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THE FLUORINATION OF 4-METHYLMORPHOLINE OVER COBALT(III) FLUORIDE

THE ISOLATION AND CHARACTERISATION OF SOME NOVEL POLYFLUORO-4-METHYLMORPHOLINES BY MASS SPECTROMETRY AND NMR SPECTROSCOPY; THE MECHANISM OF THE TITLE REACTION

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Abstract—4-Methylmorpholine has been fluorinated with cobalt(iii) fluoride to give ten highly fluorinated morpholines and one minor breakdown product. Mass spectrometry and NMR spectroscopy (^1H and ^{19}F) were utilised extensively in the assignment of product structures. A cation-radical mechanism is proposed.

The present work was initiated as part of our search for new inhalational anaesthetics.[1]

Tertiary amines bearing several fluorine substituents on C atoms α to N are essentially non-basic and similar in certain respects to highly fluorinated ethers, some of which are known to possess anaesthetic properties.[2] Thus it seemed appropriate to study some polyfluoro tertiary amines as potential anaesthetics.

Literature precedent for the exhaustive fluorination of 4-methylmorpholine is limited to an electrochemical fluorination (Simons process) from which undecafluoro-4-methylmorpholine was obtained as the only product.[3] This compound, which has also been isolated in poor yield from electrochemical fluorinations of $(HOCH_2CH_2)_2NCH_3$ and $(HOCH_2CH_2)_2NC_2H_5$,[4] is the only highly fluorinated derivative of 4-methylmorpholine to have been previously described. Nonafluoromorpholine has been prepared in low yield by electrochemical fluorinations of morpholine[3-5] and $(HOCH_2CH_2)_2NH$:[4] the best yield (31%) is claimed from a low temperature direct fluorination of morpholine.[6] Tridecafluoro - 4 - ethylmorpholine has been characterised as a product from electrochemical fluorinations of $(HOCH_2CH_2)_2NC_2H_5$[4] and 2-diethylaminoethanol $(C_2H_5)_2NCH_2CH_2OH$.[7] Higher perfluoro - 4 - alkylmorpholines have been exemplified.[8,9] Hydrogen-containing polyfluorinated derivatives of morpholine and 4-alkylmorpholines are unknown.

In this paper we discuss the fluorination of 4-methylmorpholine with cobalt(III) fluoride (CoF_3). A conventional reactor was employed[10-12] and all fluorinations were carried out at 100°.

The structures of the products (Table 1) which, with one exception, retain the morpholine ring have been deduced from a combination of mass spectrometry and NMR spectroscopy.

Mass spectrometry

Mass spectrometry (Table 2) provided considerable assistance in establishing compound structures.

As established by Burdon and Parsons for the polyfluoro - 1,4 - dioxans and -oxathians,[13] molecular ions were weak whilst peaks corresponding to polyfluoroethylene fragments were always very strong. ($C_2F_4^+$ or $C_2HF_3^+$ ions were usually the base peaks.) The assumption made by Burdon and Parsons that a strong ion for one of these latter fragments was good evidence for the presence of such a fragment in the parent heterocycle was also applied without exception to the mass spectra of our compounds. Figure 1 indicates a possible breakdown mechanism for **6**.

Analogous arguments established the structures of **3** and **5**. Similarly **4** was shown to be 2H- or 3H - heptafluoro - 4 - trifluoromethyl - morpholine whilst **6** and **8** were found to be the two possible heptafluoro - 4 - difluoromethyl - morpholines. Finally, mass spectrometry indicated that **7** was a 2H, 5H-, 2H, 6H- or 3H, 5H - hexafluoro - 4 - trifluoromethyl - morpholine whilst **9** and **10** were 2H, 5H-, 2H, 6H- or 3H, 5H - hexafluoro - 4 - difluoromethyl - morpholines.

