic stability of the α-nitrocyanoalkane anions is due to the strong-*I* effects of nitro- and cyano-groups (the Taft σ* constants are 3.9 and 3.6 respectively[71]) and also by the ability of the latter to participate in the delocalisation of the charge of the carbanion (mesomeric effect). The pK_a for certain α-nitrocyanoalkanes are listed in Table 1.

Table 1. The pK_a values for α-nitrocyanoalkanes in water.[72]

Compound	pK_a	T, °C
$NCCH_2NO_2$	4.86	27
$NCCH(C_6H_5)NO_2$	0.29	20
$NCCH(CO_2CH_3)NO_2$	−5.20	20
$NCCH(NO_2)_2$	−6.22	20

The dinitroacetonitrile anion has an almost planar structure, which follows from the results of X-ray diffraction analysis of its potassium, rubidium, and caesium salts.[22–24] Its C ≡ N bond length (1.20 Å) exceeds the C≡N bond length in cyanoalkanes (1.14–1.16 Å), while the C–C(N) bond is shorter (1.36 Å) than the usual C–C single bond (1.43 Å), which indicates the involvement of the nitrile group in conjugation. This conclusion has been confirmed by the results of IR spectroscopic[22] and ^{14}N NMR[19,20] studies on the dinitroacetonitrile anion.

It has been established by IR and UV spectroscopic methods that dinitroacetonitrile can exist in solutions in three tautomeric forms: as the ion pair (XII) (in water and polar organic solvents),[73] as the thermally labile *aci*-form (XIII) (in 100% H_2SO_4 or anhydrous dichloroethane),[74] and as the "true" dinitro-compound (XIV):



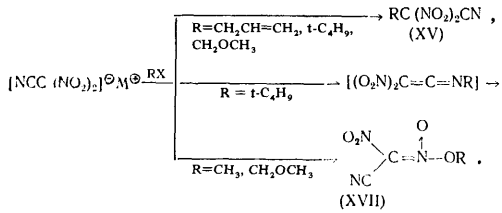
(XIV) (XII) (XIII)

The structures of the α-nitronitriles whose nitro- and cyano-groups are linked to an sp^2-hybridised carbon atom have not been investigated.

2. Reactions of α-nitronitriles with electrophiles

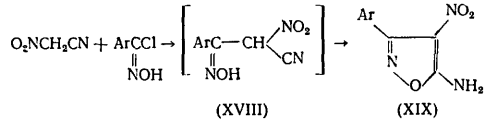
(a) Alkylation of α-nitrocyanoalkanes. The interaction of the silver salt of dinitrocyanomethane with alkylhalides can take place at the carbon atom linked to the nitro- and cyano-groups (*C*-alkylation), at the nitrogen atom of the nitrile group (*N*-alkylation), and at the oxygen atom of the nitro-group (*O*-alkylation) depending on the

nature of the alkylating agent. The reaction products are dinitrocyanoalkanes (XV), dinitrocarboxamides (XVI), and nitronic esters (XVII)[75,76,134] respectively:



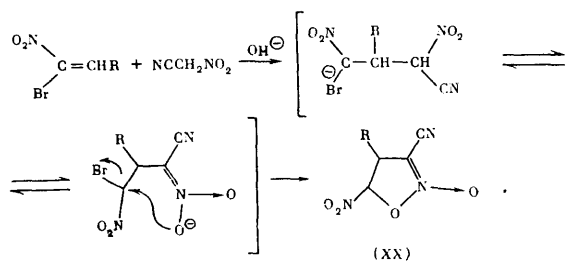
The interaction of the silver salt of phenylnitroacetonitrile with trityl chloride leads only to the *O*-alkylation product.[77] The formation of nitronic esters is observed in the alkylation of α-nitrocyanoalkanes by diazomethane.[78–80] Nitronates with a low stability can enter into further interactions under the reaction conditions.[81]

The interaction of nitroacetonitrile with Mannich bases[33,61] or with arylchloroximes[52] affords the *C*-substitution products. In the latter case the product of the cyclisation of the intermediate (XVIII)—5-amino-3-aryl-4-nitroisoxazole (XIX)—was isolated:



