Anal. Calcd. for $C_{32}H_{42}N_4Ni_2O_4$: C, 57.9; H, 6.33; N, 8.44; Ni, 17.6; mol. wt., 663. Found: C, 57.2; H, 6.17; N, 8.35; Ni, 16.9; mol. wt. (b.p. in ethylene chloride), 650.

B. R = C_2H_5.—The ethyl analog was prepared in similar fashion. The crude solid was taken up in chloroform, dried with $MgSO_4$, filtered, and concentrated. Yield of this crystallized material was 21%. It was further purified by recrystallization from chlorobenzene. The pure product decomposed sharply at 285°. Ultraviolet[17] (chloroform): 499 mμ (ε 10,900), 460 (sh) (13,900), 412 (27,600), 338 (sh) (30,300), 318.5 (33,300), 278.5 (50,600), 655.4 (592), 498 (10,700).

Anal. Calcd. for $C_{28}H_{34}N_4Ni_2O_4$: C, 55.5; H, 5.61; N, 9.23. Found: C, 55.7; H, 5.57; N, 9.46.

C. R = CH_3.—The methyl analog was prepared as above. It was obtained in 8% yield as golden platelets (from chlorobenzene) that decompose sharply at 310°. Ultraviolet[17] (chloroform): 660.0 mμ (ε 1,140), 501 (11,400), 463 (12,700), 405 (31,200), 330 (38,200), 306 (38,900), 268 (58,200).

Anal. Calcd. for $C_{24}H_{26}N_4Ni_2O_4$: C, 52.4; H, 4.72; N, 10.2. Found: C, 52.7; H, 4.91; N, 10.1.

Polymeric Chelates of 1,1,2,2-Ethanetetracarboxaldehyde (XI). M = Co (Dihydrate).—A stirred suspension of 0.142 g. of VI in 20 ml. of water was slowly heated until all the solid dissolved. Cobaltous oxide (0.075 g.) was added, and the mixture was heated at 90° and stirred for 3 hr. It was then cooled and the precipitated solid was collected by filtration and washed with water and ethanol. There was obtained 0.167 g. (84% yield) of the cobalt (II) chelate dihydrate of VI as a light pink, microcrystalline solid.

Anal. Calcd. for $C_6H_8CoO_6$: C, 30.6; H, 3.40. Found: C, 30.0; H, 3.51.

The cobalt chelate remained unchanged, except for a slight darkening, when heated up to 310°. It gave instantaneous tests with ferric chloride and 2,4-dinitrophenylhydrazine.

M = Mn (Dihydrate).—To a solution of 0.01 mole of manganous acetate in 60 ml. of water was added a solution prepared by dissolving 1 g. of the sodium salt of VI (about 90% pure), in 50 ml. of water and acidifying with excess acetic acid,[18] the latter being added to destroy carbonate impurities present in the sample. After a few minutes a precipitate started separating; the mixture was stirred and boiled for 15 min. and then allowed to cool slowly to room temperature. After 6 hr., the precipitate was filtered, washed with water and methanol, and air-dried. There was obtained 1.39 g. (72% yield) of the white manganese (II) chelate dihydrate.

Anal. Calcd. for $C_6H_8MnO_6$: C, 31.1; H, 3.46; Mn, 23.8. Found: C, 31.8; H, 2.81; Mn, 23.9.

M = Cd (Dihydrate).—This material was prepared in 90% yield by the above method. It turns yellow at 240° and slowly darkens up to 320°.

Anal. Calcd. for $C_6H_8CdO_6$: C, 25.0; H, 2.78. Found: C, 24.6; H, 2.91.

M = Zn (Monohydrate).—Zinc oxide (0.0814 g., 0.001 mole) was stirred in 25 ml. of water with 0.142 g. (0.001 mole) of VI. After stirring for 30 min., the undissolved zinc oxide was removed by filtration. A white precipitate (0.066 g.) of the zinc (II) chelate monohydrate separated from the filtrate on standing.

Anal. Calcd. for $C_6H_6O_5Zn$: C, 32.2; H, 2.69; Zn, 29.3. Found: C, 31.1; H, 2.80; Zn, 29.2.

