Peculiarities of interaction of H^+, Me_3C^+, and Me_3Si^+ ions with multifunctional molecules in the gas phase

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Peculiarities of interaction of H^+, Me_3C^+, and Me_3Si^+ ions with functional groups of molecules in the gas phase have been studied. Proton tends to form chelates with virtually all of the functional groups studied, whereas Me_3Si^+ ions exhibit no capacity for chelation. Using isomeric xylenes as examples it was shown that Me_3Si^+ ions (unlike Me_3C^+ ions) experience virtually no steric hindrance when they react with nucleophilic centers. Effects of functional groups present in molecules of nitriles on the generation of $[M+Me_3C]^+$ adducts in the gas phase and the Ritter reaction in solution were estimated.

Key word: mass spectrometry, chemical ionization; chelation, steric effects; Ritter reaction; nitriles.

Peculiarities of the interaction of electrophiles such as H^+, Me_3C^+, and Me_3Si^+ with polyfunctional molecules are determined by their size, tendency for chelation and migration, and also by the ability of the Me_3C^+ ion to form not only $[M+Me_3C]^+$ adducts, but also protonated molecular ions (PMI) with a substrate. The ratio between the latter compounds is, in turn, determined by the basicity and nucleophilicity of the substrate.

In the present work we used high-pressure chemical ionization (CI) to study susceptibilities of electrophiles with various functional groups to chelation and the role of steric effects in the formation of adducts of polyfunctional molecules with Me_3C^+ and Me_3Si^+ ions. We also estimated the general influence of the functional groups present in a molecule of a nitrile on the generation of $[M+Me_3C]^+$ adducts in the gas phase and on the Ritter reaction in solution.

Experimental

Mass spectra were obtained on a Kratos MS-30 mass spectrometer (with an energy of ionizing electrons of 200 eV and a temperature of the ion source of 150 °C). Constant pressure of the reacting gas (0.2 Torr) was maintained by using an external manometer installed on the system for its bleeding. Tetramethylsilane (Merck) of 99.7 % purity and isobutane (produced by the pilot plant of the Scientific Research Institute of Gas) with a 99.8 % content of the main compound were used. The samples were delivered through a direct injection system or through a heated direct injection bar with a heated bleeding cylinder. Data on the preparation and purity of studied compounds **1—47** have been published previously.[1]

Results and Discussion

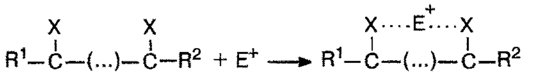
Protons are known to tend to form chelate structures,[2] whereas there is virtually no information on the generation of similar structures involving Me_3C^+ or Me_3Si^+ ions. However, whereas participation of a *tert*-butyl ion in chelate formation is very unlikely, the Si atom in a trimethylsilyl ion is in principle able to interact with two nucleophilic centers.[3]

An electrophile (E^+) adds to a monofunctional molecule RX at the functional group X. At high concentrations of substrate molecules in the ionization chamber of a mass spectrometer, generation of dimers is also possible (Eq. (1)).

$$R{-}X \xrightarrow{E^+} R{-}\overset{+}{X}{-}E \xrightarrow{RX} \underset{\textbf{A}}{R{-}X{\cdots}\overset{+}{E}{\cdots}X{-}R} \qquad (1)$$

$E = H, Me_3Si$

The formation of protonated dimers is a well known process.[4] Similar proton bridges may also arise within a molecule that contains several functional groups[2] (Eq. (2)).



$$R^1{-}\overset{X}{\overset{|}{C}}{-}(\ldots){-}\overset{X}{\overset{|}{C}}{-}R^2 + E^+ \longrightarrow R^1{-}\overset{X\cdots\overset{+}{E}\cdots X}{\overset{|\qquad\qquad|}{C{-}(\ldots){-}C}}{-}R^2 \qquad (2)$$

B

We studied the ability of various monofunctional derivatives of aliphatic compounds **1—14** (Table 1) to

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Table 1. Intensities of the peaks of $[M+E]^+$, $[2M+E]^+$, and R^+ ions ($E = H, Me_3Si^+$) in CI mass spectra (isobutane or tetramethylsilane as the reacting gas) of compounds **1—14**