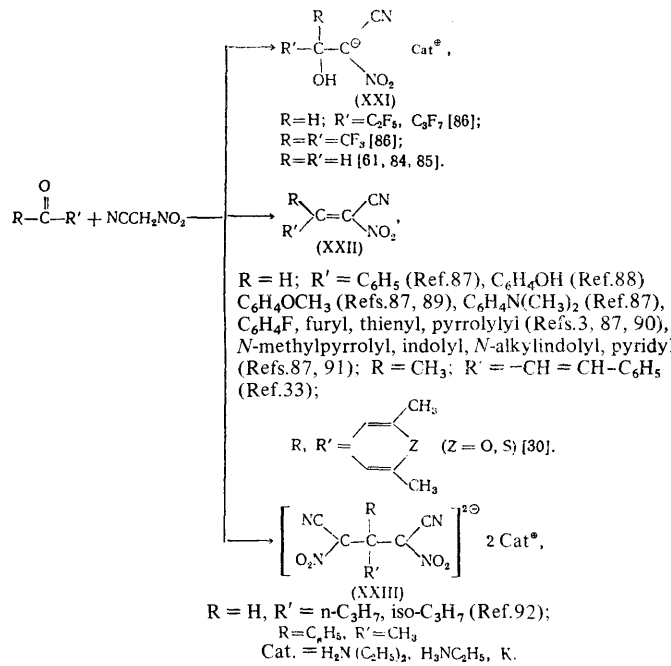
The ability of the nitrile group to enter into intramolecular condensation reactions under mild conditions is a characteristic property of α-nitronitriles, which distinguishes them from other types of cyano-compounds and makes it possible to construct on their basis various heterocyclic systems (see below).

(b) Reactions of α-nitrocyanoalkanes with alkenes containing activated double bonds. The α-nitrocyanoalkanes containing a mobile hydrogen atom in the α-position relative to the nitro- and cyano-groups are able to add to compounds containing the C = C double bond activated by strong electron-accepting substituents. The reactions of dinitroacetonitrile with methyl acrylate, acrylamide, acrolein, butenone, methylenebisacrylamide, and *NN'N''*-triacryloylperhydro-*s*-triazine lead to the formation of the corresponding Michael adducts.[76] The process does not require base catalysis owing to the high acidity of dinitroacetonitrile. The reaction of nitroacetonitrile with vinyl ketones can afford products of the addition to both the C = C double bond and to the carbonyl group.[82] The interaction of the sodium salt of nitroacetonitrile with 1-bromo-1-nitroalkenes results in the formation of 4-alkyl(aryl)-3-cyano-5-nitroisoxazolines (XX) in accordance with the following scheme:[83]

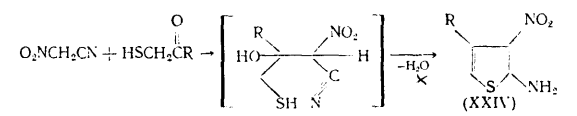


(c) Reactions of α-nitrocyanoalkanes with compounds containing C = O or C = N bonds. The interaction of nitroacetonitrile with aldehydes leads as a rule to three types of products: the salts of 1-nitro-1-cyano-2-hydroxyalkanes (XXI), 1-nitro-1-cyanoalkenes (XXII), and the salts of the dinitriles of substituted 2,4-dinitroglutaric acids (XXIII). The reaction can be stopped at the stage involving the formation of compound (XXI) by using formaldehyde,[61,84,85] perfluoroaldehydes, and perfluoroketones[86] as carbonyl components. The products of the reaction of nitroacetonitrile with aromatic and heteroaromatic aldehydes are unsaturated compounds (XXII).[6,61,87–91] When nitroacetonitrile interacts with aliphatic aldehydes, the salts (XXII) formed initially combine with a second nitroacetonitrile molecule and are converted into salts of dinitrodinitriles (XXIII).[61,92]

The reaction of nitroacetonitrile with ketones also leads to the formation of compounds (XXII) and (XXIII). The first possibility obtains in the case of benzylideneacetone,[33] 2,6-dimethyl-γ-pyrone, and 2,6-dimethyl-γ-thiapyrone[30] and the second arises in the reactions of nitroacetonitrile with acetophenone and cyclohexanone:[33]



