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The chemistry of perfluoroalkyl-substituted dicyanoethylenes

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ABSTRACT. Fundamental data on the means of obtaining and on the reactivity of perfluoroalkyl-substituted dicyanoethylenes are correlated. The principal ways of using these compounds in organic synthesis are shown. Examples are given of the practical application of perfluoroalkyl-substituted dicyanoethylenes and of the compounds derived from them.

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I. Introduction

The needs of medicine, agriculture and various modern technologies for new organic compounds possessing specific properties have enabled organofluorine chemistry to be integrated into organic chemistry in recent years. An important route for such an amalgamation is the use of synthons, which contain a perfluoroalkyl group at a multiple bond, in syntheses of organic compounds of more complex structure modified by perfluoroalkyl groups.[1] Direct analogy with reactions of unfluorinated unsaturated compounds usually fails since the presence of a perfluoroalkyl group at a multiple bond significantly affects reactivity. The present review considers the features of the chemical behaviour of perfluoroalkyl-substituted dicyanoethylenes in traditional conversions of organic synthesis.

Perfluoroalkyl-substituted dicyanoethylenes combine the properties of perfluoro-olefins,[2] polyfluorocarbonyl compounds[3,4] and their acylimines,[5] and also unfluorinated polycyanoethylenes,[6,7] the chemistry of which is widely represented in appropriate reviews. The chemistry of fluorine-containing dicyanoethylenes has not been reviewed. By filling this gap the authors hope that their work will enable bridges to be built between organofluorine chemistry and classical organic synthesis.

II. Methods of synthesis of perfluoroalkyl-substituted dicyanoethylenes

Three basic methods exist for the synthesis of fluorine-containing dicyanoethylenes. The first method described for obtaining 1,2-dicyano-1,2-bis(trifluoromethyl)ethylenes (Ia, b) and their analogues was the pyrolysis of chlorosulphite derivatives of perfluoroalkyl- and fluorohaloalkyl-cyanomethanes in the presence of sulphur.[8]

$$R_F(NC)CH-OSOCl \xrightarrow{200-800^\circ C} R_F(NC)C{=}C(R_F)CN \quad (1a, b)$$

This method is similar to the preparation of tetracyanoethylene by chlorination–dehydrochlorination of dicyanomethane.[9] The mechanism probably includes the formation of appropriate intermediates of the carbene type in both cases. Dimerisation of these intermediates leads to the ethylene derivative. In the pyrolysis of the chlorosulphite derivative of (trifluoromethyl)cyanomethane a mixture is formed of the *cis*- and *trans*-1,2-dicyano-1,2-bis(trifluoromethyl)ethylenes (Ia, b), the quantitative ratio of which is not reported. The isomeric mixture may be separated by GLC. The *cis*-isomer (Ia) is transformed readily into *trans*-1,2-dicyano-1,2-bis(trifluoromethyl)ethylene (Ib) by treatment with triethylamine.[10]

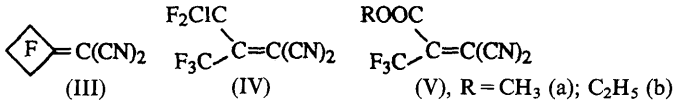
The synthesis of the initial chlorosulphite derivatives[8,10] was effected in the following way:

$$CF_3CH(OH)_2 \xrightarrow{P_2O_5/H_2SO_4} CF_3CHO \xrightarrow[C_5H_5N]{HCN} CF_3CH(CN)-OH \xrightarrow{SOCl_2} CF_3CH(CN)-OSOCl$$

The second method is based on the use of the Knoevenagel reaction under somehat modified conditions. Dicyanomethane and perfluoro- or fluorohaloketones are condensed in the presence of catalytic quantities of zinc chloride. The resulting alcohol is dehydrated with phosphorous pentoxide in the liquid phase or by passing the vapour over silica gel at 100–300 °C.[11–16] For example, the condensation of dicyanomethane and hexafluoroacetone with subsequent dehydration of the adduct with P_2O_5 leads to 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene (II) in 50% yield.[14]

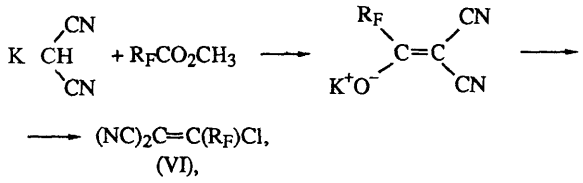
$$CH_2(CN)_2 + F_3CC(=O)CF_3 \xrightarrow{ZnCl_2} H-C(CN)_2-C(CF_3)_2-OH \xrightarrow{P_2O_5} (NC)_2C{=}C(CF_3)_2 \quad (II)$$

The corresponding fluorine-containing ylidenedicyanomethanes were obtained in a similar manner from perfluorocyclobutanone[13] and chloropentafluoroacetone,[15,16] and from the methyl (Va) and ethyl (Vb) esters of trifluoropyruvic acid (III, IV, Va, b).[17]



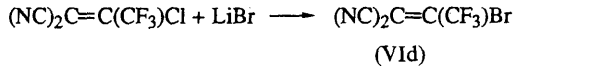
(III) (IV) (V), R = CH_3 (a); C_2H_5 (b)

At the beginning of the eighties a method was proposed for the synthesis of fluorine-containing ylidenedicyanomethanes by condensing the potassium or sodium salts of dicyanomethane with esters of perfluorocarboxylic acids with subsequent treatment of the salts of β,β-dicyano-α-(perfluoroalkyl)vinyl alcohol with phosphorus pentachloride.[13,18,19]



$R_F = CF_3$ (a), C_2F_5 (b), n-C_3H_7 (c)

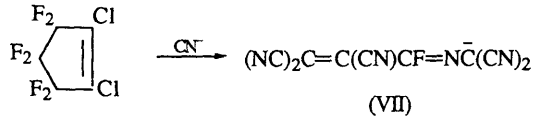
The yield of olefins (VIa–c) is increased on using $PhPCl_4$ as chlorinating agent.[19] The corresponding bromoolefin (VId) was obtained from 2-chloro-1,1-dicyano-2-(trifluoromethyl)ethylene by heating with anhydrous lithium bromide to 120 °C.[16]



(VId)

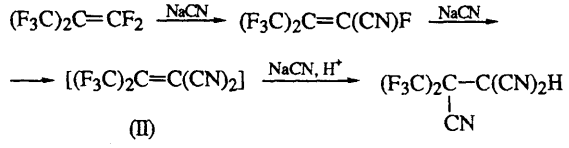
The method described for obtaining fluorine-containing ylidenedicyanomethanes has been used successfully to synthesise analogues of them containing CO_2R or CF_3 groups.[19]

While considering methods of synthesising fluorine-containing dicyanoethylenes it is impossible not to mention reactions involving the substitution of vinylic halogen atoms in perfluoroolefins and fluorohaloolefins by cyano groups. Thus the reaction of 1,2-dichloropentafluorocyclopentene with sodium cyanide leads to the formation of the 1,1,4,5,5-pentacyano-3-fluoro-2-azapentadiene anion (VII).[20]



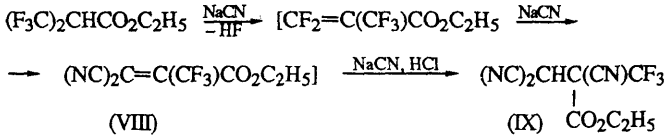
(VII)

Replacement of a vinylic fluorine by a cyano group is readily achieved in the reaction of perfluoroisobutene with sodium cyanide, though the resulting nitrile is able to react further with NaCN. It is suggested that the intermediate is 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene (II).[2,21]



(II)

The reaction of NaCN with hexafluoro-2-hydroisobutyric acid ethyl ester leads to 2,3,3-tricyano-2-(trifluoromethyl)propionic acid ethyl ester (IX). In this case 3,3-dicyano-2-trifluoromethyl)acrylic acid ethyl ester (VIII) is probably one of the intermediates.[21]



(VIII) (IX)

III. π-Complexes of perfluoroalkyl-substituted dicyanoethylenes with aromatic compounds

All the olefins considered form intensely coloured solutions on mixing with aromatic compounds or other π-bases. This colour indicates the formation of π-complexes which are characterised by intense absorption in the visible or near ultraviolet regions. The absorption maxima of complexes do not belong to either of the reactants and are attributed to a new molecular form. Several complexes, their absorption maxima and extinction coefficients (ε) are shown in Table 1.[14]

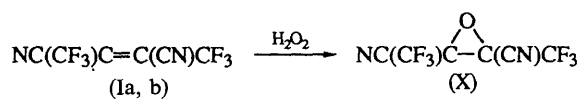
Table 1. π-Complexes of dicyanoolefins (II, III)

π-Base	π-Acid			
	(II)		(III)	
	λ, nm	ε	λ, nm	ε
Pyrene	500	3670	580	1930
Durene	386	2520	423	2430
Hexamethylbenzene	445	1060	497	1040
Benzene	316	1950	334	2170
Toluene	327	1720	358	1720

Footnote. Solvent CH_2Cl_2, temperature 24 °C.