Compound		Isobutane						Tetramethylsilane*			
		$[M+H]^+$		$[2M+H]^+$		$[R]^+$		$[M+Me_3Si]^+$		$[R]^+$	
		m/z	I_{rel} (%)	m/z	I_{rel} (%)	m/z	I_{rel} (%)	m/z	I_{rel} (%)	m/z	I_{rel} (%)
$C_6H_{13}OH$	(**1**)	103	—	205	1.2	85	100	175	36	85	100
EtOH	(**2**)	47	100	93	100	—	—	—	—	—	—
$C_6H_{13}CN$	(**3**)	112	100	223	4.4	85	8.0	184	100	85	8.0
$C_6H_{13}COOH$	(**4**)	131	100	261	0.5	85	8.0	203	100	85	20.1
$C_6H_{13}COOMe$	(**5**)	145	82.0	289	28.2	85	100	217	100	85	18.7
$C_5H_{11}COOMe$	(**6**)	131	100	261	15.6	85	8.4	—	—	—	—
MeCOOMe	(**7**)										
CD_3COCD_3	(**8**)	65	100	127	3.2	—	—	137	100	—	—
EtOEt	(**9**)	75	100	149	18.2	—	—	—	—	—	—
$C_6H_{13}NH_2$	(**10**)	102	100	203	2.8	85	2.0	174	100	85	5.7
$PrNO_2$	(**11**)	90	72.0	179	1.0	43	100	—	—	—	—
MeI	(**12**)	143	100	285	20.0	15	—	215	100	—	—
$C_6H_{13}Br$	(**13**)	165 167	— —	329 331	— —	85	100	237 239	1.2	85	100
$C_6H_{13}Cl$	(**14**)	121 123	— —	241 243	— —	85	100	193 195	0.2	85	100

* Peaks of $[2M+Me_3Si]^+$ ions are absent in the $SiMe_4$-CI mass spectra of compounds **1—14**.

dimerize with the participation of electrophiles ($E^+ = Me_3Si^+, H^+, Me_3C^+$). Most of these compounds form dimers with bridging protons. In the case of alcohols **1** and **2**, protonated ions of not only dimers, but also of trimers have been detected. The trend of carboxylic acid **4** to generate dimers is low, and aliphatic halides **13** and **14** give no protonated dimers under the experimental conditions, obviously due to the low stability of the MH^+ ions.

None of the compounds studied forms dimers with the Me_3Si^+ bridge, which indicates that the ability of the trimethylsilyl ion to form chelates is extremely low.

Study of mixtures (Table 2) of monofunctional molecules (M^1 and M^2) makes it possible to evaluate the relative abilities of the components of a mixture to generate symmetrical complexes, $M^1...E^+...M^1$, or asymmetrical complexes, $M^1...E^+...M^2$.

In the first approximation, one may assume that the relative intensities of the peaks of $2M^1E^+$, $2M^2E^+$, and $M^1M^2E^+$ ions (since they are formed under identical conditions) should reflect their relative stabilities. As the data of Table 2 indicate, for most of the compounds

Table 2. Relative intensities of the peaks of $[2M^1+H]^+$, $[2M^2+H]^+$, and $[M^1+M^2+H]^+$ ions in CI mass spectra (isobutane as the reacting gas) of mixtures **I—XIII**

