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FLUORINATIONS WITH POTASSIUM TETRAFLUOROCOBALTATE [III]. PART VIII

FLUORINATIONS OF TOLUENE AND OF PHENYLACETIC ACID

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SUMMARY

At 340 °C, toluene gave five 1-trifluoromethyl-substituted compounds:- 2*H*,4*H*,5*H*-tetrafluorocyclohexa-1,4-diene (IX); 2*H*-4*H*/5*H*-hexafluorocyclohex-1-ene (X); 2*H*-octafluorocyclohex-1-ene (IV); nonafluorocyclohex-1-ene (III); also perfluoromethylcyclohexane (II): traces of perfluorocyclohexane (I) were found. The 1-difluoromethyl-substituted analogues of these five were also obtained:- compounds XII, XV, VIII, VI, and V, respectively. A further five 1-difluoromethyl-substituted derivatives were found:- nonafluorocyclohex-3-ene (VII); an inseparable mixture of the 2*H*,4*H*- and 2*H*,5*H*-heptafluorocyclohex-1-enes (XI); 2*H*-3*H*/4*H*-hexafluorocyclohex-1-ene (probably) (XIV); and (difluoromethyl)benzene (XIII).

Structures of the unknown products were established by analysis and by nmr and ir spectroscopy. Further, the key intermediate (XII) was oxidized to difluoromalonic acid, whilst compound XV was dehydrofluorinated, to give 2*H*-(difluoromethyl)tetrafluorobenzene (XXI), together with an inseparable mixture of 2*H*,4*H*- and 2*H*,5*H*-1-(difluoromethyl)pentafluorocyclohexa-1,4-diene (XX). Dehydrofluorination of mixed heptafluoro-enes XI afforded 2*H*-1-(difluoromethyl)hexafluorocyclohexa-1,4-diene (XVIII), and mixed 2*H*-1- and 1*H*-2- (difluoromethyl)hexafluorocyclohexa-1,3-diene (XIX).

Difluoromethylundecafluorocyclohexane (V) did not dehydrofluorinate.

Phenylacetic acid was fluorinated likewise, and gave a similar range of products, but also one (originally an acid fluoride ?) which was converted to the methyl ester of tridecafluoro(cyclohexylacetic) acid (XVII).

The probable pathway of the fluorination process could be worked out.

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INTRODUCTION

The complex fluoride, potassium tetrafluorocobaltate[III] is useful for the fluorination of some organic species [1]: it reacts with arenes to give high proportions of polyfluorocyclohex-enes and -dienes. This is in contrast to fluorinations by cobalt trifluoride itself, where polyfluorocyclohexanes are the major products. The closely related complex salt, caesium tetrafluorocobaltate[III], also exhibits different reactivities, giving rise to significant proportions of polyfluoroarenes. The potassium complex has been used previously in the fluorinations of benzene and fluorobenzenes [2], hexafluoro-*m*-xylene [3] and polycyclic arenes [4].

