Fluoro-olefin Chemistry. Part IX.[1] Thermal Insertion of Hexafluoropropene into Carbon–Hydrogen Bonds in Alkylbenzenes †

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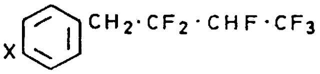
The thermal reactions (*ca.* 250 °C) of the alkylbenzenes $ArCH_2R$ (Ar = Ph, R = H, Me, or Et; Ar = *p*-ClC_6H_4, R = H; Ar = *p*-MeC_6H_4, R = H) with hexafluoropropene give mainly the 1 : 1 adducts $ArCHR\cdot CF_2\cdot CHF\cdot CF_3$, together with smaller amounts of the 1 : 1 adducts $ArCHR\cdot CF(CF_3)\cdot CHF_2$, 1-alkyl-2,2,3-trifluoro-3-trifluoromethylindanes, 1-alkyl-2,3,3-trifluoro-2-trifluoromethylindanes, and minor amounts of other products. Reaction at high pressure (autoclaves) favours 1 : 1 adduct formation whereas at lower pressure (tubes) indane formation is favoured. The reaction with cumene does not afford 1 : 1 adducts, the major products being 1,2,2,2-tetrafluoroethylbenzene, 1,1-difluoro-2-methylpropene, and the cyclobutane, $\overline{CF_2\cdot CMe_2\cdot CF(CF_3)\cdot CF_2}$; indanes are also formed in this reaction. Chlorination, bromination, and nitration of the 1 : 1 adduct $PhCH_2\cdot CF_2\cdot CHF\cdot CF_3$ gives the corresponding *ortho*- and *para*-substituted derivatives in the ratios 47 : 53, 20 : 80, and 0 : 100, respectively.

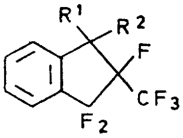
THE reaction of hexafluoropropene with toluene has been briefly reported[2] to give 2,2,3,4,4,4-hexafluorobutylbenzene (Ia) at 450 °C, but no proof of structure was given. More recently the *peroxide-initiated* reactions of hexafluoropropene with toluene, ethylbenzene, and cumene [di-t-butyl peroxide; molar ratio alkylbenzene : olefin : peroxide 1 : 1.5 : 1; 130—160 °C (6 h); neat or in $CF_2Cl\cdot CFCl_2$] have given[3] not only the expected polyfluoroalkylbenzenes, in low yield [(Ia) (16—22%) and

$PhCHR\cdot CF_2\cdot CHF\cdot CF_3$

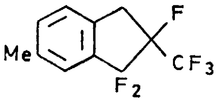
(I) a; R = H
b; R = Me
d; R = Et



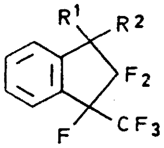
(I) e; X = Cl
f; X = Me



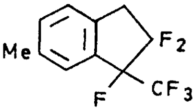
(IV) a; R¹ = R² = H
b; R¹ = H, R² = Me
c; R¹ = R² = Me



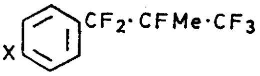
(IVf)



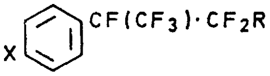
(II) a; R¹ = R² = H
b; R¹ = H, R² = Me
c; R¹ = R² = Me



(IIf)



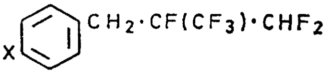
(V) a; X = H
f; X = Me



(VI) a; X = H, R = Me
b; X = H, R = Et
f; X = Me, R = Me

$PhCHR\cdot CF(CF_3)\cdot CHF_2$

(III) a; R = H
b; R = Me



(III) e; X = Cl
f; X = Me

$PhCF_2\cdot CF_2\cdot CHF\cdot CF_3$

(VII)

$PhCHF\cdot CF_3$

(VIII)

$PhCH_2\cdot CH_2\cdot CF(CF_3)\cdot CHF_2$

(IX)

$PhCH_2\cdot CH_2\cdot CF_2\cdot CHF\cdot CF_3$

(X)

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† Presented in part at the 7th International Fluorine Symposium, Santa Cruz, 1973 (R. N. Haszeldine, R. Rowland, and J. L. Moorfield).

[1] Part VIII, H. E. Evans, R. Fields, R. N. Haszeldine, and M. Illingworth, *J.C.S. Perkin I*, 1973, 649.

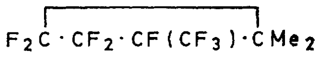
[2] I. L. Knunyants and E. Ya. Perova, *Bull. Acad. Sci., U.S.S.R.*, 1966, 1623.

[3] H. Kimoto, H. Muramatsu, and K. Inukai, *Chem. Letters*, 1974, 791.

(Ib) (2—3%)], but additionally the polyfluoroalkylindanes (IIa) (11—15%), (IIb) (11—14%), and (IIc) (6—7%), together with large amounts of higher boiling material.

$CF_2{:}CMe_2$

(XI)

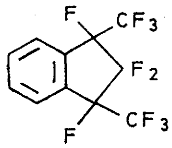


$F_2C\cdot CF_2\cdot CF(CF_3)\cdot CMe_2$

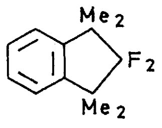
(XII)

$PhCF(CF_3)\cdot CF_2\cdot CHF\cdot CF_3$

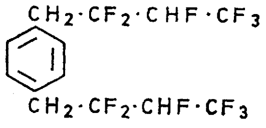
(XIII)



(XIV)



(XV)



(XVI)

We now report results on the *thermal* reactions of hexafluoropropene with a series of alkylbenzenes [4] *in the absence of added initiator*. These thermal reactions form part of a more general study of the thermal and photochemical reactions of hexafluoropropene with organic compounds.[5,6] The conditions and the results are shown in Table 1; all the reactions were carried out with a 3 : 1 molar ratio of alkylbenzene to hexafluoropropene and a reaction period of 3 days.

TABLE 1

Reactions of hexafluoropropene with alkylbenzenes

Alkyl-benzene	Reaction vessel	Temp. (°C)	Recovered reactants (%)		Products (%)								
			Olefin	Alkyl-benzene	(I)	(II)	(III)	(IV)	(V)	(VI)	(VII)	(VIII)	Others
PhMe	Tube	300	50	84	(Ia) 79	(IIa) 6	(IIIa) 2.5 [b]	(IVa) 4	(Va) 1.5	(VIa) 1	3		
PhMe	Tube [a]	300	63	87	(Ia) 71	(IIa) 21.5 [b]	(IIIa) 2.5	(IVa) [b]	(Va) 2	(VIa) 1.5	1.5		
PhMe	Autoclave	250	35	79	(Ia) 89.5	(IIa) Trace	(IIIa) 8.5	(IVa) Trace	(Va) 0.5	(VIa) 1			
PhMe	Autoclave [c]	250	3	67	(Ia) 90	(IIa) Trace	(IIIa) 9	(IVa) Trace	(Va) Trace	(VIa) Trace			
PhEt	Tube	250	65	87	(Ib) 46 [d]	(IIb) 17 [e]	(IIIb) 4.5	(IVb) 3		(VIb) 4		2	(IX) 2.5, (X) 5, others 16
PhEt	Autoclave	250	43	80	(Ib) 88 [d]	(IIb) 2.5 [e]	(IIIb) 0.5	(IVb) 0.5		(VIb) Trace		Trace	(IX) and (X) traces, others 8
$PhCHMe_2$	Tube	250	33	85		(IIc) 15		(IVc) 2				41.5 [f]	(XI) 20,[f] (XII) 21.5,[f] (XIII) and (XIV) traces
$PhCHMe_2$	Autoclave	250	21	86		(IIc) 1.5		(IVc) Trace				49 [f]	(XII) 46,[f] (XIII) and (XIV) traces, (XV) 3 [f]
$PhPr^n$	Tube	250	55	*g*	(Id) *ca.* 10 [h]								Complex mixture 90
$PhPr^n$	Autoclave [i]	250	22	74	(Id) 97 [h]								Others, 3
$PhCMe_3$	Tube	250	90	49									Tar
p-ClC_6H_4Me	Tube	250	30	77	(Ie) 91		(IIIe) 4.5						Four unidentified components 4.5
p-MeC_6H_4Me	Tube	280	65	88	(If) 80	(IIf) 1	(IIIf) 1.5	(IVf) 1.5	(Vf) 1.5	(VIf) 1			(XVI) 5, unknown $C_{11}H_8F_6$ 2

