Stable Carbonium Ions. LXXX.[1a] Protonation, Alkylation, and Acylation of Aziridine, N-Alkylaziridines, and N-Acylaziridines. Aziridinium, N-Alkylaziridinium, and N-Acylaziridinium Ions

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Abstract: Aziridinium, N-alkyl(aryl)aziridinium, and N-acylaziridinium ions were prepared either as isolated crystalline trifluoroacetate or tetrafluoroborate salts, or obtained in solution by protonation of aziridines in CF_3COOH–SO_2, HF–SbF_5–SO_2, or FSO_3H–SbF_5–SO_2 solution, by alkylation of aziridine with trialkyloxonium or alkylcarbonium ion salts and acylation of aziridine by oxocarbonium hexafluoroantimonates. Nmr parameters of the aziridinium ions are reported.

Several of the biological alkylating agents[2a] that were found effective as antineoplastic drugs,[2b] insect chemosterilants,[3] antiadrenalin, and antihistaminic agents[4] contain aziridine rings as their functional groups.

Marckwald and Frobenius first postulated the formation of an aziridinium ion in 1901.[5] The possible existence of aziridinium ions as intermediates in solvolytic reactions was reported, and the subject was adequately reviewed.[6,7]

The first stable aziridinium salts were isolated by Gulombic, Fruton, and Bergman.[8] More recently a variety of aziridinium salts became available due to the general synthetic method discovered by Leonard and coworkers.[9]

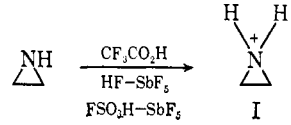
Salts of aziridine with inorganic and organic acids have been reported, although the aziridine ring is readily polymerizing in acidic media even at low temperatures. The reported salts include the chloride,[10] picrate,[11] tetrafluoroborate,[12] hydrogen phosphite, dihydrogen phosphate, hydrogen sulfate,[13] and the 2,4,6-trinitrobenzene sulfonate.[14]

Leonard and coworkers[9] reported the relatively stable N,N-diethylaziridinium ion, as well as some of the more highly substituted aziridinium salts. Neither sufficient characterization nor structural investigation of the aziridinium ion itself was reported, nor, except for N-isopropyl-2,2,3-trimethylaziridinium chloride, were any N-monoalkylaziridinium ions known.[15] No N-acylaziridinium ions were previously reported.

Results and Discussion

We wish now to report the preparation and investigation of a series of aziridinium, N-alkylaziridinium, and N-acylaziridinium ions and their nmr structural study. Since aziridinium ions are the possible intermediates in certain biological alkylating reactions as precursors of carbonium ions, they were of interest in our continued study of reactive cationic intermediates.

Aziridinium Ion. The addition of aziridine to a dimethoxyethane solution of trifluoroacetic acid at $-10°$ yielded quantitatively aziridinium trifluoroacetate (I). The white crystals were filtered under nitrogen. The material could be kept at 0° indefinitely. The same aziridinium ion was also obtained when aziridine was dissolved into HF–SbF_5–SO_2 or HSO_3F–SbF_5–SO_2 solution at $-60°$.



I

The nmr spectrum (Figure 1) shows a deceptively simple triplet at δ 2.80 of the ring protons and a broad peak at δ 8.25 of the NH_2 protons. The coupling between the methylene protons and the NH_2^+ proton is an average 6 Hz. This coupling cannot be seen in the peak due to the NH_2 protons because of the quadrupole broadening. The integration of amine to methylene protons gave the expected 1:2 ratio.

N-Alkylaziridinium Ions. The preparation of the N-methyl- and N-ethylaziridinium ion (II) was accomplished by two different routes. Aziridine was methylated by trimethyl- and triethyloxonium tetrafluoroborate,[16] and N-methyl- and N-ethylaziridine were protonated at low temperature by trifluoroacetic acid, HF–SbF_5, or FSO_3H–SbF_5. Some difficulty was experienced using the first method as the separation of the

(1) (a) Part LXXIX: A. M. White and G. A. Olah, *J. Amer. Chem. Soc.*, **91**, 2943 (1969); (b) National Institutes of Health Predoctoral Research Investigator, 1966–1968.

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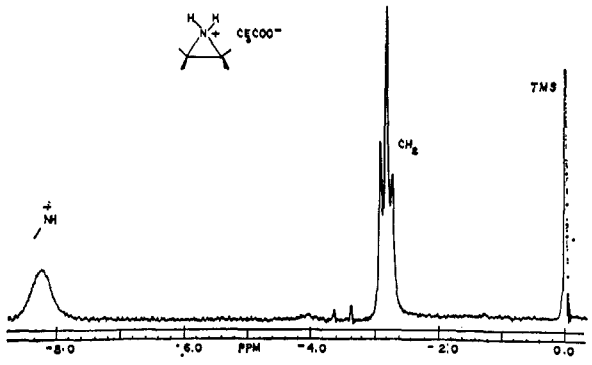


Figure 1. Aziridinium ion.

