Substitution and Addition Reactions of Aziridine
with Perfluorinated Hydrocarbons. Nuclear Magnetic Resonance Spectra
of N-Perfluoroalkyl Aziridines

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The reaction of aziridine with chlorotrifluoroethylene, perfluorobenzene, cyclic perfluoroolefins and tetracyanoethylene was investigated. The degree of substitution was affected by the ring size of the perfluoroolefin.

The temperature dependence of the nuclear magnetic resonance spectra, particularly with respect to the temperature of coalescence of the aziridinyl protons, was investigated.

Introduction.

It was expected that in the reactions of aziridine with fluoroolefins, the substitution behaviour of secondary amines would be followed. Indeed, this was observed. However, in several cases, reactions with aziridine proceeded more readily and led to a higher degree of substitution. In one case recently reported, the reaction appeared to follow a different path than substitution with amines, indicating a degree of nucleophilicity which is not comparable with amines of similar basicity (1). It is therefore conceivable that the ease of substitution is at least partially due to the small size of the aziridinyl anion. Also, the electron-donating property of the nitrogen atom was assumed to be a critical feature towards the displacement of cyano groups on tetracyanoethylene (2,3). Products reported here, with one exception, result from substitution of fluoro atoms or cyano groups by aziridine.

Results.

Perfluorobenzene Derivatives.

Substitution reactions on hexafluorobenzene can be accomplished with primary and secondary amines. Various examples are reported in the literature (4,5). Similarly, we have observed that reactions with aziridine occur readily. Aziridinylperfluorobenzene (3) and N-(β-aziridinylethyl)-perfluoroaniline (4) were isolated in a yield of 38% and 16%, respectively, when the reaction was carried out at 80° in benzene. Treatment of 4 with sodium iodide in acetone led to its dimer 5, in a yield of 23%. The

structures of products 3, 4 and 5 were evident from their nmr and infrared spectra, and structure 5 was supported by its mass spectroscopic fragmentation. Scheme I shows the major fragmentation patterns including their relative intensity. The parent ion was only observed in a low voltage spectrum.

SCHEME I
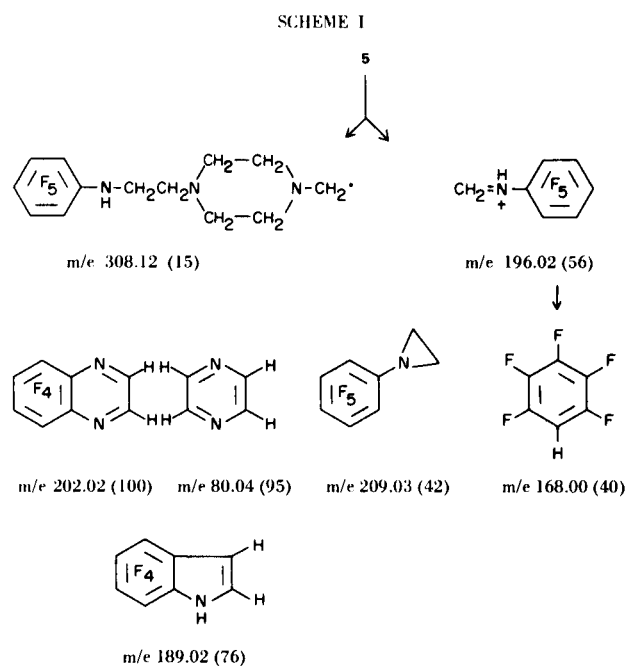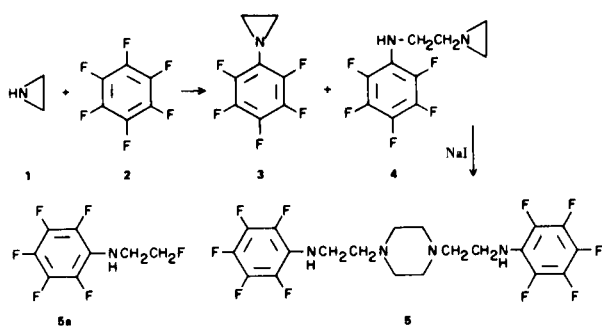
The reaction of aziridine with pentafluorocyanobenzene (7) in benzene (80°) led to p-aziridinylperfluorobenzonitrile (8) and 2,4-diaziridinylperfluorobenzonitrile (9). This behaviour is similar to the reported reactions of 7 with methanol in the presence of sodium carbonate (6), which led to o- and p-substitution, although from the reaction of 7 with dimethylamine only the p-substituted derivative had been obtained. In contrast to this, in the reaction of perfluorophenyl-substituted N-oxides, 2,6-disubstitution was achieved with secondary amines (5), which was assumed to arise from a strong nucleophilic activation of the o-fluoro atoms by the inductive effect of the N → O group.
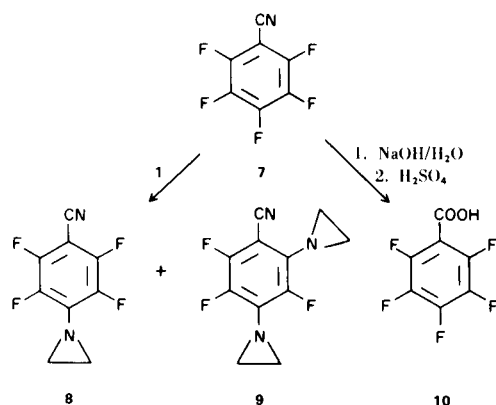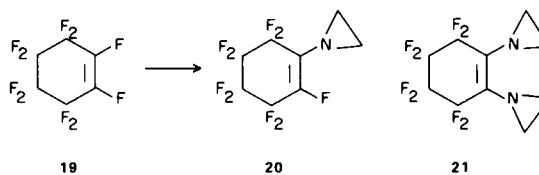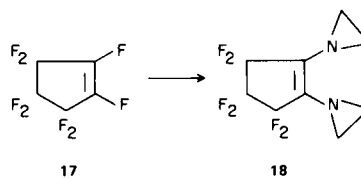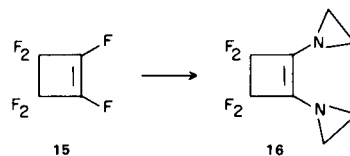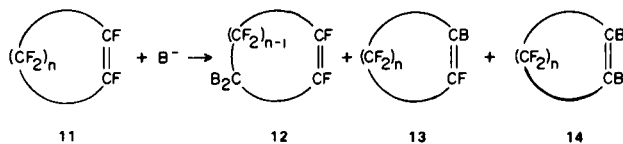