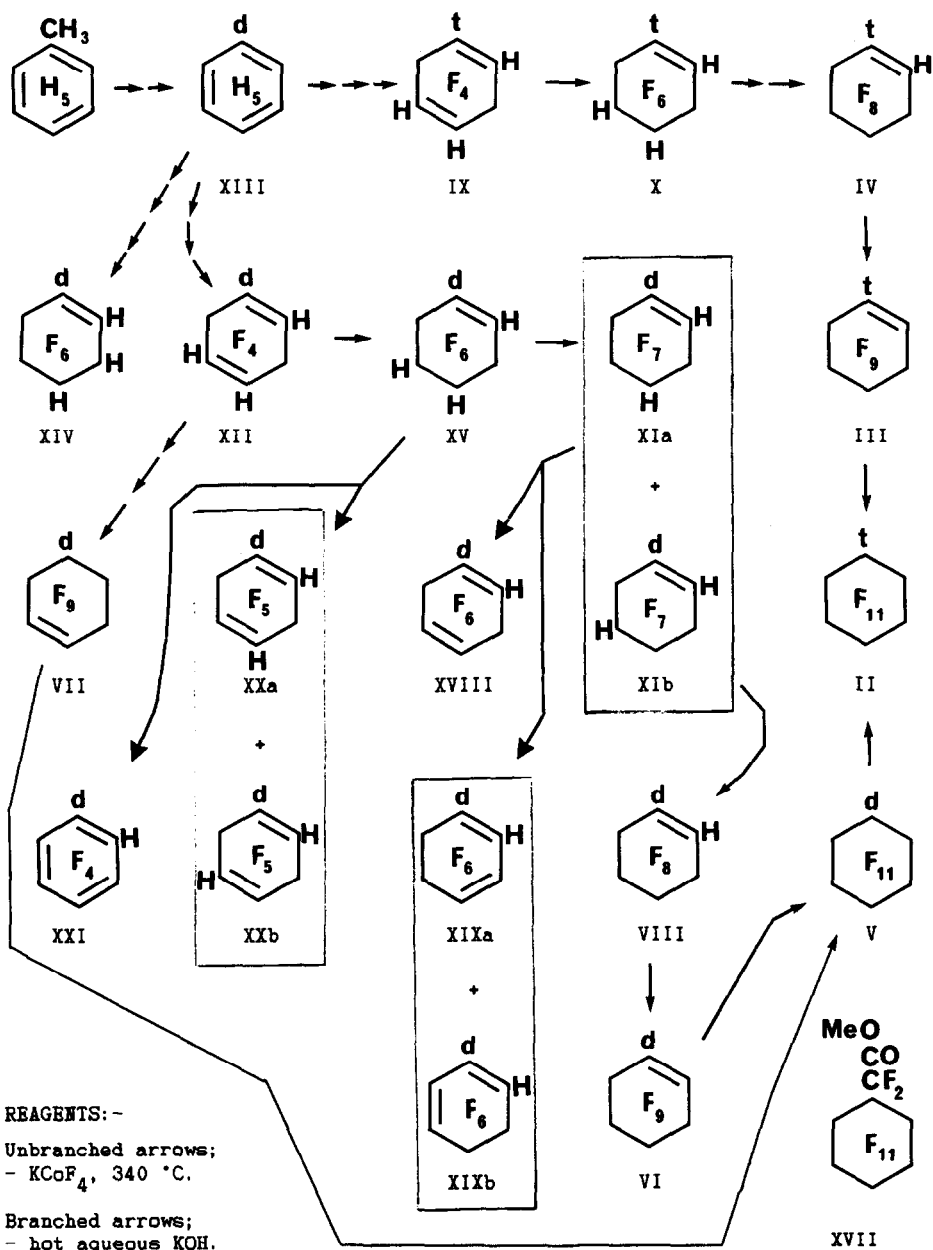
Pyridine [5] and 4-methylpyridine [5,6] were reacted similarly, but the types of products differed; they were mainly polyfluoro-azahexenes, arising by ring opening (comprising some 55 % of the total). Also found were polyfluoropyridines (ca 10 %) including a little pentafluoropyridine, and polyfluoro-*N*-methylpyrrolidines (ca 5 %) arising by ring rearrangement.

The objective of the present work was to identify the major products of the reaction of toluene with potassium tetrafluorocobaltate[III], and hence to establish the fluorination pathway. It appeared likely that this rather mild fluorinating agent might form useful amounts of polyfluorocyclohex-enes and -dienes bearing the difluoromethyl substituent, since complete fluorination of the methyl group is not easy.

RESULTS

A standard vapour-phase fluorination technique [7] was employed; 100 g portions of toluene were passed through a large reactor, kept at ca 340 °C. The products from five such runs were fractionally distilled, the fractions collected being further separated by gas-liquid chromatography. Seventeen species in all were isolated; one (benzaldehyde XVI) arose via hydrolysis in the work-up [cf 7]; another (XI) was an inseparable mixture of two isomers.

Since the products of exhaustive fluorinations become increasingly more volatile as hydrogens are replaced (beyond a 1:1 ratio), the first compounds to be isolated were the fluorocarbons, progressively followed by those with more and more hydrogen substituents remaining. In the following list of products obtained, the figures given for each are; (a) the amount isolated (expressed as % of total product, the molar yield is stated later), (b) the compound number (see Scheme) and (c) the literature reference if the product



SCHEME d = -CHF₂ : t = -CF₃

had been reported. Those isolated were:- dodecafluorocyclohexane, (<1), I, [2]; perfluoromethylcyclohexane, (5), II, [8]; 1-trifluoromethylnonafluorocyclohex-1-ene, (1), III, [8]; 2*H*-1-trifluoromethyloctafluorocyclohex-1-ene (4), IV, [9]; difluoromethylundecafluorocyclohexane, (7), V, [7]; difluoromethylnonafluorocyclohex-1-ene, (5), VI, [10]; 1-(difluoromethyl)nonafluorocyclohex-3-ene, (1), VII; 2*H*-1-(difluoromethyl)octafluorocyclohex-1-ene (9), VIII; 2*H*,4*H*,5*H*-1-(trifluoromethyl)tetrafluorocyclohexa-1,4-diene, (1), IX; 2*H*-4*H*/5*H*-1-(trifluoromethyl)hexafluorocyclohex-1-ene, (3), X; 2*H*,4*H* and 2*H*,5*H*-1-(difluoromethyl)heptafluorocyclohex-1-ene (ca 1:1 mixture, (9), XI; 2*H*,4*H*,5*H*-1-(difluoromethyl)tetrafluorocyclohexa-1,4-diene, (8), XII; (difluoromethyl)benzene, (5; benzaldehyde XVI included), XIII, [7]; 2*H*-3*H*/4*H*-1-(difluoromethyl)hexafluorocyclohex-1-ene (probably), (3), XIV; 2*H*-4*H*/5*H*-1-(difluoromethyl)hexafluorocyclohex-1-ene, (14), XV.

