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THE FLUORINATIONS OF PENTAFLUORONITROBENZENE AND PENTAFLUOROBENZALDEHYDE  
BY COBALT(III) FLUORIDE

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SUMMARY

The nitro-group survived in the fluorination of pentafluoronitrobenzene by cobalt(III) fluoride at 135-150<sup>o</sup>, the major products being undecafluoronitrocyclohexane and nonafluoro-4-nitrocyclohex-1-ene. 2H-Tetrafluoronitrobenzene similarly afforded cis- and trans- 2H-1-nitrodecafluorocyclohexane and 5H/4-nitro-octafluorocyclohex-1-ene. Pentafluorobenzaldehyde was fluorinated to give undecafluorocyclohexanecarbonyl fluoride and nonafluorocyclohex-3-enecarbonyl fluoride. Nonafluoro-4-nitrocyclohex-1-ene was oxidized to 3-nitroheptafluorohexan-1,6-dioic acid, and undecafluoronitrocyclohexane was hydrogenated over a palladium catalyst at low pressure to give decafluorocyclohexanone oxime and 1H-decafluorocyclohexanamine, accompanied by 1-aminononafluorocyclohex-1-ene.

INTRODUCTION

Some functional groups are not decomposed by high valency metallic fluorides, and appear in their original or in modified forms as substituents in the fluorinated products arising from the use of such fluorinating agents. Such has been found for carbonyl compounds [1], ethers [2], acyclic cyanides [3], and more recently for cyanides of the cyclohexane series [4,5]. In the last study, among the potentially useful polyfluoro-nitriles made was nonafluorocyclohex-3-enecarbonitrile [5]. An additional point of interest was that this was formed by fluorination of pentafluorobenzonitrile.

Hitherto, fluorinations of pentafluorophenyl derivatives ( $C_6F_5X$ ) had given fluorocyclohex- -enes or -dienes with the group X carried on a vinylic and not on a saturated carbon [6]. However, these earlier cases had not involved groups X with unsaturation, of which type the cyano-group was the first example to be investigated.

This present study had two objectives: firstly, to see whether nitro- and aldehyde- (or carbonyl fluoride) groups would survive fluorinations of fluoro-aryl compounds containing them (as did cyanide) so that useful synthetic intermediates are realisable; secondly, to see whether any -ene or -diene products had their functional groups on vinylic carbons (as with  $-CF_3$  [6]) or on saturated carbons (as with  $-CN$  [5]). The compounds fluorinated were pentafluoronitrobenzene (I), 2H-tetrafluoronitrobenzene (II) and pentafluorobenzaldehyde (III).

## RESULTS AND DISCUSSION

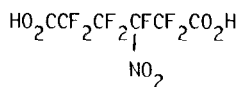
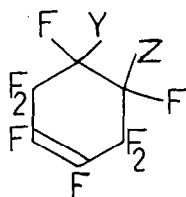
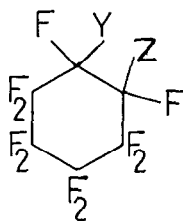
Pentafluoronitrobenzene(I) was fluorinated relatively smoothly by cobalt(III) fluoride in a standard stirred vapour-phase reactor at 135-150°. Though there was some loss of nitrogen oxides, reasonable yields of undecafluoronitrocyclohexane (IV) were obtained, together with smaller recoveries of a nonafluoronitrocyclohexene (V). The structure of product IV was clear from analysis and spectroscopy. Compound V had an ir band at  $1740\text{ cm}^{-1}$ , suggesting the presence of a  $-CF=CF-$  group. This conclusion was supported by the presence of two  $^{19}F$  nmr peaks at 148.2 and 149.9 (ratio 1:2), which were due to the tertiary fluorine and two vinylic fluorines. Probably, the two vinylic fluorines coincided at 149.9, but even if they did not and one vinylic and the tertiary fluorine absorbed at the same frequency, the 4-nitro-1-ene structure is still indicated for compound V: the peak from a vinylic fluorine adjacent to  $>C(NO_2)F$  (as in the isomeric 3-nitro-structure) would be expected to occur at lower field. Further, the chemical shift positions of the  $>CF_2$  groups were closer to those expected for the 4-nitro-structure (V) than for the 3-nitro.