Perfluorocycloolefin Derivatives.

The reaction of nucleophiles with perhaloolefins may lead to three types of derivatives (7,8,9) (Scheme II). We have isolated products of the type 13 and 14 from the reaction with aziridine and observed an influence of the ring size of the perfluoroolefin on the product distribution (13 or 14). Whereas perfluorocyclobutene 15 and perfluorocyclopentene 17 yielded the disubstitution products 16 and 18 in good yield, the predominant product in the reaction with perfluorocyclohexene 19 was found to be the mono-substituted product 20. The disubstituted product 21, if present, could not be isolated. The structures of 16, 18 and 20 were evident from both their F¹⁹ and H¹ nuclear magnetic resonance spectra. These products readily undergo polymerization and spontaneous violent polymer-

ization of 16 was observed in the solid state at room temperature.

SCHEME II

Halogenated Ethylene Derivatives.

In contrast to the direct conversion of perfluoroolefins to aziridinyl substituted products, the addition product 23a was isolated from the reaction of chlorotrifluoroethylene 22 with aziridine. No evidence was observed for the formation of the isomeric product 23b or for a monosub-

stituted product such as 24. This is in agreement with recent reports on the reaction of aziridine with chlorotrifluoroethylene, tetrafluoroethylene (10) and perfluorinated terminal olefins (11).
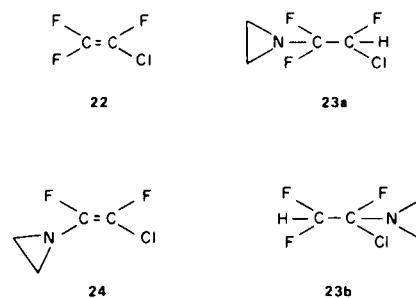
Tetracyanoethylene.

It is conceivable that the reaction of aziridine with tetracyanoethylene (25) would lead to substitution of the cyano group or addition to either the olefinic double bond or the cyano group. For example, addition of aziridine to a cyano group was observed (1), and reaction of 25 with secondary amines was reported to give either N-tricyanovinylamines and hydrogen cyanide or 1,1-diamino-2,2-dicyanoethylene (2,3) in the presence of excess of amine at elevated temperature. We have observed that reaction of aziridine with 25 at ambient temperatures led to the disubstituted product 26, which on treatment with dilute hydrochloric acid was converted to the ring-opened product 27 in good yield.