[a] Low-pressure reaction (12 mmol reactants in 300 cm³ tube); all other tube reactions 60 mmol in 300 cm³ tube. [b] As a mixture of indanes (IIa) and (IVa). [c] High-pressure reaction (4 mol in 1 dm³ autoclave; remainder 2 mol in 1 dm³ autoclave, except $PhPr^n$). [d] As two separated stereoisomers (ratio *ca.* 52 : 48). [e] As two stereoisomers. [f] Yields calculated on basis that C_3F_6 (1 mol) $\longrightarrow$ (VIII) (1 mol) + [(XI) + (XII) + (XVI)] (1 mol). [g] Not determined. [h] As two separated stereoisomers (ratio *ca.* 46 : 54). [i] Lower-pressure reaction (1.33 mol in 1 dm³ autoclave).

The majority of the products are considered to arise *via* reactions of intermediate benzyl radicals (XVII) initially formed either by homolytic fission of benzylic C–H bonds in the alkylbenzenes [equation (i)] or by interaction of thermally excited hexafluoropropene molecules with benzylic hydrogen atoms [equation (ii)]. The latter initiation is probable because of the relatively low temperature (*ca.* 250 °C) required for reaction to occur.

Traces of 1*H*,2*H*-hexafluoropropane (XVIII) were detected in the unchanged olefin fractions from many of the reactions, together with small amounts of hexafluoro-1,2-bistrifluoromethylcyclopropane (XIX) formed by dimerisation of hexafluoropropene [equation (iii)]. The 1 : 1 adducts (I) and (III) and the indanes (II) and (IV) then arise *via* bidirectional benzyl radical attack on hexafluoropropene (Scheme 1).

$$ArCHR^1R^2 \xrightarrow{\text{heat}} \underset{\text{(XVII)}}{Ar\dot{C}R^1R^2} + H\cdot \qquad \text{(i)}$$

$$ArCHR^1R^2 + [C_3F_6]^* \longrightarrow \text{(XVII)} + C_3HF_6\cdot \longrightarrow \underset{\text{(XVIII)}}{CF_3\cdot CHF\cdot CHF_2} \qquad \text{(ii)}$$

The thermal reaction of toluene with ethylene at 400 °C gives the telomers $PhCH_2\cdot[C_2H_4]_nH$ (n = 1, 2, or 3) and a similar mechanism involving benzyl radicals was proposed.[7] Formation of indane derivatives in low yields by radical reactions has also been reported [8] and

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[4] A. J. Mitchinson, Ph.D. Thesis, Manchester, 1973.

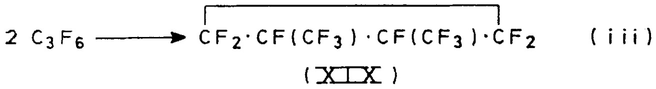
[5] R. N. Haszeldine and R. Rowland, U.S.P. 3,816,286/1947.

[6] T. Davies, R. N. Haszeldine, J. L. Moorfield, C. M. Raynor, R. Rowland, A. E. Tipping, G. Tyrrell, and B. G. Willoughby, unpublished results.

[7] E. Oltay, J. M. L. Penninger, and H. Maatman, *Angew. Chem. Internat. Edn.*, 1972, **11**, 918.

[8] V. C. R. McLoughlin and J. Thrower, *Tetrahedron*, 1969, **25**, 5921; E. L. Zaitseva, T. V. Rozantseva, I. I. Chicherina, and A. Ya. Yakubovich, *J. Org. Chem.* (*U.S.S.R.*), 1971, **7**, 2647; K. Fujita, K. Yamamoto, and T. Shono, *Nippon Kagaku Kaishi*, 1973, 1933.

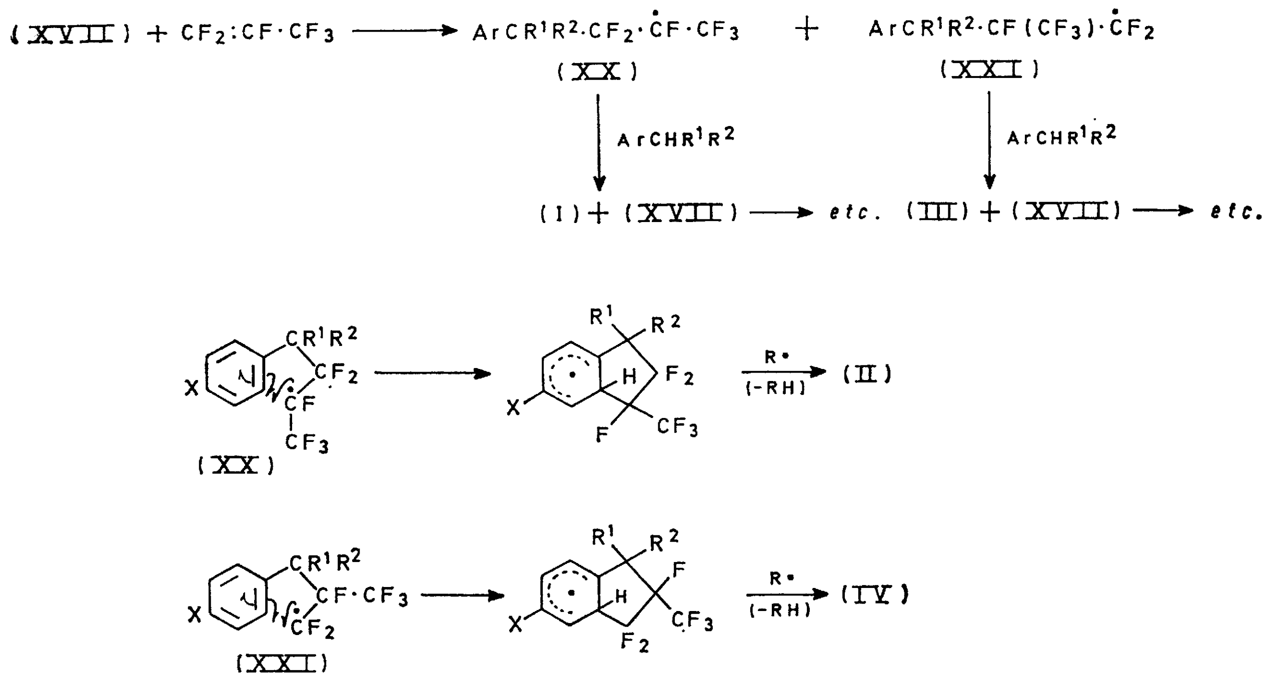
the mechanism shown in Scheme 1 was put forward to explain the products (I) and (II) from the t-butyl peroxide-initiated reactions of hexafluoropropene with alkylbenzenes.[3]



