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# THE REACTIONS OF AROMATIC COMPOUNDS WITH BROMINE TRIFLUORIDE (I) : HEXAFLUOROBENZENE AND ITS DERIVATIVES

T.W. BASTOCK, M.E. HARLEY, A.E. PEDLER and J.C. TATLOW

Department of Chemistry, University of Birmingham, P.O.Box 363,
Birmingham B15 2TT, (Great Britain)

## ABSTRACT

The reactions of mixtures of bromine trifluoride and bromine with hexa-, penta- and bromopenta-fluorobenzene, with octafluorotoluene and decafluoro-p-xylene and 2,3,4,5,6-pentafluorotoluene and -anisole have been investigated. The initial products were polyfluorocyclohexa-1,4-dienes, substituent groups being in the 1-position for electron withdrawing and the 3-position for electron donating groups respectively. The dienes then reacted further to add bromine monofluoride across one or both of the diene double bonds to give bromofluorocyclohexene or polybromofluorocyclohexane isomer mixtures. In the absence of added bromine, no reaction occurred with hexafluorobenzene and reaction was less vigorous and complete with pentafluorobenzene and 2,3,4,5,6-pentafluoroanisole. The mechanism of reaction has been discussed in terms of the ionization potential of the aromatic substrates and the formation of radical cations.

There are comparatively few detailed references to the reactions of bromine trifluoride with organic compounds. Hexachlorobenzene gave [1] compounds of empirical formula $C_6Br_2Cl_4F_6$, and with perfluoro-olefins [2,3,4] the products of reaction arose from the addition of BrF across the double bond, and suggested electrophilic attack of a bromine-containing species.

We now report reactions of $BrF_3$ and $BrF_3/Br_2$ mixtures with polyfluoroaromatic compounds. Hexafluorobenzene, with one mole per mole each of bromine and bromine trifluoride in an inert solvent, gave two products. The minor one was octafluorocyclohexa-1,4-diene (identified by IR spectroscopy), and the major one a new olefin of empirical formula $C_6BrF_9$. The position of the bromine atom was determined by reduction of the olefin to 4$\underline{H}$-nonafluorocyclohexene, together with octafluorocyclohexa-1,3 and 1,4-diene. Oxidation of the olefin gave 3-bromo-heptafluoroadipic acid isolated as dianilinium (with a consistent NMR spectrum) and di-S-benzyl thiouronium salts.

The bromo-olefin itself was treated with $BrF_3$ and $Br_2$ at 0° : no reaction occurred. This is consistent with previous work [3] where reaction between decafluorocyclohexene and this mixture required an autoclave at 265° under autogenous pressure. However, bromine alone could be added across the double bond of our bromo-olefin in UV light to form a mixture of 1,2,4-tribromononafluorocyclohexane stereoisomers.

It was suspected that octafluorocyclohexa-1,4-diene was an intermediate in the original reaction, being formed from hexafluorobenzene by a 1,4-addition of fluorine, and then giving rise to 4-bromononafluorocyclohexene by a further addition of BrF. From the reaction of octafluorocyclohexa-1,4-diene with $BrF_3/Br_2$ there was obtained only 4-bromo-nonafluorocyclohexene: under the same conditions, octafluorocyclohexa-1,3-diene gave not only the 4-bromo-olefin but also decafluorocyclohexene in equal molar proportion. It seems therefore that the 1,4-diene, but not the 1,3-diene, is an intermediate in the reaction.

Octafluorotoluene and $BrF_3/Br_2$ also gave a perfluoro-diene and a bromo-olefin. The reaction using one mole per mole of reagents yielded a small amount of a compound identified as 1-trifluoromethylheptafluorocyclohexa-1,4-diene and principally, a less volatile liquid. This showed only one peak on GLC and analysed correctly for $C_7BrF_{11}$. The $^{19}F$ NMR spectrum showed a signal at $\phi^*$ 59.8 typical of a $CF_3$-group and no tertiary fluorine atoms could be detected, showing the absence of ${}^{CF_3}_{F}{>}C{<}$ . Thus the $CF_3$-group is attached to an olefinic carbon atom. The IR spectrum showed a strong absorption at 1715 $cm^{-1}$, which was ascribed to $CF_3-\overset{|}{C}=\overset{|}{C}-F$ rather than $CF_3-\overset{|}{C}=\overset{|}{C}-Br$, for which an absorption at ~ 1620 $cm^{-1}$ might be expected (-CF = CF- [5] , 1750 $cm^{-1}$; $CF_3-\overset{|}{C}=\overset{|}{C}-F$, 1720 $cm^{-1}$; -CF = CBr- [6] 1695 $cm^{-1}$; -CBr = CBr- [6] 1610 $cm^{-1}$, all perfluorocyclohexene derivatives). Oxidation of the olefin gave tetrafluorosuccinic acid rather than a bromo-fluoro-acid. There were indications that the bromo-olefin was a mixture of isomers and it was reduced to improve the possibility of separation. With zinc/methanol, however, the product was *o*-methoxyheptafluorotoluene, the orientation being determined by a comparison of experimental with calculated $^{19}F$ NMR chemical shift parameters. Presumably the double bond is activated by the $CF_3$-group sufficiently to allow nucleophilic substitution by methoxide and this is followed by reduction/dehydrofluorination/defluorination. The bromo-olefin mixture was next fluorinated over $CoF_3$ at 200°, similar compounds [7] having suffered no loss or shift of bromine. A mixture of bromotridecafluoromethylcyclohexane isomers was obtained. The $^{19}F$ NMR spectrum showed two characteristic signals at $\phi$* 185.3 and 191.6 due to two different fluorine atoms each attached to carbon carrying a trifluoromethyl group. Thus the original olefin mixture contained at least two isomers. Attempts to substitute hydrogen for bromine in the $C_7BrF_{13}$ species by reduction with $LiAlH_4$, to give tridecafluoromethylcyclohexane isomers, were only partially successful, affording a poor recovery of the known *trans*-4*H*-tridecafluoromethylcyclohexane. Finally, 4-bromoheptafluorotoluene was fluorinated over $CoF_3$ at 200° to give 4-bromo-tridecafluoromethylcyclohexane, presumably a mixture of *cis* and *trans* isomers. The $^{19}F$ NMR spectrum of this was complex, but contained signals at $\phi$* 70.2 ($CF_3$-) and 190.6 (tertiary fluorine in $CF_3$-$CF<$ ). Thus one of the constituents of the bromopolyfluoro-olefin mixture is probably 1-trifluoromethyl -4-bromo-octafluorocyclohexene, arising by addition of BrF across the -CF=CF- double bond of 1-trifluoromethylheptafluorocyclohexa-1,4-diene formed in the initial reaction of octafluorotoluene: if so, the other product is probably the 5-bromo-isomer.

