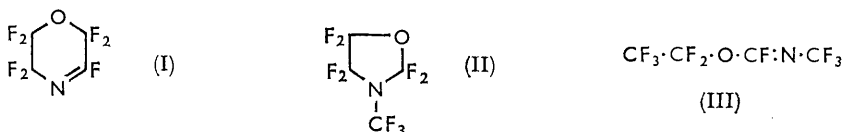


1135. Heterocyclic Polyfluoro-compounds. Part IX.¹ Some Reactions of Perfluoro-(*N*-fluoromorpholine): The Preparation of Perfluoro-5,6-dihydro-2H-1,4-oxazine and Perfluoro-(3-methyloxazolidine)

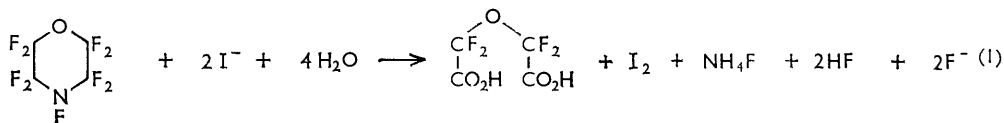
By R. E. BANKS and E. D. BURLING

Pyrolysis of perfluoro-(*N*-fluoromorpholine) in mild steel or platinum at 500—600°/1 atm. yields a mixture of perfluoro-5,6-dihydro-2H-1,4-oxazine (I), perfluoro-(3-methyloxazolidine) (II), and a compound believed to be perfluoro-4-oxa-2-azahex-2-ene (III). Ethanolysis of perfluoro-(*N*-fluoromorpholine) gives diethyl perfluoro-β-oxaglutarate, the parent acid of which is obtained by reaction of the morpholine with aqueous iodide solutions.

THE chemistry of perfluoro-(*N*-fluoromorpholine) parallels that of perfluoro-(*N*-fluoropiperidine):^{2,3} the morpholine oxidises iodide ion and ethanol, can be used to effect selective fluorination of certain organic substrates which have canonical forms with a free electron pair on carbon,⁴ can be partially defluorinated to perfluoro-5,6-dihydro-2H-1,4-oxazine (I), and undergoes thermal rearrangement to perfluoro-(3-methyloxazolidine) (II) and a product that may be perfluoro-4-oxa-2-azahex-2-ene (III).



Reductive Hydrolysis and Ethanolysis of Perfluoro-(N-fluoromorpholine).—Perfluoro-(*N*-fluoromorpholine), prepared in 8% yield by electrochemical fluorination of morpholine,⁵ is unaffected by aqueous sodium hydroxide or hydrochloric acid at 80°; but treatment with an excess of hydriodic acid or aqueous potassium iodide at 50—60° for several days, or with sodium iodide in aqueous acetone at room temperature for 1 hr., converts it into perfluoro-β-oxaglutamic acid with near quantitative (95%) liberation of iodine, according to reaction (1).



The annexed reaction scheme is suggested. Evidence in support of the postulate that the reaction is initiated by attack of iodide ion on the fluorine of the N-F bond will be presented later;⁴ compound (I), proposed here as an intermediate, has been prepared as described below and does hydrolyse readily to perfluoro-β-oxaglutamic acid with the liberation of three fluorine atoms, as fluoride ions, per molecule.

Oxidation of iodide ion is also effected by perfluoro-(*N*-fluoropiperidine),² the three isomeric perfluoro-(*N*-fluoro-methylpiperidines),¹ *NN*-difluorourea,^{6,7} *N*-fluoro-*NN'*-dimethylurea,⁷ *N*-fluoro-*NN'*-diethylurea,⁷ *N*-fluorourethane,⁷ *NN*-difluoromethylamine,⁷

¹ Part VIII, R. E. Banks, J. E. Burgess, and R. N. Haszeldine, *J.*, 1965, 2720.

² R. E. Banks, W. M. Cheng, and R. N. Haszeldine, *J.*, 1962, 3407.

³ R. E. Banks and G. E. Williamson, *Chem. & Ind.*, 1964, 1864.

⁴ R. E. Banks, E. D. Burling, and G. E. Williamson, unpublished results.