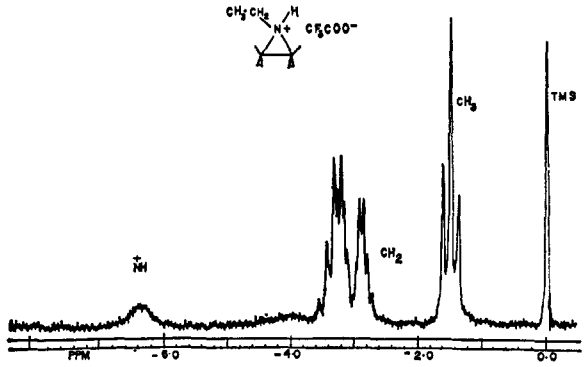


Figure 3. N-Ethylaziridinium ion.

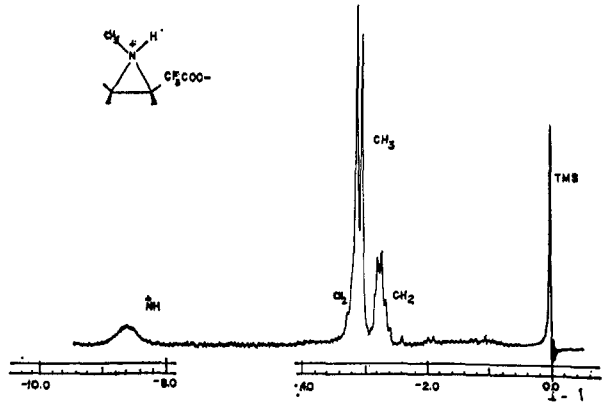


Figure 2. N-Methylaziridinium ion.

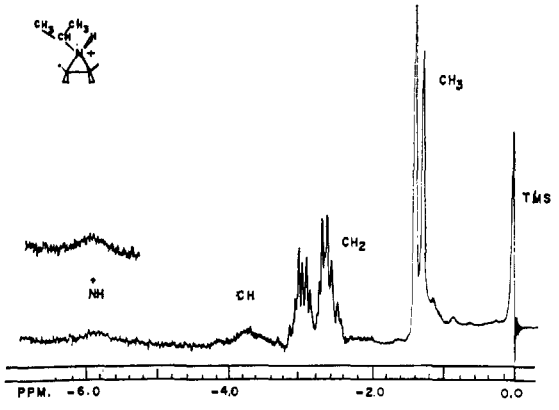
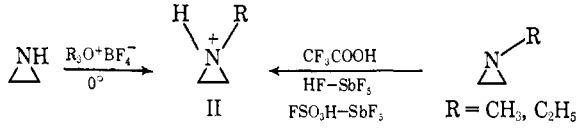


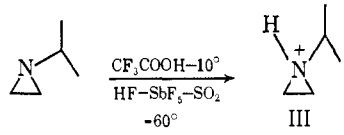
Figure 4. N-Isopropylaziridinium ion.

aziridinium salt from the unreacted oxonium salt was difficult and the material could not be readily recrystallized. Both routes gave the identical N-alkylaziridinium ions (II). The nmr spectrum (Figure 2) of the **N-methylaziridinium ion** shows a doublet for the methyl group at δ 3.05 with a coupling at 5 Hz. A complex AA'BB'X multiplet for the ring protons centered at δ 3.00, as was observed for most N-alkylaziridinium ions. In the case of the N-methylaziridinium ion, the methyl



doublet overlaps with the low-field portion of the methylene proton pattern. The protons on nitrogen appear at δ 8.47 as a broad peak. In the nmr spectrum of the **N-ethylaziridinium ion** (Figure 3) the methyl protons show a triplet with J_{HH} = 7.3 Hz. The α-methylene quartet is centered at δ 3.26, overlapping with the low-field portion of the ring methylene proton AA'BB'X pattern which centers around δ 3.10. No long-range coupling could be observed with the NH proton. The NH proton appears at δ 6.40 as a broad peak. The higher field position of this proton *vs.* the one in I reflects the larger shielding effect of the ethyl group.

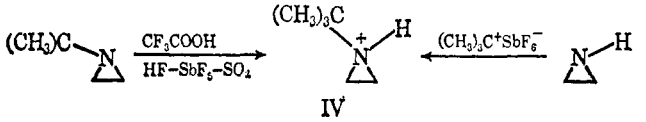
N-Isopropylaziridinium ion (III) has been prepared by the protonation of N-isopropylaziridine (Figure 4). N-Isopropylaziridine was prepared from N-isopropylaminoethyl alcohol by a modification of the method of Elderfield and Hageman.[17] The resulting N-isopropylaziridine was extracted into a 2:1 solution of SO_2 in trifluoroacetic acid at $-60°$ or into $HF–SbF_5–SO_2$ at the same temperature. The nmr spectrum of the N-isopropylaziridinium ion shows a doublet due to the methyl groups at δ 1.33 (J_{HH} = 6 Hz), a well-resolved complex AA'BB'X pattern centering at δ 2.80, a broad peak due to the methine proton at δ 3.75, and a broad peak due to the NH proton at δ 5.90. Integration of the peak areas supports the assignments.



