# N-Fluoro-compounds. Part V.[1] Photochemical Reactions of Perfluoro-N-fluoromorpholine, and a Re-investigation of its Thermal Decomposition; Preparation and Properties of Perfluoromorpholin-N-oxyl [2]

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U.v. irradiation of perfluoro-N-fluoromorpholine in the presence of perfluorocyclobutene yields perfluorobicyclobutyl, perfluoro-NN'-bimorpholyl, and perfluoro-(N-cyclobutylmorpholine). Pyrolysis of the last product gives perfluoro-(N-vinylmorpholine), photochemical bromination of which provides perfluoro-[N-(1,2-dibromoethyl)-morpholine], a compound also formed, together with N-(2-bromo-1,2,2-trifluoroethyl)octafluoromorpholine, when the vinyl derivative is subjected to photochemical hydrobromination. U.v. irradiation in silica–Pyrex apparatus of perfluoro-N-fluoromorpholine, either alone or in the presence of oxygen, yields, inter alia, the N–O–N compound perfluoro-[N-(morpholino-oxy)morpholine]. Pyrolysis of this product gives perfluoromorpholin-N-oxyl, perfluoro-NN'-bimorpholyl, perfluoro-(6-morpholino-oxy-2-aza-5-oxahex-1-ene), perfluoro-(6-morpholino-oxy-2-aza-5-oxahex-2-ene), perfluoro-5,6-dihydro-2H-1,4-oxazine, perfluoro-N-fluoromorpholine, and, if the decomposition is carried out at low pressure, a compound believed to be perfluoro-[N-(morpholino-oxymethyl)oxazolidine]. Perfluoro-(4-morpholino-oxy-3-oxabutyric) acid and its amide can be obtained via hydrolysis of the azahexenes. Perfluoromorpholin-N-oxyl reacts with nitric oxide, tetrafluoroethylene, and perfluorobut-2-yne to give perfluoromorpholyl nitrite, perfluoro-[1,2-bis(morpholino-oxy)ethane], and perfluoro-[N-(morpholino-oxy)morpholine] and perfluorobiacetyl, respectively. Flow pyrolysis of perfluoro-N-fluoromorpholine in platinum yields carbonyl fluoride, carbon tetrafluoride, hexafluoroethane, perfluoro-2-azapropene, perfluoro-2-azabut-2-ene, perfluoro-(N-methyloxazolidine), perfluoro-5,6-dihydro-2H-1,4-oxazine, and, possibly, N-fluorodifluoromethyleneamine, but apparently not perfluoro-4-oxa-2-azahex-2-ene, as proposed previously; this can be rationalised by a breakdown mechanism that is consistent with the formation of the azahexenes when perfluoro-[N-(morpholino-oxy)-morpholine] is pyrolysed and with the production of 6-chloro-octafluoro-5-oxa-2-azahex-2-ene when perfluoro-morpholine is heated with chlorine in the presence of potassium fluoride.

E.s.r. data for perfluoromorpholin-N-oxyl are presented.

ULTRAVIOLET irradiation of perfluoro-N-fluoropiperidine in the presence of oxygen and silica was shown previously to yield a colourless high-boiling liquid that decomposes when heated to give, inter alia, perfluoropiperidin-N-oxyl, a volatile purplish blue liquid.[3] The prime objective of the present investigation was to determine if perfluoro-N-fluoromorpholine could be converted into perfluoromorpholin-N-oxyl in a similar manner, and, if so, to identify the oxyl precursor. Initially, a photochemical reaction between perfluoro-N-fluoromorpholine and perfluorocyclobutene was examined to establish that u.v. irradiation of the former does smoothly yield perfluoro-N-morpholyl radicals (cf. ref. 3).

(1)   (2)   (3)

(4)   (5)   (6)
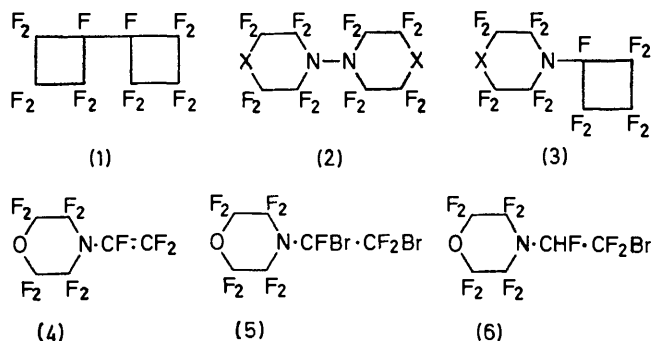
Vapour-phase u.v. irradiation of an equimolar mixture of perfluoro-N-fluoromorpholine and perfluorocyclobutene yielded perfluorobicyclobutyl (1) (21%), perfluoro-NN'-bimorpholyl (2; X = O) (12%), and per-

fluoro-(N-cyclobutylmorpholine) (3; X = O) (50%), a result that can be accommodated by a free-radical mechanism of the type suggested to account for the formation of compounds (1), (2; X = CF_2), and (3; X = CF_2) from perfluoro-N-fluoropiperidine and perfluorocyclobutene under similar conditions.[3] The structures of the new products (2; X = O) and (3; X = O) were established by standard analytical methods and, in the case of the latter, pyrolysis to perfluoro-(N-vinylmorpholine) (4) (86%) and tetrafluoroethylene. Photobromination of the vinylamine (4) gave the corresponding dibromide (5) (83%), a product also obtained (26%), together with the hydrobromide (6) (54%) and possibly traces of its isomer, $\overline{CF_2 \cdot CF_2 \cdot O \cdot CF_2 \cdot CF_2 \cdot N} \cdot CFBr \cdot CHF_2$, when the vinylamine was subjected to photochemical hydrobromination.

Photolysis of an approximately equimolar gaseous mixture of perfluoro-N-fluoromorpholine and oxygen in a Pyrex reactor equipped with a silica-encased u.v. lamp did yield a colourless liquid (ca. 60%) that decomposed when heated (>ca. 140 °C) to provide perfluoromorpholin-N-oxyl (7). The same oxyl precursor was obtained in 63% yield when the N-fluoro-compound was irradiated alone under similar conditions, so the oxygen proved to be an unnecessary reagent; presumably the product derived its oxygen via attack on the silica insert, which would also account for the formation of silicon tetrafluoride.
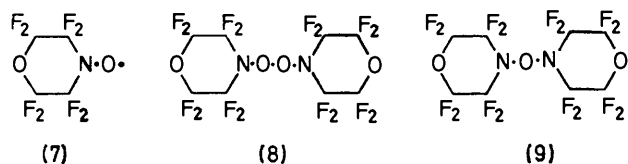
At the outset, two plausible structures, (8) and (9),

[1] Part IV, R. E. Banks, K. Mullen, W. J. Nicholson, C. Oppenheim, and A. Prakash, J.C.S. Perkin I, 1972, 1098.
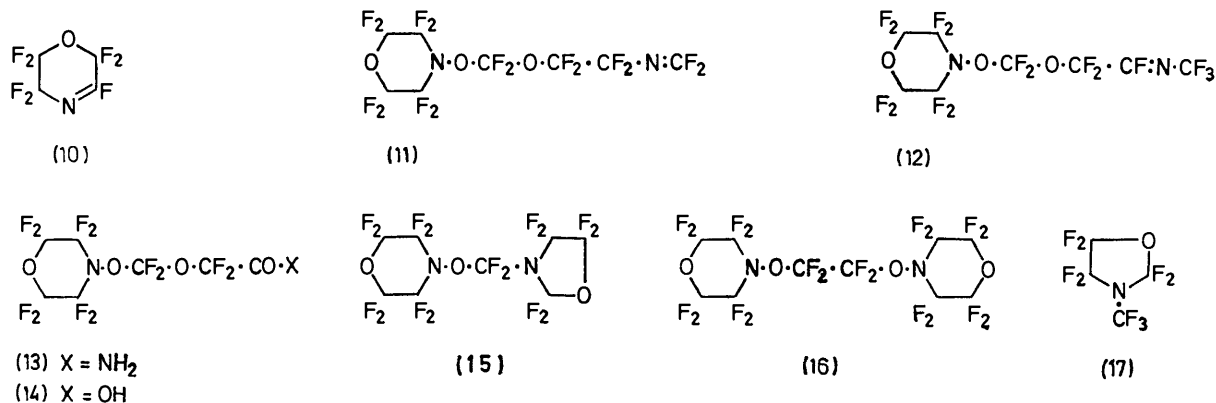
[2] Presented, in part, at the 6th International Symposium on Fluorine Chemistry, Durham University, July 1971.