Mixture	M^1	M^2	$[2M^1+H]^+$		$[2M^2+H]^+$		$[M^1+M^2+H]^+$		$I^0_{M^1H^+}$ (%)	$I^0_{M^2H^+}$ (%)
			m/z	I_{rel} (%)	m/z	I_{rel} (%)	m/z	I_{rel} (%)		
I	$C_6H_{13}OH$	$C_6H_{13}CN$	205	1.2	222	11.0	214	32.2	92.5	160.0
II	$C_6H_{13}OH$	$C_6H_{13}COOH$	205	11.0	261	1.7	233	7.0	100.0	20.0
III	$C_6H_{13}OH$	Et_2O	205	0.1	149	5.5	177	0.2	100.0	100.0
IV	$C_6H_{13}OH$	$C_5H_{11}COOMe$	205	1.5	261	5.1	233	5.6	90.0	105.0
V	$C_6H_{13}OH$	$C_6H_{13}NH_2$	205	10.0	203	6.0	204	2.8	100.0	105.0
VI	$C_5H_{11}COOMe$	Et_2O	261	1.2	149	0.2	205	1.1	135.0	36.4
VII	Et_2O	$C_6H_{13}NH_2$	149	18.2	203	12.0	176	1.5	76.0	100.0
VIII	Et_2O	EtOH	149	2.6	102	53.1	121	2.8	100.0	60.0
IX	EtOH	$C_6H_{13}NH_2$	93	100.0	203	0.5	148	0.9	100.0	110.0
X	$C_5H_{11}COOMe$	$C_6H_{13}NH_2$	261	0.7	203	4.0	232	1.0	100.0	45.0
XI	$C_6H_{13}NH_2$	$C_6H_{13}CN$	203	1.8	223	13.8	213	3.6	102.0	102.0
XII	$PrNO_2$	EtOH	179	1.0	93	14.2	136	10.5	50.7	100.0
XIII	MeI	MeOH	285	18.0	65	55.0	175	—	58.0	100.0

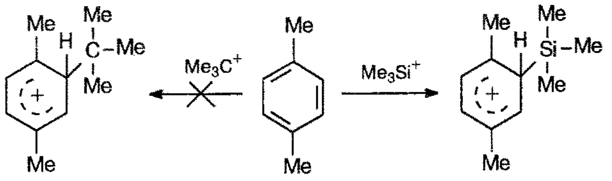
Note: I^0_{MH} is the sum of the intensities of the peaks of MH^+ ions and their fragments (the intensity of the maximum peak in the spectrum was taken as 100 %).

studied (mixtures **II**, **III**, **VI**, **VIII**, and **XII**) the $M^1...H^+...M^2$ associate is more stable than one of the dimers, $M^1...H^+...M^1$ or $M^2...H^+...M^2$. However, there are some exceptions. For example, asymmetrical associates are substantially less stable than either of the symmetrical dimers in mixtures **V** and **VII**, which contain hexylamine, possessing high proton affinity (PA), as one of the components. In hexanol—enanthonitrile (**I**) and hexanol—methylcapronate (**IV**) mixtures, the asymmetrical complex is more stable than either of the symmetrical complexes. However, the PA values of the functional groups incorporated in the components of these mixtures differ only slightly. Further investigation of mixtures of various monofunctional compounds would allow one to clarify the nature of these distinctions.

Study of interaction of Me_3C^+ and Me_3Si^+ ions with various isomers of xylene makes it possible to estimate the role of steric factors in the reactions of these ions with aromatic systems (Scheme 1). In particular, the $I_{[M+Me_3C]^+}/I_{MH^+}$ value, which characterizes the degree of alkylation with respect to protonation, decreases on going from *o*-xylene (0.60) to the *meta*- (0.36) and *para*-isomers (0.02), *i.e.*, addition of a *tert*-butyl group at an *ortho*-position is an energetically unfavorable process.[5]

One might expect that interaction of xylenes with Me_3Si^+ ions would also be governed to a large extent by steric factors. However, as shown in Table 3, the differences between the intensities of the peaks of $[M+Me_3Si]^+$ ions derived from isomeric xylenes are small.

Scheme 1



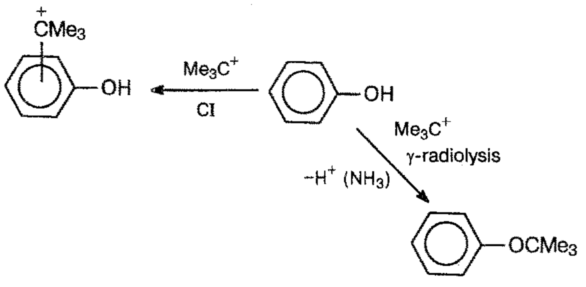
This difference between the reactions of Me_3Si^+ and Me_3C^+ ions with *p*-xylene is probably caused by the fact that a Si—C bond is longer than a C—C bond (by 20 % on the average).

