ment. A continuously recording photomonitor incorporating a Rank Cintel QVA39S (antimony–cesium) photocell in conjunction with a 1.9-mm thickness filter of Chance OX7 glass was constructed to detect and compensate for fluctuations in uv output (230–420 mμ) of the lamp with time.

At frequent intervals (5 min, initially) during an irradiation, samples (1 ml) were taken from the reactor solution (maintained constantly agitated by a stream of nitrogen) and a known volume (50 μl) of marker solution (2 ml of methyl salicylate in 10 ml of acetone solution) was added to each sample. These were analyzed quantitatively by glpc (2 m × 0.25 in. 15% polypropene glycol LB-550x, 60–80 mesh 85% Chromosorb W; nitrogen carrier, 10 psi; 125° rapidly rising to 160° after 18 min; Perkin-Elmer F11 gas chromatograph). Approximate retention times were as follows: dimethyl fumarate, 12 min; dimethyl maleate, 16 min; methyl salicylate, 29 min; *trans*-oxetane diester, 37 min; *cis*-oxetane diester, 45 min. Peak areas were estimated by cutting and weighing (precision $\pm 1.2\%$ for peak area 1 in.^{2}). Absolute concentrations (precision $\sim\pm 3.4\%$) were estimated following a calibration experiment.

Unweighted experimental data (18–26 points/curve) were submitted to a computerized polynominal least-squares curve fitting procedure in order to estimate gradients (with standard deviations) at irradiation time zero. The order fit chosen (never above 4) was the *lowest order* function consistent with estimated random error in the points.

Exceptions to this procedure were cases (production of fumarate from maleate and of maleate from fumarate (0.23 *M*) in quartz) where fewer points were submitted for analysis owing to a significant change in curve form after a limited period of irradiation. The 0.025 *M* fumarate irradiation was an extreme case. The very rapid photoisomerization of fumarate led to a photoequilibrium of maleate and fumarate with the former predominating (8.5:1) within 10-min irradiation so that after 4 points had been taken, all the curve forms had changed radically. In this case, all estimated initial gradients were based on only 4 points. However, the possible errors were greatly overestimated in order to eliminate the possibility of misleading deductions.

No 1,2,3,4-tetramethoxycarbonylcyclobutane (**3**) was detected by glpc (*cis,trans,cis* isomer, retention time 57 min at 200° on polypropylene glycol column).

Initial rates of decay of starting materials were not estimated owing to error caused by gas chromatograph overloading. However, material balance checks were conducted at longer irradiation times. The occurrence of significant side reactions was only noted in the 0.025 *M* fumarate irradiation.

Further experiments demonstrated that the photochemistry of this system was not sensitive to trace amounts of oxygen such as might have remained after degassing.

Oxygen perturbation experiments were conducted on 1 *M* chloroform (May and Baker, "Reagent" grade) solutions of dimethyl maleate and dimethyl fumarate saturated with oxygen for 15 min at 1800–2000 psi in a 5-cm, high-pressure cell, supplied by D. F. Evans. The cell was balanced against a regular 5-cm cell of the same solution and spectra were recorded on a Unicam SP800 spectrophotometer fitted with a scale expander. A base line was obtained *after* the oxygenation experiment, thus correcting for spectral changes arising from the possible formation of oxidation products.

Acknowledgments. The author is indebted to Dr. J. A. Barltrop for his guidance and encouragement throughout this work. Thanks are also due to Dr. D. F. Evans for the loan of apparatus and to Brasenose College, Oxford, and the Science Research Council for financial support.

Stable Carbonium Ions. LXV.[1] Protonation of Hydrogen Cyanide and Alkylnitriles in FSO$_3$H–SbF$_5$–SO$_2$ Solution. Comparative Study of Meerwein's N-Alkylnitrilium Ions

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Abstract: Protonation of hydrogen cyanide, alkyl- and alkenylnitriles, dinitriles, and bifunctional nitriles was studied by H^1, C^{13}, and N^{15} nuclear magnetic resonance spectroscopy in the strong acid system FSO$_3$H–SbF$_5$–SO$_2$. Nuclear magnetic resonance and infrared spectroscopic studies of Meerwein's N-alkylnitrilium ions were also undertaken and the results compared with those of protonated nitriles.

The possible formation of protonated nitriles when anhydrous HCl is dissolved in nitriles was discussed by Janz and Danyluk,[3] but they could draw no firm conclusion. Klages, *et al.*,[4] showed that no such species is formed under the conditions. The latter authors, however, succeeded in isolating acetonitrilium hexachloroantimonate, CH$_3$CNH$^+$SbCl$_6^-$. Peach and Waddington[5a] studied nitriles in anhydrous HCl and claimed the presence of $RC\equiv NH^+$ ions on the basis of conductivity measurements. Deno[5b] studied the protonation of acetonitrile, propionitrile, and benzonitrile in sulfuric acid and oleum by pmr spectroscopy under conditions where obvious rapid exchange made it impossible to obtain analyzable spectra.

As a continuation of our study of protonation of organic compounds in strong acids, we have now undertaken a study of the protonation of nitriles in FSO$_3$H–SbF$_5$–SO$_2$ solution. In addition, protonation of alkenylnitriles, dinitriles and bifunctional nitriles was also investigated. For comparison, we have also investigated Meerwein's related N-alkylnitrilium salts ($(RC\equiv NR)^+X^-$), for which no nmr data have been reported.[6]

Results and Discussion

N-Protonated nitriles were obtained by protonation of nitriles in FSO$_3$H–SbF$_5$–SO$_2$ solution generally at

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(1) Part LXIV: G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, in press.

(2) Postdoctoral Research Investigator, 1967–1968.

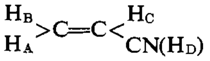
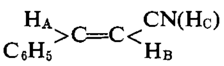
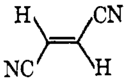
(3) G. Janz and S. Danyluk, *J. Amer. Chem. Soc.*, **81**, 3846, 3850, 3584 (1959).

