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N-Fluoro-compounds. Part II.¹ Reaction of Perfluoro-N-fluoropiperidine or Perfluoro-N-fluoromorpholine with Manganese Pentacarbonyl Hydride to give the Corresponding N-H Compounds

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Treatment of perfluoro-N-fluoropiperidine and perfluoro-N-fluoromorpholine with manganese pentacarbonyl hydride converts them into perfluoropiperidine and perfluoromorpholine, respectively. Perfluoromorpholine reacts with fuming nitric acid in trifluoroacetic anhydride to give perfluoro-N-nitromorpholine, and with anhydrous potassium fluoride to yield perfluoro-5,6-dihydro-2H-1,4-oxazine; thermal chlorination of perfluoromorpholine in the presence of anhydrous potassium fluoride gives, inter alia, 6-chloro-octafluoro-5-oxa-2-azahex-2-ene.

WHEREAS many tertiary perfluoroamines are known, no primary and only a few secondary perfluoroamines have been isolated.² These last, e.g., perfluoropiperidine,³ have been prepared hitherto by treatment of perfluoro-imines with anhydrous hydrogen fluoride.

$$\begin{array}{c} F_{2} \begin{pmatrix} X \\ F_{2} \end{pmatrix} F_{2} \\ F_{2} \end{pmatrix} F_{2} + HF \xrightarrow{40^{\circ}} F_{2} \begin{pmatrix} X \\ F_{2} \end{pmatrix} F_{2} \\ F_{2} \end{pmatrix} F_{2} \\ H \\ H \end{array}$$

Perfluoropiperidine (I; $X = CF_2$) and perfluoromorpholine (I; X = O) can now be prepared in good yields by treating perfluoro-N-fluoropiperidine and perfluoro-N-fluoromorpholine, respectively, with manganese pentacarbonvl hvdride.

Reaction of perfluoro-N-fluoromorpholine with a

ca. 10% molar excess of manganese pentacarbonyl hydride at -10 to 20 or -30 to 50° provides perfluoromorpholine in 54-67% yield, together with an unstable hygroscopic red solid that evolves in low yield an approximately equimolar mixture of perfluoromorpholine (I; X = O) and perfluoro-5,6-dihydro-2H-1,4-oxazine (II; X = 0) when heated in vacuo to 120° .

Use of a 2:1 molar ratio of carbonyl hydride to N-F compound does not increase noticeably the yield of secondary perfluoroamine obtained from perfluoro-N-fluoropiperidine: thus, with either a 1:1 or a 2:1molar reactant ratio and a reaction temperature of -20 to 20°, the yield of perfluoropiperidine (I; X = CF₂) is either 46 or 47%, which is increased to 49 or 57% by pyrolysis of the unstable hygroscopic red solids

¹ Part I, R. E. Banks, R. N. Haszeldine, and J. P. Lalu, J. Chem. Soc. (C), 1966, 1514.

² R. E. Banks, "Fluorocarbons and their Derivatives," Oldbourne Press, London, 1965, p. 82. ³ R. E. Banks, W. M. Cheng, and R. N. Haszeldine, J. Chem.

Soc., 1964, 2485.

J. Chem. Soc. (C), 1967

formed concomitantly. The pyrolysis also yields perfluoro-2,3,4,5-tetrahydropyridine (II; $X = CF_2$).

In a reaction between approximately equimolar amounts of perfluoro-N-fluoropiperidine and manganese pentacarbonyl hydride in which no control was exercised over the temperature, a vigorous exothermic reaction occurred at about $0-10^{\circ}$ and the identified products were carbon monoxide (38%), silicon tetrafluoride (a glass vessel was used), decacarbonyldimanganese (31%), perfluoropiperidine in only 17% yield, and perfluoro-2,3,4,5-tetrahydropyridine in much higher yield (58%) than in the controlled reactions.