Table 3. $I_{[M+Me_3C]^+}/I_{[M+H]^+}$ ratios in i-C_4H_{10}-CI mass spectra and $I_{[M+Me_3Si]^+}/I_{[M_{15}+Me_3Si]^+}$ ratios in $SiMe_4$-CI mass spectra of xylenes **15—17**

Compound	Isobutane, $I_{[M+Me_3C]^+}/I_{[M+H]^+}$	Tetramethylsilane, $I_{[M+Me_3Si]^+}/I_{[M_{15}+Me_3Si]^+}$
o-Xylene (**15**)	0.60	1.00*
m-Xylene (**16**)	0.36	0.80
p-Xylene (**17**)	0.02	0.82

* The concentration of a substrate in the ionization chamber was monitored using the overall ionic current of the EI mass spectrum.

Scheme 2



The previous study[6] has shown that alkylation of phenols under the conditions of CI in an isobutane atmosphere (0.3 Torr) occurs at the C atom (Scheme 2), *i.e.*, this reaction is governed by thermodynamic control, since gas-phase alkylation of phenols (γ-radiolysis, $p_{i\text{-}C_4H_{10}}$ = 720 Torr, and NH_3 as a base) governed by kinetic control yields *tert*-butyl ether (see Scheme 2).[7]

It has been shown previously[8,9] that the generation of $[M+Me_3Si]^+$ ions under the conditions of CI in a tetramethylsilane atmosphere is also subject to thermodynamic control. Therefore, the intensity of the formation of $[M+Me_3C]^+$ and $[M+Me_3Si]^+$ ions under the conditions of high-pressure CI is a measure of the stabilities of these ions.

The ability of a molecule to generate $[M+E]^+$ or MH^+ adducts in reactions with $E^+ = Me_3C^+$ or Me_3Si^+ is determined by its fundamental properties such as basicity and nucleophilicity. Since the PA of the conjugate base of the trimethylsilyl ion, dimethylsilaethylene ($Me_2Si{=}CH_2$), is very high (227 kcal mol^{-1}),[10] the principal processes occurring during interaction of most organic molecules (a rare exception is provided by some nitrogen bases having even higher PA's) with Me_3Si^+ ions amount to generation of $[M+Me_3Si]^+$ adducts and products of their decomposition.

The PA of isobutene is much lower (169 kcal mol^{-1}),[11] therefore, during interaction of most organic molecules with the *tert*-butyl ion, both generation of $[M+Me_3C]^+$ associates and formation of protonated molecular ions occur intensely.

The predominant course of one or other reaction is determined by the PA of the molecule of a substrate. For compounds with higher PA's protonation is preferred, while at a lower PA the degree of association increases. The CI mass spectrum of a molecule of a substrate allows one to find out, what particular reaction predominates. One may probably expect that if $[M+Me_3C]^+$ clusters are intensely produced under the conditions of CI, formation of similar ions in the condensed phase should occur with a high probability and their role in the subsequent transformations would be rather important.

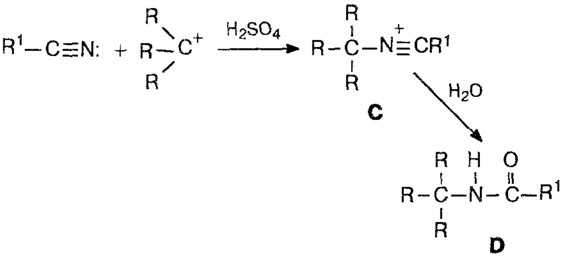
We attempted to use the CI method to evaluate the general influence of functional groups present in a nitrile molecule on the course of the Ritter reaction[12]

Table 4. i-C_4H_{10}-CI mass spectra of compounds **3**, **18—20**

Compound		$[M+Me_3C]^+$		$[M+H]^+$		$[M+H-HCN]^+$	
		m/z	I_{rel} (%)	m/z	I_{rel} (%)	m/z	I_{rel} (%)
$MeCH_2CH_2CH_2CH_2CH_2CN$	(**3**)	168	50.2	112	100.0	85	—
1-Cyanoadamantane	(**18**)	218	71.6	162	100.0	135	2.3
$Me_2C=CH(CH_2)_2C(Me)=CHCH_2CN$	(**19**)	220	100.0	164	39.6	137	5.1
3,5-Di-*tert*-butyl-4-hydroxybenzylcyanide	(**20**)	302	100.0	246	14.0	—	

(Scheme 3), whose rate-determining step is the formation of the intermediate product, nitrilium ion (**C**).