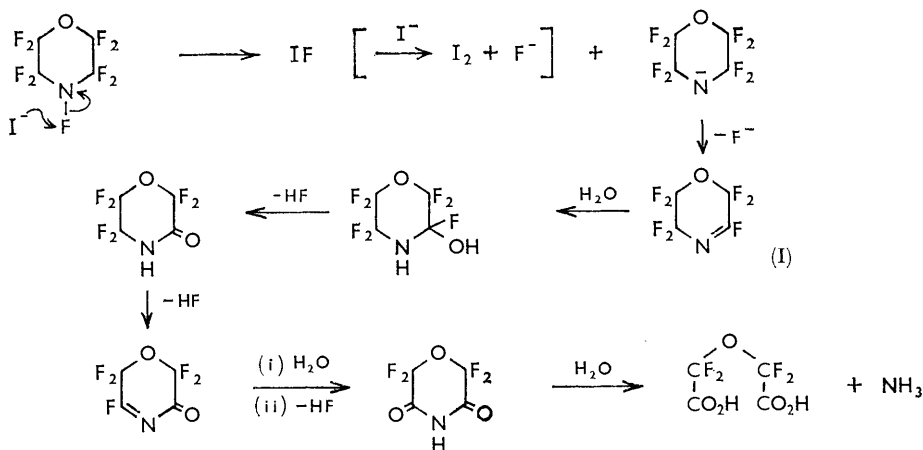
⁵ T. C. Simmons, F. W. Hoffman, R. B. Beck, H. V. Holler, T. Katz, R. J. Koshar, E. R. Larsen, J. E. Mulvaney, F. E. Rogers, B. Singleton, and R. S. Sparks, *J. Amer. Chem. Soc.*, 1957, **79**, 3429.

⁶ E. A. Lawton, E. F. C. Cain, D. F. Shefhan, and M. Warner, *J. Inorg. Nuclear Chem.*, 1961, **17**, 188.

⁷ R. E. Banks, R. N. Haszeldine, and J. P. Lulu, unpublished results.

NN-difluoroethylamine,⁷ *NN*-difluorotrifluoromethylamine,⁸ *N*-fluorobistrifluoromethylamine,⁹ *N*-fluorodifluoromethyleneimine,^{10,11} and poly-*(N*-fluorodifluoromethyleneimine);¹¹ thus it appears to be diagnostic for the N-F bond in organic compounds, and often provides an excellent simple method of structure determination.

Treatment of perfluoro-*(N*-fluoromorpholine) with ethanol at 100° gives diethyl perfluoro- β -oxagluturate in 48% yield, together with acetaldehyde, diethyl ether, and ethyl fluoride. This result can be rationalised in terms of a scheme analogous to that proposed from the ethanolysis of perfluoro-*(N*-fluoropiperidine),² and in which perfluoro-5,6-di-



hydro-2*H*-1,4-oxazine (I) is an intermediate; in a separate experiment (I) was shown to react with ethanol at 85° to give diethyl perfluoro- β -oxagluturate in 89% yield.

Pyrolytic Defluorination of Perfluoro-(N-fluoromorpholine).—When subjected to flow pyrolysis in mild steel at 500°/1 atm., perfluoro-*(N*-fluoromorpholine) undergoes both partial defluorination to perfluoro-5,6-dihydro-2*H*-1,4-oxazine (I) (68% yield) and isomerisation (discussed in the next section) to perfluoro-(3-methyloxazolidine) (II) (17%) and a compound believed to be perfluoro-4-oxa-2-azahehex-2-ene (III). The mixture of these products, distillation range 20—25°, gave only two peaks on gas chromatograms; it was separated chromatographically into a mixture of compounds (II) and (III) and perfluoro-5,6-dihydro-2*H*-1,4-oxazine (I), a colourless volatile liquid (b. p. 24.4°), the vapour of which shows a strong N:C stretching vibration at 1757 cm.⁻¹ in the infrared (i.r.) region (cf.² $\overline{\text{CF}_2} \cdot [\overline{\text{CF}_2}]_3 \cdot \overline{\text{N}} \cdot \overline{\text{CF}}$, 1754 cm.⁻¹). The structure of (I) was confirmed by ¹⁹F n.m.r. spectroscopy.

When the mixture (II + III) was shaken with aqueous sodium hydroxide, 95% of it was recovered unchanged as a colourless, dense, volatile liquid (b. p. 22.8°), which had the following properties: (i) molecular formula C₄F₉NO; (ii) an i.r. spectrum typical of a saturated fluorocarbon and not containing the 1782-cm.⁻¹ band shown by the mixture (II + III) before hydrolysis; (iii) unaffected by treatment with hot aqueous potassium iodide, mild steel at 500°, hot concentrated sulphuric acid, or hot 40% sodium hydroxide solution. On the basis of these properties, and since treatment of perfluoro-*(N*-fluoropiperidine) with mild steel at 500°/1 atm. yields, *inter alia*, perfluoro-(1-methylpyrrolidine),² this hydrolysis residue was identified as perfluoro-(3-methyloxazolidine) (II). This assignment of structure was supported by ¹⁹F n.m.r. results.