(4) F. Klages, *et al.*, *Ann.*, **626**, 60 (1959).

(5) (a) M. E. Peach and J. C. Waddington, *J. Chem. Soc.*, 600 (1962); (b) N. C. Deno, R. W. Gaugler, and M. J. Wisotsky, *J. Org. Chem.*, **31**, 1967 (1966).

(6) H. Meerwein, *et al.*, *Chem. Ber.*, **89**, 209 (1956).

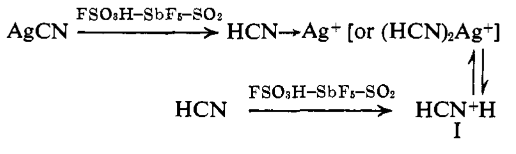
Table I. Pmr Data of Nitriles (in SO_2 Solution) and Protonated Nitriles (in FSO_3H-SbF_5-SO_2 Solution)[a]

	δ nitrile				δ protonated nitrile			
Compound	CH_3	CH_2	CH	C_6H_5	CH_3	CH_2	H	C_6H_5
HCN			−3.78 (s)				−7.50 (d) $J_{\mathrm{H-H}} = 8.5$	
$HC^{13}N$			−3.78 (d) $J_{\mathrm{C^{13}H}} = 269$				−7.50 (q) $J_{\mathrm{C^{13}H}} = 320$	
HCN^{15}							CH −7.50 (q) $J_{\mathrm{N^{15}H}} = 19.0$ NH −11.33 (q) $J_{\mathrm{N^{15}H}} = 134$	
CH_3CN	−1.77 (s)				−3.25 (d) $J_{\mathrm{H-H}} = 2.4$			
$CH_3C^{13}N$	−1.77 (d) $J_{\mathrm{C^{13}H}} = 9.8$				−3.20 (q) $J_{\mathrm{C^{13}H}} = 10.4$			
CH_3CN^{15}	−1.80 (d) $J_{\mathrm{N^{15}H}} = 1.8$				−3.20 (q) $J_{\mathrm{N^{15}H}} = 2.8$ $J_{\mathrm{H-H}} = 2.0$		−10.58 (q) $J_{\mathrm{N^{15}H}} = 136$ $J_{\mathrm{H-H}} = 2.0$	
CH_3CH_2CN	−1.03 (t)	−2.10 (q)			−1.75 (t)	−3.43 (o)		
 $\mathrm{H_B}\atop\mathrm{H_A}$>C=C<$\mathrm{H_C}\atop\mathrm{CN(H_D)}$		−5.88 (q) −5.99 (q)	−5.38 (q)			−7.36 (d) $J_{\mathrm{BC}} = 12.0$ −7.49 (d) $J_{\mathrm{AB}} = 17.5$	−6.46 (o) $J_{\mathrm{CD}} = 2.3$	
 $\mathrm{H_A}\atop\mathrm{C_6H_5}$>C=C<$\mathrm{CN(H_C)}\atop\mathrm{H_B}$		−5.75 (d) −7.21 (d)		−7.28 (m)		−8.68 (d)	−6.60 (q) $J_{\mathrm{AB}} = 17$ $J_{\mathrm{BC}} = 1.5$	−7.87 (m)
$NCCH_2CN$		−3.56 (s)				−5.47 (br)		
			−6.20 (s)				−8.07 (d, br) $J = 1.2$	
$CH_3OCH_2CH_2CN$	−3.10 (s)	−2.42 (t) −3.42 (t)			−4.64 (d)	−4.10 (t) −5.17 (t)	OH^+ −10.66 (br)	
$CH_3C({=}O)CN$	−2.28 (s)				−4.30 (s)		OH^+ −11.80 (br)	

[a] δ values in parts per million from external TMS. *J* values in hertz. Abbreviations used are: s, singlet; d, doublet; t, triplet; q, quartet; o, octet; br, broad; m, multiplet.

−60°. Pmr spectra of the nitrilium ions were obtained, and the data are summarized in Table I. Nmr spectra of the protonated species could not be observed in neat FSO_3H even at −78°, indicating fast exchange in this weaker acid system. In none of the cases studied in FSO_3H-SbF_5-SO_2 solution could the absorption due to the proton of the N^{14} nucleus be observed. This is attributed to N^{14} quadrupole broadening rather than to exchange since coupling to the NH proton was observed in most cases.

Protonated hydrogen cyanide, $H{\equiv}CNH^+$ (I), could be observed either by adding a 1:1 mixture of FSO_3H-SbF_5 to an SO_2 solution of HCN or by dissolving silver cyanide in the acid-SO_2 solution, but not by dissolving potassium cyanide in the acid mixture. When silver cyanide is used, the hydrogen cyanide-silver ion complex, reported by Dove and Hallett in HF solution,[7] may be formed first. The stronger acid, FSO_3H-SbF_5, then displaces Ag^+ from the complex. At −90° the spectrum consisted of a doublet at δ −7.50 with a vicinal coupling constant of 8.5 Hz very close to that of 9.1 Hz in acetylene.[8a] The carbon-hydrogen coupling constant $J_{\mathrm{C^{13}-H}}$ is 320 Hz (obtained with 50% enriched $HC^{13}N$), indicating the sp hybridization of the carbon atom. The values of $J_{\mathrm{C^{13}H}}$ in HCN itself and in the silver complex are 269[9] and 291 Hz,[7] respectively. The C^{13} chemical shift of neat liquid hydrogen cyanide was found to be at +83.7 ppm (relative to CS_2), in the same region as alkylnitriles. The shift was obtained with natural abundance $HC^{13}N$ by the indor method.[10] The indor spectrum of protonated 50% C^{13}-enriched hydrogen cyanide is a doublet centered at +95.7 ppm (relative to CS_2). Although neighboring positive charge usually causes deshielding of the carbon atom,[11] the shielding effect of 10 ppm relative to $HC^{13}N$ found seems consistent with the fact the $C^{13}N^-$ is deshielded relative to the alkylnitriles by *ca.* 60 ppm.[8b]



$$\begin{tikzcd} \mathrm{AgCN} \arrow[r, "\mathrm{FSO_3H{-}SbF_5{-}SO_2}"] & \mathrm{HCN{\rightarrow}Ag^+\ [or\ (HCN)_2Ag^+]} \arrow[d, shift left] \\ \mathrm{HCN} \arrow[r, "\mathrm{FSO_3H{-}SbF_5{-}SO_2}"] & \mathrm{HCN^+H} \arrow[u, shift left] \end{tikzcd}$$