IV. Oxidation–reduction reactions of perfluoroalkyl-substituted dicyanoethylenes

1,2-Dicyano-1,2-bis(trifluoromethyl)ethylene (Ia, b) react with hydrogen peroxide with the formation of the 2,3-dicyano-2,3-bis(trifluoromethyl)oxiranes (X).[10]



(Ia, b) (X)

Like alkenes (Ia, b), 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene (II) and its analogues are oxidised by hydrogen peroxide or peracids to 2,2-dicyano-3,3-bis(trifluoromethyl)oxirane (XI) and its perhaloalkyl derivatives.[12,13]

$$(CF_3)_2C{=}C(CN)_2 \xrightarrow[AcOH]{CH_3COOOH} (CF_3)_2\overset{O}{\overset{/\backslash}{C}}{-}C(CN)_2$$
(II) (XI)

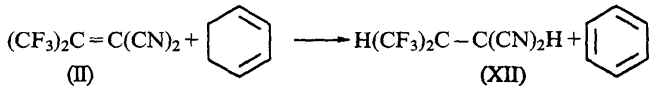
Alkene (II) forms the anion radical of 1,1,-dicyano-2,2-bis(trifluoromethyl)ethylene (XII) on electrochemical reduction in dimethylformamide at 20 °C.

$$[(CF_3)_2C{=}C(CN)_2]^{\cdot-}$$
(XII)

The ESR spectrum of this anion-radical has been investigated.[22,23]

The corresponding anion-radical was obtained from *trans*-1,2-dicyano-1,2-bis(trifluoromethyl)ethylene (Ib).[22,23] The electron affinities of (Ia, b) have been estimated on the basis of experimental ionisation potentials and their photoelectron spectra were studied.[24]

1,1-Dicyano-2,2-bis(trifluoromethyl)ethylene (II) may be reduced with cyclohexadiene to the corresponding ethane derivative (XIII).[16] No traces of the [4 + 2] cyclic adduct were detected.

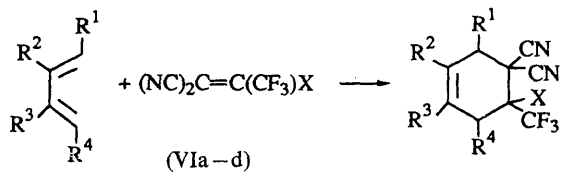

(II) (XII)

Hydrazobenzene is oxidised by alkene (II) to azobenzene.[25] Probably 1,1-dicyano-2,2-bis(trifluoromethyl)ethane (XIII) is formed in this case however it was not isolated from the reaction mixture. The dicyanoethylenes (Va, b), like the alkene (II), react with hydrazobenzene.[17]

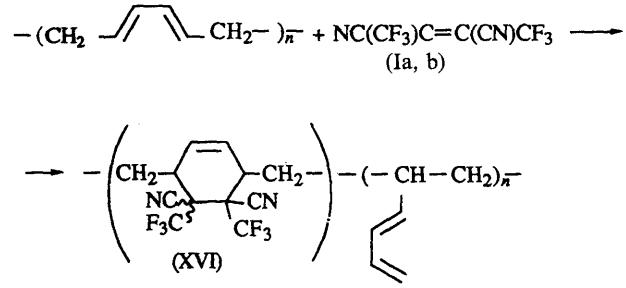
V. Cycloaddition reactions of perfluoroalkyl-substituted dicyanoethylenes

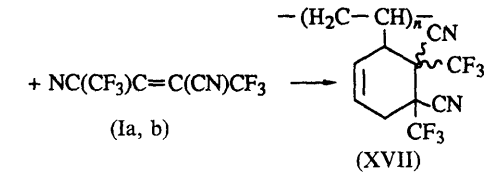
1. The Diels–Alder reaction ([4 + 2] cycloaddition)

Fluorine-containing dicyanoethylenes are reactive dienophiles in the Diels–Alder reaction. 1,1-Dicyano-2,2-bis(trifluoromethyl)-ethylene (II), 1,1-dicyano-2-(trifluoromethyl)-2-(chlorodifluoromethyl)ethylene (IV) and 1,1-dicyano-2-halo-(perfluoroalkyl)-ethylenes (VIa–d) react with 1,3-butadiene, 2,3-dimethylbutadiene, isoprene and several other linear dienes at 0–25 °C with or without a solvent giving [4 + 2] cycloaddition products (XV) in high yield.[14,16,26,27]

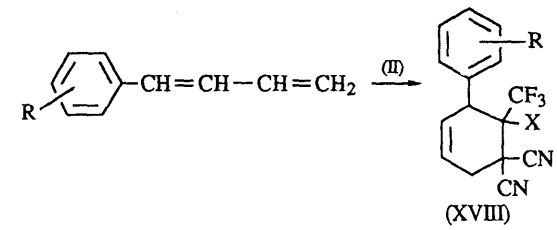

(VIa–d) (XV)

This reaction was used for the modification of various polymers of trienes. For example, polymers of 1,3,5-hexatriene, 1,3,5-heptatriene and 2,4,6-octatriene containing conjugated diene groups were modified using the Diels–Alder reaction with 1,2-dicyano-1,2-bis(trifluoromethyl)ethylene) Ia, b) at 25–80 °C in solution in benzene, toluene or tetrahydrofuran.[28,29] It was established that cyclic structures were formed in the main chain (XVI) or in the side chains (XVII) of the polymers. The conversion was from 10 to 75%.


(Ia, b) (XVI)

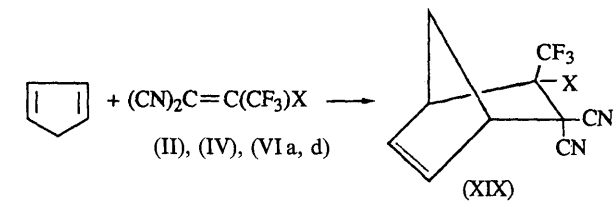

(Ia, b) (XVII)

A systematic study has been made of the [4 + 2] cycloaddition reactions of alkene (II) and *trans*-1-arylbutadienes leading to the cyclohexane derivatives (XVIII).[26,27]


(XVIII)

R = *p*-$N(CH_3)_2$, *p*-OCH_3, *p*-CH_3, H, *m*-F, *m*-Cl, *m*-CF_3, *m*-NO_2

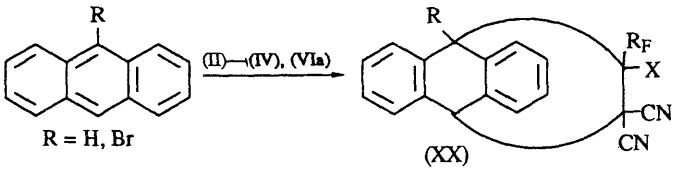
A comparison has been carried out of the relative reaction rates of various fluorine-containing dicyanoethylenes with cyclopentadiene leading to a [4 + 2] cycloaddition product (XIX).[16]


(II), (IV), (VIa, d) (XIX)

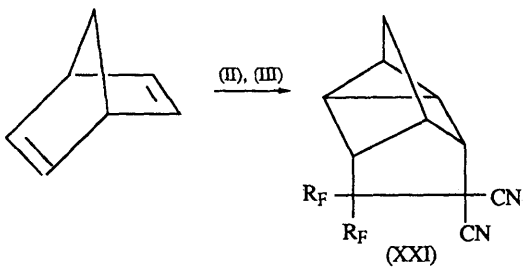
The reactivity decreases in the series $(CF_3)_2C{=}C(CN)_2$ (II) > $(CF_3)(CF_2Cl)C{=}C(CN)_2$ (IV) > $(CF_3)ClC{=}C(CN)_2$ (VIa) > $(CF_3)BrC{=}C(CN)_2$ (VId). All the alkenes considered are less reactive than tetracyanoethylene.[30]

Anthracene and certain of its derivatives may act as dienes. Dicyanomethylenehexafluorocyclobutane (III) reacts with anthracene in benzene at room temperature forming the adduct (XX) after a few minutes.[14] The reaction conditions are more forcing for alkenes (II),

(IV) and (VIa).[14,16] A temperature of 100 °C is required to form cyclic adducts with 9-bromoanthracene.[16]

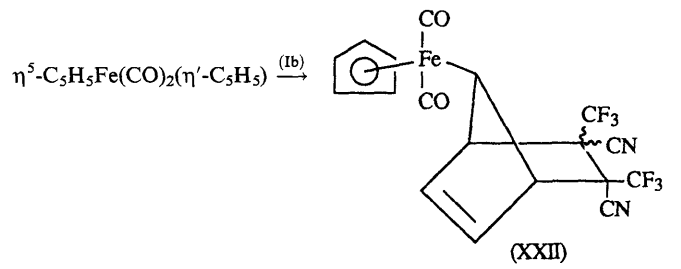


The alkenes (II) and (III) are reactive dienophiles in homo-Diels–Alder reactions.[14] Thus 1,1-dicyano-2,2-bis(trifluoromethyl)-ethylene (II) gives the cyclic adduct (XXI) with norbornadiene even at room temperature. The reaction is complete in approximately three hours, which is significantly less than for the analogous reaction of tetracyanoethylene.[31]