The fluorination of phenylacetic acid was undertaken, since in earlier work [11], carbonyl groups had been retained in this type of fluorination. The results were rather disappointing; the mixture was an almost identical range to that listed above, only compounds XIII and XIV not being detected, whilst the recoveries were relatively poor. One new compound was isolated; esterification of a high-boiling sub-fraction using methanol/sulphuric acid, gave a modest yield of the methyl ester of the fully fluorinated cyclohexylacetic acid (XVII). Presumably an acid fluoride was present originally.

The compounds that had not been described previously were characterized by using elemental analysis and mass spectrometry to establish the molecular formulae, and then from ir, uv, and nmr spectroscopic evidence. Published data on related compounds [9, 12] were used to define parameters. Details of measurements on compounds VII, VIII, IX, X, XI, XII, XIV and XV are recorded in the experimental section, and little further discussion is necessary.

Compound VII was clearly identified; also, the isomers with the double bond at C1 (VI), and at C2 [13], are both known. Diene XII was regarded as a key intermediate, and so the structure was confirmed by oxidative cleavage of the double bonds to give difluoromalonic acid. Spectroscopic parameters showed that XI was a mixture of 2*H*,4*H*- and 2*H*,5*H*-isomers, as was confirmed by dehydrofluorination. Treatment with aqueous potassium hydroxide afforded three hexafluorocyclohexadienes bearing difluoromethyl groups; the 2*H*-1-difluoromethyl-1,4-diene (XVIII), together with an inseparable mixture of two 1,3-dienes (XIX), the 1*H*-2-difluoromethyl-, and the 2*H*-1-difluoromethyl isomers. The 1,4-diene (XVIII) could arise from both isomers present in XI, but, without rearrangement, each of the latter could lose HF to give rise to

only one of the two isomers present in diene mixture XIX. The failure to separate these was unfortunate, but the conclusions were definite.

Each of the 2H-1-(difluoromethyl)hexafluorocyclohex-1-enes (XIV, XV) had nmr spectra which suggested that the two non-vinylic H atoms were located on adjacent carbons and were arranged *trans* to each other. The structure of XIV was ambiguous, since both the 3H/4H -, and the 5H/6H - arrangements could correspond to the data obtained; the chemical shift value for the H at C2 favoured the former structure, however.

The 4H/5H - compound (XV) was subjected to dehydrofluorination, to confirm the spectroscopic assignment. A *cis* configuration of H and F at C4 and C5 would ensure that one or other of these F-substituents (from C4 and C5) was eliminated preferentially, giving isomeric 1,4-dienes as the major products: in contrast, the *trans* configuration would give rise to a higher yield of the aromatic product, the loss of an F from each of the $>CF_2$ groups being more competitive [cf 14]. When XV was heated with aqueous potassium hydroxide, 2H-(difluoromethyl)tetrafluorobenzene (XXI) was the principal product. Relatively small amounts of an inseparable mixture of 2H,4H - and 2H,5H -1-(difluoromethyl)pentafluorocyclohexa-1,4-diene (XX) were generated, and, though only spectroscopic analysis of this mixture was possible, there was no doubt about the structure of XV.

It was of interest to attempt to dehydrofluorinate the alkane (V), difluoromethylundecafluorocyclohexane. It is known [15,16] that straight-chain polyfluorides bearing terminal $-CHF_2$ groups do not readily eliminate HF when treated with aqueous alkalis. Compound V could not be induced to form an alkene, even by reaction with molten KOH, though recoveries of V were very poor. Passage of V over heated sodium fluoride (an alternative approach, useful for the synthesis of fluoro-alkenes sensitive to aqueous base [cf 8]) was unsuccessful likewise, though forcing conditions led once more to losses of starting material. It seems probable that some dehydrofluorination of compound V did occur, though very sluggishly, and that the product, being an exocyclic alkene, was decomposed by the harsh conditions required.

