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α-Cyanoacetylenes

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The problems of the synthesis, physical properties, and reactivities of α-acetylene nitriles are discussed. The bibliography includes 200 references.

CONTENTS

I.	Introduction	374
II.	Methods of preparation of α-cyanoacetylenes	374
III.	Physical properties	375
IV.	Reactivities	377

I. INTRODUCTION

α-Cyanoacetylenes are nowadays of considerable interest not only because of the wide variety of their chemical properties and synthetic possibilities, but also because of their ability to give rise to ultrahigh flame temperatures on combustion in oxygen or ozone [1]. Furthermore, cyanoacetylene has been detected in cosmic space [2-6] and it has been suggested that it was involved in the prebiological synthesis of important nitrogen compounds [7,8] (purines and pyrimidines).

However, no reviews have been published hitherto on the physical and chemical properties of these interesting compounds. This paper is the first attempt at a consideration and a systematic account of the available literature data on this problem.

II. METHODS OF PREPARATION OF α-CYANOACETYLENES

α-Cyanoacetylenes were first detected in 1909 by Moureu, who also proposed a method for the synthesis of cyanoacetylene (CA), dicyanoacetylene (DAC), dicyanodiacetylene (DCDA), and other α-cyanoacetylenes [9-11]:

$$RC{\equiv}C{-}COOH \xrightarrow[H_2SO_4]{CH_3OH} RC{\equiv}C{-}COOCH_3 \xrightarrow{NH_4OH} \rightarrow RC{\equiv}C{-}CONH_2 \xrightarrow[-H_2O]{P_2O_5} RC{\equiv}C{-}C{\equiv}N \quad .$$

Since then, this method has been used fairly frequently in laboratory practice for the synthesis of small amounts of CA, DCA, and other substituted α-cyanoacetylenes [9-15]. Later many investigators [16-26] attempted to modify Moureu's method without altering its essential features. Thus Blomquist and Winslow [17] synthesised DCA in the following way:

$$HOOC{-}CH(Br)CH(Br)COOH \xrightarrow{KOH} HOOC{-}C{\equiv}C{-}COOH \rightarrow \xrightarrow[H_2SO_4]{CH_3OH} H_3COOC{-}C{\equiv}C{-}COOCH_3 \xrightarrow{NH_4OH} \rightarrow H_2NOC{-}C{\equiv}C{-}CONH_2 \xrightarrow{P_2O_5} N{\equiv}C{-}C{\equiv}C{-}C{\equiv}N \quad .$$

At 215°C and 2 mmHg, the diamide is dehydrated in 15 min, the yield of DCA amounting to 37%. Cookson et al. [22] succeeded in raising the yield of DCA to 40% by lowering the dehydration temperature of the diamide to 200°C. CA can also by synthesised under laboratory conditions by dehydrating the oxime of propargyl aldehyde with acetic anhydride [27].

The only method for the synthesis of DCDA consists in the treatment of the copper(I) derivative of propiolonitrile with aqueous potassium hexacyanoferrate(III).[11] Brockman [28] investigated the reaction in detail, but a high yield of DCDA was not achieved:

$$HC{\equiv}C{-}C{\equiv}N \xrightarrow[NH_4OH]{CuCl} CuC{\equiv}C{-}C{\equiv}N \xrightarrow[36\%]{K_3Fe(CN)_6;5^\circ;C_6H_6} N{\equiv}C{-}(C{\equiv}C)_2{-}C{\equiv}N \quad .$$

Other investigators [1,19,21] were also unable to make significant improvements to the method of synthesis of DCDA.

In the 1960s, various investigators [29-46] began to develop vigorously fundamentally new, in the main high-temperature methods for the synthesis of CA and DCA. Thus the possibility of synthesising CA from acetylene [29,30] or acetonitrile [31] on contact in the gas phase with hydrogen cyanide or dicyanogen at temperatures in the range 770 to 975°C has been demonstrated in a number of United States patents. Acrylonitrile and other impurities are formed together with CA, the yield of the latter increasing as the temperature is raised, while the yield of acrylonitrile falls. In order to determine whether or not acrylonitrile is an intermediate in the formation of CA, separate experiments were undertaken on the pyrolysis of acrylonitrile at 770° and 935°C. It was found that the yield of CA should be much lower if acrylonitrile were an intermediate. A simple radical reaction mechanism was therefore proposed:

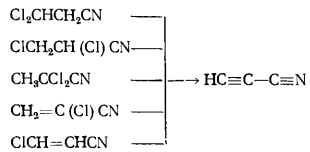
$$\left.\begin{matrix} HC{\equiv}\dot{C} + HC{\equiv}N \\ N{\equiv}\dot{C} + HC{\equiv}CH \end{matrix}\right\rbrace \rightarrow HC{\equiv}C{-}C{\equiv}N + \dot{H} \quad .$$

It is suggested that the reaction is initiated by the acetonitrile present in an amount of 0.04% in the initial hydrogen cyanide:

$$CH_3CN \rightarrow \dot{H} + CH_2CN; \quad \dot{H} + HC{\equiv}CH \rightarrow HC{\equiv}\dot{C} + H_2 \quad .$$

When a mixture of hydrogen cyanide and acetonitrile vapours with an inert gas is passed through a quartz tube at 700-900°C with a contact time of 5-0.01 s, malonodinitrile, acrylonitrile, and dicyanogen are formed preferentially. At 900-1100°C, CA is formed in 18% yield, but the main product is dicyanogen [31]. Comp [32] obtained CA in yields up to 95% by the non-catalytic reaction of acetylene with dicyanogen at 800-900°C. A satisfactory yield of CA is obtained when acetylene is highly diluted with dicyanogen and an inert gas. Substituted acetylenes react with dicyanogen under analogous conditions. Dehydrogenation of propionitrile and β-phenylpropionitrile over metal oxides at 600-800°C leads to CA and β-phenylpropiolonitrile, but the yield of the desired products has not been stated [33]. The formation of CA was

also noted when acetylene was added to active nitrogen, the yield of hydrogen cyanide, dicyanogen, and CA passing through a maximum as the supply of acetylene to the reaction zone was increased [34]. Morita and Hashimoto [35,36] recently synthesised CA by the pyrolytic cleavage of halogen-containing nitriles in a quartz tube in a stream of nitrogen, at 1000°C and a pressure of approximately 25 mmHg in the system. The yield of CA was 68–73%, depending on the initial nitrile:

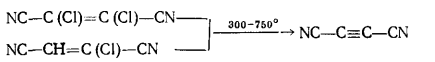


A more detailed study of the process showed that, apart from CA, monochloroacrylonitriles and acrylonitrile are formed as impurities [37]. The addition of carbon tetrachloride accelerates the pyrolysis of dichloropropionitriles and suppresses the formation of acrylonitrile. The addition of even small amounts of β-chloropropionitrile, which is converted under these conditions into acrylonitrile, leads to a sharp decrease of the yield of CA and increases the content of monochloroacrylonitriles. According to the authors [37], these data indicate that the dehydrochlorination processes under consideration have a radical mechanism. When ααβ-trichloropropionitrile, αβ-dichloroacrylonitrile, and ββ′-dichloroacrylonitrile are pyrolysed, chlorocyanoacetylene (CCA) is formed in a high yield [37].

The gas-phase interaction of acrylonitrile and chlorine at 500–1200°C and a reduced pressure (10–100 mmHg) leads to CA without an admixture of side products [38,39].

Alkyl-substituted homologues of CA may be obtained in high yields from the corresponding lithium acetylides and chlorocyanogen [40] and aryl-substituted derivatives (yield 38%) may be synthesised from phenylethynyl bromide and copper cyanide [47] or from sodium phenylacetylide and dicyanogen [48].†

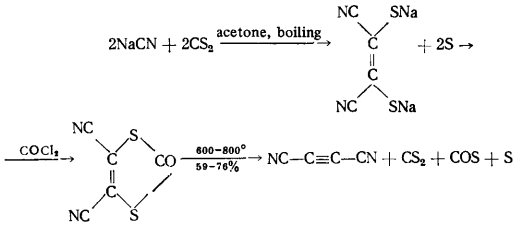
A method for the synthesis of DCA by the pyrolysis of the dichloro-derivative or its mixture with the monochloro-derivative of but-2-ene-1,4-dicarbonitrile at 300–750°C has been developed in the USA [41]:



The reaction is carried out in a pyrolysis reactor using an inert carrier gas, in particular helium (0.02–20% of the volume of the mixture). However, the pyrolysis products interact with one another so readily that the problem of their rapid separation arises even at a reduced temperature.

Zavitzanos [42,43] proposed a method for the synthesis of DCA directly from carbon and nitrogen. The latter is passed over a graphite cylinder heated to 2100–2700°C. Apart from DCA, the reaction products contain dicyanogen and DCDA. It was found that the rate of formation of DCA increases rapidly as the reaction temperature is raised from 2400 to 2700°C.

Ciganek and coworkers [40,45] obtained DCA by the pyrolysis of 4,5-dicyano-1,3-dithiol-2-one vapour:



DCA can be obtained on a preparative scale from tetracyanoethylene (yield up to 72%). [45]

DCA is also formed in the retrodiene cleavage of dimethyl 5,6-dicyano-oxabicyclo[2,2,2]hepta-2,5-dienedicarboxylate. [46] Other attempts at the synthesis of DCA, for example by the reaction of bromocyanogen with LiC≡CLi, were unsuccesful [49].