On heating, this material darkened slightly from 250° on but did not decompose up to 300°.

The chelates of Fe^{+2}, Cu^{+2}, Pb^{+2}, VO^{+2}, Al^{+3}, and Cr^{+3} were prepared by metathesis at room temperature, except for Ni^{+2}, which required boiling of the solution for 30 min. Their intractability precluded obtained good analyses although in qualitative respects (infrared spectra, carbonyl, and enol tests) they resembled the above compounds. The chelates of Cu^{+2} and Ni^{+2} had similar infrared spectra which were different from those of the other compounds, and the chelates were more stable toward hydrolysis.

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[18] 1,1,2,2-Ethanetetracarboxaldehyde salts are not affected by acetic acid. This is in contrast to the analogous salts of 3,4-diacetyl-2,5-hexanedione from which the weaker acid is immediately liberated.

Aziridines from Diazomethane and Fluorine-Substituted Imines

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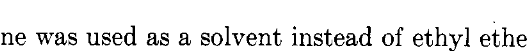
Diazomethane reacted with fluorine-substituted imines to give aziridines directly. However, when 2-(2,4-dinitrophenyl)-2H-azirine (IX) was used, no nitrogen evolution was observed and 1-(3-azido-2-methylpropenyl)-2,4-dinitrobenzene (X) was formed. The energy of activation and the frequency factor for the inversion of nitrogen in 2,2-difluoro-1-trifluoromethylazirine (IV) were found to be 5.5 ± 0.5 kcal. and 5 × 10^8 sec.$^{-1}$, respectively, by means of F^{19} n.m.r. spectroscopy.

The addition of diazomethane to various Schiff bases forms 1,2,3-triazolines.[1] Attempts to obtain aziridines by pyrolysis or photolysis of the above triazolines have failed, degradation products being obtained instead.[2] Aziridines, that were hydrolytically unstable, have been obtained by the addition of dichlorocarbene to anils,[3] and more recently, aziridinium perchlorates were prepared by the addition of diazomethane to iminium perchlorates.[4]

In this paper, the facile reaction of diazomethane with negatively substituted imines to give the corresponding aziridines is reported. The imines used were perfluoro-2-azapropene[5] (I), (1-chloro-2,2,2-trifluoroethylideneamino)pentafluorosulfur[6] (IIa), and (1-azido-2,2,2-trifluoroethylideneamino)pentafluorosulfur (IIb) prepared from IIa by treatment with sodium azide in nitrobenzene or acetonitrile.

The reaction of diazomethane with perfluoro-2-azapropene (I) in xylene at 0° evolved 1 molar equiv. of nitrogen and gave the aziridine III. The higher boiling xylene was used as a solvent instead of ethyl ether, because the volatile product could be distilled out of the mixture. In the case of the imines IIa and IIb, the reaction was run in ethyl ether and there were obtained the aziridines IVa and IVb, Va, and Vb, respectively.



I III

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[1] A. Mustafa, *J. Chem. Soc.*, 234 (1949); G. D. Buckley, *ibid.*, 1850 (1954).

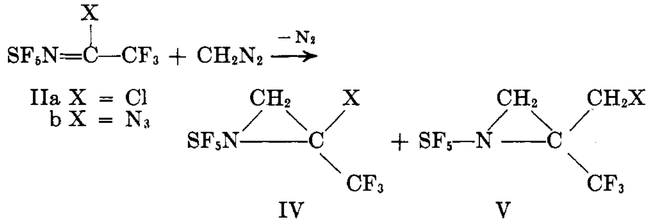
[2] P. K. Kadaba and J. O. Edwards, *J. Org. Chem.*, **26**, 2331 (1961).

[3] E. K. Fields and J. M. Sandri, *Chem. Ind.* (London), 1216 (1959); P. K. Kadaba and J. O. Edwards, *J. Org. Chem.*, **25**, 1431 (1960); A. G. Cook and E. K. Field, *ibid.*, **27**, 3686 (1962).