The interaction of nitroacetonitrile with α-mercaptoketones is accompanied by intramolecular condensation and derivatives of 1-amino-2-nitrothiophen (XXIV) are formed:[9]

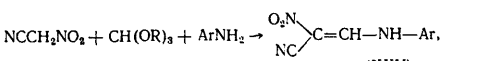


The product of the reaction of dinitroacetonitrile with formaldehyde is 2,2-dinitro-2-cyanoethanol.[76]

The reactions of α-nitrocyanoalkanes with carbonyl compounds require as a rule base[33,86,88,89,92] or acid[91] catalysis. Certain reactions take place readily also in the absence of catalysts.[31,76]

Nitroacetonitrile enters into three-component reactions with formaldehyde–amine and alkyl orthoformate–amine systems. In the former case, the process proceeds like the Mannich reaction and leads to the formation of 2-amino-1-nitro-1-cyanoalkanes[33] while in

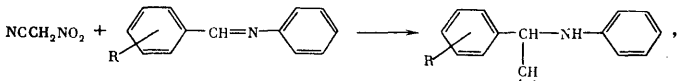
the latter derivatives of 2-amino-1-nitro-1-cyanoethylene (XXV) are prodduced:[93,94]



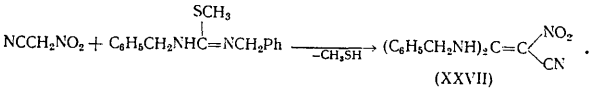
$$NCCH_2NO_2 + CH(OR)_3 + ArNH_2 \rightarrow \begin{matrix} O_2N \\ NC \end{matrix}\!\!>\!C{=}CH{-}NH{-}Ar,$$

$Ar = C_6H_5$, p-ClC_6H_4, p-$CH_3C_6H_4$. (XXV)

The addition of α-nitrocyanoalkanes to C = N double bonds has been little investigated. The interaction of nitroacetonitrile with benzylideneaniline and its derivatives is completed by the formation of the adducts (XXVI).[33] The product of the reaction of nitroacetonitrile with *NN'*-dibenzyl-*S*-methylisothiourea is 1,1-di(benzylamino)-2-nitro-2-cyanoethylene (XXVII):[34]



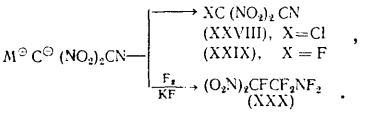
R = H, *o*-Cl, *p*-Cl. (XXVI)



$$NCCH_2NO_2 + C_6H_5CH_2NHC(SCH_3){=}NCH_2Ph \xrightarrow[-CH_3SH]{} (C_6H_5CH_2NH)_2C{=}C(NO_2)(CN)$$

(XXVII)

(d) Reactions of α-nitrocyanoalkanes leading to the formation of a carbon–heteroatom bond. The salts of α-nitro-[29,44,45] and α-dinitrocyanoalkanes[53] are readily brominated with formation of α-bromo-derivatives. The product of the interaction of the sodium salt of dinitroacetonitrile with Cl_2 is chlorodinitrocyanomethane(XXVIII).[53] Chlorine fluorosulphonate[95] and the $HCl-H_2O_2$ system[53] have also been used as chlorinating agents for the synthesis of compound (XXVIII). Fluorination of salts of dinitroacetonitrile by elemental fluorine in an aqueous medium[96] and in the CaF_2-Ni system[97] leads to the formation of fluorodinitroacetonitrile (XXIX). In the presence of KF, the nitrile (XXIX) formed initially combines with two molecules of F_2 at the C = N double bond, affording 2-difluoroamino-1,1-dinitrotrifluoroethane (XXX):[97]

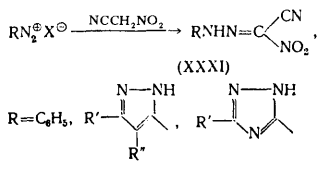


$$M^{\oplus}C^{\ominus}(NO_2)_2CN \begin{cases} \rightarrow XC(NO_2)_2CN \\ \quad (XXVIII),\ X=Cl \\ \quad (XXIX),\ X=F \\ \xrightarrow[KF]{F_2} (O_2N)_2CFCF_2NF_2 \\ \quad (XXX) \end{cases}$$