Using two moles each of bromine trifluoride and bromine per mole of octafluorotoluene the reaction products contained no diene and were principally the mixture of 1-trifluoromethyl-4- and -5-bromo-octafluorocyclohexene isomers obtained previously.

Decafluoro-*p*-xylene and one mole per mole each of $BrF_3$ and $Br_2$, gave 1,4-*bis*(trifluoromethyl)hexafluorocyclohexa-1,4-diene (principal product) and 4-bromo-1,4-*bis*(trifluoromethyl)heptafluorocyclohexene. The latter has the orientation expected for addition of BrF to $CF_3\overset{|}{C}=\overset{|}{C}F$. Even with excess bromine trifluoride and bromine the diene was still the major product. Treatment of

4-bromo-1,4-bis(trifluoromethyl)heptafluorocyclohexene with Zn/methanol gave a mixture of decafluoro-p-xylene and 2-methoxynonafluoro-p-xylene.

Bromopentafluorobenzene and one mole per mole each of bromine and bromine trifluoride gave, in addition to unchanged bromopentafluorobenzene, roughly equal amounts of 1-bromoheptafluorocyclohexa-1,4-diene and a dibromo-octafluorocyclohexene. The diene was identified by chemical analysis, IR and NMR spectrometry and mass spectrometry. Oxidation of the diene gave difluoromalonic acid, confirming the position of the bromine atom. The dibromo-octafluorocyclohexene was an inseparable mixture of isomers. Oxidation gave a good yield of 3-bromoheptafluoroadipic acid, showing the original to be a mixture of 1,4- and 1,5-dibromo-octafluorocyclohexene. Bromopentafluorobenzene and twice the molar amounts of bromine and bromine trifluoride gave no diene, but principally the dibromo-olefin mixture and also a mixture of tribromononafluorocyclohexane isomers.

From pentafluorobenzene and $BrF_3/Br_2$ there was obtained 1-bromoheptafluorocyclohexa-1,4-diene as the major product, together with the mixture of 1,4- and 1,5-dibromo-octafluorocyclohexene and the mixed tribromononafluorocyclohexane isomers, all obtained from bromopentafluorobenzene. Also separated from the product mixture was bromopentafluorobenzene itself. No hydrogen containing compounds could be isolated, although GLC revealed the presence of small amounts of additional compounds which could not be separated. The nuclear hydrogen atom in pentafluorobenzene is obviously rapidly substituted by bromine ($BrF_3/Br_2$ mixtures are powerful electrophilic brominating agents [3,4] ). In the presence of excess bromine trifluoride/bromine the major product becomes the tribromononafluorocyclohexane isomer mixture together with a dibromononafluorocyclohexane, presumably arising directly from pentafluorobenzene.

2,3,4,5,6-Pentafluorotoluene and a molar ratio of reactants at -10° (to reduce the vigour of the reaction) afforded two known dienes, 1-methyl- and 3-methyl-heptafluorocyclohexa-1,4-diene in the molar ratio 1.5:1, and a mixture of methyl-dibromononafluorocyclohexane isomers (at least three could be detected by NMR spectroscopy). No olefin was obtained. When the reaction was done at 0° using an excess of bromine trifluoride and bromine the principal product was the methyl-dibromononafluorocyclohexane isomer mixture with only a small amount of the mixed dienes. In no case were products isolated containing bromine in the methyl group.

Using 2,3,4,5,6-pentafluoroanisole at -10° and a molar ratio of reagents yielded as principal product an inseparable mixture of methoxy-dibromononafluorocyclohexane isomers, together with small amounts of 3-methoxy-heptafluorocyclohexa-1,4-diene. With an excess of bromine trifluoride/bromine at 0° the sole product was the mixed methoxy-dibromo-nonafluorocyclohexane isomers.