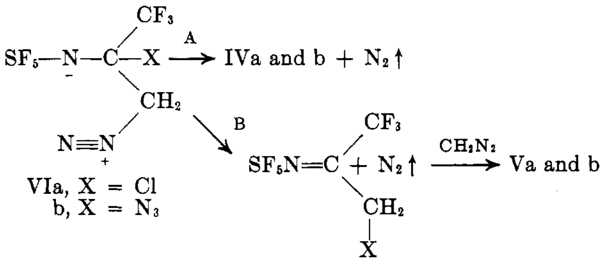
[4] N. J. Leonard and K. Jahn, *J. Am. Chem. Soc.*, **82**, 6418 (1960); **84**, 4806 (1962); N. J. Leonard, K. Jann, J. V. Paukstelis, and C. K. Steinhardt, *J. Org. Chem.*, **28**, 1499 (1963).

[5] The preparation and chemistry of perfluoro-2-azapropene is described by R. E. Banks and R. N. Haszeldine in "Advances in Inorganic and Nuclear Chemistry and Radiochemistry," Academic Press, New York, N. Y., Vol. 3, 1961, pp. 363–365.

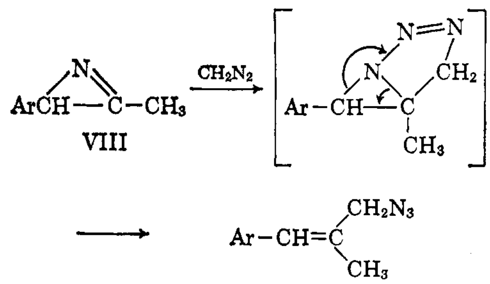
[6] C. W. Tullock, D. D. Coffman, and E. L. Muetterties, *J. Am. Chem. Soc.*, **86**, 357 (1964).


IIa X = Cl
b X = N₃
IV
V

It appears, therefore, that diazomethane adds to these fluorine-substituted imines by a nucleophilic attack to form the intermediate VI which does not cyclize to a triazoline[7] as it was observed with the Schiff bases.[1,2] The intermediate IV, being very similar to an aliphatic diazonium compound, loses nitrogen followed either by a ring closure to obtain IVa and b (process A) or by a shift of X (X = Cl, N_3) to yield VIIa and b (process B). The latter may react further with excess diazomethane to give the final product Va and b. Perfluoro-2-azapropene (I) seems to behave in a similar fashion to form III as the only product, process B (shift of a fluorine) being too unfavorable.


VIa, X = Cl
b, X = N_3
VIIIa and b

When 2-(2,4-dinitrophenyl)-3-methyl-2H-azirine (VIII)[8] was treated with diazomethane at room temperature, no nitrogen evolution was observed, and only one product was obtained in 85% yield assigned the structure of 1-(3-azido-2-methylpropenyl)-2,4-dinitrobenzene (IX). It appears that the addition of 1 molar equiv. of diazomethane to the imine bond in VII took place readily, and it was followed by an intramolecular rearrangement.[9]


VIII
IX
Ar = 2,4-dinitrophenyl

N.m.r. Spectra.—An excellent proof of structure of these new aziridines is given by their proton and fluorine n.m.r. spectra. In the case of 2,2-difluoro-1-trifluoromethylaziridine (III), the two protons of the cyclic methylene are identical, giving a single peak with no splitting from the *gem*-difluoro group. However, in the aziridines IVa, IVb, Va, and Vb these two protons are not identical, one of them being *cis* and the other *trans* with respect to the CF_3 group. These protons appear as two peaks, and they could not be further resolved to a quartet typical of an AB type.[10,11]