25   26   27
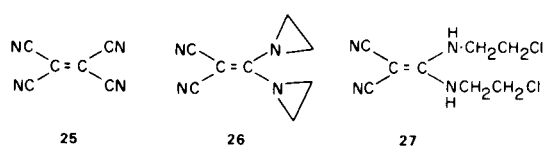
Discussion.

It has been shown that the reaction of cyclic perhaloolefins with mercaptides (12), alkoxides (13) and primary or secondary amines (14) can lead to 1,2-disubstituted reaction products. In one exceptional case a tetrasubstituted product was isolated from chlorotrifluoroethylene and dimethylamine (14). In several terminal perhaloolefins, addition products in preference to substitution products have been isolated, as for example in the reaction of methanol

SCHEME III

28   29

32   33   31   30

(15) or ethanethiol (12) with chlorotrifluoroethylene. In the latter case, only one of the two isomeric addition products was observed in high yield. Such a reaction path, as well as the isolation of only one isomer, in which the anion becomes attached to the terminal carbon atom, has been

confirmed with aziridine as reagent (10). This supports the concept that the initial addition products of the type 28 (Scheme III) can either be isolated or rapidly undergo elimination of fluoride to a mono-addition product of the type 29. The formation of the substitution product 20 from perfluorocyclohexene provides an example for this reaction. Alternatively, subsequent substitution of the α-fluorine atom may occur, and products of the type 32 as well as 33 were obtained in reactions of 1,2-dichloro-3,3,4,4-tetrafluorocyclobutene with methoxide ion (16) and in the reaction of methoxide ion with 1,2-dichlorohexafluorocyclopentene (17).

A second addition of aziridine to 29 with elimination of fluoride to give products of the type 31 was observed in the case of the more reactive perfluorocyclobutene and perfluorocyclopentene. The enhanced reactivity of the four- and five-membered olefins 15 and 17 over the six-membered homologue 19 has been observed previously in the reaction of these olefins with trivalent phosphines (18) and was attributed to the decrease of the double-bond strain in the order of ring sizes (4 > 5 > 6).

A similar addition-elimination mechanism may be involved in the reaction of aziridine with perfluorobenzene 2. The reaction followed essentially that observed for dimethylamine on 2, except that with aziridine the o- and m-disubstituted products were not detected, although such products could be present as minor components. In agreement with this observation, the reaction of 2 with nitrogen-containing heteroparaffins (5) led to very small amounts of p-disubstituted products, and a similar reaction mechanism must be active in the reaction of secondary amines with perfluoronaphthalene, which was observed to give 2-mono- and 2,6-di(N,N-disubstituted amino)fluoronaphthalenes (19).

The formation of N-(β-aziridinylethyl)perfluoroaniline 4 could arise from ring opening of the mono-addition product 3 by hydrogen fluoride and subsequent displacement of the resulting β-fluoro group in 5a by aziridine, by attack of dimerized aziridine on 2 directly, or by ring opening of 3 with excess aziridine. The recent observation (20) that the phenylcyclobutenedione (34) is converted into both 35 and 36 with aziridine but that 35 is not converted to 36 even with an excess of aziridine supports the assumption that the aziridinyl amine 4 is obtained by addition of 1 to the aziridinyl derivative 3, although a direct substitution of the fluoro atom on 2 by N-(β-aminoethyl)aziridine, the dimer of 1, can not be ruled out.
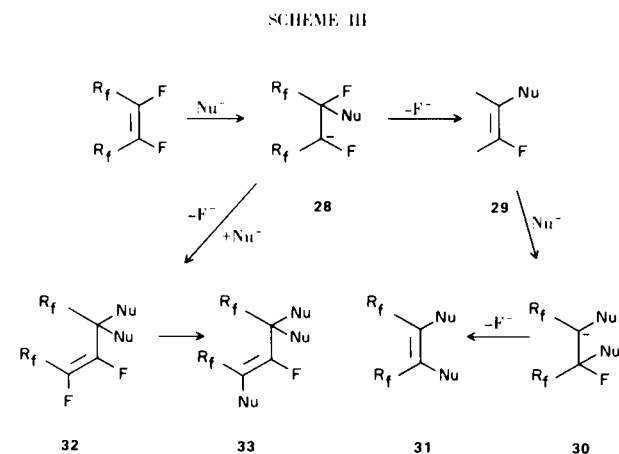
X = Cl, Br

34   35   36
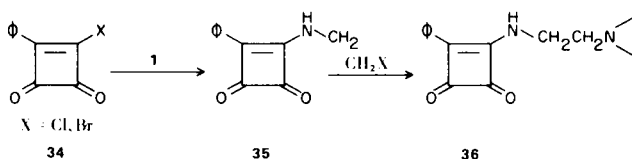
The formation of the p-substituted product **8** from pentafluorobenzonitrile (**7**) has an analogy in the reaction of **7** with dimethylamine (**21**) which only led to the p-substituted product. The isolation of the disubstituted product **9** in the reaction with aziridine confirms the o- and p-directing effect of the cyano group (**21**).