A similar fluorination was carried out on 2H-tetrafluoronitrobenzene (II) at 125°. Three products were isolated, two saturated nitrodecafluorocyclohexanes (VI and VII), and a very minor product, a nitro-octafluorocyclohexene (VIII). It seemed most likely that the saturated products (VI and VII) had 2H-1-nitro-structures, and that each had the nitro-group (significantly larger than F) in an equatorial position. Their  $^{19}F$  nmr spectra were in general conformity with this. Further, detailed comparisons

of the two spectra with those of compound IV and the 4H-tridecafluorocyclohexanes [7], indicated that compound VI had the cis- structure [1-NO<sub>2</sub>(e), 2H(a)] (>CHF peak at 234.2, tert. F at 152.2) whilst compound VII had the trans [1-NO<sub>2</sub>(e), 2H(e)] (>CHF peak at 217.9, tert. F at 139.0). The <sup>1</sup>H CHF bands at 4.33 (VI) and 4.85 (VII) were also in the range for polyfluorocyclohexanes [8].

Again in conformity with this structural allocation, the stereoisomer with equatorial hydrogen would be expected [cf. 9] to have the higher boiling point.

Cyclohexene VIII had an infrared band for CF=CF at 1745 cm<sup>-1</sup>, and, in the <sup>19</sup>F nmr spectrum, there were bands for a tertiary fluorine at 143.9, >CHF at 217.1, and two vinylic fluorines at 153.7 and 154.9, besides an AB system arising from both allylic >CF<sub>2</sub> groups. The structure corresponding to these features is 5H/4-nitro-octafluorocyclohex-1-ene (VIII). This has the same relative position for the double bond as compound V; further, it has an equatorial hydrogen corresponding to that of the major saturated product VII.



IV Y=NO<sub>2</sub>, Z=F

V Y=NO<sub>2</sub>, Z=F

XI

VI Y=NO<sub>2</sub>, Z=H(cis)

VIII Y=NO<sub>2</sub>, Z=H(trans)

VII Y=NO<sub>2</sub>, Z=H(trans)

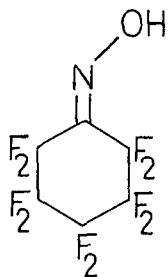
X Y=CF, Z=F

IX Y=CF, Z=F

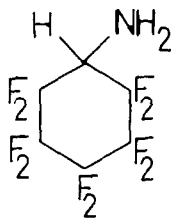
Pentafluorobenzaldehyde was fluorinated under roughly similar conditions, and gave two major products. One was the known [10] undecafluorocyclohexane carbonyl fluoride (IX), and the other a nonafluorocyclohexenecarbonyl fluoride (X). Again, there was an infrared band at 1740 cm<sup>-1</sup>, ascribable to CF=CF. In this case, the <sup>19</sup>F nmr tertiary fluorine position was at 180.7, and quite distinct from the two vinylic fluorines, which coincided at 155.6. As with compound V, there were also three AB systems, and all was specifically explained by the 3-ene structure X.

Hence, both objectives of the work were realised. Some useful synthetic intermediates with  $-\text{NO}_2$  and  $-\text{COF}$  groups are clearly obtainable by fluorinations involving high valency metallic fluorides. Further, it seems that such fluorinations of pentafluorophenyl derivatives give rise to cyclohexene derivatives with different structures depending on the nature of the functional group present. Octafluorotoluene afforded [6] mainly 1-trifluoromethylheptafluorocyclohex-1-ene, whereas in the present work, the nitro- and carbonyl fluoride groups, and also the cyano-group [5], emerged specifically on the 4-position relative to the double bond. It seems that unsaturated groups, capable perhaps of conjugating with intermediate radicals, promote saturation of double bonds on which they themselves are carried. It is tempting to invoke 1,4-diene intermediates of the type found earlier [6], the bonds carrying the unsaturated groups being fluorinated preferentially.

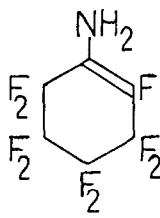
The nitro-compounds formed underwent two standard reactions. The nitro-cyclohexene (V) was oxidised normally to give 3-nitroheptafluorohexane-1,6-dioic acid (XI), characterised as its dianilinium salt (XIa), which had an appropriate  $^{19}\text{F}$  nmr spectrum. The nitro-cyclohexane (IV) was hydrogenated catalytically in ether solution using a palladium catalyst.