The rate of inversion of the nitrogen atom in 2,2-difluoro-1-trifluoromethylaziridine (III) was measured by a low-temperature study of the F^{19} n.m.r. spectra (Fig. 1). At 25°, there are two peaks, one for CF_3 and the other for CF_2, and as the temperature was decreased, the CF_3 peak became sharper but did not change otherwise, while the CF_2 peak broadened and at −28° gave two broad peaks. On further cooling to −49°, it changed to a four-line pattern characteristic for two nonequivalent fluorines of AB type with a chemical shift, $\delta = 1160$ c.p.s. and coupling constant $J = 100$ c.p.s. By measuring the chemical shifted resonances, δ, between −28 and −49°, the mean life time (τ) of the molecule in a given configuration can be calculated according to established procedures.[12] From the plot of $1/\delta\tau$ as a function of the reciprocal of the absolute temperature, the activation energy for the nitrogen inversion was calculated, $E_a = 5.5 \pm 0.5$ kcal., and the frequency factor, $\nu_0 = 5 \times 10^8$ sec.$^{-1}$. These values may be compared to $E_a = 10.0 \pm 1.0$ kcal., $\nu_0 = 5 \times 10^7$ sec.$^{-1}$, for 1,2,2-trimethylaziridine, and $E_a = 6.4 \pm 0.6$ kcal., $\nu_0 = 1 \times 10^9$ sec.$^{-1}$, for 1-methyl-2-methyleneaziridine.[11] No low-temperature n.m.r. work has been done in either IVa, IVb, Va, or Vb.

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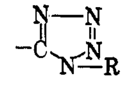
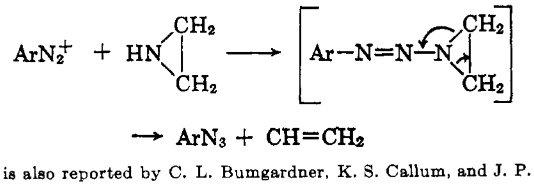
[7] The formation of triazolines appears to become unfavorable when electron-attacting substituents are found on the nitrogen of the imine. It has been similarly observed that tetrazoles,



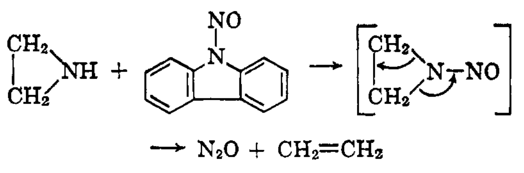
exist only when R = electron-donating group, reversing to the azide form $N_3{-}C{=}N{-}R$, when R = electron-withdrawing group [F. Eloy, *J. Org. Chem.*, **26**, 952 (1961)].

[8] P. W. Neber and A. Burgand, *Ann.*, **493**, 281 (1932); D. J. Cram and J. J. Hatch, *J. Am. Chem. Soc.*, **75**, 33 (1953).

[9] A rearrangement of similar nature is reported by C. S. Rondesvedt, Jr., and S. J. Davis, *J. Org. Chem.*, **22**, 200 (1957).



One is also reported by C. L. Bumgardner, K. S. Callum, and J. P. Freeman, *J. Am. Chem. Soc.*, **83**, 4417 (1961).



[10] S. J. Brois [*J. Org. Chem.*, **27**, 3532 (1962)] found that the coupling constant for the geminal protons, $J_{gem} = 0.6$ c.p.s., is very small for 2-phenylaziridine.

[11] A. Loewenstein, J. F. Neumer, and J. D. Roberts [*J. Am. Chem. Soc.*, **82**, 3599 (1960)] report that the *gem* hydrogens of 1,2,2-trimethylaziridine appeared as two single peaks at 25°.

[12] H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1128 (1956); J. A. Pople, W. G. Schneider, and H. S. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp. 223, 67; F. C. Nachod and W. D. Phillips, "Determination of Organic Structures by Physical Methods," Vol. 2, Academic Press, New York, N. Y., 1962, p. 437.