N-*t*-Butylaziridinium ion (IV) was prepared from N-*t*-butylaziridine in $CF_3COOH–SO_2$ or $HF–SbF_5–SO_2$ at $-60°$. The N-*t*-butylaziridine ion was also obtained (besides protonated aziridine) when aziridine was *t*-butylated with a solution of the *t*-butyl cation in $SbF_5–SO_2$ or $HF–SbF_5–SO_2$ solution. The resulting spectrum shows a singlet at δ 1.26 due to the *t*-butyl group. This could not be resolved to show any long-range coupling with the NH proton. The ring protons centered at δ 2.73, showing a considerable deshielding ($\Delta\delta$ 1.20 ppm) from unprotonated *t*-butylaziridine and have a pattern of the usual AA'BB'X spectra, although the width of this pattern is smaller (δ 0.35) in this case than observed for other N-alkylaziridinium ions. A possible explanation is that due to steric factors the proton shift (ν_{AB}) is unusually

(17) R. C. Elderfield and H. A. Hageman, *J. Org. Chem.*, **14**, 605 (1949).

small in *t*-butylaziridines.[18] Due to reduced viscosity the spectrum of ring protons was best observed at −20° where the individual peaks could be well resolved. The NH proton was observed at δ 8.00, but as usual only as a broad peak. Integration of the peak areas gave the expected 1:4:9 ratio.

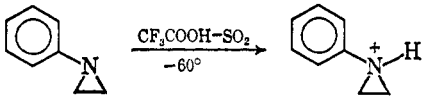


IV

N-Phenylaziridinium Ion (V). Ross and coworkers have shown that phenyldi-β-chloroethylamines differ from their purely aliphatic analogs.[19,20] Hydrolysis of these compounds is proposed to proceed by an SN1 mechanism.[21] An intramolecular mechanism is also indicated by the fact that: (a) the rate of hydrolysis of substituted phenylbis(2-chloroethyl)amines increases with increasing electron donor properties of the ring substituent and that: (b) the rate of hydrolysis falls sharply when chloride ion is added to the solution.[21-24] The formation of a stable phenylaziridinium ion as intermediate has not yet been observed. The observation and proof of this ion was expected to be difficult, since the stability of the aziridinium ring should be reduced due to the electron-attracting properties of the phenyl nucleus.

Phenylbis(2-chloroethyl)amines react faster with anions as their nucleophilicity increases. In this case, in contrast to hydrolysis, the reaction apparently proceeds by an SN2 mechanism.[20] Other sulfur and nitrogen mustards also show a mass law effect for added chloride, but still show the expected SN2 trend with nucleophilicity.[25]

N-Phenylaziridine was prepared and protonated at −60° as described in the Experimental Section.



V

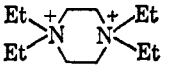
The nmr spectrum of the solution showed clearly the AA'BB'X multiplet due to the methylene protons centering at δ 3.50. The pattern is very similar to the one observed in the case of N-alkylaziridinium ions. The phenyl ring becomes a sharp singlet at δ 7.60, and the NH proton was observed at δ 9.80 as the usual broad peak. Integration of the peak areas gave the expected 1:5:4 ratios. The existence of the stable N-phenylaziridinium ion is thus proven and it seems to be feasible to suggest its involvement in the hydrolysis of the phenyldi-β-chloroethylamines. The nmr data of the N-alkyl(aryl)aziridinium ions studied are summarized in Table I.

Table I. Nmr Data of N-Alkylaziridinium Ions[a]

R	CH_2	N-H	R
H	2.80 (tr) J_{NHCH_2} = 6	8.25 (br)	
CH_3	3.00	8.47 (br)	3.03 (d) J_{CH_3-NH} = 5
C_2H_5	3.10	6.40 (br)	3.26 (qu) 1.50 (tr) $J_{CH_3-CH_2}$ = 7.3
$(CH_3)_2CH$	2.80	5.90 (br)	1.33 (d) 3.73 (m) J_{CH_3-CH} = 6
$(CH_3)_3C$	2.73 J_{NH-CH_2} = 0.35	8.00 (br)	1.26 (s)
Phenyl	3.50	9.80 (br)	7.60

[a] In δ, parts per million (ppm), from external TMS. Abbreviations used are: br, broad; s, singlet; d, doublet; tr, triplet; m, multiplet; qu, quintet. *J* values in hertz.

It is possible now to compare the ring proton spectra of N-alkylaziridinium ions with the spectra of the previously known N,N-dialkylaziridinium salts. N,N-Diethylaziridinium perchlorate,[9] tetrafluoroborate, and chloride[26] show singlets for the ring methylene protons at δ 3.08 as, due to symmetry the protons become equivalent. Similarly N,N-dimethylaziridinium salts show two overlapping singlets due to the methyl and methylene protons at δ 3.05.[26] This was taken as evidence that the spectrum was due to the aziridinium ring because the dimer, which forms as the side product, absorbs at lower fields. In the piperidinium ion (VI), the ring methylene protons appear at 3.82.[9,26,27]