I

When N^{15}-enriched (95%) HCN^{15} is protonated, the NH proton signal is observed as a doublet of doublets at δ −11.33 proving that the absence of an observable

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[7] F. A. Dove and J. G. Hallett, *Chem. Commun.*, 571 (1967).

[8] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution NMR Spectroscopy," Vol. II, Pergamon Press, Oxford, 1966: (a) p 748; (b) p 990; (c) p 1041.

[9] G. S. Raddy and J. H. Goldstein, *J. Chem. Phys.*, **39**, 3509 (1963).

[10] E. B. Baker, *ibid.*, **37**, 911 (1962); E. G. Paul and P. M. Grant, *J. Amer. Chem. Soc.*, **86**, 2977 (1964).

[11] J. B. Stothers, *Quart. Rev.* (London), **19**, 144 (1965).

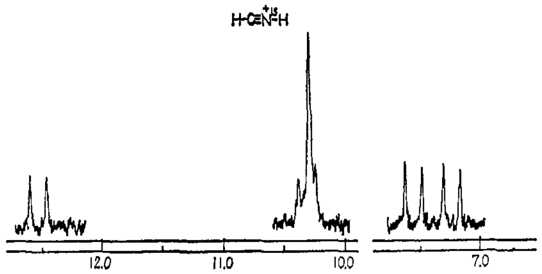

Figure 1. Pmr spectrum of N^{15}-enriched (95%) hydrogen cyanide in FSO$_3$H-SbF$_5$-SO$_2$ solution.

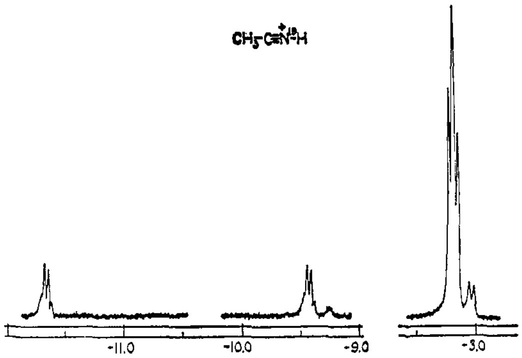

Figure 2. Pmr spectrum of N^{15}-enriched (92.5%) acetonitrile in FSO$_3$H-SbF$_5$-SO$_2$ solution. The peak at -3.03 ppm is due to an impurity.

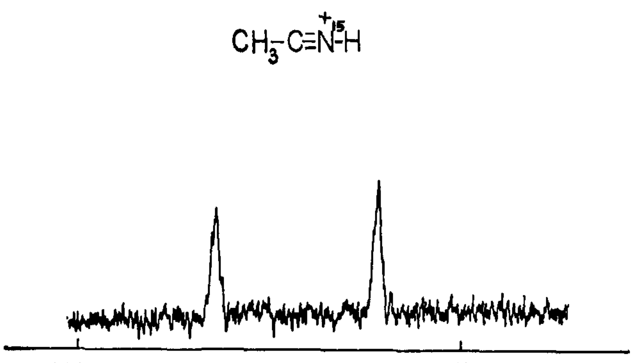

Figure 3. The N^{15} indor spectrum of 95% enriched acetonitrile in FSO$_3$H-SbF$_5$-SO$_2$ solution at $-60°$. The chemical shift is at -115.6 ppm relative to aqueous NH$_4^+$.

signal for the N^{14}H proton in protonated hydrogen cyanide is due to quadrupole broadening. The N^{15}–H coupling is 134 Hz and the H–H coupling is 8.25 Hz. The CH proton signal appears as a doublet of doublets centered at δ -7.50; the N^{15}–H coupling is 19.0 Hz. The spectrum of protonated N^{15}-enriched HCN, shown in Figure 1, has a peak between the lines of the upfield doublet at δ -10.3 which is due to water in the sample.[12]

The pmr spectrum of protonated acetonitrile (II) in FSO$_3$H-SbF$_5$-SO$_2$ solution was observed as a sharp doublet[13] at δ -3.25 corresponding to the methyl group split by the NH proton. The coupling constant $J_{\mathrm{HN-CH}}$ is 2.4 Hz compared to 2.9 Hz in methylacetylene.[8a] The spectrum is sharp and well resolved even at room temperature and does not change when the sample is allowed to stand for several days. The NH$^+$ absorption is not observable even at $-90°$. Acetonitrile

$$\mathrm{CH_3CN} \xrightarrow{\mathrm{FSO_3H-SbF_5-SO_2}} \underset{\mathbf{II}}{\mathrm{CH_3CNH^+}}$$

could be recovered from the acid–SO$_2$ solution by quenching with cold methanol.