Treatment of **7** with aqueous sodium hydroxide and subsequent acidification led to perfluorobenzoic acid (**10**) with no evidence of substitution in the p-position. Hydrolysis of **7** in the presence of aqueous base has not been attempted before. This reaction is experimentally simpler than the reaction of **7** with sulphuric acid (**22,23**) which led to **10** in yields of 16% (**22**) and 40% (**23**), respectively.

A similar addition-elimination mechanism as that suggested for the reaction of amines with tetracyanoethylene may be involved in the reaction of aziridine with that compound (**2,3**). It had been proposed that in contrast to the reaction of **25** with alcohol, the reaction of **25** with amine usually leads to monosubstitution only, as a result of the greater electron-donating property of nitrogen, which disfavours a reactive structure such as **25d** (3). The isolation of the disubstituted product **26** indicates the decreased tendency of the aziridinyl nitrogen atom to form the less reactive resonance form **25e**.
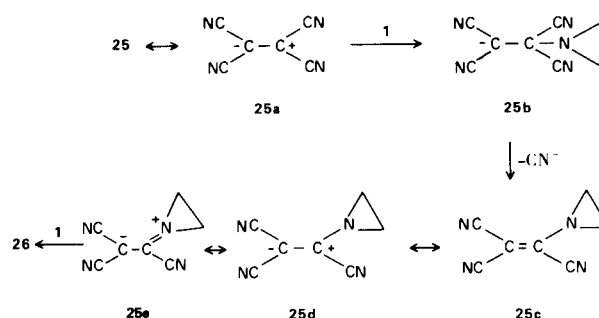
The nuclear magnetic resonance spectra of these novel aziridine derivatives, (Experimental), permit an investigation of the effect of the perfluoroalkyl group on the resonance of the aziridinyl protons. The nuclear magnetic resonance spectra of the aziridine protons of compounds **4** and **18**, recorded at various temperatures, are shown in Fig. 1. Similar spectra are obtained for the corresponding protons of the other compounds except **16**, for which only a broad singlet is observed. Table I gives coalescence temperatures T_c, and rate constants k at these temperatures, calculated from the equation $k = \pi^2 \, \nu_{AB}/2$ where ν_{AB} is the chemical shift in cps between non-equivalent pairs of aziridine protons (26). Values of k were determined from compounds **4** and **18** above the coalescence temperature using the equation

$$K = \pi \, |\nu^4 \, AB + 2\nu^2 \, AB \, \Delta\nu^2 \, -\Delta\nu^4 \,] \, \frac{1}{2}/2\Delta\nu$$

where Δ^2 is the half-width in cps (26). Corrections were made for the inaccuracies of this equation as reported and discussed elsewhere (27). A plot of log k against 1/T then enabled the energy barriers to inversion to be calculated. Values of 19.5 Kcal/mole and 3.4 Kcal/mole, obtained for **4** and **18**, respectively, are indicative of the broad range of activation energies found for substituted aziridines. Several effects (27,28), notably steric, inductive, conjugative and electrostatic affect the rate of nitrogen inversion in such compounds.