VI

For further comparison we prepared the N-ethyl-N-methylaziridinium ion (VII) by Meerwein's method.[28] N-Ethylaziridine was treated with trimethyloxonium tetrafluoroborate or N-methylaziridine with triethyloxonium tetrafluoroborate in dimethyloxethane solution. The resulting aziridinium salt was dissolved in sulfur dioxide at low temperature (−60°). The nmr spectrum showed a triplet at δ 1.40 and a quartet at δ 3.25 (J_{HH} = 7 Hz) due to the ethyl group and two singlets poorly resolved and partially overlapping with the quartet, at δ 2.97 and 3.03. The first one is assigned to the methyl group and the latter to the ring methylene protons in analogy with the N,N-diethylaziridinium salts.[26,29,30]

VII

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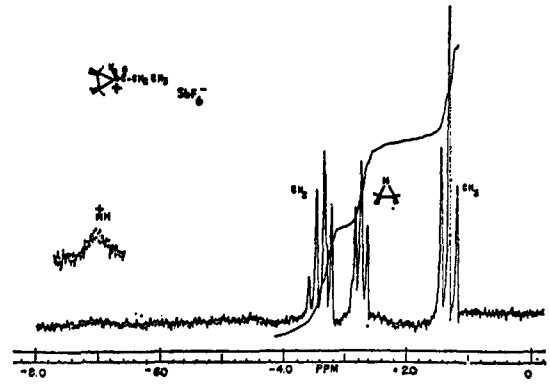


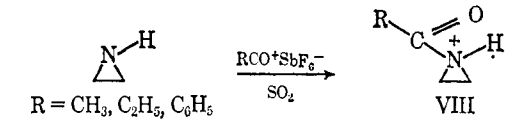
Figure 5. N-Propionylaziridinium ion.

The nmr study of N-substituted aziridines showed that, because of the suitable magnitude of nitrogen inversion rate, the ring protons give rise to AA'BB' spectra at lower temperatures.[18,31] The AA'BB' spectrum of aziridine shows a symmetrical spectrum with $J_{AB} = 10$ Hz.[32]

Recently Brois reported that ring protons *cis* to the magnetically anisotropic N-alkyl bond are shifted about 25 Hz upfield relative to the ring protons in aziridine.[18] It was proposed that intramolecular dispersion forces between the N-alkyl and the ring protons are responsible for the observed chemical shifts.

In our study of N-alkylaziridinium ions, in all cases investigated, the ring methylene protons show an AA'BB'X' pattern. By analogy with Brois' work, the upfield part of spectrum is due to the protons *cis* to the alkyl, and *trans* to the NH proton. We find that the coupling of the NH proton to the *cis*-methylene proton is always larger ($J = 4.6$ Hz) than the coupling to the *trans*-methylene protons ($J = 1.5$–2.0 Hz or less). The other coupling constants, $J_{AB'}J_{AB'}$, and $J_{BB'}$, cannot be easily determined without a complete computer analysis program. The ring spectrum overlaps with the N-alkyl substituents and it is also very difficult to observe the low intensity outside peaks. Recently Saito and coworkers have reported the following coupling constants for substituted aziridines: $J_{AB'}$ (*cis*) between 3.0 and 6.5 Hz, $J_{AB'}$ (*trans*) 1 and 4 Hz, and for $J_{AA'}$ (geminal) 5 and 7 Hz.[33] These parameters are in agreement with our findings.

N-Acylaziridinium Ions. N-Acylaziridinium ions were obtained by acetylation of aziridine with stable oxocarbonium (acylium) ion salts. The oxocarbonium ion salts were prepared as described previously.[34] Aziridine was acylated (aroylated) with methyl-, ethyl-, and phenyloxocarbonium hexafluoroantimonate ($CH_3CO^+SbF_6^-$, $CH_3CH_2CO^+SbF_6^-$, and $C_6H_5CO^+SbF_6^-$). The reactions proceed smoothly in SO_2 solution at $-60°$, and the formed N-acetylaziridinium ions (VIII) are stable at this temperature. The nmr spectrum of N-propionylaziridinium ion is representative (Figure 5). It shows the aziridinium protons



as an AA'BB'X system centered at around δ 3.00, the lower field quintet overlapping with the methylene quartet of the propionyl group. The aziridinium ring pattern is similar to that of the N-alkylaziridinium ions. The acyl group is deshielded but not as much as in the starting oxocarbonium ion salt. The nmr data of the studied N-acylaziridinium ions are summarized in Table II.

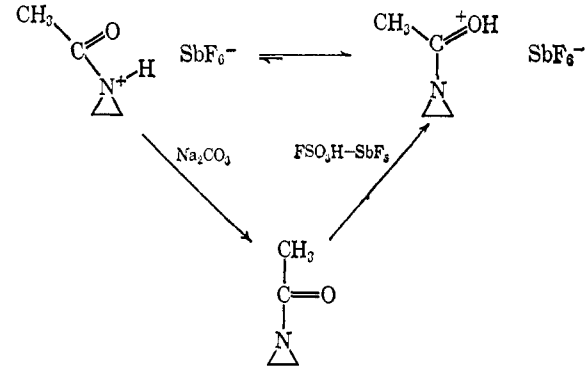
Table II. Nmr Data of N-Acylaziridinium Ions[a]

RCOHN	R	CH_2	NH
CH_3	3.16 (s)	2.93	7.00 (br)
C_2H_5	1.50 (tr)		
	3.56 (q)	3.10	7.20 (br)
	$J_{HH} = 7.5$		
C_6H_5	7.00		
	8.00 (m)	3.10	6.80 (br)

[a] In δ, parts per million (ppm), SO_2 solution at $-60°$. Abbreviations used are: s, singlet; tr, triplet; q, quadruplet; m, multiplet; br, broad. J value in hertz.