III. PHYSICAL PROPERTIES

CA is a mobile, volatile, and readily inflammable liquid boiling at 42.5°C, easily converted on cooling into crystals melting at 5°C, which are quite stable on storage at a low temperature (−70°C). [37] There is an infinite parallel arrangement of linear chains in CA crystals owing to the formation of hydrogen bonds or charge-transfer complexes [50]. The CA vapour is highly irritant to mucous membranes and has a lachrymatory effect. On storage in air, CA rapidly darkens and on combustion in oxygen gives rise to a bright colourless flame (like acetylene). CA is sparingly soluble in water and readily soluble in alcohol and acetone. Its solutions become rapidly coloured brown.

DCA is a colourless transparent liquid boiling at 76.5°C, which crystallises [45], forming crystals melting at 20.5°C. The study of the crystal structure of DCA showed that it forms monoclinic crystals at 5°C, belonging to the space group C_{2h}^{5}–$P2_1/a$. Precision [X-ray] photography established that the unit cell contains two molecules and has the following dimensions: $a = 8.93$, $b = 6.04$, $c = 3.86$ Å, and $\beta = 99°20'$. [51]

Under the usual conditoins, DCA is a toxic and volatile substance. It is potentially explosive in the pure state and in concentrated solutions, while its dilute solutions in inert solvents are stable. Pure DCA rapidly darkens in air, because it is sensitive to the presence of oxygen, but can be stored almost indefinitely in dry ice.

DCDA sublimes in the form of fine white crystals, melting at 64.5°C, which are extremely volatile and unstable [19]. However, DCDA specimens may be stored *in vacuo* or in nitrogen at room temperature. After storage for three months, an appreciable amount of DCDA was found to have sublimed from the initial specimen [19]. Even at 100°C, only partial decomposition of DCDA is observed. DCDA solutions in CS_2, CCl_4, $CHCl_3$, furan, and hexane slowly acquire an amber colour, but in cyclohexane these changes are rapid. The solution in toluene becomes slowly coloured blue, while in benzene the same colour is acquired instantaneously.

DCDA has an irritant smell and is a powerful lachrymatory agent. The physical properties of members of the series $N{\equiv}C{-}(C{\equiv}C)_n{-}C{\equiv}N$, where $n = 0$–2, agree fairly well with the general relations governing the variation of the boiling point, melting point, and density with increasing molecular weight in a homologous series. The temperature variation of DCA and DCDA vapour pressures is significantly linear for both solid and liquid states.

†A method for the introduction of the cyano-group into bromo-substituted acetylenic alcohols by their reaction with copper cyanide was reported recently [200].

DCA and DCDA are of interest for the attainment of ultrahigh temperatures, since, on combustion in a suitable amount of oxygen, they form mainly endothermic products—CO and N_2. The possibility of achieving very high combustion temperatures, actually higher than in the combustion of dicyanogen, is associated with this fact[52]. Kirshenbaum and Grosse[53] found that, when DCA is burnt in oxygen, a temperature of approximately 5260 K is developed at 1 atm and 5750 K at 40 atm. It was expected that the replacement of molecular oxygen by ozone would give a temperature of 5520 K at 1 atm. Such temperatures were indeed subsequently attained[54]. (The temperature of the DCDA flame was not investigated owing to the difficulty of obtaining a sufficient amount of the latter.)

In connection with the foregoing, the heats of formation of cyanoacetylenes, measured for the first time by Moureu[11], are of interest. Subsequently Armstrong and Marantz[55] determined more accurately the heat of combustion of DCA and reported the corrected value[56] ΔH°_{298}(comb.) = −495.5 ± 0.2 kcal mole^{-1} for the liquid substance and the heats of formation ΔH°_{298}(form.) of liquid and gaseous DCA calculated from it—119.6 and 126.5 kcal mole^{-1} respectively.

There have been numerous studies on other physicochemical properties of α-cyanoacetylenes. The infrared spectra of CA[21,57-66], DCA, and DCDA have been investigated and discussed in detail in a collected volume[67]. The infrared spectra of CA and its deuterated derivative have been investigated in the gaseous and crystalline states (at 77 K) and measurements have been made of the integral intensities of the following absorption bands assigned on the basis of the calculation of the normal vibration frequencies: 3327 (2607) cm^{-1} for the CH(CD) stretching vibrations, 2272 (2251) cm^{-1} for C≡C, 2077 (1956) cm^{-1} for C–N, and 863 cm^{-1} for C–C (in the gase phase)[68]. Analysis of the spectra led to the conclusion that molecules of this type have a linear structure. Using the observed vibration frequencies and applying the system of valence force coordinates, Miller and Hannan[59] calculated the force constants of the C≡N (16×10^5–17.5×10^5 dyn cm^{-1}) and C–C (6.0×10^5–7.5×10^5 dyn cm^{-1}) bonds in DCA.

The infrared spectra of DCDA[21] were measured in the range 35–4000 cm^{-1} in the vapour phase and in solution in carbon tetrachloride and carbon disulphide, while the Raman spectra were obtained for solutions in carbon tetrachloride, hexane, furan, and toluene. The absorption bands, assigned to the C≡N [2235 cm^{-1} (Raman), 2266 cm^{-1} (i.r.)] and C≡C [2183 cm^{-1} (Raman), 2057 cm^{-1} (i.r.)] stretching vibrations, do not interact with one another, in contrast to the two C–C vibrations with Σg^+ symmetry. The C–C stretching vibrations give rise to a smiple intense band in the infrared spectrum in the region of 717 cm^{-1}.

The thermodynamic functions of DCDA have been calculated[64] for the range 200–2000 K in terms of the rigid rotator approximation. The bond polarisabilities and the average moleculer polarisability in the ground electronic state were determined using a potential δ-function. Derivatives of molecular polarisability have been calculated for fully symmetrical vibrations. The force constants of the C≡N, C≡C, and C–C bond vibrations have been obtained: 16.823×10^5, 15.614×10^5, and 6.753×10^5 dyn cm^{-1} for the central bond, and 6.357×10^5 dyn cm^{-1} for the bonds adjoining C≡N. The force constants have also been obtained from the overall valence-force field[65]. Moffat and Knowles[66] described a method for the calculation of various thermodynamic characteristics of dicyanogen, DCA, and DCDA: entropy, heat capacity, internal and free energy, and enthalpy (the last three quantities are determined from the dissociation energy of the molecule calculated from the heats of combustion and formation), etc.

There is extremely limited information about the rotational spectra of α-cyanoacetylenes. Westenberg and Wilson[69] analysed the purely rotational spectra of several CA and deuterated CA isotopic series in the microwave region and calculated the H–C (1.057 Å), C≡C (1.203 Å), C–C (1.382 Å), and C≡N (1.157 Å) bond lengths.

The dielectric constants of CA were determined[70] in the range 8850–9500 MHz in the gas phase at 42°C, the molecular polarisation remaining constant at 278 cm^{-3}. The molecular polarisation of CA at 9400 MHz is the same as at low frequencies. Measurements have been made of the $I = 1 \leftarrow 0$ and $I = 2 \leftarrow 1$ rotational transitions in the ground vibrational state[71]. Some of the lines in the rotational spectra of CA in the microwave range are quoted for the first time in the "Strelets V2" source book[3-5,72,73].

Information about the difference between the energies of the ground and excited electronic states was obtained from the electronic spectra of α-cyanoacetylenes. The spectrum of gaseous CA has many closely spaced weak bands in the range 230–260 nm.[74] The bond lengths and angles in the CA molecule have been determined from rotational spectroscopic data. The same workers[75] investigated the diffuse absorption band of CA in the gas phase in the range 200–230 nm, but its vibrational structure could not be analysed. In other investigations[76,77], the CA spectrum was obtained with a high resolution and the bands were analysed. The ionisation potential of CA has been calculated as 11.6 eV from the observed Rydberg series. Subsequently Dibeler et al.[78] measured mass spectrometrically the ionisation potentials of CA, DCA, and DCDA, which are respectively 11.6, 11.4, and 11.4 eV.

Connors et al.[79] investigated the absorption spectrum of gaseous CA in the range 105–200 nm. The first transition (61 000–66 000 cm^{-1}), having two main bands at 62 000 and 64 500 cm^{-1}, was assigned to the $\nu_2'(\sigma^+)$ or $\nu_3'(\sigma^+)$ excitation and the transition at 69 000 cm^{-1} was assigned to the internal valence shell. The peak at 71 100 cm^{-1}, separated from the first band by 2100 cm^{-1}, can be regarded as due to the $\nu_2'(\sigma^+)$ or $\nu_3'(\sigma^+)$ active vibrations.

The spectra of DCA[80] in iso-octane solution and in the gas phase showed that the DCA molecule remains planar in the excited state and that its $D_{\infty h}$ nuclear configuration is preserved. DCA exhibits an intense absorption[79] in the range 150–165 nm, giving rise to three peaks separated by 2150 cm^{-1}, which may be assigned to the symmetrical $\nu_1'(\sigma_g^+)$ or $\nu_2'(\sigma_g^+)$ vibration. The Rydberg series (8100 to 92 440 cm^{-1}) has also been isolated.

