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FLUORINATIONS WITH COMPLEX METAL FLUORIDES. PART 9. FLUORINATIONS OF TOLUENE AND XYLENE DERIVATIVES BY MEANS OF CAESIUM TETRAFLUOROCOBALTATE[III]

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SUMMARY

Benzotrifluoride at 320 °C afforded some m-fluorobenzotrifluoride and octafluorotoluene (III), together with perfluoromethylcyclohexane (I), and also traces of 2H-heptafluorotoluene and 1-trifluoromethylnonafluorocyclohex-1-ene. Toluene itself gave (difluoromethyl)benzene, fluoro- and difluoro-methylpentafluorobenzene, difluoromethylundecafluorocyclohexane and (I); also traces of di- and tri-fluoromethylnonafluorocyclohex-1-ene: no benzotrifluoride or (III) were detected. 1,3-Bis(trifluoromethyl)benzene at 420 °C gave 4,5,6-trifluoro-1,3-bis(trifluoromethyl)benzene, decafluoro-1,3-dimethylbenzene, and perfluoro-1,3-dimethylcyclohexane. Para-xylene at 350 °C afforded 1,4-bis(difluoromethyl)tetrafluorobenzene, 1-difluoromethyl-4-trifluoromethyltetrafluorobenzene, decafluoro-1,4-dimethylbenzene (XIX), and perfluoro-1,4-dimethylcyclohexane (XVIII). Defluorination occurred to a significant extent on passage of the saturated cyclic fluorocarbons (I) and (XVIII) over the fully spent fluorinating agent (presumably caesium trifluorocobaltate) at <u>ca.</u> 400 °C; the fluorocarbon arenes, (III) and (XIX) respectively, were obtained.

INTRODUCTION

It has long been known that at 300–400 °C, caesium tetrafluorocobaltate [III] will fluorinate aromatic compounds to give significant proportions of the corresponding highly fluorinated arenes among the products [1]. First reported [2] was the direct conversion of benzene to hexa- and penta-fluoro-

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-benzene, though the major products were fluorobenzene and 3,3,6,6-tetrafluorocyclohexa-1,4-diene. Subsequently, fluorinations of naphthalene [3], benzonitrile, and the three benzenedicarbonitriles [4], pyridine and its three methyl homologues [5], and quinoline [6] have been described. Though some fluoro-arenes (having unchanged carbon skeletons) were found among the products in all cases, they were invariably accompanied by larger quantities of highly fluorinated alicyclic compounds. The fluoro-aromatic products from the bicyclic precursors had only one unsaturated ring. From all the pyridine derivatives, highly fluorinated N-alkylpyrrolidines (arising via a ring contraction) were formed in high proportions.

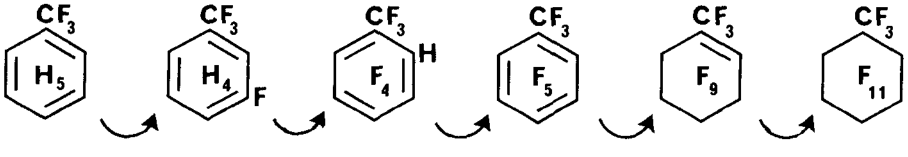
Studies of fluorinations involving caesium tetrafluorocobaltate[III] have been extended further, and this paper describes results obtained using benzotrifluoride, toluene, 1,3-bis(trifluoromethyl)benzene and p-xylene as organic substrates.

A few non-exhaustive fluorinations of this type using other reagents have been reported previously; benzotrifluoride by cobalt trifluoride [7], and by cerium tetrafluoride [8]; 1,3-bis(trifluoromethyl)benzene over potassium tetrafluorocobaltate[III] [9].

RESULTS

Fluorinations were carried out in a horizontal tubular reactor [10]; a small-scale unit was employed, containing 250 g of the caesium salt, which was stirred and heated. Around 5 g of organic substrate was used in each experiment, and the product mixtures were subjected to a standard washing procedure, pure compounds being separated by preparative glc.