Support for the assignments comes from quenching experiments with Na_2CO_3, giving the corresponding N-acylaziridines in high yield (generally better than 80%) along with some polymeric by-products.

It can be suggested that the observed N-acylaziridinium ions are in equilibrium with the O-protonated species, but the latter are present at low temperatures only in low concentration and cannot always be detected easily by nmr spectroscopy. Supporting this suggestion is the observed temperature and acid concentration dependence of O-protonated N-acetylaziridine and the observation of low intensity nmr peaks at δ 2.76 and 5.00, in the nmr spectrum of the N-acetylaziridinium ion, in the general region where the O-protonated species show resonance absorptions. Further evidence for the structure of the N-acyl-



aziridinium ions comes from the comparison of their nmr spectra with those of the N-acylpyridinium ions[35] which can be used as model compounds. Figure 6

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(35) Pyridine readily forms adducts with acyl halides, which are used in the well-known acylation method of Einhorn. W. von E. Doering and W. E. McEwen (*J. Amer. Chem. Soc.*, 73, 2104 (1951)), suggested first the N-acylpyridinium structure of these adducts. F. Klages and E. Zange, *Ann.*, 607, 35 (1957), prepared a series of tertiary N-acylammonium salts. To our best knowledge, however, no nmr investigation of any of these compounds was yet reported.

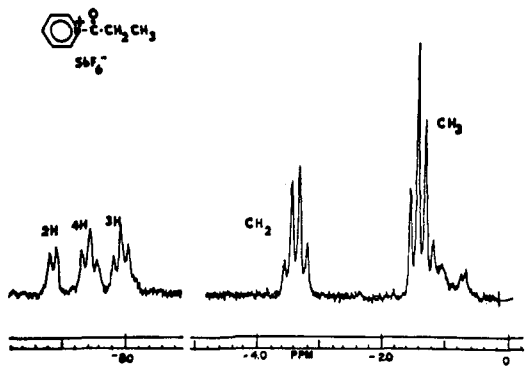


Figure 6. N-Propionylpyridinium ion.

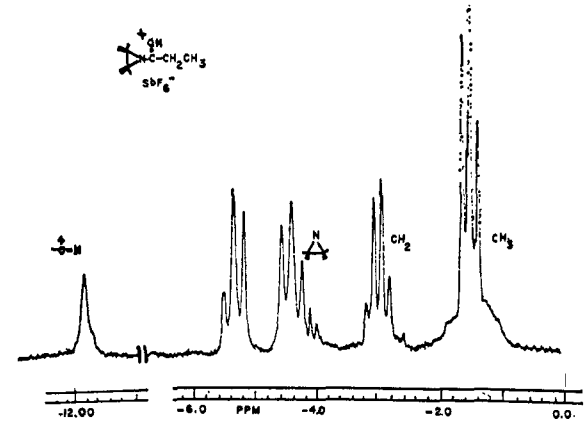
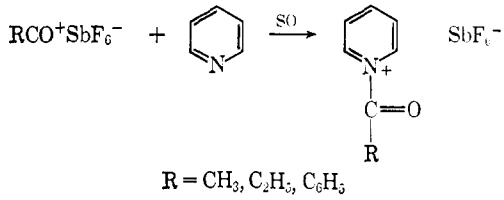


Figure 7. O-Protonated N-propionylaziridine.

shows the nmr spectrum of the N-propionylpyridinium ion which is representative. N-Acylpyridinium hexafluoroantimonates were prepared by adding an equimolecular SO_2 solution of the oxocarbonium salt ($CH_3CO^+SbF_6^-$, $CH_3CH_2CO^+SbF_6^-$, $C_6H_5CO^+SbF_6^-$) to a cold pentane solution of pyridine at $-60°$. Pyridine is slowly extracted into the SO_2 layer forming the N-acylpyridinium salt.



$R = CH_3, C_2H_5, C_6H_5$

For comparison with the N-acylaziridinium ions, the corresponding nmr data of the N-acylpyridinium ions are summarized in Table III. The ring pattern of the N-acylpyridinium ions are similar to those observed in N-nitro- and N-nitrosopyridinium ions.[36]

Table III. Nmr Data of N-Acylpyridinium Ions[a]

RCO-$NC_5H_5^+$	R	2-$NC_5H_5^+$	3-$NC_5H_5^+$	4-$NC_5H_5^+$
CH_3	2.57 (s)	8.17 (d)	7.42 (tr)	7.80 (tr)
C_2H_5	1.40 (tr) J_{HH} = 7 3.33 (q)	8.37 (d)	7.67 (tr)	7.83 (tr)
C_6H_5	7.16–8.90 (m)	8.60 (d)	7.60 (tr)	7.91 (tr)

[a] In δ, parts per million (ppm), SO_2 solution at $-60°$. Abbreviations used are: s, singlet; tr, triplet; q, quadruplet; m, multiplet; br, broad. J value in hertz.