The red solids obtained from reactions between manganese pentacarbonyl hydride and both perfluoro-Nfluoropiperidine and perfluoro-N-fluoromorpholine contain appreciable amounts of decacarbonyldimanganese, and although infrared spectra indicate the presence of polyfluoro-organic material, attempts to isolate products such as (III) or (IV) failed.

$$\begin{array}{cccc} F_2 \begin{pmatrix} X \\ F_2 \end{pmatrix} F_2 & F_2 \end{pmatrix} \\ (III) & M_n(CO)_5 & (IV) & (V) \\ & (X = CF_2 \text{ or } O) \end{array}$$

Perfluoromorpholine (I; X = O) reacts only slowly with an equimolar amount of manganese pentacarbonyl hydride, to give a low yield (29%) of the oxazine (II; X = 0), and an unidentified yellow solid. Furthermore, the reaction of perfluoro-2,3,4,5-tetrahydropyridine (II; $X = CF_{2}$ with manganese pentacarbonyl hydride is also very slow and also gives a yellow solid. Steps $(I) \longrightarrow (II) \longrightarrow (IV)$ in the possible route for the formation of the red solids thus seem unlikely.

$$\begin{array}{c} F_{2} \begin{pmatrix} X \\ F_{2} \end{pmatrix} F_{2} \\ F_{2} \end{pmatrix} \begin{array}{c} F_{2} \\ F_{2}$$

The possibility remains that the red solids are, or contain. (III), formation of which can be visualised as shown.

$$\rightarrow N^{-}F^{-}H^{-}Mn(CO)_{s} \longrightarrow HF + \rightarrow N^{-} + Mn(CO)_{s}$$

(III)

Cleavage of (III) by hydrogen fluoride would then give (I), with some loss of hydrogen fluoride by attack on the glass vessel. Cleavage of (III) by hydrogen fluoride also formed during the pyrolysis of the red solids, and loss of manganese pentacarbonyl fluoride [FMn(CO)₅; still unknown] from (III) during the pyrolysis would explain

the formation of compounds (I) and (II). Formation of a perfluoro-imine (II) from (III) in this fashion might be expected by analogy with the thermal decomposition of polyfluoroalkyl manganese compounds.⁴ Neither manganese pentacarbonyl fluoride nor the diene (V), which would be an expected pyrolysis product of (IV), were detected in the pyrolysis products from the red solids.

Properties and Reactions of Perfluoromorpholine.-Perfluoromorpholine (I; X = O) is a colourless liquid, b. p. 57.2° , the vapour of which shows strong infrared absorption at 2.93 and 6.76 μ , attributable to the N-H stretching and bending vibrations, respectively [cf. (CF₃)₂NH,⁵ 2.89 and 6.65 μ; CF₂·[CF₂]₄·NH,³ 2.90 and 6.75 μ]; it reacts with anhydrous potassium fluoride at room temperature to give an almost quantitative yield of perfluoro-5,6-dihydro-2H-1,4-oxazine (II; X = O). Thermal chlorination of perfluoromorpholine in the presence of anhydrous potassium fluoride according to the method used ⁶ to convert bistrifluoromethylamine into N-chlorobistrifluoromethylamine, gives a complex mixture from which only perfluoro-5,6-dihydro-2H-1,4-oxazine and impure 6-chloro-octafluoro-5-oxa-2-azahex-2-ene, $CF_2Cl \cdot O \cdot CF_2 \cdot CF \cdot N \cdot CF_3$, appear capable of isolation.

Nitration of perfluoromorpholine with a mixture of fuming nitric acid and trifluoroacetic anhydride gives perfluoro-N-nitromorpholine in 83% yield; use of fuming nitric acid instead of concentrated acid³ in the similar nitration of perfluoropiperidine increases the yield of perfluoro-N-nitropiperidine from 41 to 64%.

EXPERIMENTAL

Perfluoro-N-fluoropiperidine and perfluoro-N-fluoromorpholine were prepared by electrochemical fluorination of pyridine ⁷ and morpholine,⁸ respectively.

Products were identified by elemental analysis, physical properties, molecular weight determination (Regnault's method), infrared spectroscopy (Perkin-Elmer spectrophotometer model 21 with sodium chloride optics), nuclear magnetic resonance spectroscopy (Perkin-Elmer R10 instrument), mass spectrometry (A.E.I. MS/2H spectrometer), and gas-liquid chromatography.

Preparation of Perfluoromorpholine .- A mixture of perfluoro-N-fluoromorpholine (2.60 g., 10.4 mmoles) and manganese pentacarbonyl hydride (2.15 g., 11.0 mmoles), sealed in a 50-ml. Dreadnought ampoule, was allowed to warm up from -196 to -30° during 4 hr. The temperature of the straw-coloured mixture was then slowly raised during 8 hr. from -30 to 50° , during which time the mixture became dark red. Carbon monoxide (11.9 mmoles; 22%) was removed from the reaction vessel, together with a volatile condensible product that was fractionated to yield perfluoromorpholine (1.60 g., 6.9 mmoles; 67%) (Found: C, 21.0; H, 0.5; N, 6.3%; M, 229. C4HF8NO requires C, 20.8; H, 0.4; N, 6.1%; M, 231), leaving a hygroscopic red solid behind. The red solid fumed in the air and gave a

⁶ C. W. Tullock, U.S.P. 3,052,723/1962.