Benzotrifluoride did not react appreciably below 250 °C, and runs were carried out at 280, 320 and 360 °C. From the experiment at 360 °C, besides recovered benzotrifluoride (VI), the compounds isolated were :- m-fluorobenzotrifluoride (V); 2H-heptafluorotoluene (IV); octafluorotoluene (III); 1-trifluoromethylnonafluorocyclohex-1-ene (II); perfluoromethylcyclohexane

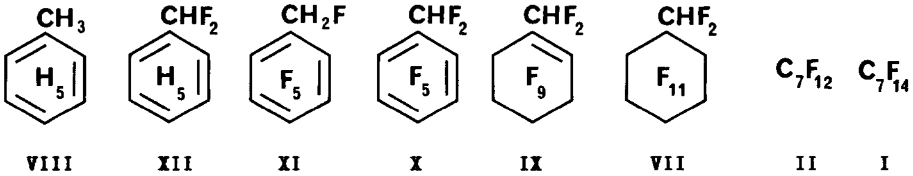


VI V IV III II I

SCHEME 1

(I); [molar yields 9, 3, 14, 2, 14 % respectively]. These same compounds were formed in the reactions at the other temperatures, though the relative amounts varied. All were known compounds, and were identified by glc and spectroscopic parameters (see Experimental section and nmr Table).

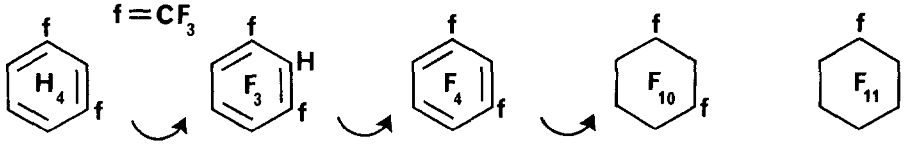
Toluene was fluorinated under generally similar conditions; as before, some starting material (VIII) was recovered. Compounds formed were:- (difluoromethyl)benzene (XII); fluoromethylpentafluorobenzene (XI); difluoromethylpentafluorobenzene (X); difluoromethylnonafluorocyclohex-1-ene (IX); difluoromethylundecafluorocyclohexane (VII); and the fluorocarbons (I and II) found before; [molar yields (for reaction at 360 °C) respectively 14, 7, 4, 2, 3, 4, 1 %]. In fact, in the main experiment, the yield of benzal fluoride (XII) was much lower, and some benzaldehyde (XIII) was isolated. It seemed likely that XIII arose by hydrolysis of XII under the work-up conditions used, and this was confirmed in a second experiment. Again, at temperatures between 280 and 360 °C, the same compounds were formed, the proportions isolated being somewhat different.



SCHEME 2

Compounds IX-XII were known: IX had arisen during further fluorination of 2,3,4,5,6-pentafluorotoluene using cobalt[III] fluoride [11]; X and XI [12], and XII [13] were obtained via halogen exchange on the corresponding side-chain chloro-derivatives. Compound VII was new; its structure followed from analysis and spectroscopy. It was noteworthy that no arenes carrying trifluoromethyl groups (eg, III-VI) could be found amongst these products, though the alicyclic fluorocarbons (I and II) were present.

Fluorination of 1,3-bis(trifluoromethyl)benzene was carried out both at 350 and 420 °C, each product containing the same five components. One was recovered starting material (XVI), and two were alicyclic fluorocarbons, perfluoro- -methyl- (I) and -1,3-dimethyl- cyclohexane (XIV). The other two were arenes, the known decafluoro-1,3-dimethylbenzene (XVII), and the new



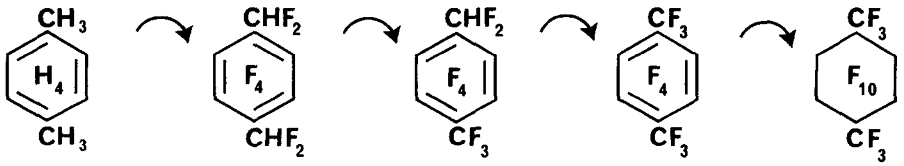
XVI XV XVII XIV I

SCHEME 3

4,5,6-trifluoro-1,3-bis(trifluoromethyl)benzene (XV). The molar yields (%) for the reaction at 350 °C were 24 (XIV), 12 (XV) and 5 (XVII).