DISCUSSION

The products from these fluorinations that were isolated and identified are all in accord with a cation-radical reaction process. This is now well established as the principal mechanistic pathway by which fluorinations with high-valency metal fluorides proceed [17]. It should be emphasised that many

of the sub-fractions that arose from the isolation techniques used were mixtures, which could not be separated into pure components. Some of the latter were the compounds obtained from other sub-fractions, but not all were. It seems certain that many extra substances were produced, additional to those listed above, but they were not major constituents. Few compounds containing small numbers of fluorine substituents were found: this is not surprising, since they are usually susceptible to further attack. Polyfluorides are more resistant, and all members of the likely reaction sequence are present. A cautious approach is therefore necessary, when working out possible reaction pathways; important reactive species may be missing, whilst stable products of no great significance may accumulate.

Clearly, attack by KCoF_4 on the toluene molecule, starting at the side chain, gives (difluoromethyl)benzene (XIII), as a major primary product. No nuclear fluorinated toluenes were found, but a multiplicity of possibilities can be invoked to reach the highly fluorinated end products. The key intermediate is 2*H*,4*H*,5*H*-1-(difluoromethyl)tetrafluorocyclohexa-1,4-diene (XII), the product of attack at the 2 and 5 positions of XIII, whatever the precise mechanistic details. XII is the exact analogue of the 1,4-diene isolated from among the products of fluorination of benzene [2]. The formation of this type of diene is characteristic of these processes, and is central to the accepted fluorination sequence [17]. All of the alicyclic products listed above, that possess difluoromethyl substituents (see Scheme), can be derived readily from XII by standard reactions.

The routes to the trifluoromethyl-containing products are less certain. Each is present in a smaller proportion than its CHF_2 analogue; some conversion of CHF_2 to CF_3 could occur (e.g. VIII \rightleftharpoons IV [cf 13]). The failure to detect any benzotrifluorides among the compounds isolated, may indicate that their generation, from XIII, is not significant. However, diene IX seems more likely to arise via 2,5-addition of fluorine to 2,5-difluorobenzotrifluoride than via substitution on diene XII (CHF_2 to CF_3).

Cyclohexenes with vinylic F (III, VI, VII) are less likely to arise via direct substitution of vinylic H [18], than by attack on the double bond and thence dehydrofluorination stages promoted by the potassium cobaltifluorides (cf the use of sodium fluoride [8]): even defluorination is possible [cf 7].

The products listed above differ markedly from those resulting from the fluorination of toluene by caesium tetrafluorocobaltate(III) [7]. Only compounds II, III, VI, and XIII are common to both processes, affording some support for the proposal [7,17] that different mechanisms apply to them.

EXPERIMENTAL

The general techniques and apparatus used have been described before [7].

Fluorination of Toluene by Potassium Tetrafluorocobaltate(III)

Toluene (100 g) was fluorinated during ca. 2 hours, using Reactor 4 at 330-340 °C, the nitrogen carrier gas flow being 20 l h⁻¹. The combined products from five such runs were washed and dried as usual, and fractionally distilled (940 g) through a glass vacuum-jacketted column (122 cm × 2.5 cm int. diam.: packing; nickel Dixon gauzes, 16 × 16 mm, 100 mesh). Based on glc control throughout (A, 100 °, 5.0; B, 70 °, 4.8), eighteen fractions were taken, leaving a still residue. Further separation by preparative glc gave compounds as follows:-

TABLE

Fraction No.	Wt(g)	Boiling range(°C)	Details of glc separation	Sub-fraction No.	Compound Number	Wt(g)
1	23.4	52- 67	D, 50°, 42	(i)	I	1.0
1			(22.0 g used)	(ii)	II	3.8
1				(iii)	mixture	9.9
1				(iv)	mixture	0.5
1111	9.9		C4, 50°, 4.0	(111a)	II	0.65
1111			(2.0 g used)	(111b)	III	0.70
2	20.0	68- 69	D, 47°, 30	(i)	II	9.6
2				(ii)	III	2.3
2				(iii)	IV	1.4
3	23.8	70- 76	D, 50°, 40	(i)	II	6.7
3				(ii)	III	0.9
3				(iii)	IV	10.8
4	19.3	77- 80	D, 70°, 50	(i)	II	0.6
4				(ii)	III	0.5
4				(iii)	mixture	10.2
4				(iv)	VI	2.0
4111	10.2		C1, 100°, 4.0	(111a)	IV	0.91
4111			(2.0 g used)	(111b)	V	0.55
5	23.4	80- 82	D, 78°, 46	(i)	mixture	0.2
5				(ii)	mixture	13.2
5				(iii)	VI	5.3
511	13.2		C1, 100°, 4.0	(11a)	IV	0.79
511			(2.2 g used)	(11b)	V	0.90

(continued)

TABLE (cont.)