[3] R. E. Banks, K. Mullen, and G. E. Williamson, J. Chem. Soc. (C), 1968, 2608.

were considered for the oxyl precursor, which showed [19]F n.m.r. absorptions of equal intensity at 10·2 ($CF_2 \cdot O \cdot CF_2$)

$F_2 \quad F_2$
$O \quad N \cdot O \cdot$
$F_2 \quad F_2$
(7)

$F_2 \quad F_2 \quad F_2 \quad F_2$
$O \quad N \cdot O \cdot O \cdot N \quad O$
$F_2 \quad F_2 \quad F_2 \quad F_2$
(8)

$F_2 \quad F_2 \quad F_2 \quad F_2$
$O \quad N \cdot O \cdot N \quad O$
$F_2 \quad F_2 \quad F_2 \quad F_2$
(9)

and 30·5 ($CF_2 \cdot N \cdot CF_2$) p.p.m. to high field of a trifluoro-acetic acid reference signal, and gave a top mass-spectral peak corresponding to the oxyl fragment (m/e 246). The thermal stability of the compound, coupled with the failure of perfluoromorpholin-N-oxyl {like $(CF_3)_2N \cdot O \cdot$ [4] or $\overline{CF_2 \cdot [CF_2]_4 \cdot N \cdot O} \cdot$ [3]} to dimerise at room temperature, militated against the peroxide structure (8); * however, this structure was favoured by C, F, and N analytical values † and, seemingly, by the ability of the compound to liberate an equimolar amount of

in this synthetic method gave a compound identical with that obtained by photolysis of perfluoro-N-fluoro-morpholine in the presence of oxygen and/or silica, and assignment of the N–O–N structure (9) was completed by a detailed study of the thermolytic formation of the oxyl.

Several pyrolyses of perfluoro-[N-(morpholino-oxy)-morpholine] (9) were carried out. For example, storage of the N–O–N compound in a Pyrex ampoule at 160 °C for 10 h gave perfluoromorpholin-N-oxyl (25%), per-fluoro-5,6-dihydro-2H-1,4-oxazine (10) ($ca.$ 36%, calculated on the basis of Scheme 1), perfluoro-N-fluoro-morpholine (trace), perfluoro-NN'-bimorpholyl (7%), and an approximately equimolar mixture (69%) of perfluoro-(6-morpholino-oxy-2-aza-5-oxahex-1-ene) (11) and perfluoro-(6-morpholino-oxy-2-aza-5-oxahex-2-ene) (12). The last product was not always detected in pyrolysis products, and presumably arose via fluoride-initiated isomerisation of the α-imine (11), a well known type of reaction.[9] Attack by adventitious moisture or

$F_2 \quad O \quad F_2$
$F_2 \quad N \quad F$
(10)

$F_2 \quad F_2$
$O \quad N \cdot O \cdot CF_2 \cdot O \cdot CF_2 \cdot CF_2 \cdot N : CF_2$
$F_2 \quad F_2$
(11)

$F_2 \quad F_2$
$O \quad N \cdot O \cdot CF_2 \cdot O \cdot CF_2 \cdot CF : N \cdot CF_3$
$F_2 \quad F_2$
(12)

$F_2 \quad F_2$
$O \quad N \cdot O \cdot CF_2 \cdot O \cdot CF_2 \cdot CO \cdot X$
$F_2 \quad F_2$
(13) X = NH_2
(14) X = OH

$F_2 \quad F_2 \quad F_2 \quad F_2$
$O \quad N \cdot O \cdot CF_2 \cdot N \quad O$
$F_2 \quad F_2 \quad F_2$
(15)

$F_2 \quad F_2 \quad F_2 \quad F_2$
$O \quad N \cdot O \cdot CF_2 \cdot CF_2 \cdot O \cdot N \quad O$
$F_2 \quad F_2 \quad F_2 \quad F_2$
(16)

$F_2 \quad O$
$F_2 \quad N \quad F_2$
CF_3
(17)

iodine from potassium iodide in wet acetone at room temperature. At about this point in the investigation, a re-examination [6] of the claim [7] that u.v. irradi-ation of bistrifluoromethyl nitroxide yields its peroxidic dimer, $(CF_3)_2N \cdot O \cdot O \cdot N(CF_3)_2$, was reaching its final stages, the conclusion being that the photoproduct was in fact perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane), $(CF_3)_2N \cdot O \cdot N(CF_3)_2$. This acyclic analogue of perfluoro-[N-(morpholino-oxy)morpholine] (9) readily oxidises iodide ion and, amongst other methods, can be obtained by treatment of perfluorobut-2-yne with bistrifluoromethyl nitroxide.[8] Application of perfluoromorpholin-N-oxyl

hot Pyrex on the fluoro-imines (10) and (11) is an obvious source of fluoride ion [10,11] and silicon tetra-fluoride was always formed; also, in one instance perfluoro-(4-morpholino-oxy-3-oxabutryamide) (13) was recovered from the reaction vessel. Intentional hydro-lysis of the azahexenes (11) and (12) did provide the carboxamide (13) or the corresponding acid (14), depend-ing on the conditions. Flow pyrolysis of the N–O–N compound (9) in platinum at 165 °C–$ca.$ 2 mmHg also gave perfluoromorpholin-N-oxyl (16%), a trace of perfluoro-N-fluoromorpholine, perfluoro-5,6-dihydro-2H-1,4-oxazine (17%), perfluoro-NN'-bimorpholyl (4%), and compound (11) (19%), but the major product (55%

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* Since this work was completed, it has been pointed out [5] that there are strong thermochemical arguments against oxygen-oxygen coupling of nitroxides ($i.e.$, N-oxyls), $D[R_2N \cdot O - O \cdot NR_2]$ having a calculated value of $ca.$ −28 kcal mol⁻¹.

† These are quoted in the Experimental section. Note that in our hands the determination of fluorine in fluorocarbon derivatives of nitrogen has so far proved much less reliable than the estimation of carbon or nitrogen.

[4] For a recent review of bistrifluoromethyl nitroxide chemis-try, see D. P. Babb and J. M. Shreeve, $Intra$-$Science$ $Chemistry$ $Reports$, 1971, 5, 55.

[5] D. F. Bowman, T. Gillan, and K. U. Ingold, $J.$ $Amer.$ $Chem.$ $Soc.$, 1971, 93, 6555.

[6] R. E. Banks, R. N. Haszeldine, and T. Myerscough, $J.C.S.$ $Perkin$ I, 1972, 1449.

[7] S. P. Makarov, A. Ya. Yakubovich, S. S. Dubov, and A. N. Medvedev, $Zhur.$ $Vsesoyuz.$ $Khim.$ $obshch.$ im $D.$ $I.$ $Mende-leeva$, 1965, 106; S. P. Makarov, M. A. Énglin, A. F. Videiko, V. A. Tobolin, and S. S. Dubov, $Doklady$ $Akad.$ $Nauk$ $S.S.S.R.$, 1966, 168, 344; S. P. Makarov, A. F. Videiko, V. A. Tobolin, and M. A. Énglin, $Zhur.$ $obshchei.$ $Khim.$, 1967, 37, 1528.

[8] R. E. Banks, R. N. Haszeldine, and T. Myerscough, $J.$ $Chem.$ $Soc.$ (C), 1971, 1951.

[9] See, for example, R. E. Banks, D. Berry, M. J. McGlinchey, and G. J. Moore, $J.$ $Chem.$ $Soc.$ (C), 1970, 1017, and references therein.

[10] R. E. Banks, ' Fluorocarbons and their Derivatives,' 2nd edn., Macdonald, London, 1970.

[11] R. E. Banks and E. D. Burling, $J.$ $Chem.$ $Soc.$, 1965, 6077.

yield), obviously formed at the expense of the azahexene (11), was a colourless liquid which showed no significant absorption in the i.r. region below 7·0 μm and accordingly, unlike (11), was unaffected by cold aqueous sodium hydroxide. This liquid has been assigned structure (15), mainly on the basis of its ^{19}F n.m.r. spectrum, which comprises six absorptions of relative intensities 2 : 2 : 1 : 1 : 1 : 1 at +10·0 (AB q), +30·0 (AB q), −11·6, −19·3, +10·0, and +15·7 p.p.m. relative to external trifluoroacetic acid, respectively; the first two absorptions reveal the presence of a perfluoromorpholino-oxy group [cf. compounds (9), (11), (12), (13), (14) (as its S-benzylthiouronium derivative), and (16), which show absorptions assigned to ring fluorines of the type $CF_2 \cdot O \cdot CF_2$ and $CF_2 \cdot N \cdot CF_2$, respectively, in the ranges 9·0—12·0 and 29·0—30·5 p.p.m., and compounds (2) and (3) for which the corresponding absorptions occur at 10·4 and 20·6, and 12·0 and 18·8 p.p.m., respectively], and the remainder are comfortably accommodated by the rest of structure (15) following analysis of the spectrum of perfluoro-(N-methyloxazolidine) (17).[11] Thermolysis of perfluoro-[N-(morpholino-oxy)morpholine] (9) at ca. 140 °C in a simple distillation apparatus did not improve the yield of perfluoromorpholin-N-oxyl, and the best yield (32%) was achieved by heating material synthesised from the oxyl and perfluorobut-2-yne at 160 °C for 10 h in a closed vessel.

The low yield of perfluoromorpholin-N-oxyl in the pyrolysis experiments immediately militates against the peroxidic structure (8) for the oxyl precursor, whereas both this and the identities of the other products can be satisfactorily explained in terms of the N—O—N structure (9) (see Scheme 1). On this basis, use of low pressure reduces the efficiency of scavenging by perfluoro-morpholin-N-oxyl and increases the opportunity for ring-closure of the radical derived from β-scission of perfluoro-N-morpholyl radical.