The structure of the nonafluoride (XV) followed from the analysis and nmr data. Calculations based on average alterations [14] to the fluorine chemical shifts of hexafluorobenzene caused by substitutions of hydrogen and of trifluoromethyl in the o-, m-, and p- positions gave a good fit with the experimental results for structure XV, but not for the other possible isomers. Also, in earlier work [9], fluorination of substrate XVI using potassium tetrafluorocobaltate gave 4-fluoro-, 5-fluoro-, and 4,5-difluoro--1,3-bis(trifluoromethyl)benzene; no other isomers were detected.

p-Xylene was chosen for study to limit the possible number of products. It was fluorinated more readily than the other substrates, and was the only one to be converted completely, none being found unreacted. From reactions at 300 and at 350 °C, the same four compounds were isolated; other products were present, but in minor amounts in inseparable mixtures. An alicyclic fluorocarbon (XVIII) was accompanied by three arenes, which were:- 1,4-bis-(difluoromethyl)tetrafluorobenzene (XXI), 1-difluoromethyl-4-trifluoromethyltetrafluorobenzene (XX), and the known decafluoro-1,4-dimethylbenzene (XIX). Respective molar yields, from the reaction at 350 °C, were 7, 9, 9 and 5 %. The structures of XIX and XX were clear from analysis and nmr. Unlike toluene, p-xylene gave some of the corresponding perfluoroarene.



XXI XX XIX XVIII

SCHEME 4

An interesting defluorination was observed on passing the saturated alicyclic fluorocarbons (I and XVIII) through a reactor containing exhausted packing (caesium trifluorocobaltate, [1,2]). First, the most reactive starting material used, p-xylene, was passed through, until no fluorinating activity remained. Perfluoromethylcyclohexane (I) was then passed over the spent reagent at 380 °C; the product contained only I and octafluorotoluene (III), in a ratio of 2:1 (recoveries were about 72 %, and the molar yield of the arene 30 %). Perfluoro-1,4-dimethylcyclohexane (XVIII) was similarly defluorinated at 400 °C; the product contained ca 3 % of unidentified aromatics, but was principally XVIII and decafluoro-1,4-dimethylbenzene (XIX), (ratio ca. 1:1, recoveries ca. 45 %, molar yield 31 %).

DISCUSSION

Clearly, caesium tetrafluorocobaltate[III] converts alkyl- and fluoroalkyl-benzenes to mixtures containing significant proportions of polyfluoroarenes. Standard reactors were used, and design of special equipment for these reactions would probably improve the yields of such compounds. The results on the arene hydrocarbons show that methyl groups are fluorinated significantly less readily than are the aromatic rings.

All the compounds found can be explained on the theory of fluorination via cation-radicals [15], as modified to cover further cases [16]. It seems likely, as suggested before [5,16], that reaction pathways for fluorinations of arenes by this reagent have many electrophilic substitution stages, until a poly- or per- fluoroarene is formed. Normal orientation rules explain the positions of the residual ring hydrogens in products where any remain.

Patterns of products arising from these reactions differ significantly from those obtained by use of potassium tetrafluorocobaltate [9,17], cerium tetrafluoride [8], or cobalt trifluoride [7]. For these, the first two give products containing big proportions of polyfluorocyclohex -enes and -dienes, and the last gives largely polyfluorocyclohexanes. The absence of dienes among the products I-XXI is noteworthy, and could be due to involvement, at the high temperatures necessary, of a disproportionation process [diene + diene ⇆ ene + arene] which has been encountered before [18]. However, the fluorination using the cerium salt required even higher temperatures [8].

The defluorination reaction is of interest: it also could be involved in the reaction pathway. Further it might offer a useful alternative in some cases to defluorinations by heated metals [19] or by metal oxides [20].

EXPERIMENTAL

General

These techniques apply also to other papers to be published soon.

