# Fluoro-olefin Chemistry. Part 18.[1] Thermal Reaction of Hexafluoropropene with Diphenylmethane, Butylbenzenes, Benzyl Alcohol, and Benzyl Methyl Ether

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The thermal reaction of hexafluoropropene with diphenylmethane gives the 1 : 1 adduct $Ph_2CHCF_2CHFCF_3$ (4a) and the rearranged adduct $PhCH_2CF_2CFPhCF_3$ (5a) *via* benzylic hydrogen abstraction. Analogous 1 : 1 adducts are formed from benzyl alcohol in low yield, *i.e.* $PhCH(OH)CF_2CHFCF_3$ (4e) and $HOCH_2CF_2CFPhCF_3$ (5b), but the reaction is complicated by decomposition of the alcohol to benzaldehyde, toluene, and water followed by the formation of the toluene–hexafluoropropene adduct $PhCH_2CF_2CHFCF_3$ (4c). A similar decomposition is observed with benzyl methyl ether and compound (4c) is the only fluorinated product isolated. With n-butylbenzene the 1 : 1 adduct $PhCHPr^nCF_2CHFCF_3$ is formed in relatively low yield due to rearrangement of the intermediate radical $PhCHPr^nCF_2\dot{C}FCF_3$ by a 1,5-hydrogen shift followed by β-scission to give the radical $Ph\dot{C}HCF_2CHFCF_3$ and propene and hence (4c) and the cyclobutane $CF_3 \cdot \dot{C}F \cdot CF_2 \cdot CH_2 \cdot \dot{C}HMe$ (8a), respectively. With isobutylbenzene the only 1 : 1 adduct isolated is $PhCH_2CMe_2CF_2CHFCF_3$, although benzylic hydrogen abstraction does occur as shown by the formation of compounds (4c) and (8a). 1 : 1 Adducts are not detected in the products from the reaction with s-butylbenzene; the intermediate radical $PhCMeEtCF_2\dot{C}FCF_3$ undergoes (i) cyclisation to give the indan (12), (ii) decomposition to give the olefin $CF_2{:}CMeEt$ and the radical $Ph\dot{C}FCF_3$ and (iii) rearrangement followed by β-scission to give ethylene and the radical $Ph\dot{C}MeCF_2CHFCF_3$.

The thermal insertion of hexafluoropropene into C–H bonds in alkanes,[2,3] trifluoromethylalkanes,[1] alkylbenzenes,[4] alkenes,[5] dialkyl sulphides,[6] ethers,[6] and halogenoalkanes [7] has been investigated extensively in this Department. The insertion reaction is considered to involve a chain mechanism initiated by hydrogen abstraction or alkane C–C bond cleavage by thermally excited hexafluoropropene (*i.e.*, see Scheme 1; where R′· is any radical formed by alkane C–C bond cleavage).
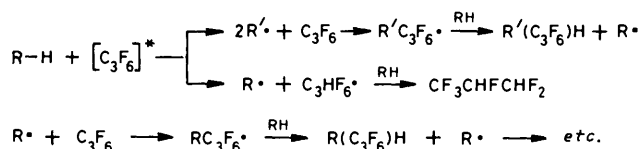

Scheme 1.

With the alkylbenzenes $PhCH_2R$ (R = H, Me or Et) the major products are the 1 : 1 adducts $PhCHRCF_2CHFCF_3$ (*ca.* 90%) and $PhCHRCF(CF_3)CHF_2$ (R = H or Me) (0.5 to 9%).[4] In contrast the reaction with cumene does not result in 1 : 1 adduct formation, the major products being 1,2,2,2-tetrafluoroethylbenzene (1), 1,1-difluoro-2-methylpropene (2), and the cyclobutane (3) [from reaction of (2) with C_3F_6], together with indans.[4]
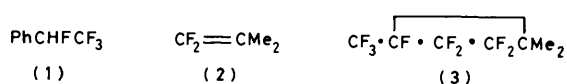
In a continuation of this study the thermal reactions of hexafluoropropene with diphenylmethane, the butylbenzenes, PhR (R = Bu^n, Bu^s, Bu^i), benzyl alcohol, and benzyl methyl ether have been investigated.

