Russian Chemical Reviews **64**(11) 1021 – 1034 (1995) ©1995 Russian Academy of Sciences and Turpion Ltd

UDC 547.315

The interaction of nitriles with electrophiles

I D Gridnev, N A Gridneva

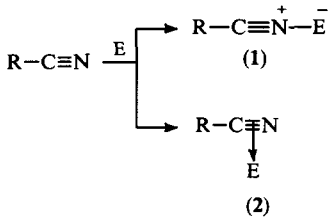
Contents

I.	Introduction	1021
II.	Interaction of nitriles with protic acids	1021
III.	Coordination of nitriles to transition metals	1023
IV.	Interaction of nitriles with Lewis acids	1024
V.	Interaction of nitriles with sulfur trioxide	1026
VI.	Alkylation of nitriles. Alkylnitrilium salts	1028
VII.	The Ritter reaction	1029
VIII.	Acylation of nitriles. Acylnitrilium salts	1030
IX.	Conclusion	1033

Abstract. The interactions of organic nitriles with various electrophiles are analysed. It is shown that the numerous processes observed in such reactions are fairly general and are largely controlled by the nucleophilic properties of the nitrile. The bibliography includes 99 references.

I. Introduction

The nucleophilic properties of nitriles are due to the lone pair of the nitrogen atom and the π-electron system of the C≡N triple bond:



This leads to two possible directions of electrophilic attack and the formation of either the *n*-complexes **1** or the π-complexes **2** as the primary products.[1–3] The direction of the primary attack by the electrophile depends on its nature, the structure of the nitrile, and the reaction conditions. For example, quantum-chemical calculations and experimental data obtained by photoelectron and X-ray electronic spectroscopy constitute evidence that the highest occupied orbital of acetonitrile is a molecular π orbital, whilst the orbital occupied by the lone pair is located in a lower position.

I D Gridnev Zelinskii Institute of Organic Chemistry, Russian Academy of Sciences, Leninskii prosp. 47, 113917 Moscow, Russian Federation. Fax (7-095) 135 53 28. Tel (7-095) 135 89 51
N A Gridneva Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, ul. Vavilova 28, 117813 Moscow, Russian Federation. Fax (7-095) 135 50 85

Received 4 July 1995
Uspekhi Khimii **64**(11) 1091–1105 (1995); translated by A K Grzybowski

In the case of benzonitrile, the π orbitals of the benzene ring have the highest energies.[4]

Hence it follows that the primary product of the charge-controlled reaction of acetonitrile with an electrophile should be a π-complex.[5] However, as a result of the influence of a whole series of factors on the populations of the orbitals, such considerations are difficult to generalise and their value is therefore small. Furthermore, only one π-complex of a nitrile with an accurately established structure is known at the present time.[3] Nevertheless, we shall see below that the wide variety of primary products, observed in the interaction of nitriles with electrophiles, can be accounted for only by resorting to the concept of the formation of π-complexes.

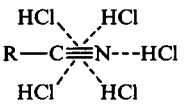
II. Interaction of nitriles with protic acids

Since protic acids catalyse a whole series of reactions of nitriles, the question of the structure of the primary products of the interaction of the latter with protic acids has been widely discussed in the literature.[1–3,6–21] Although it is regarded as generally accepted that nitriles can react with acids to form molecular π-complexes in which the proton retains its linkage with the acid anion, we are aware of only one study in which such interaction has been discussed in detail.[6]

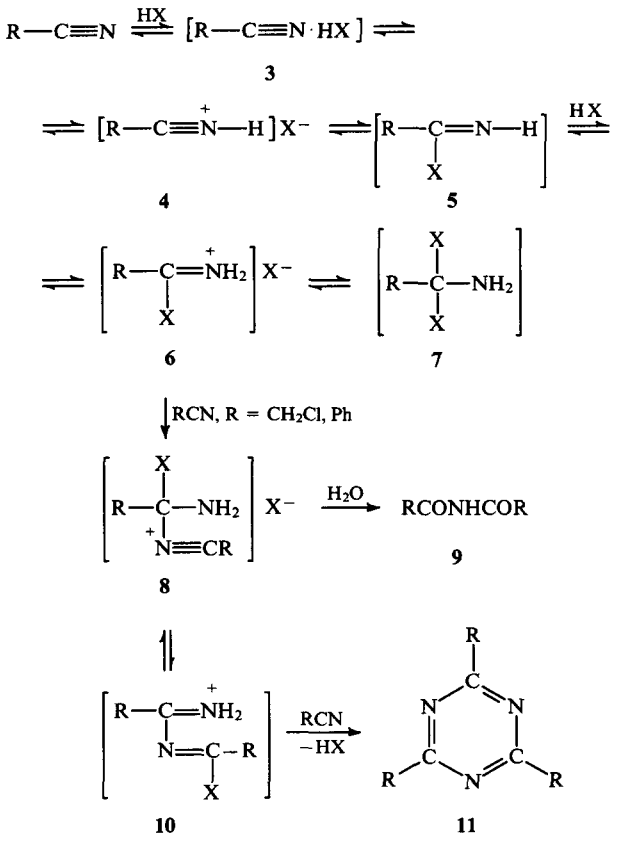
As a result of the study of the fusion diagrams for binary mixtures of hydrogen chloride with acetonitrile, propionitrile, and benzonitrile, it has been shown[6] that these nitriles can form readily fusible molecular compounds RCN·HCl. The authors[6] suggest that the lone pair of the nitrogen atom of the nitrile group participates in the formation of these compounds. The same nitriles can form the molecular compounds RCN·5HCl, RCN·7HCl, and 2RCN·3HCl with lower melting points than the compounds RCN·HCl.

Compound	T_m/°C	Compound	T_m/°C
MeCH·HCl	−63.2	2EtCH·3HCl	−117.0
2MeCN·3HCl	−88.0	EtCN·5HCl	−129.0
MeCN·5HCl	−123.6	PhCN·HCl	−80.6
MeCN·7HCl	−125.0	PhCN·5HCl	−130.0
EtCN·HCl	−97.2	2PhCN·3HCl	−109.0

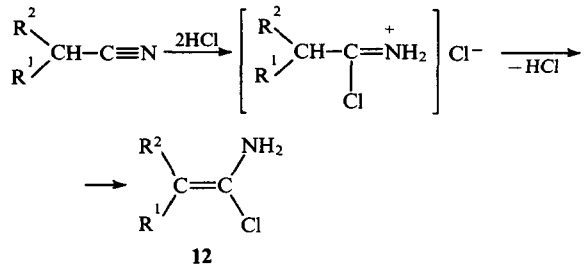
It has been suggested that these compounds are formed as a result of the interaction of HCl with the π-electron system of the nitrile, i.e. they are π-complexes.



At room and higher temperatures, nitriles react with protic acids to form salt-like compounds capable of dissociating in solution into ions, which is indicated by the results of conductimetric measurements[1,7,8] and cryoscopic studies.[9] The information accumulated hitherto makes it possible to represent all the possible products formed in the interaction of nitriles with acids in terms of the following scheme:



Although, as already noted, the formation of type **3** molecular complexes has been discussed in detail only by Murray and Schneider,[6] it is believed that this is the first stage of the interaction of nitriles with any protic acid. The formation of NH-nitrilium salts **4** has been postulated in the study of a series of acid-catalysed reactions of nitriles.[1,10,11] Indeed, in the hydrolysis of nitriles to amides or in the Hoesch reaction (acylation of phenols by nitriles), the intermediate formation of NH-nitrilium salts appears essential. However, low equilibrium concentrations of the salts **4** are sufficient for this purpose and it appears that in the case of nucleophilic anions (Hal^-, OSO_3H^-, $H_2P_2O_7^-$) the anion adds to the nitrile carbon atom with formation of type **5** compounds.[9,12] However, they are extremely unstable and the reports about the synthesis of imidoyl chloride **5** (X = Cl^-) were found to be erroneous.[1,13] The halo- and polyhalo-derivatives of immonium halides **6** (X = Hal^-, Hal_2H^-) have been isolated in a pure state and their structure has been confirmed by elemental analysis and IR spectroscopic data.[12,14,15] The same workers note that the isomeric aminochloro-derivatives **7**, the formation of which has been postulated,[13] cannot be isolated when nitriles interact with HCl. The formation of the neutral compounds **12** in the case where nitriles containing α-protons were introduced into the reaction with HCl [16] showed that the main product present in the mixture of the nitrile and HCl is the immonium halide salt.

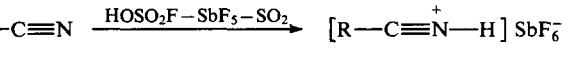


12

The reaction of α-halonitriles with acids does not stop at the immonium salt **6** stage. It has been shown[9,11,17–20] that a second nitrile molecule is added with formation of the dimer salts **8** or **10**. A choice between these two structures cannot at present be made, but the formation of the dimer salts has been confirmed by the hydrolysis to the diacylamides **9**. The trimerisation of nitriles with electron-accepting substituents is also possible, leading to the formation of the triazines **11**. However, under the conditions of the interaction of nitriles with protic acids, this reaction proceeds to only an insignificant extent.

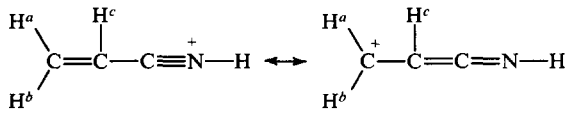
It has been observed in the reaction of fluoro- and bromo-acetonitriles with HCl [21] that, depending on the temperature, both the halo-derivatives of the immonium halides **6** and the dimer salts **8** can be obtained from the same nitriles. The former are formed at temperatures from −50 to −5 °C and the latter at room temperature. Unstable complex compounds are apparently formed initially. At a low temperature, these compounds are stabilised by the addition of a hydrogen halide molecule with formation of a halo-derivative of the immonium halide **6**. At a higher temperature, the unstable molecular complexes decompose, which increases the concentration of the free nitrile and ultimately leads to dimerisation to type **8** salts.[1]

The formation of type **4** NH-nitrilium salts can be observed in superacid media. Olah and Kiovsky[22] investigated protonated nitriles by ^1H, ^{13}C, ^{15}N NMR spectroscopy in solution in $FSO_3H-SbF_5-SO_2$ at lowered temperatures.