The reactions of $BrF_3$ which had been rigorously freed from $Br_2$ were next studied under similar conditions. With hexafluorobenzene at 0°, no reaction occurred, a good recovery of the aromatic being obtained. However the presence of only 0.05 mole $Br_2$: 1.0 mole $BrF_3$ caused the reaction to proceed normally. With pentafluorobenzene at 0° the major product was bromopentafluorobenzene together with the dibromo-octafluorocyclohexene isomer mixture and 1-bromo-heptafluorocyclohexa-1,4-diene. Thus, bromine trifluoride itself will act as a brominating agent, although in the absence of bromine the reactivity in addition reactions involving the aromatic ring is much reduced. This conclusion was confirmed when 2,3,4,5,6-pentafluoroanisole was treated with $BrF_3$ at 0°. In the presence of bromine at this temperature the sole product anticipated would be the methoxy-dibromononafluorocyclohexane isomer mixture: in the absence of bromine, 3-methoxyheptafluorocyclohexa-1,4-diene was isolated in significant quantity.

In all these reactions therefore only electron-rich aromatic compounds react in the absence of bromine. In its presence they give saturated products, whereas relatively electron-deficient substrates tend to yield dienes and olefins. The first attack is addition of fluorine to give 1,4-dienes exclusively, substituents being on the 1-position if electron-withdrawing and in the 3-position if electron-donating. These 1,4-dienes react subsequently by addition of BrF across one or both double bonds. The mixture $BrF_3/Br_2$ is a powerful electrophilic brominating agent.

In recent publications the mechanisms of fluorination of aromatic compounds with xenon fluoride and with high valency transition metal fluorides have been discussed [8,9,10] and participation of radical cations as intermediates postulated.

For fluorinations of hydrocarbon aromatics two alternative sequencies were considered [9], after initial formation of a radical cation: (a) attack by species acting as a source of fluorine atoms to give cations analogous to Wheland intermediates, (b) addition of fluoride ion to yield a radical. In each case, by loss of hydrogen reversion to fluoro-aromatic species can occur, explaining the orientations, analogous to electrophilic substitutions, observed in the primary products. At this early stage, quenching of the intermediates arising in route (a) or (b) by fluoride ions or by fluorine atoms, respectively could give dienes. However, these would be readily convertible into the same fluoro-aromatic primary products by loss of HF. Subsequently. however, in the sequence from hydrocarbon aromatics, more stable fluorocyclohexadienes can arise by this type of quenching (i.e. which cannot aromatise by HF loss) and these are the precursors for the major products, fluorocyclohex-enes and -anes. This situation applies immediately in the reactions of polyfluoroaromatics with $BrF_3$. New products can be formed only by fluorine uptake by intermediates from sequences (a) or (b) above, i.e. leading to overall addition to the ring.

For the formation of a radical cation according to

$$B + X_F \longrightarrow X_F^{\cdot +} + B^-$$

the lower the ionization potential of the aromatic compound the more facile the reaction. The ionization potentials (e.v.) of the compounds we used are [11,12] $C_6F_5CH_3$, 9.60 $<$ $C_6F_5Br$, 9.67 $<$ $C_6F_5H$, 9.84 $<$ $C_6F_6$, 9.97 $<$ $C_6F_5CF_3$, 10.4, the change in ionization potential occurring because of the effect of the substituent on the $\pi$ system, and this is order of decreasing reactivity. However, the formation of a radical cation according to the above equation in isolation would be highly endothermic and the reaction consequently slow.

The products obtained from pentafluoropyridine (1,3-dienes) and hexafluorobenzene (1,4-diene) and cobalt trifluoride may be explained best [10] via reactions of fluoride ions with the radical cations [ (b) above ] . The resulting radical then combines with a source of fluorine atoms at the point of greatest spin density to give the observed dienes. We also obtain fluorocyclohexa-1,4-dienes from the reactions of $BrF_3/Br_2$ with hexafluorobenzene and its derivatives, so that our results might also be accounted for by the same general considerations [10]. However, no calculations yet available give spin and charge densities at the various positions of a substituted polyfluoro-aromatic compound or analogous cyclohexadienyl radicals.

Questions remain concerning the nature of the initial reaction in the fluorination process, and of the electron acceptor. A variety of equilibria exist [13] in bromine trifluoride/bromine mixtures.

$$2\,BrF_3 \rightleftharpoons BrF_2^+ + BrF_4^-$$

$$BrF_3 + Br_2 \rightleftharpoons 3BrF$$

$$2Br_2 \rightleftharpoons Br_3^+ + Br^-$$

$$BrF_2^+ + Br^- \rightleftharpoons 2BrF$$

In the absence of bromine the active species in the initial oxidation may be $BrF_3$ itself or $BrF_2^+$ (although the self ionization may well be very small in media of low dielectric constant such as we have used). Pure $BrF_3$ reacted with pentafluorobenzene and 2,3,4,5,6-pentafluoroanisole, although electron-deficient aromatic compounds are probably unreactive since hexafluorobenzene was unchanged. When bromine is added the reactivity of the system is clearly increased markedly, probably due to the formation in the system of bromine monofluoride.

The reaction of BrF with a polyfluoroaromatic compound may be written in two ways :

$$Ar + BrF \longrightarrow Ar^{\bullet+} + F^- + Br^\bullet \qquad (1)$$

$$Ar + BrF \longrightarrow Ar^{\bullet+} + F^\bullet + Br^- \qquad (2)$$

Using $H_{BrF} = -14.0$; $H_{F^\bullet} = +18.4$ and $H_{Br^\bullet} = +22.7$ kcal. mole$^{-1}$, and the electron affinities of bromine and fluorine atoms as 81.6 and 83.5 kcals. g ion$^{-1}$ respectively [14], the heats of reactions (1) and (2) are (IP-28.4) and (IP-26.5) k. cals. mole$^{-1}$ respectively, where IP is the ionization potential of the aromatic compound. Since the ionization potentials of the polyfluoroaromatic compounds are ~ 10 e.v. (~ 230 k. cals. mole$^{-1}$), both these reactions are highly endothermic and can only occur given a large additional source of energy.