7 R. E. Banks, A. E. Ginsberg, and R. N. Haszeldine, J. Chem. Soc., 1961, 1740. ⁸ R. E. Banks and E. D. Burling, J. Chem. Soc., 1965, 6077.

^{P. M. Treichel and F. G. A. Stone, in "Advances in Organo-}metallic Chemistry," ed. F. G. A. Stone and R. West, Academic Press, New York, 1964, vol. 1, p. 190.
D. A. Barr and R. N. Haszeldine, J. Chem. Soc., 1955, 4169.

poorly-resolved i.r. spectrum (mull in Nujol or HCB) that revealed the presence of decacarbonyldimanganese and of a polyfluoro-organic compound or compounds (strong diffuse absorption in the C-F region). The red solid, which decomposed slowly with the evolution of carbon monoxide and hydrogen fluoride when stored in glass, was examined by liquid-solid chromatography, but the only compound isolated was decacarbonyldimanganese [eluent, light petroleum (b. p. $30-40^{\circ}$)].

In another experiment, manganese pentacarbonyl hydride (18·80 g., 96·0 mmoles) was condensed, *in vacuo*, into a 100ml. flask containing perfluoro-N-fluoromorpholine (28·8 g., 115·6 mmoles) cooled to -196° ; the flask was connected to a cold (-196°) trap filled with activated charcoal *via* a reflux condenser cooled to -85° . The reaction mixture was warmed up to -10° *in vacuo* and was then stirred for 2 hr. while the temperature was allowed to rise slowly to 20^{\circ}. During the reaction period 54·8 mmoles (12%) of carbon monoxide was adsorbed by the charcoal. The volatile product was fractionated to give traces of carbon dioxide and silicon tetrafluoride, perfluoro-N-fluoromorpholine (7·2 g., 28·9 mmoles; 25% recovery), perfluoromorpholine (10·75 g., 46·5 mmoles; 54% based on

 $CF_2 \cdot CF_2 \cdot O \cdot CF_2 \cdot CF_2 \cdot NF$ consumed), and traces of perfluoro-5,6-dihydro-2*H*-1,4-oxazine.⁸ The red solid product (24·1 g.) recovered from the flask was heated *in vacuo* to 120° (a mild explosion occurred when the temperature reached 115°), to provide carbon monoxide (17·5 mmoles), a trace of silicon tetrafluoride, perfluoromorpholine (1·3 g., 5·65 mmoles; total yield 60%), and perfluoro-5,6-dihydro-2*H*-1,4-oxazine (1·2 g., 5·7 mmoles; 6%).

The vapour pressure of perfluoromorpholine, measured over the range $0-50^{\circ}$, is given by the equation $\log_{10} p(\text{cm.}) = 7.027 - 1706/T$. The calculated b. p. is 57.2° , the Trouton constant is 23.7, and the latent heat of vaporisation is 7850 cal. mole⁻¹.

Preparation of Perfluoropiperidine.—(a) At - 20 to 20° . A mixture of perfluoro-N-fluoropiperidine (3.05 g., 10.8 mmoles) and manganese pentacarbonyl hydride (4.35 g., 22.2 mmoles), contained in a 50-ml. Dreadnought ampoule, was allowed to warm up to 20° from -20° during 48 hr. The volatile product consisted of carbon monoxide (6.3)mmoles), a trace of silicon tetrafluoride, manganese pentacarbonyl hydride (1.5 g., 7.7 mmoles; 35% recovery), perfluoropiperidine (1.35 g., 5.1 mmoles; 47% based on $C_5F_{10}NF$ consumed), and traces of perfluoro-N-fluoropiperidine and perfluoro-2,3,4,5-tetrahydropyridine. A red solid product, which had an i.r. spectrum similar to the red solid obtained from perfluoro-N-fluoromorpholine and manganese pentacarbonyl hydride, decomposed rapidly when heated in vacuo to ca. 110°, giving perfluoropiperidine (0.3 g., 1.1 mmoles; total yield 57%), perfluoro-2,3,4,5tetrahydropyridine (0.35 g., 1.4 mmoles; 13%), traces of silicon tetrafluoride, carbon monoxide, and a brown solid containing decacarbonyldimanganese [1.5 g., 3.9 mmoles; 53% based on HMn(CO)₅ consumed; extracted with light petroleum (b. p. 30-40°)].