The DCDA spectrum[79] in the range 105–200 nm has a more complex structure. The very intense transition in the range 175–190 nm was assigned to the $\nu_1'(\sigma_g^+)$ or $\nu_2'(\sigma_g^+)$ symmetrical vibration; in addition, three Rydberg series, giving a first ionisation potential of approximately 11.2 eV (90 300 cm^{-1}), were observed. A continuous absorption spectrum of gaseous DCDA[81] was also obtained in the range 230–310 nm. The fundamental characteristics of the transition suggest that the molecule is linear in both ground and excited states.

Calculations of the relative intensities in the photoelectronic spectra of CA and DCA have been published[82] and the magnetic rotation of DCA has been reported[83,84].

Analysis of the normal coordinates of CA[85,86] made it possible to determine the distribution of potential energy with respect to bonds and valence angle vibrations. Since

the application of the usual symmetry coordinates to DCA [87] leads to unduly high force constants, another set of symmetry coordinates has been proposed in which the -C-C≡C-C- chain is regarded as a system of three strongly interacting oscillators [88]. The normal DCDA coordinates have also been analysed [89] and the symmetry coordinates for the σ^+_g and σ^+_u symmetry types of the $L_\infty\omega$ group have been set up.

IV. REACTIVITIES

α-Cyanoacetylenes are capable of entering into various chemical reactions involving both the C≡C and the C≡N bond. They are particularly reactive in reactions with nucleophiles owing to the conjugation of the triple bond with the electron-accepting cyano-group.

1. Hydration

The problem of orientation in the reactions involving addition to the conjugated triple bonds is naturally of considerable interest. It has been shown, for example, that diacetylene can combine with one or two water molecules, forming acetylacetylene or diacetyl respectively [90]. On the other hand, when CA is treated with 98% sulphuric acid at 20°C and then with ice, it does not undergo any changes, while chlorocyanoacetylene (CCA) gives a 75% yield of β-chloropropiolamide under these conditions [91]. Treatment of CA with sulphuric acid under controlled conditions (at 35–40°C) gave a 20% yield of propiolamide [92].

α-Aminocyanoacetylenes are readily hydrated in an aqueous solution of THF in the presence of hydrochloric acid, cyanoacetamides (I) being isolated in almost quantitative yield [93]:

$$R_2NC{\equiv}C{-}C{\equiv}N \rightarrow \underset{(I)}{R_2NCOCH_2C{\equiv}N}$$

R=Me, or Et .

CA behaves quite differently in aqueous THF in the presence of the hydrated form of Dowex-1 anion-exchange resin. Sasaki and Shoji [94] showed that di-(β-cyanovinyl) ether (II) is then formed in a yield of up to 60%:

$$HC{\equiv}C{-}C{\equiv}N \xrightarrow[\text{Dowex-1}]{THF,\ H_2O} \underset{(II)}{N{\equiv}C{-}CH{=}CHOCH{=}CHC{\equiv}N} \quad .$$

Thus, depending on the reaction conditions, water can add to α-acetylenes in different ways.

CA and CCA can enter into the Ritter reaction forming the corresponding propiolamides (III) in a yield of 10 to 80%: [91,95]

$$HC{\equiv}C{-}C{\equiv}N \xrightarrow{R^+} HC{\equiv}C{-}\overset{+}{C}{=}NR \xrightarrow{H_2O} \underset{(III)}{HC{\equiv}C{-}CONHR} \quad ;$$

R= t-C_4H_9, $(C_6H_5)_2C$—COOH, $(CH_3)_2C$—CH_2Cl, $C_{11}H_{17}$, $C_{15}H_{15}$, or C_6H_{11}.

The extension of this reaction to more complex systems makes it possible to obtain heterocyclic compounds containing the ethynyl group. Thus the reaction of 2-methylpentane-2,4-diol with CA or CCA in sulphuric acid leads to 2-ethynyl- or 2-chloroethynyl-4,4,6-trimethyl-5,6-dihydro-1,3-oxazines. [96] Under these conditions, DCA and DCDA give rise to resins, which are difficult to treat.

2. The Addition of Alcohols and Phenols

The base-catalysed addition of methanol and ethanol to CA proceeds very readily already at 10°C, two moles of the alcohol being added with formation of ββ-dialkyoxypropionitrile (V) in 50–78% yield [18]. In the presence of KCN or potassium carbonate, it is possible to obtain a mixture of β-ethoxyacrylonitrile (IV) and diethoxypropionitrile (V):

$$HC{\equiv}C{-}C{\equiv}N \xrightarrow{ROH} \underset{(IV)}{ROCH{=}CHC{\equiv}N} \rightarrow \underset{(V)}{(RO)_2CHCH_2C{\equiv}N} \quad .$$

CA reacts similarly wtih glycols, 2-cyanomethyl-1,3-dioxolan and 2-cyanomethyl-1,3-dioxan being obtained from ethylene glycol and 1,3-propylene glycol respectively. The yields of the products were not indicated [18].

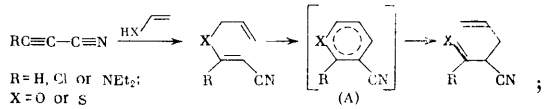
The addition of lower alcohols to CCA proceeds without catalyst at room temperature with formation of 3-alkoxy-3-chloroacrylonitrile: the reaction with allyl alcohol gave the Claisen rearrangement product (VI): [93]

$$ClC{\equiv}C{-}CN \xrightarrow{CH_2{=}CHCH_2OH} NC{-}C{\equiv}COCH_2CH{=}CH_2 \rightarrow$$

$$\xrightarrow{CH_2{=}CHCH_2OH} NC{-}CH{=}C\begin{matrix}OCH_2CH{=}CH_2\\OCH_2CH{=}CH_2\end{matrix} \rightarrow \underset{\underset{CH_2CH=CH_2}{|}}{NC{-}CHC(O)CH_2CH{=}CH_2} \quad .$$

(VI)

The reaction of cyanodiethylaminoacetylene with allyl alcohol in the presence of BF_3 etherate at room temperature gives rise to 2-cyano-*NN*-diethylpent-4-enamide. Sasaki et al. [93] proposed in such cases the mechanism of the Claisen rearrangement involving an intermediate with a quasi-cyclic structure (A):



CCA reacts with lower alcohols in the presence of sodium alkoxides, forming ββ-dialkoxyacrylonitriles (VII): [97]

$$ClC{\equiv}C{-}C{\equiv}N \xrightarrow[ROH]{NaOR} \underset{(VII)}{(RO)_2C{=}CHC{\equiv}N} \quad .$$

As shown by Moureu [11], DCA also interacts very readily with alcohols in the presence of alkaline agents, the reactivity of the alcohol decreasing with increasing length of its alkyl group. Winterfeldt et al. [98] investigated the stereochemistry of this reaction and showed that it leads to a mixture of *cis*- and *trans*-products (VIII) (yield 50 to 52%) in the proportions 4 : 1:

$$NC{-}C{\equiv}C{-}CN \xrightarrow{ROH} \underset{(VIII)}{NC{-}CH{=}C(OR)CN} \quad ;$$

R=Me, iso-Pr, or t-Bu

When piperidine is used at 0°C, the reaction proceeds stereospecifically (*cis*-adduct, 59% yield), while at 20°C a 9 : 1 mixture of the *cis*- and *trans*-adducts is obtained (yield 52%).

The addition of phenol to CA in the presence of sodium phenoxide proceeds sluggishly and leads to a mixture of monoadducts (IX) and diadducts (X), from which only the latter could be isolated [99]:

$$HC{\equiv}C{-}C{\equiv}N \xrightarrow{PhOH} \underset{(IX)}{PhOCH{=}CHC{\equiv}N} \rightarrow \underset{(X)}{(PhO)_2CHCH_2C{\equiv}N} \quad .$$

Having applied this reaction to halogenophenols, Miller [20] developed a method for the synthesis of halogeno-β-phenoxyacrylonitriles (IX) (in a yield of approximately 70%), which have found applications as agents effective against apple scab and as soil fungicides, insecticides, and herbicides.

3. The Addition of Thiols

Sasaki et al.[93] showed that the addition of propene-2-thiol to CA in the absence of a catalyst proceeds very slowly, while in the presence of sodium methoxide the reaction is accelerated and leads to a mixture of *cis*- and *trans*-β-allylthioacrylonitriles (XI) in 46% yield:

$$HC{\equiv}C{-}C{\equiv}N + HSCH_2CH{=}CH_2 \rightarrow \underset{(XI)}{H_2C{=}CHCH_2SCH{=}CHCN}$$

Like allyl alcohol, propene-3-thiol reacts with CCA and cyanodiethylaminoacetylene, forming the products of the Claisen rearrangement, for example (XII):

$$ClC{\equiv}C{-}C{\equiv}N + HSCH_2CH{=}CH_2 \rightarrow NC{-}CH{=}C(SCH_2CH{=}CH_2)_2 \rightarrow$$

$$\rightarrow NC{-}\underset{\underset{CH_2CH=CH_2}{|}}{\overset{S}{\overset{\|}{C}}H}SCH_2CH{=}CH_2 \quad \underset{(XII)}{}$$

Welle and Brandsma[40] investigated the addition of propyne-3-thiol to alkyl-α-cyanoacetylenes and found that in hexamethylphosphoramide the reaction is exothermic and proceeds without catalyst, terminating in essence at the stage of the product (XIII), which has the *cis*-configuration when R = H:

$$RC{\equiv}C{-}C{\equiv}N + HC{\equiv}C{-}CH_2SH \xrightarrow{20^\circ} \underset{(XIII)}{HC{\equiv}C{-}CH_2SC(R){=}CHC{=}N} \rightarrow \underset{(XIV)}{(HC{\equiv}C{-}CH_2S)_2C(R)CH_2C{\equiv}N};$$

R = H, or Alk .