When N^{15}-enriched (95.2%) acetonitrile is protonated the NH proton signal is observed as a doublet of quartets at δ -10.58. The doublet has a coupling constant of 136 Hz due to coupling to the N^{15} nucleus, while the quartets show a coupling constant of 2.0 Hz due to long-range coupling to the methyl group. The methyl group appears as a doublet of doublets due to splitting by the NH proton and the N^{15} nucleus ($J_{\mathrm{N^{15}H}}$ = 2.8 Hz). The spectrum is shown in Figure 2; the peaks due to the acid system are deleted for simplicity. A small impurity peak just upfield from the methyl signal which appeared as a singlet in the spectrum of protonated N^{14} acetonitrile now appears as a doublet (J = 2.4 Hz). The signal is probably due to a methyl signal split by the N^{15} nucleus, but probably not due to trimethyltriazine, since in this case a triplet would be expected.

The proton spectrum of protonated C^{13}-enriched (52.6%) acetonitrile, CH$_3$C^{13}NH$^+$, consists of three doublets centered at δ -3.20 due to the methyl groups of the C^{12} and C^{13} species coupled to the NH$^+$ proton. The C^{13}–CH$_3$ coupling constant in the protonated species, $J_{\mathrm{C^{13}H}}$ = 10.4 Hz, is very close to that in acetonitrile itself (9.8 Hz). The C^{13} spectrum of acetonitrile was observed in both SO$_2$ and FSO$_3$H-SbF$_5$-SO$_2$ solution using the indor method. The chemical shift of the nitrile carbon atom in protonated acetonitrile is at +85 ppm relative to CS$_2$, indicating linear sp hybridization. As was the case with hydrogen cyanide the nitrile carbon atom is shielded relative to the starting material by 10 ppm. The C^{13} indor spectrum of CH$_3$C^{13}$\equiv$N$^+$H appears as an equal intensity triplet. Each line of the triplet shows fine structure but was not completely resolved under the experimental conditions.

The N^{15} chemical shifts of protonated hydrogen cyanide and protonated acetonitrile were measured by the indor method and were found to be at -119.4 and -115.6 ppm, respectively, relative to external aqueous NH$_4^+$. The indor spectrum of 95% N^{15}-enriched protonated acetonitrile is shown in Figure 3. For comparison, the N^{15} chemical shifts of CN$^-$ and CH$_3$CN are at -255[14] and -218 ppm, respectively. The N^{15} chemical shifts of CN$^-$, CH$_3$CN, and CH$_3$CNH$^+$ show a pattern of increasing deshielding with increasing negative charge. This pattern contrasts with that of ammonia and ammonium ion where the ammonium ion is deshielded by 24 ppm.[15]

An empirical relationship between the amount of s character of the N^{15}–H bond and the direct N^{15}–H coupling constant has been proposed.[16] The equation,

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(12) G. A. Olah and T. E. Kiovsky, *J. Amer. Chem. Soc.*, **89**, 5692 (1967).

(13) Acetonitrilium hexachloroantimonate, $\mathrm{C\ H_3NH^+SbCl_6^-}$, in SO$_2$ solution did not give a well-resolved nmr spectrum.

(14) J. Lambert, G. B. Binsch, and J. D. Roberts, *Proc. Natl. Acad. Sci. U. S.*, **51**, 735 (1964).

(15) The N^{15} resonance work was completed after submission of the paper, and the data were inserted after acceptance of the paper.

(16) G. Binsch, J. B. Lambert, B. W. Roberts, and J. D. Roberts, *J. Amer. Chem. Soc.*, **86**, 5566 (1964).

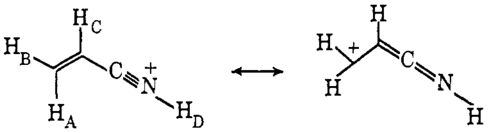
$\% s = 0.43J_{N^{15}H} = -6.0$ Hz, is based on the data for ammonium ion and $C_6H_5C{=}NH_2^+$, and was found satisfactory for a number of sp^2- and sp^3-hybridized N^{15} compounds. Protonated hydrogen cyanide, $HC{\equiv}N^{15}H^+$, and acetonitrile, $CH_3C{\equiv}N^{15}H^+$, in which N^{15} is sp hybridized (50% s character), allow a further test of this equation. The values of $J_{N^{15}-H}$ of 134 and 136 Hz for these two species yield values of the per cent s character of 52 and 53%.

Propionitrile (III), upon protonation in $FSO_3H-SbF_5-SO_2$, gives an nmr spectrum showing the methyl group as a triplet at δ −1.75 and the methylene group as a pair of quartets centered at δ −3.48. The NH absorption is again not observable but the CH_2-NH coupling is, $J_{HN-CH_2} = 2.5$ Hz.

$$CH_3CH_2CN \xrightarrow{FSO_3H-SbF_5-SO_2} CH_3CH_2CN^+H$$

III

α,β-Unsaturated nitriles, like acrylonitrile and cinnamonitrile, were also protonated. The pmr spectra of acrylonitrile and its protonated form IV are shown in Figure 4. The main effect of protonation on the spectrum is the deshielding of the H_A and H_B protons ($\Delta\delta = 1.50$)[17] substantially more that the H_C proton ($\Delta\delta = 0.63$), thus simplifying the spectrum. The fact that H_A and H_B are deshielded so much more than the H_C indicates the importance of resonance structure IVb. Coupling through the CN bond is smaller in this case, $J_{CD} = 1.5$ Hz, than in alkylnitriles. The geminal coupling is not observable in the spectrum of protonated acrylonitrile. The pmr spectrum of protonated cinnamonitrile (V) shows features similar to those of acrylonitrile.



IVa IVb

$$C_6H_5CH{=}CHCN \xrightarrow[-60°]{FSO_3H-SbF_5-SO_2} C_6H_5CH{=}CHC^+NH$$

V

Several bifunctional nitriles were also protonated in $FSO_3H-SbF_5-SO_2$ solution. The nmr data of all studied protonated nitriles are summarized in Table I. In Table II are listed the deshielding values of protonated nitriles relative to the unprotonated compounds in SO_2 solution. The fact that the deshielding values of $\Delta\delta$ for bifunctional nitriles in the strong acid systems are consistently larger than those for the monofunctional ones, together with the nmr spectral patterns, indicates diprotonation of the former. Coupling to the NH^+ proton is not clearly observable in the diprotonated species and the signals are substantially broadened.