Spectroscopy. Spectra were recorded as follows: ultraviolet (uv)- Unicam SP 800A machine (ethanol solvent; cell path 10mm): infrared (ir)- Perkin Elmer 257 grating instrument; on liquid films, unless stated otherwise; peak positions in cm^{-1} (s, strong; m, medium; w, weak): mass spectra (ms)- AEI MS9 mass spectrometer: nuclear magnetic resonance (nmr)- Perkin Elmer R10 instrument, ^{1}H spectra at 60 MH_Z using tetramethylsilane as internal reference, ^{19}F spectra at 56.4 MH_Z using trichlorofluoromethane as internal reference, carbon tetrachloride being employed as the solvent unless otherwise stated.

Gas liquid chromatography. In all cases nitrogen was the carrier gas. Units used were:- A; two glass columns, each 1 m × 4 mm, packed with Ucon fluid LB-550X on 30-60 mesh Chromosorb P (1 : 14) in a Perkin Elmer Fractometer: B; similar columns and solid support, liquid packing- Di-isodecyl phthalate (1 : 2), in a Perkin Elmer Fractometer Model 154B: C; various glass tubes (9.14 m × 8 mm) were used in a Pye Series 104 chromatograph, packings being as follows- C1, Ucon fluid LB-550X on 30-60 mesh Chromosorb P (1 : 4); C2, Ucon fluid 50-HB-2000 on 60-80 mesh Brickdust (1 : 9); C3, Silicone Gum Rubber E301 (SE 30) on 30-60 mesh Chromosorb P (1 : 6); C4, Dinonyl phthalate on Celite (1 : 2); C5, Polyethyleneglycol adipate (Peg A) on 30-60 mesh Chromosorb P (1 : 6); C6, Silicone Gum Rubber E 301 (SE 30) on Universal B (1 : 39): D; electrically-heated copper tube (gravity injection system) [cf. 21], 4.88 m × 75 mm, packed with Dinonyl phthalate on 30-60 mesh Chromosorb P (1 : 5): E; tube and packing as in D, but diam. 35 mm, and ratio 1 : 2 : F; tube as in D, packing Silicone Gum Rubber SE 30 on 60-80 mesh Celite (1 : 6): G; tube as in E, packing Carbowax 20M on 60-80 mesh Celite (1 : 5): H; Tube as in E, packing Ucon fluid 50-HB-2000 on 30-60 mesh Chromosorb P (1 : 9). Quoted for separations are (in brackets): the column used; operating temperature (°C); nitrogen carrier gas flow rate ($l\ h^{-1}$ for columns C-H; instrument scale for columns A and B).

Fluorination reactors. These were electrically-heated horizontal nickel tubes, fitted with rotating co-axial stirrer shafts carrying paddles [10]. Temperature measurements were by thermocouples. Reactor 1a, (45 cm × 5.1 cm int. diam.), paddles 4 revs. per min., thermocouple at top centre of tube, was packed with potassium tetrafluorocobaltate[III] (*ca.* 250 g). Reactor 1b was the same machine containing caesium tetrafluorocobaltate[III] (ca. 250 g). Reactor 2, (45 cm × 4.5 cm), paddles 3.5 revs. per min., was packed with cobalt [III] fluoride (ca. 200 g). Reactor 3, (110 cm × 7.5 cm), paddles 3.5 revs. per min., thermocouple in a hollow stirrer shaft, was packed with potassium tetrafluorocobaltate[III] (ca. 2 Kg). Reactor 4, (120 cm × 18 cm), paddles 3.5 revs. per min., thermocouples attached at intervals along the tube length, contained potassium tetrafluorocobaltate[III] (ca 6 Kg). Reactor 5, (120 cm × 18 cm), paddles 4 revs. per min., thermocouple in a hollow stirrer shaft, was packed with cobalt[III] fluoride (ca. 6 Kg).

Organic substrates were introduced at a steady rate in a slow stream of nitrogen carrier gas; at the end, the reactor was purged with more nitrogen for 1 hour (small scale) or 2 hours (large). Fluorinating agents were regenerated by elemental fluorine at 270-300 °C. Products were washed with water, then aqueous sodium bicarbonate, and dried ($MgSO_4$).