For the series of compounds given below, conjugation effects are considered to have a major influence upon nitrogen inversion. Apart from **4**, the carbon atom attached to the ring nitrogen is sp^2 hybridized, and maximum overlap of the unshared electron pair on nitrogen and the car-
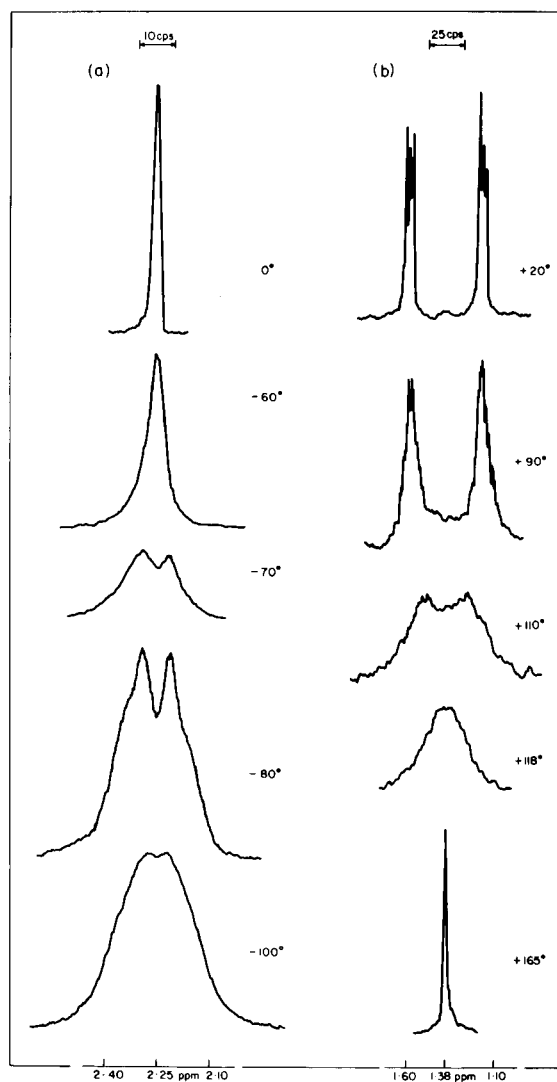
Figure 1. Variable temperature nuclear magnetic resonance spectra of Compounds **18** (a) in trichlorofluoromethane and **4** (b) in nitrobenzene. Chemical shifts in ppm downfield from tetramethylsilane.

bon p-π orbital is afforded in the planar transition state of inversion thus enhancing the inversion rate. The coalescence temperatures T_c as found in Table 1 are in the range -45° to -80° for these compounds, although T_c for **16** could not be established. When the carbon atom attached to the nitrogen is sp³ hybridized, as in **4**, then the rate of inversion is considerably decreased and T_c is raised by more than 150°. Such is the case for other alkyl substituted aziridines, though when a t-butyl group is attached to the ring nitrogen the inversion rate apparently increases. If, however, the chemical shift difference of the ring proton pairs is much smaller than the magnitude of the ring coupling constants then only a single line will be observed (29), even at temperatures below T_c. This fact may account for the failure to observe peak separation at low temperatures in the spectrum of compound **16**. A marked decrease in the chemical shift difference ν_{AB} is found as the attached fluorinated ring size decreases. Thus ν_{AB} decreases from 17.4 cps to 4.5 cps when the attached six-membered ring is replaced by a five-membered ring. It is perhaps reasonable to assume that ν_{AB} will further decrease if the attached ring is four-membered as in **16**.

One explanation of the considerable broadening of the ring proton signal of **16** found at low temperatures is that a slow-down of rotation about the C-N bond occurs, perhaps caused by steric hindrance between the two adjacent aziridine rings. If this hypothesis is correct a similar effect in the spectrum of **18** would be expected where the two rings are closer together. A maximum separation of ν_{AB} in **18** due to slow inversion was found at -80°. Below this temperature further broadening occurred and the separation ν_{AB} decreased from 4.5 cps to 2.5 cps at -100°. It is possible, therefore, that restriction of rotation becomes apparent at these tempratures.

It would appear that fluorine substitution on the ring has little effect on the rate of inversion as evidenced by comparing 1-phenyl aziridine (30) with 1-perfluorophenyl aziridine, **3**. The coalescence temperatures T_c for the two compounds in carbon disulfide are -40° and -45°, respectively.

It was hoped that, as the rate of inversion about the aziridine nitrogen atom decreased, changes in the F^{19}-spectra would be observed. Apart from signal broadening at coalescence temperatures, no significant changes were found with the exception of compound **4**. As mentioned previously, a shift of the ortho and para-fluorine signals of 0.7 ppm to low field, (relative to hexafluorobenzene), occurred on increasing the temperature above T_c. These shifts are most likely caused by increased conjugation between the ring π-electrons and the unshared electrons on the adjacent nitrogen atom as the temperature is raised.