The reaction of the sodium salt of dinitroacetonitrile with perchloryl fluoride does not permit the synthesis of compound (XXIX),[98] but fluorination of the potassium salt of ethyl nitrocyanoacetate by this fluorinating agent affords ethyl fluoronitrocyanoacetate.[99]

Dinitroacetonitrile is smoothly nitrated by fuming HNO_3 and sulphuric acid–nitric acid mixtures to trinitroacetonitrile.[53] The reaction is described by a third-order kinetic equation, which includes the concentrations of dinitroacetonitrile, HNO_3, and the water or H_2SO_4 present in the system.[100]

The interaction of nitroacetonitrile with aromatic[29] and heteroaromatic[32] diazonium salts leads to the formation of the corresponding hydrazones of nitrocyanoformaldehyde (XXXI):

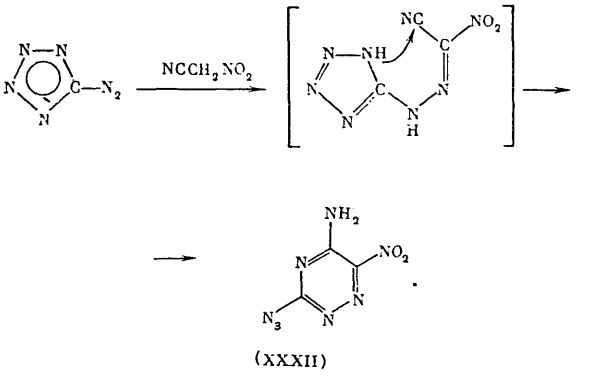


$$RN_2^{\oplus}X^{\ominus} \xrightarrow{NCCH_2NO_2} RNHN{=}C(CN)(NO_2),$$

(XXXI)

$R = C_6H_5$, R' = 1,2,4-triazol-3-yl, R' = 1,2,4-triazol-4-yl.

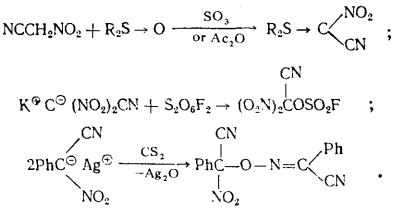
In the case of diazotetrazole, the process cannot be stopped at the hydrazone formation stage; the hydrazone is converted under the reaction conditions into 5-amino-3-azido-1,2,4-triazine (XXXII), which cannot be obtained in other ways:[101]



(XXXII)

In contrast to nitroacetonitrile, dinitroacetonitrile reacts with aromatic diazo-compounds to form only arenediazonium salts containing the anion $(O_2N)_2\bar{C}CN$.[102]

In a number of instances, the reactions of α-nitrocyanoalkanes with electrophiles lead to the formation of a bond between the carbon atom and the atoms of Group VI elements. The formation of the ylide C ← S bond is observed in the interaction of nitroacetonitrile and its salts with dialkyl sulphoxides[103,104] [Eqn. (1)]. The formation of the C–O bond accompanies the reactions of the potassium salt of dinitroacetonitrile with peroxysulphuryl difluoride[105] [Eqn. (2)] and of the silver salt of α-nitrophenylacetonitrile with CS_2[106,107] [Eqn. (3)]:



$$NCCH_2NO_2 + R_2S \rightarrow O \xrightarrow[or\ Ac_2O]{SO_3} R_2S \rightarrow C(NO_2)(CN); \quad (1)$$

$$K^{\oplus}C^{\ominus}(NO_2)_2CN + S_2O_6F_2 \rightarrow (O_2N)_2C(CN)OSO_2F; \quad (2)$$

$$2PhC^{\ominus}(CN)(NO_2)Ag^{\oplus} \xrightarrow[-Ag_2O]{CS_2} PhC(CN)(NO_2)-O-N{=}C(Ph)(CN). \quad (3)$$

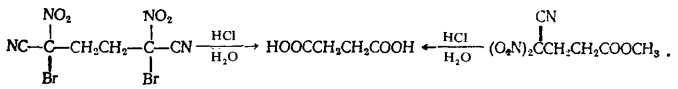
3. Reactions of α-nitronitriles with nucleophiles

(a) Reactions of α-nitrocyanoalkanes with nucleophiles accompanied by the elimination of functional groups. α-Nitrocyanoalkanes exhibit dual reactivity in relation to nucleophiles. The attack by a nucleophile on the carbon atom of the nitrile group leads to the formation of adducts. The attack on the carbon atom linked to the nitro- and cyano-group is accompanied by the elimination of one of them.