⁸ R. E. Banks, R. N. Haszeldine, and R. Hatton, unpublished results.

⁹ J. A. Young, W. S. Durrell, and R. D. Dresdner, *J. Amer. Chem. Soc.*, 1959, **81**, 1587.

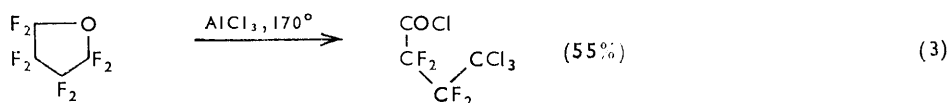
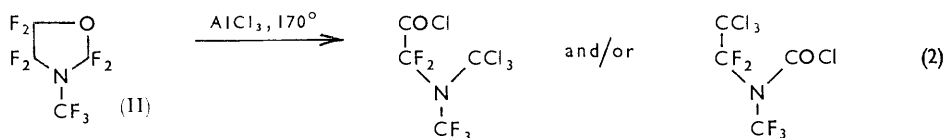
¹⁰ J. A. Cuculo and L. A. Bigelow, *J. Amer. Chem. Soc.*, 1952, **74**, 710.

¹¹ R. E. Banks, R. N. Haszeldine, and M. D. Hawkins, unpublished results.

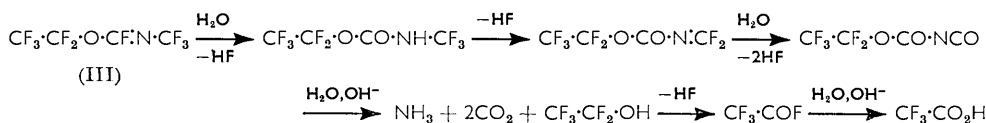
In an effort to provide further chemical proof of structure for the oxazolidine (II), it was heated with aluminium trichloride in order to cleave the ether link in the fashion typical for cyclic perfluoro-ethers containing no α -perfluoroalkyl substituents¹² (reaction 2; cf.¹³ reaction 3). This proved unsuccessful: only unchanged oxazolidine, phosgene, carbon dioxide, unidentified chlorine-containing material, and a tar were obtained.

The synthesis of perfluoro-(3-methyloxazolidine) by pyrolysis of perfluoro-(*N*-fluoromorpholine) over mild steel may be the first of this compound; a product C_4F_9NO , b. p. 22° , believed to be perfluoro-(3-methyloxazolidine) although its ^{19}F n.m.r. spectrum did not fully substantiate this structure, has been obtained previously by electrochemical fluorination of the methyl ester or *NN*-dimethylamide of *NN*-dimethylglycine.¹⁴

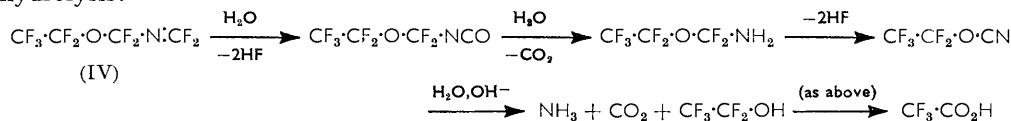
The hydrolysate obtained by treatment of the mixture (II + III) with aqueous sodium hydroxide contained both fluoride and trifluoroacetate ions; this, coupled with the know-



ledge that (i) the i.r. spectrum of (III) contained a band (1782 cm^{-1}) characteristic of an N:C bond in a perfluoro-compound,² and (ii) thermal isomerisation of perfluoro-(*N*-fluoropiperidine) yields perfluoro-(*n*-butylidenemethylamine), $\text{CF}_3 \cdot [\text{CF}_2]_2 \cdot \text{CF} \cdot \text{N} \cdot \text{CF}_3$ (N:C str. 1773 cm^{-1}), as well as perfluoro-(1-methylpyrrolidine),² leads us to believe that (III) is perfluoro-4-oxa-2-azahex-2-ene. Hydrolysis of (III) to trifluoroacetic acid is readily accounted for:



However, since the isomeric compound (IV) would also yield trifluoroacetic acid on hydrolysis:



it can be argued that we are wrong in assuming that the thermal isomerisation of perfluoro-(*N*-fluoromorpholine) will follow *exactly* the same pattern as that of perfluoro-(*N*-fluoropiperidine), so that either (IV) is the acyclic isomer formed or the product is a mixture of (III) and (IV). The latter possibility is considered unlikely since gas chromatography did not reveal the presence of another isomer, yet, according to the known physical properties¹⁵ of isomeric compounds of type $R_F\text{N} \cdot \text{CF}_2$ and $R_F\text{N} \cdot \text{CFR}_F''$ ($R_F, R_F', R_F'' =$ perfluoroalkyl), isomer (IV) should boil *ca.* 15° higher than (III). The i.r. spectroscopic evidence militates

¹² R. E. Banks, "Fluorocarbons and Their Derivatives," Oldbourne Press, London, 1964.