The existence of free ions in solvents of low dielectric constant is energetically unfavourable; ions in such solvents must exist largely as ion pairs, The coulombic energy for an ion pair between a halide ion and the cation radical formed according to the equations :

$$Ar^{\bullet+} + F^- \longrightarrow [Ar^{\bullet+}, F^-] \qquad (3)$$

$$Ar^{\bullet+} + Br^- \longrightarrow [Ar^{\bullet+}, Br^-] \qquad (4)$$

may be obtained knowing the equilibrium separation of the charges. These may be estimated as 2.2 and 2.7 Å for the ion pairs involving fluoride and bromide ions respectively. These values have been obtained using a calculated [15] equilibrium separation of 1.38 Å for the proton-ring distance in the $C_6H_6.H^+$ cation and ionic radii for $F^-$ and $Br^-$ corrected for their change in coordination number. [16] The coulombic energies for the ion pairs $[Ar^{\bullet+}, F^-]$ and $[Ar^{\bullet+}, Br^-]$ may then be estimated as 150 and 120 kcals mole$^{-1}$ respectively. Although these values are only approximate due to the neglect of other intermolecular forces, the calculations show a significant difference in energy between ion pairs involving fluoride and bromide ions (arising from the greater size of the bromide ion). For hexafluorobenzene and the simple derivatives we have studied, the charge separation between the radical cation and halide ion probably remains approximately constant, so that the coulombic energy will be independent of the aromatic substrate.

Thus the overall reaction with hexafluorobenzene may be written as :

$$C_6F_6 + BrF \longrightarrow [C_6F_6^{\bullet+}, F^-] + Br^{\bullet} \qquad (5)$$

or

$$C_6F_6 + BrF \longrightarrow [C_6F_6^{\bullet+}, Br^-] + F^{\bullet} \qquad (6)$$

for which the heats are approximately $\Delta H_5 = +52$ and $\Delta H_6 = +83$ k.cals.mole$^{-1}$, indicating that reaction (5) is the more probable. The ion pair formed in (5) must subsequently rearrange to form the heptafluorocyclohexadienyl radical, which then reacts with a fluorine atom source to produce the first isolable product, octafluorocyclohexa-1,4-diene.

Similar considerations apply to the substituted polyfluoro-aromatic compounds we have studied, since the thermochemical quantities and coulombic energies remain largely unaltered, although the ionization potentials vary as described above. Thus it is not surprising that the reactivity of the system varies with ionization potential in a simple fashion, the endothermicity rising with increasing ionization potential.

This type of calculation may be repeated for the reactions with bromine trifluoride, the most likely possible reaction with hexafluorobenzene being :

$$C_6F_6 + BrF_3 \longrightarrow [C_6F_6^{\bullet+}, F^-] + BrF + F^{\bullet} \qquad (7)$$

for which $\Delta H = +80$ k.cals.mole$^{-1}$ ($H_{BrF_3} = -61.1$ k.cals.mole$^{-1}$) [14]. This result demonstrates the significantly greater endothermicity of reactions involving $BrF_3$, and the observed lack of reaction between $BrF_3$ and $C_6F_6$ is not surprising.

The data used in these calculations refer only to the gas phase, and solvation effects have been ignored. It seems unlikely that these would seriously perturb the relative magnitude of the results and we regard the calculations as confirming the relative order of reactivity BrF $>$ $BrF_3$. The absolute reactivities are also in accord with the calculations. Bromine trifluoride is unreactive in fluorination with compounds of ionization potential in excess of 9.6-9.7 e.g. $C_6F_5Br$; bromine monofluoride fluorinates octafluorotoluene (IP 10.4 e.v.), although not octafluorocyclohexa-1,4-diene (IP 10.9 e.v.) [17]. The difference between these values ($\sim$ 1 e.v.; $\sim$ 23 k.cals.mole$^{-1}$) is close to the calculated difference in heat of reaction of $BrF_3$ and BrF with similar substrates ($\sim$ 28 k.cals.mole$^{-1}$).

The subsequent reactions of the diene produced in the initial reactions depend on the structure and reactivity of the compound. The authors cited above [10] suggest that the diene could be fluorinated via a radical cation mechanism to yield polyfluoro-olefins. We observe that the dienes react further, although with greater difficulty than the parent aromatic, to yield generally a bromo-olefin or dibromocyclohexane by the addition of bromine monofluoride across one or both of the double bonds.

In general, fluorination of the dienes is not observed. This suggests that the ionization potentials of the 1,4-dienes may be sufficiently high to render fluorination by the modified radical cation and ion pair formation process outlined above energetically too difficult. Measurement of the potentials using photoionization [17] for octafluorocyclohexa-1,4-diene and 1,3-diene yields values of 10.9 and 10.0 e.v. respectively ($C_6F_6$ = 9.93, cited [12] 9.97 e.v.), and it may be significant that the 1,3-diene does indeed yield decafluorocyclohexene with $BrF_3/Br_2$ mixtures, whereas the 1,4-diene does not. Thus we believe that in our system the 1,4-diene intermediates react with BrF to yield bromonium ions, which are converted to the bromocyclohexenes by trans addition of fluoride ion, according to the commonly accepted electrophilic mechanism for such addition reactions.