Results and Discussion

The results obtained are shown in the Table.
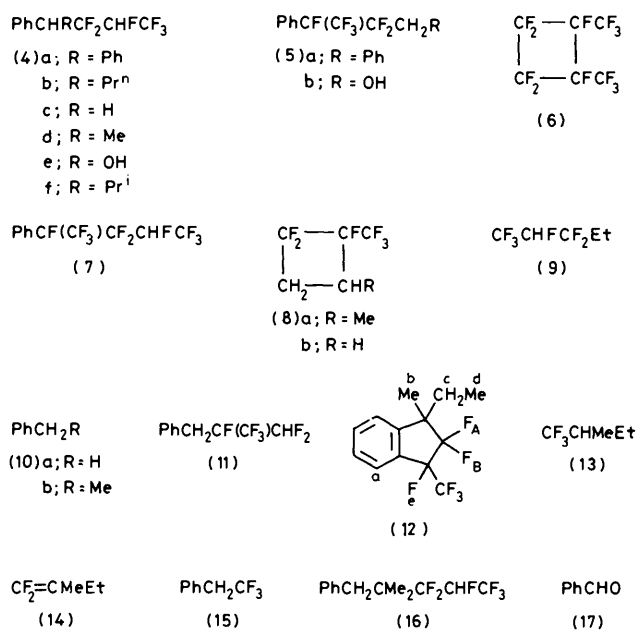
(a) *Alkylbenzenes.*—1 : 1 Adducts were isolated as major products from all the reactions except that involving s-butylbenzene (*cf.* cumene [4]). Two such adducts were formed in the diphenylmethane reaction *via* abstraction of a benzylic hydrogen atom (Scheme 2). However, in contrast to results obtained with other alkylbenzenes,[4] the formation of the major adduct (5a) involved a 1,3-phenyl migration in the intermediate radical (18), presumably because chain transfer with reactant alkylbenzene is sterically hindered thus allowing rearrangement to compete effectively.
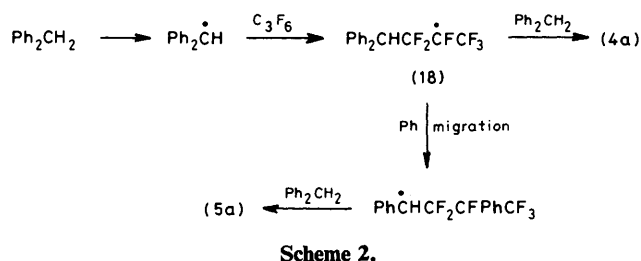
The radicals Ph$\dot{C}$HR (R = H or Me) undergo bidirectional addition to hexafluoropropene,[4] but the more bulky radical (R = Ph) apparently attacks the fluoro-olefin exclusively at the less hindered terminal CF_2 group.

With n-butylbenzene the 1 : 1 adduct (4b) as two isomers,

Table. Reaction of hexafluoropropene with benzene derivatives PhR (1 : 3 molar ratio) (figures for percentage yields are given in italics)

R	Temp. (°C)	Recov. alkane (%)	Recov. C_3F_6 (%)	Products (%)[b,c]		
				1 : 1 Adducts	Cyclobutanes	Others
CH_2Ph [a]	260—280	90	50	(4a) 9 (20.5) (5a) 23 (53)	(6) 8 [d]	(1) Trace, (7) Trace
CH_2Ph	250	74	2	(4a) 22 (27) (5a) 46 (58)	(6) 4 [d]	
Bu^n	250	84		(4b) 18.5 (39) [e]	(6) 1 [d] (8a) 16 [d]	(9) 2.5, (10a) (1), (4c) + (11) 17 (36)
Bu^s	250	82			(6) 1 [d] (8b) 10	(1) 13.5 (25), (4d) 10.5 (19.5) [f] (9) 1, (10b) (1.5), (12) (9.5),[d] (13) 8, (14) 1, (15) 3 (5)
Bu^i	250	85		(16) 10 (22)	(6) 1 [d] (8a) 14 [d]	(1) 2.5 (5.5), (4c) 14 (30), (10a) (1)
CH_2OH [a]	240	3	64	(4e) 18 (2.5) [g] (5b) 11 (1.5)		(4c) 28 (3.5), (10a) (21), (17) (46)
CH_2OMe [a]	230	55	46			(4c) 12.5 (5), (10a) (23), (17) (17)

[a] Tube reactions; remaining reactions carried out in autoclaves. [b] Yields are based on C_3F_6 consumed except those in parentheses which are based on aromatic consumed. [c] A number of unidentified compounds (mainly minor) and tar were also formed. [d] Mixture of cis- and trans-isomers (1 : 1 ratio). [e] Two isomers formed (17 : 20 ratio). [f] Two isomers formed (3 : 4 ratio). [g] Tentatively identified.

$$Ph_2CH_2 \longrightarrow Ph_2\overset{\bullet}{C}H \xrightarrow{C_3F_6} Ph_2CHCF_2\overset{\bullet}{C}FCF_3 \xrightarrow{Ph_2CH_2} (4a)$$
(18)

Ph | migration ↓

$$(5a) \xleftarrow{Ph_2CH_2} Ph\overset{\bullet}{C}HCF_2CFPhCF_3$$
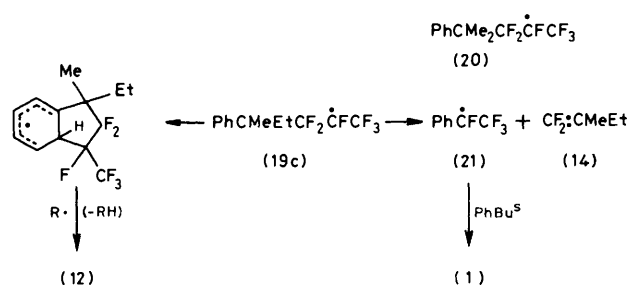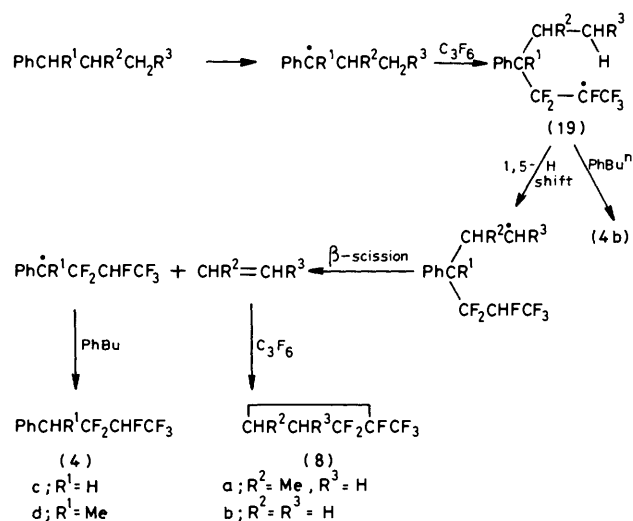
Scheme 2.