The mode of elimination depends on the nature of the nucleophile and the structure of the α-nitrocyanoalkane. Thus, treatment of trinitroacetonitrile[53] or fluorodinitroacetonitrile[98] with the OH^- anion, which has a high oxidation potential, results in the nitrile group being split off. However, the reactions of trinitroacetonitrile with reductants (H_2S, $Br^{\ominus}$) lead to the elimination of the nitro-group.[53,54]

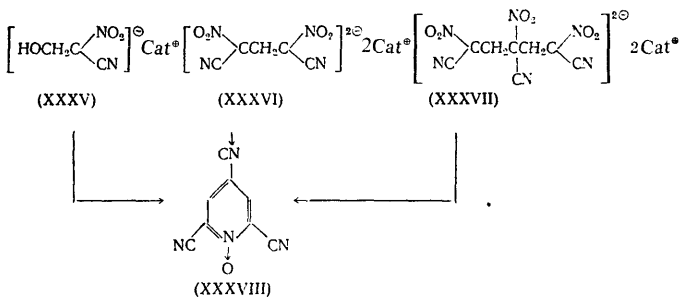
Treatment of alkyl derivatives of nitro- and dinitro-acetonitrile is accompanied in all cases by decyanation and the formation of the salts of the corresponding nitroalkanes.[45,56,76] Under fairly severe conditions (heating with aqueous alkali), the salts of α-nitrocyanoalkanes also undergo decyanation on treatment with nucleophiles.[44,57]

The elimination of functional groups is observed in the reactions of α-nitrocyanoalkanes with aqueous acids. The product of the reactions of compounds (XXXIII) and (XXXIV) with HCl is succinic acid;[45,76]



(XXXIII) (XXXIV)

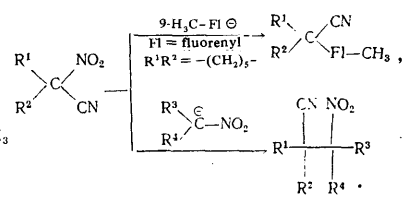
The acid hydrolysis of the salts (XXXV)–(XXXVII) proceeds with retention of the cyano-groups and the formation of 2,4,6-tricyanopyridine *N*-oxide (XXXVIII):[61,84,85]



(XXXV) (XXXVI) (XXXVII) (XXXVIII)

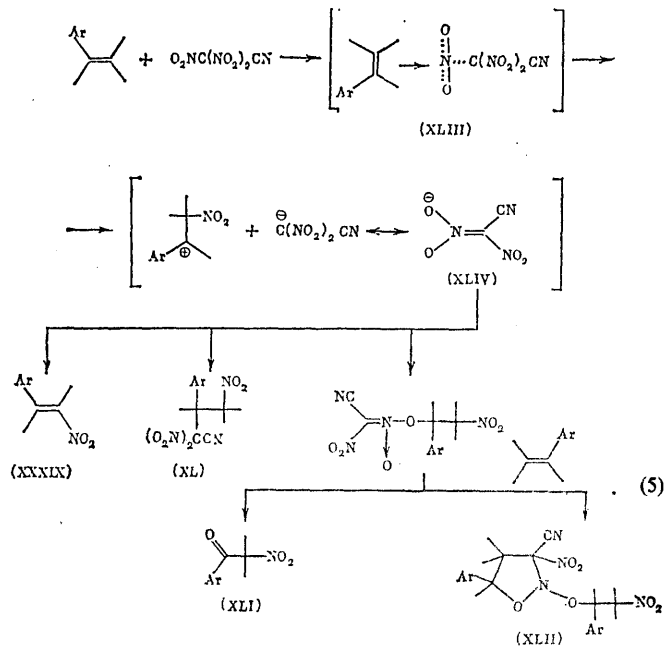
The cyano-groups are retained also in the reactions involving the "degradative alkylation" of dialkyl derivatives of nitroacetonitrile by the 9-methylfluorenyl anion[108] or salts of nitroalkanes,[109–111] leading to the formation of highly branched cyano-compounds [Eqn. (4)]:

R^1, R^2	R^3, R^4
$-(CH_2)_4-$	CH_3, CH_3
CH_3, CH_3	CH_3, CH_3
CH_3, CH_3	$-(CH_2)_5-$
CH_3, CH_3	CH_3, $CH_2CH_2COOCH_3$



(4)

The reaction of trinitroacetonitrile with arylalkenes, which behave in this case as nucleophiles, is accompanied by denitration. The reaction may result in the formation of a whole series of products: conjugated nitroalkenes (XXXIX), 1-cyano-1,1,3-trinitroalkanes (XL), α-nitroketones (XLI), and 2-(β-nitroalkoxy)-3-cyano-3-nitroisoxazolidines (XLII).[112–115] A reaction mechanism has been proposed,[113,115] including the formation of a charge-transfer complex (XLIII) and an ion pair (XLIV), which is stabilised either by splitting off H^+ from the cation or by the *C*- or *O*-alkylation of the dinitroacetonitrile anion [Eqn. (5)]:

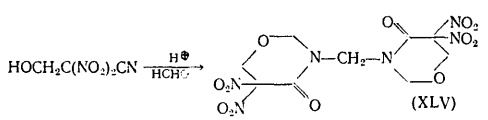


(XLIII) (XLIV) (XXXIX) (XL) (XLI) (XLII)

(5)

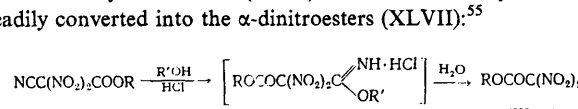
(b) Reactions of α-nitrocyanoalkanes with nucleophiles accompanied by addition to the C ≡ N bond. The nitrile group in α-nitrocyanoalkanes is activated by the neighbouring nitro-group and readily combines with nucleophiles: water, alcohols, amines, and chlorine fluorosulphate.

The hydrolysis of α-nitrocyanoalkanes can be stopped at the stage involving the formation of amides of carboxylic α-nitroacids on treatment with HCl in inert organic solvents[96,116] or when the reaction is carried out in 85–99% H_2SO_4.[99,117] The hydrolysis of 2,2-dinitro-2-cyanoethanol in the presence of formaldehyde is accompanied by condensation reactions and leads to the formation of the bicyclic methylenebisamide (XLV):[76]



(XLV)

The products of the reactions of α-nitrocyanoalkanes with alcohols in the presence of HCl are iminoester hydrochlorides (the Pinner reactions).[55,118] In the case of dinitrocyanoacetates, the imonoester hydrochlorides (XLVI) have a low stability and are readily converted into the α-dinitroesters (XLVII):[55]

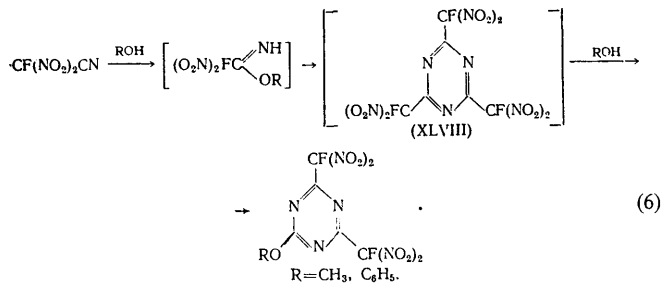


(XLVI) (XLVII)

R = CH_3, C_2H_5, n-C_4H_9, C_6H_{11}, CH_2CH_2Br, $CH_2CH_2ONO_2$.