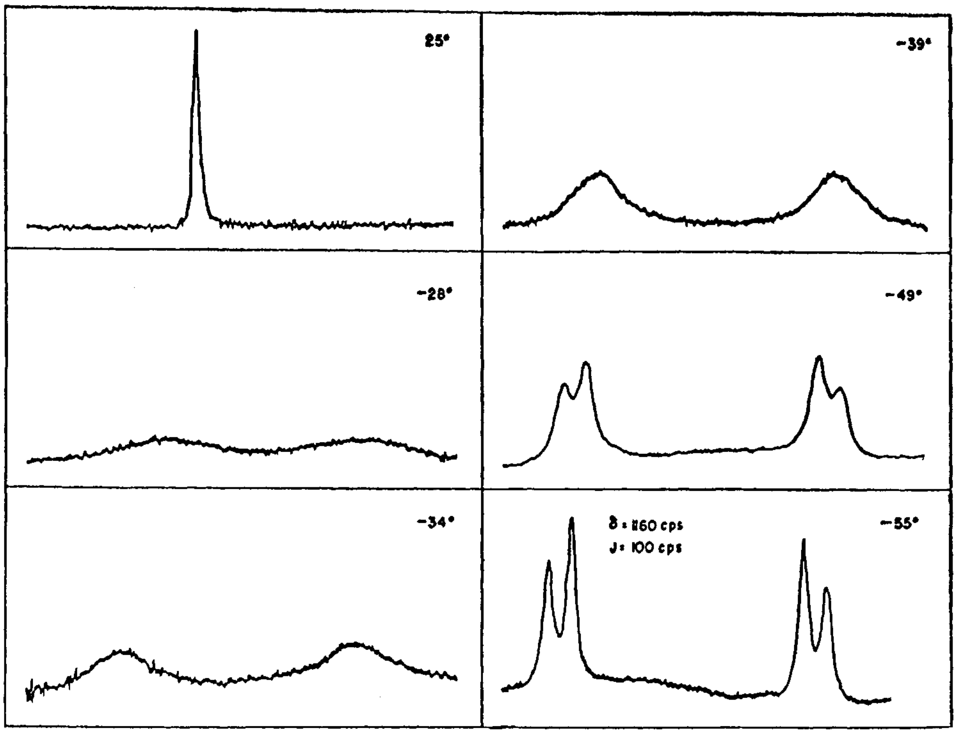


Fig. 1.—The F^{19} magnetic resonance spectra of the CF_2 group in 1-trifluoromethyl-2,2-difluoroaziridine at several temperatures (56.4 Mc.).

Experimental[13]

2,2-Difluoro-1-(trifluoromethyl)aziridine (III).—To a dry solution of diazomethane in 300 ml. of xylene (approximately 0.25 mole) cooled in an ice bath, was added slowly by means of a gas inlet tube 20 g. (0.15 mole) of perfluoro-2-azapropene.[5] Nitrogen evolution totaled 3100 ml. (0.15 mole). The volatile products were distilled out of the solution into a Dry Ice trap by applying vacuum. Gas chromatographic analysis indicated the presence of two major peaks, one corresponding to the dimer of perfluoro-2-azapropene (~20%, retention time 3.2 min.) and the other to 2,2-difluoro-1-(trifluoromethyl)aziridine (~64%, retention time 4.5 min.). This latter compound was isolated by preparative gas chromatography; infrared maxima (gas) were observed at 3.3, 6.65, 7.74, 8.10, 8.35, and 10.4 μ; mol. wt. 147 (mass spectrum); proton n.m.r. spectra (neat) showed peaks in τ-values at 7.65 (singlet, CH)$_2$ and F^{19} n.m.r. at −334 (broad, CF_3) and +3116 c.p.s. (CF_2). From the vapor pressure equation, $\log P = 1970/T + 9.23$, the boiling point was estimated to be 25 ± 0.5°, $\Delta H_{vap} = 9000$ cal./mole, and Troutons constant = 30.1.

(2-Chloro-2-trifluoromethyl-1-aziridyl)pentafluorosulfur (IVa) and (2-Chloromethyl-2-trifluoromethyl-1-aziridyl)pentafluorosulfur (Va).—To an ethereal solution of diazomethane (approx. 0.20 mole), cooled in an ice bath, was added dropwise 20 g. (0.078 mole) of (1-chloro-2,2,2-trifluoromethylideneamino)pentafluorosulfur.[6] After 1 hr. at 25°, the solution was fractionated to give 4.0 g. (19.5%) of (2-chloro-2-trifluoromethyl-1-aziridyl)pentafluorosulfur (IVa) as a stable colorless liquid, b.p. 100°; infrared maxima (neat) were observed at 3.22 and 3.30 (CH_2), transparent in the 6.0-μ region. The F^{19} n.m.r. spectrum showed peaks at −7570 (multiplet) and 680 c.p.s. (singlet) characteristic for SF_5[14] and CF_3 groups, respectively, and proton n.m.r. (neat) in τ-values at 7.27 and 7.10 (singlets, $C\langle^{H_1}_{H_2}$).