formed *via* benzylic hydrogen abstraction, was isolated in relatively low yield (contrast $PhPr^n$),[4] while with isobutyl-benzene and s-butylbenzene no such adducts were isolated. Other products were formed in all three reactions *via* the intermediate radical precursors (19) to the 1 : 1 adducts and it is postulated that, in contrast to the reactions of the shorter-chain alkylbenzenes studied previously,[4] there is increased steric hindrance in the intermediate radicals to chain transfer. This, coupled with the presence of longer alkyl chains, allows rearrangement of the intermediate radicals by 1,5-hydrogen shifts followed by β-scission to compete effectively with chain transfer (Scheme 3).

In addition to the products resulting from these decompositions, *i.e.* compounds (4c) and (8a) from the $PhBu^n$ ($R^1 = R^2 = H$, $R^3 = Me$) and $PhBu^i$ ($R^1 = R^3 = H$, $R^2 = Me$) reactions and compounds (4d) and (8b) from the $PhBu^s$ ($R^1 = Me$, $R^2 = R^3 = H$) reaction, propene and ethylene, respectively, were detected in the low-boiling product mixtures.

The 1 : 1 adduct (16) isolated from the isobutylbenzene reaction was formed *via* abstraction of the tertiary hydrogen atom; the reaction of hexafluoropropene with ethylbenzene has been reported [4] to give adducts in low yield formed *via* abstraction of a non-benzylic β-hydrogen atom.

The intermediate radical (20) formed in the cumene reaction underwent (i) cyclisation to give an indan and (ii) decomposition to give the tetrafluorobenzyl radical (21) and 1,1-difluoro-2-methylpropene (2).[4] Analogous reactions of the intermediate radical (19c; $R^1 = Me$, $R^2 = R^3 = H$) formed from s-butylbenzene took place (see Scheme 4).

The olefin (14) was present in low yield (1%) but its hydrogen fluoride adduct (13) (8%) was also isolated.

$$PhCHR^1CHR^2CH_2R^3 \longrightarrow Ph\overset{\bullet}{C}R^1CHR^2CH_2R^3 \xrightarrow{C_3F_6} Ph\overset{\bullet}{C}R^1 \begin{smallmatrix} CHR^2-CHR^3 \\ | \quad | \\ CF_2-\overset{\bullet}{C}FCF_3 \end{smallmatrix}$$

structure (19) with H

1,5-H shift / PhBu[n]

$$Ph\overset{\bullet}{C}R^1CF_2CHFCF_3 + CHR^2=CHR^3 \xleftarrow{\beta\text{-scission}} Ph\overset{\bullet}{C}R^1 \begin{smallmatrix} CHR^2\overset{\bullet}{C}HR^3 \\ | \\ CF_2CHFCF_3 \end{smallmatrix}$$

(4b)

↓ PhBu   ↓ C_3F_6

$$PhCHR^1CF_2CHFCF_3 \qquad CHR^2CHR^3CF_2CFCF_3$$
(4)   (8)
c; $R^1 = H$ a; $R^2 = Me$, $R^3 = H$
d; $R^1 = Me$ b; $R^2 = R^3 = H$

Scheme 3.

$$PhCMe_2CF_2\overset{\bullet}{C}FCF_3$$
(20)

structure (12) with Me, Et, F_2, F, CF_3, H ; R· (−RH)

$$\longleftarrow PhCMeEtCF_2\overset{\bullet}{C}FCF_3 \longrightarrow Ph\overset{\bullet}{C}FCF_3 + CF_2{:}CMeEt$$
(19c)   (21)   (14)

↓ $PhBu^s$

(1)

Scheme 4.

The isolation of 1,3,3,3-tetrafluoroethylbenzene (1) in low yield from the isobutylbenzene reaction indicated that a corresponding decomposition of intermediate radical (19b; $R^1 = R^3 = H$, $R^2 = Me$) had occurred but the expected co-

product 1,1-difluoro-3-methylbut-1-ene or compounds formed from it were not detected.

The lower molecular-weight alkylbenzenes isolated from the reactions are considered to arise either *via* C–C fission in the reactant alkane or *via* non-benzylic hydrogen abstraction followed by β-scission to give the intermediate benzyl radicals PhĊHR (R = H or Me).

The intermediacy of the radical PhĊH$_2$ also accounts for the formation of compound (11) since this radical is reported to undergo bidirectional addition to hexafluoropropene.[4]

From the reactions involving n-butylbenzene and s-butylbenzene the 1 : 1 adduct (9) of ethane and hexafluoropropene was isolated in low yield. This compound has been reported [2] previously from the thermal reaction of ethane with hexafluoropropene and its formation in the present reactions indicates the intermediacy of ethyl radicals.

The cyclodimer of hexafluoropropene (6)[8] was isolated as a 1 : 1 mixture of the *cis*- and *trans*-isomers.

Compound (7), isolated in low yield from the diphenylmethane reaction, arose *via* reaction of the radical (21) with hexafluoropropene as was postulated previously for its formation in the cumene reaction.[4]

The only remaining identified product was 2,2,2-trifluoroethylbenzene (15) formed in the s-butylbenzene reaction. It is not apparent how this compound arose.

