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HIGHLY FLUORINATED HETEROCYCLES. PART XVI.

POLYFLUORINATED DERIVATIVES OF 1-METHYLPYRROLIDINE, 1-METHYLPYRROL-3-INE AND 1-METHYLPYRROLE

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SUMMARY

Fluorination of 1-methylpyrrole with cobalt(III) fluoride gave six major products, 1-fluoromethyl- and 1-difluoromethyl- -octa-, -3H-hepta-, and-3H,4H-hexa-fluoropyrrolidine. Similar fluorination of 1-methylpyrrolidine gave better total recoveries of the same six products, together with 1-trifluoromethyloctafluoropyrrolidine, and 1-fluoromethyl- and 1-difluoromethyl- -2H-heptafluoropyrrolidine. 1-Fluoromethyl- and 1-difluoromethyl- -3H-heptafluoropyrrolidine each gave the corresponding polyfluoropyrrol-3-ine on dehydrofluorination with potassium hydroxide, but the 1-difluoromethyl-2H-heptafluoride could not be dehydrofluorinated. 1-Methyl- and 1-fluoromethyl- -3H,4H-hexafluoropyrrolidine similarly gave the corresponding 3H-3-ine, but no pyrrole. Reaction of 1-methyl-3H,4H-hexafluoropyrrolidine with 'old' aluminium chloride gave a little 1-methyl-2,5-dichlorodifluoropyrrole, the only fluoropyrrole we have obtained so far. Freshly sublimed $AlCl_3$ afforded 1-methyltetrachloropyrrole (obtained also from 1-methylpyrrole and sulphuryl chloride) : fluorination of this with $KCo(III)F_4$ gave 1-methyl- and 1-fluoromethyl- -3,4-dichloro-tetrafluoropyrrol-3-ine.

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INTRODUCTION

Part XV of this series [1] reported attempts to make fluoropyrroles from polyfluoro-1-alkylpyrrolidines by defluorination with heated iron. Polyfluoro-1-alkylpyrrolidines were among the products of the fluorination of pyridines by high valency metallic fluorides, a ring contraction occurring. Such a product was formed in the pyridine/KCo(III)F_4 reaction [2], another was found later, and others from pyridine/CoF_3 [3]. Among the products of fluorination of pyridine [4], and the three picolines [5], by caesium tetrafluorocobaltate, significant proportions of polyfluoro-1-alkylpyrrolidines were found. They are interesting compounds in their own right, as well as being possible precursors to fluoropyrroles.