Thermolysis of Perfluoro-N-fluoromorpholine.—Consideration of the thermal decomposition of perfluoro-[N-(morpholino-oxy)morpholine] (9) led us to reflect on the pyrolytic reorganisation of perfluoro-N-fluoro-morpholine and of the related perfluoro-N-fluoro-piperidine.

Originally,[12] the two isomerisation mechanisms shown in Scheme 2 were tentatively suggested following the discovery that flow pyrolysis of nitrogen-diluted per-fluoro-N-fluoropiperidine at 550 °C in platinum yields perfluoro-(N-methylpyrrolidine) (18) (ca. 20%) and perfluoro-2-azahex-2-ene (19) (ca. 20%), together with products arising from defluorination [perfluoro-2,3,4,5-tetrahydropyridine (5%)] and fragmentation (carbon tetrafluoride, hexafluoroethane, and perfluoro-2-aza-propene). Subsequently,[11] similar pyrolysis of perfluoro-N-fluoromorpholine at 600 °C was found to follow an analogous pattern, the products being carbon tetra-fluoride, hexafluoroethane, perfluoro-2-azapropene, carbonyl fluoride, perfluoro-5,6-dihydro-2H-1,4-oxazine (10)

[12] R. E. Banks, W. M. Cheng, and R. N. Haszeldine, *J. Chem. Soc.*, 1962, 3407.

(22%), perfluoro-(N-methyloxazolidine) (17) (ca. 44%), and material that might have been perfluoro-4-oxa-2-azahex-2-ene (20) (ca. 2%) since it showed absorption in the i.r. region characteristic of a compound containing
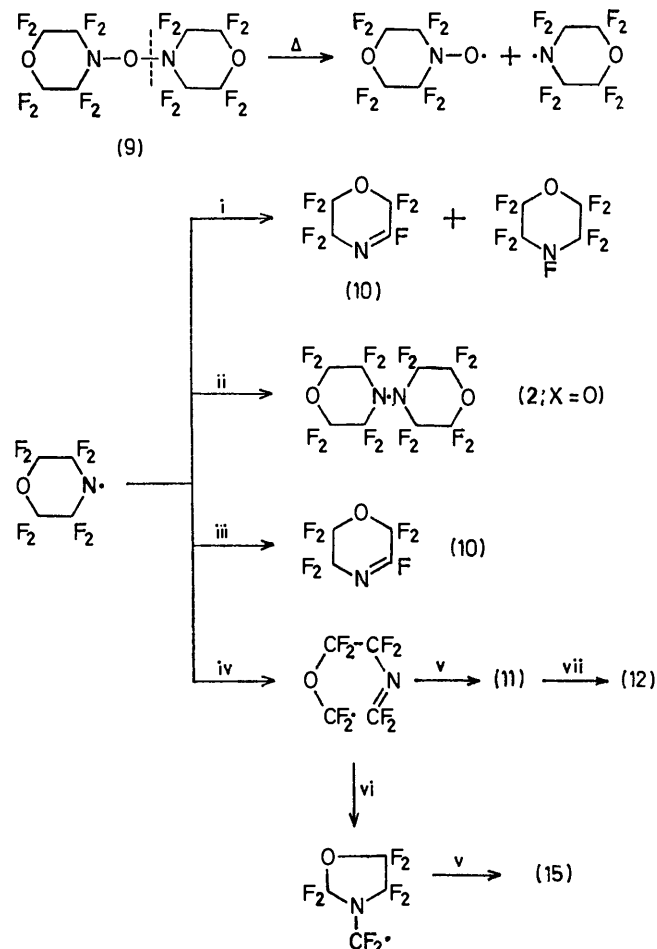
SCHEME 1 i, Disproportionation; ii, dimerisation; iii, defluorination at wall; iv, β-scission; v, combination with perfluoromorpholin-N-oxyl; vi, intramolecular closure; vii, isomerisation

the imine function $CF_3 \cdot N \colon CFR_F$ (R_F = fluorocarbon-based group) and gave trifluoroacetic acid when hydrolysed.
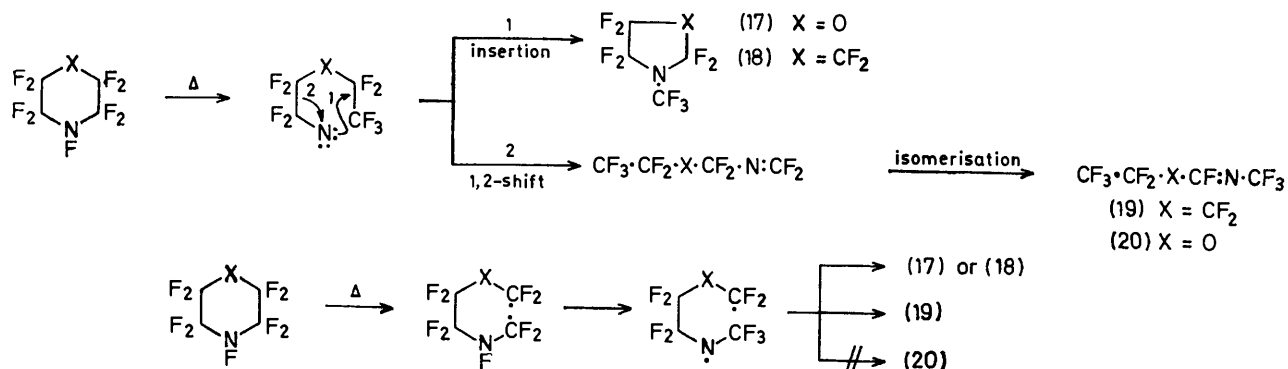
In the present work, it was confirmed initially that pyrolysis of perfluoro-N-fluoromorpholine diluted with nitrogen in platinum does yield a hydrolytic source of trifluoroacetic acid; detailed investigation of the pyrolysate, however, failed to reveal the presence of perfluoro-4-oxa-2-azahex-2-ene (20) but showed that the azabutenes $CF_3 \cdot CF_2 \cdot N \colon CF_2$ and $CF_3 \cdot CF \colon N \cdot CF_3$, both of which hydrolyse to trifluoroacetic acid, had been formed. In fact, the pyrolysate, after treatment with mercury to remove material believed to be the imine $CF_2 \colon NF$,[13] comprised perfluoro-(N-methyloxazolidine) (17) (17% yield), perfluoro-5,6-dihydro-2H-1,4-oxazine (10) (20%),

[13] J. A. Cuculo and L. A. Bigelow, *J. Amer. Chem. Soc.*, 1952, **74**, 710; R. E. Banks, R. N. Haszeldine, and M. D. Hawkins, unpublished results.
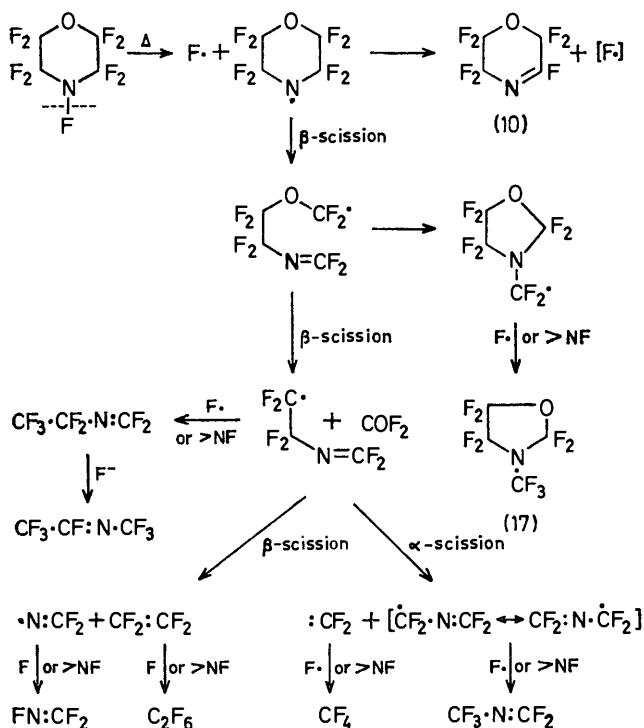
perfluoro-2-azabut-1-ene (9%), perfluoro-2-azabut-2-ene (30%), perfluoro-2-azapropene (11%), carbonyl fluoride (29%), hexafluoroethane (13%), carbon tetrafluoride, carbon dioxide, and silicon tetrafluoride (the last two products presumably arose from attack of the pyrolysate on glass traps).