The presence of protonated nitriles under the given conditions is indicated by the existence of spin–spin coupling of the proton attached to the nitrogen atom with the protons of the alkyl group in the nitrile. For example, the signal of the methyl group in the protonated acetonitrile is a doublet (δ = 3.25 ppm) with $^4J_{H-H}$ = 2.4 Hz, which is comparable in magnitude to the analogous constant for methyl-ethyne (2.9 Hz). In the ^{13}C NMR spectrum of the protonated [^{13}C]acetonitrile, the signal of the nitrile carbon atom is displaced downfield by 10 ppm relative to the signal of acetonitrile, but the chemical shift nevertheless indicates the retention of *sp* hybridisation of this carbon atom.[22]

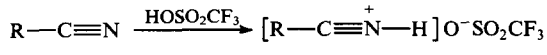
An appreciably greater downfield shift of the H^a and H^b protons than for the H^c proton (1.5 and 0.6 ppm respectively) is observed in the ^1H NMR spectrum of the protonated acrylonitrile. This apparently indicates appreciable delocalisation of the carbonium ion centre in protonated unsaturated nitriles.



It is interesting to note that Olah and Kiovsky[22] were unable to achieve the protonation of nitriles by fluorosulfonic acid, which they attribute to the insufficient acidity of the medium in

the given instant. This fact makes it necessary to treat with caution reports about the preparation of type **4** NH-nitrilium salts by the interaction of nitriles with even weaker acids.

The formation of NH-nitrilium salts on dissolution of trifluoromethanesulfonic acid in nitriles has been reported.[11]



4a

R = Me, Pr, Ph.

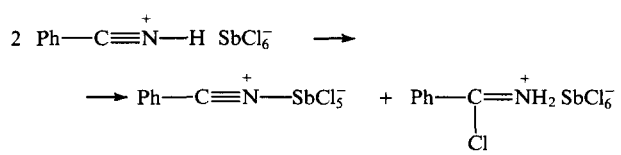
Nitrilium trifluoromethanesulfonates **4a** were isolated from solution in the form of a red oil. The IR spectra of these compounds show a 50 cm^{-1} hypsochromic shift of the $\nu(C\equiv N)$ vibrational frequency compared with the free nitriles, which led the authors[2] to attribute to them the structure of the nitrilium salts **4**. However, other data confirming this hypothesis are not quoted. Solutions of trifluoromethanesulfonic acid in nitriles are able to interact with phenols and their ethers via a reaction analogous to the Hoesch reaction.[11] After 20–30 days, the yields reach 70%–80% and acylation takes place in the *para*-position.



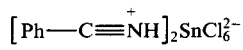
R = Alk, Ph; R′ = Me, Pr.

Halonitriles dimerise on treatment with CF_3SO_3H, which indicates the fundamentally similar nature of the interaction of nitriles with various protic acids.

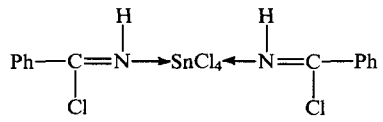
It is also essential to mention the NH-nitrilium salts with complex anions. The synthesis of such compounds has been reported in a number of communications.[1,12,14] The most detailed study[12] showed that the formation of the nitrilium salt **4** ($X = SbCl_6^-$) is not observed in the interaction of HCl with the complex $PhCN-SbCl_5$, which the authors attribute to the instantaneous disproportionation of the salt.



The only NH-nitrilium salt which it has been possible to isolate is apparently compound **13**. It has been shown by conductimetric measurements that it is not the donor–acceptor complex **14**.[12]



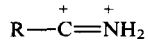
13



14

However, the salt **13** also disproportionates above 50 °C.

A recent investigation of the Houben–Hoesch reaction showed[23] that the most probable species undergoing acylation is the dication



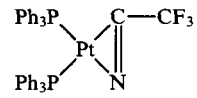
This hypothesis has been confirmed by the fact that the monocationic reagent *N*-methylbenzonitrilium triflate reacts with benzene only in the presence of an acid as strong as the $CF_3SO_3H-SbF_5$ mixture, whereas trifluoroacetic acid does not catalyse the process at all. Trifluoromethanesulfonic acid without added SbF_5 has only a slight catalytic effect.

It is also of interest to note that the complexes of nitriles with $FeCl_3$ and $AlCl_3$ do not react with HCl at all even at temperatures above 120 °C.

Thus the principal types of interaction of nitriles with protic acids are the formation of the immonium salts **6** in the case of aliphatic nitriles and the formation of the dimer salts **8** in the case of aromatic and α-halo-substituted nitriles. The formation of NH-nitrilium salts **4** can be detected only in superacid media for aliphatic nitriles.

III. Coordination of nitriles to transition metals

It has been suggested that in the complexes of nitriles with transition metals there is a possibility of interaction of the acceptor (the metal ion) both with the π-electron system of the triple bond of the nitrile and with the lone pair of the nitrogen atom.[3] In the IR spectrum of compound **15**, the frequency $\nu(C\equiv N)$ is 1780 cm^{-1}, which is 350 cm^{-1} lower than in the initial nitrile.

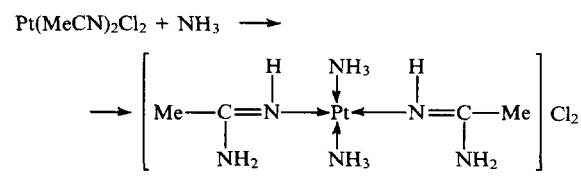


15

Such a low stretching vibrational frequency has been attributed to the formation of a π-complex with the platinum atom.

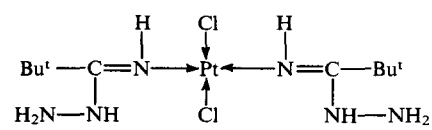
For the majority of the complexes between nitriles and transition metals, X-ray diffraction studies have shown that the MNC angle is close to 180°, whilst the length of the C≡N bond diminishes on coordination to the metal atom,[24] i.e. its strength increases. The frequency $\nu(C\equiv N)$ increases under these conditions by 50–300 cm^{-1}.[4,25,26] However, despite this, the coordinated nitriles have enhanced electrophilic properties, which is reflected in a number of reactions.

For example, coordinated nitriles interact much more readily with amines and other nitrogen bases than the free nitriles. The nitrile complexes are converted quantitatively into amidine complexes at room temperature.[27]



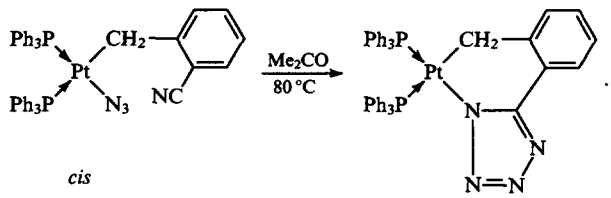
Similar reactions have been observed for the complexes $Re(RCN)_2Cl_4$ (R = Me, Ph) and a series of aromatic amines.[27]

It has been shown[28] that nitriles may be converted into amidines on treatment with hydrazine. The interaction of *trans*-$Pt(Bu^tCN)_2Cl_2$ with hydrazine hydrate in solution in ethanol leads to the formation of complex **16**.



16

An interesting example of intramolecular cyclisation has also been observed:[29]



cis

Such cyclisation does not occur when the initial complex is the *trans*-isomer.

The catalytic effect of transition metal ions on the rate of hydrolysis of nitriles, noted in a number of investigations,[29-31] has been attributed to the intermediate formation of nitrile complexes with subsequent conversion of the inner-sphere nitriles into the amides of the corresponding acids.[3] It is also believed that the facilitation of the reactions with nucleophiles when the nitrile is coordinated to a transition metal atom is associated with the decrease in the electron density on the nitrile carbon atom as a consequence of its displacement towards the central atom.[3,32]

It has been noted[4,33] that the introduction of strongly electron-accepting substituents into the nitrile molecule may alter the nature of its participation in complex formation, transforming it from an electron-donating to an electron-accepting component. For example, in the formation of complexes between nitriles and electron acceptors containing a central metal atom with populated *d* orbitals (Rh, Ru, Co, Mo), the transfer of electron density from the nitrile group to the metal may be accompanied by the additional formation of a donor–acceptor bond as a result of the interaction of the electrons of the metal *d* orbitals and the unoccupied π^* orbitals of the nitrile.[4] The participation of the π MO of the nitrile in the η^5-cyclopentadienylmanganese dicarbonyl and phosphine-molybdenum dicarbonyl complexes of nitriles has been demonstrated by electronic spectroscopic methods.[34,35] The intense charge-transfer band at $\lambda \approx 500$ nm, observed in the electronic spectra of these compounds, constitutes, according to Michurin et al.,[4] definite confirmation of the manifestation of π-electron-accepting properties by the nitrile in these complexes.

The π-electron-accepting properties of nitriles are exhibited also in complexes of the type Et_3N-SO_2-RCN, where $R = CCl_3$ or p-$NO_2C_6H_4$. The appreciable bathochromic shift of $\nu(C\equiv N)$ (by 20–30 cm^{-1}) in the IR spectra of these compounds indicates the transfer of electron density to the antibonding π MO of the nitrile.[36]

IV. Interaction of nitriles with Lewis acids

Nitriles are extremely effective electron donors in complex formation with Lewis acids.[4] The formation of complexes can be detected even for weak Lewis acids such as the halogens and interhalogen compounds.[37-39] It was shown in the above studies by UV spectroscopy that the equilibrium constants for the complex formation reactions between nitriles and the halogens increase in the sequence $Br_2 < I_2 < IBr < ICl$. An increase in the equilibrium constant is favoured also by an increase in the electron-donating capacity of the hydrocarbon group in the nitrile.[37-39]

The complexes of nitriles with metal halides have been thoroughly investigated. They are formed on simple mixing of the reactants and can be readily isolated in a pure form and characterised. Table 1 shows that the hypsochromic shift of the $\nu(C\equiv N)$ vibrational frequency is observed in all the complexes of nitriles with metal halides, which is a common phenomenon for all the complexes of nitriles whose formation involves the lone pair of the nitrogen atom.[4]

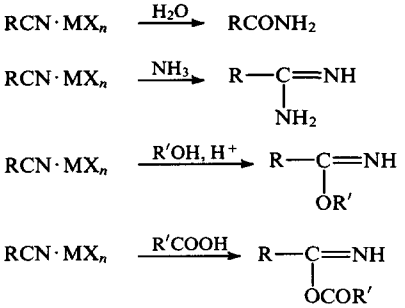
Table 1. The quantities $\nu(C\equiv N)$ and $\Delta\nu$ for the complexes of nitriles with Lewis acids.