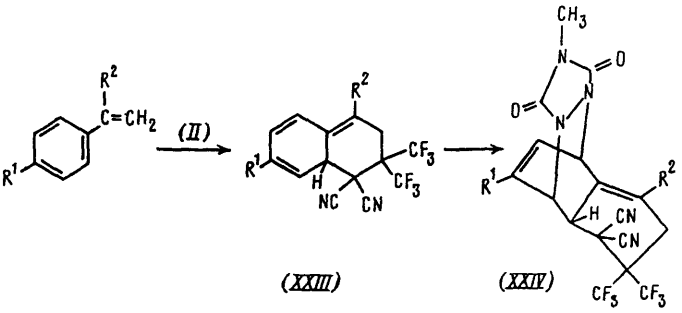


The high reactivity of the alkenes (II) and (III) compared with tetracyanoethylene in the reaction with norbornadiene is explained by their more readily polarisability and the possibility of forming an intermediate or transition state with a larger charge separation.[14]

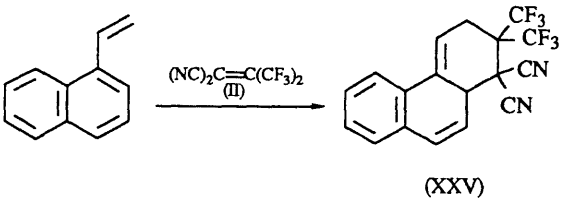
The diene system may be part of an unsaturated hydrocarbon ligand in a transition metal complex. The reaction of η^5-$C_5H_5Fe(CO_2)(\eta'$-$C_5H_5)$ with *trans*-1,2-dicyano-1,2-bis(trifluoromethyl)ethylene (Ib) leads to the 1:1 adduct (XXII) containing a norbornyl ring.[32]



Reactions of [4 + 2] cycloaddition have been reported in which the aromatic benzene nucleus acts as part of a diene system.[33,34] Derivatives of styrene and 1,1-dicyano-2,2-bis(trifluoromethyl)-ethylene (II) are subject to a reversible Diels–Alder reaction. The nonaromatic adduct (XXIII) was isolated and was in its turn the substrate in a [4 + 2] cycloaddition reaction with *N*-methyltriazolinedione leading to the tricyclic product (XXIV).



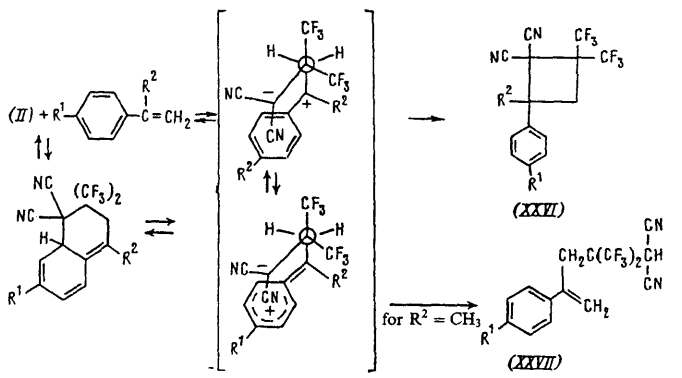
The effects of substituents R^1 and R^2 and the influence of solvent polarity on the reaction rate are in agreement with a synchronous reaction mechanism.[34] It was noted that if part of the initial diene is a naphthalene system then the cycloaddition product (XXV) is stable and the Diels–Alder reaction is irreversible.[34]



(XXV)

This phenomenon is due to the lower loss of resonance energy by the naphthalene system compared with benzene.

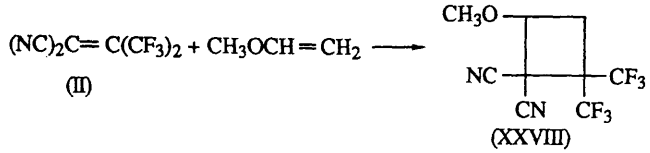
In a detailed study of the conversions occurring in the styrene—1,1-dicyano-2,2-bis(trifluoromethyl)ethylene (II) system it was shown that at 20 °C a slow irreversible reaction forming the cyclobutane derivatives (XXVI), i.e. a [2 + 2] cycloaddition, competes with the rapid reversible Diels–Alder cycloaddition. Products (XXVII) of the ene reaction were also detected. The overall scheme of these conversions is as follows.[33]



2. [2 + 2] Cycloaddition reactions

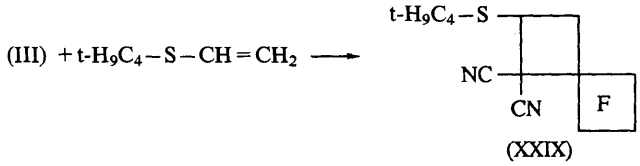
The formation of cyclobutane derivatives together with Diels–Alder reaction products was recorded on reacting the alkene (II) with 1-chloro-1,3-butadiene,[16] 1,1-diarylbutadiene[26] and 1-aryl-1,3-butadiene.[26,27] In the case of 1,1-diarylbutadiene the [2 + 2]

cycloaddition product was the main product.[35] The [2 + 2] cycloaddition reaction with olefins occupies a special place in the chemistry of fluorine-containing dicyanoethylenes as they are often effected under exceptionally mild conditions.[14] Thus 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene (II) reacts practically instantaneously with methyl vinyl ether even at −78 °C forming 1,1-dicyano-2,2-bis-(trifluoromethyl)-4-methoxycyclobutane (XXVIII) in 87% yield.



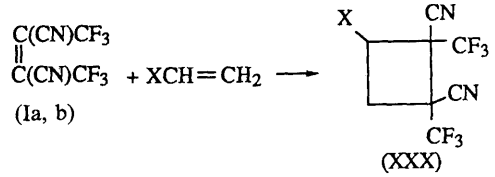
(XXVIII)

The alkene (II) gives a cyclic adduct of type (XXVI) after a few minutes with styrene, 4-methoxystyrene and α-methylstyrene at 0 °C in solvents such as pentane or carbon tetrachloride. No formation of Diels–Alder reaction products is observed at reduced temperatures.[11–14] Under the same conditions t-butyl vinyl sulphide and α-methylstyrene react with dicyanomethylenehexafluorocyclobutane (III) forming the corresponding spiro derivatives of cyclobutane, such as (XXIX).



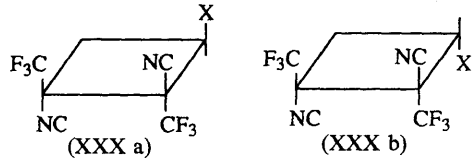
(XXIX)

The stereochemistry of the [2 + 2] cycloadditions of *cis*- and *trans*-1,2-dicyano-1,2-bis(trifluoromethyl)ethylenes (Ia) and (Ib) has been studied.[36] It was found that these alkenes react at room temperature with alkyl vinyl ethers, alkyl vinyl sulphides and 4-alkoxystyrenes forming the cyclobutanes (XXX). The solvent polarity exerts a strong effect on the reaction rate.

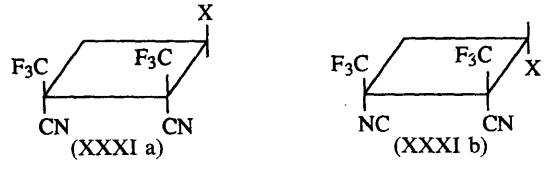


(XXX)

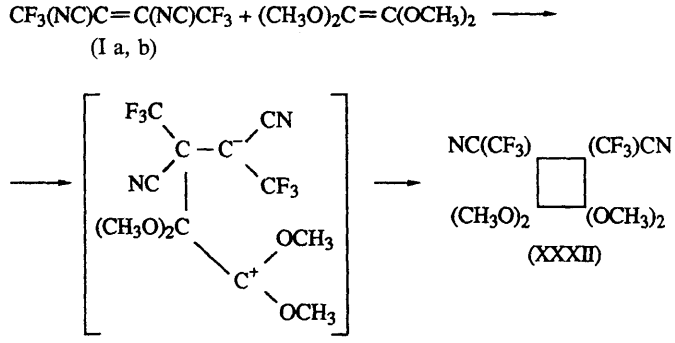
The reaction of (Ib) with the above olefins is stereoselective in the absence of solvent and gives exclusively the cyclobutane diastereomers (XXXa, b).



The corresponding reaction of the *cis* isomer (Ia) leads to the diastereomers (XXXIa, b).