Table II. Deshielding Values for Mono- and Bifunctional Nitriles in $FSO_3H-SbF_5-SO_2$ Relative to the Starting Materials in SO_2 Solution

	$\Delta\delta$		
Compd	CH_3	CH_2	CH
Acetonitrile	1.50		
Propionitrile		1.38	
Acrylonitrile		1.50	0.63
Malonitrile		1.91	
Fumaronitrile		1.87	
β-Methoxypropionitrile		1.68, 1.75	
Pyruvonitrile	2.02		

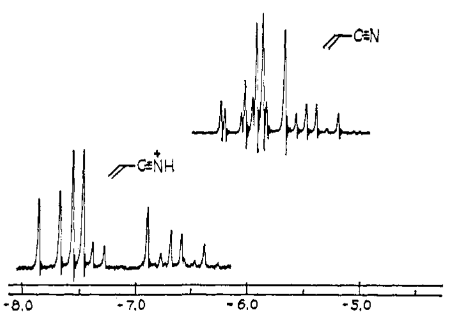
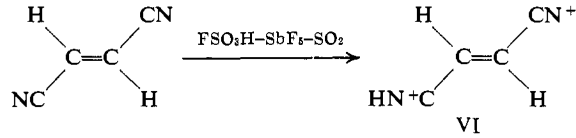


Figure 4. Pmr spectrum of acrylonitrile in liquid SO_2 and in $FSO_3H-SbF_5-SO_2$.

When fumaronitrile was dissolved in $FSO_3H-SbF_5-SO_2$ at −80°, a broadened doublet at δ −8.07 was observed as the major signal along with a minor peak at δ −7.96. The major peak is attributed to diprotonated fumaronitrile (VI) due to the large deshielding value and the fact that fumaronitrile could be recovered from the acid solution by quenching.



VI

The pmr spectra of *diprotonated β-methoxypropionitrile*, $CH_3O(H)^+CH_2CH_2CNH^+$ (VII), at −25° in $HSO_3F-SbF_5-SO_2$ consists of two broadened triplets due to the methylene protons and a broadened singlet due to the methoxyl protons. At −70° the methoxyl signal appears as a doublet due to coupling to the OH^+ proton. The methylene peaks lose almost all fine structure due to coupling and viscosity of the acid system at this temperature. At −90° the OH^+ proton can also be observed at δ −10.66. The OH^+ proton of diprotonated pyruvonitrile (VIII) can also be observed at −90° at δ 11.8. The deshielding value for the methyl singlet is 2.02 ppm.

Comparative Study of Meerwein's N-Alkylnitrilium Ions. N-Alkylnitrilium tetrafluoroborates were prepared according to the procedure of Meerwein[6] from nitriles and trialkyloxonium tetrafluoroborates.[18] N-Alkylnitrilium hexachloroantimonates were prepared according to the method of Klages[4] from nitrile–antimony pentachloride complexes and alkyl chlorides.

$$RCN + R_3'O^+BF_4^- \longrightarrow RCN^+R'BF_4^- + R_2'O$$

$$RCN{\rightarrow}SbCl_5 + R'Cl \longrightarrow RCN^+R'SbCl_6^-$$

The infrared spectra of the very hygroscopic nitrilium complexes could be examined in the usual way as Nujol mulls with the exclusion of moisture. Unless sufficient care was taken to exclude moisture, peaks

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(17) Chemical shifts and coupling constants for protonated acrylonitrile were taken from the 100-MHz spectrum.

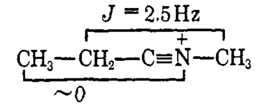
(18) H. Meerwein in "Die Methoden der organischen Chemie," Vol. 5, Houben-Weyl, Ed., Georg Thieme Verlag, Stuttgart, Germany, 1965, p 325.

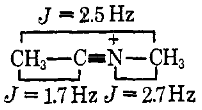
appeared in the carbonyl region due to hydrolysis to the amides. The infrared studies summarized in Table III show the C≡N stretching frequencies of N-alkylnitrilium complexes to be raised relative to that of the parent nitriles similar to nitrile–Lewis acid halide complexes.[19]

Table III. C≡N Stretching Frequencies in Nitrilium Complexes

Compound	Frequency, cm^{-1}	$\Delta\nu$, cm^{-1}
CH_3CN	2245	. . .
$CH_3CNH^+SbCl_6^-$	2310	76
$CH_3CN^+CH_3BF_4^-$	2420	180
$CH_3CN^+CH_2CH_3BF_4^-$	2400	160
$CH_3CN^+C(CH_3)_3SbCl_6^-$	2370	130
CH_3CH_2CN	2240	. . .
$CH_3CH_2CN^+CH_3BF_4^-$	2400	160
C_6H_5CN	2215	. . .
$C_6H_5CN^+CH_3SbCl_6^-$	2360	145
$C_6H_5CN^+CH_2CH_3BF_4^-$	2345	130
$C_6H_5CN^+C(CH_3)_3SbCl_6^-$	2300	85

groups to the N^{14} nucleus. Double-irradiation experiments in which the alkyl groups were decoupled from each other and from nitrogen allowed the H′–H′ and H′–N^{14} coupling constants to be determined. The spectrum of N-methylacetonitrilium ion before and after such decoupling is shown in Figure 5. The coupling constants are shown in the diagrams. The H′–H′ coupling constant of 2.5 Hz through the C≡N bond is comparable to that of 2.1 to 2.9 Hz through the C≡C bond in substituted acetylenes.[8a]





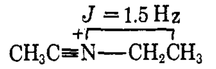


Table IV. Nmr Data of Nitrilium Ions[a]