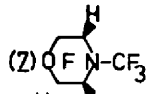
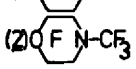
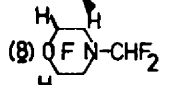
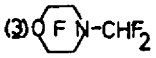
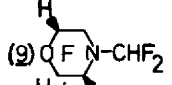
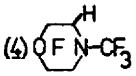
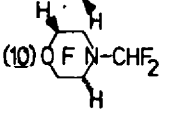
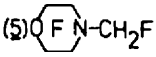
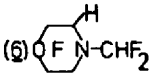
NMR spectroscopy

In general ^1H NMR spectra (Table 3) were only of limited value. Thus, the chemical shifts (5.6–5.9δ) and geminal H–F coupling constants ($J_{CHFO} \sim 50$–52 Hz; $J_{CHFN} \sim 52$–54 Hz) of ring H atoms did not allow unequivocal assignments of their positions to be made whilst the signals themselves were too complex for more detailed analyses to be carried out. H atoms in NCH_2F groups (one example: 5.53δ; $J_{CH_2F} = 52.3$ Hz) and $NCHF_2$ groups (6.6–6.9δ; $J_{CHF_2} \sim 55$–62 Hz) were only coupled to geminal F atoms.

The ^{19}F NMR spectra (Table 3) of our morpholines were often quite complex, but could be analysed on the basis that the molecules adopted chair conformations in which the greatest possible number of ring F atoms were axial and on the assumption that signals were either AB or simple first order patterns (cf. the polyfluoro-cyclohexanes,[18] -dioxans[19] and -oxathians[19]). Although chemical shift and coupling constant data may not be wholly reliable in some instances (due to non-first order behaviour), the observed chemical shift values were secure enough to be utilised in calculating parameters from which the structures of **9** and **10** were deduced.

F-substituted N-Me groups appeared in characteristic portions of the spectra: CH_2F fluorine at 176.4ϕ (one

Table 1. Major products from the fluorination of 4-methylmorpholine with CoF_3

Structure[a]	Percentage by weight	Structure	Percentage by weight
(1) 	2.0[b]	(7) 	4.9
(2) 		(8) 	3.1
(3) 	13.7	(9) 	1.2
(4) 	4.7	(10) 	1.6
(5) 	12.0	(11) $(CF_3)_2NCH_2F$	4.7
(6) 	30.7		

[a] 'F' inside ring signifies that all unmarked bonds are to fluorine.

[b] 1 and 2 were not resolved by g.l.c. ^{19}F n.m.r. (see experimental) suggested a ratio of 1:2 = 7:1.

Table 2. Fragments from the mass spectra of some polyfluoro-(N-polyfluoromethyl-) morpholines[a]

Compound No.	1[b] + 2	3	4	5	6	7	8	9	10
Fragment									
M	> 1 for each	32	3	2	9	3	7	1	6
114 (C_2F_4N)	100	38	10	16	2	<1	22	<1	1
100 (C_2F_4)	74	100	100	100	100	2	100	<1	2
96 (C_2HF_3N)	<1	14	37	9	28	11	16	8	31
82 (C_2HF_3)	<1	<1	70	<1	51	100	45	100	100
78 ($C_2H_2F_2N$)	<1	<1	<1	19	8	3	1	10	38

[a] Intensities are quoted as percentages of the base peak.

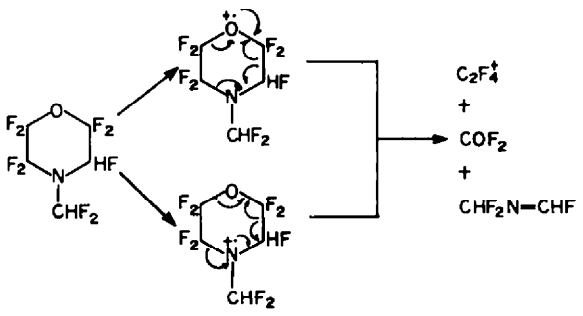
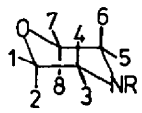


Fig. 1. A similar mechanism would account for the formation of $C_2HF_3^+$ fragments.