Fluorodinitroacetonitrile combines with alcohols in the presence of basic catalysts [CH_3ONa, $N(C_2H_5)_3$][97] or without a catalyst,[98] affording the free iminoesters. The iminoester formation stage apparently includes the cyclotrimerisation of fluorodinitroacetonitrile to 1,3,5-triazine derivatives (XLVIII) in the presence of alcohols

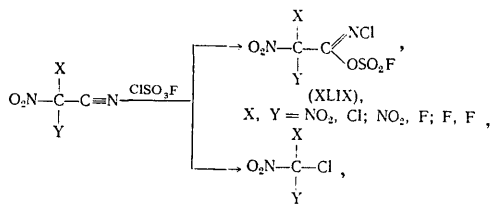
under a pressure of 8–10 kbar in accordance with reaction (6):[119]



(6)

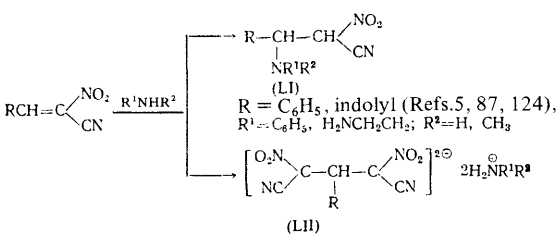
The interaction of α-nitrocyanoalkanes with amines usually leads to the formation of amidines.[97,120] In a number of cases, amidines are capable of undergoing further interactions (hydrolysis,[10] cyclisation[121]) under the reaction conditions. The addition of hydroxylamine to nitroacetonitrile results in the formation of the amidoxime of nitroacetic acid.[29]

Chlorine fluorosulphate adds to the C≡N bond of chlorodinitro-, fluorodinitro-, and difluoronitro-acetonitriles, affording chloroimino-fluorosulphonylesters (XLIX).[95,122] However, the reaction with ethyl dinitrocyanoacetate leads not to the adduct but to the product (L) of the substitution of the nitrile group by chlorine:[95]



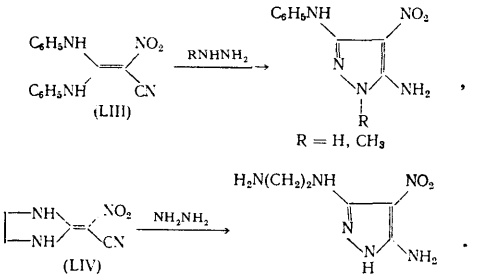
(L), X = NO_2, Y = $CO_2C_2H_5$.

(c) Reactions of α-nitronitriles whose functional groups are linked to an sp^2-hybridised carbon atom with nucleophiles. α-Nitrocyanoalkenes can combine with nucleophiles in the β-position. The interaction of 1-aryl- and 1-heteroaryl-2-nitro-2-cyanoethylenes with amines affords two types of products depending on the basicity of the amines: 1-amino-2-nitro-2-cyanoethylenes (LI) and the salts of the dinitriles of 3-substituted 2,4-dinitro-glutaric acids (LII). The less basic aromatic amines (pK_b = 9.0–9.5) form the adducts (LI),[5,87,124] while alkylamines (pK_b = 3.0–4.8) (with the exception of ethylenediamine) afford the salts (LII):[87–89,123,126,128]

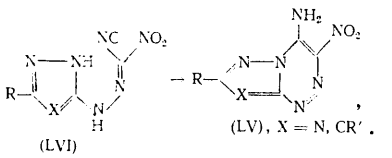


R = C_6H_5 (Refs.87, 123), thienyl (Refs.125, 126, 128), C_6H_4OH (Ref.88), $C_6H_4OCH_3$ (Ref.89), C_6H_4F (Ref.3), furyl (Ref.127);
R, R^1 = H, alkyl, cycloalkyl.

In a number of instances, the addition of nucleophiles to derivatives of 1-nitro-1-cyanoethylene may be accompanied by intramolecular condensation involving the nitrile group. Thus the reaction of nitrocyanoketen aminals (LIII) and (LIV) with hydrazine leads to polyfunctional compounds of the pyrazole series:[129]



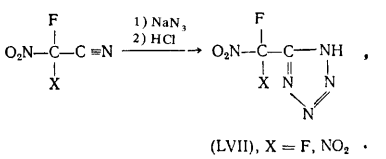
Cyclisation with formation of condensed derivatives of 1,2,4-triazine (LV) is observed in the case of pyrazolyl- and triazolyl-hydrazones of cyanonitroformaldehyde (LVI).[32] One of the nitrogen atoms of the heterocycle plays the role of the nucleophile attacking the carbon atom of the nitrile group under these conditions:



4. Cycloaddition reactions of α-nitronitriles

α-Nitrocyanoalkanes are capable of entering into 1,3-dipolar cycloaddition reactions. The dipolarophile activity of the nitrile group in these compounds exceeds the activity of the majority of aliphatic nitriles owing to the presence in their composition of the electron-accepting nitro-groups.