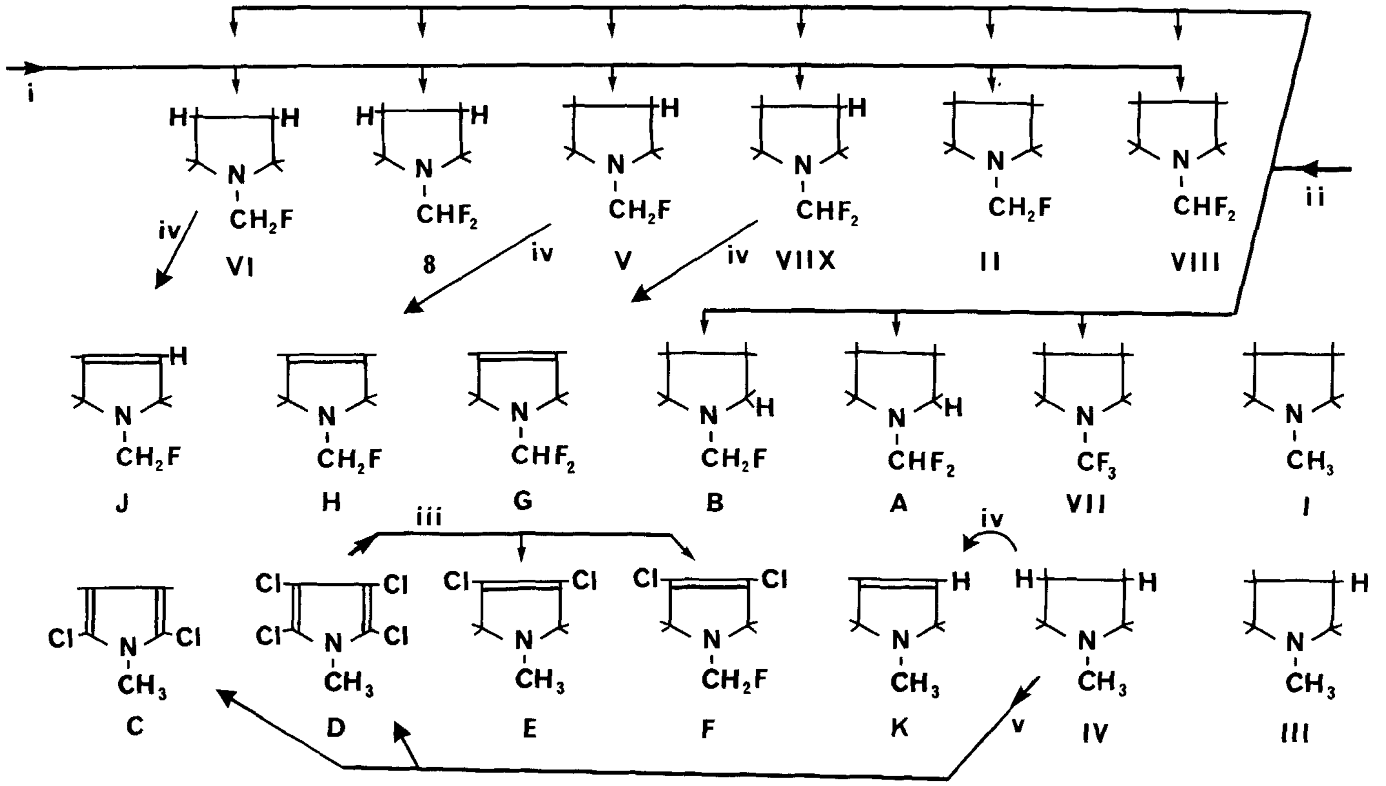
The straightforward route, direct fluorination of 1-methylpyrrole, was later found to be an effective and more general method for their synthesis [6]. 1-Methylpyrrole and potassium tetrafluorocobaltate(III) at 220-240° gave six products (I - VI; see Scheme). There were pyrrolidines with N-methyl groups on 3H,4H-hexafluoro-(IV), 3H-heptafluoro-(III), and octafluoro-(I) substituted rings, and the N-fluoromethyl-analogues (VI, V, and II, respectively), interesting types of fluoro-tertiary amines. A preliminary small-scale fluorination of N-methylpyrrole over cobalt(III) fluoride at 140° gave five of these products (III was missing), whilst 1-methyloctafluoropyrrolidine(I) and CoF_3 at 140° gave the 1-fluoromethyl-(II), 1-difluoromethyl-(VIII) and 1-trifluoromethyl-(VII) compounds [6].

This paper reports further work on fluoro-1-methylpyrrolidines, involving larger-scale fluorinations of 1-methylpyrrole and 1-methylpyrrolidine by cobalt(III) fluoride, dehydrofluorinations of several of the polyfluoro-1-methylpyrrolidines, and also fluorination of 1-methyltetrachloropyrrole by potassium tetrafluorocobaltate(III).

RESULTS

Fluorinations

Compounds involved in the work are represented in the Scheme: those described earlier, in Part XIII of this series, are given the same Roman numerals as in that paper [6]; compound IX of Part VI of a series [2] is VIIX; compound 8 is also known [3]. Compounds designated by letters are new products from the present study.



i CoF$_3$/ 1-Methylpyrrole ; ii CoF$_3$/ 1-Methylpyrrolidine ; iii KCoF$_4$; iv KOH ; v AlCl$_3$.

SCHEME (All unmarked bonds to FLUORINE)

Fluorinations on 1-methylpyrrole were done in a large reactor (10 Kg CoF_3) at 120-140° using 45 g of the heterocycle (ca. 8% only of the available fluorine was consumed). Six products were obtained, but not all the same as from the small-scale reaction [6]. None had N-methyl groups, i.e. I and IV were missing. Present were 1-fluoromethyl compounds with 3H,4H-hexafluoro-(VI), 3H-heptafluoro-(V) and octafluoro-(II) rings (all obtained before [6]), and the 1-difluoromethyl-analogues (8, VIIX and VIII, respectively). These last three had not been found from this reaction before [6], though they were known. Compound 8 had been obtained from pyridine/$KCoF_4$ [3], VIIX likewise [2], and VIII from Compound I/ CoF_3 [6].