XII



XIII



XIV

Isolation when its glc peak was at its maximum yielded an intermediate, found to be decafluorocyclohexanone oxime (XII). Allowing the reaction to run to completion gave the known decafluorocyclohexanamine (XIII) [11], accompanied by 1-aminononafluorocyclohex-1-ene (XIV) (ir  $\text{C}=\text{C}$  band at  $1720\text{ cm}^{-1}$ ;  $^{19}\text{F}$  nmr showed 4 singlet  $>\text{CF}_2$  peaks, and a vinylic fluorine at 168.6). Use of acetic acid as solvent gave the oxime XII and the enamine (XIV). Lithium aluminium hydride reduction of nitro-compound (IV) gave products XIII and XIV, but in poor yield. Clearly, reduction of the nitro-group in IV is followed by loss of HF, as soon as an NH-bond is formed at  $\text{C}_1$ , giving the oxime XII as an isolatable intermediate. Subsequent further

reduction gives the amine XIII, expected to be labile towards elimination of HF between C<sub>1</sub> and C<sub>2</sub> with formation of enamine XIV (cf. the formation of its nitroso-imidazolidone derivative [12]). Enamine XIV is the postulated primary product of the reaction between ammonia and decafluorocyclohexene [13] but could not be isolated in the original work. Subsequently, a product of this type was found in poor yield in the products of the analogous reaction between ammonia and dodecafluorocycloheptene [14], and later work has given some of them from decafluorocyclohexene [15].

## EXPERIMENTAL

### General

Fluorinations, glc separations and spectroscopic measurements were done as described in an earlier paper [4]. Two further glc semi-preparative columns were used: column F, dinonyl phthalate/Chromasorb P30-60 (1:9); column G, Silicone rubber SE 30/Universal support B (1:9). Given for each separation are the column used, temperature (°C) and nitrogen overpressure (p.s.i.). <sup>1</sup>H and <sup>19</sup>F nmr spectra are recorded in the Table, δF values are actually negative, relative to CFCl<sub>3</sub> as internal standard.

### Fluorination of pentafluoronitrobenzene (I) with cobalt(III) fluoride

Pentafluoronitrobenzene (I) (3.9 g) was added dropwise over 1 hour to a small stirred fluorination reactor (containing 150 g CoF<sub>3</sub>) at 135-150°C and which was being swept with a nitrogen stream (2 l h<sup>-1</sup>). Products were collected in a glass trap cooled in liquid nitrogen. The reactor was then swept with nitrogen (4 l h<sup>-1</sup>) for an hour. The product was washed with ice-water (some NO<sub>2</sub> present), sodium hydrogen carbonate solution, and dried (MgSO<sub>4</sub>). An aliquot (1.36 g) of the combined product (15.5 g) from four such runs was separated by glc (F, 90°, 15) to give:- (i), nitrogen oxides (0.1 g): (ii), undecafluoronitrocyclohexane (IV) nc (0.92 g), b.p. 96-98°C (Found: F, 63.8%. C<sub>6</sub>F<sub>11</sub>NO<sub>2</sub> requires F, 63.9%); M/e 308 (M-F), 281 (M-NO<sub>2</sub>), 262 (C<sub>6</sub>F<sub>10</sub>), base peak 46 (NO<sub>2</sub>); ν<sub>max</sub> 1610 cm<sup>-1</sup> (vs; NO<sub>2</sub>): (iii), nonafluoro-4-nitrocyclohex-1-ene (V) nc (0.17 g), b.p. 100-101°C (Found: C, 24.8; F, 59.7%. C<sub>6</sub>F<sub>9</sub>NO<sub>2</sub> requires C, 24.9; F, 59.2%); M/e 243 (M-NO<sub>2</sub>), base peak 46 (NO<sub>2</sub>); ν<sub>max</sub> 1740 cm<sup>-1</sup> (s; C=C), 1610 cm<sup>-1</sup> (vs; NO<sub>2</sub>).

TABLE

## Nmr Spectra of Products

Compound	Chemical Shifts	Relative Intensities	Positions	Couplings
IV	F 120.2 and 133.9	4	2,6	AB, J=282
	124.1 and 139.0	4	3,5	AB, J=282
	124.0 and 140.6	2	4	AB, J=282
	140.3	1	1	s
V	F 109.5 and 115.8	2	3	AB, J=276
	116.6	2	6	s
	123.4 and 127.6	2	5	AB, J=276
	148.2	1	4	s
	149.9	2	1,2	s
VI	F 123.1 and 139.8	2	6	AB, J=285
	125.3 and 142.4	2	5	AB, J=282
	126.3 and 146.8	2	4	AB, J=282