Thiophenol readily reacts with CA in the presence of sodium methoxide on cooling, the yield of β-phenylthiolacrylonitrile (XV) reaching 75%. ββ-Di(phenylthio)-propionitrile (XVI) was obtained together with the adduct (XV) under analogous conditions in the presence of an excess of thiophenol[99]:

$$HC{\equiv}C{-}C{\equiv}N \xrightarrow[MeONa]{PhSH} \underset{(XV)}{PhSCH{=}CHC{\equiv}N} \rightarrow \underset{(XVI)}{(PhS)_2CHCH_2C{\equiv}N} \quad .$$

CA reacts just as readily with *p*-methylbenzenethiol (at a reduced temperature in methanol solution in the presence of sodium *p*-methylbenzenethiolate), forming exclusively the *cis*-adduct in 100% yield[100,101]. Truce and Wolf[102] discovered a new reaction involving the addition of toluene-*p*-sulphonyl iodide to acetylenes, which proceeds stereoselectively and leads to the *trans*-adduct (XVII):

$$NC{-}C{\equiv}CH + n\text{-}CH_3C_6H_4SO_2I \rightarrow \underset{(XVII)}{\overset{NC}{\underset{I}{}}\!\!>C{=}C<\!\!\overset{SO_2C_6H_4CH_3\text{-}n}{\underset{H}{}}}$$

The reaction begins even when the components are mixed in the cold and is strongly accelerated by ultraviolet light.

4. The Addition of Amines, Hydrazines, and Their Derivatives

α-Cyanoacetylenes readily react with a wide variety of amines. Murahashi et al[99] obtained β-piperidinoacrylonitrile by the exothermic reaction of CA with piperidine in benzene. According to the same workers[99], the analogous reaction with aniline leads to the monoadduct (XVIII) and the diadduct (XIX):

$$HC{\equiv}C{-}C{\equiv}N + PhNH_2 \rightarrow \underset{(XVIII)}{PhNHCH{=}CHC{\equiv}N} \rightarrow \underset{(XIX)}{(PhNH)_2CHCH_2CN} \quad .$$

In a later study by Sasaki et al.[103], the monoadduct (XVIII) was not obtained and the yield of (XIX) was 65%. It was shown[103] that the 1 : 1 products of the addition of cyclic secondary amines (morpholine, pyrrolidine, piperidine, aziridine, and imidazole) to CA have the *trans*-configuration. The reaction of CA with other amines proceeds similarly[104-107], the monoadducts, with both the *cis*- and *trans*-configurations, having been isolated. CA reacts with aqueous 28% ammonia solution, giving rise to β-aminoacrylonitrile.[99] The addition of ammonia and amines to DCA was first reported by Moureu and Bongrand[11], who showed that ammonia and primary and secondary amines interact vigorously with 2-cyano-1-phenylacetylene and DCA with formation of β-aminoacrylonitriles, which readily hydrolyse to β-ketonitriles (XXI):

$$RC{\equiv}C{-}CN \xrightarrow{NHR^1R^2} \underset{(XX)}{RC(NR^1R^2){=}CHCN} \xrightarrow{H_2O} \underset{(XXI)}{RCOCH_2CN} \quad ;$$

R = Ph, or CN .

Since compounds (XX) have not been characterised, Weis[108] repeated this investigation and found that 1-arylamino-1,2-dicyanoethylenes are formed quantitatively when DCA reacts with primary aromatic amines, while in the reaction with aliphatic amines the reaction mixture chars.

Sasaki et al.[109] investigated the possibility of synthesising ynamines by the reaction of CCA with secondary amines. It is known[67] that α-halogenoacetylenes enter into nucleophilic substitution reactions with trialkylamines and (mainly) into addition reactions involving the C≡C bond with secondary amines. The presence of the cyano-group in CCA suggests an increase in the reactivity of the chlorine in nucleophilic substitutions, so that treatment of CCA in ether with sodamide makes it possible to obtain malonodinitrile (XXII) in a satisfactory yield[109]:

$$NC{-}C{\equiv}CCl + NaNH_2 \rightarrow \underset{(B)}{[H_2NC{\equiv}C{-}CN]} \rightarrow \underset{(XXII)}{NC{-}CH_2CN} \quad .$$

It has been suggested that the amine (B) is an intermediate in the reaction and is converted into the nitrile (XXII) as a result of prototropic isomerisation. Secondary amines (dimethylamine, diethylamine, piperidine, morpholine, and pyrrolidine) react with CCA to give the corresponding cyanoynamines (XXIII):

$$NC{-}C{\equiv}CCl + HNR_2 \rightarrow \underset{(XXIII)}{NC{-}C{\equiv}CNR_2} \quad .$$

A higher yield of compound (XXIII) is achieved when the reaction is carried out at −50°C with a twofold excess of the amines. The ynamines (XXIII) readily undergo acid hydrolysis, being converted into cyanoacetamides in almost quantitative yield. They also readily react with amines, alcohols, and other compounds[109].

The interaction of CCA with allylamine[93] proceeds in a more complex manner—with formation of compound (XXIV):

$$NC{-}C{\equiv}CCl \xrightarrow{H_2NCH_2CH=CH_2} \underset{(XXIV)}{\begin{matrix} NC{-}CH{=}C\!<\!\!\begin{matrix}NHCH_2CH{=}CH_2\\ NCH_2CH{=}CH_2\end{matrix} \\ NC{-}CH{=}C\!<\!\!NHCH_2CH{=}CH_2 \end{matrix}} \quad .$$

Depending on the conditions in the reaction between CCA and diallylamine, compound (XXV) or (XXVI) is obtained[93,109]:

$$\underset{(XXV)}{NC{-}C{\equiv}CN(CH_2CH{=}CH_2)_2}; \quad \underset{(XXVI)}{NC{-}CH{=}C[N(CH_2CH{=}CH_2)_2]_2} \quad .$$

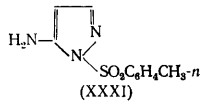
Hydrazines and semicarbazides are stronger bases and nucleophiles than amines, and can therefore react with CA

via both the triple bond and via the nitrile group or can simultaneously attack both reaction centres. For example, hydrazine hydrate in ethereal solution reacts with CA to form 1,2-di-(β-cyanovinyl)hydrazine (XXVII), while thiosemicarbazide in methanol at 20°C gives rise to β-thiosemicarbazidoacrylonitrile (XXIX)[99]:

$$NC{-}CH{=}CHNHNHCH{=}CHCN;\quad NC{-}CH{=}CHNHNH_2;$$
(XXVII) (XXVIII)
$$NC{-}CH{=}CHNHNHCSNH_2;\quad PhNHNHCH{=}CHCN$$
(XXIX) (XXX)

Under other conditions, CA reacts with hydrazine hydrate to give a 3 : 1 mixture of compound (XXVII) and β-cyanovinylhydrazine (XXVIII). CA and phenylhydrazine, taken in equimolar proportions in ether at −40°C, react to form a 1 : 1 adduct having the *trans*-configuration (XXX).[99]

The attempt to cyclise compounds (XXVIII) and (XXX) by heating in protic or aprotic solvents were unsuccessful[92]. However, CA reacts with tosylhydrazine to form 5-amino-1-*p*-tosylpyrazole (XXXI) in approximately 50% yield and only 23% of the non-cyclic product[97]:

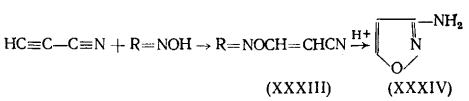

(XXXI)

5-Amino-1-arenesulphonylpyrazoles, which are used as analgesics, diuretics, and chemotherapeutic agents, have been obtained by the same reaction (in benzene at 90°C).[110]

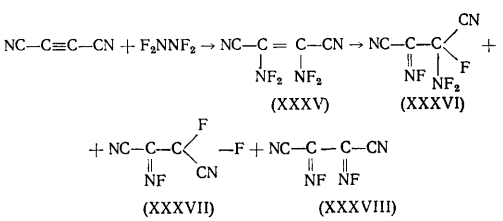
A solution of semicarbazide in methanol reacts with CA via the following mechanism and gives a 99% yield of cyanoacetaldehyde semicarbazone (XXXII):[97]

$$HC{\equiv}C{-}C{\equiv}N + H_2NNHCONH_2 \xrightarrow{MeOH} (MeO)_2CHCH_2CN \rightarrow \underset{(XXXII)}{NC{-}CH_2CH{=}NNHCONH_2}$$

Alkylideneiminoxyacrylonitriles (XXXIII), which readily cyclise to 3-aminoisoxoazole (XXXIV), have been obtained by the reaction of CA with alkanone oximes[111]:


(XXXIII) (XXXIV)

Tetrafluorohydrazine adds to DCA under more severe conditions (140°C, 5 h), which can probably be accounted for by the decrease of the nucleophilic reactivity of hydrazine when fluorine atoms are introduced into its molecule[112]. Bisdifluoroamino-1,2-dicyanoethylene (XXXV) is probably formed initially and then isomerises to the final dinitrile (XXXVI) (yield 33%) and disproportionates to side products of this reaction, namely (XXXVII) (12%) and (XXXVIII) (15):


(XXXV) (XXXVI)

(XXXVII) (XXXVIII)

3-Aminoisoxazole was obtained by the condensation of DCA with *N*-hydroxyurethane[113] and was then converted into 3-sulphanilamidoisoxazole, which exhibits bactericidal activity.