TABLE I

Compound	T_c, °C	ν_{AB} max (cps)	k (sec⁻¹)
3	-45	42.5	94
4	+115	51.0	113
9	-68	36.5	81
16	<-150		
18	-65	4.5	10
20	-80	17.4	39
22	ca. -80		

EXPERIMENTAL

Nuclear magnetic resonance spectra were recorded on a JEOLCO JNM-4H-100 spectrometer equipped with variable temperature accessory. A copper-constantan thermocouple inserted into a tube in the probe recorded the temperature over the range +150° to -150°. Quoted temperatures are considered to be accurate to ± 2° over the complete range. Chemical shift and coupling constant data were obtained from spectra of 5-20% solutions of the compounds in deuterochloroform using tetramethylsilane and trichlorofluoromethane as references for H^1 and F^{19} studies, respectively. Trichlorofluoromethane and carbon disulfide were used as solvents for low temperature studies with the exception of compound **16**, where chlorotrifluoroethylene was utilized to attain temperatures lower than -110°. Nitrobenzene and hexachlorobutadiene were used as solvents for high temperature studies of compound **4**.

Infrared spectra were recorded on a Perkin-Elmer 521 grating instrument either in potassium bromide pellets (for solids) or neat (for liquids).

The Reaction of 1 with Hexafluorobenzene. Aziridinylperfluorobenzene (3) and N-(β-aziridinylethyl)perfluoroaniline (4).

To a solution of 186 g. (1 mole) of hexafluorobenzene in 300 ml. of benzene was added dropwise 258 g. (6 moles) of **1**. The solution was heated to 55°. After 48 hours, 2% of the hexafluorobenzene remained unreacted. Benzene was evaporated and the crystalline residue washed with water. The air-dried product was dissolved in methylene chloride, the solution dried over magnesium sulfate, filtered, and the volatile components evaporated on a rotary evaporator. The residue was distilled to give two fractions, (a) b.p. 55-65°/1 mm. Hg; 80 g., m.p. 36-42° (**3**) and (b) 92-98°/0.5 mm. Hg; 38 g.; m.p. 58-63° (**4**).

Recrystallization of **3** from pentane yielded a product of m.p. 40.5-43°. The ir spectrum of **3** shows strong absorption bands at 3010, 1510, 1325, 1255, 1162, 1118, 1088, 1015, 995-985, 830 in addition to intense bands arising from the C-F and C=C bonds in the region of 1450 to 1190 cm⁻¹.

Anal. Calcd. for $C_8H_4F_5N$: C, 45.78; H, 1.99; N, 6.96. Found: C, 45.95; H, 1.94; N, 7.09.

The H^1 nmr spectrum shows signals at δ 2.25 for CH_2CH_2 (s in fluorotrichloromethane, t in carbon disulfide or deuteriochloroform, with J_{HF} = 1.1 Hz).

The F^{19} nmr spectrum: ϕ_o 154.2 (J_{op} = 6.5 Hz); ϕ_m 164.7 (J_{mp} = 26.8 Hz); ϕ_p 166.7.

Sublimation of **4** provided an analytical sample, m.p. 59.5-62.5°. The ir spectrum of **4** shows bands at 3220, 3000, 2960, 2850, 1660, 1550, 1520, 1485, 1355, 1268, 1188, 1123, 1073, 1018, 998, 970, 922 in addition to intense bands arising from C-F and C=C bonds

in the region of 1450 to 1050 cm^{-1}.

Anal. Calcd. for $C_{10}H_9F_5N_2$: C, 47.61; H, 3.59; N, 11.11. Found: C, 47.35; H, 3.65; N, 10.90.

The H^1 nmr spectrum shows signals at δ 4.52 for NH (broad s); 3.42 for -CH$_2$NH- (broad m), 2.35 for -CH$_2$N◁ (t); 1.58 and 1.07 for ring CH$_2$CH$_2$ (AA'XX', J_g = -1.4 Hz, J_c = +6.1 Hz, J_t = 3.4 Hz) (24,25).

The F^{19} nmr spectrum: ϕ_o 160.2 (J_{op} = 4.0 Hz); ϕ_m 165.1 (J_{mp} = 23.5 Hz); ϕ_p 175.1.

Dimerization of 1-Perfluoroanilinyl-2-aziridinylethane (4) to give N-(β-aziridinylethyl)perfluoroaniline (5).