It was not made clear in Part XIII [6], that the quoted small-scale fluorination was done in a small reactor (100 g CoF_3; mentioned in this Experimental section), the 1-methylpyrrole (6 g) being fluorinated in two experiments (3 g each: N_2 2 ℓ h^{-1}), and in each ca. 50% of the available fluorine of the reactor was consumed.

The present larger-scale run was a more exhaustive fluorination. The methyl group is fluorinated less readily than the ring, and this is shown particularly with the less reactive $KCoF_4$ [6], which is the better reagent for the preparation of compounds I, III, and IV. With CoF_3, the methyl group is fluorinated fairly readily, and this reagent is superior for making compounds with $-CH_2F$ and $-CHF_2$ groups. With neither reagent, starting from 1-methylpyrrole, were any 2H-compounds found, suggesting that there are directional effects operating in the fluorination of the pyrrole ring.

The fluorination of 1-methylpyrrolidine, under slightly milder conditions, gave significantly greater recoveries of crude product mixture than did 1-methylpyrrole. The same six products as before were isolated, together with the perfluoride VII [6], and two new compounds. These were shown to be 1-fluoromethyl- (B) and 1-difluoromethyl- (A) -2H-heptafluoropyrrolidine. For each, the mass spectral cracking pattern suggested hydrogen at position 2 [cf. 6]. This was confirmed by the ^{19}F nmr spectra, each compound showing one lower-field peak due to $>CF_2$ and one due to $>CHF$ (both adjacent to nitrogen) and two $>CF_2$ peaks at around 130 p.p.m. in the normal fluorocarbon range. The spectra also showed a $-CHF_2$ group (A) and $-CH_2F$ group (B).

Quantities of 2H-compounds (A + B) present were rather greater than of 3H-compounds (VIIX + V), so the fluorination of 1-methylpyrrolidine appears not to proceed via dehydrogenation to the pyrrole.

Reactions of Products

In earlier work [6], fluorine adjacent to nitrogen in compounds I and IV had been replaced readily using sulphuric acid, to give the corresponding diones (N-methyl-tetrafluoro- and -difluoro-succinimides). Now, a similar reaction was achieved with the perfluoro-compound (VII) but only under very forcing conditions, and complete hydrolysis to tetrafluorosuccinic acid resulted. The order of reactivity was IV > I >> VII. The perfluoro-compound (VII) does not have the extreme stability of saturated cyclic fluorocarbons, nitrogen destabilizing the $>CF_2$ groups adjacent to it, as do fluorovinyl groups [7].

Compound VI had been found also [6] to react selectively with aluminium chloride, only the fluorine of the $-CH_2F$ group being replaced by chlorine. The N-methyl analogue (IV) was now treated under comparable conditions, but only a small yield of product was formed. However, it was 1-methyl-2,5-dichlorodifluoropyrrole (C) the only fluoropyrrole isolated in our work so far. Presumably, the four fluorines in the 2 and 5 positions are all replaced by chlorine, followed by dehydrochlorination. In an attempt to improve the process, freshly sublimed aluminium chloride was used, but it was more reactive and the product (in much better yield) was 1-methyltetrachloropyrrole (D). It was found that this could also be made quite readily from 1-methylpyrrole and sulphuryl chloride. It was fluorinated over potassium tetrafluorocobaltate(III) at 180°.

Two products were obtained, 1-methyl- (E) and 1-fluoromethyl- (F) - 3,4-dichlorotetrafluoropyrrol-3-ine. Again, the 2 and 5 positions, next to nitrogen are the most reactive.

Dehydrofluorinations of the polyfluoropyrrolidines were of interest. Only one example of such a reaction had been reported, that of compound III [6], the product being 1-methylhexafluoropyrrol-3-ine. The only suitable reagent found was a suspension of potassium hydroxide powder in benzene. The reactions with the 1-difluoromethyl- (VIIX) and 1-fluoromethyl- (V) analogues were now found to proceed analogously, affording 1-difluoromethyl- (G) and 1-fluoromethyl- (H) -hexafluoropyrrol-3-ine, respectively. Structures were proved by ir (C=C bands at _ca._ 1800 cm^{-1}) and ^{19}F nmr (symmetrical structures; 2 low-field $>CF_2$ groups; adjacent to nitrogen).