5. Halogenation and Hydrohalogenation

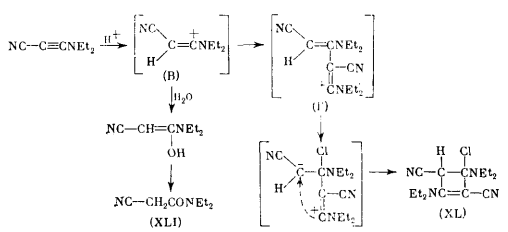
The addition of bromine and iodine to CA in alkaline solutions of KBr and KI proceeds with low yields of trihalogenoacrylonitriles[114]. Like other acetylenes, CA is readily halogenated with a high degree of selectivity at 30–60°C in alcoholic and aqueous alcoholic solutions of copper(II) chloride and bromide, forming αβ-dibromo-αβ-dichloro- and tribromo-derivatives of acrylonitrile[115,116].

Bromocyanoacetylene is halogenated under similar conditions. The halogenation of CA in methanol solutions of a mixture of $CuCl_2$ and $CuBr_2$ leads to the formation of α-bromo-β-chloroacrylonitrile. In aqueous solutions of the corresponding hydrogen halides and copper(I) halides at 30–35°C, CA readily gives rise exclusively to *cis*-β-halogeno-derivatives of acrylonitrile (XXXIX),[117] in agreement with the generally accepted ideas concerning the electron shift in CA:

$$HC{\equiv}C{-}C{\equiv}N \xrightarrow[CuHal]{HHal} \underset{(XXXIX)}{CHHal{=}CHCN}$$

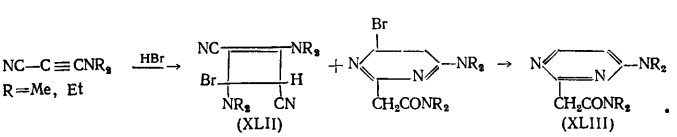
The hydrohalogenation of bromocyanoacetylene and iodocyanoacetylene proceeds under analogous conditions. The addition of HCl to CA in sulphuric acid in the presence of boron trifluoride etherate leads to ββ-dichloropropionitrile[91]. In research designed to synthesise Little's model of a one-dimensional organic superconductor, the products of the addition of HBr and ICN to DCA were used to introduce 1,2-dicyanovinyl groups into azo-, cyanine, and merocyanine dyes[24].

Aminocyanoacetylenes behave quite differently in the presence of hydrogen halides[118,119]. Sasaki[118] established that the reaction of cyano-*NN*-diethylaminoacetylene in solution in methylene chloride at 0–5°C with gaseous hydrogen chloride leads to the cyclobutene (XL) in 85% yield. The mechanism of the formation of this cyclobutene apparently involves the initial protonation of the ynamine with formation of the intermediate (C), which reacts further with the nucleophilic centre of the initial compound and gives rise to the intermediate (D):

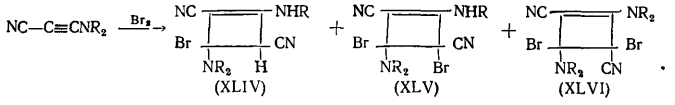

(B) (C) (D)

(XLI) (XL)

The latter is rapidly attacked by the chloride anion with subsequent cyclisation to the cyclobutene (XL). The analogous reaction in the presence of small amounts of water leads exclusively to the cyanoacetamide (XLI). The addition of hydrogen bromide to the initial ynamine at 0°C proceeds in two ways with formation of products (XLII) and (XLIII):


(XLII) (XLIII)

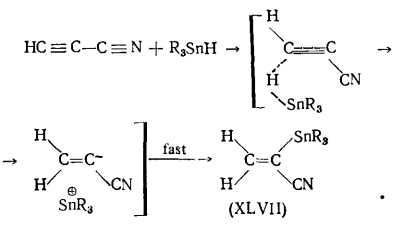
When these ynamines were allowed to react with bromine, cyclobutene derivatives (XLIV)–(XLVI) were again obtained in proportions which depend on the amount of bromine employed[118]:



(XLIV) (XLV) (XLVI)

6. The Reactions of α-Cyanoacetylenes with Metal Compounds

CA reacts exothermically with tin monohydrides via the *trans*-addition mechanism, which has been confirmed by experiments with deuterated transalkylstannanes[120–122]:



(XLVII)

The reaction is of second order overall: in terms of their influence on its rate, the substituents R in tin hydrides can be arranged in the following sequence: pH ≪ Me < Et, iso-Bu[121,123]. Lead hydrides[124] can also react with CA, but in this case a mixture of compounds (XLVIII)–(L) is formed:

$$H_2C{=}C(PbR_3)CN;\quad R_3PbCH{=}CHCN;\quad R_3PbCH{=}CHCN$$

(XLVIII), 50% (XLIX), 45%, *cis*- (L), 5%, *trans*-

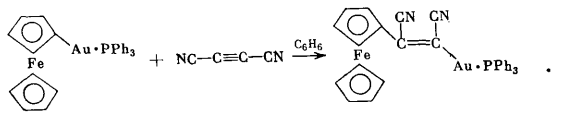
The stereochemistry of this process was not investigated in detail; it was suggested that compounds (XLVIII) and (XLIX) are formed via the *trans*-addition mechanism, while compound (L) is obtained as a result of the rearrangement of compound (XLIX) in the presence of the initial lead hydride[124].

Leusink, Noltes, and coworkers observed the exchange of hydride hydrogen between organic derivatives of tin and lead. When R_3PbOAc and Ph_3SnH are mixed in THF at −80°C and then treated with CA, a 3 : 7 mixture of products (XLVIII) and (XLIX) is formed[125].

Quintard and Pereyre showed[126] that the reaction of DCA with tributylstannane in methanol proceeds with the reduction of the triple bond:

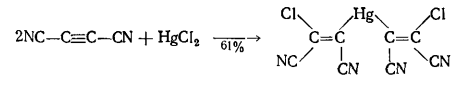
$$NC{-}C{\equiv}C{-}CN \xrightarrow{Bu_3SnH} NC{-}CH{=}C(SnBu_3)CN \xrightarrow{MeOH} \rightarrow NC{-}CH{=}CHCN + Bu_3SnOMe$$

Nesmeyanov and coworkers[127] investigated the reactivity of the complex of ferrocenylgold with triphenylphosphine in relation to tetracyanoethylene and DCA. It was found that DCA is inserted (20°C, 15 min) in the C–Au bond with formation of 1,2-dicyano-1-ferrocenyl-2-(triphenylphosphinegold)ethylene (LI) in 76% yield:



(LI)

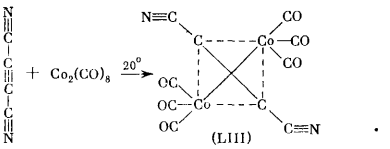
In a saturated aqueous NaCl solution, mercury(II) chloride adds to DCA (5–10°C, 20 min)[108]:



(LII)

It has been shown that in aqueous ethanol the $[Co(CN)_5]^{3-}$ ion forms stable compounds having the composition $K_6[Co_2(CN)_{10}A].2H_2O$ with acetylenes (A) having electron-accepting substituents (such compounds include DCA).[128]

Dickson and Jawhey[129] obtained hexacarbonyl-m-dicyanoacetylenedicobalt (LIII) by the reaction of DCA with dicobalt octacarbonyl in hexane:

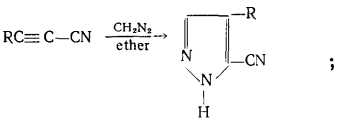


(LIII)

When DCA was allowed to react with $(Ph_3P)_2Ir(CO)Cl$ and nickelocene, complexes were obtained in low yields in which the metal atom is linked by a π-bond with the acetylenic ligand[130].

7. 1,3-Dipolar Cycloaddition

Numerous examples of the reactions of alkynes, particularly conjugated alkynes, with various types of dipoles are known[67]. For example, the method of synthesis of 4-R-5-cyanopyrazoles (LIV) is based on the reaction of α-cyanoacetylenes with diazoalkanes[92,131]:

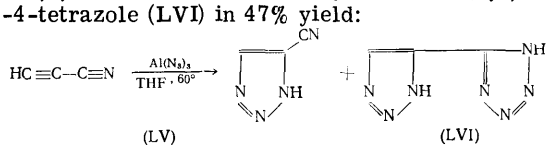


R=H, Cl, or Br (LIV)

Such pyrazoles may be used to synthesise pyrazole-3,5-dicarboxylic acid, which exhibits hypoglycaemic activity.