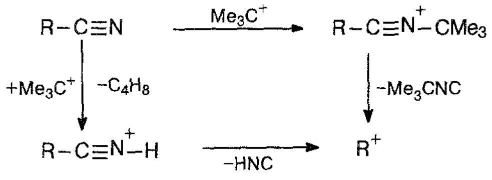
Scheme 3



In the present study we considered the effects of various structural factors on the ability of a nitrile group to form associates with carbenium ions under the conditions of CI.

The reaction of a nitrile group in aliphatic or alicyclic nitrile **3** or **18** with *tert*-butyl cation (i-C_4H_{10} as the reacting gas) (Scheme 4) is accompanied by its protonation and alkylation (Table 4).

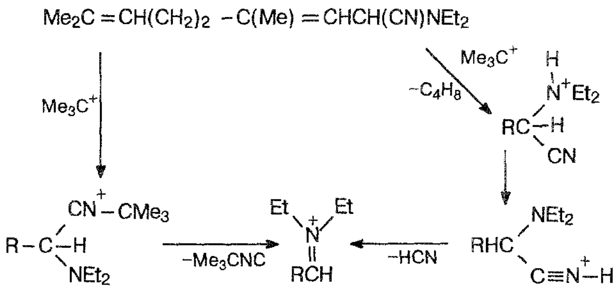
Scheme 4



If the molecule of a nitrile contains a double bond (**19**) or a benzene ring (**20**), they compete with the nitrile group to a small extent; the latter probably acts as the reaction center both in protonation and alkylation. In fact, the contribution of the formation of $[M+Me_3C]^+$ ions (under the conditions of CI) in benzene or alkenes amounts to 5 % of the main process, *viz*., protolysis. Previously[6] it has been shown that the intensity of peaks of $[M+Me_3C]^+$ ions produced in the alkylation of the aromatic ring in compound **20** is only 2.5 %. The presence of a nitrile group in the molecule results in the peaks of $[M+Me_3C]^+$ ions becoming the most intense in the CI mass spectra of compounds **19** and **20**.

If a nitrile molecule contains other functional groups, the intensity of the formation of nitrilium ions is determined to a large extent by the electron-donating abilities of these additional groups (Table 5). In fact, introduction of an electron-donating substituent at the α-position with respect to the nitrile group (compounds **21—25**) is accompanied by a decrease in the intensity of the $[M+Me_3C]^+$ ion peak; in the case of PMI **21—24** this may be primarily due to the decrease in the stabilities of the $[M+E]^+$ ions caused by the dramatic increase in the rate of elimination of HCN. The stability of the PMI derived from compound **25** is high, however, peaks of $[M+Me_3C]^+$ ions are practically missing from the CI mass spectrum. Since PA's of the α-substituents in structures **21—25** are much higher than the PA of the CN group, the reaction of Me_3C^+ ion with a molecule preferably occurs as protonation at the amine fragment. The intense elimination of an HCN molecule from PMI **21—24** indicates that the proton of the reacting gas moves to the nitrile group and also that the activation energy (E_a) of the elimination of hydrocyanic acid is low, which is apparently due to the formation of a stable product (Scheme 5).

Scheme 5



Compound **25** is protonated at the α-substituent, however, no elimination of HCN is observed, since it would lead to the formation of a less stable ion, $H_2NC(O)CH_2^+$.

Table 5. *i*-C_4H_{10}-CI mass spectra of compounds **21—26**

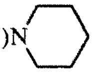
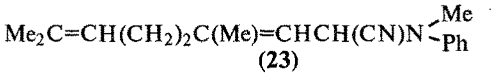
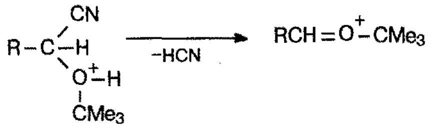
Compound	$[M+Me_3C]^+$		$[M+H]^+$		$[M-CN]^+$	
	m/z	I_{rel} (%)	*m/z*	I_{rel} (%)	*m/z*	I_{rel} (%)
$Me_2C=CH(CH_2)_2C(Me)=CHCH(CN)NEt_2$ **(21)**	291	1.2	235	7.5	208	100
$Me_2C=CH(CH_2)_2C(Me)=CHCH(CN)N$  **(22)**	303	0.2	247	3.6	220	100
 $Me_2C=CH(CH_2)_2C(Me)=CHCH(CN)N\genfrac{}{}{0pt}{}{Me}{Ph}$ **(23)**	325	0.3	269	10.0	242	100
$Me_2C=CH(CH_2)_2C(Me)=CHCH(CN)N$  **(24)**	305	0.1	249	6.3	222	100
$H_2N(O)CCH_2CN$ **(25)**	141	—	85	100.0	58	—
$Me_2C=CH(CH_2)_2C(Me)=CH=CH(CN)OH$ **(26)**	236	3.8	180	3.8	153	100