## EXPERIMENTAL

### Gas Liquid Chromatography

The following columns were used for the separation of product mixtures: unit I, 488 cm x 75 mm i.d., dinonyl phthalate:celite = 1:2, $N_2$ flow rate 60$\ell$ h$^{-1}$;

unit 2, 488 cm x 75 mm i.d., di-isodecylphthalate:chromosorb P = 1:5, $N_2$ flow rate 60ℓ $h^{-1}$; unit 3, 488 cm x 75 mm i.d., dinonyl phthalate: chromosorb P = 1:5, $N_2$ flow rate 60ℓ $h^{-1}$; unit 4, 920 cm x 7 mm i.d., Ucon oil 50-HB2000: chromosorb P = 1:10, $N_2$ pressure 1.05 Kg $cm^{-2}$; unit 5, 488 cm x 35 mm i.d., dinonylphthalate:celite = 1:2, $N_2$ flow rate 15ℓ $h^{-1}$; unit 6, 900 cm x 8 mm i.d., PEG "A":chromosorb P = 1:6, $N_2$ flow rate 20 ℓ $h^{-1}$; unit 7, 488 cm x 35 mm i.d., Ucon oil 50-HB2000:chromosorb P = 1:10, $N_2$ flow rate 17 ℓ $h^{-1}$; unit 8, 488 cm x 75 mm i.d., silicone gum:celite = 1:6, $N_2$ flow rate 70 ℓ $h^{-1}$; unit 9, 920 cm x 7 mm i.d., silicone gum:Universal B = 1:40, $N_2$ pressure 1.05 Kg $cm^{-2}$; unit 10, 180 cm x 4 mm i.d., silicone gum:Universal B = 1:40, $N_2$ pressure 0.35 Kg $cm^{-2}$.

## Spectroscopy

Mass spectra were measured on an A.E.I. MS.9 Mass Spectrometer. All NMR spectra were measured on a Perkin Elmer R.10 Spectrometer at 60 MHz for $^1H$ and 56.4 MHz for $^{19}F$ spectra, except those marked + which were measured on an H.A.100 Spectrometer at 100 MHz for $^1H$ and 94.1 MHz for $^{19}F$ spectra. Except where otherwise indicated samples were dissolved in carbon tetrachloride. Proton and fluorine chemical shifts, measured against T.M.S. and trichlorofluoromethane as internal standards respectively, are quoted in $\tau$ and $\phi$ * values.

Infra red spectra were measured using a Perkin Elmer 257 Spectrophotometer.

## Starting Materials

Hexafluoro-, pentafluoro- and bromopentafluorobenzene were supplied by Imperial Smelting Corporation, Avonmouth: octafluorocyclohexa-1,3- and -1,4 -diene, 2,3,4,5,6-pentafluorotoluene, octafluorotoluene, decafluoro-p-xylene, and 2,3,4,5,6-pentafluoroanisole were prepared by known methods [18]. For the reactions of polyfluoroaromatic compounds in the presence of molar or twice molar proportions of bromine, the bromine trifluoride used was obtained from B.D.H. In the remaining experiments bromine trifluoride prepared by the fluorination of bromine [19] was used in order to ensure complete absence of bromine.

## General Procedure

The polyfluoroaromatic compound and solvent were placed in a nickel vessel of 100 $cm^3$ volume with a brass lid, which was fitted with a stainless steel stirrer, copper condenser and a thermometer pocket. The mixture was brought to the appropriate temperature and the required weight of bromine added through the condenser, followed by the bromine trifluoride, at a rate which caused no temperature increase. The mixture was then stirred, and at the end of the reaction water was added to destroy excess bromine trifluoride. The organic layer was separated, washed with sodium metabisulphite solution (10%), water, and then dried ($MgSO_4$). The organic product was then separated by distillation and preparative scale GLC.

## Hexafluorobenzene and $BrF_3/Br_2$

Hexafluorobenzene (10.0 g), decafluoro-p-dimethylcyclohexane (40 $cm^3$) and bromine (8.6 g) were stirred at 0°, and bromine trifluoride (7.3 g) added slowly. The mixture was then stirred at 0° for 1 h and, after the standard work up procedure, the organic mixture was separated by preparative scale GLC (Unit I, 85°) to give, in addition to solvent, (i) octafluorocyclohexa-1,4-diene [20] (1.1 g), identified by I.R. spectroscopy, and (ii) 4-bromo-nonafluorocyclohexene (7.6 g), b.p. 99° (Found: C, 22.5; H, 0.0; Br, 24.4; F, 52.7. $C_6BrF_9$ requires C, 22.3; H, 0.0; Br, 24.8; F, 52.9%). Mass spectrometry gave a top mass peak 324 (one bromine atom): $C_6BrF_9^+$ requires 324. The IR spectrum showed an absorption at 1747 $cm^{-1}$ (-CF=CF-).