	131.3	2	3	cs
	152.2	1	1	s
	234.2	1	2	cd, $J_d=46$
H	4.33	-	2	cdd, $J_d=42, J_q=12$
<hr/>				
VII	F 120.8 and 131.2	2	3	AB, $J=305$
	123.1 and 134.6	2	6	AB, $J=288$
	127.1 and 141.1	4	4,5	AB, $J=285$
	139.0	1	1	s
	217.9	1	2	cd, $J=44$
H	4.85	-	2	dq, $J_d=42, J_q=5$
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VIII	F 106.5 and 119.0	4	3 and 6	AB, $J=268$
	143.9	1	4	s
	153.7	1	2	s
	154.9	1	1	s
	217.1	1	5	cd, $J_d=45$
H	5.00	-	5	bd, $J_d=45$

(continued overleaf)

TABLE (Cont.)

Compound	Chemical Shifts	Relative Intensities	Positions	Couplings
IX (done neat)	F -35.3	1	1 (O=C-F)	cm
	121.0 and 133.6	4	2,6	AB, J=307
	125.9 and 142.3	4	3,5	AB, J=288
	125.8 and 144.9	2	4	AB, J=279
	182.1	1	1 (tert. F)	cm
X (done neat)	F -35.0	1	1 (O=C-F)	s
	108.7 and 118.7	2	2	AB, J=293
	114.2 and 126.9	2	5	AB, J=288
	122.2 and 132.6	2	6	AB, J=285
	155.6	2	3,4	cm
	180.7	1	1 (tert. F)	s
XIa (done in DMSO)	F 107.2	2	2	cm
	115.1	4	4,5	cm
	136.0	1	3	ct, J <sub>F</sub> =16



	H	0.75	3	$\text{NH}_3^+$	s
		2.72	5	aryl H	c
XII	F	114.5	1	2	s
		127.3	1	6	s
		133.6	3	3,4,5	cm, J=17, J=10, J=4.5
	H	5.2	-	NOH	b
XIII	F	124.7 and 143.5	2	2,6	AB, J=286
		125.9 and 142.1	2	3,5	AB, J=293
		128.1	1	4	c
	H	6.2	1	1 (CH)	s
		8.2	2	1 ( $\text{NH}_2$ )	s
XIV	F	116.4	2	3	s
		118.8	2	6	s
		135.4	2	4	s
		136.4	2	5	s
		168.6	1	2	s
	H	6.2	-	1	s

Fluorination of 2H-tetrafluoronitrobenzene (II)

Compound II [16] was fluorinated as for compound I, each run (3.2 g) at a reactor temperature of 125°C. A part (2.6 g) of the product (9.05 g) from two such runs was separated by glc (F, 80°, 15) to give: (i), a mixture (0.14 g) principally product IV (glc and ir): (ii), 2H/1-nitro/-decafluorocyclohexane (VI) nc (0.20 g), b.p. 97-98°C (Found: C, 23.5; H, 0.3; N, 4.7.  $C_6H_6F_{10}NO_2$  requires C, 23.3; H, 0.3; F, 61.5; N, 4.5%); M/e 263 (M-NO<sub>2</sub>), 46 (NO<sub>2</sub>);  $\nu_{\max}$  1605 cm<sup>-1</sup> (vs): (iii), 2H/1-nitrodecafluorocyclohexane (VII) nc (0.81 g), b.p. 109-111°C (Found: C, 23.4; H, 0.4; F, 61.7; N, 4.7%); M/e 263, 46;  $\nu_{\max}$  1600 cm<sup>-1</sup>: (iv), 5H/4-nitrooctafluorocyclohex-1-ene (VIII) nc (0.03 g), b.p. 119-121°C;  $\nu_{\max}$  1745 cm<sup>-1</sup> (s), 1610 cm<sup>-1</sup> (s).

Fluorination of pentafluorobenzaldehyde (III)

Carried out as for I but at a reactor temperature of 135°C, compound III (4.0 g; fluorinated in two runs of 2.0 g; each added over 30 min) gave crude product (4.37 g). Glc (C, 90°, 20) on 2.37 g afforded: (i), a mixture (0.2 g) of dodecafluorocyclohexane and tetradecafluoromethylcyclohexane (glc and ir): (ii), undecafluorocyclohexanecarbonyl fluoride (IX) (0.7 g), b.p. 80-82°C (cited [10] 77-78°); M/e 328 (M), 309 (M-F), 281 (M-COF), 47 (COF);  $\nu_{\max}$  1870 cm<sup>-1</sup> (vs, FC=0): (iii), nonafluorocyclohex-3-enecarbonyl fluoride (X) nc (0.5 g), b.p. 86-89°C (Found: C, 28.3%; M/e 289.973.  $C_7F_{10}O$  requires C, 29.0%; M, 289.979); M/e 290 (M), 262 (M-CO), 243 (M-COF), 47 (COF);  $\nu_{\max}$  1870 (vs), 1740 (s) cm<sup>-1</sup>.