Anal. Calcd. for $C_3H_2CFN_8S$: Cl, 13.05; F, 55.97; N, 5.26; S, 11.81. Found: Cl, 13.01; F, 55.99; N, 5.29; S, 11.53.

On further fractionation, 15.5 g. (76%) of (2-chloromethyl-2-trifluoromethyl-1-aziridyl)pentafluorosulfur (Va) was obtained as a colorless liquid, b.p. 75–76° (100 mm.), $n^{25}D$ 1.3580, infrared maxima (neat) at 3.25 and 3.32 (CH_2), transparent in the 6.0-μ region. The F^{19} n.m.r. showed peaks at −7580 (multiplet) and at 470 c.p.s. (singlet) characteristic for SF_5[14] and CF_3 groups and proton n.m.r. (neat) in τ-values at 7.18 and 7.02 (broad peaks, $C\langle^{H^1}_{H_2}$), and 5.95 (singlet, CH_2–X).

Anal. Calcd. for $C_4H_4ClF_8NS$: C, 16.82; H, 1.40; Cl, 12.42; F, 53.22; N, 4.91; S, 11.23. Found: C, 17.66; H, 1.77; Cl, 12.24; F, 53.10; N, 4.81; S, 11.15.

(1-Azido-2,2,2-trifluoroethylideneamino)pentafluorosulfur (IIb).—To a suspension of 25 g. (0.38 mole) of sodium azide in 300 ml. of nitrobenzene was added 80 g. (0.31 mole) of (1-chloro-2,2,2-trifluoroethylideneamino)pentafluorosulfur (IIa),[6] and the mixture was stirred at 60° for 3 hr. (1-Azido-2,2,2-trifluoroethylidine-1-amino)pentafluorosulfur (IIb, 67 g., 82%) was obtained on distillation as a colorless stable liquid, b.p. 48° (60 mm.), $n^{25}D$ 1.3410, infrared maxima (neat) were observed at 4.6 (N_3) and 6.0 (C=N). F^{19} n.m.r. showed peaks at −7800 (multiplet) and at −235 c.p.s. (quintet, $J_{F-F} = 11$ c.p.s.) characteristic for SF_5[14] and CF_3 groups, respectively.

Anal. Calcd. for $C_2H_4F_8S$: F, 57.56; N, 21.22; S, 12.15; mol. wt., 264. Found: F, 56.83; N, 21.37; S, 12.36; mol. wt., 264 (mass spectrum).

An acetonitrile solution of 2.6 g. of the azide IIb was heated to reflux with excess cyclohexene until the theoretical amount of nitrogen was evolved. On distillation, [1-(cyclohexylideneamino)-2,2,2-trifluoroethylideneamino]pentafluorosulfur was obtained as a colorless liquid, b.p. 53° (0.1 mm.), $n^{25}D$ 1.4068; infrared maxima (neat) were observed at 5.90 (C=N) and 6.15 μ (C=N); proton n.m.r. was typical of cyclohexylidene, and F^{19} n.m.r. showed peaks characteristic for SF_5 and CF_3 groups.

Anal. Calcd. for $C_8H_{10}F_8N_2S$: C, 30.19; H, 3.15; F, 47.75; N, 8.79; S, 10.08. Found: C, 30.67; H, 3.47; F, 46.94; N, 8.80; S, 10.09.