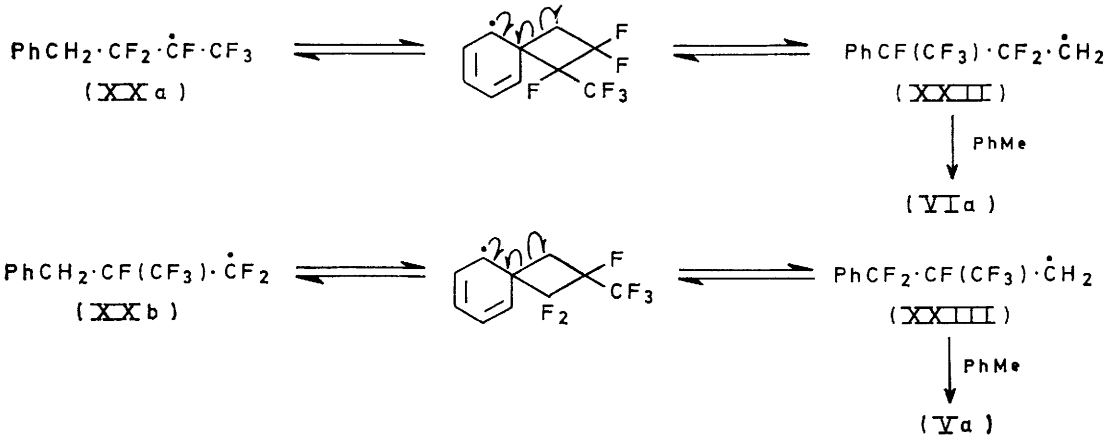
$$2\,C_3F_6 \longrightarrow \overline{CF_2\cdot CF(CF_3)\cdot CF(CF_3)\cdot CF_2} \quad \text{(iii)}$$

(XIX)

The 1 : 1 adducts (Ib and d) were formed in both cases as two stereoisomers in the ratio *ca.* 50 : 50; these arise because of the presence of two asymmetric carbon atoms in the molecule $PhCHR\cdot CF_2\cdot CHF\cdot CF_3$ (R = Me or Et). Similarly the indane (IIb) was present as two diastereoisomers, but although two diastereoisomers are also possible for the indane (IVb) only one was detected, possibly that in which the adjacent bulky CH_3 and CF_3 groups are *trans*.

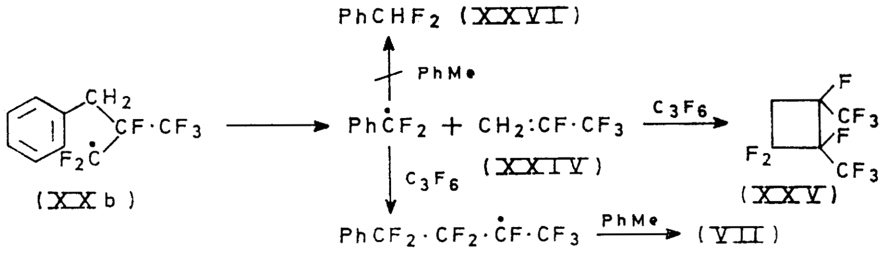


SCHEME 1 R· is any radical present in the system



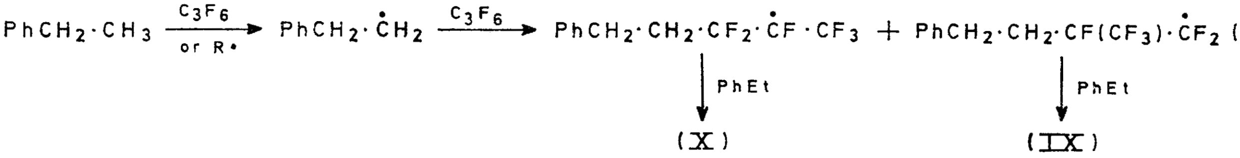
SCHEME 2

The other 1 : 1 adducts (V) and (VI) formed in the toluene reactions and the ethylbenzene and *p*-xylene tube reactions probably arise *via* rearrangement of the intermediate radicals (XX) and (XXI) as shown for the toluene adducts (Va) and (VIa) in Scheme 2. The indanes (II) and (IV) may arise in part *via* cyclisation of radicals of type (XXII) and (XXIII). The remaining product (VII) isolated from the toluene tube reactions possibly arises *via* decomposition of radical (XXb) (Scheme 3). However, if this mechanism is correct it is surprising that difluoromethylbenzene (XXVI) and products derived from similar breakdown of the major intermediate radical (XXa), *e.g.* $PhCHF\cdot CF_3$ (VIII), were not detected; compound (VIII) was found in the products from the ethylbenzene and cumene reactions. Nor was the olefin (XXIV) or its cyclodimer with hexafluoropropene (XXV) detected, although if formed they would be in such small amounts that they may well have remained undetected in the recovered olefin fraction.

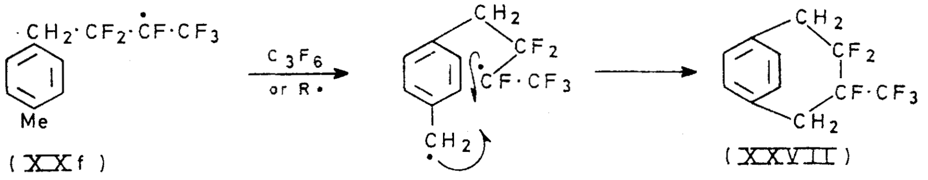


SCHEME 3

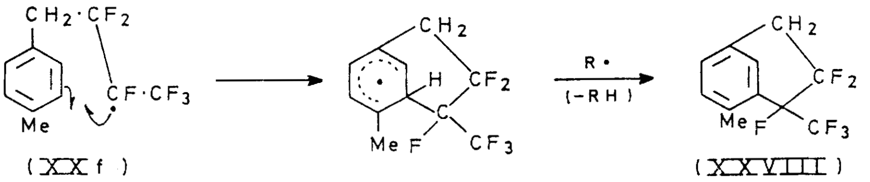
The ethylbenzene reactions also, surprisingly, gave the 1 : 1 adducts (IX) and (X), albeit in low yield, derived from abstraction of a β-hydrogen atom [equation (iv)]. A small amount of 1,2,2,2-tetrafluoroethylbenzene (VIII) was detected in the products; its formation is discussed later.



The *p*-xylene reaction was similar to the toluene reaction in that the major product was the 1 : 1 adduct (If), and the 1 : 1 adducts (IIIf), (Vf), and (VIf) were also formed. However, some of the 1 : 1 adduct (If) reacted further at the free methyl group to give the 2 : 1 adduct (XVI), and three products of formula $C_{11}H_8F_6$, *i.e.* 1 : 1 adducts — H_2, were detected. Two of these were the indanes (IIf) and (IVf), but the third cannot be an indane. The mass spectra of all the indanes detected in the present reactions showed relatively strong parent ion peaks (*ca.* 50%), but in the spectrum of the unknown compound the parent ion peak was the base peak. It is possible that the unknown compound has structure (XXVII) or (XXVIII), formed *via* (XXf) [equations (v) and (vi)]. This is considered less likely, however, because such compounds were not detected in the products from the reactions of the other alkylbenzenes.



(v)



(vi)

The reaction of hexafluoropropene with cumene was different from the other reactions in that 1 : 1 adducts were not found. The major products in both autoclave and tube reactions were the polyfluoroalkylbenzene (VIII) and the cyclobutane (XII), but the tube reaction also gave the olefin (XI) as a major product. These compounds are considered to arise *via* intermediate cumyl radicals as shown (Scheme 4). The olefin (XI) has been prepared previously by reduction with lithium aluminium hydride of the olefin $CF_2Cl{\cdot}CMe{:}CH_2$.[9]

Although the indane (IIc), arising *via* cyclisation of radical (XXIX), was also formed, the favoured reaction is decomposition of the radical (XXIX). This decomposition is probably a direct result of the methyl hydrogen atoms in radical (XXIX) hindering the chain-transfer step to give the adduct (Ic); also the decomposition would relieve steric congestion at the benzylic carbon atom. The detection of a small amount of compound (VIII) in the ethylbenzene reactions indicates that one methyl group in the benzylic position of the intermediate radical (XX) causes sufficient steric congestion to allow decomposition of the intermediate radical to compete with chain transfer and cyclisation.