A suspension of 2.5 g. (0.1 mole) of 4 and 15 g. (0.1 mole) of sodium iodide in 100 ml. of acetone was refluxed for 5 days. Upon standing at -20° for 48 hours, the crystalline sodium iodide (8.7 g.) was removed by filtration. After evaporation of acetone, the remaining solid was stirred with diethyl ether. The resulting solution was evaporated to dryness and the residual oil was extracted with hot hexane. On cooling this solution to -20°, 0.58 g. of a crystalline product separated, m.p. 102-108°. Sublimation of 0.27 g. gives 0.2 g. of a sublimed fraction, m.p. 112-115°, and 0.06 g. of a non-sublimable residue, which was not further identified. The ir spectrum (potassium bromide) shows major absorption bands at 3300, 2940, 2810, 1655, 1525-1510, 1480, 1468, 1458, 1455, 1448, 1345, 1305, 1272, 1245, 1215, 1155, 1095, 1025, 1010, 975 and 952 cm^{-1}.

Anal. Calcd. for $C_{20}H_{18}F_{10}N_4$: C, 47.61; H, 3.59; N, 11.11. Found: C, 47.56; H, 3.77; N, 10.97.

The Reaction of Aziridine with Perfluorobenzonitrile (7). p-Aziridinylperfluorobenzonitrile (8) and 2,4-Diaziridinylperfluorobenzonitrile (9).

To a solution of 2.1 g. (0.01 mole) of 7 in 20 ml. of methylene chloride was added dropwise at an internal temperature of -30°, 4.4 g. (0.1 mole) of 1, and the temperature was then maintained at -20° for 12 hours. The solution was shaken with dilute sodium carbonate, dried over magnesium sulfate, and then methylene chloride distilled off at normal pressure to give 1.79 g. of a crystalline residue, m.p. 92-108°. Upon fractional recrystallization from hexane, two products 8 (m.p. 61.5-63°) and 9 (m.p. 132-134.5°) were isolated. Major infrared absorption bands were observed at 2240, 1640, 1480, 1428, 1255, 1160 and 985 cm^{-1} for compound 8.

Anal. Calcd. for $C_9H_4N_2F_4$: C, 50.00; H, 1.85; N, 12.96. Found: C, 49.87; H, 2.03; N, 13.15.

Major ir absorptions were observed at 2225, 1625, 1485, 1282, 1168, 1160, 985, 950, 815 and 755 cm^{-1} for compound 9.

Anal. Calcd. for $C_{11}H_8N_3F_3$: C, 55.23; H, 3.35; N, 17.57. Found: C, 54.88; H, 3.20; N, 17.36.

The H^1 nmr spectrum shows signals at δ 2.41 for ring CH$_2$CH$_2$ *ortho* to -CN group (d, J_{HF} = 1.2 Hz); 2.37 for ring CH$_2$CH$_2$ *para* to -CN group (t, J_{HF} = 1.2 Hz).

The F^{19} nmr spectrum: ϕ137.5, 143.4 and 156.8 (J = 20.5 Hz, J = 11.0 Hz).

Reaction of 1 with Perfluorocyclobutene. 1,2-Diaziridinylperfluorocyclobutene (16).

To a solution of 31.0 g. (0.19 mole) of perfluorocyclobutene (15) in 100 ml. of diethyl ether was added dropwise with cooling to -25°, 36.0 g. (0.836 mole) of 1. The reaction was initially exothermic and good stirring was required to prevent an appreciable temperature increase. After 25 hours at -25°, a white precipitate (assumed to be the hydrogen fluoride salt of 1) was filtered off, and the remaining solution was evaporated until a crystalline residue

was left (34 g.). Upon recrystallization of 10 g. from hexane and sublimation, 8.4 g. of a colourless product, m.p. 38-41°, was obtained. The ir spectrum of 16 shows major absorption bands at 3010, 1690, 1400, 1335, 1265, 1250, 1142, 970 and 820 cm^{-1}.

In one instance a violent explosion of 16 was observed when the material was kept at ambient temperature.

Anal. Calcd. for $C_8H_4N_2F_4$: C, 46.15; H, 3.84; N, 13.46. Found: C, 46.56; H, 3.73; N, 13.43.

The H^1 nmr spectrum shows a signal at δ 2.11 for ring CH$_2$CH$_2$ (s) and the F^{19} nmr spectrum at ϕ 115.5 (s).

Reaction of 1 with Perfluorocyclopentene. 1,2-Diaziridinylperfluorocyclopentene (18).

The reaction between 21.7 g. (0.1 mole) of 17 with 18.4 g. (0.43 mole) of 1 was carried out as described in the reaction of 1 with 15. The crude crystalline reaction product was extracted with pentane. Evaporation of the solvent from this extract left 18.5 g. of 18, m.p. 36.5-39.5° after sublimation.