Table 3. Chemical shifts in polyfluoro-1,4-morpholines[a]

All compounds numbered as in 

Compound Number	Position Number								Coupling Constants (Hz)			
	1	2	3	4	5	6	7	8	J_{12}	J_{34}	J_{56}	J_{78}
1[14,15]	85.9		110.0		110.0		85.9		-	-	-	-
2[14,15]	86.1		93.9		93.9		86.1		-	-	-	-
3	87.75		95.45		95.45		87.75		-	-	-	-
4	83.5	74.8	5.62[b]	150.6	104.35	88.95	88.0	86.0	162.35	53.0	190	146
5	88.6		96.9		96.9		88.6		-	-	-	-
6	84.6	76.3	5.85[b]	151.6	106.3	84.7	88.7	84.9	161.0	52.3	197	146
7	85.3	75.4	5.68[b]	152.8	5.68[b]	152.8	85.3	75.4	166	53.8	53.8	166
8	5.85[b]	139.4	101.1	78.5	100.5	89.7	91.3	82.1	50.4	209	198	151
9	5.80[b]	134.4	90.15	82.15	145.1	5.80[b]	73.3	78.9	52	202	52	162.8
10	5.69[b]	139.0 (139.4[17])	109.8 (106.9[17])	73.8 (73.5[17])	5.75[b]	152.5 (151.6[17])	87.15 (87.2[17])	73.55 (73.5[17])	50.3	208.0	54	163.3

[a] ^{19}F shifts in ϕ units.

[b] ^{1}H shifts in δ units.

example), CHF_2 fluorines at 93–106ϕ (complex AB patterns, J ~ 214–221 Hz, in asymmetrical molecules) and CF_3 fluorines at 52–62ϕ. These F atoms were usually coupled (J ~ 7–14 Hz) to one or more fluorines present in the 3- and 5-positions.

F atoms in CHFO groups appeared at 134–140ϕ as broadened doublets (J ~ 50–52 Hz) whilst those in CHFN groups appeared at 145–153ϕ as doublets (J ~ 52–54 Hz) of multiplets.

Ring CF_2 groups in **3** and **5** appeared as broadened singlets or complex multiplets in two distinct regions of the spectra: CF_2O groups at 87.75ϕ (**3**) and 88.6ϕ (**5**) and CF_2N groups at 95.45ϕ (**3**) and 96.9ϕ (**5**). These values were within *ca* 3 ppm of the corresponding shifts for octafluoro - 4 - trifluoromethyl - morpholine (**2**).

F atoms in ring CF_2 groups of morpholines with ring H-substituents appeared as complex AB patterns. Thus fluorines in CF_2O groups were observed at 73–92ϕ (J ~ 146–166 Hz; cf. 140–170 Hz for the polyfluoro-dioxans,[19] -oxathians[19] and -tetrahydro - 2 - trifluoromethyl - 1,2 - oxazines[20]) whilst those in CF_2N groups appeared at 73–109ϕ (J ~ 190–209 Hz; cf. 191–199 Hz for the polyfluorotetrahydro - 2 - trifluoromethyl - 1,2 - oxazines[20]).

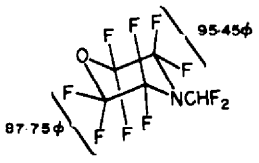
All but one of the structural assignment problems which remained after the original analysis of the mass spectra could be resolved by combining data from the appropriate mass spectrum with information from the corresponding ^{1}H and ^{19}F NMR spectra.

Thus **4**, a heptafluoro - 4 - trifluoromethyl - morpholine, was established as the 3H-isomer since the geminal F–F coupling constants of the three ring CF_2 groups could only be consistent with the presence of two CF_2O groups and one CF_2N group. A similar argument enabled the structures of **6** and **8** to be fully assigned.

The structure of **7** was not determined with certainty. However, the six possibilities remaining after analysis by mass spectrometry were easily reduced to two (3H/5H- or 3H,5H/ - hexafluoro - 4 - trifluoromethyl - morpholine). Thus the ^{19}F NMR spectrum was composed of only three sets of signals, eliminating the possible 2H, 5H-isomers whilst the value (166 Hz) of the geminal F–F coupling constant of the two equivalent ring CF_2 groups was only compatible with the presence of CF_2O groups, eliminating the possible 2H, 6H-isomers. In the absence of any evidence (e.g. chemical shift parameter calculations) which would have enabled the structure of **7** to be assigned absolutely, the chemical shift and coupling constant data for its ring F atoms were compared with those of the equivalent fluorines in **4**. Such marked similarities were found that, if the assumption holds that the H atom in **4** is equatorial, it follows that both H atoms in **7** are probably equatorial. **7** is therefore likely to be the 3H, 5H/-isomer.