Composition of complex	$\nu(C\equiv N)/cm^{-1}$	$\Delta\nu/cm^{-1}$	Ref.
$MeCN\cdot BF_3$	2359	111	40
$MeCN\cdot BCl_3$	2328	81	41
$PhCN\cdot BCl_3$	2304	75	41
$MeCN\cdot AlCl_3$	2330	77	42
$MeCN\cdot AlBr_3$	2335	82	42
$2\,MeCN\cdot ZnCl_2$	2306	44	43
$2\,MeCN\cdot SnCl_4$	2300	38	44
$PhCN\cdot SnCl_4$	2258	27	45
$2\,MeCN\cdot NiCl_2$	2286	41	46
$2\,PhCN\cdot TiCl_4$	2269	38	47
$4\,EtCN\cdot NiBr_2$	2290	42	48
$4\,MeCN\cdot RuCl_2$	2270	29	49
$H_2C{=}CHCN\cdot NbCl_5$	2264	36	50
$H_2C{=}CHCN\cdot FeCl_2$	2257	29	51
$H_2C{=}CHCN\cdot CoCl_2$	2260	32	51
$2\,MeCN\cdot ReCl_4$	2310	59	52
$2\,MeCN\cdot TiCl_4$	2280	26	53

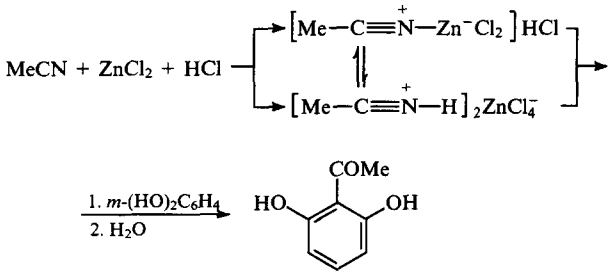
The causes of such increase in the vibrational frequency of the C≡N bond have not been fully elucidated. Initially, this phenomenon was attributed to the increasing charge separation and hence to a larger dipole moment of the C≡N bond in the complexes.[54] In a later study,[55] it was shown that one of the causes may be the kinematic interaction between the stretching vibration of the N–B and C–B bonds with the normal C≡N mode in the complexes $MeCN\cdot BX_3$ (X = Cl, F, Br). However, according to the results of Bittie and Gilson,[56] the observed increase in $\nu(C\equiv N)$ cannot be accounted for solely by the kinematic effect, since calculation yields a shift of 25 cm^{-1}, whilst the observed experimental values are 70–100 cm^{-1}. Nevertheless the shift of the $\nu(C\equiv N)$ vibrational frequency is regarded as a reliable criterion of the formation of complexes of nitriles via the lone pair of the nitrogen atom.[1,2,4]

This conclusion has been confirmed by X-ray diffraction for a series of complexes of acetonitrile with Lewis acids.[11,44,57] A linear $Me-C\equiv N-MX_n$ coordination and a shortening of the C≡N bond (1.10–1.15 Å) were observed in all these investigations.

The chemical properties of the nitrile–Lewis acid complexes are characterised by a greater ease of nucleophilic attack on the nitrile carbon atom compared with the free nitrile. This is manifested in their interactions with water, organic acids, alcohols, and nitrogen bases. In fact, all these reactions proceed smoothly only in the presence of Lewis acids.[1-3]

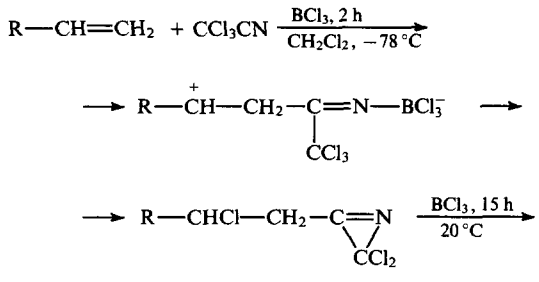


The Hoesch reaction, which was already known at the beginning of the century, also proceeds in the presence of a Lewis acid — $ZnCl_2$.[11]

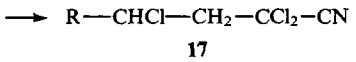


The recently discovered reaction of complexes of nitriles containing electrophilic substituents with BCl_3 and BBr_3 is of the greatest synthetic interest.[57-59] Japanese investigators[57,58] observed that, in the presence of BCl_3, trichloroacetonitrile interacts with a wide range of alkenes, affording the products of the electrophilic attack by the nitrile on the double bond of the unsaturated compound. The mode of the reaction then depends significantly on the structure of the unsaturated compound.

Thus, it has been shown that the interaction of α-alkenes with trichloroacetonitrile in the presence of BCl_3 in methylene chloride at −78 °C leads to satisfactory yields of dichloroaziridines **16**, which may be converted into the corresponding dichloronitriles.[57]



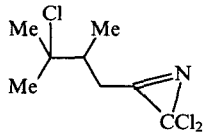
16



17

R	Yield (%)	
	16	**17**
n-C_6H_{13}	90	60
Bu^n	90	66
Bu^{iso}	90	77
$EtMe_2C$	92	59
Bu^t	68	65
$PhCH_2$	44	19

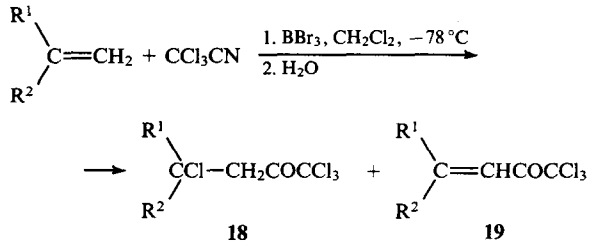
In the case of compound **16** (R = Bu^t, $PhCH_2$), the reaction lasted 15 h and in the case where R = Bu^t the compound



was isolated as a side product in 28% yield.

The use of BBr_3 as the catalyst in this reaction leads to the formation of the same product, which shows that the carbonium ion is stabilised by a chlorine atom in trichloroacetonitrile.[57]

A different mode of reaction has been observed for 1,1-disubstituted alkenes — aziridines are not formed and the stabilisation of the carbonium ion is achieved either by the 'abstraction' of a halide ion from the catalyst or as a result of the elimination of an α-proton. A different origin of the halogen from that in the preceding reaction is indicated by the formation of a bromoketone when BBr_3 is employed as the catalyst.[57]



18 **19**

In the case of *tert*-butyl(methyl)ethene, an increase of the reaction temperature to room temperature leads to the formation of rearrangement products (Table 2).

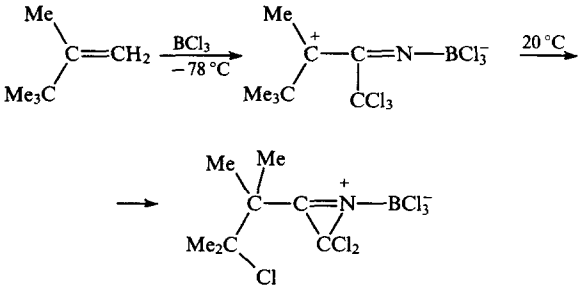
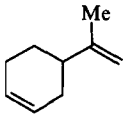
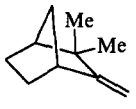


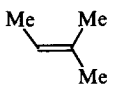
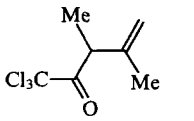
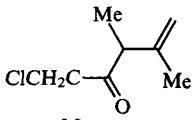
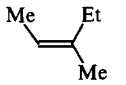
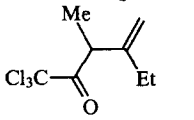
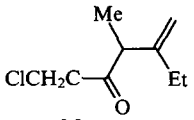
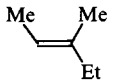
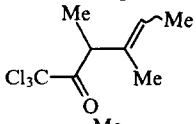
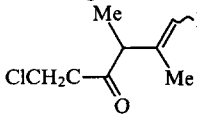
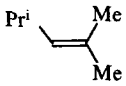
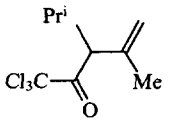
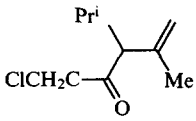
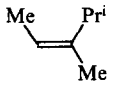
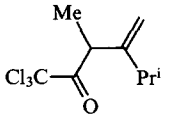
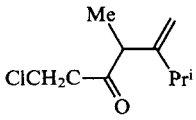
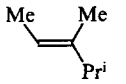
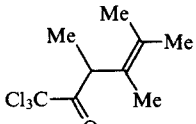
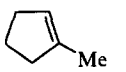
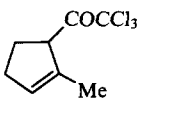
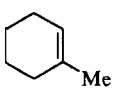
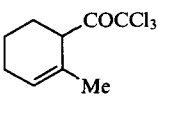
Table 2. The yields and ratios of the products **18** and **19**.

Alkene	Overall yield (%)	Compound **18**: compound **19**
	92	80:20
	90	80:20
	91	86:14
	95	0:100
	89	0:100
	75	0:100

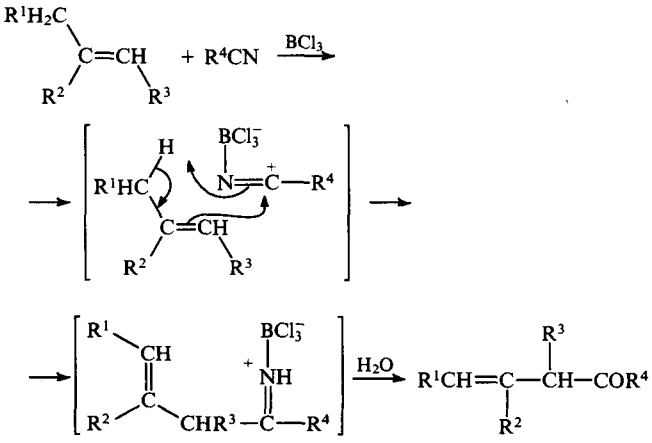
The causes of the different modes of reaction for different alkenes are not discussed in the communication of Hamana and Sugasawa.[57] It is noted that only BCl_3 and BBr_3 are suitable as catalysts. When $AlCl_3$, $TiCl_4$, or $BF_3.OEt_2$ and nitriles with less strongly electron-accepting substituents than CCl_3 are employed, the reaction does not occur.

A different mode of reaction occurs for trisubstituted alkenes. β,γ-Unsaturated ketones are formed exclusively in this instance. It is believed[58] that the reaction proceeds via the 'ene' mechanism.

Table 3. Conditions in the preparation and yields of the β, γ-unsaturated ketones **20**.

Alkene	Nitrile	Product	Yield (%)
	Cl_3CCN		70
	H_2CClCN		74
	Cl_3CCN		76
	H_2CClCN		70
	Cl_3CCN		74
	H_2CClCN		70
	Cl_3CCN		74
	H_2CClCN		71
	Cl_3CCN		74
	H_2CClCN		71
	Cl_3CCN		45
	Cl_3CCN[a]		90
	Cl_3CCN[a]		90

Note. When CCl_3CN was used, the reaction was carried out at −78 °C for 2 h, whereas in the case of $ClCH_2CN$ it was carried out at 20 °C for 20 h.
[a] The reaction time 5 h.

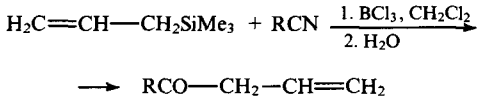


20

Table 3 shows clearly the difference between the reactivities of trichloroacetonitrile and chloroacetonitrile. In the latter case, the reaction requires room temperature and a time longer by a factor of 10.