This result seems best interpreted as shown in Scheme

change (11) ⟶ (12), p. 6].[9,10] Support for the thermolysis mechanism envisaged is provided by the formation of 6-chloro-octafluoro-5-oxa-2-azahex-2-ene (21) when perfluoromorpholine is heated with chlorine in the presence of anhydrous potassium fluoride;[14] apparently chlorine, like perfluoromorpholin-N-oxyl (see Scheme 1), is able to effectively intercept the new radical

SCHEME 2

3, which, like Scheme 1, relies heavily on the formation and subsequent β-scission of perfluoro-N-morpholyl radical. The assumption that perfluoro-2-azabut-1-ene formed initially becomes converted partly into perfluoro-2-azabut-2-ene during work-up is based on the known

formed by β-scission of perfluoro-N-morpholyl radical (see Scheme 4).[15]

SCHEME 4

The products obtained by pyrolysis of perfluoro-N-fluoropiperidine (for which the calculated[16] N–F thermochemical bond energy $= 73$ kcal mol^{-1}) in platinum[13] are consistent with Scheme 3, since in this case the new radical formed by β-scission of perfluoro-N-piperidyl radical does not have such an agreeable fragmentation fate as its morpholyl counterpart, so the formation of perfluoro-2-azahex-1-ene and thence the observed perfluoro-2-azahex-2-ene (19) is not unexpected.

*Properties of Perfluoromorpholin-*N*-oxyl.*—The oxyl is

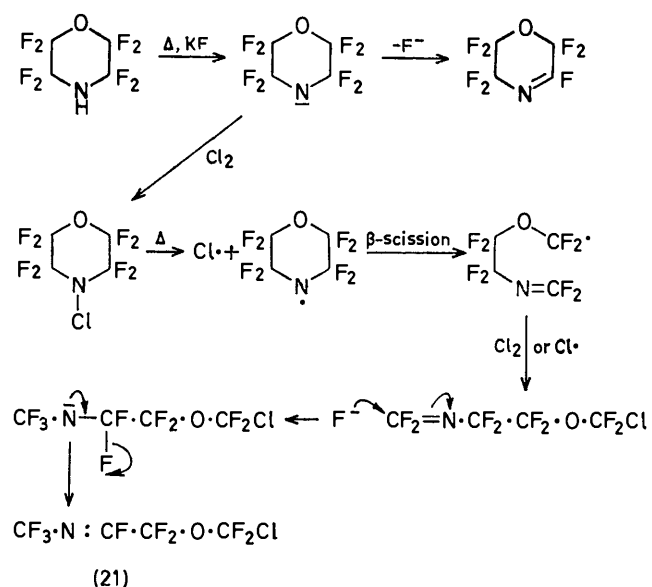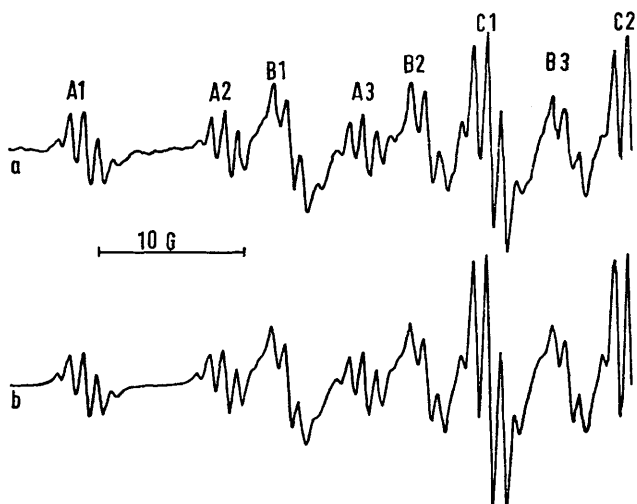SCHEME 3   (>NF = perfluoro-N-fluoromorpholine)

ease of fluoride-initiated isomerisation of fluorocarbon imines to their internal counterparts [cf. the suggested

[14] R. E. Banks, R. N. Haszeldine, and R. Hatton, *J. Chem. Soc. (C)*, 1967, 427.
[15] R. Hatton, Ph.D. Thesis, University of Manchester, 1967.

[16] W. D. Good, S. S. Todd, J. F. Messerly, J. L. Lacina, J. P. Dawson, D. W. Scott, and J. P. McCullough, *J. Phys. Chem.*, 1963, **67**, 1306.

a volatile (b.p. 51 °C), deep blue liquid with a purplish hue. It can be stored unchanged in Pyrex at room temperature in the dark for long periods, and seems to be unaffected by contact with water, aqueous sodium hydroxide, or perfluoro-N-fluoromorpholine; however, its vapour attacks Apiezon grease, presumably giving perfluoro-N-hydroxymorpholine (*cf.* hydrogen-abstraction reactions of perfluoropiperidin-N-oxyl [3]), so it is recommended that ground-glass joints or stopcocks liable to come in contact with the oxyl should be lubricated with Kel-F [poly(chlorotrifluoroethylene)] grease. The ability of perfluoromorpholin-N-oxyl to convert perfluorobut-2-yne into perfluorobiacetyl with, as mentioned previously (see p. 6), concomitant formation of perfluoro-[N-(morpholino-oxy)morpholine] (9), mirrors that of its acyclic analogue $(CF_3)_2N \cdot O \cdot$;[8] additionally, the oxyl combines readily with nitric oxide ($\longrightarrow \overline{CF_2 \cdot CF_2 \cdot O \cdot CF_2 \cdot CF_2 \cdot N} \cdot O \cdot NO$) and with tetra-fluoroethylene [$\longrightarrow (R_F)_2 N \cdot O \cdot CF_2 \cdot CF_2 \cdot O \cdot N(R_F)_2$; $(R_F)_2 = {}^-CF_2 \cdot CF_2 \cdot O \cdot CF_2 \cdot CF_2{}^-$], in keeping with the chemistry of both $(CF_3)_2 N \cdot O \cdot$ [17] and $\overline{CF_2 \cdot [CF_2]_4 \cdot N} \cdot O \cdot$.[3,18]

a, E.s.r. spectrum obtained at room temperature from a *ca.* 0·002M solution of perfluoromorpholin-N-oxyl in perfluoro-N-fluoromorpholine (only the low-field half is shown). b, Computer simulated spectrum produced using Lorentzian lineshape, linewidths 0·49 and 0·74 G for lines A and B, respectively, and the following hyperfine splitting constants: A_N 9·3, $A_{\beta\text{-}F}$ 13·4, $A_{\gamma\text{-}F}$ 0·9 G

E.s.r. studies. E.s.r. spectra were recorded for *ca.* 0·002M solutions of perfluoromorpholin-N-oxyl in per-fluoro-N-fluoromorpholine. The low-field half of a spectrum obtained at room temperature is reproduced in Figure a; as expected, the g value for the oxyl (2·0074 ± 0·0004) is quite close to that for its acyclic analogue $(CF_3)_2N \cdot O \cdot$ ($g = 2·0075$ [19]) and higher than that typical

* The positional nomenclature used here conforms with that employed by e.s.r. specialists, *viz.* $-\overset{\gamma}{C}-\overset{\beta}{C}-\overset{\alpha}{N}-O \cdot$.[21]

[17] R. E. Banks, R. N. Haszeldine, and M. J. Stevenson, *J. Chem. Soc. (C)*, 1966, 901.

[18] R. E. Banks and K. Mullen, unpublished results.

[19] T. J. Schaafsma and D. Kivelson, *J. Chem. Phys.*, 1968, **49**, 5235.

of a hydrocarbon N-oxyl of the same structural type (g *ca.* 2·0055 [20]). The pattern of lines in the whole spectrum is ascribed to contributions from (a) nitrogen hyperfine splitting [$A_N = 9·3 \pm 0·1$ G; *cf.* $(CF_3)_2N \cdot O \cdot$ 9·3, $(MeO_2C \cdot CF_2 \cdot CF_2)_2N \cdot O \cdot$ 9·4 G [21]]; (b) splitting arising from the four β-fluorines * [$\overline{CF_2 \cdot CF_2 \cdot O \cdot CF_2 \cdot CF_2 \cdot N} \cdot O \cdot$; $A_{\beta\text{-}F} = 13·4 \pm 0·1$ G, *cf.* $(CF_3)_2N \cdot O \cdot$ 8·2, $(MeO_2C \cdot CF_2 \cdot CF_2)_2N \cdot O \cdot$ 13·8 G [21]] [note, however, that the five sets of lines observed (Figure a) do not possess relative height ratios of 1 : 4 : 6 : 4 : 1, a point discussed below]; and (c) a further five-line splitting owing to the presence of four γ-fluorines ($\overline{CF_2 \cdot CF_2 \cdot O \cdot CF_2 \cdot CF_2 \cdot N} \cdot O \cdot$; $A_{\gamma\text{-}F} = 0·9 \pm 0·1$ G). By contrast with perfluoro-morpholin-N-oxyl, morpholin-N-oxyl at room temperature is characterised by a larger A_N value (18·1 G) and smaller splittings arising from β- and γ-substituents ($A_{\beta\text{-}H} = 12·5$ G; $A_{\gamma\text{-}H}$ not observable).[22]