Table 6. *i*-C_4H_{10}-CI mass spectra of compounds **27—30**

Compound	$[M+Me_3C]^+$		$[M+H]^+$		$[M+H+HCN]^+$	
	m/z	I_{rel} (%)	*m/z*	I_{rel} (%)	*m/z*	I_{rel} (%)
$O=CHCH_2CH_2C(Me)ClCN$ **(27)**	202 (204)	100.0 (58)	146 (148)	71 33	119 (121)	23.8 6.8
$O=C(Me)CH_2CH_2C(Me)ClCN$ **(28)**	216 (218)	21.8 18.6	160 (162)	100 42	133 (135)	7.3 2.3
$O=C(Pr)CH_2CH_2C(Me)ClCN$ **(29)**	244 (246)	8.7 2.3	188 190	100 23.8	161 (163)	10.1 4.2
$NCCH_2CN$ **(30)**	123	18.7	67	100	40	2.0

The proton affinity of an OH group is much lower than that of an amino group; therefore, in the case of hydroxynitrile **26**, association with the Me_3C^+ ion occurs, despite the intense fragmentation of the PMI. However, the E_a value of elimination of HCN is still rather low, which is indicated by the intense abstraction of HCN from the cluster ion (Scheme 6).

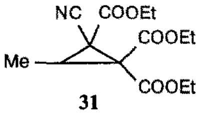
Scheme 6



Further increase in the electron-withdrawing properties of the substituent in a nitrile molecule, which occurs on going to chlorinated derivatives **27—29** (Cl and CN are attached to the same C atom), is accompanied by a substantial increase in the intensities of peaks of nitrilium ions (Table 6).

The electron acceptors, such as ethoxycarbonyl, present in nitriles of the cyclopropane series **31—33** (Table 7), do not prevent the formation of nitrilium ions. It should be noted that the formation of associates is not typical of ester groups. For molecule **31**, which incorpo-

Table 7. *i*-C_4H_{10}-CI mass spectra of compounds **31—33**



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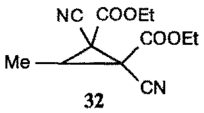

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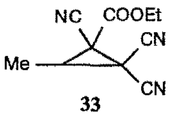

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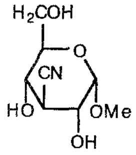
Compound	$[M+Me_3C]^+$		$[M+H]^+$	
	m/z	I_{rel} (%)	*m/z*	I_{rel} (%)
31	354	79.9	298	100.0
32	308	100.0	252	13.8
33	261	100.0	205	9.8

* Compounds **31—33** are mixtures of isomers.

Table 8. i-C_4H_{10}-CI mass spectra of compounds **34—44**



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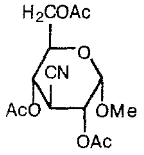

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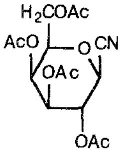

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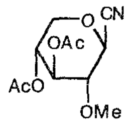

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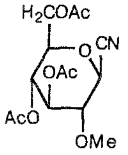

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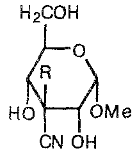
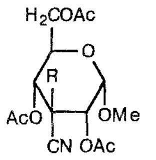
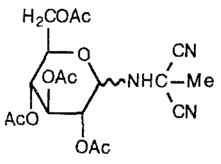