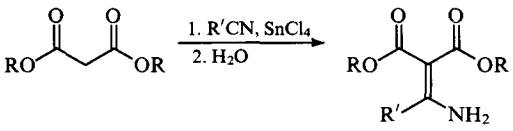
The concerted reaction mechanism of the 'ene' type is confirmed by the rigorous regiospecificity of the reaction. When two possible modes of reaction are possible, the proton is abstracted from the alkyl group located in the *cis*-position relative to the vinyl proton.

In the interaction of trichloroacetonitrile and chloroacetonitrile with allyltrimethylsilane in the presence of BCl_3, allylketones are formed.[59]



R = CCl_3, CH_2Cl.

It has been also observed recently that the complexes of nitriles with tin tetrachloride may be alkylated by malonic acid esters, which leads to the formation of derivatives of α,β-dehydroaminoacids in 20%–60% yields.[60]

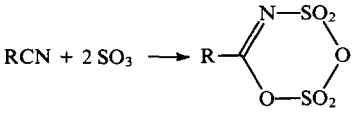


R′ = Me, Et, Ph, CH=CHPh, CH=CHMe.

Thus, although numerous studies were devoted to the investigation of the structures and physicochemical properties of complexes of nitriles with Lewis acids already in the 1960–1970s, the study of their synthetic possibilities as acylating agents is only just beginning.

V. Interaction of nitriles with sulfur trioxide

The interaction of nitriles with sulfur trioxide has been described in detail in the communications of Bodrikov, Michurin, and coworkers.[61,62] Thus it has been shown that the reaction with SO_3, leading to the formation of 1,3,2,4,5-dioxadithiazine 2,2,4,4-tetroxides **21**, is a general reaction of nitriles (Table 4).



21

Table 4. Some characteristics of 1,3,2,4,5-dioxadithiazine 2,2,4,4-tetroxides **21**.

R	Yield (%)	T_m/°C	ν(C≡N)/cm^{-1}
Me	96	40–42	1665
Et	97	46–48	1662
Bu^t	92	57–59	1660
H_2C=C(Me)	95	45–48	1636
CCl_3	98	46–48	1670
CBr_3	92	76–78	1668
$CHCl_2$	97	54–56	1672
Ph	98	81–83	1645
p-MeC_6H_4	97	165–167	1642
p-ClC_6H_4	99	132–134	1650
m-$O_2NC_6H_4$	95	193	1658
p-$O_2NC_6H_4$	96	177–180	1657
3,5-$(O_2N)_2C_6H_3$	98	140–142	1665

For alkylnitriles and nitriles with unsaturated substituents, the reaction temperature varies from −75 to −60 °C, whilst for halonitriles and aromatic nitriles it varies from −40 to −25 °C. The structure of compound **21** has been confirmed by X-ray diffraction.[63]

However, it has been found[64] that 1,3,2,4,5-dioxadithiazine 2,2,4,4-tetroxides are not the primary products of the interaction of SO_3 with nitriles. This is indicated by the hypsochromic shift of ν(C≡N) when nitriles are mixed with SO_3 in CCl_4. The absorption frequencies of the cyano-group of the nitriles (ν) and their mixtures with SO_3 in CCl_4 (ν') are given below.

R	ν(C≡N)/cm^{-1}	ν'(C≡N)/cm^{-1}
Me	2255	2285
Et	2251	2282
Bu^t	2239	2283
H_2C=C(Me)	2232	2262
Ph	2231	2261
p-MeC_6H_4	2231	2260
p-ClC_6H_4	2234	2267
m-$O_2NC_6H_4$	2238	2270
p-$O_2NC_6H_4$	2238	2270
m-MeC_6H_4	2232	2259
p-$MeOC_6H_4$	2229	2258

For nitriles with strongly electron-accepting substituents [R = CCl_3, CBr_3, 3,5-$(NO_2)_2C_6H_3$], the presence of SO_3 does not induce a hypsochromic shift of ν(C≡N) in the IR spectrum but gives rise to a decrease in the intensity of this band.

It has been suggested[64] that the observed changes in the IR spectra of nitriles in the presence of SO_3 should be regarded as the result of the formation of the donor–acceptor complexes **22**.

The initial formation of the donor–acceptor complexes on mixing nitriles with SO_3 has also been confirmed by the observed kinetic features in the formation of the tetroxide **21**. These features are consistent with a two-stage mechanism.[65]

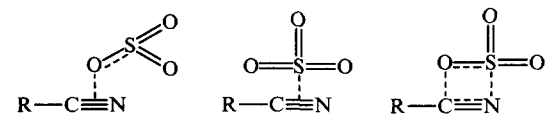
$$RCN + SO_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} RCN\cdot SO_3$$

22

$$RCN\cdot SO_3 + SO_3 \xrightarrow{k_2} \mathbf{21}$$

$k_2 > k_1$.

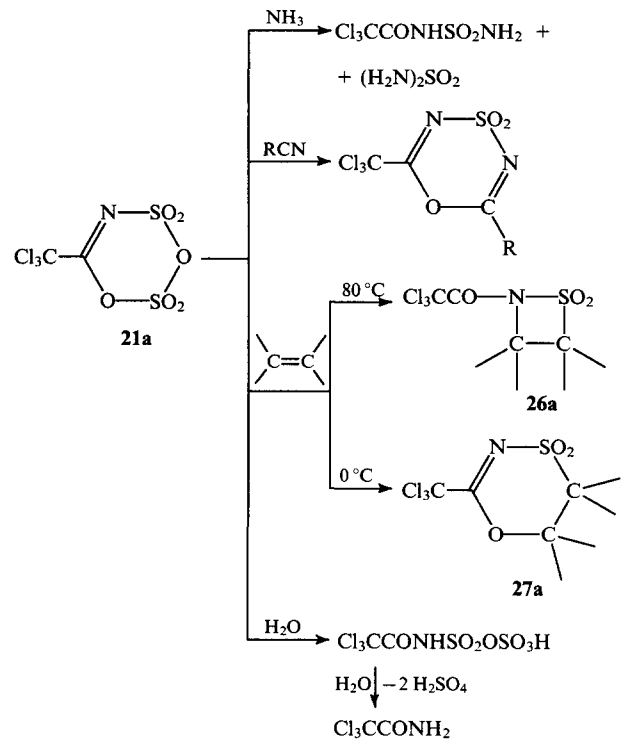
Quantum-chemical analysis of the possible forms of the donor–acceptor complexes of nitriles with SO_3 has shown that the most probable form of the complexes of nitriles having strongly electron-accepting substituents with SO_3 is form **23**, whilst for the remaining nitriles forms **24** and **25** are equally probable.



23 **24** **25**

The chemical properties of 1,3,2,4,5-dioxadithiazine 2,2,4,4-tetroxides depend on the structure of the group R in the nitrile entering into the composition of the tetroxide. Tetroxides having strongly electron-accepting substituents interact with nucleophiles with retention of the C–O bond in the tetroxide (Scheme 1).[6]

Scheme 1



In the interaction of nitriles having strongly electron-accepting substituents with tertiary amines, the dipolar compounds **29** are formed. Their structure has been demonstrated by X-ray diffraction.[67]

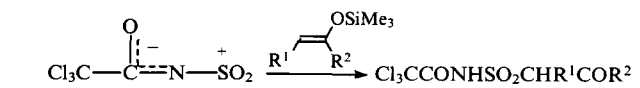
$$\mathbf{21} + NEt_3 \xrightarrow[-SO_3\cdot NEt_3]{} R{-}\overset{O}{\overset{\|}{C}}{=}\overset{-}{\underset{|}{}}\!\!N\!\!\overset{+}{\underset{|}{}}{-}SO_2$$

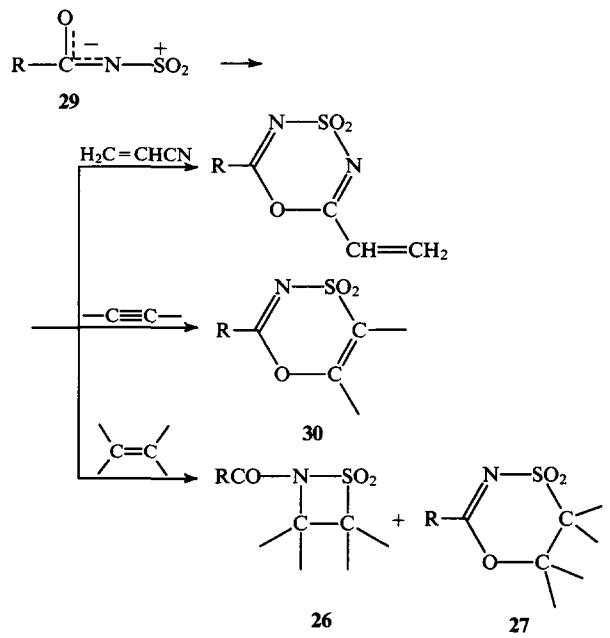
29

R = CCl_3, CBr_3, 3,5-$(O_2N)_2C_6H_3$.

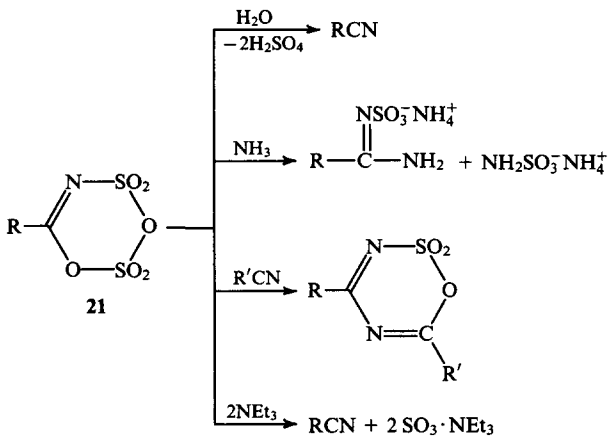
Like the tetroxides **21**, compound **29** reacts with unsaturated compounds.[68]

The formation of compounds **26** may be detected only when trimethylethene or styrene is used as the substrate. In all the remaining cases (in the reactions with allyl chloride, allylbenzene, *p*-methylallylbenzene, *p*,β-dimethylstyrene, isoprene, phenylethyne, diphenylethyne, and *tert*-butylethyne), the [4+2]-cycloaddition reaction takes place with formation of compound **27** or **30** respectively.[69] The interaction of compounds **29** with the trimethylsilyl ethers of enols proceeds with formation of 2-oxosulfonamides.