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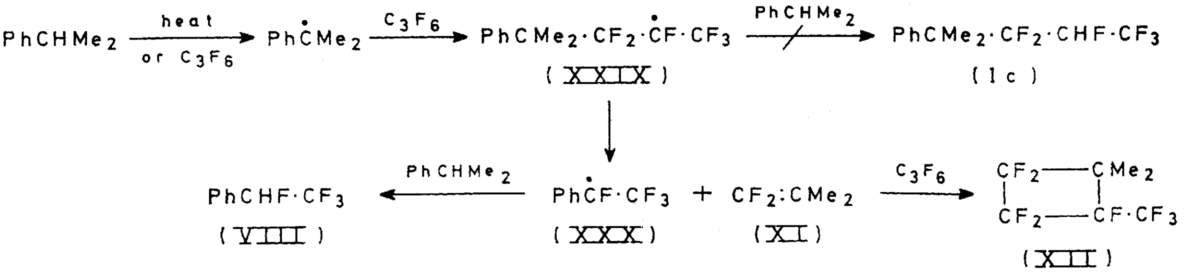
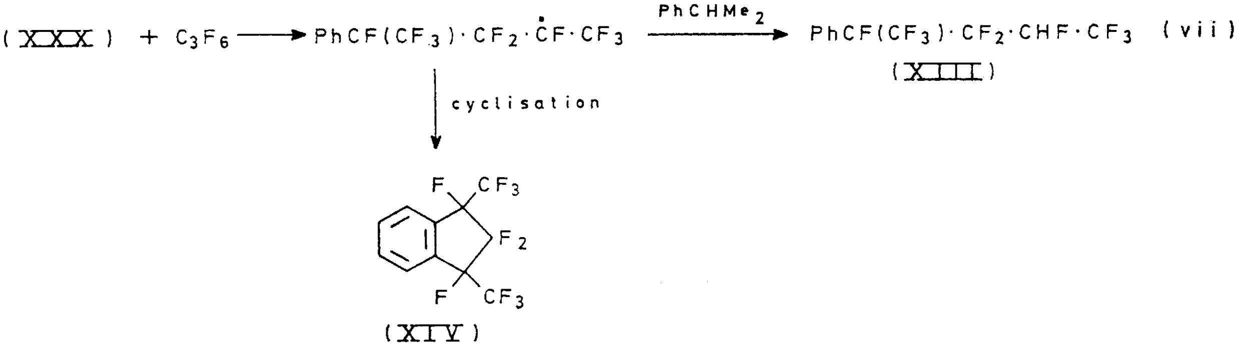
[9] R. S. Corley, S. G. Cohen, M. S. Simon, and H. T. Woloskinski, *J. Amer. Chem. Soc.*, 1956, **78**, 2608.

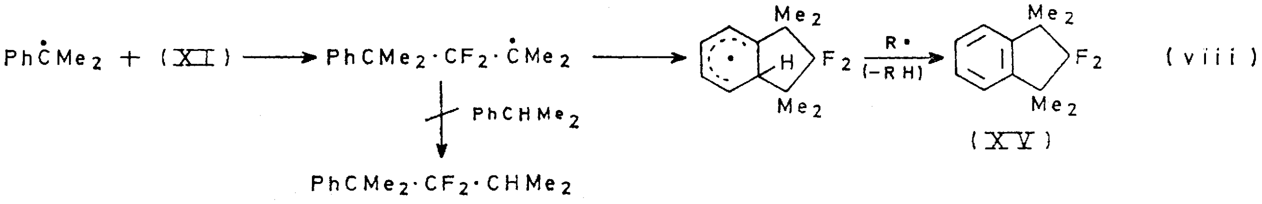
Compounds (XIII) and (XIV), formed in trace amounts, involve further reactions of the tetrafluorobenzyl radical (XXX) [equation (vii)]. The indane (XV) formed in the autoclave reaction arises *via* cumyl radical attack on olefin (XI) [equation (viii)]. The only compound detected in the products which was formed *via* cumyl radical attack at the central carbon atom of hexafluoropropene was the indane (IVc) [equation (ix)]; however, it is possible that decomposition of the intermediate radical (XXIf) did occur to some extent, but the products were formed in too low a yield to be detected.



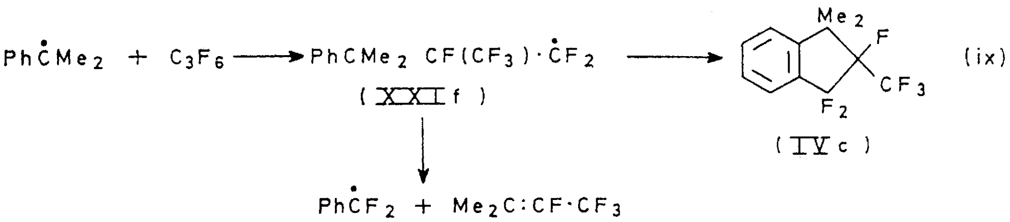
SCHEME 4



(vii)



(viii)



(ix)

In the attempted reaction of hexafluoropropene with t-butylbenzene most of the olefin was recovered (90%) and products were not detected apart from tar. The tube reactions with n-, iso-, and s-butylbenzenes were complex; the results obtained[10] from autoclave reactions will be reported later.

The results in Table 1 show that the autoclave reactions gave considerably higher yields of the 1 : 1 adducts (I) and (III) (88.5—99%) than the corresponding tube reactions (10—81.5%). The tube reactions in general gave higher yields of the indanes (II) and (IV) (up to 21.5%) than the autoclave reactions (up to 3%), but more complex mixtures of products were formed in the tube reactions. This can be explained on the basis of the higher pressures used in the autoclave reactions, which results in more hexafluoropropene being dissolved in the liquid phase thus allowing considerable reaction to occur in the liquid phase where chain-transfer reactions (excess of alkylbenzene present) of the intermediate radicals (XX) and (XXI) are favoured. In the lower-pressure tube reactions considerable reaction occurs in

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[10] R. N. Haszeldine, C. M. Raynor, and A. E. Tipping, unpublished results.

the vapour phase, where there is a deficiency of alkylbenzene, and so reactions of the intermediate radicals (XX) and (XXI), other than chain transfer, become more favoured. This is illustrated by the two tube reactions of toluene with hexafluoropropene; in the lower-pressure reaction the yield of adducts (I) and (III) is 73.5% and the yield of indanes (II) and (IV) is 21.5%, whereas in the higher-pressure reactions the yields are 81.5 and 10%, respectively.

One apparent anomaly is that the n-propylbenzene autoclave reactions, carried out at lower pressure than the other autoclave reactions, gave the highest yield of 1 : 1 adduct (I) (97%), but the tube reaction gave a much lower yield of adduct (I) (10%) than the yields obtained from the other alkylbenzenes (46—91%).