Compound	δ_{R-C} CH$_3$	δ_{R-C} CH$_2$	δ_{R-C} C$_6$H$_5$	δ_{N-R} CH$_3$	δ_{N-R} CH$_2$	δ_{N-R} C$_6$H$_5$
$CH_3CN^+HSbCl_6^-$	−2.33 (br)					
$CH_3CN^+CH_3BF_4^-$	−2.67 (m) $J_{H-H} = 2.4$ $J_{N-H} = 1.7$			−3.66 (m) $J_{H-H} = 2.4$ $J_{N-H} = 2.7$		
$CH_3CN^+CH_2CH_3BF_4^-$	−2.77 (m)			−1.42 (m) $J_{H-H} = 7.0$ $J_{N-H} = 1.5$	−4.02 (m)	
$CH_3CN^+C(CH_3)_3SbCl_6^-$	−2.83 $J_{N-H} = 1$			−1.61 (br)		
$CH_3CN^+C_6H_5$ (in HSO_3F)	−3.40 (t) $J_{N-H} = 1.4$					−7.85 (m)
$CH_3CH_2CN^+CH_3BF_4^-$	−1.47 (t)	−3.17 (m)		−3.78 (m) $J_{H-H} = 2.5$ $J_{N-H} = 2.7$		
$C_6H_5CN^+CH_3BF_4^-$			−7.60 (m)	−3.93 (br)		
$C_6H_5CN^+C(CH_3)_3SbCl_6^-$			−7.33 (m)	−1.67 (br)		

[a] δ values are in parts per million. J values are in hertz. Abbreviations used are: br, broad; m, multiplet; t, triplet.

The pmr spectra of N-alkylnitrilium ions were obtained in sulfur dioxide solution. Representative spectra are shown in Figures 5 and 6 and the data are summarized in Table IV.

Methyl and methylene groups on the nitrogen atom show more deshielding than alkyl groups on the nitrile carbon atom. For example, the chemical shifts of the N-methyl groups in $CH_3CN^+CH_3$ and $CH_3CH_2CN^+CH_3$ are at δ −3.66 and −3.78, respectively, while the C-methyl shifts in $CH_3CN^+CH_3$ and $CH_3CN^+CH_2CH_3$ are at δ −2.67 and −2.77, respectively. These shifts compare well to those of methyl groups on charged nitrogen. The methyl shift in tetramethylammonium bromide is δ −3.13 while the N-methyl shift in $CH_3C{\equiv}NCH_3$ is −3.66.

The complex pmr peaks of nitrilium ions as shown, for example, in Figure 5 were found to be due to long-range coupling of the N- and C-alkyl groups through the C≡N bond in addition to coupling of the alkyl groups to the N^{14} nucleus.

The N^{14}–H coupling is much larger than the 0.5 Hz observed in tetrahedrally symmetric tetramethylammonium bromide. In contrast to the N^{14}–H coupling in isopropyl isocyanide where the coupling to the β protons is greater than that to the α protons,[8c] the α coupling is greater in nitrilium ions.

The N^{14} chemical shift in $(CH_3C{\equiv}NCH_3)^+$ relative to that of NH_4^+, as determined by the indor method, is 107 ppm to lower field.[20] The N^{14} chemical shift of acetonitrile is −217 ppm relative to NH_4^+;[8c] thus N-alkylation of the nitrile causes a shift to higher field of about 110 ppm.

Nmr investigation of the compound reported by Klages and Grill[21] to be $C_6H_5CN^+CH_3SbCl_6^-$, which was obtained from $SbCl_5$ and N-methylbenzimide chloride, showed that the compound was instead the two isomers IX and X of the N-methylbenzimide chloride–antimony pentachloride donor–acceptor complex. The spectrum of the imidochloride in SO_2 solution at −20° consists of a broad singlet at δ −2.95 and a broad multiplet at δ −7.64 corresponding to the methyl and phenyl groups. At −50° the methyl

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(19) For a discussion see D. Cook in "Friedel-Crafts and Related Reactions," Vol. I, G. A. Olah, Ed., Interscience Publishers, New York, N. Y., 1963, pp 808–809. (b) For a complete infrared investigation of N-methylacetonitrilium ion, see G. C. Turrell and J. E. Gordon, *J. Chem. Phys.*, **30**, 895 (1959). (c) Infrared shifts of nitrile–Lewis acid complexes and nitrilium tetrachloroborates have been recently reported by P. K. Unmat and K. Wade, *J. Chem. Soc.*, *A*, 1612 (1967).

(20) The chemical shift of nitrogen in the ion was obtained in FSO_3H–SbF_5 solution.

(21) F. Klages and W. Grill, *Ann.*, **594**, 21 (1956).

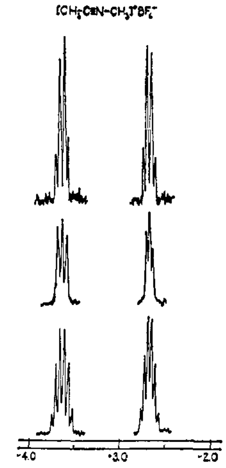
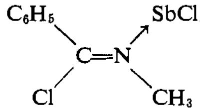
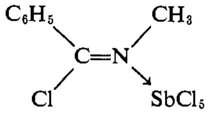


Figure 5. Pmr spectrum of N-methylacetonitrilium ion with no decoupling (bottom), with the methyl protons decoupled from each other (middle), and with nitrogen decoupled (top).

resonance is resolved into two peaks at δ −2.92 and −3.02 indicating the "freezing out" of the *cis* and *trans* isomers. When a solution of $SbCl_5$ in SO_2 was added to a solution of N-methylbenzimide chloride in SO_2 solution, an orange precipitate formed. The pmr spectrum of this solid in SO_2 solution shows two methyl peaks even at +20° indicating the presence of the isomers IX and X.