Fraction No.	Wt(g)	Boiling range(°C)	Details of glc separation	Sub-fraction No.	Compound Number	Wt(g)
6	83.6	82- 86	D, 85°, 50	(i)	V	36.8
6			(in 3 batches)	(ii)	VI	27.2
6				(iii)	mixture	3.9
7	26.0	87- 92	D, 87°, 70	(i)	V	4.2
7				(ii)	mixture	6.4
7				(iii)	mixture	5.3
7				(iv)	VIII	5.2
7ii	6.4		C1, 100°, 4.0	(iia)	VI	1.05
7ii			(3.0 g used)	(iib)	VII	1.30
8	65.0	93- 97	C1, 110°, 4.0	(i)	mixture	0.09
8			(1.0 g used)	(ii)	VIII	0.62
9	31.6	98-104	D, 80°, 75	(i)	VIII	5.4
9				(ii)	mixture	11.0
9				(iii)	mixture	9.5
9ii	11.0		C1, 90°, 3.5	(iia)	mixture	1.35
9ii			(2.2 g used)	(iib)	IX	0.20
10	29.6	105-109	C1, 110°, 4.0	-	mixture	-
11	23.1	109-113	C1, 110°, 4.5	(i)	X	1.25
11			(2.4 g used)	(ii)	mixture	0.15
11				(iii)	XI	0.30
11				(iv)	XII	0.30
12	96.3	113-116	C1, 115°, 4.5	(i)	X	0.18
12			(3.0 g used)	(ii)	mixture	0.09
12				(iii)	XI	1.00
12				(iv)	XII	0.75
13	42.7	116-119	C1, 115°, 4.5	(i)	mixture	0.10
13			(4.0 g used)	(ii)	XI	1.48
13				(iii)	XII	1.23
13				(iv)	mixture	0.08
14	38.2	119-123	D, 95°, 60	(i)	mixture	10.9
14			(20 g used)	(ii)	mixture	3.1
14				(iii)	XIII	2.6
15	37.3	123-129	C1, 120°, 4.0	(i)	XIV	1.45
15			(3.0 g used)	(ii)	mixture	0.80
15				(iii)	XIII	0.25

(continued)

TABLE (cont.)

Fraction No.	Wt(g)	Boiling range(°C)	Details of glc separation	Sub-fraction No.	Compound Number	Wt(g)
16	45.3	129-134	D, 100°, 70	(i)	mixture	2.3
16			(27 g used)	(ii)	mixture	4.4
16				(iii)	XV	14.4
17	92.7	134-138	C1, 140°, 4.5	(i)	XV	1.35
17			(1.8 g used)	(ii)	mixture	0.10
18	35.3	138-148	C1, 140°, 5.0	-	mixture	-
19	130.0	residue	(7.0 g distilled in vacuo)			
19	6.3		C5, 190°, 4.5	(i)	mixture	0.55
19			(1.8 g used)	(ii)	mixture	0.45
19				(iii)	XVI	0.25

The following fractions and sub-fractions were mixtures, and were not separated further (minimum numbers of components in brackets):-

11v (3); 5i (3); 6iii (3); 7iii (4; by glc, the major one (ca 40 %) was VIII); 8i (5); 9iia (3; by glc, the major one (ca 55 %) was VIII); 9iii (7); 10 (9); 11ii (3); 12ii (3); 13i (3); 13iv (4); 14i (7); by glc (C1, 100°, 4.0), the major ones were XI (ca 20 %) and XII (ca 25 %); 14ii (2); 15ii (3); 16i (3); 16ii (3); 17ii (3); 18 (complex; glc (C1, 140°, 5.0) indicated the presence of ca 12 % of XV); 19i and 19ii (both multicomponent).

Characterization of compounds. Compound I was dodecafluorocyclohexane, and II was perfluoromethylcyclohexane; III was 1-trifluoromethylnonafluorocyclohex-1-ene [8]; V was difluoromethylundecafluorocyclohexane [7]; VI was difluoromethylnonafluorocyclohex-1-ene [10, 7]; XIII was (difluoromethyl)benzene and XVI was benzaldehyde (cf [7]).

New compounds (nc) were characterized as follows:-

IV (sub-fractions 2iii, 3iii, 4iia, 5ia) was 2H-1-(trifluoromethyl)-octafluorocyclohex-1-ene; b.p. 81 °C; M/e, 294 (M); (Found: C, 28.3; H, 0.5; F, 71.6. Calc. for C_7HF_{11} : C, 28.6; H, 0.3; F, 71.1 %); nmr as [9].