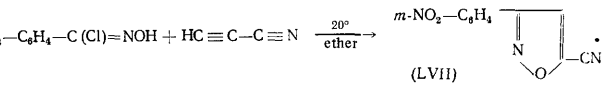
Sasaki et al.[132] described the synthesis of 5-cyano-3-(5-nitrofuryl)pyrazole in 36% yield from CA and 5-nitro-2-furyldiazomethane in ether at 20°C in the presence of triethylamine.

In 1969, Arnold and Thatcher[133] achieved the cyclisation of CA with aluminium azide and obtained a mixture of 4-cyano-1,2,3-triazole (LV) in 32% yield and 5-(1,2,3-triazolyl)-4-tetrazole (LVI) in 47% yield:



(LV) (LVI)

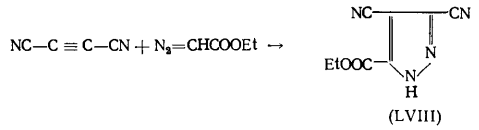
5-Cyanoisoxazole (LVII) has been obtained in 35% yield by the condensation of CA with the chloride of *m*-nitrophenylhydroxamic acid[134]:



(LVII)

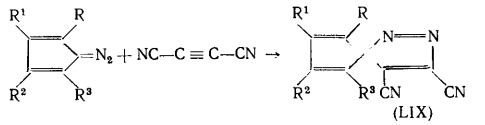
Weis[108] found that the addition of DCA to the *N*-oxide of benzonitrile or diazomethane leads respectively to 4,5-dicyano-3-phenylisoxazole in 81% yield or 3,4-dicyano-*N*-methylpyrazole in 99% yield. Ethyl 3,4-dicyanopyrazole-5-carboxylate (LVIII) has been synthesised from DCA

and ethyl diazoacetate[135] in 40% yield and then converted into 3,4,5-tricyanopyrazole:



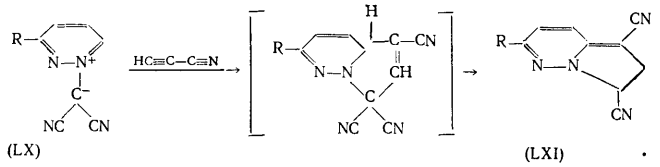
(LVIII)

Various polycyclic adducts can be obtained by the reaction with diazo-compounds. For example, Dürr and coworkers[136,137] achieved the 1,3-dipolar cycloaddition of diazocyclopentadienes to DCA (20°C, 1–2 h) and obtained spiropyrazoles (LIX):



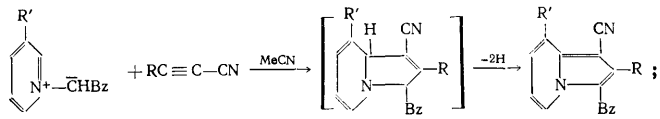
(LIX)

The 1,3-dipolar cycloaddition to CA to *N*-ylids (LX) in acetone (20°C, 4–12 h) results in the formation (in 30 to 80% yield) of pyrrolo[1,2-*c*]pyridazines (LXI):[138]



(LX) (LXI)

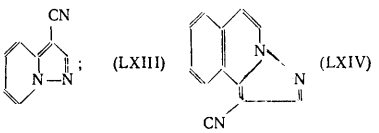
The analogous condensation of DCA with isoquinolinium ylid in dimethylformamide (DMF) leads to 1,2,3-tricyanopyrrolo[2,1-*a*]isoquinoline[139]. Sasaki et al.[140] achieved the 1,3-dipolar cycloaddition of CA and CCA to *N*-ylids and *N*-imines, but the yield of final products did not exceed 5–25%:



(LXII)

R=H, Cl; R′=H, or Me .

1-Aminopyridinium and 2-aminoisoquinolinium iodides react with CA in DMF (with added K_2CO_3) at 20°C, forming respectively 3-cyanopyrazolo[1,5-*a*]pyridine (LXIII) and 1-cyanopyrazolo-[5,1-*a*]isoquinoline (LXIV):



(LXIII) (LXIV)

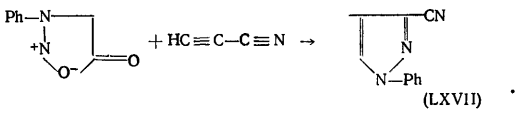
The interaction of pyridinium and triphenylphosphonium 1-cyclopentadienides with CA (−50°C, N_2) leads to the corresponding ylids of 1-(2-trans-β-cyanovinyl)cyclopentadiene.

5-Cyano-3-(5-nitro-2-furyl)-1-phenylpyrazole (LXVI) has been synthesised by the condensation of CA with the phenylhydrazone (XLV) in a THF–benzene mixture at 20°C in the presence of lead tetra-acetate[141]:



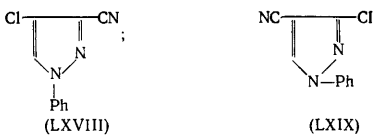
(LXV) (LXVI), 55%

Pyrazole (LXVII) has been obtained in satisfactory yield by the reaction of CA with *N*-phenylsydnone in chlorobenzene at 110°C:



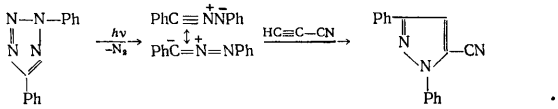
(LXVII)

Under analogous conditions, the reaction with CCA gives a 2:3 mixture of the isomeric pyrazoles (LXVIII) and (LXIX):



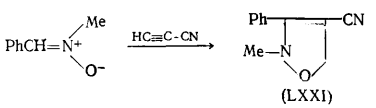
(LXVIII) (LXIX)

Diphenylnitrileimine[92], which was obtained by the ultraviolet irradiation of a solution of 2,5-diphenyltetrazole in THF, readily reacts with CA and yields 5-cyano-1,3-diphenylpyrazole (LXX):



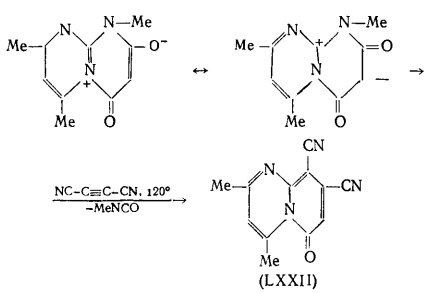
(LXX), 64%

Sims and Houk[142] established that CA reacts with *N*-methyl-*C*-phenylnitrone in benzene at 25°C to form exclusively 4-cyano-2(*N*)-methyl-3-phenylisoxazoline (LXXI), while the reaction with *N*-t-butylnitrone gives a 1:1 mixture of 4-cyano- and 5-cyano-*N*-t-butylisoxazolines:



(LXXI)

DCA enters into a 1,4-cycloaddition reaction as an acetylenic dipolarophile with the anhydro-2-hydroxy-1,6,8-trimethyl-4-oxopyrimido[1,2-*a*]pyrimidinium system[143]—a new heteroaromatic betaine with condensed rings:

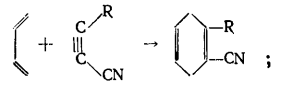


(LXXII)

8. α-Cyanoacetylenes in the Diels–Alder Reaction

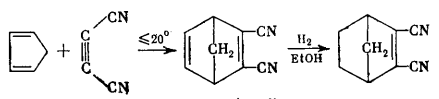
Diene synthesis is one of the convenient methods for obtaining cyclic and heterocyclic systems based on a wide variety of unsaturated compounds. CA and particularly DCA are used fairly frequently nowadays as dienophiles of the acetylenic series. The dienophilic activity of α-cyanoacetylenes is consistent with the fact that the rate of diene synthesis increases following the introduction of electron-donating substituents into the dienes and electron-accepting

substituents into the dienophiles, the reactions proceeding in accordance with the general mechanism



R=H, or CN .

In 1945, Blomquist and Winslow [17] were the first to use DCA as a dienophile in the reaction with one of the commonest reactive dienes—cyclopenta-1,3-diene (CPD)—in order to obtain insecticides having the properties of pyrethrum:

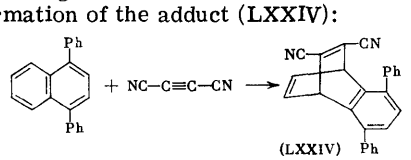


(LXXIII), 83%

The adduct (LXXIII) was also obtained by other workers [22,144]. CA reacts with CPD with much more difficulty than does DCA: thus 1,3-dicyanobicyclo[2,1,2]hepta-1,3-diene is formed in 37% yield in petroleum ether (30°C, 12 h). [99] Subsequently numerous dienes with a wide variety of structures were introduced into diene synthesis with α-cyanoacetylenes: butadiene [99,108], isoprene and chloroprene [93], allo-ocimene [145], cyclohexa-1,3-diene [22,108,144], 3-diphenylcyclohexa-1,4-diene [146], cyclo-octatetraene [108], fluorocyclo-octatetraene [147], furan [46,108], thiophen [148-150], benzene [151] and its derivatives (durene, veratrol, m-cresyl methyl ether, arsabenzene) [22,144,151,152], naphthalene and 1,4-diphenylnaphthalene [22,153], anthracene [22,108,154,155], 9,10-diphenylanthracene [156], naphthacene [157], dimethyl- and diphenyl-fulvenes [17,22], bicyclo[2,2,1]heptadiene [22,108], bicyclo[2,2,2]octa-2,5,7-triene [158], *cis*-bicyclo[6,1,0]nonatriene [159,160], spiro[2,6]nonatriene [161], norbornadiene [162], [2,2]paracyclophane [151], ergosteryl acetate [163], [8](2,5)furanophane [164], and 6-chloro-3-cyano-2,4-bis(dimethylamino)-pyridine [165].