The present results show certain differences from the results reported [3] for the t-butyl peroxide-initiated reactions carried out at 160 °C. In the peroxide-initiated reactions bidirectional benzyl radical addition to hexafluoropropene was not detected and the major products were compounds boiling higher than the 1 : 1 adducts or indanes. These higher boiling products are possibly telomeric, a result of using an excess of hexafluoropropene rather than the 3 : 1 ratio of alkylbenzene to hexafluoropropene employed in the present work. The peroxide-initiated reactions were carried out in an attempt to maximise the yields of indanes (II),[3] but the present tube reactions, where indane formation is favoured, gave higher yields of indanes (from toluene, 21.5%; from ethylbenzene, 20%; from cumene, 17%) than the peroxide-initiated reactions (15, 14, and 7%, respectively). It is also surprising that although no 1 : 1 adduct (Ic) was found in the peroxide-initiated reaction with cumene, in agreement with the present results, the benzene derivative (VIII) was not reported, although this is the major aromatic product in the thermally initiated reaction.

Since the yields of adducts plus indanes were much lower in the peroxide-initiated reactions than in the present thermally initiated reactions it is possible that bidirectional benzyl radical attack on hexafluoropropene also occurred in the former reactions, but the products from central carbon atom attack in the olefin were present in too low a yield to allow their separation and identification. It would be expected that at the lower temperature employed in the peroxide-initiated reactions (160 °C) the benzyl radicals would be more selective in their attack on hexafluoropropene and so less radical attack on the central carbon atom of the olefin would occur than at the 250 °C employed in the present work.

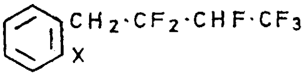
The ratios of bidirectional attack on hexafluoropropene by the various benzyl radicals are shown in Table 2. Radical attack on hexafluoropropene by the majority of radicals occurs to a major extent on the terminal CF_2 group, *e.g.* CF_3· (80%),[11] $(CF_3)_2N$· (96%),[12] but as the electrophilicity of the radical increases so does the proportion of radical attack on the central carbon atom, *e.g.*, MeS· 91 : 9, CF_3·S· 45 : 55;[13] Me_3Si· 95 : 5, Cl_3Si· 35 : 65.[14] As hydrogen atoms in the benzyl radical are successively replaced by electron-releasing alkyl groups so the electrophilicity of the radical decreases and the proportion of radical attack on the terminal CF_2 group of the olefin increases. It is also possible that the observed trend is due, at least in part, to increased steric hindrance to attack on the central olefinic carbon atom as the benzyl radical becomes more bulky. The apparent decreased electrophilicity of the *p*-chloro- and *p*-methylbenzyl radicals relative to the benzyl radical can be explained by resonance stabilisation of the lone electron by the chlorine atom and inductive stabilisation by the methyl group.

TABLE 2

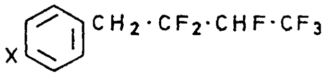
Benzyl radical attack on hexafluoropropene

Radical	Reaction	Ratio of radical attack CF_2	 $=CF·CF_3$
$PhCH_2$·	Tube	89	11
$PhCH_2$·	Autoclave	91	9
$Ph\dot{C}HMe$	Autoclave	99	1
$Ph\dot{C}Me_2$	Tube	98	2
$Ph\dot{C}Me_2$	Autoclave	>99	<1
$Ph\dot{C}HEt$	Autoclave	100	0
p-ClC_6H_4·CH_2·	Tube	95	5
p-MeC_6H_4·CH_2·	Tube	95	5

Ring-substitution Reactions.—Chlorination of the adduct (Ia) with chlorine and an iron catalyst gave the *o*-chloro-derivative (XXXI) (47%) and the *p*-chloro-compound (Ie) (53%), identical with the major product from the reaction of *p*-chlorotoluene with hexafluoro propene. A corresponding bromination gave the *o*-bromo-derivative (XXXII) (20%) and the *p*-bromo-compound (XXXIII) (80%); nitration, surprisingly, gave only the *p*-nitro-derivative (XXXIV) (98%).



(XXXI) X = Cl
(XXXII) X = Br



(Ie) X = Cl
(XXXIII) X = Br
(XXXIV) X = NO_2

It has been reported previously that *o* : *p*-substitution ratios for nitration,[15] chlorination,[16] and bromination [16] of toluene are 59 : 41, 60 : 40, and 41 : 69, respectively, and for t-butylbenzene they are 13 : 87,[15] 22 : 78,[16] and 8 : 92,[16] respectively. These results show the effect of steric hindrance on the *o* : *p* ratio in changing from a methyl to a tertiary butyl group. The *o* : *p* ratios for chlorination and bromination of the polyfluoroalkylbenzene (Ia) indicate that steric hindrance to *ortho* attack is greater than with toluene but less than with t-butylbenzene. The nitration result is anomalous in that exclusive *para*-nitration of (Ia) took place, whereas

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[11] J. Brown and R. N. Haszeldine, unpublished results.

[12] G. L. Fleming, R. N. Haszeldine, and A. E. Tipping, *J. Chem. Soc.* (*C*), 1971, 3833.

[13] J. F. Harris and F. W. Stacey, *J. Amer. Chem. Soc.*, 1961, **83**, 840.

[14] C. J. Attridge, Ph.D. Thesis, Manchester, 1967.

[15] P. B. D. de la Mare and J. H. Ridd, 'Aromatic Substitution: Nitration and Halogenation,' Butterworths, London, 1959.

[16] P. B. D. de la Mare, J. T. Harvey, M. Hassan, and S. Varma, *J. Chem. Soc.*, 1956, 2756.

for toluene and t-butylbenzene the *o* : *p* nitration ratios are intermediate between those found for chlorination and for bromination; the reason for this anomaly is not apparent.

EXPERIMENTAL

Care was taken to ensure the purity of reactants, the exclusion of peroxides, *etc.*, and volatile reactants and products were manipulated in a vacuum system to avoid contamination with air or moisture. Tube reactions were carried out *in vacuo* in Pyrex tubes (*ca.* 300 cm^3) and autoclave reactions were carried out *in vacuo* in Hastelloy autoclaves (*ca.* 1 dm^3). The less volatile products were fractionated through a spinning-band column (2 m) which separated them into a recovered alkylbenzene fraction and a higher boiling (product) fraction; with cumene a product fraction boiling lower than the recovered cumene was also obtained. Individual components were separated from the product fractions by g.l.c. [Perkin-Elmer F 21 instrument; columns of trixylyl phosphate (TXP), Apiezon L grease (APL), polyethyleneglycol adipate (PEGA) or Silicone SE 30 oil (each 25% on Celite) as indicated in the text] and were examined by i.r. spectroscopy (Perkin-Elmer 257 spectrophotometer with sodium chloride optics), n.m.r. spectroscopy (Perkin-Elmer R10 spectrometer operating at 60.0 MHz for ^{1}H and 56.46 MHz for ^{19}F or a Varian HA-100 spectrometer operating at 100.0 MHz for ^{1}H and 94.1 MHz for ^{19}F and with internal tetramethylsilane and external trifluoroacetic acid as the respective references), and mass spectrometry (A.E.I. MS 902 spectrometer). The mass spectra of individual components of complex mixtures were obtained by coupled g.l.c.–mass spectrometry. Spectral data for compounds indicated with an asterisk are available as Supplementary Publication No. SUP 21628 (22 pp., 1 microfiche).† B.p.s were determined by Siwoloboff's method. The alkylbenzenes were distilled before use and their purity was checked by n.m.r. and g.l.c.