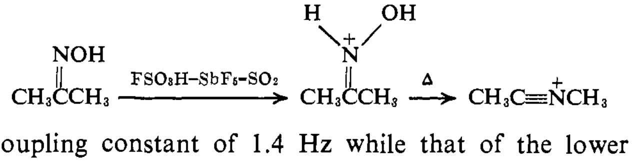


IX



X

We found in our studies that N-alkylnitrilium ions can also be prepared by Beckmann rearrangement of ketoximes in HSO_3F–SbF_5–SO_2 solution or in neat fluorosulfonic acid. When acetone oxime was dissolved in FSO_3H–SbF_5–SO_2 solution, the spectrum of the protonated oxime was observed. The spectrum consists of two doublets at δ −2.20 and −2.26, corresponding to the two methyl groups split by the NH proton, and two broad low-field peaks at δ −11.1 and −12.0, corresponding to the OH and NH protons, respectively. The higher field methyl doublet shows a



$$CH_3\overset{\overset{NOH}{\|}}{C}CH_3 \xrightarrow{FSO_3H-SbF_5-SO_2} CH_3\overset{\overset{H\diagdown\overset{+}{N}\diagup OH}{\|}}{C}CH_3 \xrightarrow{\Delta} CH_3C{\equiv}\overset{+}{N}CH_3$$

coupling constant of 1.4 Hz while that of the lower field one is 1.1 Hz. The larger coupling constant is assumed to be due to *trans* coupling. Upon heating in a sealed tube at 100° for 30 min, the characteristic spectrum of the N-methylacetonitrilium ion appears. Similar observations were made using acetophenone oxime in neat fluorosulfonic acid. The spectrum of the protonated oxime is similar to that of protonated acetone oxime. Upon heating the sample to 100°, an equal intensity triplet arises at δ −3.50. After about 15 min, the peak due to the methyl group of the oxime completely disappears. The triplet, which is due to the methyl group of the ion $(CH_3C{\equiv}NC_6H_5)^+$, degenerates to a broadened singlet at lower temperatures. The coupling constant of 1.4 Hz is consistent with long-range coupling to the N^{14} nucleus.

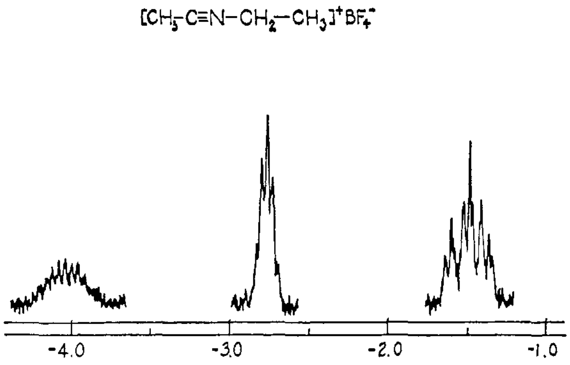


Figure 6. Pmr spectrum of N-ethylacetonitrilium ion in SO_2 solution.

Conclusions

Both protonated nitriles and N-alkylnitrilium ions appear to have linear configurations involving the $-C{\equiv}N^+-$ bond as evidenced by the nmr studies (including C^{13} and N^{15} resonance data) and the observation of only one isomer in all cases studied. Iminocarbonium ion character $-C{\equiv}N^+-$ should give rise to two isomers. Thus all observations indicate that the latter form is only a minor contributor in protonated nitriles and N-alkylnitrilium ions.

The direct observation of protonated hydrogen cyanide and alkylnitriles has direct bearing on our better understanding of the mechanism of Friedel–Crafts type reactions like the Gatterman and Houben–Hoesch reactions, as well as the Ritter reaction.

Experimental Section

All nitriles were of commercially available highest purity. $KC^{13}N$, KCN^{15}, and CH_3CN^{15} were obtained from Merck Sharpe and Dohme, Ltd., Montreal, Canada. Protonation of the nitriles was accomplished by dissolving 0.2 g of the nitrile in 2 ml of sulfur dioxide, cooling to −78°, and adding 2 ml of cold 1:1 FSO_3H–SbF_5. Upon stirring, a clear colorless solution was obtained.

Fifty per cent C^{13}-enriched acetonitrile, $CH_3C^{13}N$, was prepared from C^{13}-enriched $NaC^{13}N$ and methyl sulfate.[22] The acetonitrile was separated from the ether extract by gas chromatography rather than by distillation using an Aerograph Autoprep equipped with a 5-ft DEGS column at 70°.

Quenching of the protonated nitriles was accomplished by pouring the acid solution into cold methanol, adding water, and extracting with ether. The ether solutions were analyzed by gas–liquid partition chromatography using a 5-ft DEGS column. No quantitative measurements were made.

Nitrilium Salts. All of the nitrilium salts except N-methylacetonitrilium tetrafluoroborate were prepared according to the method of Meerwein[6] or, in the case of acetonitrilium hexachloroantimonate, according to the method of Klages and Grill.[4]

N-Methylacetonitrilium tetrafluoroborate was prepared by adding to trimethyloxonium tetrafluoroborate[10] an equimolar amount of carefully dried acetonitrile and allowing the mixture to stand for a few days in a flask protected from moisture with a drying tube. The mixture solidified and could be readily recrystallized from benzonitrile. N-Methylacetonitrilium hexachloroantimonate was prepared by allowing a mixture of the acetonitrile–antimony pentachloride complex and excess methyl chloride to react in a sealed tube at room temperature for 4 or 5 weeks. The salt crystallizes as large yellow cubes and has the same nmr spectrum in SO_2 solution as the tetrafluoroborate.

Pure dry samples of the salts were difficult to obtain due to the very hygroscopic nature of the compounds. The samples used for

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[22] P. Walden, *Ber.*, **40**, 3215 (1907).

the ir spectra were recrystallized twice from benzonitrile, washed twice with CCl_4, and pumped dry under vacuum. Nujol mulls were made up by grinding in a drybox.