The hyperfine splitting caused by the β-fluorines in perfluoromorpholin-N-oxyl can be interpreted in terms of ring inversion (*cf.* ref. 21). If inversion were rapid enough at room temperature to render the axial and equatorial β-fluorines equivalent, the sets of lines marked A1, B1, and C1 in Figure a would have relative height ratios of 1 : 4 : 6. This is not the case: the sets of lines marked B are broader than the rest of the spectrum. This type of linewidth alternation has been discussed by Hudson and Hussain [22] in terms of the theory given by Fraenkel,[23] who defines the derivative peak–peak width (ΔH) of any component in the e.s.r. spectrum as in equation (1) where γ is the magnetogyric ratio, τ is the

$$\Delta H = (\gamma/4\sqrt{3}) \tau (A_{ax} - A_{eq})^2 (m_1 - m_2)^2 + \Delta H^o \quad (1)$$

mean time between ring inversions, A_{ax} and A_{eq} are the hyperfine coupling constants and m_1 and m_2 are the nuclear spin quantum numbers of the two sets of β-substituents, and ΔH^o is the contribution to the line-width from any process which does not depend on m. The linewidth of any component depends on the quantity $(m_1 - m_2)^2$, and the *broadening* of a component may be defined as $\Delta H - \Delta H^o$, which is equal to $(m_1 - m_2)^2$ in units of $(\gamma\tau/4\sqrt{3})(A_{ax} - A_{eq})^2$. The broadening of the components under discussion for perfluoromorpholin-N-oxyl is listed in the Table; M_I is the total nuclear magnetic quantum number for the particular e.s.r. transition concerned. The lines marked B in Figure a are therefore broadened by 1 unit relative to the lines marked A; and the lines marked C are composed of four parts with the same linewidth as A added to two parts with a broadening of four units. For a given intensity, the height of the derivative peak is inversely proportional to the square of the linewidth, therefore the broadened parts of lines C will contribute little to the total height of those lines. Thus the relative heights of lines A and C would be expected to be *ca.* 1 : 4 rather than 1 : 6, the

[20] R. Briere, H. Lemaire, and A. Rassat, *Bull. Soc. chim. France*, 1965, 3273.

[21] E. G. Janzen, *Topics Stereochem.*, 1971, **6**, 177.

[22] A. Hudson and A. Hussain, *J. Chem. Soc. (B)*, 1968, 251.

[23] G. K. Fraenkel, *J. Phys. Chem.*, 1967, **71**, 139.

value consistent with rapid interchange of axial and equatorial β-fluorines. Even at 100 °C, the relative height ratios of lines A1, B1, and C1 were only ca. 1 : 3·5 : 5, compared with ca. 1 : 2 : 3·3 at room temperature.

Line broadening for interconversion between two pairs of equivalent fluorine nuclei (after ref. 22)

Designation of line (see Figure 1a)	M_I	m_1	m_2	Degeneracy	Broadening[a]
A	2	1	1	1	0
B	1	1	0	2⎫ 4	1
		0	1	2⎭	1
C	0	0	0	4⎫	0
		−1	1	1⎬6	4
		1	−1	1⎭	4

[a] In units of $(\gamma\tau/4\sqrt{3})(A_{ax} - A_{eq})^2$.

In order to check the interpretation of the hyperfine splitting pattern for perfluoromorpholin-N-oxyl and to obtain an estimate of the linewidths, a computer simulation of the e.s.r. spectrum was undertaken using linewidths assigned on the basis of the data in the Table. The method employed was to sum the heights of first derivative lineshapes for each hyperfine component, allowing for a change in linewidth between sets of lines A and B (Figure a). The C lines were treated originally as having a degeneracy of 4 units with a linewidth equal to that of the A lines; to this was added another lineshape function for each component of set C, having a degeneracy of 2 units with a linewidth equal to four times the difference between the linewidths of B and A (see Table). The four γ-fluorines were assumed to be equivalent, giving rise to a set of components with relative height ratios of 1 : 4 : 6 : 4 : 1. Lorentzian lineshape functions were found to give better fits than Gaussian functions, and the linewidths used in the production of the spectrum (Figure b) were 0·49 G for lines A and 0·74 G for lines B; the hyperfine splitting constants employed were those extracted from the observed spectrum (Figure a).

EXPERIMENTAL

Perfluoro-N-fluoromorpholine was prepared by electrochemical fluorination of morpholine.[11] Perfluorocyclobutene was obtained by zinc-dechlorination of 1,2-dichlorohexafluorocyclobutane procured by thermal dimerisation of commercial chlorotrifluoroethylene.[24]

Products were identified by elemental analysis, i.r. spectroscopy (Perkin-Elmer spectrophotometer model 257), [19]F n.m.r. spectroscopy (Perkin-Elmer R10 instrument operating at 56·46 MHz and 35 °C), and mass spectrometry (A.E.I. MS/2H instrument).

E.s.r. spectra were recorded on a Decca Radar Ltd. spectrometer (Type XI instrument operating at 9270 ± 1 MHz; 100 kHz field modulation, phase-sensitive detection) equipped with a Decca variable-temperature cavity insert. The g-value of perfluoromorpholin-N-oxyl was measured relative to that of polycrystalline diphenylpicrylhydrazyl (g = 2·0036) and, for determination of hyperfine splitting constants, the magnetic field was calibrated by proton

resonance, the calibration being checked with the aid of an aqueous solution containing [·O·N(SO₃)₂]²⁻ ions. Computer simulations of the e.s.r. spectra were carried out initially using the Atlas computer of the Department of Computer Science of the University of Manchester; later, the I.C.L. 1900 Series computers (1905F and 1906A) of the University of Manchester Regional Computer Centre were used.

Photolysis of Perfluoro-N-fluoromorpholine.—(a) In the presence of perfluorocyclobutene. This was carried out as described previously,[3] using perfluoro-N-fluoromorpholine (28·3 g, 0·114 mol) and perfluorocyclobutene (18·5 g, 0·114 mol), but with a 25 l photochemical reactor and a 90 h irradiation period. The product was shown by a combination of trap-to-trap fractional condensation in vacuo, i.r. spectroscopy, and g.l.c. analysis to contain 23·4 g (57·0 mmol, 50% yield) of perfluoro-(N-cyclobutylmorpholine) (3; X = O), 4·4 g (12·2 mmol, 21%) of perfluorobicyclobutyl (1), 3·1 g (6·7 mmol, 12%) of perfluoro-NN'-bimorpholyl (2; X = O), 3·52 g (21·6 mmol, 19% recovery) of perfluorocyclobutene, and 1·45 g (5·82 mmol, 5% recovery) of perfluoro-N-fluoromorpholine, together with silicon tetrafluoride and unidentified material. Distillation of the material boiling above room temperature through a Haage 100 × 0·8 cm spinning-band column gave perfluorobicyclobutyl (8·2 g), perfluoro-(N-cyclobutylmorpholine) (3; X = O) (10·8 g) (Found: C, 23·6; N, 3·1. C₈F₁₅NO requires C, 23·4; N, 3·4%), b.p. 112·5 °C, n_D^{21} 1·3018, top mass peak m/e 392 [M − F (C₈F₁₄NO⁺)], $\lambda_{max.}$ (vapour) 7·08vw, 7·35w, 7·52m, 7·63w, 7·84m, 8·14s, 8·35w, 8·48w, 8·72m, 9·03m-w, 9·8w, 10·55w, 10·95w, 11·75vw, 12·60w-m, 12·95w, and 14·73vw μm, δ (external CF₃·CO₂H), +12·0 (CF₂·O·CF₂, s), +18·8br (CF₂·N·CF₂, s), +53·0br (CF₂·CF₂·CF₂·CF·N, AB q, J_{AB} 241 Hz), +57·4 (CF₂·CF₂·CF₂·CF·N, AB q, J_{AB} 234 Hz), and +63·5br (>CF·N, s) p.p.m. (rel. int. 4 : 4 : 4 : 2 : 1), and a fraction, b.p. 69 °C at 59 mmHg, the major component of which was isolated by preparative g.l.c. (4 m silicone MS550 oil-Celite; 70 °C) and found to be perfluoro-NN'-bimorpholyl (2; X = O) (2·1 g) (Found: C, 20·7; N, 6·1%; M (mass spec.), 460. C₈F₁₆N₂O₂ requires C, 20·9; N, 6·1%), b.p. 137 °C, n_D^{22} 1·3096, $\lambda_{max.}$ (vapour) 7·44w, 7·71m, 7·91w, 8·15s, 8·47m, 8·70m-s, 8·95m, and 10·75w μm, δ (external CF₃·CO₂H) +10·4 (CF₂·O·CF₂, s) and +20·6 (CF₂·N·CF₂, s) p.p.m. (rel. int. 1 : 1).