A g.l.c.–mass spectrometric examination of the minor products from the butylbenzene reactions showed the presence of (i) other 1 : 1 adducts (m/z 284, M^+) with base peaks at m/z 91 (C$_7$H$_7^+$; PhBu^n reaction), m/z 105 (C$_8$H$_9^+$) or 91 (PhBu^s reaction) and m/z 43 (C$_3$H$_7^+$, PhBu^i reaction); (ii) compounds corresponding to 1 : 1 adducts – H$_2$ (m/z 282, M^+) with base peaks at m/z 131 $(M − C_3F_6H)^+$ which are probably indans; and (iii) 2 : 1 adducts (m/z 434, M^+) which were detected from the n-butylbenzene reaction only. It has been shown previously in the reactions of n-butane and n-pentane with hexafluoropropene [3] that 1 : 1 adducts are the precursors of the 2 : 1 adducts and that C–H bonds α- and β- to the C$_3$HF$_6$ group in the 1 : 1 adducts are deactivated towards hydrogen abstraction. Only the 1 : 1 adduct (4b) from the n-butylbenzene reaction contains favourable hydrogen atoms (γ- and δ-) available for abstraction to give 2 : 1 adducts (see Scheme 5).
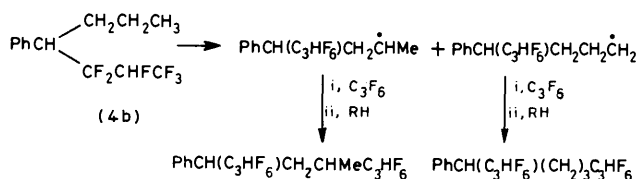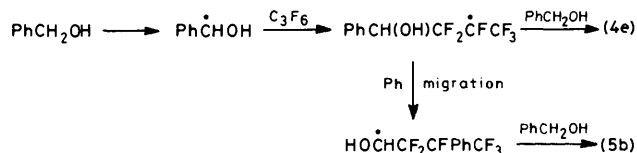
Scheme 5.

(b) *Benzyl Alcohol and Benzyl Methyl Ether.*—When these two compounds were heated alone in Pyrex at 240 °C low conversions (6—7%) to toluene, benzaldehyde, and water or dimethyl ether (1 : 1 : 1 ratio) were observed.

Despite these findings initial reactions of the two compounds with hexafluoropropene were investigated. Two 1 : 1 adducts were isolated from the benzyl alcohol reaction with the minor adduct (5b) resulting from phenyl migration. Although the second adduct was not fully characterised it is probably (4e) (see Scheme 6).

1 : 1 Adducts were not detected either in the reaction involving the ether and the major products from both reactions were toluene, benzaldehyde, and the toluene adduct (4c).

The yields of benzaldehyde and toluene were much higher

Scheme 6.

than those observed when the substrates were heated alone perhaps indicating that hydrogen fluoride formed during the reactions catalysed the rearrangements.

Experimental

Experimental techniques were as described previously [5] except that g.l.c. employed columns of Silicone SE30 oil, trixylyl phosphate (TXP), or polyethyleneglycol adipate (PEGA) (15—25% on Celite). N.m.r. chemical shifts to low-field of reference [external tetramethylsilane for ^{1}H (unless stated otherwise) and external trifluoroacetic acid for ^{19}F spectra] are positive.

The reactant benzene derivatives were commercial samples which were carefully purified before use.

Reaction of Hexafluoropropene with Diphenylmethane.—(a) *Tube reaction.* A mixture of hexafluoropropene (2.25 g, 15.0 mmol) and the alkane (7.56 g, 45.0 mmol), sealed *in vacuo* in a Pyrex tube (*ca.* 300 cm^3) and heated at 280 °C (72 h), gave (i) unchanged hexafluoropropene (0.92 g, 6.2 mmol, 41% recovered), (ii) a mixture of *cis*- and *trans*-perfluoro-(1,2-dimethylcyclobutane) (6) (0.11 g, 0.40 mmol, 10% on C$_3$F$_6$) contaminated with a trace of 1H,2H-hexafluoropropane, (iii) a non-volatile fraction (7.86 g) which was shown by g.l.c. (2 m SE 30 at 170 °C) to contain one major component (unchanged alkane), components with shorter retention times than diphenylmethane (trace), and two components with longer retention times than the alkane, and (iv) carbonaceous material (*ca.* 0.9 g) which was not examined further.

A further four experiments using the same amounts of reactants at 270 °C (72 h), 270 °C (96 h), 270 °C (168 h), and 260 °C (168 h) gave (i) unchanged hexafluoropropene (48, 54, 16, and 56% recovered, respectively), (ii) a mixture of *cis*- and *trans*-perfluoro-(1,2-dimethylcyclobutane) (6) (8, 6, 8, and 6%, respectively), (iii) non-volatile fractions (7.74, 7.92, 6.97, and 7.76 g, respectively), and (iv) small amounts of carbonaceous residues.