Oxidation of nonafluoro-4-nitrocyclohex-1-ene (V)

Nitro-ene V (1.0 g) was added slowly and with stirring to potassium permanganate (0.58 g) in dry acetone (200 cm<sup>3</sup>). After 30 min at ca. 15°C, water (200 cm<sup>3</sup>) was added, and the bulk of the acetone evaporated off at reduced pressure. After being acidified with dilute sulphuric acid, and decolourized by having sulphur dioxide bubbled through it, the solution was extracted with ether, and the dried extract treated with freshly distilled aniline (0.8 g). The precipitate was filtered off (1.2 g; m.p. 177-179°C) and a portion recrystallised from carbon tetrachloride/diethyl ether to give the dianilinium salt of 3-nitroheptafluorohexan-1,6-dioic acid (XIa) nc, m.p. 179-181°C (Found: C, 42.9; H, 3.5; F, 26.5; N, 8.4.  $C_{18}H_{16}F_7N_3O_6$  requires C, 42.9; H, 3.2; F, 26.4; N, 8.4%);  $\nu_{\max}$  1685 cm<sup>-1</sup> (s; NO<sub>2</sub>).

Hydrogenation of undecafluoronitrocyclohexane (IV)

(a) The nitro-compound (IV) (1.0 g), dry diethyl ether (5 cm<sup>3</sup>), and palladium on charcoal catalyst (0.1 g), were shaken together in an atmosphere of hydrogen in a flask fitted with a septum cap and mounted in a standard low-pressure hydrogenator. The reaction was monitored by glc (column type G) to optimise the first-formed (long-retained) product peak. The solution was filtered through Celite, and the filtrate and washings were then concentrated by distillation. Glc (G, 150<sup>o</sup>, 30) afforded: (i), diethyl ether and starting material IV (glc and ir): (ii), decafluorocyclohexanone oxime (XII) nc (0.21 g), b.p. 136-138<sup>o</sup>C (Found: M/e 292.986. C<sub>6</sub>H<sub>10</sub>F<sub>10</sub>NO requires M 292.9898); M/e 293 (M), 276 (M-OH), 273 (M-HF), 243 (M-CF<sub>2</sub>);  $\nu_{\max}$  1650 cm<sup>-1</sup> (w; C=N).

(b) In a similar experiment, the reaction was continued until the glc peak due to compound XII had almost disappeared (ca. 8 hours), which coincided with a lessening of the rate of uptake of hydrogen. Isolation as above followed by glc (G, 90<sup>o</sup>, 20) gave: (i), diethyl ether: (ii), 1H-decafluorocyclohexanamine (XIII) (0.13 g), m.p. 40-42<sup>o</sup>C, ir spectrum identical with that of material made by a different route [11] (cited m.p. 43-44<sup>o</sup>C): (iii), 1-aminononafluorocyclohex-1-ene (XIV) nc (0.21 g), b.p. 129-131<sup>o</sup>C (Found: C, 27.5; H, 0.9; N, 5.4%; M/e 259.006. C<sub>6</sub>H<sub>2</sub>F<sub>9</sub>N requires C, 27.8; H, 0.8; N, 5.4%; M, 259.004); M/e 259 (M), 239 (M-HF), base peak 159 (C<sub>4</sub>F<sub>5</sub>NH<sub>2</sub>);  $\nu_{\max}$  3520, 3440 cm<sup>-1</sup> (s; NH), 1720 (s, C=C).

(c) Use of acetic acid as solvent, reaction being continued until hydrogen uptake ceased, gave compound XIV (0.15 g; slightly impure) and compound XII (0.3 g).

(d) Reaction of compound IV with lithium aluminium hydride in diethyl ether, at 0<sup>o</sup> for 30 min, and at ca. 15<sup>o</sup>C for 30 min, gave compounds XIII and XIV (ratio 2:1) in recovery lower than from expt. (b).

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