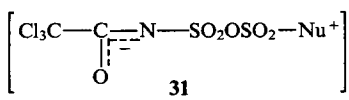




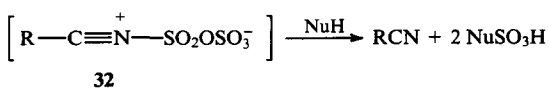
On the other hand, tetroxides containing electron-donating and weakly electron-accepting substituents react with nucleophiles with dissociation of the C–O bond.[63–65]



It has been suggested[65] that the observed differences in the behaviour of tetroxides **21** with strongly electron-accepting substituents and with electron-donating or weakly electron-accepting substituents are due to the fact that in the former case the reaction proceeds via the relatively stabilised intermediate **31**.



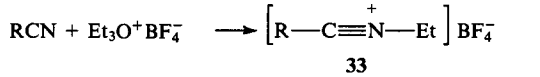
On the other hand, in the case of electron-donating substituents, the formation of the azacarbenium type intermediate **32**, the decomposition of which affords the initial nitrile, proves to be favourable.[65]



VI. Alkylation of nitriles. Alkylnitrilium salts

Meerwein et al.[69] reported in 1956 the synthesis of a large number of alkylnitrilium salts for nitriles and various alkylating agents. This study still remains the main source of information about alkylnitrilium salts.

Alkylnitrilium salts may be obtained by the reaction of nitriles with triethyloxonium tetrafluoroborate followed by the removal of ether (Table 5).[70]

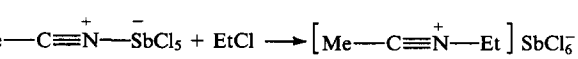


Nitrilium tetrafluoroborates and tetrachloroaluminates are extremely hygroscopic, deliquesceing in air almost instantaneously. The composition of the compounds obtained has been confirmed by elemental analysis for the halogen.

Table 5. The alkylnitrilium salts obtained by alkylating nitriles with triethyloxonium salts.

Alkylnitrilium salt	T_{decomp}/°C	Yield (%)
$[MeC{\equiv}N^+Et]BF_4^-$	—	89
$[EtC{\equiv}N^+Et]BF_4^-$	68–75	70
$[PhC{\equiv}N^+Et]BF_4^-$	92–98	64
$[PhC{\equiv}N^+Et]SbCl_6^-$	170–172	64
$[PhC{\equiv}N^+Et]AlCl_4^-$	—	36

Nitrilium salts can also be obtained from complexes of nitriles with Lewis acids and alkyl halides.[69]



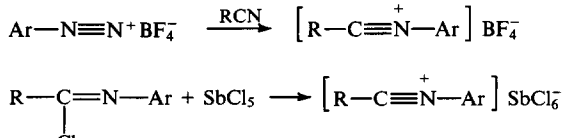
The alkylation time then depends on the ease of the formation of the carbonium ion from the alkyl halide (Table 6).

Table 6. Conditions in the alkylation of the complex $PhCN^+ - SbCl_5^-$.

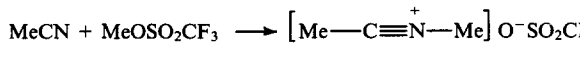
Alkyl chloride	Nitrilium salt	PhCN : RCl	Time	Yield (%)
EtCl	$PhCN^+ - Et\,SbCl_6^-$	1 : 12	1 month	75
Pr^iCl	$PhCN^+ - Pr^i\,SbCl_6^-$	1 : 10	1 month	83
Bu^tCl	$PhCN^+ - Bu^t\,SbCl_6^-$	1 : 2.2	1 min	90

This method of synthesis of alkylnitrilium salts is extremely convenient and is widely used on the preparative scale.

The methods described above are not suitable for the synthesis of *N*-arylnitrilium salts, and the latter are therefore synthesised by the interaction of nitriles with arenediazonium salts or by treating iminohalo-derivatives with Lewis acids.[70]

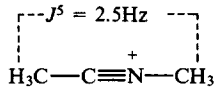


The synthesis of alkylnitrilium triflates by the interaction of nitriles with methyl triflate has been reported:[70]



The structure of alkylnitrilium salts has been investigated by IR and NMR spectroscopy. The IR spectra of alkylnitrilium

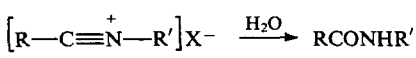
salts, like those of the protonated nitriles and their complexes with Lewis acids,[21,70,71] exhibit an 80–100 cm^{-1} hypsochromic shift of $\nu(C\equiv N)$. It has been suggested that this finding indicates unambiguously that the main contribution to the structure of the nitrilium salts comes from the form with the charge localised on the nitrogen atom.[71] The ^1H NMR spectra of the nitrilium salts indicate the existence of spin–spin coupling between the alkyl group at the nitrogen atom and the α-protons of the nitrile.[21]



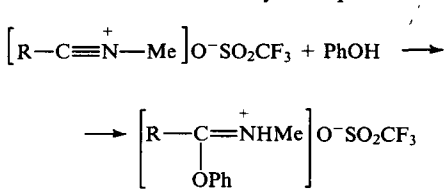
δ = 2.67 ppm δ = 3.66 ppm

The linear structure of the alkylnitrilium ions has been confirmed by an X-ray diffraction study of *N*-(2,6-dimethylphenyl)acetonitrilium tetrafluoroborate.[72]

N-Alkyl- and *N*-aryl-nitrilium salts interact with nucleophiles at the nitrile carbon atom. For example, their hydrolysis leads to *N*-alkylamides.[69]

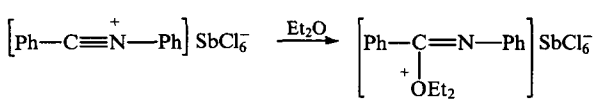


Nitrilium salts react similarly with phenol.[70]

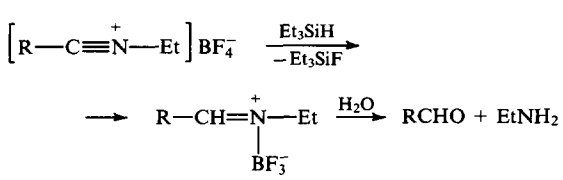


R = Me, Ph.

An unstable compound of an *N*-arylnitrilium salt with ether has been obtained.[69]

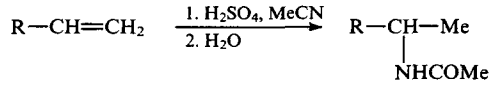


The interaction of *N*-alkylnitrilium salts with triethylsilane leads to the formation of aldehydes and amines.[73]

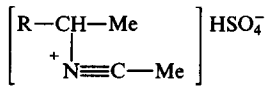


VII. The Ritter reaction

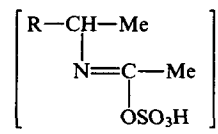
The classical version of the Ritter reaction involves the alkylation of nitriles by the carbonium ions generated in an acid medium from alkenes and alcohols with subsequent hydrolysis, which leads to *N*-alkylamides.[74,75]



The reaction mechanism presupposes the intermediate formation of the alkylnitrilium salt **34**.



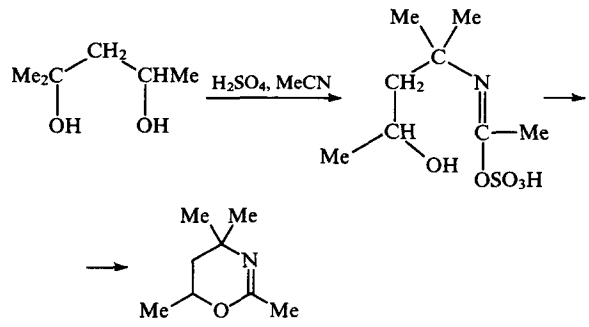
34



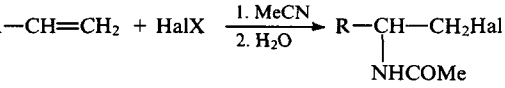
35

However, the direct detection of such intermediates in the Ritter reaction has not so far been reported in the literature. Bearing in mind the complexity of the chemical behaviour of nitriles in acid media (see Section I), it is fairly difficult to imagine the true reaction mechanism. The majority of investigators, including Ritter himself, prefer to represent the intermediate by formula **35** with a covalently bound anion.

The development of the synthetic possibilities of the Ritter reaction arose primarily from its use in the reaction of the nitrile with molecules having a variety of functional groups. Thus heterocyclic compounds may be synthesised by the Ritter reaction.[76,77]

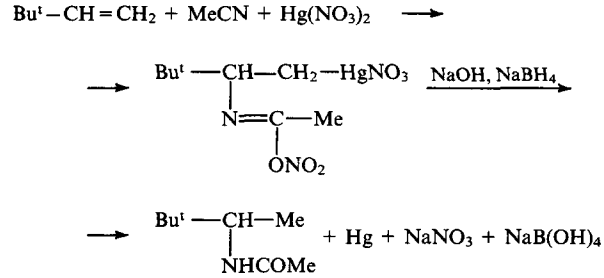


Another direction in the synthetic development of the Ritter reaction involved the employment of electrophiles other than the proton. For example, the halogens have been used as the electrophiles.[78–80]

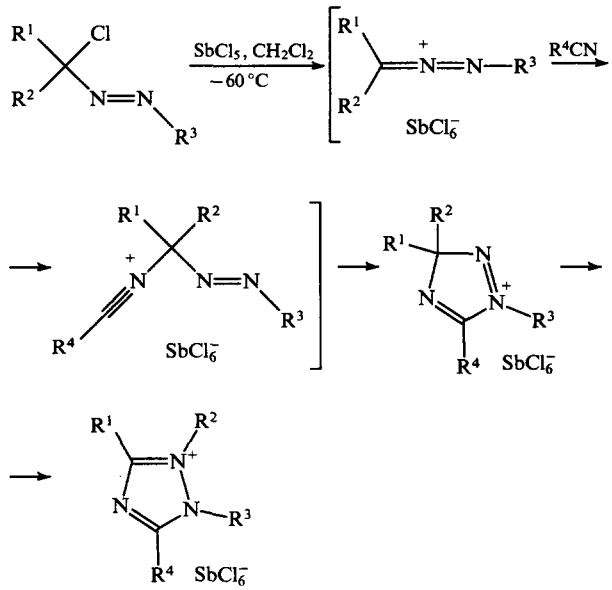


Hal = Cl, Br; X = Cl, Br, OH, N_3, HCONH, ClNCOOEt.