In contrast, 1-difluoromethyl-2H-heptafluoropyrrolidine (A) could not be dehydrofluorinated: it was unchanged when treated as above, whilst bubbling through molten potassium hydroxide gave poor recoveries of a complex mixture.

It was hoped that dehydrofluorinations of 1-methyl-(IV) and 1-fluoromethyl-(VI) -3H,4H-hexafluoropyrrolidines might give pyrroles, by analogy with the reaction of IV with aluminium chloride. With compound IV, it was found better to use KOH powder in perfluorodimethylcyclohexane. The only product found was 1-methyl-3H-pentafluoropyrrol-3-ine (K) (ir C=C band at ca. 1710 cm^{-1} : ^{19}F nmr spectra showing two low-field $>CF_2$ groups, one vinylic fluorine :one vinylic hydrogen, one methyl). Compound VI was first dehydrofluorinated by molten potash. The one product, in poor yield, was J, the 1-fluoromethyl-analogue of K (appropriate spectroscopic properties). A small dehydrofluorination of VI using KOH/benzene gave only the same product J, but in much better recovery.

EXPERIMENTAL

Gas chromatography

Analytical and semi-preparative runs were done by Pye Series 104 and 105 machines with flame ionisation detectors. Semi-preparative columns were of glass 9.1 m x 7 mm int. diam. packed as follows: tube a, dinonyl phthalate/Celite (1:2) : tube b, polyethylene-glycol adipate/Chromasorb P 30-60 (1:6) : tube c, dinonyl phthalate/ Chromasorb P (1:9) : tube d, silicone gum SE 30/Supasorb 60-80 (1:9) : tube e, silicone gum/Chromasorb P (1:7) : tube f, Ucon LB 550X/Chromasorb P (1:4) : tube g, di-isodecyl phthalate/Chromasorb P (1:3). A larger scale preparative column (tube p) was of copper 4.8 m x 35 mm diam., packed with dinonyl phthalate on Chromasorb P30-60 (1:5). Quoted for each separation, are the tube used, temperature, and nitrogen flow rate.

Spectroscopy

Nuclear magnetic resonance spectra were measured on a Perkin-Elmer R12B machine, ^{1}H at 60 MHz using tetramethyl silane as internal reference (τ units) and ^{19}F at 56.4 MHz using trichlorofluoromethane as internal reference (δ units, negative). Unless otherwise stated samples were measured in solution in deuterochloroform. Signals are denoted by s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, c = complex. All results are given in Table 1.

Fluorination of 1-methylpyrrole with cobalt(III) trifluoride

A standard reactor was used 1.3 m long x 180 mm int. diameter, containing CoF_3 (ca. 10 Kg). Starting material (45 g) was dripped into the reactor at 120-140° in a nitrogen stream (10 ℓ h^{-1}) during 2.5 h, the products being collected in a copper vessel cooled by solid CO_2. The nitrogen stream was continued at 25 ℓ h^{-1} for 2 h further. The product, after being washed with iced water, sodium bicarbonate solution, dried ($MgSO_4$) (31.0 g) was separated by glc (p, 70°, 20: 21.8 g passed). The following fractions were obtained:- (i) 5.3 g; (ii) 4.3 g; (iii) 3.9 g; (iv) 1.2 g.

Fraction (i), by further glc (a, 80°, 9) gave:- (i)a, 1-difluoromethyloctafluoropyrrolidine(VIII)(1.9 g) [6]: (i)b, 1-fluoromethyloctafluoropyrrolidine(II) (1.2 g) [6] : (i)c, unidentified mixture (0.3 g).

Fraction (ii) was 1-difluoromethyl-3H-heptafluoropyrrolidine(VIIX) [2].

Fraction (iii), by further glc (b, 80°, 9) afforded:- (iii)a, 1-fluoromethyl-3H-heptafluoropyrrolidine(V) (1.45 g) [6] : (iii)b, 1-difluoromethyl-3H,4H-hexafluoropyrrolidine (8) (1.36 g) [3].

Fraction (iv) was 1-fluoromethyl-3H,4H-hexafluoropyrrolidine(VI) [6].

All compounds were characterised by glc and ir, and VIIX by nmr as well.