The greater deshielding observed in the acyl groups of N-acylpyridinium ions as compared with those of the corresponding N-acylaziridinium ions indicates that the aziridine ring delocalizes charge preferentially to the pyridinium ring.[36,37]

N-Acylaziridinium ions represent an interesting case of N-protonated amides. Direct protonation of amides generally results in carbonyl oxygen and not nitrogen protonation.[37-39] It was, therefore, of interest to study the protonation of N-acylaziridines in order to obtain the expected O-protonated isomeric ions.

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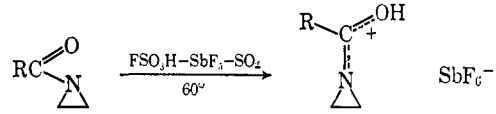
The protonation of N-acylaziridines was carried out in FSO_3H–SbF_5–SO_2 solution at $-60°$. The N-acylaziridine was usually carefully extracted from petroleum ether (bp 30–60°) or *n*-pentane solution into the acid layer. Some polymerization took place, but the insoluble polymer precipitated and the clear separated solution contained the protonated N-acylaziridines.



$R = CH_3, C_2H_5, C_3H_7, C_6H_5, C_{10}H_7$

The following protonated N-acylaziridines were observed: N-acetyl-, N-propionyl-, N-butyryl-, N-benzoyl-, and N-naphthoylaziridine. The spectra are consistent with the oxygen-protonated species. The alkyl and aryl groups are somewhat deshielded, the aziridine ring protons are around δ 5.00. The greater deshielding as compared to that of about δ 3.00 in the N-alkylaziridinium ions, is suggested to be due to the sp^2 character of the nitrogen atom in the protonated N-acylaziridinium ions.

The nmr spectra of protonated N-propionylaziridine is representative of N-acylaziridines in FSO_3H–SbF_5–SO_2 solution (Figure 7). Chemical shifts and coupling constants are summarized in Table IV.

Table IV. Nmr Data of Protonated N-Acylaziridines[a]

	R	Ring CH_2	OH
CH_3	2.96 (s)	5.00 (m)	9.06 (s)
C_2H_5	1.58 (tr) 3.07 (q)	4.75 (m)	9.94 (s)
C_3H_7	1.60 (tr) 1.83 (s) 2.76 (tr)	4.83 (m)	10.56 (s)
C_6H_5	8.00 (br, s)	4.80 (m)	10.40 (s)
$C_{10}H_7$	7.80, 8.00 (m)	4.40 (m)	8.40 (s)

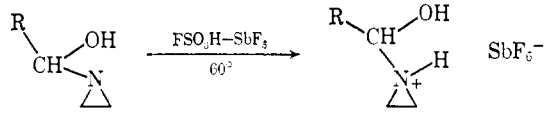
[a] In δ, parts per million (ppm), FSO_3H-SbF_5-SO_2 solution at $-60°$. Abbreviations used are: s, singlet; tr, triplet; q, quadruplet; m, multiplet; br, broad.

The protonation of N-acylaziridines in strongly acidic solutions without opening of the ring is noteworthy. Aziridine derivatives which contain substituents capable of stabilizing a negative charge,

usually undergo ring-opening reactions with nucleophiles easily even in the absence of an acid catalyst.[40-43] The ability of the N-acyl substituent to conjugate with the partial negative charge on the aziridine nitrogen atom greatly reduces the activation energy needed for reaction with nucleophiles compared with N-alkyl-substituted aziridines.[44]

The protonation without ring opening of N-acylaziridines seems to depend on the addition of aziridines to excess of very strongly acidic solutions, where all aziridines present will be in the protonated form and consequently SN1 type reactions will be prevented. The extremely low nucleophilicity of the gegenions also prevents ring opening reactions.

Similarly to the protonated of N-acylaziridine, 1-aziridinylethanol, and 1-aziridinylpropanol (prepared by the method of Rabourn and Howard[45]) are also protonated in FSO_3H–SbF_5–SO_2 solution at −60° without ring opening. Protonation takes place on the nitrogen atom. Supporting this assignment is the fact that on warming the samples to about −20° protonated aziridine and protonated acetaldehyde (propionaldehyde) formed.



R = CH_3, C_2H_5

The nmr spectra show the expected features a triplet at δ 1.50 due to the overlapping methyl groups, coupled to the CH proton, a complex multiplet at δ 2.83 due to the ring protons. The methine proton appears at δ 4.76 and 4.53 as a quartet. The two broad peaks, one at δ 6.63 (6.26) and the other at 7.66 (7.03), assigned to the NH and OH protons, respectively (Table V).

Table V. Nmr Chemical Shifts of Protonated N-Aziridine-1-ols[a]

R	CH_3CH_2	CH	Ring CH_2	NH	OH
CH_3	1.50 (d)	4.76 (q)	2.83 (tr)	6.63 (br)	7.66 (br)
C_2H_5	0.93 (tr)	4.53 (q)	2.83 (tr)	6.26 (br)	7.03 (br)
	1.86 (q)				

[a] In δ, parts per million (ppm), FSO_3H–SbF_5–SO_2 at −60° Abbreviations used are: d, doublet; tr, triplet; q, quadruplet; br, broad.