Thermal Reactions of Hexafluoropropene with Alkylbenzenes.—(a) *With toluene in Pyrex tubes*. A mixture of toluene (42.0 g, 0.455 mol) and the olefin (22.5 g, 0.15 mol), sealed *in vacuo* in ten Pyrex tubes (*ca.* 3 dm^3 total capacity) and heated at 300 °C (3 days), gave unchanged olefin (11.3 g, 75.3 mmol, 50% recovered), unchanged toluene (35.27 g, 0.382 mol, 84% recovered), and a higher boiling fraction (17.93 g), which was separated by g.l.c. (3.5 m TXP at 120 °C) into its six components identified as (i) 1,2,2-*trifluoro*-1-*trifluoromethylpropylbenzene* (VIa) * (0.27 g, 1.1 mmol, 1.5%) (Found: C, 49.7; H, 3.4%; M^+, 242. $C_{10}H_8F_6$ requires C, 49.6; H, 3.3%; *M*, 242), (ii) 1,1,2-*trifluoro*-1-*trifluoromethylpropylbenzene* (Va) * (0.18 g, 0.74 mmol, 1%) (Found: C, 49.7; H, 3.1%; M^+, 242), b.p. 167 °C, (iii) 1,1,2,2,3,4,4,4-octafluorobutylbenzene (VII) * (0.53 g, 2.2 mmol, 3%) (Found: M^+, 278. Calc. for $C_{10}H_6F_8$: *M*, 278), (iv) 2,3,3-*trifluoro*-2-*trifluoromethylpropylbenzene* (IIIa) * (0.44 g, 1.82 mmol, 2.5%) (Found: C, 49.7; H, 3.4; F, 47.3%; M^+, 242. $C_{10}H_8F_6$ requires C, 49.6; H, 3.3; F, 47.1%; *M*, 242), b.p. 169 °C, (v) 2,2,3,4,4,4-hexafluorobutylbenzene (Ia) * (14.6 g, 59.0 mmol, 79%) (Found: C, 49.7; H, 3.4; F, 47.3%; M^+, 242), b.p. 174 °C; and (vi) a mixture * (1.80 g, 7.50 mmol, 10%) (Found: C, 49.9; H, 2.7; F, 47.0%; M^+, 240. Calc. for $C_{10}H_6F_6$: C, 50.0; H, 2.5; F, 47.5%; *M*, 240), b.p. 183 °C, of 1,2,2-trifluoro-1-trifluoromethylindane (IIa) (1.08 g, 4.5 mmol, 6%) and 1,1,2-trifluoro-2-trifluoromethylindane (IVa) (0.72 g, 3.0 mmol, 4%) in the ratio 60 : 40 as determined by n.m.r. spectroscopy.

A second reaction carried out at lower pressure, with a mixture of toluene (0.83 g, 9.0 mmol) and hexafluoropropene (0.45 g, 3.0 mmol) heated at 300 °C (3 days), gave unchanged hexafluoropropene (0.284 g, 1.89 mmol, 63% recovered) and higher boiling material (0.996 g) shown by g.l.c. (2 m TXP at 120 °C) and coupled g.l.c. (as above)–mass spectrometry to consist of unchanged toluene (0.72 g, 7.83 mmol, 87% recovered), (VIa) (1.5%), (Va) (2%), (VII) (1.5%), (IIIa) (2.5%), (Ia) (71%), and a mixture (21.5%) of the indanes (IIa) and (IVa).

(b) *Autoclave reaction with toluene*. A mixture of toluene (138 g, 1.5 mol) and the olefin (75.0 g, 0.50 mol), heated at 250 °C (3 days), gave unchanged hexafluoropropene (26.25 g, 0.177 mol, 35% recovered) and a higher boiling fraction (186.8 g) which was fractionated to give unchanged toluene (109 g, 1.18 mol, 79% recovered), b.p. 110 °C, and a higher boiling residue (77.75 g), b.p. >110 °C, shown by g.l.c. (2 m TXP at 120 °C) and coupled g.l.c. (as above)–mass spectrometry to consist of compounds (VIa) (1%), (Va) (0.5%), (IIIa) (8.5%), and (Ia) (89.5%), and a mixture (*ca.* 0.1%) of the indanes (IIa) and (IVa).

In a second higher-pressure reaction with a mixture of toluene (267 g, 3.0 mol) and hexafluoropropene (150 g, 1.0 mol) the products were unchanged hexafluoropropene (4.5 g, 33.0 mmol, 3% recovered) contaminated with small amounts of 1*H*,2*H*-hexafluoropropane and 1,2-bis(trifluoromethyl)hexafluorocyclobutane (i.r.), unchanged toluene (186.8 g, 2.01 mol, 67% recovered), and a higher boiling fraction (234 g) which was shown by g.l.c. (2 m TXP at 120 °C) to consist of compounds (VIa) (trace), (Va) (trace), (IIIa) (9%), and (Ia) (90%), and a mixture (trace) of the indanes (IIa) and (IVa).

(c) *With* p-*chlorotoluene*. A mixture of *p*-chlorotoluene (5.96 g, 45.0 mmol) and hexafluoropropene (2.25 g, 15.0 mmol), heated at 250 °C (3 days) gave unchanged hexafluoropropene (0.67 g, 4.5 mmol, 30% recovered) and higher boiling material (7.26 g) which was fractionated to give unchanged *p*-chlorotoluene (4.35 g, 34.5 mmol, 77% recovered), b.p. 162 °C, and a residue (2.9 g), b.p. >162 °C. The residue was shown by g.l.c. (3.5 m TXP at 135 °C) to contain two major components and four minor components; the major components were separated and identified as (i) 1-*chloro*-4-(2,3,3-*trifluoro*-2-*trifluoromethylpropyl*)*benzene* (IIIe) * (0.10 g, 0.4 mmol, 4.5%) (Found: C, 43.5; H, 2.7; Cl, 13.2; F, 44.1%; M^+, 278 and 276. $C_{10}H_7ClF_6$ requires C, 43.5; H, 2.5; Cl, 12.7; F, 44.3%; *M*, 276.5), and (ii) 1-*chloro*-4-(2,2,3,4,4,4-*hexafluorobutyl*)*benzene* (Ie) * (2.66 g, 9.65 mmol, 91%) (Found: C, 43.6; H, 2.7; F, 44.4; Cl, 12.7%; M^+, 278 and 276).

(d) *With* p-*xylene*. A mixture of *p*-xylene (47 g, 0.45 mol) and hexafluoropropene (22.5 g, 0.15 mol), sealed in ten Pyrex tubes (3 dm^3 total capacity) and heated at 280 °C (3 days), gave unchanged hexafluoropropene (14.63 g, 97.0 mmol, 65% recovered) and a higher boiling fraction (54.87 g), which was fractionated to afford unchanged *p*-xylene (41.8 g, 0.40 mol, 88% recovered), b.p. 138 °C, and a residue (13.07 g), b.p. >138 °C, which was separated by g.l.c. (3.5 m TXP programmed from 120 to 150 °C) into its components, identified as (i) 1-methyl-4-(1,2,2-trifluoro-1-trifluoromethylpropyl)benzene (VIf) * (0.13 g, 0.5 mmol,

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† For details of Supplementary Publications see Notice to Authors No. 7, *J.C.S. Perkin I*, 1974, Index issue.

1%), (ii) 1-methyl-4-(2,3,3-trifluoro-2-trifluoromethylpropyl)benzene (IIIf) (0.19 g, 0.75 mmol, 1.5%), (iii) 1-methyl-4-(1,1,2-trifluoro-2-trifluoromethylpropyl)benzene (Vf) * (0.19 g, 0.75 mmol, 1.5%), (iv) 1-*methyl*-4-(2,2,3,4,4,4-*hexafluorobutyl*)*benzene* (If) * (10.80 g, 42.2 mmol, 80%) (Found: C, 51.7; H, 4.1%; M^+, 256. $C_{11}H_{10}F_6$ requires C, 51.6; H, 3.9%; *M*, 256), b.p. 196 °C, (v) the indane (IIf) * (0.13 g, 0.51 mmol, 1%), (vi) an unknown compound * (0.23 g, 0.9 mmol, 2%), (vii) the indane (IVf) * (0.19 g, 0.75 mmol, 1.5%), and (viii) 1,4-*bis*-(2,2,3,4,4,4-*hexafluorobutyl*)*benzene* (XVI) * (1.08 g, 2.65 mmol, 5%) (Found: F, 55.9%; M^+, 406. $C_{14}H_{10}F_{12}$ requires F, 56.2%, *M*, 406), m.p. 64 °C. A number of unidentified minor components were also formed.