(2-Azido-2-trifluoromethyl-1-aziridyl)pentafluorosulfur (IV).—To a dry diazomethane solution (approximately 0.18 mole) in 400 ml. of ethyl ether cooled in an ice bath was added dropwise 25 g. (0.095 mole) of (1-azido-2,2,2-trifluoroethylidine-1-amino)-

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(13) The proton n.m.r. spectra were determined with a Varian A-60 spectrometer. The fluorine n.m.r. spectra were obtained with a high-resolution n.m.r. spectrometer and associated electromagnet both of which were manufactured by Varian Associates operating at 56.4 Mc./sec. and approximately 14,000 gauss. Spectra are calibrated in terms of displacements in cycles per second (c.p.s.) from "Freon-112" (1,2-difluoro-1,1,2,2-tetrachloroethane). The gas chromatographic analyses were run on a 6-ft. column containing 20% Kel-F ester (trade-name for ethyl ester of perhalooctanoic acid, Kel-F acid 8114, from Minnesota Mining and Manufacturing Co.) on firebrick at 24° with a helium flow rate of 60 ml./min.

(14) N. Müller, P. C. Lauterbur, and G. F. Stratos, *J. Am. Chem. Soc.*, **79**, 1043 (1957); C. J. Merrill, S. M. Williams, G. H. Cady, and D. F. Eggers, Jr., *J. Inorg. Chem.*, **1**, 215 (1962).

pentafluorosulfur (IIb) in 50 ml. of ethyl ether. Evolution of nitrogen continued even after the addition was complete and a total of 5 l. (0.22 mole) was evolved. The solution was distilled to give 10 g. (40%) of (2-azido-2-trifluoromethyl-1-aziridyl)pentafluorosulfur (IVb) as an unstable colorless liquid which on standing slowly loses nitrogen, b.p. 75–76° (150 mm.), $n^{25}\text{D}$ 1.3538; infrared maxima (neat) were observed at 4.68 (N_3) and it was transparent in the 6.0-μ region. The F^{19} n.m.r. spectrum showed peaks typical for SF_5 and CF_3 groups and proton n.m.r. (neat) in τ-values at 7.37 and 7.16 (broad peaks, $C\langle^{H_1}_{H_2}$).

Anal. Calcd. for $C_3H_2F_8N_4S$: F, 54.66; N, 20.15; S, 11.53. Found: F, 54.60; N, 19.97; S, 11.57.

On further distillation, there was obtained 3.5 g. of a liquid, b.p. 63–68° (20 mm.). Infrared maxima (neat) were observed at 4.70 (N_3), impurity at 5.9 μ (C=N). F^{19} n.m.r. showed peaks for CF_3 and SF_5, along with unassigned small peaks due to impurities and proton n.m.r. (neat) in τ-values at 7.28 and 7.10 (broad peaks, $C\langle^{H_1}_{H_2}$), 6.10 (singlet, CH_2X). Repeated distillation did not remove the impurities. It is concluded that the major component is (2-azidomethyl-2-trifluoromethyl-1-axiridyl)pentafluoro sulfur (Vb).

1-(3-Azido-2-methylpropenyl)-2,4-dinitrobenzene (IX).—To a dry ethereal diazomethane solution (approximately 0.04 mole) was added 2.0 g. (0.009 mole) of 2-(2,4-dinitrophenyl)-3-methyl-2H-azirine (VIII)[7] in 5 ml. of benzene, and the solution was allowed to stand at 25° for 18 hr. The solvent was evaporated *in vacuo* to give a brown oil which was decolorized by passing it through a column of Woelm neutral alumina using a mixture of 20% benzene–80% petroleum ether (b.p. 00–00°) as eluent. There was obtained 2.0 g. (85%) of 1-(3-azido-2-methylpropenyl)-2,4-dinitrobenzene as a light yellow oil; infrared maxima (neat) were observed at 4.76 (N_3) and 6.06 μ (C=C); ultraviolet maxima in acetonitrile at 245 mμ (ϵ 10,600) and 290 (ϵ 8650); proton n.m.r. in τ-values at 8.9 (singlet CH_3), 6.75 (singlet, CH_2–), 3.97 (singlet, =CH), the aromatic protons being typical for 1,2,4-trisubstituted benzene.

Anal. Calcd. for $C_{10}H_9N_5O_4$: C, 45.63; H, 3.45; N, 26.61. Found: C, 45.72; H, 3.71; N, 26.69.