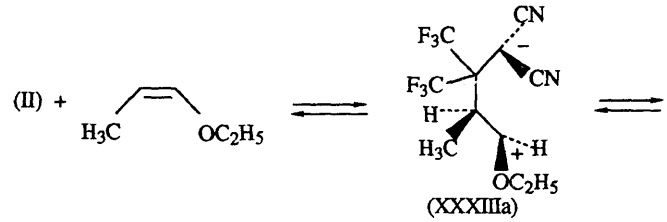


The [2 + 2] cycloaddition of 1,2-dicyano-1,2-bis(trifluoromethyl)-ethylenes (Ia, b) with tetramethoxyethylene has been studied and a zwitterionic mechanism has been proposed for the formation of the adducts (XXXII).[37]

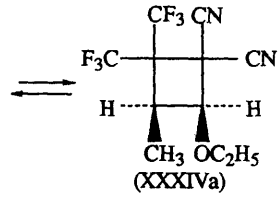


(XXXII)

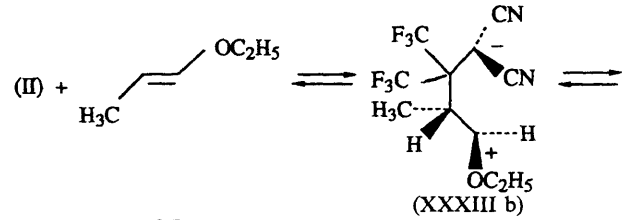
The features and mechanism of the [2 + 2] cycloaddition of 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene (II) and alkyl vinyl ethers has been studied in detail by Huisgen and Bruckner.[38] It was found that the cyclobutane derivatives (XXXIV) are formed through a 1,4-dipolar intermediate which was trapped by reaction with ethanol or acetic acid. No regioisomer (XXXIV) was recorded on NMR investigation of the reaction products. Since the cyano groups stabilise the negative charge better than the trifluoromethyl groups in the 1,4-dipolar intermediate (XXXIII) and the reaction of *cis*- and *trans*-1-ethoxypropene with (II) is not stereospecific, the following [2 + 2] cycloaddition mechanism is proposed.



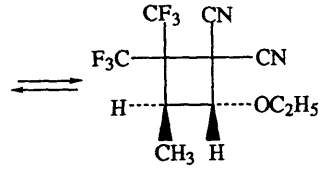
(XXXIIIa)



(XXXIVa)



(XXXIII b)



(XXXIV b)

The reaction of the cyclobutanes (XXIVa, b) with ethanol (2 d, 20 °C) leads to the acetal (XXXV).[38,39]

$$\text{(XXXIV a or b)} \xrightarrow{C_2H_5OH} H(CN)_2C-C(CF_3)_2-CH_2CH(OC_2H_5)_2$$

(XXXV)

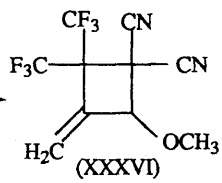
This result is a consequence of the equilibrium (XXXIII) ⇄ (XXXIV). A similar trapping of the 1,4-dipole also occurs on reaction with acetic acid.

A study of the kinetics of the reaction of (II) with ethyl vinyl ether showed the marked effect of solvent polarity on the reaction rate.[35] The rate constants are increased on introducing donor substituents into the α-position of the ethyl vinyl ether while a β-methyl group leads to the opposite effect, probably due to the increased role of steric factors.

Olefins having a cumulative diene system also readily undergo [2 + 2] cycloaddition. For example, 1-methoxy-1,2-propadiene reacts with the alkene (II) leading to the adduct (XXXVI) with an exocyclic double bond.[35]

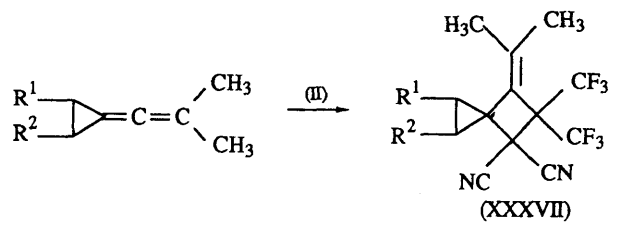
$$H_2C{=}C{=}CHOCH_3 + (NC)_2C{=}C(CF_3)_2 \longrightarrow$$

(II)



(XXXVI)

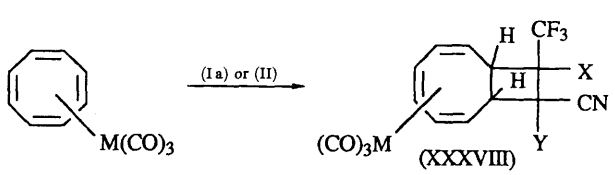
Similar results were obtained for the reaction of 1-(2-methylpropylidene)-2-phenylcyclopropane and 7-(2-methylpropenylidene)-bicyclo[4,1,0]heptane with 1,1-dicyano-2,2-bis(trifluoromethyl)-ethylene (II). In the first case (R^1 = C_6H_5, R^2 = H) an isomeric mixture of the cyclic adducts (XXXVII) is formed.[40]



(XXXVII)

A radical mechanism has been proposed for cycloaddition reactions of cumulene systems with the dicyanoethylene (II).[41] The retention of the cyclopropane ring, indicating the formation of a phenylcyclopropenyl radical which undergoes ring fission with more difficulty than a phenylcyclopropenyl cation, points in favour of this mechanism.

As with the Diels–Alder reaction the [2 + 2] cycloaddition of fluorine-containing dicyanoethylenes may occur with an unsaturated hydrocarbon ligand in a transition metal complex. Thus alkanes (Ib) and (II) react with tricarbonylcyclooctatetraeneruthenium and iron forming adducts of composition 1 : 1 which are assigned the structure (XXXVIII) on the basis of ^1H and ^{19}F NMR spectral data.[41]

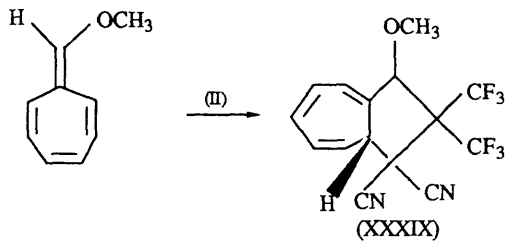


(XXXVIII)

By comparing the reactivity of the alkanes (Ia, b) and (II), (III) with the reactivity of tetracyanoethylene (TCE)[42,43] in reactions occurring by the zwitterionic mechanism, it may be concluded that reactivity decreases in the series (III) > (II) > (TCE) > (Ia, b). Middleton[14] explains the higher reactivity of (II) and (III) compared to TCE and (Ia, b) by their higher polarisability and greater inclination towards the formation of polar intermediates.

3. Other cycloaddition reactions of perfluoroalkyl substituted dicyanoethylenes

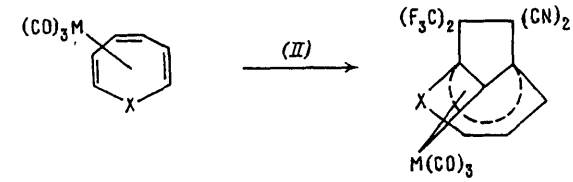
It is known that heptafulvenes with electron-donating substituents may react with fluorine-containing dicyanoethylenes according to an [8 + 2] cycloaddtion. For example, 8-methoxyfulvene and 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene (II) give the cyclic adduct (XXXIX).[44]



(XXXIX)

The reaction is regiospecific and leads to a diastereomeric mixture of hydroazulenes (XXXIX).[44]

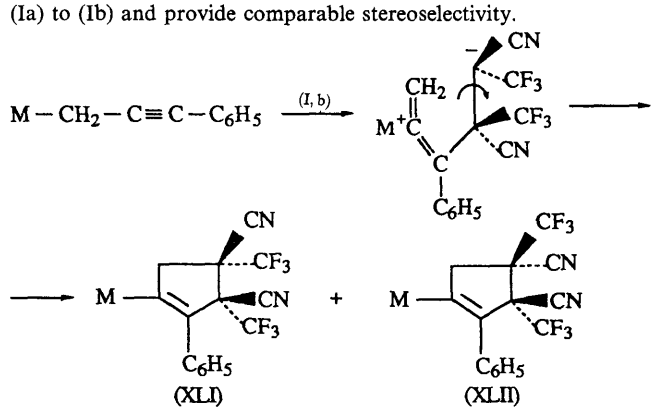
The *exo*-1,3-cyclic adducts (XL) of alkene (II) and tricarbonyl-(η-cycloheptа-2,4,6-trien-1-one) iron and tricarbonyl(η-*N*-methoxy-carbonyl-1H-azepines) iron or ruthenium have been described.[45]



M = Ru, Fe; X = CH_2, NCO_2CH_3 (XL)

A zwitterionic mechanism is proposed for this reaction.