Experimental Section

Materials. Aziridine and N-ethylaziridine were obtained from the Dow Chemical Company. N-Methylaziridine was prepared from 2-methylaminoethanol and N-*t*-butylaziridine from 2-*t*-butylaminoethanol,[46,47] N-isopropylaziridine, and N-isopropylaminoethanol were prepared by the Elderfield-Hageman modification of Wenkert's synthesis.[47] N-Phenylaziridine was prepared from N-β-bromoethylaniline-hydrogen bromide[48] by the Gabriel synthesis as described by Heine and Kapur.[49] Trimethyl- and triethyloxonium tetrafluoroborates were prepared by Meerwein's general method.[28] Trifluoroacetic acid was the commercially available grade (Aldrich Chemical Company). Hydrogen fluoride–antimony pentafluoride and fluorosulfuric acid–antimony pentafluoride were purified as previously discussed.[50]

Preparation of Aziridinium Ions. Aziridinium Trifluoroacetate (I). In a 100-ml, three-necked flask, under N_2 stream, and magnetic stirring, 11.4 g (0.1 mol) of trifluoroacetic acid in 50 ml of dimethoxyethane (DME) was cooled to −10°. To this solution was added 4.2 ml (0.1 mol) of precooled aziridine in 10 ml of DME. The solution was stirred vigorously. After the addition was completed, the solution was left to warm at room temperature. White crystals of aziridinium trifluoroacetate fall out almost quantitatively. To avoid decomposition by humidity, the crystals were vacuum filtered under nitrogen stream at −60°. These crystals melted at 60–62°. The material is stable at 0° indefinitely. Nmr samples were prepared by dissolving it in SO_2 at −60°. It should be noted that, if a solution of aziridine were added directly to a mixture of SO_2–CF_3COOH solution, rapid polymerization was observed even at −60°. Furthermore, the same spectra were observed by extracting aziridine from petroleum ether into a solution of FSO_3H–SbF_5–SO_2 or HF–SbF_5–SO_2 at −50°. The lower acid layer contained the protonated aziridine. This method of preparation was, however, somewhat less advantageous.

N-Methyl- and N-ethylaziridinium tetrafluoroborates were prepared by adding 0.1 mol of trimethyloxonium or triethyloxonium tetrafluoroborate in 100 ml of dry DME to 3.9 g (0.1 mol) of aziridine in 10 ml of DME at 0°. The solution was stirred for 15 min and the salts precipitated by adding dry dichloromethane. The crystals were filtered under nitrogen and a yield of 85 and 83%, respectively, was obtained. The aziridinium salts could be dissolved in SO_2 at −60° without polymerization or decomposition.

N-Ethyl-N-methylaziridinium Tetrafluoroborate. The addition of 5 g (0.1 mol) of N-ethylaziridine in 10 ml of DME to 12.3 g (0.1 mol) of trimethyloxonium tetrafluoroborate in 50 ml of DME at 0° with subsequent precipitation by methylene chloride resulted in an 82% yield of the N-ethyl-N-methylaziridinium tetrafluoroborate salt. Similarly the same compound was prepared by adding 5 ml of N-methylaziridine in 10 ml of DME to 15 g of trimethyloxonium tetrafluoroborate in 50 ml of DME at −10°. The salt precipitated with methylene chloride. The white crystalline salt when dissolved in SO_2 gave an identical nmr spectrum with samples obtained from both reactions.

N-Alkylaziridinium Ions by Protonation of N-Alkylaziridines. The protonation of N-substituted aziridines was carried out in the following way. A 1:1 solution of trifluoroacetic acid, HF–SbF_5, or FSO_3H–SbF_5 in SO_2 was prepared and cooled to −60°. A solution of the specific aziridine in pentane or petroleum ether (bp 30–60°) was also cooled and carefully added to the cooled acid solution with vigorous agitation. The aziridinium salt was thus extracted into the SO_2 layer, which was separated and used directly in spectroscopic studies.

Protonation of N-Acylaziridines. N-Acetylaziridine (Dow Chemical Co.), N-butyrylaziridine (Dow Chemical Co.), and N-naphthoylaziridine (Aldrich Chemical Co.) were used without further purification. N-Benzoylaziridine was prepared by the method of Goldberg and Kelly[51] and also by a new route reacting benzoyl fluoride and aziridyllithium in ether solution.[52,53] To a 0.22 mol solution of aziridyllithium in 140 ml of ether 0.22 mol of benzoyl fluoride in 50 ml of ether was added dropwise with vigorous stirring. Care was taken to keep the mixtures at around 0°. After the addition was completed the solution was hydrolyzed and the ether layer separated and dried. The ether was carefully evaporated *in vacuo*. The remaining N-benzoylaziridine was 95% and could be crystallized upon cooling (mp +8°), but could not be purified by distillation. The yield was 72%. N-Propionylaziridine was similarly prepared from propionyl fluoride and aziridyllithium in 66% yield.

The protonation of N-acylaziridine was carried out by adding to 2 ml of solution of 1:1 of HF–SbF_5–SO_2 or FSO_3H–SbF_5–SO_2 the appropriate N-acylaziridine in *n*-pentane. Where possible the solutions were precooled to −60°. With vigorous agitation the acylaziridine salts were extracted into the SO_2 layer.