(b) In the presence of oxygen. A mixture of perfluoro-N-fluoromorpholine (4·3 g, 17 mmol) and oxygen (0·55 g, 17·2 mmol) was irradiated with u.v. light for 20 h in a photochemical reactor (1 l) of the type described previously.[25] The volatile product was pumped into cold (−196 °C) traps and then subjected to trap-to-trap fractional condensation in vacuo, to give (i) (−23 °C trap) perfluoro-[N-(morpholino-oxy)morpholine] (9) (2·39 g, 5·02 mmol; 59%), m.p. ca. 21 °C, b.p. 144 °C (decomp.), n_D^{23} 1·3087, $\lambda_{max.}$ (vapour) 7·28vw, 7·46w, 7·68m, 7·76m (dblt), 8·16vs, 8·50w, 8·68s, 8·33s, 8·96m, 10·60vw, 10·70vw, and 10·80w (t) μm, δ (external CF₃·CO₂H) +10·2 (CF₂·O·CF₂, s) and +30·5 (CF₂·N·CF₂, s) p.p.m. (rel. int. 1 : 1), with an unsatisfactory elemental analysis (Found: C, 19·8; F, 60·0; N, 5·8. C₈F₁₆N₂O₃ requires C, 20·2; F, 63·9; N, 5·9%. C₈F₁₆N₂O₄ requires C, 19·5; F, 61·8; N, 5·7%), (ii) (−72 °C trap) a mixture (0·05 g; analysed by g.l.c. and i.r. techniques) of perfluoro-N-fluoromorpholine and perfluoro-5,6-dihydro-2H-1,4-oxazine (10), and (iii) (−196 °C

[24] A. L. Henne and R. P. Ruh, J. Amer. Chem. Soc., 1947, 69, 279.

[25] A. H. Dinwoodie and R. N. Haszeldine, J. Chem. Soc., 1965, 1675.

trap) silicon tetrafluoride contaminated with traces of the components of the $-72\ ^\circ C$ fraction.

The reaction was repeated on a larger scale (5 l reactor), and the $-23\ ^\circ C$ fraction (9·13 g) obtained by fractionation of the product was heated in a simple Vigreux still fitted with a cold-finger (methylated spirit–Drikold) take-off head; when the stillpot bath temperature reached ca. 140 $^\circ C$, the distilland turned purplish blue and 1·88 g of coloured distillate was collected; re-distillation of this material gave perfluoromorpholin-N-oxyl (7) (shown by i.r. spectroscopy to be contaminated with a small amount of perfluoro-5,6-dihydro-$2H$-1,4-oxazine) (10) (0·5 g) (Found: C, 19·7; N, 5·5. $C_4F_8NO_2$ requires C, 19·5; N, 5·7%), a deep purplish blue liquid, b.p. 51 $^\circ C$, top mass peak m/e 230 $[M - O\ (C_4F_8NO^+,\ 22\%)]$, base peak m/e 100 $(C_2F_4^+)$, δ [ca. 30% w/w soln. in $CFCl_3$ (internal ref.)] $+87\ (CF_2\cdot O\cdot CF_2$, s) and $+112\ (CF_2\cdot N\cdot CF_2$, s) p.p.m. (rel. int. 1 : 1). Fractionation of the original colourless distillation residue in a semi-micro Vigreux unit gave an unsaturated [$\lambda_{max.}$ 4·37 (C:N str.) and 5·57 (C:C or C:N str.) μm] oil, b.p. 144 $^\circ C$, part of which, when stored in a lightly stoppered tube at room temperature for a few days, changed into a solid identified as *perfluoro-(4-morpholino-oxy-3-oxabutyramide)* (13) (Found: C, 21·0; H, 0·7; F, 56·6; N, 6·4. $C_7H_2F_{12}N_2O_4$ requires C, 20·7; H, 0·5; F, 56·2; N, 6·9%), m.p. 77 $^\circ C$, by i.r. [$\lambda_{max.}$ (mull) 2·91m, 3·03w, 3·11m (N–H str.), 5·90s (C=O str.), 6·04w (H-bonded C=O str.), 6·13w (NH$_2$ def.), and 6·92w (N–C:O str.) μm], n.m.r. [δ_F (external $CF_3\cdot CO_2H$; ca. 20% w/w soln. in ether) $+9\cdot 5$br $CF_2\cdot CF_2\cdot O\cdot CF_2\cdot CF_2$, AB q), $+29\cdot 6$br ($CF_2\cdot N\cdot CF_2$, AB q), $-16\cdot 0$br (N·O·CF_2·O, s), and $+2\cdot 5$ ($CF_2\cdot CO\cdot NH_2$, t) p.p.m. (rel. int. 2 : 2 : 1 : 1); δ_H (external C_6H_6) 0·9vbr (s) p.p.m.], and mass [top mass peak m/e 387 $(\overset{+\cdot}{M} - F$, $<1\%$), base peak m/e 44 (O:C:$\overset{+}{N}H_2$)] spectroscopy.

The unsaturated distillation residue from a similar experiment was examined by ^{19}F n.m.r. spectroscopy before any hydrolysis had occurred, and was found to contain perfluoro-NN'-bimorpholyl (2; X = O), perfluoro-[N-(morpholino-oxy)morpholine] (9), and perfluoro-(6-morpholino-oxy-2-aza-5-oxahex-1-ene) (11) [δ (external $CF_3\cdot CO_2H$) $+10\cdot 0$ ($CF_2\cdot O\cdot CF_2$, AB q), $+29\cdot 5$ ($CF_2\cdot N\cdot CF_2$, AB q), $-16\cdot 0$ (N·O·CF_2·O), $+13\cdot 0$ ($CF_2\cdot CF_2\cdot N$:CF_2), $+20\cdot 5$ ($CF_2\cdot N$:CF_2), and $-21\cdot 0$ and $-31\cdot 0$ (N:CF_2) p.p.m. (rel. int. 2 : 2 : 1 : 1 : 1 : 1)]. A sample of the residue (1·63 g) was shaken with 0·1M-sodium hydroxide (15 ml) at room temperature and the hydrolysate was worked up by standard techniques to give the amide (13) (0·75 g).

(c) *Alone.* Perfluoro-N-fluoromorpholine (6·15 g, 24·7 mmol) was irradiated for 30 h in a 1 l photochemical reactor. Fractionation of the product gave ($-23\ ^\circ C$ trap) a mixture of perfluoro-NN'-bimorpholyl (2; X = O) (0·56 g, 1·22 mmol; 10%) and perfluoro-[N-(morpholino-oxy)morpholine] (9) (3·74 g, 7·84 mmol; 63%), a mixture (0·42 g; $-72\ ^\circ C$ trap) of perfluoro-N-fluoromorpholine, perfluoro-5,6-dihydro-$2H$-1,4-oxazine (10), and traces of material unidentifiable by i.r. spectroscopy, and silicon tetrafluoride (1·2 g, 11·5 mmol; $-196\ ^\circ C$ trap) contaminated with carbonyl fluoride, perfluoro-N-fluoromorpholine, and perfluoro-5,6-dihydro-$2H$-1,4-oxazine (10). A sample (1·80 g) of the $-23\ ^\circ C$ fraction was heated at 160 $^\circ C$ in a Pyrex ampoule (250 ml) for 10 h to give the amide (13) (0·06 g, 0·15 mmol), m.p. 77 $^\circ C$, and a volatile product containing perfluoromorpholin-N-oxyl (7) [estimated as the tetrafluoroethylene adduct (16); yield, based on the

amount of the N-(morpholino-oxy)morpholine (9) in the starting material = 25%], perfluoro-5,6-dihydro-$2H$-1,4-oxazine (10) (30%), perfluoro-(6-morpholino-oxy-2-aza-5-oxahex-1-ene) (11) plus perfluoro-(6-morpholino-oxy-2-aza-5-oxahex-2-ene) (12) (60%), and perfluoro-NN'-bimorpholyl (2; X = O) (6%).

Pyrolysis of Perfluoro-[N-(morpholino-oxy)morpholine] (9). —(a) *Static pyrolysis.* Perfluoro-[N-(morpholino-oxy)morpholine] (9) (2·53 g, 5·32 mmol) was heated in the absence of air in a sealed Pyrex tube (250 ml) at 160 $^\circ C$ for 10 h. The volatile product was subjected to trap-to-trap fractional condensation *in vacuo*, to give (i) ($-196\ ^\circ C$ trap) a mixture of perfluoromorpholin-N-oxyl (7), perfluoro-5,6-dihydro-$2H$-1,4-oxazine (10), perfluoro-N-fluoromorpholine (trace), and silicon tetrafluoride, and (ii) ($-23\ ^\circ C$ trap) a mixture which was shown by g.l.c. and i.r. and ^{19}F n.m.r. spectroscopy to comprise perfluoro-NN'-bimorpholyl (2; X = O) (0·09 g, 0·19 mmol; 7%) and an approximately equimolar mixture (1·74 g, 3·65 mmol; 69%) of compounds (11) [$\lambda_{max.}$ (vapour) 5·54 μm (CF·N=CF_2 str.)] and (12) [$\lambda_{max.}$ (vapour) 5·61 μm (CF=N·CF_3 str.)]; δ (external $CF_3\cdot CO_2H$) $+10\cdot 0$ ($CF_2\cdot O\cdot CF_2$, AB q), $+29\cdot 5$ ($CF_2\cdot N\cdot CF_2$, AB q), $-16\cdot 0$ (N·O·CF_2·O), $+0\cdot 8$ ($CF_2\cdot CF$:N·CF_3), $-45\cdot 0$ (CF:N·CF_3), and $-19\cdot 0$ (N·CF_3) p.p.m. (rel. int. 4 : 4 : 2 : 2 : 1 : 3). A sample of the $-23\ ^\circ C$ fraction (1·70 g) was heated under reflux with 0·1M-sodium hydroxide (15 ml) for 1 week, and the hydrolysate was worked up by standard procedures to yield *S-benzylthiouronium perfluoro-(4-morpholino-oxy-3-oxabutyrate)* (1·0 g) (Found: C, 31·4; H, 2·2. $C_{15}H_{11}F_{12}N_3O_5S$ requires C, 31·4; H, 1·9%), m.p. 151 $^\circ C$ (from aqueous ethanol), $\lambda_{max.}$ (mull) 6·0br μm (asym. CO_2^- str.), δ (external $CF_3\cdot CO_2H$; ca. 20% w/w soln. in ethanol) $+9\cdot 0$ ($CF_2\cdot O\cdot CF_2$, AB q), $+29\cdot 0$ ($CF_2\cdot N\cdot CF_2$, AB q), $-17\cdot 0$ ($CF_2\cdot O\cdot CF_2\cdot CO_2^-$), and $+1\cdot 0$ ($CF_2\cdot CO_2^-$) p.p.m. (rel. int. 2 : 2 : 1 : 1). The $-196\ ^\circ C$ fraction was vaporised and mixed with tetrafluoroethylene (*ca.* 1 g) in a Pyrex bulb (1 l) at room temperature; the colour of the N-oxyl disappeared, and the product was fractionated to yield perfluoro-[1,2-bis(morpholino-oxy)-ethane] (16) (0·38 g, 0·65 mmol; equivalent to 25% yield of the N-oxyl) and perfluoro-5,6-dihydro-$2H$-1,4-oxazine (10) (0·4 g, 1·9 mmol; 36%) contaminated with perfluoro-N-fluoromorpholine.