(e) *With ethylbenzene in Pyrex tubes.* A mixture of ethylbenzene (4.8 g, 45.0 mmol) and hexafluoropropene (2.25 g, 15.0 mmol), heated at 250 °C (3 days), gave unchanged olefin (1.46 g, 9.75 mmol, 65% recovered) contaminated with a small amount of 1*H*,2*H*-hexafluoropropane (i.r.) and higher boiling material (5.59 g), which was fractionated to afford unchanged ethylbenzene (4.2 g, 39.5 mmol, 87% recovered), b.p. 136 °C, and a residue (1.35 g), b.p. >136 °C. The two major components of the residue were separated by g.l.c. (3.5 m TXP at 120 °C) and identified as 2,2,3,4,4,4-*hexafluoro*-1-*methylbutylbenzene diastereoisomer A* (Ib_1) * (0.325 g, 1.36 mmol 24%) (Found: C, 51.6; H, 4.2; F, 44.2%; M^+, 256. $C_{11}H_{10}F_6$ requires C, 51.6; H, 3.9; F, 44.5%; *M*, 256), b.p. 179 °C, and *diastereoisomer B* (Ib_2) * (0.30 g, 1.15 mmol, 22%) (Found: C, 51.5; H, 4.0; F, 44.5%; M^+, 256), b.p. 191 °C. The remainder of the fraction (0.73 g) was a complex mixture, but the following compounds were identified by coupled g.l.c. (3.5 m TXP at 150 °C)–mass spectrometry: (i) 1,2,2,2-tetrafluoroethylbenzene (VIII) (*ca.* 2%) (Found: M^+, 178. Calc. for $C_8H_6F_4$: *M*, 178), the mass spectrum of which was identical with that of a pure sample obtained from the products of the cumene reaction [experiment (h)], (ii) 1,2,2-trifluoro-1-trifluoromethylbutylbenzene (VIb) * (*ca.* 4%) (Found: M^+, 256. Calc. for $C_{11}H_{10}F_6$: *M*, 256), (iii) 2,3,3-trifluoro-1-methyl-2-trifluoromethylpropylbenzene (IIIb) * (*ca.* 4.5%) (Found: M^+, 256. Calc. for $C_{11}H_{10}F_6$: *M*, 256), (iv) 3,4,4-trifluoro-3-trifluoromethylbutylbenzene (IX) * (*ca.* 2.5%) (Found: M^+, 256. Calc. for $C_{11}H_{10}F_6$: *M*, 256), (v) 2,3,3-trifluoro-1-methyl-3-trifluoromethylindane diastereoisomer A (IIb_1) * (*ca.* 8%) (Found: M^+, 254. Calc. for $C_{11}H_8F_6$: *M*, 254), (vi) 2,3,3-trifluoro-1-methyl-2-trifluoromethylindane (IVb) * (*ca.* 3%) (Found: M^+, 254), (vii) 2,2,3-trifluoro-1-methyl-3-trifluoromethylindane stereoisomer B (IIb_2) * (*ca.* 9%) (Found: M^+, 254), and (viii) 3,3,4,5,5,5-hexafluoropentylbenzene (X) * (*ca.* 5%) (Found: M^+, 256. Calc. for $C_{11}H_{10}F_6$: *M*, 256).

(f) *Autoclave reaction with ethylbenzene.* A mixture of ethylbenzene (159 g, 1.5 mol) and hexafluoropropene (75 g, 0.5 mol), heated in an autoclave at 300 °C (3 days), gave unchanged hexafluoropropene (32.0 g, 0.214 mol, 43% recovered), contaminated with traces of 1*H*,2*H*-hexafluoropropane and 1,2-bis(trifluoromethyl)hexafluorocyclobutane (i.r.), and higher boiling material (202 g) which was fractionated to afford unchanged ethylbenzene (128.8 g, 1.22 mol, 80% recovered), b.p. 136 °C, and a residue (73.2 g), b.p. >136 °C. The residue was shown by g.l.c. (3.5 m TXP at 120 °C) to contain two major components and a number of minor components; the two major components were separated (g.l.c. as above) and identified as 2,2,3,4,4,4-hexafluoro-1-methylbutylbenzene diastereoisomer A (Ib_1) (33.7 g, 0.130 mol, 46%), and the diastereoisomer B (Ib_2) (30.8 g, 0.120 mol, 42%); the following minor components were identified by g.l.c. (as above)–mass spectrometry: (IIIb) (0.5%), (IIb_1) (0.5%), (IVb) (0.5%), and (IIb_2) (2%).

(g) *With n-propylbenzene.* A mixture of n-propylbenzene (120 g, 1.0 mol) and hexafluoropropene (50.0 g, 0.33 mol), heated in an autoclave at 250 °C (3 days), gave unchanged hexafluoropropene (11.0 g, 73.0 mol, 22% recovered), contaminated with traces of 1*H*,2*H*-hexafluoropropane and 1,2-bis(trifluoromethyl)hexafluorocyclobutane (i.r.) and a higher boiling fraction (159 g), which was fractionated to afford unchanged n-propylbenzene (88.8 g, 0.74 mol, 74% recovered), b.p. 159 °C, and a residue (70.2 g), b.p. >159 °C. The residue was shown by g.l.c. (3.5 m TXP) to contain four components, two minor and two major; the four components were separated and the minor components were shown by n.m.r. spectroscopy to be complex mixtures which could not be identified, but the major components were identified as 1-*ethyl*-2,2,3,4,4,4-*hexafluorobutylbenzene diastereoisomer A* (Id_1) * (31.6 g, 0.177 mol, 45%) (Found: C, 53.0; H, 4.4; F, 42.2%; M^+, 270. $C_{12}H_{12}F_6$ requires C, 53.3; H, 4.4; F, 42.2%; *M*, 270), b.p. 199 °C, and *diastereoisomer B* (Id_2) * (36.50 g, 0.135 mol, 52%) (Found: C, 53.4; H, 4.5; F, 42.4%; M^+, 270), b.p. 205 °C.

In a tube reaction a mixture of n-propylbenzene (5.4 g, 45.0 mmol) and hexafluoropropene (2.25 g, 15.0 mmol), heated at 250 °C (3 days), gave unchanged hexafluoropropene (1.24 g, 8.25 mmol, 55% recovered) and higher-boiling material which was shown by g.l.c. (2.5 m TXP at 120 °C) to contain unchanged n-propylbenzene and *ca.* twenty components of longer retention times none of which were major; two were identified as the 1 : 1 adducts (Id_1) (*ca.* 5%) and (Id_2) (*ca.* 5%) by coupled g.l.c.–mass spectrometry.