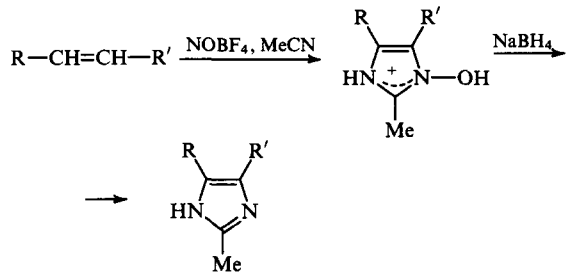
The use of mercury(II) nitrate and acetonitrile leads ultimately to the same products as the Ritter reaction, but makes it possible to avoid acid conditions. The value of this approach has been demonstrated in the reaction of acetonitrile with *tert*-butylethene, which occurs without a skeletal rearrangement.[81]



The diversity of the carbonium ions capable of allylating nitriles is well illustrated by their reactions with 1-aza-2-azonioallene salts.[82]

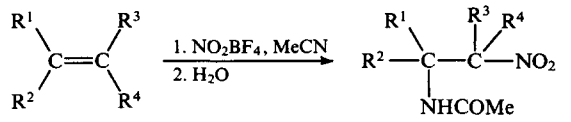


An interesting example of a modified Ritter reaction is the interaction of nitrosonium[83] and nitronium[84,85] tetrafluoroborates with alkenes. The yield of the imidazole derivatives depends on the structure of the alkene.

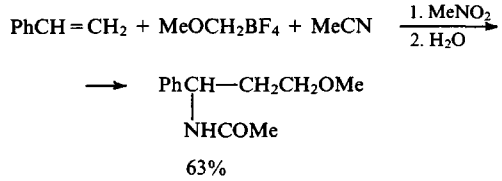


R = Me, R′ = H (80%); R = R′ = Me (80%);
R = Ph, R′ = H (50%); R + R′ = $(CH_2)_4$ (50%).

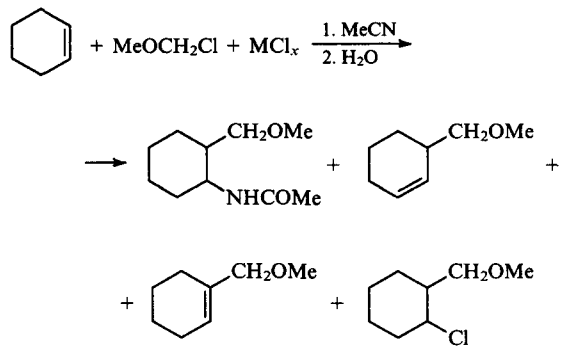
Nitronium tetrafluoroborate interacts with alkenes in acetonitrile, giving rise to β-*N*-acylaminonitro-derivatives after hydrolysis.[84,85] The best yields in this reaction (80%–90%) have been obtained for substituted styrenes.[85]



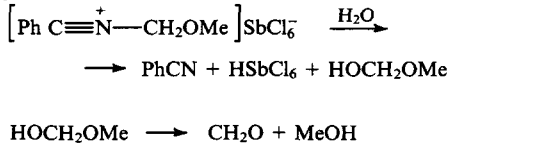
The reaction involving the coupled formation of C–C and C–N bonds is of special interest. It was first described[86] in relation to styrene.



The possibility of the employment of the chloromethoxymethane–Lewis acid–acetonitrile system for this reaction was investigated in a later study,[87] but the yields of the target products do not exceed 40% in this instance and the formation of side products is observed.



It is interesting to note that, according to Meerwein's data, alkylnitrilium salts of the type $[Me-C\equiv N-CH_2.OMe]^+X^-$ should be formed under the conditions of the last two reactions. However, in contrast to the remaining known nitrilium salts, their interaction with a nucleophile (in the given instance with an alkene) involves an alkyl and not the nitrile carbon atom. This finding agrees well with Meerwein's data for the interaction of a similar alkylnitrilium salt with water. This was the only instance in which he observed that hydrolysis entailed the formation of the initial nitrile and not an *N*-alkylamide.[69]

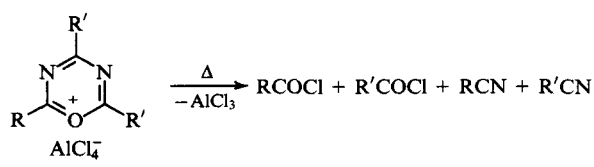


VIII. Acylation of nitriles. Acylnitrilium salts

The syntheses of a series of acylnitrilium salts via the acylation of a series of complexes of nitriles with Lewis acids by acyl halides have been described in Meerwein's classical paper.[69] The compositions of the reaction products were confirmed by elemental analysis for the halogen.

PhCN·$PhCOZnCl_3$ (**36**),
2 PhCN·$PhCOAlCl_4$ (**37**),
2 PhCN·$PhCOSbCl_6$ (**38**),
2 MeCN·$MeCOSbCl_6$ (**39**),
2 PhCN·$PhSO_2SbCl_6$ (**40**),
3 PhCN·$MeCOSbCl_6$ (**41**),
3 PhCN·$(PhCO)_2SnCl_4$ (**42**),
3 PhCN·$MeCOAlCl_4$ (**43**).

Meerwein et al.[69] believe that the acylnitrilium salt PhCN.$PhCOZnCl_3$ **36** constitutes benzonitrile acylated at the nitrogen atom. They attribute the structure of the diazapyrylium salts **44** to the salts **37**–**40**, which has been confirmed by their thermal decomposition, in which exchange of substituent groups is observed.

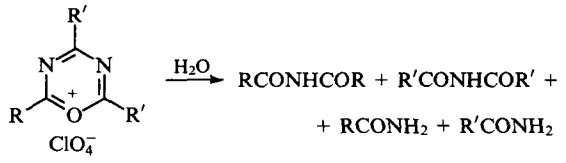


44

For complexes **41**–**43**, the authors consider the structure of acylated triazines, but they present no data whatever to confirm this hypothesis.

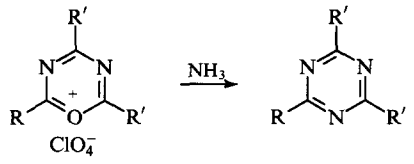
In Schmidt's study,[88] the structure of aryldiazapyrylium salts obtained by Meerwein's method, involving the heating of the

benzonitrile–Lewis acid complex with an acyl halide, was confirmed by a series of chemical reactions. Thus their hydrolysis leads to a mixture of two amides and two acylamides.



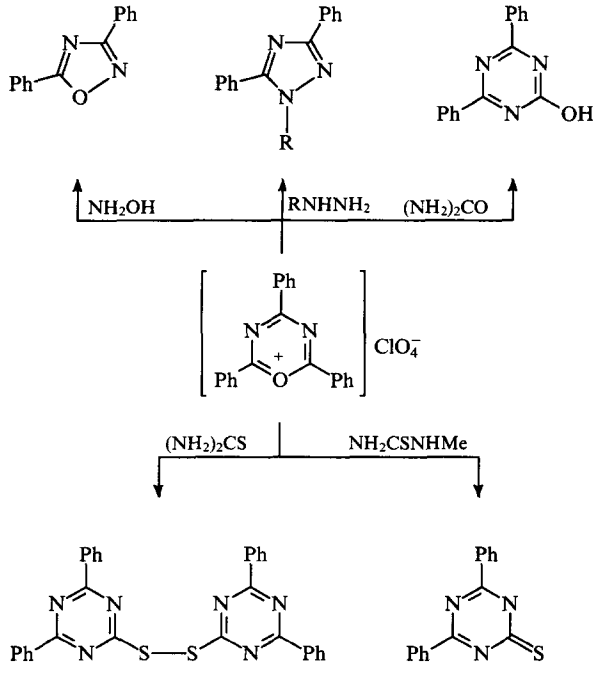
R, R′ = Ar.

Reaction with ammonia converts the diazapyrylium salts into triazines.

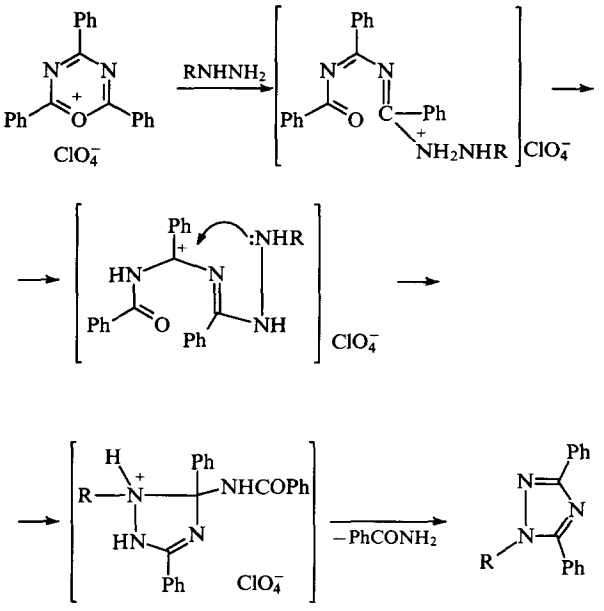


R, R′ = Ar.

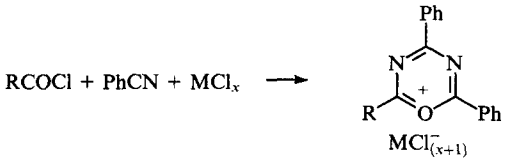
Schmidt also observed a series of reactions of triphenyldiazapyrylium perchlorate, which take place with elimination of benzamide.



Apparently the primary attack by the nucleophile is directed to the nitrile carbon atom linked to oxygen.



The IR spectra of a series of diazapyrylium salts synthesised by the interaction of acyl halides with Lewis acids and benzonitrile in nitrobenzene, dichloroethane, or without a solvent have been investigated.[89]

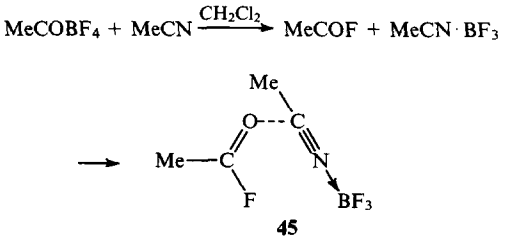


R = Me, Ph, CH_2Cl; MCl_x = $SbCl_5$, $SbCl_3$, $SnCl_4$.

It is of interest to note the differences between the conditions in the synthesis of the diazapyrylium salts mentioned by Sumarokova et al.[89] Thus the reaction of the complex $PhCN.SbCl_5$ with acyl halides takes place rapidly at room temperature, whereas the synthesis of the diazapyrylium salts involving the use of $SnCl_4$ or $SbCl_3$ as the Lewis acid requires prolonged maintenance at 80 °C and the yields of the target products are in this case lower.