Precise assignments of structure for **9** and **10** could now be made. Both compounds showed two sets of AB patterns (due to ring CF_2 groups) and two sets of broadened doublets (due to ring CHF groups). The 2H, 6H- and 3H, 5H-structures were eliminated on this basis. Also the relative magnitudes of the geminal F–F coupling constants were such that each compound required the presence of one CF_2O group and one CF_2N group. Chemical shift parameters were utilised to assign specific stereochemistry to **9** and **10**, thus established as the two 2H, 5H - hexafluoro - 4 - difluoromethyl - morpholines (cf. the polyfluoro-dioxans[19] and -oxathians[19]).

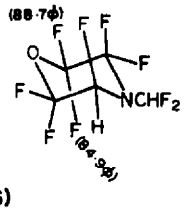
Ideally the required base values would have been the chemical shifts of the axial and equatorial fluorines adjacent to oxygen and nitrogen in **3** (Fig. 2). At temperatures down to −90°, **3** interconverts rapidly between



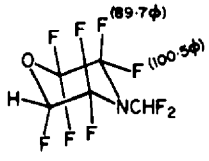
(3)

Fig. 2.

the two possible chair forms and only an averaged value of axial and equatorial fluorine chemical shifts is obtainable. However, the required data could be derived from the spectra of **6** and **8** (Fig. 3).



(6)



(8)

Fig. 3.

The averaged values of the two sets of chemical shifts for **6** and **8** shown in Fig. 3 should be the same as the corresponding values for **3** given in Fig. 2, assuming that there is a negligible error due to the effect of γ hydrogen substituents. A series of parameters (Table 4) was calculated from the base values and the remaining chemical shifts for the ring CF_2 groups in **6** and **8**.

The chemical shifts of the ring fluorines in 2H/5H - hexafluoro - 4 - difluoromethyl - morpholine were estimated from the information given in Table 4 (see Burdon and Parsons paper[19] for a similar calculation). Clearly the correlation between the predicted shifts and those actually observed for **10** (Table 3) provides good evidence that **10** is the 2H/5H-isomer. **9** therefore becomes the 2H,5H/-isomer.

Compound **11** was unambiguously characterised as bis-trifluoromethyl - monofluoromethylamine by mass spectrometry and NMR spectroscopy.

DISCUSSION

The average number of F atoms per (identified) product molecule is 9.0–9.5 whilst the average number of H atoms per (identified) product molecule is 1.5–2.0 (Table 1). Earlier studies on the fluorination of 1,4-

Table 4. ^{19}F NMR chemical shift parameters[a] for CF_2 groups in polyfluoro-4-difluoromethyl-morpholines

Position of fluorine	Base value[b]	Substituent position[c] α Heq	β Heq
Fax (α to O)	84.9	-8.6	-2.8
Feq (α to O)	88.7	-4.1	+2.6
Fax (α to N)	89.7	-11.2	-5.0
Feq (α to N)	100.5	+0.6	+5.8

[a] Parameters in p.p.m. (upfield from CCl_3F).

[b] In ϕ units.

[c] Ring hydrogen atoms are considered as substituents.

Table 5. Distillation of product from fluorination of 4-methylmorpholine

Fraction Number	Wt. (g)	Boiling Range	Fraction Number	Wt. (g)	Boiling Range
Volatiles	9.9	≤25°	9	43.7	81°
1	33.6	20-28°	10	44.0	81°
2	21.7	28-54°	11	44.7	81°
3	14.7	54-63°	12	47.2	81-85°
4	46.1	63-65°	13	25.2	85-97°
5	36.4	65-68°	14	23.1	97-111°
6	36.4	68-76°	15	17.3	111-124°
7	31.3	76-80°	16	73.2	>124°
8	30.7	80-81°			

dioxan[13] with CoF_3 at 100° indicated an average number of F atoms per product molecule of about 5.5 and an average number of H atoms per product molecule of about 2.5. These results can be rationalised by the theory that the major reaction pathways in fluorinations by high valency transition metal fluorides begin with an initial oxidation to a cation-radical,[21,22] followed by various quenching processes[23] and further oxidation-quenching steps.