## Reactions of 4-Bromo-nonafluorocyclohexene

### (i) Reduction

The title compound (4.5 g), zinc powder (1.2 g) and methanol (30 $cm^3$) were stirred under reflux for 2 h, when the mixture was fractionally distilled, and the distillate (10 $cm^3$) poured into water (20 $cm^3$). The organic layer (2.8 g) was separated by preparative scale GLC (unit I, 85°) to give (i) octafluorocyclohexa-1,4-diene (0.1 g), (ii) octafluorocyclohexa-1,3-diene [20] (trace), (iii) 4H-nonafluorocyclohexene [21] (0.3 g) and (iv) 4-bromo-nonafluorocyclohexene (1.7 g), all identified by a comparison of their IR spectra with those of authentic samples.

(ii) Oxidation

4-Bromo-nonafluorocyclohexene (1.3 g), was dissolved in dry acetone (50 $cm^3$) containing $KMnO_4$ (2.5 g) and the mixture refluxed for 30 min. Water (50 $cm^3$) was added, the solution evaporated to remove acetone, and the residue decolourized with $SO_2$. The aqueous solution was acidified ($H_2SO_4$) and continuously extracted with ether for 24 h. The ethereal extracts were dried ($MgSO_4$), evaporated to a small bulk, and the dianilinium salt precipitated with freshly distilled aniline. Recrystallization of the precipitate from ethanol/chloroform gave di-anilinium 3-bromoheptafluoroadipate (2.0 g), m.p. 206-7° (Found: C, 40.3; H, 3.2; F, 24.7; N, 5.2. $C_{18}H_{16}BrF_7N_2O_4$ requires C, 40.2; H, 3.0; F, 24.8; N, 5.2%). The $^{19}F$ NMR spectrum (in deuterated DMSO) consisted of five signals at $\phi$ * 115.9 ($>$ CFBr), 113.3 and 111.6 (both collapsed AB systems ascribed to two $> CF_2$ groups), 109.0 and 107.2 (the inner lines of an AB system due to a $> CF_2$ group). The signals had acceptable intensity ratios and were consistent with the proposed structure.

The adipate was dissolved in warm water (5 $cm^3$) and S-benzyl thiouronium chloride added. The precipitate was filtered and dried to give di-S-benzyl thiouronium 3-bromoheptafluoroadipate (1.7 g), m.p. 219° (Found: C, 38.9; H, 3.3; N, 8.4. $C_{22}H_{22}BrF_7N_4O_4S_2$ requires C, 38.7; H, 3.2; N, 8.2%).

(iii) Reaction with Bromine

4-Bromo-nonafluorocyclohexene (5.5 g) and bromine (3.0 g) were irradiated with UV light in a quartz vessel for 72 h. The product was washed with aq $NaHSO_3$ and water to give a product (5.0 g), which after distillation from $P_2O_5$ in vacuum, afforded 1,2,4-tribromononafluorocyclohexane (3.2 g), b.p. 185° (Found: C, 14.5; H, 0.0; Br, 50.0; F, 35.1. $C_6Br_3F_9$ requires C, 14.9; H, 0.0; Br, 49.7; F, 35.4%). Mass spectrometry gave a top mass peak of 486 with three bromine atoms ($C_6Br_3F_9^+$ requires 486).

(iv) Reaction with $BrF_3/Br_2$ –

The cyclohexene (5.0 g), perfluoro-p-dimethylcyclohexane (30 $cm^3$) and bromine (2.5 g) were stirred at 0° and bromine trifluoride (2.0 g) added slowly. After 1 h the mixture was worked up to give starting material (3.2 g) only.

### Octafluorocyclohexa-1,4-diene and BrF$_3$/Br$_2$ –

A mixture of the diene (10.0 g) 1,1,2-trichlorotrifluoroethane (60 cm$^3$) bromine (7.0 g) and bromine trifluoride (6.1 g) was left for 2 h at 0° and then treated as above. Separation (GLC Unit 1, 85°) gave, in addition to solvent 4-bromononafluorocyclohexene (7.2 g) as the sole product, identified by IR spectroscopy.

### Octafluorocyclohexa-1,3-diene and BrF$_3$/Br$_2$ –

The diene (10.0 g), bromine (7.0 g) and 1,1,2-trichlorotrifluoroethane (60 cm$^3$) were stirred together at 0° and bromine trifluoride (6.1 g) added slowly. The mixture was stirred for 2 h and gave (GLC unit 3, 80°) (i) decafluorocyclohexene [22] (3.3 g), (ii) 1,1,2-trichlorotrifluoroethane and (iii) 4-bromo-nonafluorocyclohexene (4.2 g), all identified by IR spectroscopy.

### Octafluorotoluene and BrF$_3$/Br$_2$ –

Octafluorotoluene (10.0 g) and 1,1,2-trichlorotrifluoroethane (60 cm$^3$) were stirred together at 0°. Bromine (7.2 g) and bromine trifluoride (6.2 g) were slowly added, and the whole stirred for 2 h. The residue (18.8 g) after removal of solvent was separated (GLC unit 3, 80°) to give (i) (with S.F.Campbell and R.Stephens) 1-trifluoromethylheptafluorocyclohexa-1,4-diene (0.6 g) b.p. 78-79° (Found: C, 30.6; H, 0.0. $C_7F_{10}$ requires, C, 30.7; H, 0.0%). The IR spectrum showed absorptions at 1780 cm$^{-1}$ (-CF = CF-) and 1720 cm$^{-1}$ ($-CF=\overset{|}{C}-CF_3$) with a UV spectrum (ethanol) $\lambda_{max}$ 2650 ($\epsilon$ 765). Mass spectrometry gave a top mass peak of 274 ($C_7F_{10}$ requires 274). (ii) 1,1,2-Trichlorotrifluoroethane (3.6 g), (iii) a mixture of 1-trifluoromethyl-bromo-octafluorocyclohexene isomers (8.2 g) (Found: C, 22.2; H, 0.1; Br, 21.5; F, 56.3. $C_7BrF_{11}$ requires C, 22.5; H, 0.0; Br, 21.4; F, 56.1%) and (iv) octafluorotoluene (0.8 g), identified by IR.