Fluorination of 1-methylpyrrolidine with cobalt(III) trifluoride

1-Methylpyrrolidine (50 g) was swept by a nitrogen stream (20 ℓ h^{-1}), during 1.5 h, into the reactor at 90°. The nitrogen stream was continued for 2 h further, and, after treatment as before, the dried product (54.6 g) was distilled in vacuo to give a clear liquid (52.2 g). Separation of a portion (30 g) by glc (p, 70°, 20) gave:- (i), 1-trifluoromethyloctafluoropyrrolidine(VII) (0.8 g) [6] : (ii), VIII (7.8 g) : (iii), II (4.1 g): (iv), 1-difluoromethyl-2H-heptafluoropyrrolidine (A) nc (2.6 g) b.p. 82-83° (Found: C, 24.5; H, 0.7; F, 69.4; N, 6.0. $C_5H_2F_9N$ requires C, 24.3; H, 0.8; F, 69.2; N, 5.7%); m/e 247 (M), 147 ($M-C_2F_4$), 100 (C_2F_4), base peak 51 (CHF_2) : (v), VIIX (1.4 g) : (vi),(2.1 g) a mixture : (vii), (2.6 g) a mixture. Mixture (vi) was separated (b, 80°, 9) to give:- (vi)a, V (0.91 g) : (vi)b, 8 (0.79 g). Mixture (vii) was separated (b, 80°, 9) into:- (vii)a, 1-fluoromethyl-2H-heptafluoropyrrolidine (B) nc (0.78 g) b.p. 103-105° (Found: M; 229.0091. $C_5H_3F_8N$ requires 229.0138); m/e 210 (M-F), 129 ($M-C_2F_4$), 100 (C_2F_4), base peak 33 (CH_2F) : (vii)b, VI (1.05 g). Known compounds were identified by glc and ir.

TABLE 1

^1H and ^{19}F nmr data for all new compounds

Compound letter		Chemical shifts	Relative intensity	Position in formula	Couplings
A	F	89.2	2	5	AB; $J=169$, $\Delta\nu=102$
		97.9	2	$1(C\underline{F}_2H)$	dAB; $J_{AB}=220$
		129.2	2	4	AB; $J=248$, $\Delta\nu=619$
		131.5	2	3	AB; $J=254$, $\Delta\nu=658$
		144.2	1	2	cd; $J_{2F2H}=63.6$
	H	3.40	1	$1(C\underline{H}F_2)$	t; $J_{1H1F}=58.8$
		4.18	1	2	cd; $J_{2H2F}=63.6$
B	F	90.5	2	5	AB; J=ca 175, $\Delta\nu$=ca 103
		129.6	2	4	AB; $J=248$, $\Delta\nu=580$
		131.5	2	3	AB; $J=259$, $\Delta\nu=688$
		142.1	1	2	cd; $J_{2F2H}=66.4$
		172.0	1	$1(C\underline{F}H_2)$	tdt; $J_{1F1H}=54, J_{12}=J_{15}=11$
	H	4.39	1	2	cd; $J_{2H2F}=66.4$
		4.64	2	$1(C\underline{H_2}F)$	d; $J_{1H1F}=54$
C (in CCl_4)	F	175.2	-	3,4	s
	H	6.53	-	$1(CH_3)$	s
D (in CD_3COCD_3)	H	6.40	-	$1(CH_3)$	s
E	F	89.7	-	2,5	q; $J_{FH}=1.3$
	H	7.22	-	$1(CH_3)$	p; $J_{HF}=1.3$

TABLE 1(Cont.)

Compound letter		Chemical shifts	Relative intensity	Position in formula	Couplings
F	F	86.0	4	2,5	d; $J_{21F}=J_{51F}=8$
		170.0	1	$1(C\underline{F}H_2)$	tp; $J_{1F1H}=55, J_{1F2}=J_{1F5}=8$
	H	4.52	-	$1(C\underline{H}_2F)$	d; $J_{1H1F}=55$
G (in CCl_4)	F	88.7	2	2,5	q; $J_{23}=J_{21F}=J_{54}=J_{51F}=7$
		99.2	1	$1(C\underline{F_2}H)$	dp; $J_{1F1H}=59, J_{12}=J_{15}=7$
		157.8	1	3,4	c
	H	3.50	-	$1(C\underline{H}F_2)$	t; $J_{1H1F}=58$
H (neat)	F	90.4	4	2,5	dd; $J_{21F}=J_{51F}=8, J_{23}=J_{54}=5$
		159.0	2	3,4	ct; $J_{32}=J_{45}=5$
		171.4	1	$1(C\underline{F}H_2)$	tp; $J_{1F1H}=55, J_{1F2}=J_{1F5}=8$
	H	4.67	-	$1(C\underline{H_2}F)$	d; $J_{1H1F}=55$
J	F	82.1	2	2	c
		91.5	2	5	c
		132.7	1	4	ctt
		170.3	1	$1(C\underline{F}H_2)$	ttt; $J_{1F1H}=55.5$, $J_{1F2}=J_{1F5}=8$
	H	4.18	1	3	ctd
		4.60	2	$1(C\underline{H_2}F)$	d; $J_{1H1F}=55.5$
K (in CCl_4)	F	86.3	2	2	c
		95.3	2	5	c
		133.6	1	4	c
	H	4.35	1	3	c
		7.27	3	1	s