Ionisation potentials of tertiary amines are low compared with those of 1,4-dioxan (9.13 eV) and diethyl ether (9.6 eV),[24] for which cation-radical mechanisms of fluorination (with CoF_3 and $KCoF_4$) have been proposed.[13,25] Assuming that the ionisation potentials of intermediates containing an equivalent number of F substituents from fluorinations of 4-methylmorpholine and 1,4-dioxan behave in the same way, a higher average number of F atoms per product molecule is to be expected in the former case.

Initial oxidation of 4-methylmorpholine seems most likely to occur at the N atom. A sequence is shown in Fig. 4 from the resultant cation-radical (A) to all the major isolated products via 3 - fluoro - 4 - methyl - morpholine (B) and a 2H, 3H, 5H, 6H - tetrafluoro - 4 - polyfluoromethyl - morpholine (C).

Figure 5 shows a mechanism for the formation of 1 and 11. This has a number of features in common with the mechanism previously described for the thermolysis of 1,[26] from which carbon tetrafluoride, hexafluoroethane, pentafluoro - 2 - azapropene, carbonyl fluoride, heptafluoro - 5,6 - dihydro - 2H - 1,4 - oxazine, nonafluoro - 3 - methyloxazolidine and (possibly) nonafluoro - 4 - oxa - 2 - azahex - 2 - ene were obtained.

Surprisingly, the novel compounds described in this paper were of no value as anaesthetics.

†Further details of glc separations, NMR and mass spectra are available on request from the authors.

‡When the NMR sample was shaken for a few seconds at room temperature with a solution (200 μl) of NaI (30%) in acetone/water (10:1), a dark red colour was generated due to the liberation of I_2, which confirmed the presence of an N–F bond.[5]

EXPERIMENTAL†

IR spectra, recorded on all pure samples, were measured on a Perkin Elmer Model 157 Spectrophotometer. ^1H NMR spectra (samples in $CDCl_3$ soln with internal TMS as standard) were measured on Varian HA 100D (100 MHz), Varian A60 (60 MHz) or Perkin Elmer R 12 (60 MHz) instruments. ^{19}F NMR spectra (samples in $CDCl_3$ soln with internal CCl_3F as standard) were measured on Varian HA 100D (100 MHz), Varian A60 (60 MHz) or Perkin Elmer R 12 (60 MHz) instruments. ^{19}F NMR spectra integrals were always consistent with the proposed structures. Mass spectra (MS) were recorded on an AEI MS9 instrument, *m/e* values being obtained in a.m.u. Entries such as NMR or MS after a compound indicate that details of these measurements appear elsewhere.

Pye 104 and 105 glc machines were used under standard conditions for analytical and preparative separations, respectively. Both machines were equipped with glass columns containing either Di (2-ethyl hexyl) Sebacate (15%) on Universal Support or Carbowax 20M (20%) on Chromosorb W (Columns A and B respectively, for the Pye 105). Details of some intermediate fractions have been omitted from descriptions of the preparative glc separations.

Fluorination of 4-methylmorpholine with CoF_3

4-Methylmorpholine (35 ml; 32 g) was injected over 3 hr into a stirred bed of CoF_3 (3 kg) at 100° in a stream of dry N_2 (300 ml min^{-1}). Product, collected in a trap at −78°, was removed after the system had been purged with N_2 (500 ml min^{-1}) for a further 2 hr at 100–200°. Products accumulated from several such fluorinations were washed with ice-water and excess sat. $NaHCO_3$aq. After drying ($MgSO_4$) the mixture (592 g) was distilled (Table 5).

Compositions of distillation fractions

Volatiles. (9.9 g; b.p. ≤ 25°): an inseparable mixture (1.6 g) of 1 and 2, 11 (3.6 g) and three unidentified components (analytical glc).