The combined non-volatile fractions (38.25 g) were fractionated on a spinning-band column to give the following. (i) A multicomponent mixture (0.01 g), b.p. <120 °C at 10 mmHg, from which two components were identified *via* g.l.c. (2 m SE 30 at 170 °C)–mass spectrometry as 1,2,2,2-tetrafluoroethylbenzene [4,9] (1) (trace), m/z 178 (30%, M^+) and 109 (100, PhCHF$^+$), and (1,2,2,3,4,4,4-heptafluoro-1-trifluoromethylbutyl)benzene [4,9] (7) (trace), m/z 328 (25%, M^+) and 177 (100, PhCF CF$_3^+$). (ii) Unchanged diphenylmethane (34.06 g, 0.203 mol, 90% recovered), b.p. 120 °C at 10 mmHg. (iii) A higher-boiling fraction (4.19 g), b.p. >120 °C at 10 mmHg, which was shown by g.l.c. to contain two components in the ratio 28 : 72. These components were separated by g.l.c. (2 m SE 30 at 145 °C) to give (1) (2,2,3,4,4,4-*hexafluoro*-1-*phenylbutyl*)*benzene* (4a) (1.17 g, 3.7 mmol, 9% on C$_3$F$_6$, 20.5% on alkane) (Found: C, 60.9; H, 4.1; F, 35.9%; M^+ 318. C$_{16}$H$_{12}$F$_6$ requires C, 60.4; H, 3.8; F, 35.8%; M, 318), b.p. 130 °C at 10 mmHg, m/z 318 (19%, M^+), 167 (100, C$_{13}$H$_{11}^+$), 165 (28, C$_{13}$H$_9^+$), 152 (14, C$_{12}$H$_8^+$), and 91 (14, C$_7$H$_7^+$),

n.m.r. bands for Ph$_2$CHCF$_2$CHFCF$_3$ at δ$_F$ + 4.6 (3 F, qd,

F$_f$, J_{cf} $\simeq$ J_{et} 11, J_{df} 6 Hz), -35.2 (2 F, mult F$_c$), and -131.4 (1 F, dsexd, F$_e$, J_{de} 44, J_{ce} 11, J_{be} 3 Hz) and δ_H (benzene ref.) $+0.14$ (10 H, mult, H$_\alpha$), -2.30 (1 H, ddquin, H$_d$, J_{cBd} 6 Hz), and -2.40 (1 H, ddd, H$_b$, J_{cAb} 25, J_{cBb} 13 Hz); and (ii) (2,2,3,4,4,4-*hexafluoro*-3-*phenylbutyl*)*benzene* (5a) (3.02 g, 9.5 mmol, 23% on C$_3$F$_6$, 53% on alkane) (Found: C, 60.4; H, 4.0; F, 35.6%; M^+, 318), b.p. 130 °C at 10 mmHg, m/z 318 (31%, M^+), 141 (100, C$_8$H$_7$F$_2^+$), and 91 (99, C$_7$H$_7^+$), n.m.r. bands for PhCH$_2$CF$_2$CFPhCF$_3$ at δ_F + 4.6 (3 F, td, F$_f$, J_{cf} 11.5, J_{df} 6.5 Hz), -30.3 (2 F, mult, F$_c$), and -101.4 (1 F, mult, F$_d$) and δ_H (benzene ref.) -0.14 (10 H, mult, H$_a$ and H$_e$) and $+3.98$ (2 H, ddd, H$_b$, J_{cAb} 20, J_{cBb} 17, J_{db} 4 Hz).

(b) *Autoclave reaction.* A mixture of hexafluoropropene (75.0 g, 0.50 mol) and diphenylmethane (252 g, 1.50 mol), heated *in vacuo* in an autoclave (*ca.* 500 cm³) in a rocking furnace at 250 °C (72 h), gave the products shown in the Table.

Reaction of Hexafluoropropene with the Butylbenzenes.—
(a) *n-Butylbenzene.* A mixture of hexafluoropropene (75.0 g, 0.50 mol) and n-butylbenzene (201.0 g, 1.50 mol), heated *in vacuo* in a rocked autoclave (*ca.* 500 cm³) at 250 °C (72 h), gave the following. (i) A highly volatile fraction (0.18 g, 3.2 mmol; M, 56) which was shown by i.r. spectroscopy to consist of propene, silicon tetrafluoride, and unidentified compounds. (ii) A mixture of the *cis-* and *trans*-isomers of compound (6) (0.78 g, 2.6 mmol, 1%). (iii) A non-volatile fraction (257.8 g). (iv) A carbonaceous residue (*ca.* 17 g) which was not examined further.

The non-volatile fraction was distilled (spinning-band column) to give the following: (1) a mixture (42.6 g), b.p. <183 °C; (ii) unchanged n-butylbenzene (168.8 g, 1.26 mol, 84% recovered), b.p. 183 °C; (iii) a mixture (46.4 g), b.p. >183 °C. Mixture (i) was shown by g.l.c. (3 m TXP at 65 °C) to contain five major components and a number of minor components. The major components were separated by g.l.c. (7 m TXP at 85 °C and 6 m PEGA at 120 °C) to give: 1,1,1,2,3,3-hexafluoropentane (9) (2.2 g, 12.2 mmol, 2.5% on C$_3$F$_6$) as shown by a comparison of its n.m.r. and mass spectra with those of an authentic sample; [2,10] *trans*-1,1,2-trifluoro-3-methyl-2-trifluoromethylcyclobutane (8a) (7.8 g, 40.6 mmol, 8%) as shown by a comparison of its n.m.r. and mass spectra with those reported; [5] *cis*-1,1,2-trifluoro-3-methyl-2-trifluoromethylcyclobutane (8a) (7.8 g, 40.6 mmol, 8%) as shown by a comparison of its n.m.r. and mass spectra with those reported; [5] toluene (1.8 g, 19.6 mmol, 1% on alkane); and a mixture of 2,2,3,4,4,4-hexafluorobutylbenzene (4c) and 2,3,3-trifluoro-2-trifluoromethylpropylbenzene (11) (20.8 g, 85.9 mmol, 17% on C$_3$F$_6$, 36% on alkane) in the ratio 98 : 2 (n.m.r.) as shown by a comparison of their n.m.r. and mass spectra with those reported. [11]