Similarly, perfluoro-N-fluoropiperidine (13.9 g., 49.0 mmoles) and manganese pentacarbonyl hydride (9.8 g., 50.0 mmoles) gave carbon monoxide, traces of silicon tetrafluoride, perfluoropiperidine (6.0 g., 22.6 mmoles; 46%), and a red solid that decomposed when heated to

⁹ R. E. Banks, W. M. Cheng, and R. N. Haszeldine, J. Chem. Soc., 1962, 3407.

 120° in vacuo, giving carbon monoxide, silicon tetrafluoride, perfluoropiperidine (0.35 g., 1.3 mmoles; total yield 49%), perfluoro-2,3,4,5-tetrahydropyridine (0.40 g., 1.6 mmoles; 3%), and a dark brown solid residue containing deca-carbonyldimanganese (by i.r. spectroscopy).

Vacuum sublimation of the red solid from a duplicate experiment gave carbon monoxide, silicon tetrafluoride, perfluoropiperidine, perfluoro-2,3,4,5-tetrahydropyridine, decacarbonyldimanganese, and a dark brown-black residue.

(b) Without temperature control. A mixture of manganese pentacarbonyl hydride (1.95 g., 10.0 mmoles) and per-fluoro-N-fluoropiperidine (2.75 g., 9.7 mmoles) contained in a 50-ml. Dreadnought ampoule, was warmed fairly quickly from -196° to somewhere between 0 and 10° . A vigorous exothermic reaction set in and no attempt was made to control this by cooling. After 30 min. the product consisted of carbon monoxide (19.2 mmoles; 38%), silicon tetrafluoride, perfluoropiperidine (0.43 g., 1.6 mmoles; 17%) perfluoro-2,3,4,5-tetrahydropyridine (1.38 g., 5.6 mmoles; 58%), and a red solid from which decacarbonyldimanganese (0.6 g., 1.5 mmoles; 31%) was isolated by extraction with light petroleum (b. p. 30-40°).

Reactions of Perfluoromorpholine.—(a) Dehydrofluorination. Perfluoromorpholine (1.15 g., 5.0 mmoles) was condensed, in vacuo, into a 300-ml. silica tube containing anhydrous potassium fluoride (10 g.), and cooled to -196° . The tube was sealed and allowed to warm up to 20° whilst being rotated about its longitudinal axis. After 16 hr., the volatile product was fractionated to provide perfluoro-5,6-dihydro-2H-1,4-oxazine (1.00 g., 4.75 mmoles; 95%) (Found: M, 208. Calc. for C₄F₇NO: M, 211), with correct i.r. spectrum.

(b) Chlorination. A mixture of perfluoromorpholine (5.40 g., 23.4 mmoles), chlorine (1.56 g., 22.0 mmoles), and anhydrous potassium fluoride (10 g.), contained in a horizontal rotating 300-ml. silica ampoule, was heated at 100° for 1 hr. and then at 200° for 1 hr., 250° for 1 hr., and, finally, 325° for 1 hr. The volatile product was then removed from the ampoule and left in contact ⁶ with anhydrous powdered sulphur (10 g.) for 12 hr. in a 300-ml. Dreadnought ampoule. The final very complex product was examined by a combination of fractionation, g.l.c., i.r., and mass spectrometric techniques and found to contain sulphur monochloride (0.6 g.), silicon tetrafluoride, carbon dioxide, carbonyl fluoride, perfluoromorpholine, perfluoro-5,6-dihydro-2H-(estimated yield 1,4-oxazine 35%), chloroform, compound shown by ¹⁹F n.m.r. spectroscopy to be 6-chlorooctafluoro-5-oxa-2-azahex-2-ene (estimated yield 38%), and at least seven unidentified chlorofluoro-compounds, including some containing >NH, >NF, N.C, CN, and N:C:O groups (by i.r. spectroscopy). Using g.l.c. techniques (4 m. \times 5 mm. Kel-F No. 10 oil–Celite at 50°) small samples of perfluoro-5,6-dihydro-2H-1,4-oxazine (Found: C, 22.7; N, 6.5%; M, 207. Calc. for C₄F₇NO: C, 22.8; N, 6.6%; M, 211), $\lambda_{\text{max.}}$ 5.69 μ (C:N str.), and impure 6-chloro-octafluoro-5-oxa-2-azahex-2-ene (Found: C, 19.5; Cl, 11.0; N, 5.5. Calc. for C₄ClF₈NO: C, 18.1; Cl, 13.3; N, 5.3%) were isolated. The latter product attacked glass at room temperature and gave a mass spectrum with major peaks at m/e values (per cent rel. intensities and assignments in parentheses) of 164 (77.2; $CF_3 \cdot N \cdot CF \cdot CF_2^+$), 114 (52.4; $CF_3 \cdot N \cdot CF^+$), 85 (100.0; CF_2Cl^+), 69 (50.6; CF_3^+), and 50 (10.2; CF_2^+), but showing no parent ion; the i.r. spectrum of the azahexene contained a strong C:N absorption at $5{\cdot}60\,\mu$ in keeping with the presence of a CF₃·N:CF·CF₂ group.⁹