(b) *Flow pyrolysis.* The vapour of perfluoro-[N-(morpholino-oxy)morpholine] (9) (1·21 g, 2·54 mmol) was passed at *ca.* 2 mmHg pressure through a 100 $\times$ 0·7 cm platinum tube heated to 165 $^\circ C$ over 50 cm of its length. The product, trapped at $-196\ ^\circ C$, was subjected to trap-to-trap fractional condensation *in vacuo* to give (i) ($-196\ ^\circ C$ trap) a mixture (0·25 g) of silicon tetrafluoride (from attack of hot pyrolysate on the glass traps), perfluoro-N-fluoropiperidine (trace), perfluoro-5,6-dihydro-$2H$-1,4-oxazine (10) (estimated yield 0·43 mmol, 17%), and perfluoromorpholin-N-oxyl (7) [0·10 g, 0·41 mmol, 16%; determined by treatment of the fraction with tetrafluoroethylene and subsequent isolation of compound (16) thus formed, as in the static pyrolysis experiment], and (ii) ($-23\ ^\circ C$ trap) (0·94 g) a mixture which was shown by i.r. and ^{19}F n.m.r. spectroscopy to contain compound (11) (0·23 g, 0·48 mmol; 19%), a compound believed to be perfluoro-[N-(morpholino-oxy-methyl)oxazolidine] (15) (0·66 g, 1·38 mmol; 55%), and perfluoro-NN'-bimorpholyl (2; X = O) (0·05 g, 0·11 mmol; 4%). A sample of the suspected oxazolidine (15) contaminated with perfluoro-NN'-bimorpholyl (2; X = O) (Found: C, 20·3; N, 6·0. Calc. for $C_8F_{16}N_2O_3$: C, 20·2; N, 5·9%), b.p. 131 $^\circ C$, n_D^{20} 1·2988, $\lambda_{max.}$ (vapour) 7·04vw, 7·39s, 7·57s,

7·70s, 7·93s, 8·11sh,vs, 8·15vs, 8·70s, 8·86m-s, 9·24m, and 9·82m-s μm, δ (external $CF_3 \cdot CO_2H$) +10·0 ($CF_2 \cdot CF_2 \cdot O \cdot CF_2 \cdot CF_2$, AB q), +30·0 ($CF_2 \cdot CF_2 \cdot N \cdot CF_2 \cdot CF_2$, ABq), −11·6br(N·O·$CF_2$·N, complex), −19·3br(N·$CF_2$·O, s), +10·0 (N·$CF_2 \cdot CF_2$·O, s showing signs of triplet splitting), and +15·7 (N·$CF_2 \cdot CF_2$·O, m) p.p.m. (rel. int. 2 : 2 : 1 : 1 : 1 : 1), top mass peak m/e 296 ($C_5F_{10}NO_2{}^+$, 1%) [the main peaks in the mass spectrum possessed m/e values of 230 ($C_4F_8NO^+$, 83%), 164 ($C_3F_6N^+$, 100), 114 ($C_2F_4N^+$, 76), 100 (C_2F_4, 16), 69 ($CF_3{}^+$, 17), and 50 ($CF_2{}^+$, 51); the main peaks in the mass spectrum of perfluoro-NN'-bimorpholyl (2; X = O) occur at m/e 460 (M, 7%), 441 (M − F, 11), 311 (10), 119 ($C_2F_5{}^+$, 35), 114 ($C_2F_4N^+$, 14), 100 ($C_2F_4{}^+$, 100), 69 ($CF_3{}^+$, 19), 58 ($CNO_2{}^+$, 17), and 43 (C_2F^+, 37)] was isolated from the −23 °C fraction by removing the azahexene with aqueous sodium hydroxide.

Reaction of Perfluoro-[N-*(morpholino-oxy)morpholine*] (9) *with Potassium Iodide.*—The N–O–N compound (0·1743 g, 0·366 mmol) was shaken at room temperature with potassium iodide (0·2 g, 1·2 mmol) in acetone containing 10% v/v of water (20 ml). Iodine was liberated immediately in an exothermic reaction, and after the reaction mixture had been shaken for 4 h the product was neutralised (NaHCO₃) and titrated against 0·1002M-sodium thiosulphate (free iodine 0·0906 g, 0·357 mmol; 98%).

The N–O–N compound (0·64 g) was recovered almost quantitatively (0·63 g) after being shaken for 3 days with anhydrous hydrogen iodide. Lack of reaction is attributed to immiscibility of the reactants.

Pyrolysis of Perfluoro-(N-*cyclobutylmorpholine*) (3; X = O).—The vapour of perfluoro-(N-cyclobutylmorpholine) (0·62 g, 1·51 mmol) was passed at *ca.* 2 mmHg pressure through a 100 × 0·7 cm platinum tube heated to 700 °C over 50 cm of its length. The product, collected at −196 °C, was separated by trap-to-trap fractional condensation *in vacuo* into a mixture (0·21 g; −196 °C trap) of silicon tetrafluoride, carbonyl fluoride (products presumed to arise *via* attack on the glass traps by hot pyrolysate), unknown material showing C:C and/or C:N absorptions in the i.r. region at 5·56 and 5·79 μm, and (mainly) tetrafluoroethylene, and (−72 °C trap) *perfluoro-*(N-*vinylmorpholine*) (4) (0·40 g, 1·30 mmol; 86%) (Found: C, 23·2; N, 4·4%; M (mass spec.), 311. $C_6F_{11}NO$ requires C, 23·15; N, 4·5%; M, 311), b.p. 63·5 °C (isoteniscope), $n_D{}^{21·5}$ 1·2895, $\lambda_{max.}$ (vapour) 5·49w (C=C str.), 7·02w, 7·05w (dblt), 7·36m, 7·51s, 7·73m, 7·95s,sh, 8·01s, 8·18s, 8·72s, 9·01s, 10·31w, 10·75w, 11·70w, 11·93w, and 14·49w μm, δ (external $CF_3 \cdot CO_2H$) +11·2vbr ($CF_2 \cdot O \cdot CF_2$, AB q), +18·5vbr ($CF_2 \cdot N \cdot CF_2$, AB q), +19·6 (*trans*-FC:C·N, dd, $J_{FF}{}^{cis}$ 58·4, $J_{FF}{}^{gem}$ 50·2 Hz), +34·2 (*cis*-FC:C·N, dd, $J_{FF}{}^{trans}$ 119·1 Hz), and +69·4 (CF_2:CF·N, dd) p.p.m.

Reactions of Perfluoro-(N-*vinylmorpholine*) (4).—(a) *Bromination.* The vinyl compound (0·49 g, 1·58 mmol) and bromine (0·29 g, 1·81 mmol) were irradiated, in silica (250 ml ampoule), with u.v. light from a Hanovia S500 lamp placed 25 cm distant. After 2 h, the product was shaken with mercury to remove free bromine, leaving *perfluoro-*[N-(1,2-*dibromoethyl*)*morpholine*] (5) (0·71 g, 1·51 mmol; 83%) (Found: C, 15·1; N, 3·1. $C_6Br_2F_{11}NO$ requires C, 15·3; N, 3·0%), δ (external $CF_3 \cdot CO_2H$) −19·1 (CF_2Br), +7·3 ($CF_2 \cdot O \cdot CF_2$), +11·5 ($CF_2 \cdot N \cdot CF_2$), and +20·5 ($CFBr$) p.p.m. (rel. int. 2 : 4 : 4 : 1).