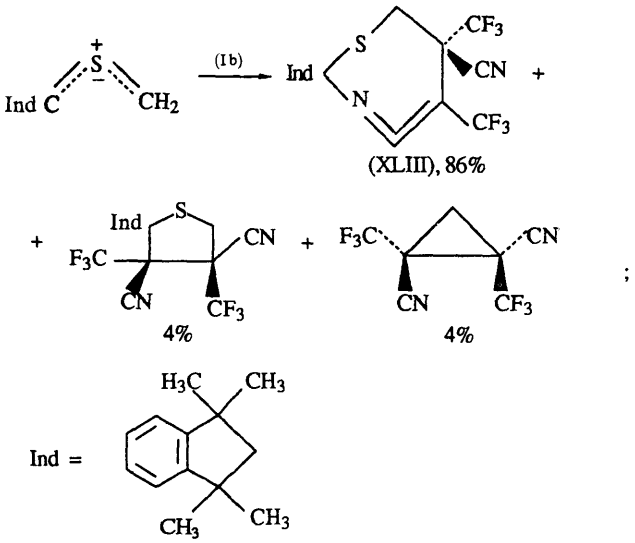
Another example of the cycloaddition of the alkenes (Ia, b) to the unsaturated hydrocarbon ligand of a transition metal complex is the reaction of η^5-$C_6H_5Fe(CO)_2CH_2C{\equiv}CC_6H_5$ with (Ib) in benzene at 20 °C. This leads to compounds (XLI) and (XLII) with 75% regioselectivity.[46] The analogous reactions for the *cis*-isomer (Ia), at least partially if not completely, occur through the isomerisation of (Ia) to (Ib) and provide comparable stereoselectivity.



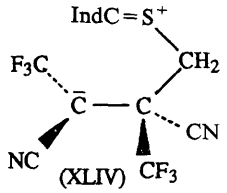
(XLI) (XLII)

M = η^5-$C_5H_5Fe(CO)_2$, $Mn(CO)_5$, $Re(CO)_5$

The [3 + 4] cycloaddition of 1,1,3,3-tetramethylindane-2-thione *S*-methylide and 2,3-bis(trifluoromethyl)fumaronitrile leading to the ketenimine (XLIII) has been studied by Huisgen and collaborators.[47]

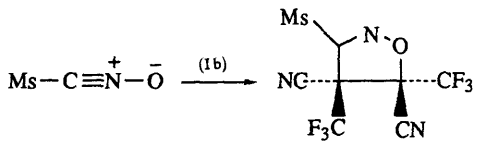


The zwitterion (XLIV) is the probable intermediate.



Similar results are obtained for the cycloadditions of (Ia) and other sulphur methylides.[48]

The mechanism of the 1,3-dipolar cycloaddition of nitrile oxides to the *trans* isomer of alkene (Ib) was studied.[49]

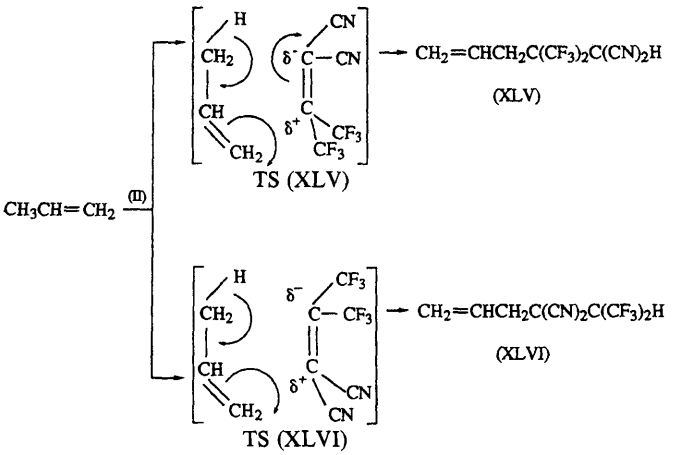


This reaction occurs stereospecifically according to a synchronous cycloaddition mechanism.

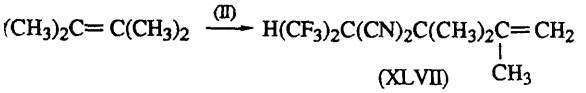
In concluding this section mention must be made of the attempts at computer prediction of the spatial structure of the products of the six-electron cycloaddition of electron-deficient alkenes, such as (Ib), to various olefins.[50]

VI. Reactions of perfluoroalkyl-substituted dicyanoethylenes with olefins involving the allylic hydrogen

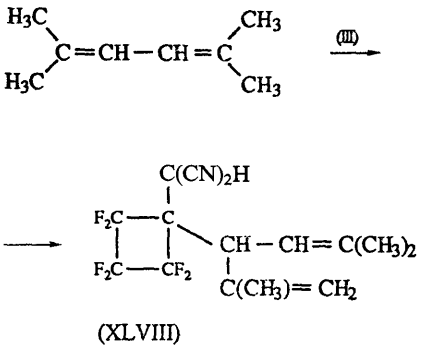
Unactivated olefins which contain an allylic hydrogen atom enter into ene reactions with alkenes (II) and (III). For example, 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene (II) gives a mixture of isomeric adducts (XLVI) and (XLVII) on reaction with propylene at 150 °C.[14]



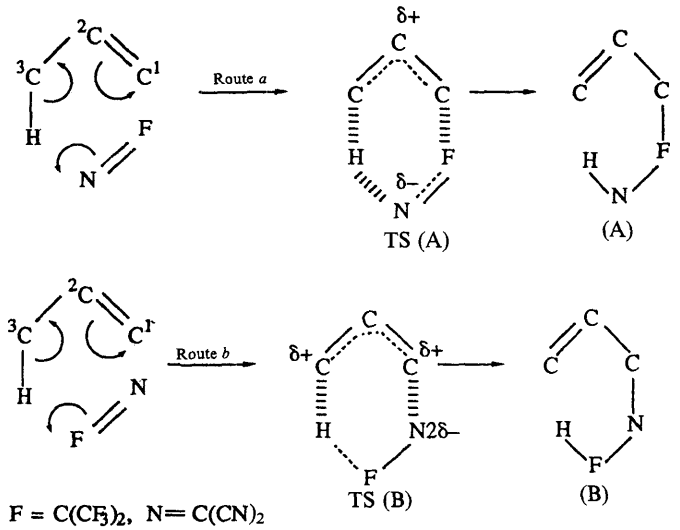
The product (XLV) is formed in good yield which is explained by the high probability of implementing the transition state [TS (XLV)].[14] The formation of the isomer (XLVI) is more favoured. This conclusion is in accordance with the fact that the sterically hindered tetramethylethylene gives a single product (XLVII) at room temperature.[14]



The reaction of alkene (II) with 1,1,4,4-tetramethylbutadiene at 20 °C also leads to the product of the ene reaction (XLVIII).[14]

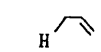
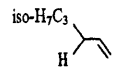
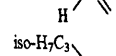
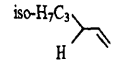
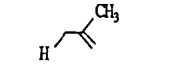
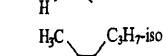


A detailed study of the reaction of 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene (II) with various olefins has been carried out.[51] The reaction mechanism may be represented as follows using the symbols taken from the original work.



The usual enophiles (maleic anhydride, azodicarboxylic ester, formaldehyde, etc.) are carbophilic, i.e. the new C–C bond is more developed in the transition state than X–H (X = C, N, O ...). The charge distribution for the alkene (II) is determined by the ability of the cyano groups to stabilise the negative charge. Reaction of the F portion of the alkene (II) with C(1) leads to a zwitterion with simultaneous transfer of hydride ion reducing the ionic character of the TS (A). A terminal CH(CN) group appears in the reaction product in this case. On implementing TS (B) the hydride transfer and the formation of the $(CF_3)_2C-H$ bond precede the formation of the C–C bond. The negative charge of the carbanion formed from alkene (II) is better stabilised by the CN groups than by the trifluoromethyl groups in TS (A). In this case the reaction product will contain a terminal $H(CF_3)_2C$ group.

Table 2. Products of the ene reactions of 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene with olefins at 20 °C.[51]

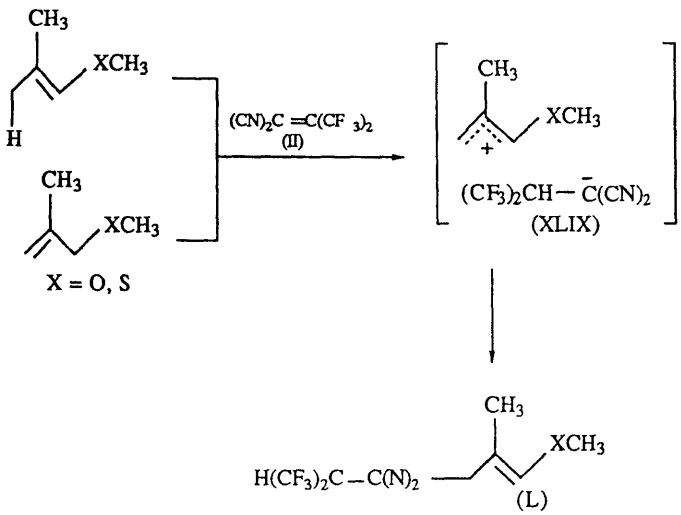
Olefin	Reaction time	Relative amount of products, %	
		(A)	(B)
	12 h	93	7
	18 d	67	33
	141 d	0	100
	18 d	100	0
	40 h	61	39
	29 d	100	0

Both one-stage reactions (*a*) and (*b*) occur with a compulsory shift of the double bond. Recognition of the terminal group of the ene reaction product suggests the implementation of TS (A) or TS (B).[51]

The results of some reactions of alkene (II) with olefins are shown in Table 2.