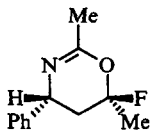
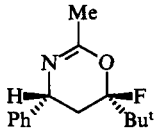
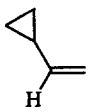
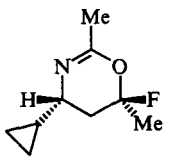
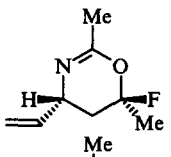
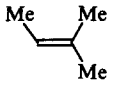
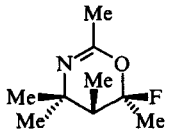
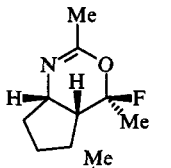
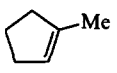
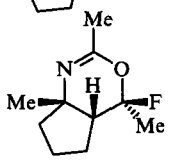
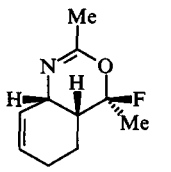
The diazapyrylium salts have been obtained in the form of yellow or orange crystals; their structure has been confirmed by measurements of the molecular mass (by the cryoscopic method), by elemental analysis, and by IR spectroscopy. The IR spectra of the diazapyrylium salts contain no absorption bands above 1650 cm^{-1}, but they do contain a group of bands in the region 1540–1640 cm^{-1}, which Sumarkova et al.[89] assigned to the diazapyrylium ring vibrations.

The interaction of acetyl tetrafluoroborate with acetonitrile in methylene chloride has been studied in detail.[90] It was shown by NMR spectroscopy that this interaction involves the transfer of boron trifluoride from acetyl fluoride to acetonitrile, which leads to the reformation of complex **45**, in which the oxygen atom of the acetyl fluoride is coordinated to the electrophilic carbon atom of the complex $MeCN.BF_3$.

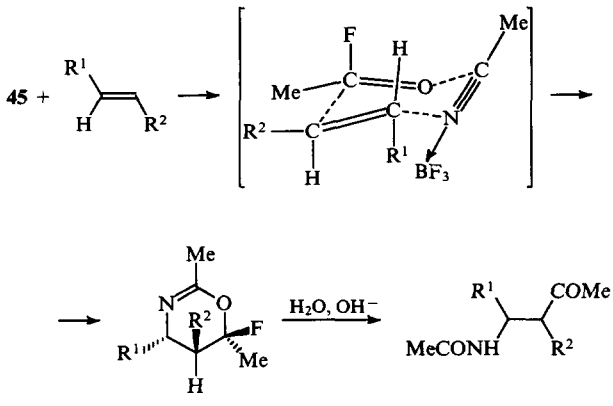


45

Table 7. The structure of the fluorooxazines obtained by the acylamidation reaction.

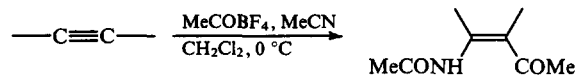
Reagent	T/°C	Product	Yield (%)
	0		62
	0		52
	−10		35
	−10		33
	0		57
	0		48[a]
	0		66[a]
	−20		25[b]

[a] Approximately 20% of the corresponding 3-acetylcyclopentene was isolated. [b] The low yield is due to the polymerisation of the product.

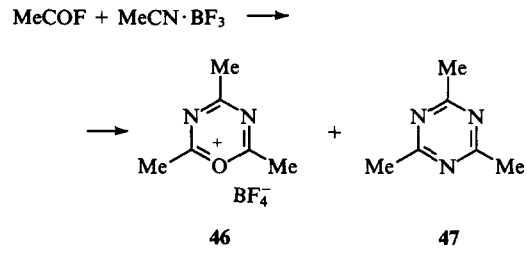


The formation of complex **45** is confirmed by the fact that, when an unsaturated hydrocarbon is added to the MeCOF–MeCN–BF_3 system, the acylamidation reaction, leading to the *syn*-stereospecific formation of the corresponding 6-fluoro-5,6-dihydro-1,3-oxazines, takes place (Table 7).[90–94]

The reactions with ethynes, which give stereospecifically products of the *syn*-acylamidation of the triple bond, take place similarly (Table 8).[95]



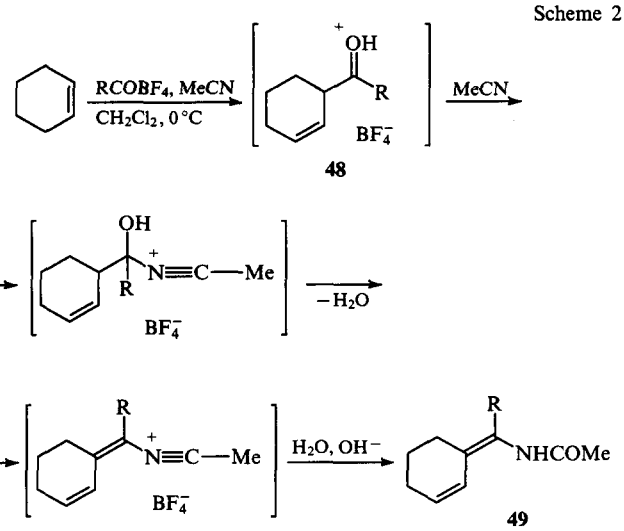
When the MeCOF–MeCN–BF_3 system is kept for a long time in a sealed tube, the formation of a dark-red solution, containing the diazapyrylium salt **46** and the triazine **47**, is observed. This solution does not interact with unsaturated hydrocarbons.[90]



46 **47**

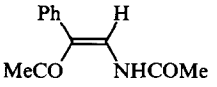
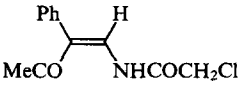
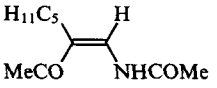
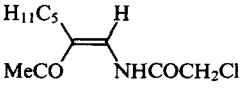
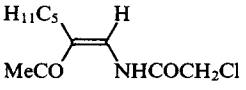
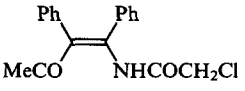
The complexity of the processes occurring in the acyl fluoride–nitrile–boron trifluoride system is indicated by the results of a study of the influence of the structure of the unsaturated substrate on the nature of the acylamidation reaction.[96–98] For example, in contrast to cyclopentene, cyclohexene does not afford 1,2-adducts on interaction with the MeCOF–MeCN–BF_3 system. The diene amide **49**, isolated in this reaction (Scheme 2), is formed via the interaction of the protonated unsaturated ketone **48** with the nitrile.[96] Thus in certain cases complex **45** can function also as an acylating agent.

Scheme 2



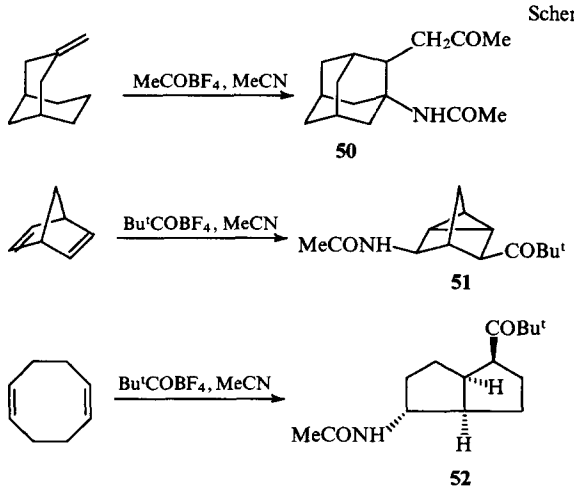
Nonconjugated cyclic dienes interact with the acyl fluoride–nitrile–boron trifluoride system to form the polycyclic amides **50–52**, which are the products of transannular cyclisation (Scheme 3).[97,98] The acylating properties of complex **45** are apparently also manifested in these reactions, but the unusually high stereospecificity observed in these reactions[98,99] may be evidence that in this case too the nitrile does not behave simply as an external nucleophile, participating in some way in the transition state of the reaction.[98]

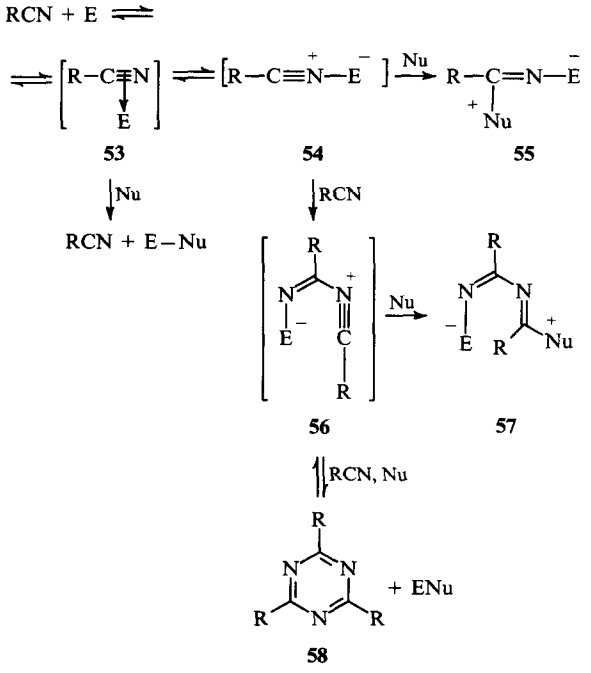
Table 8. The acylamidation of ethynes.

Ethyne	Nitrile	Conditions		Product	Yield (%)
		T/°C	time/h		
Ph–C≡CH	MeCN	20	1		35
Ph–C≡CH	$ClCH_2CN$	0	1		41
n-C_5H_{11}–C≡CH	MeCN	20	1		45
n-C_5H_{11}–C≡CH	$ClCH_2CN$	0	1		39
Ph–C≡C–Ph	MeCN	42[a]	—		0
		42[a]	—		44

[a] The reaction was carried out by refluxing in CH_2Cl_2.

Scheme 3





IX. Conclusion

In conclusion of the consideration of the reactions of nitriles with electrophiles, mention should be made of the fact that they are common to different electrophiles.

The majority of investigators believe that the primary products of the interaction of nitriles with electrophiles are donor–acceptor complexes **53**. A sufficiently strong interaction between the nitrile and the electrophile has not yet been manifested in these π-complexes, so that their treatment with nucleophiles leads to the regeneration of the nitrile. Under appropriate conditions (usually at higher temperatures), the π-complexes **53** are converted into the n-complexes **54**. The n-complexes **54** have a linear structure, their C≡N bond is shortened, and attack by the nucleophile is directed to the nitrile carbon atom with formation of type **55** compounds.

Under favourable conditions (usually in those cases where R is a fairly strong electron-accepting substituent), the second nitrile molecule behaves as the nucleophile and the dimeric salts **56** are formed. These may be stabilised by interaction with the former electrophile, affording compounds having the general formula **57**. Attack by the nucleophile in its interaction with compound **57** is usually directed to the nitrile carbon atom of the second nitrile molecule. Finally, the triazine **58** may be formed; this reaction path is also favoured by electron-accepting substituents R.

The understanding of the by no means simple pattern in the interaction of nitriles with electrophiles, achieved only recently, makes it possible to seek new reactions of nitriles, which will undoubtedly enrich synthetic organic chemistry.