(b) *Hydrobromination.* The vinyl compound was recovered in 92% yield (0·162 g) by fractional condensation techniques after 0·177 g (0·569 mmol) of it had been stored

in a silica ampoule (250 ml) with an excess of hydrogen bromide (0·1 g, 1·2 mmol) at 22 °C in the dark for 1 week.

Fractionation of the product obtained by u.v. irradiation of a mixture of perfluoro-(N-vinylmorpholine) (0·7 g, 2·25 mmol) and hydrogen bromide (0·4 g, 5·0 mmol) in a silica ampoule (250 ml) for 2·5 days gave (−23 °C trap) a liquid (0·80 g) which was shown by n.m.r. spectroscopy to contain perfluoro-[N-(1,2-dibromoethyl)morpholine] (5) (0·28 g, 0·60 mmol; 26%), N-(2-bromo-1,2,2-trifluoroethyl)-2,2,3,3,5,5,6,6-octafluoromorpholine (6) (0·48 g, 1·20 mmol; 54%) [δ (external $CF_3 \cdot CO_2H$) −14·8 (CF_2Br), +9·4 ($CF_2 \cdot O \cdot CF_2$), +15·2 ($CF_2 \cdot N \cdot CF_2$), and +87·8 (CHF) p.p.m.; δ (external benzene) +0·63 (CHF; dt, $J_{HF}{}^{gem}$ 42, $J_{HF}{}^{vic}$ 8 Hz) p.p.m.] and a small amount of unknown material which gave a weak absorption at 32 p.p.m. upfield from $CF_3 \cdot CO_2H$ in the ^{19}F spectrum characteristic of a CHF_2 group and might, therefore, have been the other $\overline{HBr\text{-adduct } CF_2 \cdot CF_2 \cdot O \cdot CF_2 \cdot CF_2 \cdot N \cdot CFBr \cdot CHF_2}$ (the yields of the two identified products were calculated on the basis of the presence of 0·12 mmol of this adduct in the mixture).

*Reactions of Perfluoromorpholin-*N-*oxyl* (7).—(a) *With nitric oxide.* Nitric oxide (0·12 g, 4·00 mmol) was condensed, *in vacuo*, onto solid perfluoromorpholin-N-oxyl (0·20 g, 0·81 mmol) in a Pyrex tube (100 ml) at −196 °C. The tube was sealed and allowed to warm slowly to 20 °C. Fractionation of the brown liquid product gave perfluoro-N-morpholyl nitrite (0·14 g, 0·51 mmol; 63%) (Found: N, 9·9. Calc. for $C_4F_8N_2O_3$: N, 10·2%), identified spectroscopically $\lambda_{max.}$ (vapour) 5·46s and 5·55m (dblt) μm [O·NO group; *cf.* ($CF_3)_2N \cdot O \cdot NO$, 5·47 and 5·55 (dblt) μm [26], δ (*ca.* 30% w/w soln. in $CFCl_3$, used as internal ref.) +88·0br ($CF_2 \cdot O \cdot CF_2$, s) and +107·2br ($CF_2 \cdot N \cdot CF_2$, s) p.p.m. (rel. int. 1 : 1).

(b) *With tetrafluoroethylene.* Perfluoromorpholin-N-oxyl (0·32 g, 1·30 mmol) and tetrafluoroethylene (0·5 g, 5·0 mmol) were condensed separately into a cold (−196 °C), evacuated, Pyrex tube (250 ml). The tube was sealed and allowed to warm to room temperature; the colour of the nitroxide quickly disappeared, and after removal of the unchanged tetrafluoroethylene, the solid product was sublimed to give *compound* (16) (0·40 g, 0·67 mmol; 100%) (Found: C, 20·2; N, 4·8. $C_{10}F_{20}N_2O_2$ requires C, 20·3; N, 4·7%), m.p. 72·5 °C, δ (*ca.* 20% soln. in $CF_2Cl \cdot CFCl_2$; external $CF_3 \cdot CO_2H$) +12·0br ($CF_2 \cdot O \cdot CF_2$, complex m) and +29·0br ($CF_2 \cdot N \cdot CF_2$ and N·O·$CF_2 \cdot CF_2$, complex unsymmetrical band) p.p.m. (rel. int. 2 : 3).

(c) *With perfluorobut-2-yne.* Perfluoromorpholin-N-oxyl (3·0 g, 12 mmol) contaminated with perfluoro-N-fluoromorpholine was heated at 80 °C for 2 days with perfluorobut-2-yne (0·5 g, 3·0 mmol) in a Pyrex ampoule (250 ml). The yellowish green volatile product was shown by a combination of fractionation, g.l.c., and spectroscopic methods to contain perfluorobiacetyl (*ca.* 0·32 g, 2·0 mmol), perfluoro-N-fluoromorpholine, perfluorobut-2-yne (0·04 g, 0·25 mmol; 8% recovery), silicon tetrafluoride, perfluoro-[N-(morpholino-oxy)morpholine] (9) (2·02 g, 4·24 mmol), and perfluoromorpholin-N-oxyl (0·74 g, 3·0 mmol).

A sample (0·49 g, 1·0 mmol) of perfluoro-[N-(morpholino-oxy)morpholine] (9) from the above experiment was heated in a Pyrex ampoule (250 ml) at 160 °C for 10 h. The volatile product was found to contain perfluoromorpholin-N-oxyl (7) (0·32 mmol, 32%), silicon tetrafluoride, perfluoro-5,6-dihydro-2H-1,4-oxazine (10), perfluoro-NN'-bimorpholyl

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(2; X = O) (0·05 mmol, 10%), and compound (12) (0·45 mmol, 45%). The amide (13) (0·25 mmol, 25%) was recovered from the reaction vessel.

Pyrolysis of Perfluoro-N-fluoromorpholine.—A slow stream of dry nitrogen was passed (13 h) through a reservoir containing perfluoro-N-fluoromorpholine (26·0 g, 0·10 mol) and thence through a 100 × 0·7 cm platinum tube heated to 600 °C over 50 cm of its length. The pyrolysate was collected in two Pyrex traps cooled to −72 and −196 °C, respectively. The condensate in the −72 °C trap, which showed C:N str. absorptions [11,12] in the i.r. at 5·54 ($CF_3 \cdot N = CF_2$), 5·59 ($CF_3 \cdot CF = N \cdot CF_3$), and 5·69 ($\overline{CF_2 \cdot CF_2 \cdot O \cdot CF_2 \cdot CF = N}$) μm, was subjected to trap-to-trap fractional condensation *in vacuo* using two traps cooled to −72 and −196 °C, respectively. The −196 °C fraction was hydrolysed with 0·1M-sodium hydroxide, and the hydrolysate (pH adjusted to 4) was treated with aqueous S-benzylthiouronium chloride, to give S-benzylthiouronium trifluoroacetate (Found: C, 42·7; H, 4·0. Calc. for $C_{10}H_{11}F_3N_2O_2S$: C, 42·9; H, 3·9%), m.p. 180 °C after recrystallisation from aqueous ethanol (lit.,[11] 179 °C).

The experiment was repeated using 27·6 g (0·11 mol) of perfluoro-N-fluoromorpholine. The pyrolysate (27·2 g) was expanded into a Pyrex bulb (10 l) containing a pool of mercury; the bulb was shaken gently and the mercury rapidly became tarnished and started to 'tail' on the glass. The volatile residue was shown by distillation in a semi-automatic low-temperature unit [27] followed by coupled g.l.c.–i.r. analysis of the fractions [using a Perkin-Elmer spectrophotometer model 137 (Infracord) coupled to a g.l.c. apparatus *via* a Wilks Scientific model 41 GC-IR attachment, and recording the i.r. spectrum of each component separately] to contain carbon dioxide, silicon tetrafluoride, carbon tetrafluoride, hexafluoroethane (14 mmol, 13% yield), carbonyl fluoride (32 mmol, 29%), perfluoro-2-azapropene (12 mmol, 11%), perfluoro-2-azabut-1-ene (10 mmol, 9%), perfluoro-2-azabut-2-ene (34 mmol, 30%), perfluoro-(N-methyloxazolidine) (19 mmol, 17%), perfluoro-5,6-dihydro-2H-1,4-oxazine (22 mmol, 20%), and traces of two unidentified compounds (neither of which showed C=N absorption in the i.r. region). A fraction with boiling range −20 to −8 °C (4·4 g, 24 mmol) was shown by [19]F n.m.r. spectroscopy to be essentially perfluoro-2-azabut-2-ene [three absorptions of relative intensities 1 : 3 : 3 at −44·0vbr ($CF_2^{.}N$), −17·6br ($CF_3 \cdot N_{..}^{..}$, d), and −0·8 ($CF_3 \cdot CF$, s) p.p.m. (ext. $CF_3 \cdot CO_2H$), respectively]; g.l.c.–i.r. analysis revealed the presence of perfluoro-2-azabut-1-ene.

[27] R. E. Banks and H. Sutcliffe, *Chem. and Ind.*, 1962, 979.