The introduction of an isopropyl or phenyl group into the C(3) position enables stabilisation of the quasi-allylic cation TS (B). Route *b* is effected in these cases by 33 and 100% respectively. Substituents at C(2) make the quasi-carbocation RS (A) tertiary and consequently aid the formation of the product (A).

The reaction of isobutenyl or methylallyl ethers and thioethers with 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene (II) involving the allylic hydrogen atom has been investigated systematically.[52] In this the ion pair (XLIX) generated in the hydride transfer is the intermediate in the main reaction pathway.



The better stabilisation of the negative charge of (XLIX) by the cyano groups leads to the formation of adducts with terminal $(CF_3)_2CH$ groups. Allyl ethers and thioethers react similarly.

Although the dimethylacetal of dimethylketene is subject only to a [2 + 2] cycloaddition with the alkene (II),[35] the corresponding slow reaction of the dithioacetal gives the product (LI).[52]

$$(CH_3)_2C{=}\,C(SCH_3)_2 + (NC)_2C{=}C(CF_3)_2 \longrightarrow$$

$$\longrightarrow H(CF_3)_2C(CN)_2CH_2C{=}\,C(SCH_3)_2$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad CH_3$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad (LI)$$

It may be concluded from the above that 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene (II) and dicyanomethylenehexafluorocyclobutane (III) are unique enophiles with a marked ability to split off hydride ion from the allyl carbon atom. The alkene (II) is the sole known representative of the ethylene series reacting with unactivated olefins at room temperature without a catalyst.

VII. Reactions of perfluoroalkyl-substituted dicyanoethylenes with nucleophiles

The fluorine-containing dicyanoethylenes readily react with nucleophiles due to their electrophilic nature.

1. Reaction with water and alcohols

1,1-Dicyano-2,2-bis(trifluoromethyl)ethylene (II) readily adds water without a catalyst forming 2,2-dicyano-1,1-bis(trifluoromethyl)ethanol (LII).[14]

$$(NC)_2C{=}\,C(CF_3)_2 + H_2O \longrightarrow H(NC)_2C{-}\,C(CF_3)_2OH$$
(II) (LII)

In strongly acidic medium (II) may be hydrolysed to the diamide (LIII).[14]

$$(NC)_2C{=}\,C(CF_3)_2 \xrightarrow{H_2SO_4/H_2O} (CF_3)_2C{=}\,C(CONH_2)_2$$
(II) (LIII)

The reaction of adding alcohols to the alkene (II) is reversible and leads to the unstable adduct (LIV) which decomposes to the starting materials even on vacuum distillation. The position of the equilibrium depends on the size of the hydrocarbon group of the alcohol. The equilibrium is shifted to the right in the reaction of (II) with methanol and ethanol. The opposite picture is seen with t-butyl alcohol. Isopropanol and the alkene (II) give approximately equal quantities of the product (LVI) and the starting materials of equilibrium.[14]

$$(II) + ROH \rightleftharpoons H(CN)_2C{-}\,C(CF_3)_2OR$$
(LIV)

The reaction of 2-chloro-1,1-dicyano-2-(trifluoromethyl)ethylene (VIa) with alcohols is irreversible and leads, probably according to an addition–elimination mechanism, to 2-alkoxy-1,1-dicyano-2-(trifluoromethyl)ethylenes (LV).[18]

$$(NC)_2C{=}\,C(CF_3)Cl + ROH \longrightarrow (NC)_2C{=}\,C(CF_3)OR$$
(VIa) (LV)

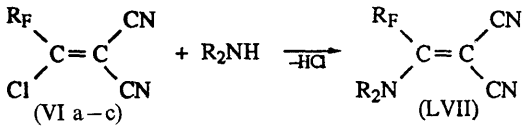
R = CH_3, C_2H_5

2. Reaction with nitrogen-containing nucleophiles

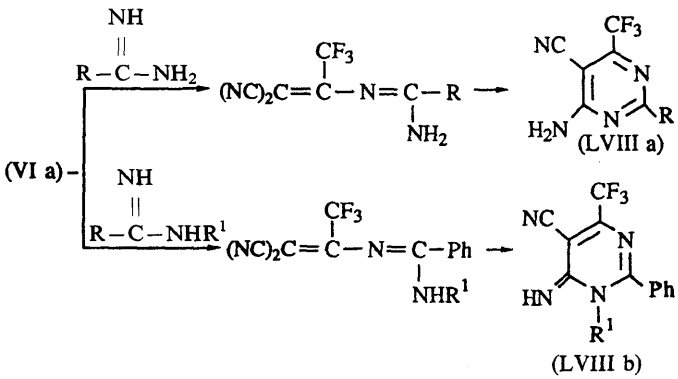
The alkene (II) adds ammonia at the double bond forming an amphoteric amine which was isolated as the tetraethylammonium salt (LVI).[14]

$$(CF_3)_2C{=}\,C(CN)_2 + NH_3 \xrightarrow[-HCl]{N(C_2H_5)_4Cl} H_2N{-}\,C(CF_3)_2{-}\,C(CN)_2{-}\,{}^{+}N(C_2H_5)_4$$
(II) (LVI)

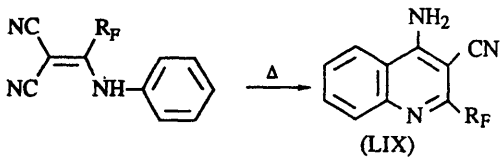
The 1,1-dicyano-2-chloro-2-(perfluoroalkyl)ethylenes (VIa–c) react with primary and secondary aliphatic, primary aromatic amines and amidines with the formation of *N*-vinylation products (LVII).[18,19]



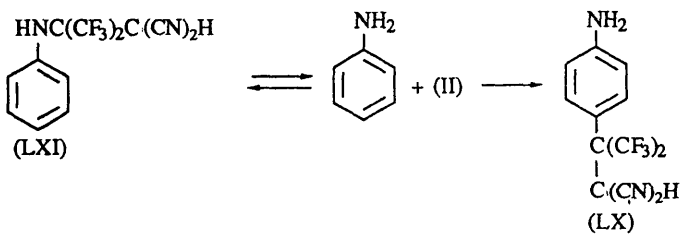
In several cases the resulting *N*-vinyl derivatives undergo further intramolecular cyclisation with the participation of the cyano group. Thus the products of the *N*-vinylation of amidines are cyclised into 5-cyano-4-trifluoromethylpyrimidines (LVIIIa, b).[53]



The *N*-vinyl derivatives of aniline are converted on heating into 4-amino-3-cyano-2-(perfluoroalkyl)quinolines (LIX).[19]

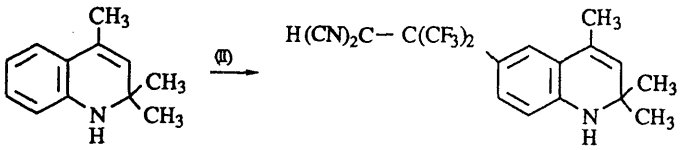


In contrast to dicyanoethylenes containing vinylic halogen atoms 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene (II) reacts with aniline to give the C(4) alkylation product (LX).[11,14,25] It was shown recently that the reaction is complex. The unstable *N*-alkylation product (LXI) is formed first and is in equilibrium with the initial aniline and alkene under the reaction conditions (20 °C, Freon 113). A competing slow irreversible reaction leads to the 4-substituted aniline derivative (LX).[25]



The presence of a substituent in the 2 position to the amino group in *o*-toluidine generates steric hindrance to the formation of an *N*-alkylation product shifting the equilibrium in the *N*-alkylation

product—[arylamine + (II)] system to the right. An increase in the concentrations of the starting materials increases the overall rate of formation of the *C*(4)-alkylation product. The same effect assists rapid *C*(4)-alkylation of the *N*-alkylanilines by the alkene (II). The reaction of alkene (II) with 2,2,4-trimethyl-1,2-dihydroisoquinoline, representing secondary arylamines, also leads to the product of alkylation in the *para* position to the amino group (LXII).[25]

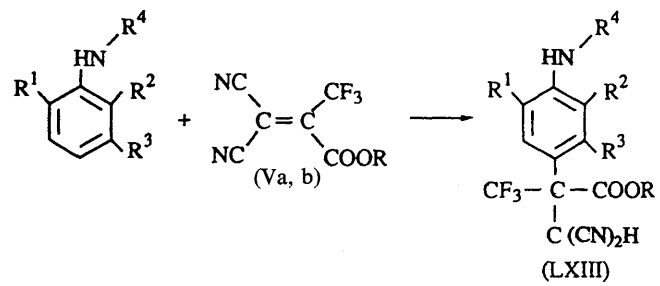


(LXII)