Acknowledgment.—The author wishes to thank Dr. C. G. Krespan for valuable discussions during the course of this work, Mrs. Adah Richmond for the gas chromatographic analyses, and Mr. C. B. Matthews for the n.m.r. spectra.

Activated Aziridines. I. Reaction of Anilines with O-Ethyl-N,N-Ethyleneurethane. Mechanism and Hammett ρ-Constant

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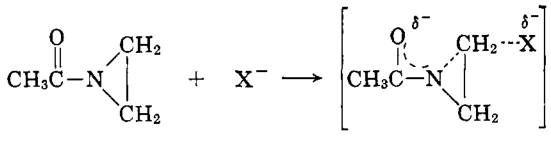
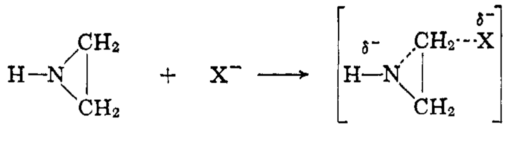
Classification of N-substituted aziridines into two groups of compounds is proposed. The term "activated" aziridines is suggested for those derivatives which contain substituents capable of stabilizing a negative charge which is formed on the aziridine nitrogen in the transition state when the derivative reacts with a nucleophile. The reaction of aniline or *meta*- or *para*-substituted anilines with the activated aziridine O-ethyl-N,N-ethyleneurethane in anhydrous ethanol at 50° was found to be first order in the aniline derivative and first order in activated aziridine. The reaction gave only a single ring-opened product, O-ethyl-N-(2-anilinoethyl)urethane. Electron-supplying groups in the aniline increased the rate while electron-withdrawing groups caused a decrease. The Hammett ρ-constant under these conditions was found to be −1.47. The data were all consistent with the proposal that the reaction proceeds through a bimolecular displacement by the aniline nitrogen on the aziridine carbon.

Aziridines may be broadly divided into two groups of compounds based on their reactivity toward nucleophilic materials and general properties. These groups are (1) compounds which contain substituents capable of stabilizing a negative charge which is formed on the aziridine nitrogen in the transition state when the compound reacts with a nucleophile, *e.g.*, 1-acetyl aziridine and (2) compounds which contain no such substituent, *e.g.*, ethylenimine, or compounds containing a basic aziridine nitrogen. The ability of the substituent to conjugate with the partial negative charge on the aziridine nitrogen in eq. 1 greatly reduces the activation energy needed to attain this state from that required to attain the transition state 2.[1]


(1)


(2)

The activated aziridines will readily undergo ring-opening reactions with nucleophilic materials in the absence of an acid catalyst as shown by their reaction with amines.[2–5] A number of activated aziridines have also been isomerized or dimerized by heating with nucleophilic ions such as iodide ion.[6] This reaction is presumed to involve nucleophilic attack by the ion on the carbon of the aziridine ring.

Ring-opening reactions involving those compounds in the second group may, in practically all reported cases, be ascribed to the reactivity of the protonated or quaternized aziridine or the Lewis acid adduct of the aziridine. Amines or ammonia react readily with aziridines containing a basic aziridine nitrogen but only

[1] It should also be noted that such substituents conjugate more readily with nonaziridine nitrogen than with aziridine nitrogen. See H. C. Brown and A. Tsukamoto, *J. Am. Chem. Soc.*, **83**, 4551 (1961). Thus much of the lowering of activation energy may be due to increased conjugation of the substituent with the nitrogen as it proceeds from aziridine nitrogen to nonaziridine nitrogen.

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[4] W. Gauss, P. Moser, and G. Schwartzenbach, *Helv. Chim. Acta*, **35**, 2359 (1952).

[5] N. P. Grechkin, *Dokl. Akad. Nauk SSSR*, **133**, 592 (1960).

[6] For a review of this isomerization, see H. W. Heine, *Agnew. Chem.* **74**, 772 (1962); *Agnew. Chem., Intern. Ed. Engl.*, **1**, 528 (1962).