The ir spectrum shows major absorption bands at 3010, 1650, 1582, 1528, 1285, 1240, 1188, 1160, 1130, 1095, 1025, 995, 970, 830, 790, 575 cm^{-1}.

Anal. Calcd. for $C_9H_8N_2F_6$: C, 41.86; H, 3.10; N, 10.85. Found: C, 42.07; H, 3.29; N, 10.88.

The H^1 nmr spectrum shows signals at δ 2.25 for CH$_2$CH$_2$ of both rings (s) and the F^{19} nmr spectrum at ϕ 112.5 (t); 131.5 (m, J_{FF} = 5.8 Hz).

Aziridinylperfluorocyclohexene (20).

To a solution of 52.6 g. (0.20 mole) of 19 in 200 ml. of diethyl ether was added dropwise at -20°, 52.1 g. (1.215 mole) of 1. After maintaining the temperature at -25° for 48 hours, a precipitate was filtered off under nitrogen atmosphere and the resulting solution was distilled under reduced pressure to give 34 g. (59%) of 20, b.p. 55°/12 mm., n$_D^{20}$ = 1.3690. The ir spectrum (neat) shows major absorption bands at 3020, 1670, 1370, 1344, 1330, 1280, 1245, 1210, 1170, 1155, 1070, 1032, 990, 970, 828, 815, 662, 562 and 513 cm^{-1}.

The H^1 nmr spectrum shows signals at δ 2.33 for ring CH$_2$CH$_2$ (d or t), J_{FH} = 1.4 Hz, J_{F_2H} = 0.4 Hz), and the F^{19} nmr spectrum at ϕ 113.8 (m); 116.9 (m); 134.3 (m); 135.1 (m) and 151.1 (m).

The Reaction of 1 with Tetracyanoethylene. 1,1-Diaziridinyl-2,2-dicyanoethylene (26).

To a solution of 19.2 g. (0.15 mole) of 25 in 2 l. of anhydrous diethyl ether was added dropwise with stirring 12.9 g. (0.3 mole) of 1. After stirring for approximately 1 hour, a heavy precipitate had formed, which was filtered off and air-dried to give 14 g. of 26, m.p. 171° dec. Partial evaporation of the ether gave another 4.9 g. of product, total yield 79%. Recrystallization of the crude product from ethyl acetate-hexane (8:2) did not increase the melting point of the material. The ir spectrum showed major absorption bands at 2219, 2209, 1520, 1468, 1445, 1420, 1305, 1165, 1150, 1140, 828, 808 cm^{-1}, with a weak absorption band at 3010 cm^{-1} indicating the presence of aziridinyl (C-H) groups.

Anal. Calcd. for $C_8H_8N_4$: C, 60.00; H, 5.00; N, 35.00. Found: C, 59.90; H, 5.05; N, 34.65.

The H^1 nmr spectrum shows a signal at δ 2.51 for ring CH$_2$CH$_2$ (s).

The Reaction of 1,1-Aziridinyl-2,2-cyanoethylene with Hydrochloric Acid to give (27).

A suspension of 1.6 g. of 26 in 20 ml. of dilute hydrochloric acid was stirred for 20 minutes at 40°, the crystalline product was filtered off and air-dried to give 1 g. (43%) of 27, m.p. 103.5-107°.

Recrystallization from water produced a pale yellow product, m.p. 106-109°. Major ir absorptions are observed at 3300, 2205, 2180, 1595, 1565, 1385, 1340 and 1247 cm^{-1}.

Anal. Calcd. for $C_8H_{10}N_4Cl_2$: C, 41.20; H, 4.29; N, 24.03; Cl, 30.47. Found: C, 41.12; H, 4.45; N, 23.96; Cl, 30.42.

The Reaction of Perfluorobenzonitrile with Sodium Hydroxide. Perfluorobenzoic Acid (10).

A suspension of 9.7 g. (0.05 mole) of perfluorobenzonitrile in 40 ml. of 25% of aqueous sodium hydroxide was refluxed for 50 minutes after which time the organic layer had dissolved. The solution was neutralized with carbon dioxide and filtered to give 7.4 g. (71%) of crude **10**, (m.p. 79-84°). Recrystallization from toluene and drying over phosphorous pentoxide provided an analytical sample, m.p. 146-148° (vacc.).

Anal. Calcd. for $C_7HO_2F_5$: C, 39.62; H, 0.47. Found: C, 40.10; H, 0.55.

The crude reaction mixture was not analyzed for the presence of p-hydroxytetrafluorobenzoic acid.

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