Diphenylamine, in spite of significant steric hindrance to *N*-alkylation, is substituted significantly more slowly which is linked with the reduced nucleophilicity of the benzene nuclei compared with the *N*-alkylanilines. 4-Substituted anilines do not form stable products with the alkene (II).[25]

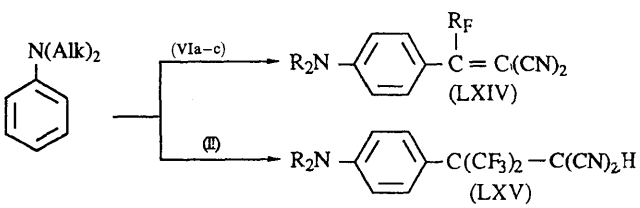
The features of the reaction of anilines with alkene (II) correspond mainly with the results of the tricyanovinylation of aniline with tetracyanoethylene.[54–56]

The reaction of primary and secondary arylamines with the esters of 3,3-dicyano-2-(trifluoromethyl)acrylic acid (Va, b) has also been studied systematically. It was noted that the range of anilines clearly subject to C(4) alkylation by the alkenes (Va, b) was reduced compared to the alkene (II). Positive results were obtained for 2,6-dimethyl- and 2,5-dimethoxyanilines and for diphenylamine. The corresponding derivatives of 4-[2,2-dicyano-1-alkoxycarbonyl-1-(trifluoromethyl)ethyl]aniline (LXIII) were isolated.[17]



(LXIII)

N,N-Dialkylanilines are alkylated at C(4) under mild conditions by the alkenes (VIa–c) and (II) with the formation of the products (LXIV) and (LXV).[16,18,25,27]

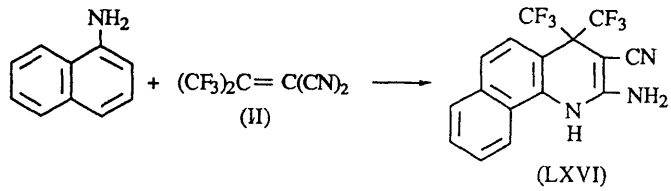


(LXIV)

(LXV)

N,N-Dimethylaniline was successfully alkylated at C(4) by esters of 3,3-dicyano-2-(trifluoromethyl)acrylic acid (Va, b) in acetic acid solution.[17]

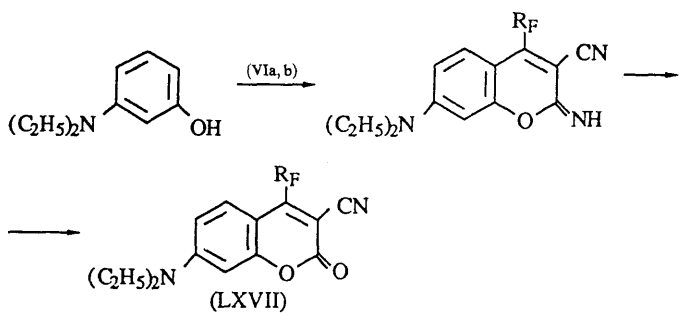
Cases when the *C*-alkylation of the aromatic nucleus is accompanied by heterocyclisation involving the cyano or some other functional group of the electrophilic alkene are of particular interest. Stable heterocyclic compounds modified by perfluoroalkyl groups are formed. For example, the regiospecific alkylation of 1-aminonaphthalene at C(2) by alkene (II) is accompanied by an intramolecular cyclisation involving a cyano and the amino group leading to the benzoquinoline derivative (LXVII).[25,58]



(II)

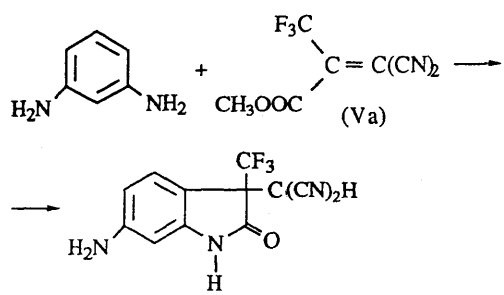
(LXVI)

Cyclisation involving the hydroxyl group of the nucleophile and a cyano group of 2-chloro-1,1-dicyano-2-(trifluoroalkyl)ethylenes (VIa, b) was used in the synthesis of the perfluoroalkyl substituted coumarin derivatives (LXVII).[57]



(LXVII)

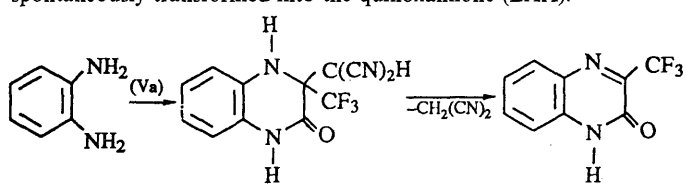
On reacting the acrylic acid derivative (Va) with *m*-phenylenediamine the *C*-alkylation is accompanied by the formation of a lactam (LXVIII).[17]



(Va)

(LXVIII)

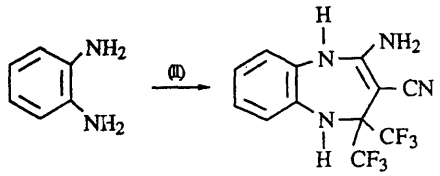
Lactamisation reaches *N*-alkylation in the case of *o*-phenylenediamine. The dihydroquinoxaline (LXIX) is formed which is spontaneously transformed into the quinoxalinone (LXX).[17]



(LXIX)

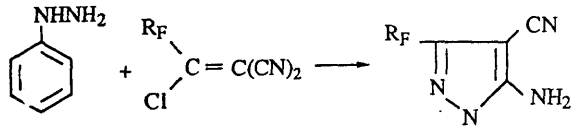
(LXX)

The reacton of *o*-phenylenediamine with 1,1-dicyano-2,2-bis-(trifluoromethyl)ethylene (II) terminates with the formation of the dihydro-1,5-benzodiazepine (LXXI).[17,59]



(LXXI)

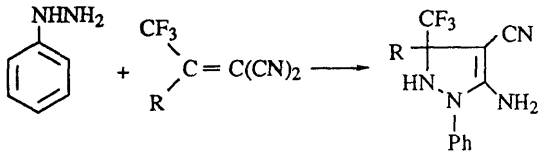
Phenylhydrazine reacts with the dicyanoethylenes (VIa–c) with the formation of the pyrazole derivatives (LXXII).[18,19]



(VIa–c)

(LXXII)

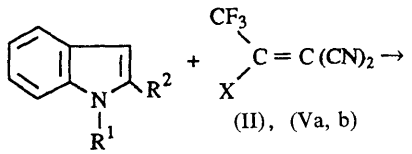
The analogous reaction with 1,1-dicyano-2-(trifluoromethyl)ethylenes (II) and (Va) leads to the pyrazoline derivative (LXXIII).[17,25,60]



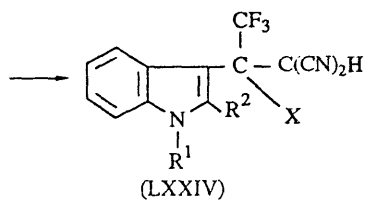
(LXXIII)

R = CF_3 (II); COOMe (Va)

There are only limited data on the *C*-alkylation reactions of nitrogen-containing heteroaromatic compounds with perfluoroalkyl substituted dicyanoethylenes. In addition it is known that indole, 2-methylindole and *N*-methyl-2-phenylindole react under mild conditions with 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene (II) and with esters of 3,3-dicyano-2-(trifluoromethyl)acrylic acid (Va, b) with the formation of products (LXXIV) of substitution of the indole nucleus of C(3).[61]



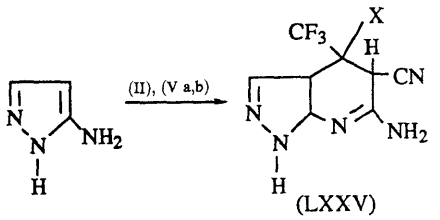
(II), (Va, b)



(LXXIV)

X = CF_3, $COOCH_3$, $COOC_2H_5$

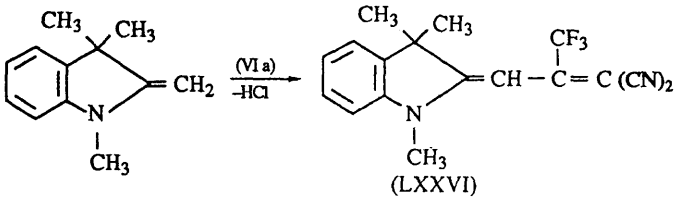
The *C*-alkylation of 3-aminopyrazole is accompanied by heterocyclisation leading to the dihydropyrazolopyridine (LXXV).[17,25]



(LXXV)