The fraction (46.4 g), b.p. >183 °C, was shown by g.l.c. (2 m PEGA at 140 °C) to contain twelve components only two of which were major; these major components were separated by g.l.c. (6 m PEGA at 150 °C) and were identified as (2,2,3,4,4,4-*hexafluoropropyl*)*butylbenzene* (isomer 1) (4b) (12.1 g, 42.6 mmol, 8.5% on C$_3$F$_6$, 17.5% on alkane) (Found: C, 55.2; H, 5.0; F, 40.5%; M^+, 284. C$_{13}$H$_{14}$F$_6$ requires C, 54.9; H, 5.0; F, 40.1%; M, 284), b.p. 209 °C, m/z 284 (8%, M^+), 133 (33, C$_{10}$H$_{13}^+$), 91 (100, C$_7$H$_7^+$), and 43 (19, C$_3$H$_7^+$), n.m.r. bands for PhCH(CH$_2$CH$_2$CH$_3$)CF$_2$CHFCF$_3$ at δ_F + 3.3 (3 F, qd, F$_h$, J_{AB-h} $\simeq$ J_{gh} 10, J_{fh} 6 Hz), -39.0 and -43.9 (2 F, AB mult, F$_A$ and F$_B$, J_{AB} 260 Hz), and -133.2

21.5% on alkane) (Found: C, 55.1; H, 4.9; F, 40.5%; M^+, 284), b.p. 211 °C, m/z 284 (14%, M^+), 140 (6, C$_8$H$_6$F$_2^+$), 133 (39), 91 (100), and 43 (18), n.m.r. bands at δ_F + 3.5 (3 F, qd, F$_h$, J_{AB-h} $\simeq$ J_{gh} 10, J_{fh} 6 Hz), -36.1 (2 F, AB mult, F$_A$ and F$_B$), and -134.6 (1 F, d sex, F$_g$, J_{fg} 43, J_{hg} $\simeq$ J_{AB-g} 10 Hz), and δ_H (SiMe$_4$ ref.) 0.50 (3 H, t, H$_e$ J_{de} 6 Hz), 0.84 (2 H, mult, H$_d$), 1.60 (2 H, q, H$_c$, J_{bc} $\simeq$ J_{dc} 8 Hz), 2.92 (1 H, tt, H$_b$, J_{AB-b} 16, J_{bc} 8 Hz), 4.36 (1 H, dtq, H$_f$, J_{gf} 43, J_{AB-f} 11, J_{Hf} 6 Hz), and 6.90 (5 H, mult, H$_a$).

The alkane when heated alone at 270 °C (72 h) was recovered unchanged.

(b) *s-Butylbenzene.* A mixture of hexafluoropropene (75.0 g, 0.50 mol) and s-butylbenzene (201.0 g, 1.50 mol), heated *in vacuo* in a rocked autoclave (*ca.* 500 cm³) at 250 °C (72 h), gave the following. (i) A highly volatile fraction (0.42 g, 9.8 mmol; M, 43) which was shown by i.r. spectroscopy to consist of ethylene, silicon tetrafluoride, and unidentified components. (ii) A mixture of *cis-* and *trans*-(6) (0.84 g, 2.8 mmol, 1%). (iii) A non-volatile fraction (247.4 g). (iv) A residue of carbonaceous material (*ca.* 27 g) which was not examined further.