Benzene derivatives are relatively inert as dienes in Diels–Alder reactions, but are capable of condensing with DCA, the reaction having been shown by Ciganek [151] to be strongly accelerated by aluminium chloride. Thus, 2,3-dicyanobicyclo[2,2,2]octa-2,5,7-triene is formed in 14% yield in the reaction of benzene with DCA (180°C, 48 h), while in the presence of $AlCl_3$ at 20°C the yield is 63%. The condensation of DCA with hexamethylbenzene (in benzene, 130°C) is much faster than the condensation with unsubstituted benzene and gives a satisfactory yield of the desired product (83%).

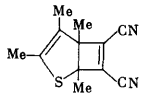
DCA readily condenses with naphthalene [22], anthracene [22,108], and 1,4-diphenylnaphthalene [153], the attack in the last case being directed to the unsubstituted benzene ring with formation of the adduct (LXXIV):



(LXXIV)

On being refluxed with anthracene (100°C, 1 h), DCA gives rise quantitatively to the 1 : 1 9,10-addition product [108], while the 2 : 1 adduct is formed in the reaction with 9,10-diphenylanthracene [156].

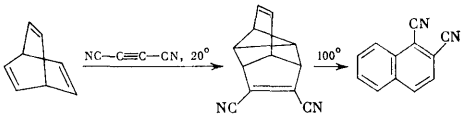
In contrast to benzene, thiophenes do not enter into the Diels–Alder reaction with acetylenes as dienes. In the study of the reaction of DCA and thiophen [148-150], a considerable influence of aluminium chloride on the mode of condensation was discovered. According to Wynberg and Helder [149], this involves a single-stage expansion of the thiophen ring to give thiepin (57% yield). Other workers showed by ^{13}C NMR that 2-thiabicyclo[3,2,0]hepta-3,6-diene (LXXV) is formed in this case, i.e. substituted thiophens undergo [2+2]-cyclo addition to DCA: [150]



(LXXV)

The cycloaddition to α-cyanoacetylenes of dienes such as norbornadienes [108,162], cyclohexa-1,4-diene [146], or barrelene [158] can be regarded as a kind of extension of the Diels–Alder reaction.

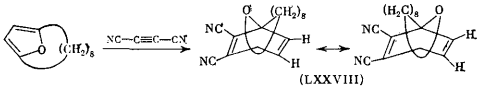
On condensation with DCA [158], barrelene is converted into the naphthalene derivative (LXXVII). The intermediate (LXXVI), isolated at lower temperatures, rearranges to 9,10-dihydronaphthalene, which is converted into the final product in 63% yield:



(LXXVI) (LXXVII)

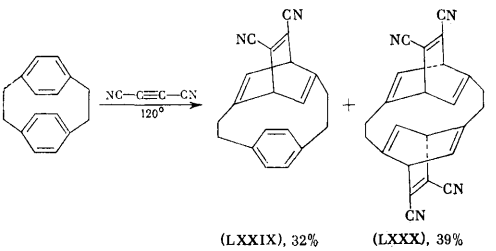
Other cyclopolyenes [147,159-161] condense similarly with DCA.

The Diels–Alder addition of DCA to certain cyclophanes [151,164] leads to unusual tricyclic systems (LXXVIII):



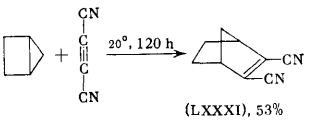
(LXXVIII)

When DCA is heated with [2,2]paracyclophane [151], a mixture of the polycyclic products (LXXIX) and (LXXX) is formed:



(LXXIX), 32% (LXXX), 39%

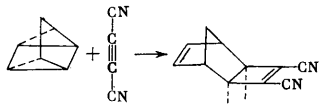
Strained alicyclic systems readily undergo the Diels–Alder reaction with DCA. Thus DCA adds to bicyclo[2,1,0]pentane [166,167] with rupture of the three-membered ring to form the adduct (LXXXI):



(LXXXI), 53%

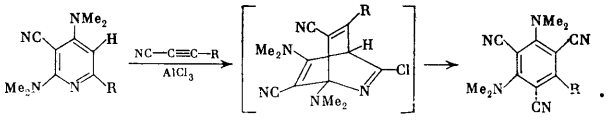
Tricyclo[4,1,0,$0^{3,7}$]heptane [168] reacts with DCA under more severe conditions (70°C, 14 h) to form a 1 : 1 adduct (via a radical mechanism). "Propellerane" or tricyclo-[3,2,1,$0^{1,5}$]octane, synthesised by Gassman et al. [169], reacts very vigorously with DCA at 20°C and somewhat more slowly at −78°C. The reaction of quadricyclane [170] with

DCA in methylene chloride is exothermic and leads to the formation of the 1 : 1 adduct (LXXXII) in 78% yield:



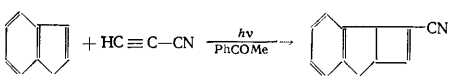
(LXXXII)

On heating in the presence of a small amount of $AlCl_3$, CA reacts with 6-chloro-3-cyano-2,4-bis(dimethylamino)-pyridine [165]. The reaction proceeds via a cyclic intermediate (D) and terminates with formation of 1,3,5-tricyano-2,4-bis(dimethylamino)benzene (LXXXIII):



R = H, Cl (D) (LXXXIII), 4%

When Indene and CA were photolysed [171,172] in benzene in the presence of a sensitiser (acetophenone), cyanocyclobutene (LXXXIV) was obtained in a satisfactory yield:



(LXXXIV)

9. Cyanoacetylene in Substitution Reactions

The mobility of the hydrogen atom in CA is caused not only by the very nature of the acetylenic linkage but also by the presence of the electron-accepting cyano-group. Thus the acidity of the acetylenic hydrogen in CA is reflected in its distinct ability to form hydrogen bonds not only with typical basic proton acceptors, but also with the electrons of the triple bond (self-association) [50]. The tendency of CA to undergo substitution reactions is shown primarily in its reaction with metals. Thus copper cyanoacetylide [21] has been obtained as a yellow deposit when a CuCl solution in aqueous ammonia was treated with CA. The attempt to obtain the sodium derivative of CA in liquid ammonia was unsuccessful [25]. Lithium cyanoacetylide [25] has been obtained from butyl-lithium and CA at −70°C. The magnesium bromide derivative of CA (LXXXV) is formed smoothly at a reduced temperature in absolute ether and can react virtually with all reagents capable of involvement in organomagnesium syntheses [173]. In the presence of CuCl, compound (LXXXV) reacts with organic halides, for example with allyl bromide:

$$H_2C{=}CHCH_2Br + BrMgC{\equiv}C{-}CN \xrightarrow{THF,\ Et_2O} \underset{(LXXXV)}{H_2C{=}CHCH_2{-}C{\equiv}C{-}CN} \quad \underset{(LXXXVI)}{}$$

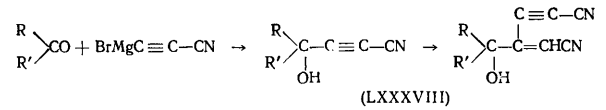
When compound (LXXXV) is treated with phosgene, bromocyanoacetylene is formed, while treatment with ethyl chlorocarbonate results in the formation of 1,6-dicyano-3-ethoxyhex-2-en-4-yne. Acetic anhydride adds to the triple bond of complex (LXXXV) and gives rise to 2,3-diacetyl-3-bromoacrylonitrile. *trans*-Acrylonitriles (LXXXVII) have been obtained by the reactions with epoxyethane and epoxypropane:

$$\underset{\underset{R}{|}}{BrCH_2CHOCH{=}CHCN} \quad ;$$

(LXXXVII)

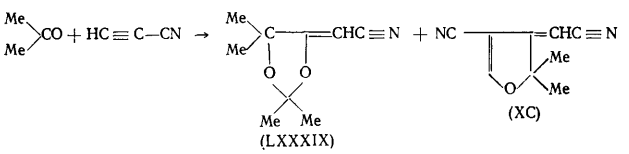
R=H, or Me .