Fraction 1 (33.6 g; b.p. 20–28°). Separation (A, 51°) of an aliquot (1.01 g) gave: (i) a 7:1 (^{19}F NMR integration) mixture (0.12 g) of 1 and 2, nonafluoromorpholine and octafluoro - 4 - trifluoromethyl - morpholine respectively, identified by b.p. [32–34°; lit.[3,5] for 1, 34.5°], IR [$\nu_{max(N-F)}$ 975 and 930 cm^{-1}; lit.[5] for 1, 975 and 922 cm^{-1}], ^{19}F NMR, MS and chemical means;‡ and (ii) 11, *bis - trifluoromethyl - monofluoromethylamine* (0.27 g), b.p. 25–27°, ^1H (CH_2F, doublet, J = 53.5 Hz, of complex multiplets at 5.44δ) and $^{19}F[(CF_3)_2N$, doublet, J = 5.0 Hz, at 58.0φ; CH_2F, triplet, J = 53.5 Hz, of complex multiplets at 171.5φ]

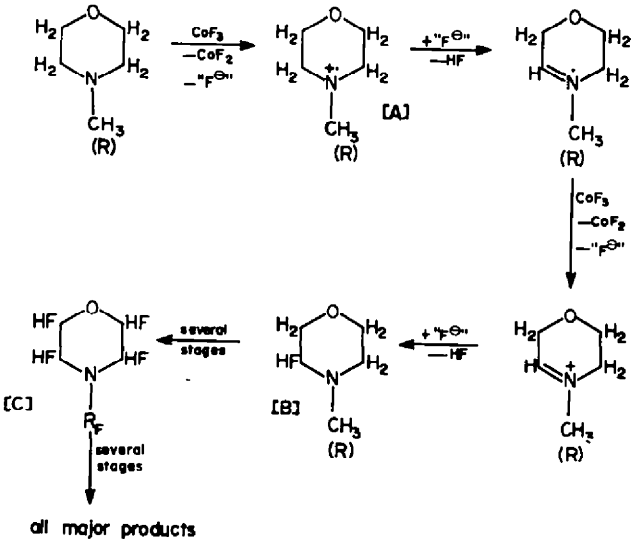


Fig. 4.

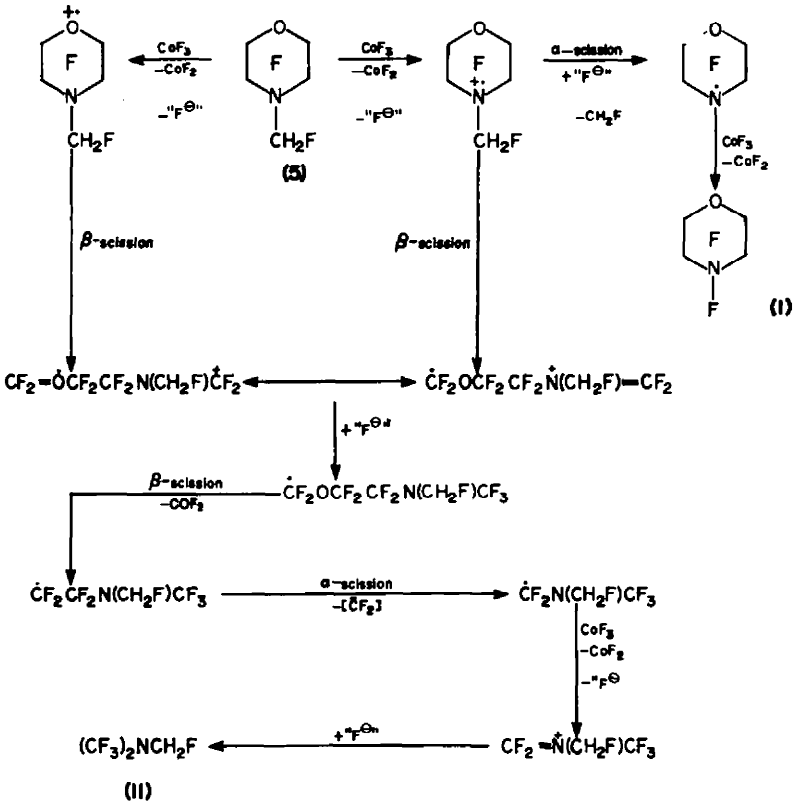


Fig. 5

NMR, MS [*m/e* at 185 ($C_3H_2F_7N$), 184.001 (C_3HF_7N requires: 184.000), 166 ($C_3H_2F_6N$), 114 (C_2F_4N), 96 (C_2HF_3N), 78 ($C_2H_2F_2N$), 69 (CF_3), 33 (CH_2F)].