VII (7iib) was 1-(difluoromethyl)nonafluorocyclohex-3-ene; b.p. 94-95 °C; M/e, 294 (M); (Found: C, 28.3; H, 0.6; F, 71.0 %); ir 1750(m) (-FC=CF-).

VIII (7iv, 8ii, 9i) was 2H-1-(difluoromethyl)octafluorocyclohex-1-ene; b.p. 100 °C; M/e, 276 (M); (Found: C, 30.6; H, 1.0; F, 68.9. $C_7H_2F_{10}$ requires C, 30.4; H, 0.7; F, 68.8 %); ir ca 1700(vw) (RC=CF), ca 3080 (vw).

IX (9iib) was 2H,4H,5H-1-(trifluoromethyl)tetrafluorocyclohexa-1,4-diene; b.p. 104 °C; identified concurrently with Dr. I.W.Parsons, of this

Department, who isolated IX (Found: C, 38.5; H, 1.7; F, 60.9. $C_7H_3F_7$ requires C, 38.2; H, 1.4; F, 60.4 %), in higher proportion, from the mixture obtained by the fluorination of benzotrifluoride over $KCoF_4$.

X (11i, 12i) was 2H-4H/5H-1-(trifluoromethyl)hexafluorocyclohex-1-ene; b.p. 118 °C; M/e, 258 (M); (Found: C, 32.7; H, 1.4; F, 66.1. $C_7H_3F_9$ requires C, 32.6; H, 1.2; F, 66.3 %).

XI (11iii, 12iii, 13ii) was an approximately 1:1 mixture of 2H,4H- and 2H,5H-1-(difluoromethyl)heptafluorocyclohex-1-ene; b.p. 120 °C; M/e, 258 (M); (Found: C, 32.2; H, 1.6; F, 65.9 %); ir 1710(vw), 2980(w), 3080(w).

XII (11iv, 12iv, 13iii) was 2H,4H,5H-1-(difluoromethyl)tetrafluorocyclohexa-1,4-diene; b.p. 121 °C; M/e 202 (M); (Found: C, 41.5; H, 2.1; F, 56.9; $C_7H_4F_6$ requires C, 41.6; H, 2.0; F, 56.4 %); ir 1710(w), 1760 (vw), 2980(vw), 3080(w); no strong uv absorption in the range 220-300 nm. Aqueous alkaline permanganate [cf 8] afforded difluoromalonic acid (isolated as the dianilinium salt, yield 70 %).

XIV (15i) was a 2H-1-(difluoromethyl)hexafluorocyclohex-1-ene (3H/4H, probably); b.p. 132 °C; M/e, 240 (M); (Found: C, 34.9; H, 1.9; F, 63.6. $C_7H_4F_8$ requires C, 35.0; H, 1.7; F, 63.3 %).

XV (16iii, 17i) was 2H-4H/5H-1-(difluoromethyl)hexafluorocyclohex-1-ene; b.p. 142 °C; M/e, 240 (M); (Found: C, 34.6; H, 1.8; F, 63.4 %); ir 2980(w), 3080(vw).

Yields of Compounds

Compound number	I	II	III	IV	V	VI	VII	VIII
% of isolated product	<1	5	1	4	7	5	1	9
molar yield (%)	<1	3	1	3	4	3	1	6
Compound number	IX	X	XI	XII	XIII+XVI	XIV	XV	
% of isolated product	1	3	9	8	5	3	14	
molar yield (%)	1	2	7	7	7	2	11	

Fluorination of Phenylacetic Acid by Potassium Tetrafluorocobaltate(III)

The acid was introduced, as a fine powder, into Reactor 3 in a nitrogen stream (15 l h⁻¹). Fluorinations were carried out at 360 °C, on ca 40 g portions of substrate, each passed through the reactor during 1 hour. The combined products (200 g) from five runs (total input, 220 g) were washed rapidly with a little water and dried. To the clear liquid (185 g) was added acetone (75 cm³), and the solution was then distilled azeotropically (column as above). Acetone was removed from the appropriate fractions by washing with water. Residue (b.p. >56 °C) was fractionally distilled (column of above type, 61x2.5 cm), and that with b.p. >94 °C was distilled at 15 mm

Hg pressure (glass Vigreux column, 100 x 8 mm). Separations of fractions by glc, similar to the above, afforded the following compounds (the bracketed figures are respectively the %ages in the isolated product, and the molar yields:- I (1, trace); II (11,4); III (6,3), IV (1, trace), V (10,4); VI (8, 3); VII (1,1); VIII (2,1); IX (trace, trace); X (2,1); XI, (4,2); XII (5,4); XV (8,4). Compounds XIII and XIV were not detected.