An additional method of preparation was found to be successful. The methylacetonitrilium ion was obtained by adding an SO_2 solution of CH_3CN to a solution of CH_3Cl in SbF_5–SO_2. The presence of the ion was detected in the nmr spectrum, but no attempt was made to isolate the salt. The spectrum of the ion appears after only a few minutes at temperatures below −10°,

$$CH_3Cl\rightarrow SbF_5 + CH_3CN \xrightarrow{SO_2} CH_3CNCH_3SbF_5Cl$$

while the preparation from CH_3CN-$SbCl_5$ + CH_3Cl required weeks of standing at room temperature.

Ir and Nmr Spectra. A Beckman IR-10 infrared spectrophotometer was used for all ir spectra. Varian Associates Models A-56/60, HA 100, and HA 60 nmr spectrometers were used for the nmr spectra. Nitrogen and carbon decoupling experiments were performed with the aid of a NMR Specialties Model SD-60B heteronuclear spin-spin decoupler. Indor spectra were taken as previously described[23] using a Hewlett-Packard function generator.

Acknowledgment. Support of the work by grants of the National Science Foundation and the National Institutes of Health is gratefully acknowledged. Dr. A. M. White is thanked for the C^{13} measurements and helpful discussions.

(23) G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, 90, 1884 (1968).

Stable Carbonium Ions. LXVI.[1] Protonation of Diketones in FSO_3H–SbF_5–SO_2 Solution

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Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. *Received February 8, 1968*

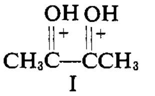
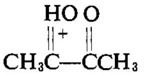
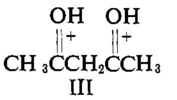
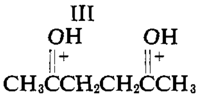
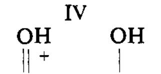
Abstract: 1,2-, 1,3-, and 1,4-diketones were protonated (diprotonated) in FSO_3H–SbF_5–SO_2 solution at −60°. Pmr spectroscopy allowed study of the protonated products.

In continuation of our studies of protonated heteroatom compounds,[3] including protonated ketones,[4] we wish now to report on the investigation of protonated diketones. After our studies were completed, a brief communication by Brouwer[5] appeared, reporting the protonation of acetylacetone, benzoylacetone, and dibenzoylmethane in HF–SbF_5 solution. As our own studies (in FSO_3H–SbF_5 solution) included only one of the diketones investigated by Brouwer (*e.g.*, acetylacetone) and even in this case our observations contain significant new findings, we report them in full.

Results and Discussion

Protonated Aliphatic Open-Chain Diketones. The pmr parameters of protonated diketones have been measured in FSO_3H–SbF_5–SO_2 solution at −60°. It was found that aliphatic diketones like 2,3-butanedione, 2,4-pentanedione, and 2,5-hexanedione are diprotonated in excess 1:1 *M* SbF_5–FSO_3H solution (diluted with sulfur dioxide). At a low concentration of acid (1.5 mol/mol of diketone) there is a tendency toward monoprotonation (as in the case of 2,3-butanedione and 2,3-pentanedione). In all cases there is no indication of resolvable fine structure in the OH resonance (although the peaks are broad), indicating exchange of the proton on oxygen. Table I summarizes the pmr data of protonated aliphatic ketones obtained in FSO_3H–SbF_5–SO_2 solution at −60°.

Table I. Pmr Chemical Shifts of Protonated Aliphatic Diketones[a]

	δ, ppm		
Ion	CH_3	CH_2	$\overset{+}{=OH}$
 $CH_3\overset{\overset{OH}{\Vert +}}{C}-\overset{\overset{OH}{\Vert +}}{C}CH_3$ I	−4.0 (−2.3)	. . .	b
 $CH_3\overset{\overset{HO}{\Vert +}}{C}-\overset{\overset{O}{\Vert}}{C}CH_3$ II	−3.23 (−2.32)	. . .	. . .
 $CH_3\overset{\overset{OH}{\Vert +}}{C}CH_2\overset{\overset{OH}{\Vert +}}{C}CH_3$ III	−3.6 (−2.1) (tr, J = 1.0)	−5.70 (−2.3) (q, J = 1.0)	−16.6 (br)
 $CH_3\overset{\overset{OH}{\Vert +}}{C}CH_2CH_2\overset{\overset{OH}{\Vert +}}{C}CH_3$ IV	−3.5 (2.2)	−4.3 (−2.7)	−15.5 (br)
 $CH_3\overset{\overset{OH}{\Vert +}}{C}-CH=\overset{\overset{OH}{\vert}}{C}CH_3$ V	−2.52 (br)	−6.13 (br)	. . .

[a] Chemical shifts of parent ketones are in parentheses. J values in hertz. Abbreviations used: br, broad; q, quartet; tr, triplet; [b] Not observable even at −100°.

2,3-Butanedione (diacetyl) in excess 1:1 FSO_3H–SbF_5–SO_2 shows a single methyl absorption at −4.0 ppm (Figure 1a). The absorption peak, although somewhat broadened, showed no observable coupling. We interpret the highly deshielded single methyl absorption

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(1) Part LXV: G. A. Olah and T. E. Kiovsky, *J. Amer. Chem. Soc.*, **90**, 4666 (1968).

(2) Postdoctoral Research Investigator, 1966–1967.

(3) For a review see G. A. Olah, *Chem. Eng. News*, **45**, 76 (March 27, 1967).

(4) (a) G. A. Olah, M. Calin, and D. H. O'Brien, *J. Amer. Chem. Soc.*, **89**, 3586 (1967); (b) G. A. Olah and M. Calin, *ibid.*, **90**, 938 (1968).

(5) D. M. Brouwer, *Chem. Commun.*, 515 (1967).