¹³ G. V. D. Tiers, *J. Amer. Chem. Soc.*, 1955, **77**, 6704.

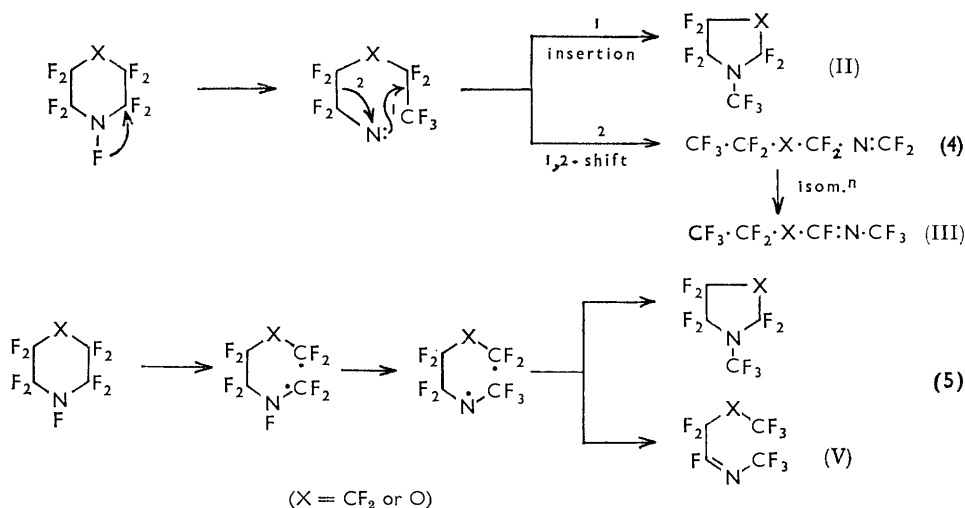
¹⁴ J. A. Young and R. D. Dresdner, *J. Amer. Chem. Soc.*, 1958, **80**, 1889.

¹⁵ D. A. Barr, R. N. Haszeldine, and C. J. Willis, *J.*, 1961, 1351.

strongly against the possibility that (IV) is the sole acyclic isomer formed, since the N:C stretching vibration occurs in the position (1782 cm^{-1}) expected for a perfluoro-compound containing the structural element $\cdot\text{CF}\cdot\text{N}\cdot\text{CF}_3$ (*e.g.*,^{15,16} $\text{CF}_3\cdot\text{CF}\cdot\text{N}\cdot\text{CF}_3$ 1786 cm^{-1} , $\text{CF}_3\cdot\text{CF}_2\cdot\text{CF}\cdot\text{N}\cdot\text{CF}_3$ 1786 cm^{-1} , and $\text{CF}_3\cdot[\text{CF}_2]_2\cdot\text{CF}\cdot\text{N}\cdot\text{CF}_3$ 1773 cm^{-1}) and at higher wavelength than is found with compounds containing a $\cdot\text{N}\cdot\text{CF}_2$ group (*e.g.*,^{15,17} $\text{CF}_3\cdot\text{N}\cdot\text{CF}_2$ 1808 cm^{-1} , $\text{C}_2\text{F}_5\cdot\text{N}\cdot\text{CF}_2$ 1812 cm^{-1} , and $n\text{-C}_3\text{F}_7\cdot\text{N}\cdot\text{CF}_2$ 1815 cm^{-1}). Clinching structural evidence could not be obtained using n.m.r. spectroscopy, since the proportion of (III) (<5%) present in the mixture (II + III) was too low to allow its spectrum to be observed.

Thermal Isomerisation of Perfluoro-(N-fluoromorpholine).—Pyrolysis of perfluoro-(*N*-fluoromorpholine) in the absence of a defluorinating agent favours thermal rearrangement leading to formation of perfluoro-(3-methyloxazolidine) and perfluoro-4-oxa-2-azahex-2-ene at the expense of defluorination to perfluoro-5,6-dihydro-2*H*-1,4-oxazine; thus, pyrolysis of the morpholine in platinum at $600^\circ/1\text{ atm.}$ yields 46% of (II + III) and 22% of (I), together with degradation products [tetrafluoromethane, hexafluoroethane, perfluoro(methylenemethylamine), carbonyl fluoride, and, by attack of the pyrolysate on glass traps, silicon tetrafluoride].