The non-volatile fraction was distilled (spinning-band column) to give the following. (i) A mixture (32.8 g), b.p. <173 °C. (ii) Unchanged s-butylbenzene (164.4 g, 1.23 mol, 82% recovered), b.p. 173 °C. (iii) A mixture (50.2 g), b.p. <173 °C. The mixture b.p. <173 °C was shown by g.l.c. (3 m TXP at 65 °C) to contain four major components which were separated by g.l.c. (7 m TXP at 80 °C and 6 m PEGA at 130 °C) to give the following. A mixture (6.0 g) of 1,1,1-trifluoro-2-methylbutane (13) (5.3 g, 41.9 mmol, 8% on C$_3$F$_6$) and 1,1-difluoro-2-methylbut-1-ene (14) (0.7 g, 6.5 mmol, 1%), b.p. 44 °C, identified by a comparison of their n.m.r. and mass spectra with those of authentic samples; [12] 1,1,1,2,3,3-hexafluoropentane (0.8 g, 4.4 mmol, 1%) (9), 1,1,2-trifluoro-2-trifluoromethylcyclobutane (8b) (9.0 g, 50.6 mmol, 10%), identified by a comparison of its n.m.r. and mass spectra with those of an authentic sample; [5] and a mixture of 1,2,2,2-tetrafluoroethylbenzene (1) (12.0 g, 67.4 mmol, 13.5% on C$_3$F$_6$, 25% on alkane), 2,2,2-trifluoroethylbenzene (15) (2.1 g, 13.1 mmol, 3% on C$_3$F$_6$, 5% on alkane), and ethylbenzene (0.5 g, 4.5 mmol, 1.5% on alkane). Compound (15) was identified by a comparison of its n.m.r. and mass spectra with those reported. [13] The fraction, b.p. >173 °C, was shown by g.l.c. (2 m PEGA at 120 °C) to contain 16 components and the three major components were separated by g.l.c. (6 m PEGA at 130 °C) to give the following. (2,2,3,4,4,4-Hexafluoro-1-methylbutyl)benzene (isomer 1) (4d) (5.7 g, 22.3 mmol 4.5% on C$_3$F$_6$, 8% on alkane) as shown by a comparison of its n.m.r. and mass spectra with those reported; [9,11] (2,2,3,4,4,4-hexafluoro-1-methylbutyl)benzene [9,11] (isomer 2) (4d) (7.9 g, 30.8 mmol, 6% on C$_3$F$_6$, 11.5% on alkane); and a 1 : 1 mixture of cis- and trans-1-*ethyl*-2,2,3-*trifluoro*-1-*methyl*-3-*trifluoromethylindan* (12) (7.2 g, 25.5 mmol, 5% on C$_3$F$_6$, 9.5% on alkane) (Found: C, 55.4; H, 4.5; F, 40.6%; M^+, 282. C$_{13}$H$_{12}$F$_6$ requires C, 55.3; H, 4.3; F, 40.4%; M, 282), b.p. 217 °C, m/z 282 (41%, M^+), 267 [20, $(M - \text{Me})^+$], 253 [100, $(M - \text{Et})^+$], 117 (48, C$_9$H$_9^+$), and 91 (26, C$_7$H$_7^+$), n.m.r. bands at δ_F + 3.5 (6 F, mult, F$_f$ in both isomers), -38.0 and -40.7 (2 F, AB mult, F$_A$ and F$_B$ in one isomer, J_{AB} 250 Hz), -40.7 (2 F, mult, F$_A$ and F$_B$ in second isomer), -74.6 (1 F, mult F$_e$ in one isomer), and -75.5 (1 F, mult, F$_e$ in second isomer) and δ_H (SiMe$_4$ ref.) 0.9—1.0 (8 H, complex, H$_b$ + H$_c$ + H$_d$) and 6.80 (4 H, mult. H$_a$).

following. (i) A low boiling-mixture (0.16 g, 2.8 mmol; M, 58) of propene, silicon tetrafluoride, and unidentified components (i.r.). (ii) A mixture of *cis*- and *trans*- (6) (0.66 g, 2.2 mmol, 1%). (iii) A non-volatile fraction (253.8 g). (iv) A carbonaceous residue (*ca.* 21 g) which was not examined further.

The non-volatile fraction was distilled (spinning band column) to give the following. (i) A fraction (18.6 g), b.p. <173 °C; (ii) a fraction (187 g), b.p. 173 °C; and (iii) a fraction (48.2 g) b.p. >173 °C. Fraction (i) was shown by g.l.c. (2 m PEGA at 60 °C) to contain four major components which were separated by g.l.c. (6 m PEGA at 65 °C and 120 °C) to give: *trans*-1,1,2-trifluoro-3-methyl-2-trifluoromethyl-cyclobutane (8a) (6.4 g, 33.3 mmol, 7% on C_3F_6); *cis*-1,1,2-trifluoro-3-methyl-2-trifluoromethylcyclobutane (8a) (6.4 g, 33.3 mmol, 7%); toluene (1.4 g, 15.2 mmol, 6.5% on alkane); and 1,2,2,2-tetrafluoroethylbenzene (1) (2.2 g, 12.4 mmol, 2.5% on C_3F_6, 5.5% on alkane). The intermediate fraction was shown by g.l.c. (2 m PEGA at 120 °C), n.m.r. spectroscopy, and mass spectroscopy to consist of unchanged isobutyl-benzene (170.4 g, 1.27 mol, 85% recovered) and 2,2,3,4,4,4-hexafluorobutylbenzene (4c) (16.6 g, 68.6 mmol, 14% on C_3F_6, 30% on alkane), while the higher-boiling fraction contained 14 components (g.l.c.; 2 m PEGA at 140 °C) from which the major component was separated by g.l.c. (6 m PEGA at 160 °C) and identified as (3,3,4,5,5,5-*hexafluoro*-2,2-*dimethylpentyl*)*benzene* (16) (14.6 g, 51.4 mmol, 10% on C_3F_6, 22% on alkane) (Found: C, 54.9; H, 4.6; F, 39.6%; M^+, 284. $C_{13}H_{14}F_6$ requires C, 54.9; H, 5.0; F, 40.1%; M, 284), m/z 284 (5%, M^+), 117 (5, $C_9H_9^+$), 91 (100, $C_7H_7^+$), 78 (10, $C_6H_6^+$), and 65 (8, $C_5H_5^+$), n.m.r. bands for PhCH$_2$CMe$_2$CF$_2$CHFCF$_3$ with labels a, b, c, AB, d, e, f at δ_F + 3.5 (3 F, qd, F$_f$, $J_{ef} \simeq J_{AB-f}$ 10, J_{df} 6 Hz), −38.9 and −46.0 (2 F, AB mult, F$_A$ + F$_B$, J_{AB} 268 Hz), and −128.0 (1 F, d mult, F$_e$, J_{de} 44 Hz) and δ_H (SiMe$_4$ ref.) 0.64 (6 H, s, H$_c$), 2.38 (2 H, s, H$_b$), 4.56 (1 H, dd, mult, H$_d$), and 6.82 (5 H, mult, H$_a$).