Fluorination of Benzotrifluoride by Caesium Tetrafluorocobaltate[III]

Benzotrifluoride (5 g) was fluorinated (Reactor 1b) at 320 °C during 20 min (nitrogen flow 1.5 l h^{-1}). The product (5.7 g) was distilled in vacuo to yield a clear liquid (5.4 g); an aliquot (4.1 g), separated by glc (C1, 130°, 4.0) gave five fractions. The first was further separated (C4, 70°, 4.5) to give perfluoromethylcyclohexane (I) (0.47 g) [22], and 1-trifluoromethylnonafluorocyclohex-1-ene (II) (0.08 g) [7]: the other four original fractions were octafluorotoluene (III) (0.58 g) [22]; 2H-heptafluorotoluene (IV) (0.06 g) [23]; m-fluorobenzotrifluoride (V) (0.28 g) [24]; recovered benzotrifluoride (VI) (1.50 g). All were identified by glc, ir and nmr.

From similar fluorinations, yields of the compounds (as percentages of the total products, established by glc calibrations) were:

Compound number	I	II	III	IV	V	VI
Reaction Temperature 280°	9	3	5	0	11	72
320°	20	4	18	2	9	47
360°	26	3	17	3	7	40

Perfluoromethylcyclohexane (I) and Caesium Fluorocobaltates

I was passed over fully regenerated caesium tetrafluorocobaltate[III] as above, but at 380 °C. Only I itself (recoveries >95 %) was detectable by glc and ir. In another experiment, in a preliminary stage, p-xylene was passed over the fluorinating agent until no further fluorination of it could be detected. Perfluoromethylcyclohexane (I), in aliquots (5 g), was then passed over the bed of exhausted fluorinating agent (presumably caesium trifluorocobaltate) at 380 °C. Recoveries of product from three successive aliquots were 3.1, 3.0 and 3.2 g, respectively. By glc (A, 70°, 5.0), all three products contained the same two compounds, I and III. Part (1.0 g) of the first product was separated (C1, 140°, 4.5) to give starting material (I) (0.50 g), and octafluorotoluene (III) (0.25 g).

Fluorination of Toluene by Caesium Tetrafluorocobaltate[III]

Toluene (5 g) was passed during approx. 20 min. through Reactor 1b held at 360 °C (nitrogen flow as above). The product (ca. 23 g) from four such runs was washed, dried, filtered (20.1 g) and fractionally distilled through a glass vacuum-jacketed spinning band column (27 cm × 6 mm int. diam.). Based on glc control (A, 135°, 5.0; B, 120°, 5.5), fractions 1-7 were taken, and then further separated by preparative glc to give pure compounds:

Fraction No.	Wt(g)	Boiling range(°C)	Details of glc separation	Sub-fraction No.	Compound Number	Wt(g)
1	0.80	65- 70	C4, 60°, 3.5	(i)	I	0.52
1				(ii)	II	0.09
2	2.30	70- 78	C4, 60°, 3.5	(i)	I	1.05
2			(1.80 g used)	(ii)	II	0.15
2				(iii)	VII	0.17
3	0.50	78- 88	C4, 85°, 4.5	(i)	I	9 %
3			(not	(ii)	II	5 %
3			isolated)	(iii)	VII	77 %
3				(iv)	VIII	9 %
4	1.21	88- 94	C1, 100°, 4.0	(i)	I+II	trace
4				(ii)	VII	0.66
4				(iii)	IX	0.17
4				(iv)	VIII	trace
5	2.22	94-108	C1, 100°, 4.0	(i)	I(>90%)	0.27
5				(ii)	mixture	0.67
5				(iii)	VIII	0.60
6	2.49	108-125	C5, 130°, 4.0	(i)	mixture	trace
6				(ii)	X	1.41
6				(iii)	VIII	0.30
6				(iv)	XI	0.17
6				(v)	XII	trace

Fraction 7 (8.02 g) was distilled in vacuo to yield a liquid (6.02 g), and a tarry residue (1.50 g), the latter not being examined further. The liquid consisted of two layers. The lower layer 7L (0.60 g) was a complex mixture containing at least five components, ir peaks at 1650 and 1510 indicating the presence of some polyfluoroaromatic species; it was not examined further.