Reaction of 1-methyl-3H,4H-hexafluoropyrrolidine(IV) with aluminium chloride

(a) Compound IV (2.0 g) in dry dichloromethane (5 cm^3) was added dropwise during 30 min to a stirred suspension of aluminium chloride (2.1 g; normal laboratory reagent) in dry dichloromethane (10 cm^3) at 0°. After 1 hour further at 0°, the mixture was allowed to warm up to 15°, filtered, and the residue washed with more solvent. Dichloromethane was distilled from the combined liquid layers to leave a crude product (2.2 g) with many peaks on analytical glc. Semi-preparative glc (e, 100°, 4.5) gave, as the only isolatable product, 1-methyl-2,5-dichloro-3,4-difluoropyrrole (C) nc (0.15 g) (Found: C, 32.7; H, 1.6; F, 20.5; N, 7.3. $C_5H_3Cl_2F_2N$ requires C, 32.3; H, 1.6; F, 20.4; N, 7.5%); m/e 189, 187, 185 (M).

(b) The title compound (4.0 g) in dry CH_2Cl_2 (5 cm^3) was added during 1 hour to stirred $AlCl_3$ (4.2 g; freshly sublimed) in dry CH_2Cl_2 (10 cm^3) at 0° The mixture was allowed to warm to 15° and stirred for 12 hours. Isolation as before left a solid (3.8 g), recrystallized from methanol to give 1-methyl-2,3,4,5-tetrachloropyrrole (D) (2.6 g) m.p. 120-121° (Found: C, 27.7; H, 1.6; Cl, 64.9; N, 6.5. $C_5H_3Cl_4N$ requires C, 27.4; H, 1.4; Cl, 64.8; N, 6.4%); m/e 223, 221, 219, 217 (M), (cited [9] m.p. 118-119°).

1-Methyltetrachloropyrrole (D) from 1-methylpyrrole Sulphuryl chloride (54 g) was added dropwise to a well-stirred solution of 1-methylpyrrole (8.1 g) in dry diethyl ether (35 cm^3) at 0°, during 1 hour. Stirring was continued whilst the solution was allowed to warm to 15°, and then for 2 hours further. Evaporation left a solid (16.7 g) which was recrystallized from methanol to give 1-methyltetrachloropyrrole (D) (10.1 g), m.p. 118.5-119.5° (correct ir).

Fluorination of 1-methyltetrachloropyrrole (D) with potassium tetrafluorocobaltate(III) The reactor used was 0.45 m long x 40 mm int. diameter, containing $KCoF_4$ (ca. 100 g); the temperature was 180° and nitrogen flow rate 2 $\ell\ h^{-1}$. Compound D (2.5 g) was introduced in portions of 0.5 g every 15 minutes, and, when the addition was complete, nitrogen was passed at 4 $\ell\ h^{-1}$ for 4 hours further. The products, collected in a glass trap cooled in liquid air, were washed with aqueous sodium bicarbonate, dried ($MgSO_4$), and filtered (1.6 g). Glc showed two major components, and separation (b, 95°, 9) afforded: (i) 1-methyl-3,4-dichloro-2,2,5,5-tetrafluoropyrrol-3-ine (E) nc (0.93 g), b.p. 128-130° (Found: C, 26.6; H, 1.4; Cl, 31.6; F, 34.2; N, 6.3. $C_5H_3Cl_2F_4N$ requires C, 26.8; H, 1.3; Cl, 31.7; F, 33.9; N, 6.3%); m/e 227, 225, 223 (M),208, 206, 204 (M-F), 190, 188 (M-Cl) ; ir, 1660cm^{-1} : (ii), 1-fluoromethyl-3,4-dichloro-2,2,5,5-tetrafluoropyrrol-3-ine (F) nc (0.24 g), b.p. 142-144° (Found: C, 24.6; H, 1.0; Cl, 29.2; F, 39.8; N, 5.7. $C_5H_2Cl_2F_5N$ requires C, 24.8; H, 0.8; Cl, 29.3; F, 39.3; N, 5.8%); m/e 245, 243, 241 (M), base peak 33 (CH_2F) ; ir 1660 cm^{-1}.