Acylation of Aziridine. Methyl-, ethyl-, and phenyloxocarbonium hexafluoroantimonates were prepared as described previously.[34] The oxocarbonium ion salt (0.005 mol) was dissolved in 2 ml of SO_2 at −60° with complete exclusion of moisture (in a

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drybox). An equimolar amount of aziridine was dissolved in 2 ml of *n*-pentane and the cold solution added with vigorous agitation to the SO_2 solution of the oxocarbonium ion salt. The solutions of the N-acylaziridinium ions were used directly in the nmr spectroscopic studies. The N-acylpyridinium ions were prepared similarly to the N-acylaziridinium ions.

Protonation of N-Aziridin-1-ols. N-Aziridine-1-ethanol and N-aziridine-1-propanol were prepared by the method described by Rabourn and Howard,[4b] condensing acetaldehyde (propionylaldehyde) and aziridine at 0 to −5°. Protonation was carried out in CF_3COOH–SO_2 solution at −40 to −60°.

Nmr Spectra. Varian Associates A-56/60A spectrometer with a variable-temperature probe was used for all spectra. Coupling constants are believed accurate to ±0.1 Hz. Samples of isolated aziridinium ions in SO_2 at −60° or solutions of protonated N-alkylaziridinium ions made up as described in acid–SO_2 solutions at −60° were used for all the nmr studies. Small solvent effects on the chemical shift were observed ($\Delta\delta$ 0.2 ppm) when acid concentrations or gegenions were changed.

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Stable Carbonium Ions. LXXXI.[1] Alkyl(aryl)halocarbonium Ions and Haloarylcarbonium Ions[2]

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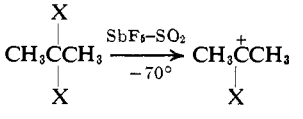
Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. *Received October 30, 1968*

Abstract: Sixteen stable alkyl(aryl)halocarbonium ions and haloarylcarbonium ions containing conjugatable halogen have been prepared and examined using ^1H and ^{19}F nmr spectroscopy. The charge distributions in these ions are discussed.

In previous publications[4] from these laboratories it has been shown that a wide variety of heteroatom-substituted carbonium ions can easily be formed. As expected, these ions exhibit an enhanced stability relative to the corresponding ions with hydrocarbon fragments in place of the heteroatom. This work describes related work with halogen as the heteroatom. Part of this work has been reported in preliminary communications.[5]

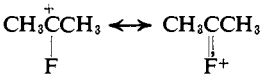
Results

Dimethylhalocarbonium Ions. When 2,2-dihalopropane (**1**) is treated with SbF_5 in SO_2 at −70°, the corresponding dimethylhalocarbonium ion **2** is formed.



1-F, X = F **2**-F, X = F
1-Cl, X = Cl **2**-Cl, X = Cl
1-Br, X = Br **2**-Br, X = Br

The pmr spectra of **1**-F and **2**-F (Figure 1) shows that the methyl groups in the ion are considerably deshielded from those of the precursor **1**-F, indicating carbonium ion formation. The methyl absorption of **1**-F is split into a triplet by the two equivalent fluorine nuclei (J_{HF} = 17.6 Hz), while the pmr spectra of the ion **2**-F, is a doublet (J_{HF} = 25.4 Hz), showing coupling to only one fluorine nucleus. The fluorine nmr spectra of **1**-F and **2**-F (Figure 1) is completely consistent with the conclusions reached from the proton spectra and illustrates the importance of charge delocalization onto fluorine. The ^{19}F resonance of the ion **2**-F is at ϕ −181.91, 267 ppm deshielded from the resonance of **1**-F.



The proton resonance of **2**-Cl (singlet δ 4.06) is deshielded from that of its precursor **1**-Cl. The same is true for the spectra of **1**-Br and **2**-Br.

Both **2**-F and **2**-Cl are stable to −30° for at least 30 min. In contrast, ion **2**-Br is only stable below −70°; above this temperature **2**-Br is converted to ion **2**-F. Whether this is due to the ion's low C–Br bond strength (as compared to that of C–F and C–Cl) or if the ion is inherently unstable because of a lesser amount of charge delocalization onto bromine is unknown. The nmr spectra of the dimethylhalocarbonium ions and their precursors are tabulated in Table I.

Table I. Chemical Shifts of Dimethylhalocarbonium Ions

X	Precursors $(CH_3)_2$–CX_2, **1** CH_3	^{19}F	Ion CH_3–CX–CH_3, **2** CH_3	^{19}F
F	1.30[a]	ϕ +84.93[a]	3.83[b]	ϕ −181.91[b]
Cl	1.89		4.06	
Br	2.38		3.82	

[a] J_{CH_3-F} = 17.6 Hz. [b] J_{CH_3-F} = 25.4 Hz.

Phenylmethylhalocarbonium Ions. When α,α-dihaloethylbenzene (**3**) is treated with SbF_5 in SO_2 at −70°,

(1) Part LXXX: G. A. Olah and P. J. Szilagyi, *J. Amer. Chem. Soc.*, **91**, 2949 (1969).
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