A part (5.00 g) of the upper layer (5.60 g) was separated by glc (C3, 170°, 5.0) into two sub-fractions, 7i (3.10 g) and 7ii. Further separation (C1, 140°, 5.0) of 7i (2.40 g) afforded:- 7ia; compound X, (0.51 g): 7ib; XI, (0.92 g): 7ic; XII, (0.49 g). Sub-fraction 7ii (1.20 g) was compound XIII.

Characterization of compounds. Compound I was perfluoromethylcyclohexane, II was trifluoromethylnonafluorocyclohex-1-ene, VIII was toluene and XIII was benzaldehyde; all had glc and ir data similar to those of authentic specimens.

VII (sub-fractions 2iii, 3iii and 4ii) was difluoromethylundecafluorocyclohexane (nc); b.p. 87 °C; M/e, 313 (M-19); (Found: C, 25.6; F, 73.9. C_7HF_{13} requires C, 25.3; F, 74.4 %); consistent ir.

IX (4iii) was difluoromethylnonafluorocyclohex-1-ene [11]; b.p. 90-91 °C; M/e, 294 (M); (Found: C, 28.5; F. 70.7. Calc. for C_7HF_{11}: C, 28.6; F, 71.1 %); consistent ir and nmr.

Sub-fraction 5ii had ir peaks at 1520, 1501 (polyfluoroaromatic).

X (6ii, 7ia) was difluoromethylpentafluorobenzene [12]; b.p. 125-126 °C ; M/e, 218 (M); (Found: C, 38.6; H, 0.8; F, 61.0. Calc. for C_7HF_7 : C, 38.5; H, 0.5; F, 61.0 %); ir 1660 and 1510.

XI (6iv, 7ib) was fluoromethylpentafluorobenzene [12]; b.p. 134-135 °C; M/e, 200 (M); (Found: C, 42.2; H, 1.3; F, 56.7. Calc for $C_7H_2F_6$: C, 42.0; H, 1.0; F, 57.0 %); ir 1650 and 1510.

XII (6v, 7ic) was (difluoromethyl)benzene [13,22]; b.p. 135 °C; M/e, 128 (M); (Found: C, 65.4; H, 4.7; F, 30.1. Calc for $C_7H_6F_2$: C, 65.6; H, 4.7; F, 29.7 %); consistent ir and nmr.

Other Fluorinations of Toluene by Caesium Tetrafluorocobaltate(III)

Material from the reactor trap, following a fluorination similar to the above, was washed rapidly with minimal water and dried (5.6 g). Part (4.00 g) was separated (C1, 140°,5.0) by glc into six fractions, each of which was analysed further (C4, 70°, 4.0).

Fluorinations followed by normal work-up and distillation, as in the main experiment above, were carried out at 280 °C and at 300 °C.

Yields of compounds obtained (as percentages of the total products), were established for all the fluorinations by glc calibrations, as follows:

Compound number	I	II	VII	VIII	IX	X	XI	XII
Analysis number 1	14	2	9	17	3	7	12	17
2	14	2	16	17	4	5	10	21
3	6	1	14	13	2	9	9	30
4	2	trace	6	7	2	15	5	49

Analysis 1 was based on fluorinations at 360 °C, followed by normal washing, fractional distillation and glc separation; the figure for benzal fluoride (XII) was the actual amount + that for benzaldehyde (XIII). Analysis 2 was based on a fluorination at 360 °C, followed by minimal washing, and then a direct glc separation. Analyses 3 and 4 followed fluorinations at 300 °C and 280 °C, respectively, followed by normal work-up, and then direct glc analysis (again, no fractional distillation stage).

No benzotrifluoride (VI) or octafluorotoluene (III) could be detected in any of these product mixtures by glc techniques.