The IR spectrum of (iii) showed an absorption at 1715 cm$^{-1}$ and mass spectrometry gave a top mass peak of 374, with one bromine atom ($C_7BrF_{11}^+$ requires 374). The $^{19}$F NMR spectrum was complex, but showed a signal at $\phi$* 59.8 typical of a CF$_3$-group; no tertiary fluorine atoms were detected. The remaining fluorine signals formed a complex system not susceptible to analysis.

The reaction was repeated using octafluorotoluene (11.8 g), bromine (16.4 g) and bromine trifluoride (13.7 g) in 1,1,2-trichlorotrifluoroethane at 0° as described above. The excess solvent was distilled off to leave a residue (17.1 g), which was fractionally distilled through a Vigreux column to give (i) solvent (1.5 g), (ii) a mixture of 1-trifluoromethyl-bromo-octafluorocyclohexene isomers (13.0 g), and a residue (2.2 g) for which mass spectrometry gave a top mass peak 436, with two bromine atoms ($C_7Br_2F_{10}^+$ requires 436).

## Attempted Identification of 1-trifluoromethyl-bromo-octafluorocyclohexene isomer mixture

### (i) Oxidation

The 1-trifluoromethyl-bromo-octafluorocyclohexene isomer mixture (1.1 g), and $KMnO_4$ (1.5 g) in acetone (30 cm$^3$) as described above, gave (from ethanol/chloroform) dianilinium tetrafluorosuccinate (1.4 g), m.p. 222-223° (cited [20] 224-225°), with IR and $^{19}F$ NMR spectra identical with those of an authentic sample.

The bromocyclohexene (1.1 g) and aqueous alkaline $KMnO_4$ likewise gave dianilinium tetrafluorosuccinate (1.9 g).

### (ii) Reduction

The olefin mixture (3.0 g), methanol (40 cm$^3$) and zinc dust (1.0 g) were stirred and refluxed together for 16 h. Water (100 cm$^3$) was then added, the mixture ether extracted (3 x 30 cm$^3$) and the extracts washed, dried and evaporated. The residue (2.3 g) gave (GLC unit 4, 100°) (i) ether (0.3 g), (ii) a mixture of three compounds (0.3 g), which were not separated and (iii) o-methoxyheptafluorotoluene (1.2 g), b.p. 148-149° (Found: C, 38.9; H, 1.2; F, 53.5. $C_8H_3F_7O$ requires C, 38.7; H, 1.2; F, 53.6%). The IR spectrum showed three weak absorption maxima at 3010, 2940 and 2870 cm$^{-1}$ (aliphatic C-H) and a strong absorption at 1650 cm$^{-1}$ (aromatic C-F). The mass spectrum gave a top mass peak of 248 ($C_8H_3F_7O^+$ requires 248). The $^{19}F$ NMR spectrum consisted of five signals in the ratio 3:1:1:1:1 at $\phi$ * 56.4 (d, J = 27.6 Hz), 154.5 (d of d, J = 16.6 and 8.3 Hz), 149.9 (d of tr, J = 5.5 and 19.3 Hz), 161.8 (tr, J = 16.6 Hz), and 140.6 (multiplet) respectively. A consideration of chemical shift parameters gives expected $\phi$ * values for a meta substituted compound of 133.6, 143.1, 162.5 and 139.8, and for an ortho derivative of 155.9, 149.7, 162.1 and 140.1.

The $^1$H NMR spectrum consisted of one signal $\tau$ 6.0 (d) typical of $CH_3O$- attached to an aromatic ring.

### (iv) Fluorination of the mixed 1-trifluoromethyl-bromo-olefin

A mixture of the olefins (1.4 g) was fluorinated over $CoF_3$ at 200° in the usual way to give a product (1.1 g) shown by GLC analysis to consist largely of a single component. Separation by preparative scale GLC (unit 5, 80°) gave a mixture of bromo-tridecafluoromethylcyclohexane isomers (0.7 g) (Found: C, 20.4; Br, 19.5; F, 59.8. $C_7BrF_{13}$ requires C, 20.6; Br, 19.6; F, 60.1%). The IR spectrum showed no $>C=C<$ absorption and mass spectrometry gave a top mass peak of 412, with one bromine atom ($C_7BrF_{13}^+$ requires 412). The $^{19}$F NMR spectrum $^+$ consisted of a signal at $\phi$ * 69.6 ($CF_3$-) and two signals at $\phi$ * 185.3 and 191.6 (tertiary fluorine atoms $CF_3$-$CF<$); the remainder of the $^{19}$F spectrum was a complex set of AB signals not susceptible to analysis.