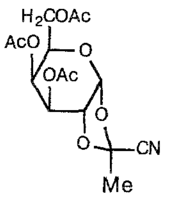
39: R = $CONH_2$



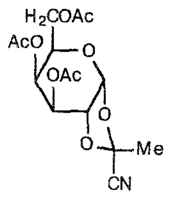
40: R = $CONH_2$



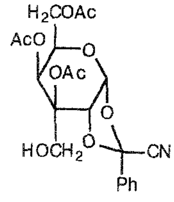
41



42



43



44

Compound	$[M+Me_3C]^+$		$[M+H]^+$		$[M+H-HCN]^+$	
	m/z	I_{rel} (%)	m/z	I_{rel} (%)	m/z	I_{rel} (%)
34	260	100.0	204	73.0	—	
35	386	100.0	330	77.0	—	
36	414	100.0	358	100.0	331	11.2
37	286	14.0	230	100.0	203	4.5
38	386	10.4	330	100.0	303	2.3
39	303	2.6	247	100.0	—	
40	429	7.4	373	100.0	—	
41	455	—	398	100.0	371	88.1
42	415	—	358	4.6	331	100.0
43	415	0.5	358	1.2	331	100.0
44	477	—	420	2.3	393	100.0

rates one CN group, the intensities of the peaks of association and protonation products are comparable. If a molecule contains two or three nitrile groups, the $[M+Me_3C]^+$ ions predominate, and the intensity of PMI is low.

The CN group in unsaturated monosaccharides **34** and their acetates **35** and **36** (Table 8) is rather prone to association with carbenium ions. The presence of methoxy groups at the C(2) atoms in monosaccharide acetates **37** and **38** decreases the ability of these compounds to form $[M+Me_3C]^+$ ions. The presence of $CONH_2$ groups in the molecules of monosaccharides **39** and **40** also suppresses the formation of the $[M+Me_3C]^+$ ion, and this effect is observed even with molecule **41**, which contains two nitrile groups. The dioxolane ring in monosaccharides **42—44** also suppresses association with Me_3C^+. This is caused by both the ease of elimination of HCN yielding a stable structure and the high susceptibility of the dioxolane system to protonation, which is confirmed by the fragmentation of PMI **42—44**, accompanied by elimination of a MeC(O)CN molecule (Scheme 7).

The nitrile group in the benzene ring of compound **45** and the nitrile group at the double bond of dinitrile **46** are prone to form nitrilium ions (Table 9). The CN group in the α-position of the pyridine ring of compound **47** is not liable to association.

It should be noted that the ability of nitriles to form nitrilium ions in the gas phase correlates with the extent to which Ritter reaction occurs in solution.[12]

Scheme 7

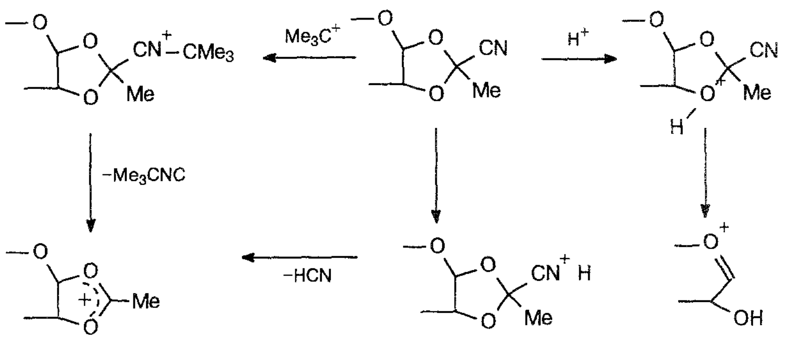


Table 9. *i*-C_4H_{10}-CI mass spectra of compounds **45—49**

Compound		$[M+Me_3C]^+$		$[M+H]^+$	
		m/z	I_{rel} (%)	m/z	I_{rel} (%)
Benzonitrile	(**45**)	159	15.6	103	100.0
Benzylidene-malonodinitrile	(**46**)	211	100.0	155	62.5
2-Cyanopyridine	(**47**)	161	—	105	100.0

The experiments carried out have shown that electron-donating groups retard the formation of $[M+Me_3C]^+$ ions, while electron-withdrawing substituents do not hamper this process. Thus, the CI method allows one to evaluate the effects of functional groups present in a molecule of a nitrile on the ratio between $[M+H]^+$ and $[M+Me_3C]^+$ ions and can be used to predict the possibility of the occurrence of the Ritter reaction in solution.

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