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(c) Nitration. Perfluoromorpholine (2.35 g., 10.3 mmoles) was added during 15 min. to a stirred mixture of fuming nitric acid (2 ml.) and trifluoroacetic anhydride (10 ml.) held at 0° in a 50-ml. Pyrex flask fitted with a reflux condenser cooled to -72° . The mixture was warmed slowly to 40° during 2 hr. and then cooled to -5° and carefully neutralised with sodium carbonate; a few drops of water were added periodically during the last operation to prevent the mixture solidifying. The volatile product, separated in vacuo and condensed at -196° , was washed successively with 2M-sodium hydroxide (5 ml.) and water (5 ml.), and then dried (P2O5), to give perfluoro-N-nitromorpholine (2.35 g., 8.5 mmoles; 83%) (Found: C, 17.4; N, 10.3%; M, 278. C₄F₈N₂O₃ requires C, 17.4; N, 10.2%; M, 276), b. p. 73.4° (isoteniscope), the vapour of which showed a strong absorption in the i.r. region at 5.95 μ , attributable to the presence of the nitro-group [cf. $(CF_3)_2$ N·NO₂¹⁰ 5.99 μ ;

$CF_2 \cdot [CF_2]_4 \cdot N \cdot NO_2$, 3 5.93, 6.00 μ (doublet)].

(d) With manganese pentacarbonyl hydride. Perfluoromorpholine (1.00 g., 4.32 mmoles) was condensed, in vacuo, into a cold (-196°) 50-ml. Dreadnought tube containing manganese pentacarbonyl hydride (0.85 g., 4.34 mmoles). The tube was sealed and warmed fairly quickly to -20° ; it was then allowed to warm up slowly to room temperature (ca. 24 hr.). The volatile products were carbon monoxide (1.00 mmole), perfluoromorpholine (3.20 mmoles; 74%) recovery), manganese pentacarbonyl hydride (2.70 mmoles; 62% recovery), and perfluoro-5,6-dihydro-2H-1,4-oxazine (0.33 mmole; 29% based upon perfluoromorpholine consumed). A moist bright yellow solid flecked with red that remained in the tube was heated gently, in vacuo, to give silicon tetrafluoride containing traces of perfluoro-5,6-dihydro-2H-1,4-oxazine, a brown solid, and some yellow crystals. The last two products were shaken with light petroleum (b. p. 30-40°), and the yellow solution obtained was decanted from insoluble brown material and then evaporated, to yield decacarbonyldimanganese (0.1 g.; identified by i.r. spectroscopy). Extraction of the brown material with chloroform-acetone (50: 50 v/v) gave a small amount of brown solid, which was shown by i.r. spectroscopy to contain fluorocarbon material (broad strong absorption in the region $7.5 - 9.5 \mu$), possibly with carboxylic acid groups present (broad absorption centred at 3.15 and carbonyl absorption at 5.7μ), together with a metal carbonyl (strong absorption in the region $4 \cdot 6 - 5 \cdot 0 \mu$).

Preparation of Perfluoro-N-nitropiperidine.—Perfluoropiperidine (2.50 g., 9.4 mmoles) was nitrated as described above for perfluoromorpholine, to give perfluoro-N-nitropiperidine (1.85 g., 6.0 mmoles; 64%) (Found: C, 19.4; N, 8.5%; M, 308. Calc. for $C_5F_{10}N_2O_2$: C, 19.4; N, 9.0%; M, 310), b. p. 87.5°, with correct i.r. spectrum.