Of the two mechanisms proposed to rationalise the thermal rearrangement of perfluoro-(*N*-fluoropiperidine),² only that involving a nitrene intermediate (reaction 4) can account for the formation of isomer (III).



According to the other mechanism (reaction 5), the acyclic isomer obtained from perfluoro-(*N*-fluoromorpholine) would be perfluoro-5-oxa-2-azahex-2-ene (V; X = O). Hydrolysis of compound (V; X = O), which would show C:N absorption in the i.r. region near 1780 cm^{-1} , would yield the acid $\text{CF}_3\cdot\text{O}\cdot\text{CF}_2\cdot\text{CO}_2\text{H}$; only trifluoroacetic acid was isolated after destruction with aqueous base of the acyclic product of rearrangement of perfluoro-(*N*-fluoromorpholine) (see the previous section). Interestingly, an approximately equimolar mixture of perfluoro-(1-methylpyrrolidine) and perfluoro-(*n*-butyldenemethylamine) arises from thermal isomerisation of perfluoro-(*N*-fluoropiperidine), yet the ratio of cyclic to acyclic isomer (II to III) from the corresponding reaction of perfluoro-(*N*-fluoromorpholine) is *ca.* 95 : 5; the preference for ring-closure shown by the presumptive nitrene

¹⁶ J. B. Hynes, B. C. Bishop, P. Bandyopadhyay, and L. A. Bigelow, *J. Amer. Chem. Soc.*, 1963, **85**, 83; R. E. Banks, W. M. Cheng, and R. N. Haszeldine, *J.*, 1962, 3407; E. Halpern and J. Goldenson, *Appl. Spectroscopy*, 1957, **11**, 173.

¹⁷ D. A. Barr and R. N. Haszeldine, *J.*, 1955, 1881; 1956, 3416.

derived from the morpholine can be ascribed to the molecular flexibility arising from the presence of the ether link.

EXPERIMENTAL

Volatile materials were manipulated in a conventional Pyrex vacuum system to minimise handling losses and attack by moisture. Products were identified by physical properties, elemental analysis, molecular-weight determination (Regnault's method), i.r. spectroscopy (Perkin-Elmer spectrophotometers models 21 and 137 equipped with sodium chloride optics), ^{19}F nuclear magnetic resonance (n.m.r.) spectroscopy (A.E.I. RS2 spectrometer operating at 60 Mc./sec.), and gas-liquid chromatography (g.l.c.) (Perkin-Elmer Fraktometer model 116).

Preparation of Perfluoro-(N-fluoromorpholine).—A 2 mole % solution of morpholine in anhydrous hydrogen fluoride was electrolysed at 20A and 5.0v in the electrochemical fluorination apparatus described previously.¹⁸ The product which collected in the -78° trap was vaporised and carried by a stream of nitrogen through 10% aqueous sodium hydroxide (to remove any HF), then over calcium sulphate, and finally into a trap cooled to -78° . The condensate was distilled through a 60×2.5 cm. adiabatic Vigreux column to remove most of the perfluoro-diethyl ether, b. p. 4.5° , and the stillpot residue was carefully fractionated using a 30×0.8 cm. Podbielniak Heli-grid column to provide more perfluoro-diethyl ether (total yield 30%) and g.l.c.-pure (10 m. dinonyl phthalate-Celite at 22°) perfluoro-(N-fluoromorpholine) (8% yield) (Found: C, 19.3; N, 5.3%; *M*, 250. Calc. for $\text{C}_4\text{F}_9\text{NO}$: C, 19.3; N, 5.5%; *M*, 249), b. p. 34.5° (lit.,⁵ $30.3\text{--}33.0/730$ mm.), the vapour of which showed N-F absorption in the i.r. region at 975 and 922 cm.^{-1} .

Reactions of Perfluoro-(N-fluoromorpholine).—(a) *Attempted hydrolysis.* Perfluoro-(N-fluoromorpholine) was recovered unchanged after treatment with (i) 2N-sodium hydroxide at 80° for 5 weeks and (ii) 5N-hydrochloric acid at 80° for 5 days.

(b) *With iodide ion.* Perfluoro-(N-fluoromorpholine) (4.00 g., 16.1 mmoles) and an excess of 2N-potassium iodide (40 ml.) were vigorously shaken in a 250-ml. Pyrex ampoule at 60° for 2 days. After neutralisation (NaHCO_3), the product was made up to 120.0 ml. and titrated against 0.1N-sodium thiosulphate (free iodine 3.88 g., 15.3 mmoles; 95%). The solution, free of iodine, was then evaporated *in vacuo* and the white residue extracted with absolute ethanol (450 ml.). The residue from evaporation of the ethanolic extract was dissolved in water (110 ml.), and the solution (pH adjusted to 4) was treated with aqueous *S*-benzylthiuronium chloride, to give *di-(S-benzylthiuronium) perfluoro- β -oxagutarate* (3.30 g., 38%) (Found: C, 44.7; H, 4.1; N, 10.5. $\text{C}_{20}\text{H}_{22}\text{F}_4\text{N}_4\text{O}_5\text{S}_2$ requires C, 44.6; H, 4.1; N, 10.4%), m. p. (decomp.) $190.5\text{--}191^\circ$, recrystallised from water (charcoal).