Dehydrofluorinations of fluoropyrrolidines

(a) 1-Difluoromethyl-3H-heptafluoropyrrolidine(VIIX)

To this (2.0 g) in dry benzene (4 cm^3), was added finely divided potassium hydroxide (1.9 g) with stirring. Heat was evolved. After 1 hour, the volatile components were distilled off in vacuo and separated by glc (g, 130°, 7) to give: (i), 1-difluoromethylhexafluoropyrrol-3-ine (G) nc (1.4 g), b.p. 62-63° (Found: C, 27.1; H, 1.2; F, 67.0; N, 6.4. C_5HF_8N requires C, 26.4; H, 0.5; F, 66.9; N, 6.2%); m/e 227 (M), 208 (M-F); ir 1805 cm^{-1} : (ii), benzene.

(b) 1-Difluoromethyl-2H-heptafluoropyrrolidine (A)

Reactions similar to that in (a), followed by refluxing for 6 hours, gave only unreacted A (recoveries ca. 75%). Bubbling A in a stream of nitrogen through molten potassium hydroxide at 200° gave poor recoveries of a complex mixture.

(c) 1-Fluoromethyl-3H-heptafluoropyrrolidine(V)

Powdered potassium hydroxide (5.6 g) was added to stirred V (4.6 g) in dry benzene (8 cm^3) at 15°. After 3 hours at 80°, the volatile part was distilled off and separated by glc (c, 95°, 9) to give:- (i), 1-fluoromethylhexafluoropyrrol-3-ine (H) nc (2.2 g), b.p. 81-83° (Found: C, 28.7; H, 0.9; F, 63.3; N, 6.8. $C_5H_2F_7N$ requires C, 28.7; H, 1.0; F, 63.6; N, 6.7%); m/e 209 (M), base peak 33 (CH_2F); ir 1800 cm^{-1} : (ii), benzene.

(d) 1-Fluoromethyl-3H,4H-hexafluoropyrrolidine(VI)

Compound VI (1.8 g) was volatilized in a nitrogen stream (1.5 ℓ h^{-1}) which was bubbled through molten potassium hydroxide at 210°. The organic product was purified by glc (a, 95°, 5) to give:- 1-fluoromethyl-3H-pentafluoropyrrol-3-ine (J) nc (0.09 g) b.p. 107-109°; m/e 191 (M), 190 (M-H), 172 (M-F), 158 (M-CH_2F), 33 (CH_2F); ir 1715 cm^{-1}.

(e) 1-Methyl-3H,4H-hexafluoropyrrolidine(IV)

Compound IV (2.0 g) in perfluorodimethylcyclohexane (3 cm^3) was stirred at 85° with powdered KOH (1.0 g) for 2 hours. The liquid was distilled off in vacuo and separated by glc (a, 90°, 4) to give:- (i), 1-methyl-3Hpentafluoropyrrol-3-ine (K) nc (1.4 g), b.p. 71° (Found: C, 34.7; H, 2.5; F, 55.4; N, 8.3. $C_5H_4F_5N$ requires C, 34.7; H, 2.3; F, 54.9; N, 8.1%); m/e 173 (M); ir 1710 cm^{-1} : (ii), perfluorodimethylcyclohexane

Reaction of 1-trifluoromethyloctafluoropyrrolidine(VII) with sulphuric acid Sulphuric acid (7.0 g; 98%) and VII (2.0 g) were shaken in a sealed glass Carius tube at 265° for 3 days. The product was poured carefully into ice-water (30 cm^3) and extracted with ether. Evaporation of the dried ether extracts and recrystallisation from benzene afforded tetrafluorosuccinic acid monohydrate (1.1 g) m.p. 90° (cited 87°, [8]) analysing correctly, which gave a dianilinium salt, m.p. 224-225° (cited 224° [8]).

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