Part (3.2 g) of one fraction (b.p. 78-110 °C /15 mm Hg; 19 g); methanol (16.0 cm³) and sulphuric acid (1.0 cm³) were refluxed for 24 hours. Work-up as usual afforded a liquid (2.45 g): glc (C3, 150°, 4.5) on part (2.05 g) gave :- (i) (trace), mixture: (ii) (0.83 g), the methyl ester of tridecafluoro(cyclohexylacetic) acid (XVII) [19]; M/e, 371 (M-19); (Found: C, 27.4; H, 1.0; F, 63.1. Calc. for C₉H₃F₁₃O₂ C, 27.7; H, 0.8; F, 63.3 %); ir 1790(s), 2980(w): (iii) (0.50 g) mixture.

Dehydrofluorinations of Compounds

2H,4H - and 2H,5H -1-(Difluoromethyl)heptafluorocyclohex-1-ene (XI). XI (3.0 g) was added to a solution of potassium hydroxide (3.0 g) in water (7.0 cm³), the system then being stirred magnetically at 70 °C for 45 min. After being washed and dried, the product (1.9 g) was separated by glc (C1, 140°, 4.5) to give:- (i) (0.60 g), 2H-1-(difluoromethyl)hexafluorocyclohexa-1,4-diene (XVIII) (nc); b.p. 103 °C; M/e, 238 (M); (Found: C, 34.9; H, 1.0; F, 64.0. C₇H₂F₈ requires C, 35.3; H, 0.8; F, 63.8 %); ir 1710(vw), 1770(m), 2980(w); no strong uv absorptions in the range 220-300 nm: (ii) (0.45 g), 1:1 mixture of 2H-1-(difluoromethyl)- and 1H-2-(difluoromethyl)-hexafluorocyclohexa-1,3-diene (XIX) (nc); b.p. 114 °C; M/e, 238 (M); (Found: C, 35.0; H, 0.9; F, 64.2 %); ir 1660(m), 1735(m), 2980(w); uv, λ_{max} 262nm (ε_{max} 3.7 x 10³): (iii) (0.40 g), recovered XI.

2H-4H/5H -1-(Difluoromethyl)hexafluorocyclohex-1-ene (XV). The reaction was carried out as for XI, but at 50 °C for 1 hour. Glc (C5, 130°, 4.5) on the product afforded:- (i) (0.10 g), tentatively identified as a 1:1 mixture of 2H,4H - and 2H,5H -1-(difluoromethyl)hexafluorocyclohexa-1,4-diene (XX): (ii) (0.25 g), 2H-(difluoromethyl)tetrafluorobenzene (XXI) (nc); b.p. 122 °C; M/e, 200 (M); (Found: C, 41.7; H, 1.2; F, 57.4. C₇H₂F₆ requires C, 42.0; H, 1.0; F, 57.0 %); ir 1500(s), 1530(s), 1640(m), 2980(vw), 3090(w): (iii) (0.08 g), an inseparable mixture of at least four components: (iv) (0.62 g) recovered XV.

Difluoromethylundecafluorocyclohexane (V). When compound V, in a stream of nitrogen, was passed through molten KOH [cf 20], only V itself (14 %) was recovered. Passage over heated sodium fluoride [8] at 440, at 500, and at

560 °C, left V unchanged (recovers 83-90 %): at 650 °C, unidentifiable products (3 %) were formed, but recovered V (59 %) still predominated.

TABLE

NMR SPECTRA OF COMPOUNDS VII, VIII, IX, X, XI.

b = broad, c = complex, d = doublet, m = multiplet, s = singlet, t = triplet

Compound Number		Chemical Shifts	Relative Intensity	Position in Formula	Type of Signal and Couplings
VII	H	6.35	-	-CHF ₂	t of d; J = 52.0, 9.0
	F	109.1; 119.0	4	2, 5	AB; J = 293
		129.8; 133.8	2	6	AB; J = 282
		132.9	2	-CF ₂ H	d of m; J = 52.0
		152.8	1	3 or 4	bs
		153.8	1	3 or 4	bs
		194.1	1	→CF	s
VIII	H	6.45	1	-CHF ₂	t; J = 53.1
		6.69	1	2	s
	F	109.9	2	6	s
		113.5	2	3	s
		120.7	2	-CF ₂ H	d; J = 53.1
		135.9	4	4, 5	bs
IX	H	6.35	2	4, 5	bs
		6.78	1	2	bs
	F	64.0	3	-CF ₃	s
		96.0	2	6	bs
		99.0	2	3	bs
X	H	4.97	2	4, 5	d of m; J = 48.0
		6.72	1	2	bs
	F	65.6	3	-CF ₃	s
		103.4; 107.4	2	6	AB; J = 304
		107.9; 110.7	2	3	AB; J = 299
		219.4	2	4, 5	m
XI	H	5.00	1	4 and 5	d of m; J = 47.9
		6.42	1	-CHF ₂	t; J = 53.6
		6.63	1	2	s
	F	94.3-137.5	6	3, 4, 6 & 3, 5, 6	series of cm
		121.5	2	-CF ₂ H	d of m; J = 53.6
		218.6	0.5	4 or 5	d of m; J = 47.9
		220.6	0.5	4 or 5	d of m; J = 47.9