In a similar experiment, perfluoro-(N-fluoromorpholine) (6.50 g., 26.1 mmoles) and n-hydriodic acid (100 ml.) were shaken at 50° for 2 weeks. After this time the organic layer had disappeared, and the solution was strongly coloured by free iodine. After neutralisation (NaHCO_3), the solution was extracted with carbon tetrachloride to remove the iodine, acidified (H_2SO_4), and further extracted continuously with ether for 48 hr. The ethereal extract was dried (MgSO_4) and treated with aniline, to yield *dianilinium perfluoro- β -oxagutarate* (3.30 g., 32%) (Found: C, 48.7; H, 4.0; N, 7.0%; Equiv. 195. $\text{C}_{16}\text{H}_{16}\text{F}_4\text{N}_2\text{O}_5$ requires C, 49.0; H, 4.1; N, 7.1%; Equiv. 196), m. p. (decomp.) $189\text{--}190^\circ$, recrystallised from 1 : 1 chloroform-acetone (charcoal). The iodine (6.60 g., 26.0 mmoles; 100%) in the carbon tetrachloride extract was estimated with 0.1N-sodium thiosulphate.

Reaction between perfluoro-(N-fluoromorpholine) and a solution of sodium iodide in acetone containing 10% by volume of water was almost complete after 1 hr. at room temperature, since 95% of the theoretical amount of iodine was liberated.

(c) *With ethanol.* Perfluoro-(N-fluoromorpholine) (5.13 g., 20.6 mmoles) and absolute ethanol (15 ml.) were heated together in a 50-ml. Dreadnought ampoule at 100° for 4 weeks. A volatile product (0.10 g.) was identified as ethyl fluoride by i.r. spectroscopy. The liquid product (13.30 g.) was distilled through a 10×0.5 cm. adiabatic Vigreux column, to give (i) a fraction (6.80 g.), b. p. $35\text{--}95^\circ$, which was shown by g.l.c. and i.r. spectroscopy to be ethanol containing traces of acetaldehyde and diethyl ether, and (ii) *diethyl perfluoro- β -oxagutarate* (2.60 g., 48%) (Found: C, 36.7; H, 3.9%; Equiv. 133. $\text{C}_8\text{H}_{10}\text{F}_4\text{O}_5$ requires C, 36.6; H, 3.8%; Equiv. 131), b. p. $52\text{--}54^\circ/\text{ca. } 2\text{ mm.}$, ν_{max} 1786 cm.^{-1} (C=O str.).

¹⁸ R. N. Haszeldine and F. Nyman, *J.*, 1956, 2684.

(d) *Pyrolysis in mild steel.* In a preliminary experiment, perfluoro-(*N*-fluoromorpholine) (2.00 g.) was passed in a slow stream of nitrogen at atmospheric pressure through a 100×1.5 cm. mild-steel tube heated to 500° over 56 cm. of its length; the contact time was 48 min. The pyrolysate (1.54 g. Found: *M*, 199) which collected in a trap cooled to -72° gave two peaks on a gas chromatogram [10 m. dinonyl phthalate-Celite at 22° ; retention times relative to perfluoro-(*N*-fluoromorpholine): peak 1, 0.86; peak 2, 1.96; area ratio peak 1 : peak 2 = 0.36], and its vapour showed i.r. absorption at 1757 (strong) and 1782 cm.^{-1} (medium), indicating the presence of C:N and/or C:C groups.

In a large-scale experiment, perfluoro-(*N*-fluoromorpholine) (20.0 g.) was pyrolysed as above. The pyrolysate (15.6 g.), trapped at -72° , was distilled through a 30×0.8 cm. Podbielniak Heli-grid column to give a fraction (10.5 g.), b. p. $20-23^\circ$, which contained both g.l.c. peak 1 and peak 2 materials, and a stillpot residue (4.0 g.) that consisted mainly (95%) of peak 2 material. Separation of part of the former by g.l.c. (10 m. \times 5 mm. dinonyl phthalate-Celite at room temperature) afforded a volatile colourless liquid (peak 1, 0.13 g.) (Found: C, 19.3; N, 5.3%; *M*, 249. $\text{C}_4\text{F}_9\text{NO}$ requires C, 19.3; N, 5.6%; *M*, 249), with i.r. absorption at 1782 cm.^{-1} , and perfluoro-5,6-dihydro-2*H*-1,4-oxazine (peak 2, 0.35 g.) (Found: C, 22.7; N, 6.6%; *M*, 211. $\text{C}_4\text{F}_7\text{NO}$ requires C, 22.8; N, 6.6%; *M*, 211), with strong i.r. absorption at 1757 cm.^{-1} .