1,3-Bis(Trifluoromethyl)benzene with Caesium Tetrafluorocobaltate[III]

The title compound was fluorinated (Reactor 1b) as for toluene, but at 420 °C; the product (*ca.* 19 g) from four runs being fractionated (18.0 g) under glc control (A, 98°, 5.2; B, 102°, 4.8) to give fractions 1-5, which were further separated by preparative glc as follows:

Fraction		Boiling	Details of glc	Sub-fraction	Compound	
No.	Wt(g)	range(°C)	separation	No.	Number	Wt(g)
1	1.80	65- 75	C4, 65°, 3.5	(i)	mixture	0.20
1			(1.30 g used)	(ii)	I	0.50
1				(iii)	XIV	0.20
2	2.63	75- 80	C4, 65°, 3.5	(i)	I	0.08
2			(1.00 g used)	(ii)	XIV	0.71
3	3.01	80- 85	C4, 60°, 3.0	(i)	XIV	>95 %
4	5.97	85- 95	C1, 125°, 4.0	(i)	XIV	2.50
4			(4.50 g used)	(ii)	XV	0.20
4				(iii)	mixture	0.20
4				(iv)	XVI	0.60
5	3.30	residue	(distilled in vacuo)			
5	3.20	-	C1, 125°, 4.0	(i)	XV	0.58
5			(2.30 g used)	(ii)	XVII	0.47
5				(iii)	XVI	0.70

A similar fluorination was carried out at 350 °C; after the initial washing, the product (4.50 g) was distilled in vacuo (4.43 g), and a part (4.00 g) separated by glc (C1, 110°, 4.0). Isolated were:- (i), a mixture (2.0 g), shown by glc (C4, 65°, 4.0) and ir to be principally compound XIV (ca. 80 %); (ii), XV (0.52 g); (iii), XVII (0.20 g); (iv), XVI (0.41 g).

Characterization of compounds. Compound XIV was perfluoro-1,3-dimethylcyclohexane [22]: XVI was unreacted starting material: XVII was decafluoro-1,3-dimethylbenzene [25]: XV (4ii, 5i) was 4,5,6-trifluoro-1,3-bis-(trifluoromethyl)benzene (nc); b.p. 118-119 °C; M/e, 268 (M); (Found; C, 35.8; H, 0.6; F, 63.6. C_8HF_9 requires C, 35.8; H, 0.4; F, 63.8 %); ir, 1505(m), 1640(m), 3090(vw). Two sub-fractions were mixtures: 1i had at least two components, and 4iii at least three (containing some XVII); they were not examined further.

Fluorination of para-Xylene over Caesium Tetrafluorocobaltate[III]

Five runs on p-xylene (19.0 g in all), carried out as for toluene but at 350 °C, yielded product (18.4 g) which was fractionally distilled, through a small Vigreux column (24 cm × 8mm int. diam.). Based on glc analysis (C1, 140°, 5.0; C5, 132°, 5.5), fractions 1-5 were taken, and separated further by glc as follows:

Fraction No.	Fraction Wt(g)	Boiling range(°C)	Details of glc separation	Sub-fraction No.	Compound Number	Compound Wt(g)
1	4.21	80- 98	C4, 65°, 3.5	(i)	mixture	0.81
1				(ii)	XVIII	2.45
2	4.73	98-110	C1, 140°, 4.5	(i)	XVIII	1.50
2			(3.30 g used)	(ii)	mixture	0.10
2				(iii)	XIX	0.50
2				(iv)	XX	0.30
3	3.50	110-130	C1, 140°, 4.5	(i)	XIX	0.60
3			(3.00 g used)	(ii)	XX	1.20
3				(iii)	XXI	0.40
4	2.49	130-140	C5, 190°, 4.5	(i)	XIX	0.08
4				(ii)	XX	0.50
4				(iii)	XXI	1.40
4				(iv)	mixture	0.15
5	2.30	residue	(distilled in vacuo)			
5	2.25	-	C5, 190°, 4.5	(i)	XXI	0.45
5			(1.00 g used)	(ii)	mixture	0.26

TABLE

NMR SPECTRA OF COMPOUNDS IV, VII, X, XI, XV, XX, XXI.