Reaction of Manganese Pentacarbonyl Hydride with Perfluoro-2,3,4,5-tetrahydropyridine.—A mixture of manganese pentacarbonyl hydride (1.0 g., 5.1 mmoles) and perfluoro-2,3,4,5-tetrahydropyridine (1.35 g., 5.5 mmoles) was stored in a 50-ml. Dreadnought ampoule at 20° for 2 weeks. Since no reaction appeared to have occurred, the ampoule was then left at 20° for a further 6 weeks. The volatile condensable product was shown by i.r. and ¹⁹F n.m.r. spectroscopy to be silicon tetrafluoride and a complex mixture (0.25 g.) of fluorinated compounds containing some unchanged perfluoro-2,3,4,5-tetrahydropyridine and material with C.C, N-H, and C-H bonds. A solid yellow product was not removed from the tube, but was heated to *ca.* 150° *in vacuo*, to give traces of silicon tetrafluoride and material which was shown by i.r. spectroscopy to be fluoro-carbon in nature and to contain N-H and C.N groups; the brown residue remaining in the tube was not examined.

N.m.r. Spectra.—(a) Perfluoromorpholine. The ¹H 60·00 Mc./sec. spectrum consists of a broad singlet at 2·2 p.p.m. to high field of external benzene. The 56·46 Mc./sec. ¹⁹F spectrum shows two absorption band systems of equal intensity at 11·7 and 14·8 p.p.m. to high field of external trifluoroacetic acid, which are assigned, respectively, to the fluorines of the type $CF_2 \cdot O \cdot CF_2$ and $CF_2 \cdot NH \cdot CF_2$. The 11·7 p.p.m. band shows poorly-resolved fine structure, while the 14·8 p.p.m. band is a broad singlet (width at half-height 7·5 c./sec.) due to the adjacent ¹⁴N quadrupole.

(b) Perfluoro-N-nitromorpholine. The 56.46 Mc./sec. ¹⁹F spectrum consists of two absorption band systems of equal intensity at 8.85 and 22.6 p.p.m. to high field of external trifluoroacetic acid, which are assigned, respectively, to the fluorines of the $CF_2 \cdot O \cdot CF_2$ and $CF_2 \cdot N(NO_2) \cdot CF_2$ groups. Both absorption bands show poorly-resolved fine structure.

(c) Perfluoropiperidine. The 60.00 Mc./sec. ¹H spectrum is a broad singlet at 2.31 p.p.m. to high field of external benzene. The 56.46 Mc./sec. ¹⁹F spectrum shows two absorption regions of relative intensity 4.0:5.9 at 14.6 and 57.6 p.p.m. to high field of external trifluoroacetic acid; these are assigned, respectively, to the fluorines of the CF₂·NH·CF₂ group and the fluorines at C-3, C-4, and C-5.

(d) Perfluoro-N-nitropiperidine. The 56.46 Mc./sec. ¹⁹F spectrum shows three absorption band systems of relative intensities 2:2:1 at 24.0, 55.5, and 58.0 p.p.m. to high field of external trifluoroacetic acid, which are assigned to the fluorine nuclei in the α , β , and γ -positions, respectively. Each band system shows poorly-resolved fine structure.

(e) 6-Chloro-octafluoro-5-oxa-2-azahex-2-ene.

(1) (2) (3) (4)
$$CF_2CI \cdot O \cdot CF_2 \cdot CF \cdot N \cdot CF_3$$

The 56·46 Mc./sec. spectrum shows four absorption band systems of relative intensities 2:1:3:2 at 50·0, $45\cdot8$, and $19\cdot2$ p.p.m. to low field, and $1\cdot2$ p.p.m. to high field of external trifluoroacetic acid. These are assigned, respectively, to the fluorine nuclei of type (1), (3), (4), and (2). The band at $-50\cdot0$ p.p.m. appears as a triplet 5 [coupling to F(2)], while the $-45\cdot8$ p.p.m. band is a broadened quartet [coupling to F(4)]; the $-19\cdot2$ p.p.m. band is a doublet [coupling to F(3)] and that at $1\cdot2$ p.p.m. is a triplet of doublets [coupling to F(1) and F(3)]. The following coupling constants were extracted from the spectrum: $|J_{12}| =$ $10\cdot5; |J_{23}| = 3\cdot4;$ and $|J_{34}| = 13\cdot6$ c./sec. The spectrum showed impurity bands estimated to be due to the presence of *ca.* 10% of unidentified material.

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¹⁰ J. A. Young, S. N. Tsoukalas, and R. D. Dresdner, J. Amer. Chem. Soc., 1958, **80**, 3604.