The vapour pressure of perfluoro-5,6-dihydro-2*H*-1,4-oxazine, measured over the range $-24-20^\circ$, is given by the equation $\log p \text{ (cm.)} = 6.686 - 1428/T$. The calculated b. p. is 24.4° , Trouton's constant is 22.0, and the latent heat of vaporisation is $6539 \text{ cal.mole}^{-1}$.

Material (0.40 g.) yielding g.l.c. peak 1 was shaken (2 hr.) with 2*N*-sodium hydroxide (4 ml.) in a 20-ml. Pyrex ampoule at room temperature. Part of the sample was hydrolysed with the evolution of heat; the organic residue (0.36 g., 95%), recovered by distillation *in vacuo* and dried (P_2O_5), was perfluoro-(3-methyloxazolidine) (Found: C, 19.3; N, 5.6%; *M*, 249. $\text{C}_4\text{F}_9\text{NO}$ requires C, 19.3; N, 5.6%; *M*, 249). Comparison of the i.r. spectrum of this compound with that of g.l.c. peak 1 material showed that the 1782 cm.^{-1} band had disappeared. The hydrolysate from this experiment gave a positive test for fluoride ions and contained trifluoroacetate ions, which were isolated in the form of *S*-benzylthiuronium trifluoroacetate (10.6 mg.), m. p. and mixed m. p. 179° after recrystallisation twice from water (charcoal).

The vapour pressure of perfluoro-(3-methyloxazolidine), measured over the range $-24-20^\circ$, is given by the equation $\log p \text{ (cm.)} = 6.712 - 1429/T$. The calculated b. p. is 22.8° , Trouton's constant is 22.1, and the latent heat of vaporisation is $6540 \text{ cal.mole}^{-1}$.

(e) *Pyrolysis in platinum.* At atmospheric pressure, perfluoro-(*N*-fluoromorpholine) (10.6 g.) was passed (0.5 g./hr.) in a slow stream of nitrogen through a 100×1 cm. platinum tube heated to 600° over 56 cm. of its length. The pyrolysate was collected in two Pyrex traps cooled to -72 and -196° , respectively. The condensate in the -196° trap (2.35 g.) was shown by i.r. spectroscopy to be a mixture of the compounds tetrafluoromethane, hexafluoroethane, perfluoro-(methylenemethylamine), carbonyl fluoride, and silicon tetrafluoride. The product (6.90 g.) in the -72° trap was shown by g.l.c. analysis (10 m. dinonyl phthalate-Celite at room temperature) and i.r. spectroscopy to consist of perfluoro-(3-methyloxazolidine), perfluoro-4-oxa-2-azahex-2-ene (total 71%, in the approximate ratio 95:5; these constitute g.l.c. peak 1 referred to earlier), and perfluoro-5,6-dihydro-2*H*-1,4-oxazine (29%; g.l.c. peak 2). No unchanged perfluoro-(*N*-fluoromorpholine) was detected.

Reactions of Perfluoro-5,6-dihydro-2H-1,4-oxazine.—(a) *Hydrolysis.* A thin-walled Pyrex ampoule containing perfluoro-5,6-dihydro-2*H*-1,4-oxazine (0.0624 g., 0.295 mmole) was crushed under the surface of *N*-sodium hydroxide (30 ml.). After being shaken for 2 hr. the solution contained free fluoride ions (0.01579 g., 0.8407 mmole; 97% of 3F).

When the oxazine (0.50 g.) was shaken with 2*N*-sodium hydroxide (10 ml.) for 45 min., the hydrolysate, after adjustment of its pH to 4, afforded di-(*S*-benzylthiuronium) perfluoro- β -oxaglutarate (0.66 g., 55%) (Found: C, 44.6; H, 4.1; N, 10.5. Calc. for $\text{C}_{20}\text{H}_{22}\text{F}_4\text{N}_4\text{O}_5\text{S}_2$: C, 44.6; H, 4.1; N, 10.4%), m. p. (decomp.) 192° (from water).