Compound Number		Chemical Shifts	Relative Intensity	Position in Formula	Type of Signal and Couplings
IV	H	7.28	-	2-H	cm
	F	61.6	3	$-CF_3$	d; J = 13.5
		137.1	1	3	cm
		139.3	1	6	cm
		148.9	1	4	cm
		152.5	1	5	t of m; J = 17.4
VII	H	6.35	-	$-CHF_2$	t of d; J = 51.3, 9.0
	F	117-146	10	$>CF_2$	series of cm
		131.8	2	$-CF_2H$	d of m; J = 51.3
		198.9	1	$>CF$	bs
X	H	6.91	-	$-CHF_2$	t; J = 52.3
	F	114.9	2	$-CF_2H$	d of t of d; J = 52.3, 8.5, 2.3
		144.3	2	2,6	m
		150.3	1	4	t of m; J = 21.2
		162.0	2	3,5	m
XI	H	5.44	-	$-CH_2F$	d of t; J = 48.0, 1.7
	F	144.2	2	2,6	d of m; J = 20.8
		152.5	1	4	t of m; J = 20.8
		162.9	2	3,5	t of m; J = 19.8
		212.7	1	$-CFH_2$	t; J = 48.0
XV	H	7.73	-	2-H	t of m; J = 7.0
	F	62.9	6	$-CF_3$	m
		128.0	2	4,6	m
		154.6	1	5	t; J = 19.7
XX	H	6.97	-	$-CHF_2$	t; J = 52.5
	F	58.1	3	$-CF_3$	t; J = 22.6
		116.1	2	$-CF_2H$	d of t; J = 52.5, 8.9
		139.9	2	3,5	m
		142.6	2	2,6	m
XXI	H	6.93	-	$-CHF_2$	t; J = 53.9
	F	115.9	4	$-CF_2H$	d; J = 53.9
		143.4	4	2,3,5,6	s

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

Fluorinations at 300 °C were also carried out on p-xylene (2 × 3.0 g) and the product was washed as usual, and then distilled in vacuo (4.72 g). By glc analysis based on calibration (C1, 140°, 5.0), it was shown to contain XVIII (20 %): XIX (12 %): XX (17 %): XXI (21 %).

Characterization of compounds. Compound XVIII was perfluoro-1,4-dimethylcyclohexane [22]: XIX was decafluoro-1,4-dimethylbenzene [19]: XX (2iv, 3ii, 4ii) was 1-difluoromethyl-4-trifluoromethyltetrafluorobenzene (nc); b.p. 143 °C; M/e, 268 (M); (Found: C, 35.6; H, 0.5; F, 63.4. C_8HF_9 requires C, 35.8; H, 0.4; F, 63.8 %); ir, 1500 (s): XXI was 1,4-bis-(difluoromethyl)tetrafluorobenzene (nc); m.p. 45-50 °C; M/e, 250 (M); (Found: C, 38.5; H, 1.0; F, 60.7. $C_8H_2F_8$ requires C, 38.4; H, 0.8; F, 60.8 %); ir, 1500 (s). Four sub-fractions were mixtures:- 1i had at least three components; 2ii at least two; 4iv had three; 5ii at least five; they were not studied further.

Perfluoro-1,4-dimethylcyclohexane (XVIII) and Caesium Fluorocobaltates

Compound XVIII was passed over fully regenerated caesium tetrafluorocobaltate[III] at 400 °C: only unreacted XVIII (recoveries >95 %) could be detected in the products. Experiments with exhausted fluorinating agent were carried out like those on perfluoromethylcyclohexane (I), but at 400 °C and using nitrogen flows of 2.0 l h^{-1}. In three runs, XVIII (18.0 g) gave combined product (8.3 g) containing almost 50 % each of starting material (XVIII) and decafluoro-1,4-dimethylbenzene (XIX): also present in trace amount was an unidentified component having an ir peak at 1510 (aromatic).

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