References

1. E N Zil'berman *Reaktsii Nitrilov* (Reactions of Nitriles) (Moscow: Khimiya, 1972)
2. S Patai (Ed.) *Chemistry of the Cyano Group* (New York: Wiley-Interscience, 1970)
3. Yu N Kukushkin *Koord. Khim.* **7** 323 (1981)
4. A A Michurin, V L Krasnov, I V Bodrikov *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* **20** 1744 (1977)
5. G Klopman (Ed.), in *Chemical Reactivity and Reaction Paths* (New York: Wiley-Interscience, 1974) (Translated into Russian; Moscow: Mir, 1977) p. 128
6. F E Murray, W G Schneider *Can. J. Chem.* **33** 797 (1955)
7. J Janz, S S Danyluk *J. Am. Chem. Soc.* **81** 3854 (1959)
8. E N Zil'berman, T S Ivcher, E M Perepletchikova *Zh. Obshch. Khim.* **31** 2037 (1961)
9. M E Peach, T C Waddington *J. Chem. Soc.* 600 (1962)
10. N C Deno, R W Gangler, M J Wisotsky *J. Org. Chem.* **31** 1967 (1966)
11. B L Booth, G F Noori *J. Chem. Soc., Perkin Trans. 1* 2894 (1980)
12. E Allenstein, A Schmidt *Spectrochim. Acta* **20** 1451 (1964)
13. F Klages, R Ruhnau, W Hauser *Liebigs Ann. Chem.* **626** 60 (1959)
14. F Klages, W Grill *Liebigs Ann. Chem.* **594** 21 (1955)
15. A Hantzsch *Berichte* **64** 667 (1931)
16. G Simchen, W Kramer *Berichte* **102** 3656 (1969)
17. Sh Yanadiga, S Komori *Synthesis* 189 (1973)
18. Sh Yanadiga, S Ohoka, S Komori *J. Org. Chem.* **34** 4127 (1969)
19. C Grundmann, G Wiese, S Seide *Liebigs Ann. Chem.* **577** 77 (1952)
20. E N Zil'berman, F Ya Lazaris *Zh. Org. Khim.* **31** 1321 (1961)
21. F Ya Lazaris, E N Zil'berman, O N Strizhakov *Zh. Org. Khim.* **32** 900 (1962)
22. G A Olah, T E Kiovsky *J. Am. Chem. Soc.* **90** 4666 (1968)
23. M Yato, T Ohwada, K Shudo *J. Am. Chem. Soc.* **113** 691 (1991)
24. B N Storhoff, H C Lewis *Coord. Chem. Rev.* **23** 1 (1977)
25. J R Stricklev, D E Wigley *Organometallics* **9** 1665 (1990)
26. H Shumann, M Speis, W P Bosman, J M M Smits, P T Beurskens *J. Organomet. Chem.* **403** 165 (1991)
27. N C Stephenson *J. Inorg. Nucl. Chem.* **24** 801 (1962)
28. R Ros, J Renald, R Roulet *J. Organomet. Chem.* **104** 393 (1976)
29. S Komiya, S Suzuki, K Watanabe *Bull. Chem. Soc. Jpn.* **44** 1440 (1971)
30. P F B Barnard *J. Chem. Soc., A* 2140 (1969)
31. M A Bennet, T Yoshida *J. Am. Chem. Soc.* **95** 3030 (1973)
32. P Diversi, L Ermini, G Ingrosso, A Lucherini *J. Organomet. Chem.* **447** 291 (1993)
33. J Yarwood *Spectroscopy and Structure of Molecular Complexes* (New York: Plenum, 1973)
34. M Herberhold, H Brabetz *Berichte* **103** 3896 (1970)
35. F Hohman, H T Diek *J. Organomet. Chem.* **9** 495 (1975)
36. O M Titova, V K Bel'skii, A A Michurin, I V Bodrikov *Zh. Org. Khim.* **24** 670 (1988)
37. J A Maguire, J J J Banewicz *J. Phys. Chem.* **76** 2098 (1973)
38. K Kimura, I Achiba, S Kastumata *J. Phys. Chem.* **76** 2098 (1973)
39. G E Hawkes, J H P Utley *J. Chem. Soc., Perkin Trans. 2* 128 (1973)
40. H J Coerver, C J Curran *J. Am. Chem. Soc.* **80** 3522 (1958)
41. W Gerrard, M F Lappert, H Piszora, W J Wollis *J. Chem. Soc.* 2182 (1960)
42. A Terenin, W Filimonow, D Bystrow *Z. Electrochem.* **62** 180 (1958)
43. J C Evans *J. Chem. Soc., A* 1849 (1969)
44. H Webster, H E Bluden *J. Chem. Soc., A* 2443 (1969)
45. T L Brown, M J Kibota *J. Am. Chem. Soc.* **83** 331 (1961)
46. Yu F Kharitonov, Kh U Ikramov, A B Babaeva *Zh. Neorg. Khim.* **10** 2424 (1965)
47. A D Pomogailo, I L Leonov *Dokl. Akad. Nauk SSSR* **202** 1083 (1972)
48. W F Newton, J E Searles *Inorg. Chim. Acta* **7** 349 (1973)
49. G W A Fowles, K F Cadd *J. Chem. Soc. A* 2232 (1970)
50. M F Farona, G R Tompkin *Spectrochim. Acta, Part A* **24** 788 (1968)
51. A P Hamer, R A Walton *Synth. React. Inorg. Metal-Org. Chem.* **4** 573 (1974)
52. R P Cooney, P B Fraser *Aust. J. Chem.* **27** 1885 (1974)
53. G Rouschias, G Wilkinson *J. Chem. Soc. A* 489 (1968)
54. R A Walton *Quart. Rev.* **19** 126 (1965)
55. D E Shriver, B Swanson *Inorg. Chem.* **10** 1354 (1971)
56. I R Beattie, T J Gilson *J. Chem. Soc.* 2292 (1964)
57. H Hamana, T Sugasawa *Chem. Lett.* 571 (1985)
58. H Hamana, T Sugasawa *Chem. Lett.* 575 (1985)
59. H Hamana, T Sugasawa *Chem. Lett.* 921 (1985)
60. F Scavo, P Helquist *Tetrahedron Lett.* **26** 2603 (1985)
61. A A Michurin, E A Sivenkov, E N Zil'berman *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* **12** 1534 (1969)
62. I V Bodrikov, A A Michurin, V L Krasnov *Zh. Org. Khim.* **11** 2217 (1975)
63. V K Bel'skii, A A Michurin, A V Zhivoderov, I V Bodrikov *Dokl. Akad. Nauk SSSR* **268** 1399 (1983)
64. I V Bodrikov, E A Lyapdaev, A A Michurin *Zh. Org. Khim.* **13** 1965 (1977)
65. A A Michurin, V L Krasnov, I V Bodrikov *Zh. Org. Khim.* **11** 2448 (1975)
66. I V Bodrikov, G B Sergeev, A A Michurin, V L Krasnov, V V Smirnov *Dokl. Akad. Nauk SSSR* **227** 863 (1976)
67. V K Belsky, I V Bodrikov, A A Michurin, L I Chumakova, A V Zhivoderov *Tetrahedron Lett.* **26** 5689 (1986)
68. A A Michurin, I V Bodrikov, V K Bel'skii, O M Titova, A V Zhivoderov *Zh. Org. Khim.* **24** 1978 (1988)
69. H Meerwein, P Laasch, R Mersch, J Spille *Berichte* **89** 209 (1956)
70. B L Booth, K O Jibodi, M F Proenca *J. Chem. Soc., Perkin Trans. 1* 1067 (1983)
71. A F Hegarty *Acc. Chem. Res.* **13** 448 (1980)
72. A K Gjoystdal, Ch Romming *Acta Chem. Scand., Ser. B* **31** 56 (1977)
73. G L Fry, R A Ott *J. Org. Chem.* **46** 602 (1980)
74. J J Ritter, P P Mimieri *J. Am. Chem. Soc.* **70** 4045 (1948)
75. J J Ritter, P P Mimieri *J. Am. Chem. Soc.* **70** 4048 (1948)
76. E J Tillmans, J J Ritter *J. Org. Chem.* **22** 839 (1957)
77. A A Gevorkyan, G G Tokmadzyan *Arm. Khim. Zh.* **30** 269 (1977)
78. L I Krimen, D J Cota *Org. React.* **17** 246 (1969)
79. F Boerwinkle, A Hassner *Tetrahedron Lett.* **9** 3921 (1968)
80. Y Wada, R Oda *Bull. Chem. Soc. Jpn.* **43** 2167 (1970)
81. H C Brown, J T Kurek *J. Am. Chem. Soc.* **91** 5647 (1969)
82. Q Wang, J C Jochims, S Köhlbrandt, L Dahlenburg, M Al-Talib, A Hamed, A El-H Ismail *Synthesis* 710 (1992)
83. M L Scheinbaum, M B Dines *Tetrahedron Lett.* **12** 2205 (1971)
84. M L Scheinbaum, M B Dines *J. Org. Chem.* **36** 3641 (1971)
85. A J Bloom, M Fleischman, J M Mellor *J. Chem. Soc., Perkin Trans. 1* 2357 (1984)
86. W A Smit, A V Semenovsky, V F Kucherov, A T Chernova, M Z Krimer, O V Lubinskaya *Tetrahedron Lett.* **12** 3101 (1971)
87. Y Wada, T Yamazaki, K Nishiura, S Tanimoto, M Okano *Bull. Chem. Soc. Jpn.* **51** 1821 (1978)
88. R R Schmidt *Berichte* **98** 334 (1965)
89. T N Sumarokova, R A Slavitskaya, I G Litvyak, N Yu Vykhrest *Zh. Obshch. Khim.* **50** 2331 (1980)
90. I D Gridnev, A V Shastin, E S Balenkova *Tetrahedron* **29** 5577 (1991)
91. A V Shastin, E S Balenkova *Zh. Org. Khim.* **20** 1357 (1984)
92. I D Gridnev, A V Shastin, E S Balenkova *Zh. Org. Khim.* **23** 1546 (1987)
93. I D Gridnev, A V Buevich, N M Sergeyev, T S Balenkova *Tetrahedron Lett.* **30** 1987 (1989)
94. I D Gridnev, E S Balenkova *Zh. Org. Khim.* **26** 46 (1990)
95. I D Gridnev, E S Balenkova *Zh. Org. Khim.* **24** 1605 (1988)
96. I D Gridnev, E S Balenkova *Zh. Org. Khim.* **26** 50 (1990)
97. V K Gubernatorov, V A Sokolenko, I D Gridnev, E S Balenkova *Zh. Org. Khim.* **24** 892 (1988)
98. I D Gridnev, E S Balenkova, A V Buevich *Zh. Org. Khim.* **26** 760 (1990)
99. I D Gridnev, I F Leshcheva, N M Sergeyev, V A Chertkov *Magn. Reson. Chem.* **30** 817 (1992)