(h) *With cumene in a Pyrex tube.* A mixture of cumene (5.4 g, 45.0 mmol) and hexafluoropropene (2.25 g, 15.0 mmol), heated at 250 °C (3 days), gave a mixture (1.03 g, 7.87 mmol; *M*, 131) of unchanged hexafluoropropene (0.79 g, 5.25 mmol, 33% recovered) and 1,1-difluoro-2-methylpropene (XI) (0.24 g, 2.62 mmol, 20% based on CF_2 content in C_3F_6 consumed), i.r. $\lambda_{max.}$ 5.66 μm (CF_2:C< str.) (lit.,[9] 5.67 μm), *m/e* 92 (90%, M^+) and 77 [100%, $(M - Me)^+$], and higher boiling material (6.6 g), which when fractionated afforded (i) a mixture (1.61 g), b.p. <152 °C, (ii) unchanged cumene (4.55 g, 38.0 mmol, 85% recovered), b.p. 152 °C, and (iii) a residue (0.44 g), b.p. >152 °C. The fraction of b.p. < 152 °C was separated by g.l.c. (3 m APL at 130 °C) into its four components: (i) 1,1,2,2,3-*pentafluoro*-4,4-*dimethyl*-3-*trifluoromethylcyclobutane* (XII) * (0.66 g, 2.73 mmol, 21.5%) (Found: C, 35.0; H, 2.8; F, 62.8%; M^+, 242. $C_7H_6F_8$ requires C, 34.7; H, 2.5; F, 62.8%; *M*, 242), b.p. 81 °C, (ii) 1,2,2,3,4,4,4-heptafluoro-1-trifluoromethylbutylbenzene (XIII) * (trace), (iii) 1,2,2,3-tetrafluoro-1,3-bis(trifluoromethyl)indane (XIV) * (trace), and (iv) 1,2,2,2-*tetrafluoroethylbenzene* (VIII) * (0.95 g, 5.35 mmol, 41.5%) (Found: C, 53.9; H, 3.4; F, 42.7%, M^+, 178. $C_8H_6F_4$ requires C, 53.9; H, 3.4; F, 42.7%; *M*, 178), b.p. 133 °C. The residue from the distillation was separated by g.l.c. (3 m APL at 130 °C) into its two components: 2,2,3-*trifluoro*-1,1-*dimethyl*-3-*trifluoromethylindane* (IIc) * (0.39 g, 1.45 mmol, 15%) (Found: F, 42.4%; M^+, 268. $C_{12}H_{10}F_6$ requires F, 42.6%; *M*, 268), b.p. 201 °C (lit.[3] 200 °C), and 2,3,3-trifluoro-1,1-dimethyl-2-trifluoromethylindane (IVc) * (0.05 g, 0.2 mmol, 2%).

(j) *Autoclave reaction with cumene.* A mixture of cumene

(180 g, 1.5 mol) and hexafluoropropene (75.0 g, 0.50 mol), heated in an autoclave at 250 °C (3 days), gave unchanged hexafluoropropene (15.75 g, 0.105 mol, 21% recovered), contaminated with a trace of 1*H*,2*H*-hexafluoropropane (i.r.) and higher boiling material (239.25 g) which was fractionated to give a fraction (81.1 g), b.p. <152 °C, unchanged cumene 154.4 g, 1.28 mol, 86% recovered), b.p. 152 °C, and a residue (3.7 g), b.p. >152 °C. The four components in the lower boiling fraction were separated by g.l.c. (3 m APL at 130 °C) and identified as (XII) (45.6 g, 0.189 mol, 46%), (XIII) (trace), (XIV) (trace), and (VIII) (35.5 g, 0.200 mol, 49%), and the three components in the high boiling residue were separated by g.l.c. (as above) and identified as (IIc) (1.5 g, 6.0 mmol, 1.5%), (IVc) (trace), and 2,2-*difluoro*-1,1,3,3-*tetramethylindane* (XV) * (2.2 g, 11.0 mmol, 3%) (Found: C, 74.1; H, 7.8%, M^+, 210. $C_{13}H_{16}F_2$ requires C, 74.3; H, 7.6%; M 210).

(k) *With t-butylbenzene.* A mixture of t-butylbenzene (6.04 g, 45.0 mmol) and hexafluoropropene (2.25 g, 15.0 mmol), heated at 250 °C (3 days), gave unchanged olefin (2.02 g, 13.5 mmol, 90% recovered) and a black tar which was extracted with ether (2 × 10 cm^3) to afford, after removal of the ether, unchanged t-butylbenzene (3.0 g, 21.8 mmol, 49% recovered).

(l) *With other alkylbenzenes.* The reactions of n-, s-, and iso-butylbenzenes with hexafluoropropene, carried out as in experiment (k), gave unchanged olefin (60, 81, and 81% recovered, respectively) and higher boiling material which was shown by g.l.c. (2 m TXP at 120 °C or 2 m APL at 110 °C) to contain the appropriate unchanged butylbenzene and numerous (>20) other components, none of which were major.

Reactions of 2,2,3,4,4,4-*Hexafluorobutylbenzene.*—(a) *Chlorination.* Chlorine was passed into a mixture of the polyfluoroalkylbenzene (10.0 g, 42.0 mmol) and iron filings (0.25 g) in a round-bottomed flask fitted with a cold finger (−78 °C) until almost the theoretical gain in weight was achieved. The resultant liquid (11.15 g, 90% conversion) was separated into its components by g.l.c. (3.5 m TXP at 150 °C): (i) unchanged polyfluoroalkylbenzene (1.0 g, 4.2 mmol, 10% recovered), (ii) 1-*chloro*-2-(2,2,3,4,4,4-*hexafluorobutyl)benzene* (XXXI) * (4.80 g, 17.8 mmol, 47%) (Found: C, 43.5; H, 2.6; F, 44.1%; M^+, 276. $C_{10}H_7ClF_6$ requires C, 43.5; H, 2.8; F, 44.3%; M, 276), and (iii) 1-chloro-4-(2,2,3,4,4,4-hexafluorobutyl)benzene (Ie) (5.45 g, 19.7 mmol, 53%), the i.r., n.m.r., and mass spectra of which were identical with those of a sample prepared by the reaction of *p*-chlorotoluene with hexafluoropropene [experiment (c)].

(b) *Nitration.* The polyfluoroalkylbenzene (12.1 g, 50.0 mmol) was added slowly to a mixture of concentrated sulphuric (20 cm^3) and nitric acids (17 cm^3) and the solution was heated at 80 °C (1 h). The mixture was poured into water (200 cm^3) and the organic phase extracted with ether (3 × 25 cm^3). The extract was washed with water (3 × 25 cm^3), dried ($CaCl_2$), and then distilled to afford 1-*nitro*-4-(2,2,3,4,4,4-*hexafluorobutyl)benzene* (XXXIV) * (13.9 g, 49.0 mmol, 98%) (Found: C, 42.1; H, 2.5; N, 4.7; F, 39.4%; M^+, 287. $C_{10}H_7F_6NO_2$ requires C, 41.8; H, 2.4; N, 4.9; F, 39.7%; M, 287), b.p. 81 °C at 0.01 mmHg.

(c) *Bromination.* Bromine (12.5 g, 75.0 mmol) was added slowly to a mixture of the polyfluoroalkylbenzene (12.1 g, 50.0 mmol) and iron filings (0.1 g) and the mixture was heated at 60 °C (1 h) and then at 80 °C (30 min). The brown product was shaken with aqueous sodium hydroxide (2%) until neutral, washed with water (3 × 25 ml), and then filtered to afford a mixture which was separated by g.l.c. (3.5 m TXP at 150 °C) into its comodnents: (i) unchanged 2,2,3,4,4,4-hexafluorobutylbenzene (1.2 g, 5.0 mmol, 10% recovered), (ii) 1-*bromo*-2-(2,2,3,4,4,4-*hexafluorobutyl*)-*benzene* (XXXII) * (2.89 g, 9.0 mmol, 20%) (Found: C, 37.2; H, 2.3. $C_{10}H_7BrF_6$ requires C, 37.4; H, 2.2%), b.p. 199 °C, and (iii) 1-*bromo*-4-(2,2,3,4,4,4-*hexafluorobutyl*)-*benzene* (XXXIII) * (11.5 g, 36.0 mmol, 80%) (Found: C, 37.1; H, 2.1%), b.p. 218 °C.

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