Carbonyl compounds (acetone, cyclohexanone, formaldehyde, etc.) react with compound (LXXXV) to form the corresponding carbinols (LXXXVIII), which can undergo further reactions involving the addition of another CA molecule [173]:



(LXXXVIII)

The reaction of CA with acetone [173] in the presence of a 20% aqueous solution of NaOH leads to the dioxolan (LXXXIX) and the dihydrofuran (XC):



(LXXXIX) (XC)

The magnesium iodide derivative of CA gives cyanoiodoacetylene and not CCA on treatment with toluene-*p*-sulphenyl chloride [25]:

$$IMgC{\equiv}C{-}CN + p\text{-}CH_3C_6H_4SO_2Cl \rightarrow IC{\equiv}C{-}CN$$

CCA can be obtained only via lithium acetylide:

$$HC{\equiv}C{-}CN \xrightarrow{BuLi} LiC{\equiv}C{-}CN \xrightarrow[30\%]{Cl_2} ClC{\equiv}C{-}CN$$

In contrast to CCA, bromo- and iodo-cyanoacetylenes are obtained by the reaction of CA with bromine or iodine respectively, in aqueous alkaline solutions of KBr and KI in yields of 40–60% [174].

The dimerisation of CA is known [27] to occur in the presence of potassium hexacyanoferrate (III). The same method can be used for asymmetric coupling. Thus, Jones and coworkers [175] described the synthesis of 7-cyanohept-2-ene-4,6-diynol from CA and pent-2-en-4-ynol. The acetylenic compounds are initially converted into copper acetylides and then treated with potassium hexacyanoferrate(III).

It has been shown recently [176] that CA can also undergo the Chodkiewicz condensation, but its use is limited by the occurrence of side reactions and the instability of the products. CA has been used successfully in the synthesis of a natural acetylene analogue (XCI):

$$NC{-}C{\equiv}CH + BrC{\equiv}C(CH_2)_3OH \xrightarrow{CuCl,\ NH_2OH{\cdot}HCl,\ EtNH_2}$$

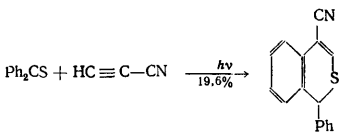
$$\rightarrow [NC{-}C{\equiv}C{-}C{\equiv}C(CH_2)_3OH] \rightarrow \underset{(XCI),\ 9\%}{NC{-}C{\equiv}C{-}CH{=}\overline{C(CH_2)_3O}}$$

5-Aminoisoxazole was isolated as a side product [176].

10. Other Reactions of α-Cyanoacetylenes

Apart from those already discussed, a number of non-general reactions of α-cyanoacetylenes have been described.

On being irradiated with light from a sodium lamp, CA undergoes photocycloaddition to diphenyl thione [177] with formation of compound (XCII):

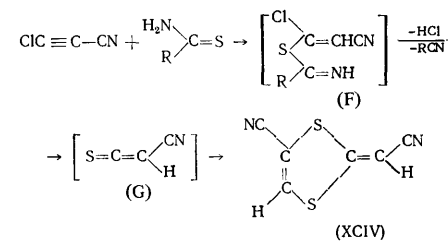


(XCII)

The high-temperature reaction of benzene with CA proceeds with a low conversion (1–2%), benzonitrile and biphenyl having been isolated from the reaction products[178]. When CA was allowed to react with a formate ester[179] in the presence of $HgCl_2$ or $CuCl_2$–$Zn(Ac)_2$, the cyanoacrylate (XCIII) was obtained:

$$HC\equiv C-CN + HCOOR \rightarrow NC-CH=CHCOOR \quad (XCIII)$$

Sasaki et al.[180] found that the reaction of equimolar amounts of CCA and thioacetamide in methanol at 0°C leads to 1,4-dithiofulvene (XCIV). CCA reacts similarly with other thiocarbonyl compounds: thiourea, *NN*-dimethylthiourea, and *N*-phenylthiourea:

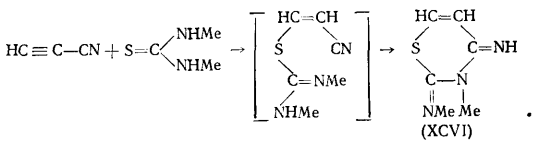


The authors believe that the reaction begins with nucleophilic attack by the thiocarbonyl group on the triple bond with formation of an intermediate (F), which loses a molecule of hydrogen chloride and RCN, is converted into the unstable thioketen (G), and dimerises to compound (XCIV).

The reaction of CA and methyl- and phenyl-cyanoacetylenes with thiourea and ammonium dithiocarbamate[181] in alcohol proceeds stereospecifically and results in the synthesis of *cis,cis*-thiodiacrylonitriles (XCV):

$$RC\equiv C-CN + H_2NCSNH_2 \text{ or } H_2NCS_2NH_4 \rightarrow NC-CH=C(R)SC(R)=CHCN \quad (XCV)$$

Sasaki et al.[180] found that other thiocarbonyl compounds (thioacetamide and *N*-phenyl-, *N*-methyl-*N'*-phenyl-, and *NN'*-diphenyl-thioureas) react with CA under analogous conditions in methanol or acetone solution to form thiodiacrylonitriles in 70–90% yield. The reaction with *NN'*-dimethylthiourea led to the isolation of 4-imino-3-methyl-2-methylimino-2,3-dihydro-1,3-thiazin (XCVI) in 60% yield:



Bushby[182] described the reaction between DCA and ethers. On heating for 16 h a mixture of DCA and THF, he obtained tetrahydro-2-furylfumaronitrile (37% yield), the photochemical isomerisation of which leads to the formation of tetrahydro-2-furylmaleonitrile. 1-Ethoxyethylfumaronitrile was obtained similarly in 48% yield from diethyl ether and DCA, while 1,2-dimethoxyethane gave a mixture of 1,2-dimethoxyethylfumaronitrile (6%) and (2-methoxyethoxy)methylfumaronitrile (6% yield).

Reddy and Weis[183] obtained the product of the addition of DCA to triphenylphosphine (in acetonitrile at 25–30°C) having the structure of 1,2,3,4,5,6-hexacyanohexa-2,4-diene-1,6-diylidene-1,6-bistriphenylphosphorane according to revised data[184].

11. The Polymerisation of Cyanoethylenes

New polyconjugated systems have been obtained on the basis of CA [185,186], namely polypropiolonitrile and its copolymer with phenylacetylene, which exhibit a high thermal stability and electrical resistance.

A number of workers[187–191] have shown that, at a reduced temperature, CA forms low-molecular-weight polymers under the influence of anionic catalysts. For example, the polymerisation of CA and its copolymerisation with acrylonitrile are initiated by CH_3ONa or KSCN.[189] It is believed that the polymerisation involves the acetylenic linkage, since the polymers readily interact with H_2O_2 via the cyano-group, forming amides. In another instance, the polymerisation of CA was initiated by BuLi.[191] The polymerisation of CA in the presence of Ziegler–Natta catalysts[192] leads to a mixture of trimethylsuccinonitrile and polypropiolonitrile in a low yield. It has been established by infrared spectroscopy that polypropiolonitrile has the structure $[-CH=C(CN)-]_n$.

In the presence of initiators of free-radical polymerisation in THF solution, CA forms copolymers with olefinic compounds, for example *N*-vinylcarbazole[193].

Chukhadzhyan and coworkers[194,195] showed that π-allyl derivatives of nickel are active catalysts of the polymerisation of CA. They believe that the polymerisation proceeds via the triple bond of the acetylenic group; the resulting polymer has a conjugated chain of double bonds with a *trans*-structure, which has been confirmed by infrared spectra and a number of chemical reactions.

The homopolymerisation of DCA was achieved for the first time[196] in the presence of an anionic catalyst, namely butyl-lithium (in heptane–THF at −73°C) and led to the formation of a powdered polymer in 90% yield. The infrared spectra of the latter showed absorption bands characteristic of systems of conjugated bonds with cyano-groups, while the ESR spectrum contained a single narrow signal without a definite structure (the number of unpaired electrons is approximately 10^{18} per gram). The polymerisation of DCA in the presence of lithionaphthalene proceeds with a large exothermic heat change, requires large amounts of the catalyst, and results in the formation of oligomers (having molecular weights in the range 400 to 500) soluble in acetone, alcohols, DMF, THF, water, and sulphuric acid and having a resistivity (*in vacuo* at 20°C) of approximately 10^9–10^{12} Ω cm.[197]

Byrd[49,198] homopolymerised DCA under free-radical conditions [in the presence of 2-azobisisobutyrodinitrile (ABIBN) for 1400 h at 55°C], the yield of the polymer being 7%. In the copolymerisation of DCA with styrene in THF, acetone, or toluene in the presence of the same catalyst, the conversion reached 80–97%.

Rembaum and Henry[199] proposed a method for the synthesis of the DCA copolymers with various vinyl (5–90 wt.%) compounds: styrene, methyl methacrylate, butadiene, isoprene, isobutene; acrylonitrile, ethylene, and propene. The polymerisation is carried out in polar organic solvents (THF, dioxan, ethyl methyl ketone, etc.) in the presence of ABIBN, benzoyl peroxide, t-butyl hydroperoxide, butyl-lithium, butylmagnesium bromide, and sodionaphthalene (for 10–30 h at 40–70°C and 10^{-5} mmHg, yield 70–95%). The resulting copolymers exhibit a moderate thermal stability (they are stable up to 280°C) and are semiconductors, which permits their employment in transistors and solar batteries.

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