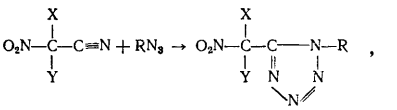
Fluorodinitro-, and difluoronitro-acetonitriles readily combine with NaN_3, forming the corresponding tetrazole derivatives (LVII):[130,131]



(LVII), X = F, NO_2.

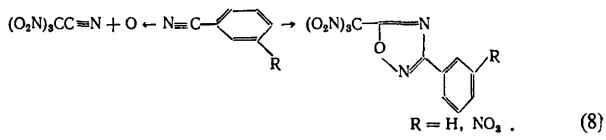
Sodium azide adds also to the salts of α-nitrocyanoalkanes, but the reaction requires much more severe conditions.[132]

The reactions of α-nitrocyanoalkanes with organic azides lead as a rule to the formation of 1,5-disubstituted tetrazole derivatives. The reaction conditions depend on the steric structure of the azide. Whereas methyl azide adds to fluoridinitro- and difluoronitro-acetonitrile even at room temperature,[130] the cycloaddition of the sterically more hindered n-hexyl and trimethylsilyl azides occurs only after heating for many hours at 60–70 °C[131] [Eqn. (7)]:



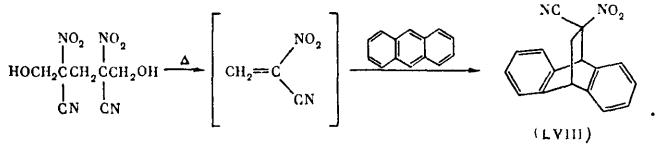
X = Y = F; R = CH_3;
X = NO_2, Y = F; R = CH_3, n-C_6H_{13}, Si $(CH_3)_3$;
X = Y = NO_2; R = Si $(CH_3)_3$. (7)

The reaction of trinitroacetonitrile with aromatic nitrile oxides, leading to the trinitromethyl derivatives of 1,2,4-oxadiazole in high yields[133] [Eqn. (8)], takes place under mild conditions:



(8)

α-Nitrocyanoalkenes can enter into the Diels–Alder reaction. 1-Nitro-1-cyanoethylene, generated *in situ* from the dinitrile of 2,4-di(hydroxymethyl)-2,4-dinitroglutaric acid, combines with anthracene to form the adduct (LVIII):[61]



(LVIII)

IV. Applications of α-nitronitriles

Many α-nitronitriles whose functional groups are linked to an sp^2-hybridised carbon atom exhibit biological activity. Thus 2-(nitrocyanomethylene)-1,3-dithiacyclobutane exhibits a fungicidal activity.[1] The arylhydrazones of cyanonitroformaldehyde possess insecticidal and fungicidal activities.[2]

The bis-2,2-dichlorodiethylammonium salt of 2,4-dinitro-3-phenylglutaronitrile exhibits an antitumour activity[32] and a number of nitronitrile salts are inhibitors of the thermooxidative ageing of polymers.[5]

The potassium, sodium, and barium salts of dinitroacetonitrile have been recommended as regulators of the rate of combustion of rocket fuels.[6,7]

α-Dinitrocyanoacetates have been proposed as additives to explosive and combustible mixtures, as initiators of chain polymerisation reactions, and as reagents for the determination of OH and NH_2 groups.[4]

Epoxy-αα-dinitrocyanoalkanes have been patented at monomers for the synthesis of high-energy polymeric binders.[8] Trinitro- and fluorodinitro-acetonitriles can be used as intermediates for the preparation of mixtures of trinitromethyl- and fluorodinitromethyltetrazoles—components of solid rocket fuels.[11,12]

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