The alkane when heated alone at 270 °C (72 h) was recovered unchanged.

Reaction of Hexafluoropropene with Benzyl Alcohol.—A mixture of hexafluoropropene (2.25 g, 15.0 mmol) and benzyl alcohol (4.86 g, 45.0 mmol), heated *in vacuo* in a Pyrex ampoule (*ca.* 300 cm³) at 240 °C (72 h), gave (i) unchanged hexafluoropropene (1.44 g, 9.6 mmol, 64% recovered), (ii) a non-volatile fraction (5.11 g), and (iii) a charred residue (*ca.* 0.5 g) which was not examined further. The non-volatile fraction was shown by g.l.c. (2 m PEGA at 180 °C) to contain nine compounds (A—I, ratio 10 : 7 : 42 : 3 : 3 : 17 : 5 : 2 : 11) which were examined by g.l.c. (as above)–mass spectrometry; components A—E were identified as toluene (0.51 g, 5.5 mmol, 12% on alcohol), 2,2,3,4,4,4-hexafluorobutylbenzene (4c) (0.36 g, 1.5 mmol, 28% on C_3F_6; 3.5% on alcohol), benzaldehyde (2.14 g, 20.0 mmol, 46% on alcohol), unchanged benzyl alcohol (0.15 g, 1.4 mmol, 3% recovered), and 2,2,3,4,4,4-hexafluoro-3-phenylbutanol (5b) (0.15 g, 0.58 mmol, 11% on C_3F_6, 1.5% on alcohol) (Found: M^+, 258. Calc. for $C_{10}H_8F_6O$: M, 258), m/z 258 (19%, M^+), 177 (100, $C_8H_5F_4^+$), 127 (36, $C_7H_5F_2^+$), 81 (7, CF$_2$CH$_2$OH$^+$), 79 (23, CF$_2$CHO$^+$), and 77 (27, $C_6H_5^+$), n.m.r. bands for CF$_3$CFPhCF$_2$CH$_2$OH with labels a, b, c, d, e, f at δ_F + 4.0 (3 F, td, F$_a$, J_{da} 11.0, J_{ba} 6.0 Hz), −32.4 (2 F, mult, F$_d$) and −102.6 (1 F, mult, F$_b$) and δ_H (SiMe$_4$ ref.) 6.95 (5 H, mult, H$_c$), 4.36 (1 H, broad, H$_f$), and 3.75 (2 H, mult, H$_e$).

Component G was tentatively identified as 2,2,3,4,4,4-hexa-fluoro-1-phenylbutanol (4e) (0.26 g, 1.0 mmol, 18% on C_3F_6, 3% on alcohol) (Found: M^+, 258), but components F, H, and I were not identified.

The alcohol (2.16 g, 20.0 mmol) when heated alone in a Pyrex ampoule (*ca.* 100 cm³) at 240 °C (72 h) gave a mixture (2.16 g) of four compounds (ratio 6 : 6 : 88 : 6) as shown by g.l.c. (2 m PEGA at 180 °C) and n.m.r. spectroscopy which were identified as toluene (0.11 g, 1.20 mmol, 6% on initial alcohol), benzaldehyde (0.13 g, 1.2 mmol, 6%), unchanged benzyl alcohol (1.90 g, 17.6 mmol, 88% recovered), and water (0.02 g, 1.2 mmol, 6%).

Reaction of Hexafluoropropene with Benzyl Methyl Ether.—A mixture of hexafluoropropene (2.25 g, 15.0 mmol) and the ether (5.49 g, 45.0 mmol), heated *in vacuo* in a Pyrex ampoule (*ca.* 300 cm³) at 230 °C (72 h), gave (i) unchanged hexafluoro-propene (1.04 g, 6.9 mmol, 46% recovered), (ii) a higher-boiling fraction (4.14 g), and (iii) a carbonaceous residue (*ca.* 2.5 g) which was not examined further. The higher-boiling fraction was shown by g.l.c. to contain eight minor components (3% of fraction) and four major components (ratio 12 : 6 : 73 : 9) which were identified by g.l.c. (2 m PEGA at 130 °C)–mass spectrometry as toluene (0.50 g, 5.4 mmol, 23% on ether), 2,2,3,4,4,4-hexafluorobutylbenzene (4c) (0.25 g, 1.0 mmol, 12.5% on C_3F_6, 5% on ether), unchanged ether (3.02 g, 24.7 mmol, 55% recovered), and benzaldehyde (0.37 g, 3.5 mmol, 17% on ether).

The ether (2.44 g, 20.0 mmol), heated alone *in vacuo* in a Pyrex ampoule (*ca.* 100 cm³) at 240 °C (72 h) gave (i) dimethyl ether (0.03 g, 0.8 mmol, 8%) and a mixture (2.38 g) of toluene (0.13 g, 1.4 mmol, 7% on initial ether), unchanged benzyl methyl ether (2.10 g, 17.2 mmol, 86% recovered), and benz-aldehyde (0.15 g, 1.4 mmol, 7%) in the ratio 7 : 86 : 7 as shown by g.l.c. (2 m PEGA at 130 °C).

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