X = CF_3, $COOCH_3$, $COOC_2H_5$

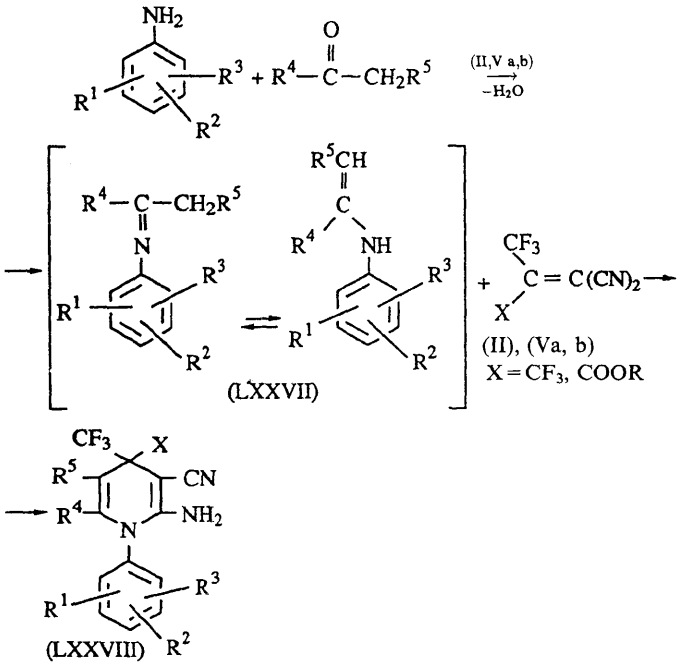
The *C*-alkenylation of 1,3,3-trimethyl-2-methyleneindoline with 2-chloro-1,1-dicyano-2-(trifluoromethyl)ethylene (VIa) is an example of the reaction of perfluoroalkyl substituted dicyanoethylenes with enamines. The strongly coloured compound (LXXVI) is formed.[18]



(LXXVI)

It has been suggested that certain acyclic enamines may react with 1,1-dicyano-2-(trifluoromethyl)ethylenes (II) and (Va, b) with the formation of dihydrobenzene derivatives.[62] The product of β-*C*-alkylation in this case is stabilised by cyclisation involving the nitrile group and the β′-CH fragment of the enamine.

A nonstandard example of the use of compounds existing in a state of imine–enamine equilibrium is the three component reaction of anilines, ketones and 1,1-dicyano-2-(trifluoromethyl)ethylenes (II) and (Va, b) leading to the *N*-phenyl-1,4-dihydropyridine derivative (LXXVII).[62]



(LXXVII)

(II), (Va, b)
X = CF_3, COOR

(LXXVIII)

The key stage of the process is the formation of the Schiff's bases (LXXVII) which are subject to β-*C*-alkylation in their enamine form with subsequent intramolecular cyclisation. A similar heterocyclisation is also effected on reacting alkenes (II) and (Va, b) with anils obtained from aldehydes.[62]

3. Reactions with salts of CH-acids

1,1-Dicyano-2,2-bis(trifluoromethyl)ethylene (II) reacts with sodium cyanide in acetonitrile forming the adduct (LXXIX) which is stable below 300 °C.[14]

$$(NC)_2C=C(CF_3)_2 + NaCN \longrightarrow Na(NC)_2C-C(CF_3)_2CN$$

(II) (LXXIX)

The reaction of alkene (VIa) with the sodium salt of dicyanomethane is known. The tetramethylammonium salt (LXXX) is formed in the presence of tetramethylammonium chloride.[16]

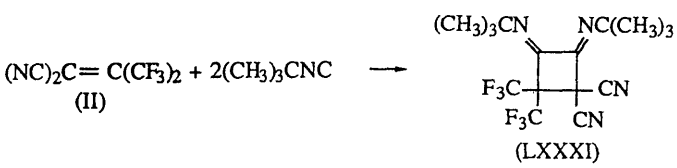
$$(NC)_2C=C(CF_3)CL + (NC)_2CHNa \xrightarrow{N(CH_3)_4Cl} (NC)_2C=C(CF_3)\overline{C}(CN)_2.\overset{+}{N}(CH_3)_4$$

(VIa) (LXXX)

VIII. Other reactions of perfluoroalkyl substituted dicyanoethylenes

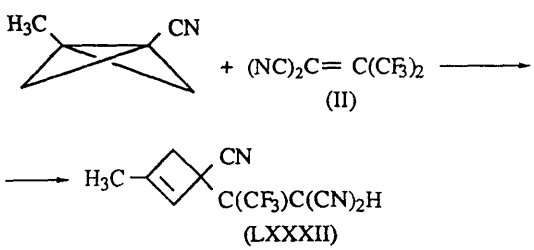
Data are included in this section on chemical conversions of fluorine-containing dicyanoethylenes which have not been systematically covered in the literature or belong to a special area of heteroorganic chemistry but are sufficiently important when creating a more complete picture of the chemical properties of the alkenes under consideration.

The first type includes the reaction of 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene (II) with t-butyl isocyanide at 0 °C. The resulting crystalline adduct of composition 1 : 2 was assigned the structure (LXXXI).[14]



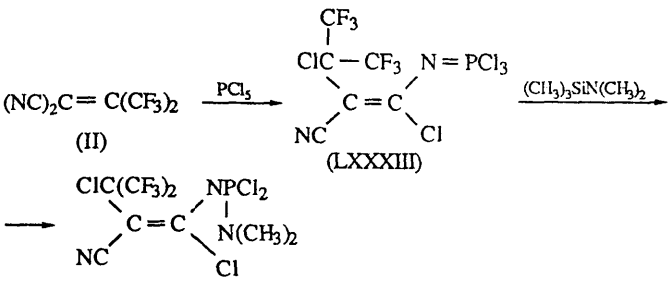
(LXXXI)

The reaction of (II) with bicyclo[1,1,0]butane is an example of an electrophilic addition leading to the cyclobutane derivative (LXXXII).[63]



(LXXXII)

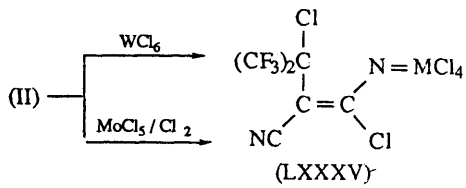
The reaction of the alkene (II) with phosphorus pentachloride leads to the (phosphoranilidenamino)ethylene (LXXXIII), treatment of which with $(CH_3)_3SiN(CH_3)_2$ gives the compound (LXXXIV).[64]



(LXXXIII)

(LXXXIV)

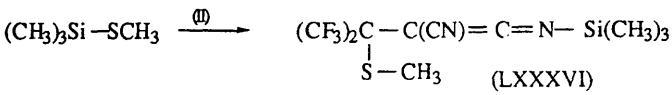
The acyclic nitrenes (LXXXV) may be obtained by the reaction of tungsten hexachloride or molybdenum pentachloride with the alkene (II).[65]



(LXXXV)

M = W, Mo

The olefin (II) reacts under mild conditions by insertion into Si–Si, Si–As, B–S or B–N bonds forming ketenimino derivatives such as compound (LXXXVI).[15,65]



(LXXXVI)

The reactions of alkenes (Ia, b) and (II) with transition metal complexes have been studied fairly widely.[66–70]

IX. Applications of perfluoroalkyl-substituted dicyanoethylenes and compounds obtained from them

1,2-Dicyano-1,2-bis(trifluoromethyl)ethylenes (Ia, b) are patented as stabilising additives for chlorinated hydrocarbons.[71]

The electron-accepting properties of fluorine-containing dicyanoethylenes were used in a study of the photo-dimerisation of 1,4,4a,5,8,8a-hexahydro-1,4,5,8-*endo*, *endo*-dimethanonaphthalene.[72]

Polymers of conjugated trienes, modified with the alkenes (Ia, b) by the Diels–Alder reaction,[28] acquire a high stability towards various actions and also improved electrical insulating properties.

Dicyano-*S*-diaminomethylenesulphilidenes, obtained from 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene oxide and thiourea derivatives, have been proposed for bleaching paper.[12]

The reaction of alkene (II) with aniline gives 4-[2,2-dicyano-1,1-bis(trifluoromethyl)ethyl]aniline (LX) which after diazotisation and coupling with β-naphthol gives an orange dye for wool.[11] Compounds (LXIV) and (LXXIV), which are intensely coloured, may also be used as dyes.[18]

The purpose-directed synthesis of 2,2-dicyanonorbornene derivatives (XIX) from the alkenes (II) and (VIa–d) and study of their biological activity has been carried out by Dupont.[16] It turned out these these compounds are exceptionally toxic (LD50 < 4 mg kg^{-1}) but 2,2-dicyano-3,3-bis(trifluoromethyl)norbornene has an absolutely lethal dose on oral administration to rats of the order of 1.5 mg kg^{-1}, i.e. it is more toxic than sodium cyanide. In addition

the heterocyclic compounds synthesised from trifluoromethyl substituted dicyanoethylenes are obviously interesting from the point of view of searching for new biologically active compounds.

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