Fractions 2 *and* 3 (36.4 g; b.p. 28–63°): inseparable mixture (3.1 g) of **1** and **2**, **11** (5.2 g), **3** (15.2 g) and **4** (5.4 g) and at least 6 unidentified components (analytical glc).

Fraction 4 (46.1 g; b.p. 63–65°). A partial separation (A, 107°) of an aliquot (3.07 g) gave a mixture (2.08 g), a portion (0.73 g) of which was further separated (A, 26°) to give: (i) **3**, *octafluoro - 4 - difluoromethyl - morpholine* (0.28 g), b.p. 66.0–67.0°, NMR, MS(Found: *m/e* at 280.989. $C_5HF_{10}NO$ requires: 280.990); and (ii) **4**, 3H - *heptafluoro - 4 - trifluoromethyl - morpholine* (0.05 g), b.p. 63.5–64.5°, NMR, MS. (Found: *m/e* at 261.992. C_5HF_9NO requires: 261.991).

Fractions 5–8 (134.8 g; b.p. 65–81°): mainly **3** (34.3 g), **4** (11.4 g), **5** (23.7 g), **6** (57.1 g), **7** (6.5 g) and **8** (0.5 g) (analytical glc).

Fraction 9 (43.7 g; b.p. 81°). Separation (A, 114°) of an aliquot (8.84 g) gave: (i) an impure compound (1.84 g), a portion (1.70 g) of which was further purified (A, 60°) to give **5**, *octafluoro - 4 - monofluoromethyl - morpholine* (1.48 g), b.p. 80.0–81.0°, NMR, MS. (Found: *m/e* at 262.999. $C_5H_2F_9NO$ requires: 262.999); and (ii) **6**, 3H - *heptafluoro - 4 - difluoromethyl - morpholine* (4.51 g), b.p. 82.5°, NMR, MS. (Found: *m/e* at 262.997).

Fractions 10–12 (135.9 g; b.p. 81–85°): mainly **5** (29.7 g), **6** (85.1 g), **7** (14.9 g) and **8** (4.8 g) (analytical glc).

Fraction 13 (25.2 g; b.p. 85–97°). Separation (A, 118°) of an aliquot (5.90 g) gave: (i) a mixture (0.84 g), a portion (0.74 g) of which was further separated (B, 83°) to give (i) (a) a complex mixture (0.24 g), (i) (b) **5**† (0.09 g), (i) (c) **7**, 3H,5H/ - *hexafluoro - 4 - trifluoromethyl - morpholine* (0.10 g), b.p. 83.0–84.0°, NMR, MS. (Found: *m/e* at 262.997) and (i) (d) **6**† (0.04 g); (ii) mainly **6**† (0.78 g); and (iii) **8**, 2H - *heptafluoro - 4 - difluoromethyl - morpholine* (1.57 g), b.p. 93.5–94.5°, NMR, MS. (Found: *m/e* at 262.999).

Fraction 14 (23.1 g; b.p. 97–111°). This material was redistilled to give various sub-fractions, an aliquot (5.03 g) of that (5.3 g) containing the highest proportions of **9** and **10** being chosen for preparative glc separation (B, 110°): (i) a complex mixture (2.17 g), believed to be mainly decomposition products; and (ii) a mixture (1.93 g), a portion (1.18 g) of which was further separated (B, 94°) to give (ii) (a) **9**, 2H,5H/*-hexafluoro - 4 - difluoromethyl - morpholine* (0.23 g), b.p. 109–111°, NMR, MS. (Found: *m/e* at 245.009. $C_5H_3F_8NO$ requires 245.009) and (ii) (b) **10**, 2H/5H - *hexafluoro - 4 - difluoromethyl - morpholine* (0.40 g), b.p. 107–109°, NMR, MS. (Found: *m/e* at 245.009).

Fraction 15 (90.5 g; b.p. > 111°): **7** (0.2 g), **8** (0.5 g), **9** (1.4 g), **10** (1.7 g) and numerous unidentified components (analytical glc).

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