(b) *Ethanolysis.* Perfluoro-5,6-dihydro-2*H*-1,4-oxazine (1.00 g., 4.74 mmoles) and absolute ethanol (8.7 ml.) were shaken together in a 25-ml. Pyrex ampoule at 85° for 6 days. Distillation of the product gave ethyl fluoride (*ca.* 0.03 g.) and spectroscopically pure diethyl perfluoro- β -oxaglutarate (1.11 g., 4.24 mmoles; 89%), b. p. $54^\circ/\text{ca. } 2 \text{ mm.}$, which gave only one peak on a gas chromatogram (2 m. Apiezon L-Celite at 150°).

Reactions of Perfluoro-(3-methyloxazolidine).—(a) No reaction occurred when the oxazolidine

(0.11—0.21 g.) was shaken with (i) 2*N*-potassium iodide (4 ml.) at 60° for 6 days, (ii) 40% aqueous sodium hydroxide (6 ml.) at 60° for 5 days, or (iii) concentrated sulphuric acid (4 ml.) at 60° for 5 days.

(b) The oxazolidine (0.61 g.) was recovered in 95% yield after being heated at 500° for 2 hr. in a 30-ml. autoclave packed tightly with clean mild-steel wool. It was also recovered unchanged (96% yield) after passage at the rate of 0.5 g./hr. in a slow stream of nitrogen through a 100 × 1.5 cm. mild-steel tube heated to 500° over 56 cm. of its length.

(c) The oxazolidine (2.40 g.) and finely powdered aluminium trichloride (1.93 g.) were heated at 170° for 11 hr. in a 35-ml. stainless steel autoclave. The volatile product was shown by g.l.c. (8 m. Kel-F No. 3 oil-Celite at room temperature) and i.r. spectroscopy to consist of perfluoro-(3-methyloxazolidine) (65% by weight), phosgene (20%), carbon dioxide (13%), and unidentified chlorine-containing material (2%). A black tar (*ca.* 2.5 g.) remained in the autoclave.

Nuclear Magnetic Resonance Spectra.—(a) *Perfluoro-5,6-dihydro-2H-1,4-oxazine*. The ¹⁹F n.m.r. spectrum of (I) consists of four absorption regions, the chemical shifts relative to external CF₃·CO₂H being -21.2, 0.16, 14.6, and 20.5 p.p.m., severally. The lowest-field absorption is a broad structureless band that is assigned to the N·CF group by comparison with the chemical shift value (-24.2 p.p.m.) for the same group in perfluoro-2,3,4,5-tetrahydropyridine (VI).² The absorption at 0.16 p.p.m. is a doublet of triplets with further unresolved structure; this band is assigned to the 2-fluorine nuclei, which interact with the 3-fluorine nucleus ($J_{2,3} = 21.4$ c./sec.) and also with the 6-fluorine nuclei ($J_{2,6} = 4.6$ c./sec.) [cf. (VI), for which $J_{5,6} = 24$ c./sec. and $J_{3,5} = 7.6$ c./sec.]. The absorption at 14.6 p.p.m. is a complex group of bands which has not been analysed; it is assigned to the 6-fluorine nuclei. The highest-field absorption (20.5 p.p.m.) is a rather broad, structureless band that is assigned to the 5-fluorine nuclei [cf.² chemical shift for the 2-fluorine nuclei in (VI) = 16.7 p.p.m.].

(b) *Perfluoro-(3-methyloxazolidine)*.—The ¹⁹F n.m.r. spectrum (CF₃·CO₂H as external reference) consists of three absorption regions. The lowest field absorption (-18.9 and -18.2 p.p.m.) consists of a quintet-like structure and a single broad band; the former is assigned to the CF₂·N group, the fine structure arising from spin-spin interaction with the two CF₂·N groups; the



broad singlet is assigned to the N·CF₂·O group. An absorption at 10.35 p.p.m., predominantly a single band showing a small triplet splitting, is assigned to the 5-fluorine nuclei (O·CF₂), the splitting being the result of interaction with the two fluorine substituents of the C-4 CF₂·N group. The third absorption, at 16.85 p.p.m., is a 1 : 3 : 3 : 1 quartet and is assigned to the C-4 fluorine substituents, the multiplet structure arising from interaction with the N·CF₃ group. The spectrum showed weak impurity bands at 9.65, 12.45, and 33.7 p.p.m.; one of the impurities was probably perfluoro-(*N*-fluoromorpholine), the ¹⁹F n.m.r. spectrum of which consists of three absorption regions, two of estimated equal intensity at 9.77 and 33.9 p.p.m. (from CF₃·CO₂H) and a weak band at 36.4 p.p.m.¹⁹

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¹⁹ J. Lee and K. G. Orrell, unpublished results.