TABLE

NMR SPECTRA OF COMPOUNDS XII, XIV, XV, XVII, XVIII.

Compound Number	Chemical Shifts	Relative Intensity	Position in Formula	Type of Signal and Couplings	
XII	H	6.34	4,5	s	
		6.41	-CHF ₂	t; J = 54.0	
		6.65	2	bs	
	F	96.5	2	6	s
		99.8	2	3	s
		121.2	2	-CF ₂ H	d; J = 54.0
XIV	H	4.60-5.80	3,4 or 5,6	cm	
		6.32	-CHF ₂	t of d; J = 54.1, 4.2	
		6.32	2	s	
	F	101.2; 122.5	2	3 or 6	AB; J = 305
		120.4; 130.4	2	-CF ₂ H	AB; J _{AB} = 305, J _{HF} = 54.1
		134.4	-	4 or 5	cm
		197.8	1	3 or 6	d; J = 45.7
		216.1	1	4 or 5	d of m; J = 47.0
XV	H	4.92	4,5	d of m; J = 46.5	
		6.37	-CHF ₂	t; J = 54.0	
		6.56	2	s	
	F	103.7; 106.6	2	6	AB; J = 299
		107.6; 111.1	2	3	AB; J = 293
		119.9; 122.5	2	-CF ₂ H	AB; J _{AB} = 303, J _{HF} = 54.0
		216.9	2	4,5	cm
XVII	H	4.18	-CH ₃	s	
	F	110.9	α-CF ₂	m	
		116.2; 128.0	4	2,6	AB; J = 307
		122.3; 140.2	4	3,5	AB; J = 296
		124.2; 142.4	2	4	AB; J = 289
		187.3	1	>CF	bs
XVIII	H	6.45	-CHF ₂	t; J = 53.9	
		6.62	2	bs	
	F	105.4	2	6	s
		108.1	2	3	s
		121.3	2	-CF ₂ H	d; J = 53.9
		156.2	2	4,5	bs

(continued)

TABLE

NMR SPECTRA OF COMPOUNDS XIX, XX, XXI.

Compound Number	Chemical Shifts	Relative Intensity	Position in Formula	Type of Signal and Couplings	
XIX	H	6.40	1	-CHF ₂ (both)	t; J = 54.9
		6.30	0.5	2 (isomer a)	bm
		6.70	0.5	1 (isomer b)	bm
	F	120.6; 121.7	2	-CF ₂ H (both)	d; J = 54.9
		120.1	1	6 (isomer b)	collapsed AB
		123.4	1	6 (isomer a)	s
		127.5	2	5 (both)	2 x t
		137.3; 147.8	1	3 (both)	2 x s
156.7; 157.7	1	4 (both)	2 x m		
XX	H	6.00	1	4(a); 5(b)	bs
		6.44	1	-CHF ₂ (both)	t; J = 54.1
		6.67	0.5	2 (isomer a)	bs
		6.97	0.5	2 (isomer b)	bs
	F	92.6	1	6 (isomer b)	s
		95.5	1	3 (isomer a)	s
		108.4	1	6 (isomer a)	d of m; J = 16.4
		111.5	1	3 (isomer b)	d of m; J = 16.4
	121.1	2	-CF ₂ H (both)	2 x d; J = 54.1	
	126.2	1	5(a); 4(b)	m	
XXI	H	6.85	1	-CHF ₂	t; J = 55.5
		7.26	1	2	m
	F	116.9	2	-CF ₂ H	d; J = 55.5
		139.3	1	3	m
		147.7	1	6	m
		153.5	1	4	m
		156.5	1	5	t; J = 17.0

Proton chemical shift values are in δ units (p.p.m. to low field of the internal standard, tetramethylsilane) and fluorine values in δ units (p.p.m. to high field of the internal standard, trichlorofluoromethane).

Tetrachloromethane was used as solvent throughout.

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