### (v) Reduction of the Bromo-tridecafluorocyclohexane isomers

The mixed bromotridecafluorocyclohexane isomers (3.0 g) in dry ether (10 $cm^3$) were added to a stirred mixture of $LiA\ell H_4$ (0.3 g) in ether (30 $cm^3$) at 0°. The mixture was then stirred at 0° for 2 h, when water (50 $cm^3$) and N $H_2SO_4$ (20 $cm^3$) was added. The ether layer was separated, dried ($MgSO_4$) and evaporated. The product (1.65 g) (GLC unit 4, 70°) gave (i) ether (0.16 g), (ii) trans-4H-tridecafluoromethylcyclohexane [23] (0.3 g), b.p. 93°, identified by IR and (iii) a complex mixture of products (0.6 g), which would not readily be separated by GLC, but which was shown by IR spectroscopy to contain olefinic compounds.

Repeat experiments at -15°, and using diglyme as solvent gave a similar reaction mixture to the above. Additional experiments using methyl magnesium bromide in ether/THF at -70° as the reducing agent gave no reaction, starting material being recovered in good yield.

### (vi) Fluorination of 4-bromo-heptafluorotoluene

The title compound [24] (2.0 g) was fluorinated over $CoF_3$ at 200° in a flow of $N_2$ in the usual way. The product was washed with aq $NaHSO_3$ and water, and distilled in vacuo from phosphorus pentoxide to give a mixture

(2.3 g) of two compounds (GLC). An aliquot (1.0 g) was separated by preparative scale GLC (unit 5, 80°) into (i) perfluoromethylcyclohexane [25] (0.1 g) and (ii) 4-bromo-tridecafluoromethylcyclohexane (0.6 g) (Found: C, 20.1; F, 59.6. $C_7BrF_{13}$ requires C, 20.4; F, 60.1%). Mass spectrometry gave a top mass peak of 412, with one bromine atom ($C_7BrF_{13}^+$ requires 412). The $^{19}F$ NMR spectrum $^{+}$ contained signals at $\phi^*$ 70.2 ($CF_3$-) and 190.6 (tertiary fluorine in $CF_3$-CF< ); the remainder of the spectrum consisted of a complex set of overlapping AB signals not susceptible to analysis.

## Decafluoro-*p*-xylene and $BrF_3/Br_2$

To decafluoro-*p*-xylene (10.0 g) and bromine (5.6 g) in 1,1,2-trichlorotrifluoroethane at 0° was added slowly, with stirring, bromine trifluoride (4.8 g), and the reaction mixture stirred for 2 h. Isolation gave a residue (12.2 g) and thence (GLC unit 3, 80°) (i) 1,4-*bis*(trifluoromethyl)-hexafluorocyclohexa-1, 4-diene [26] (3.5 g), identified by IR spectroscopy, (ii) 1,1,2-trichlorotrifluoroethane (2.6 g), (iii) 4-bromo-1,4-*bis*(trifluoromethyl)heptafluorocyclohexene (1.7 g), b.p. 105-6° (Found: C, 22.9; Br, 19.0; F, 58.4. $C_8BrF_{13}$ requires C, 22.7; Br, 18.9; F, 58.4%). The mass spectrum gave a top mass peak of 424, with one bromine atom ($C_8BrF_{13}^+$ requires 424) and the IR spectrum showed an absorption at 1720 $cm^{-1}$ ($CF_3$-C=C-F). The $^{19}F$ NMR spectrum showed signals at $\phi^*$ 59.3 and 63.5 due to the trifluoromethyl-groups at positions 1- and 4- respectively, each of intensity ratio 3, together with a further set of signals of total intensity ratio 7, consisting of two AB systems, chemical shifts $\phi^*$ A, 98.5; B, 116.9 (J. 320 Hz); A, 92.2; B, 116.4 (J 320 Hz), a collapsed AB system $\phi^*$ 117.4, and a vinylic fluorine signal at $\phi^*$ 109.5, consistent with the proposed structure. No tertiary fluorine was present.

The reaction was repeated using perfluoro-*p*-xylene (10.0 g), bromine (11.2 g) and bromine trifluoride (9.6 g) in 1,1,2-trichlorotrifluoroethane (40 $cm^3$) at 0°. The residue (15.3 g) gave (i) 1,4-*bis*(trifluoromethyl)hexafluorocyclohexa-1,4-diene (5.3 g), (ii) solvent (1.6 g) and (iii) 4-bromo-1, 4-*bis*(trifluoromethyl)heptafluorocyclohexene (3.5 g), all identified by IR spectroscopy.

### Reduction of 4-bromo-1,4-bis(trifluoromethyl)heptafluorocyclohexene

The cyclohexene (1.4 g) was refluxed and stirred for 16 h with zinc (1.0 g) and methanol (20 cm$^3$). The reaction mixture was poured into water (150 cm$^3$) and the solution ether extracted. The residue (1.1 g) (GLC unit 4, 100°) gave (i) ether (0.1 g), (ii) decafluoro-p-xylene (0.6 g) and (iii) 2-methoxynonafluoro-p-xylene [27] (0.2 g), all identified by IR spectroscopy.

### Bromopentafluorobenzene and BrF$_3$/Br$_2$

To the aromatic (10.0 g) in 1,1,2-trichlorotrifluoroethane (60 cm$^3$) at 0° was added, with stirring, bromine (5.2 g) and bromine trifluoride (4.5 g) and the mixture stirred for 2 h. After the usual work up, solvent was distilled from the product through a short fractionating column and the residue (12.3 g), fractionally distilled to give I, (4.1 g), b.p. 47-49°, (largely solvent), II (2.3 g), b.p. 79-106°, III (3.4 g), b.p. 106-120° and IV residue (1.3 g). IV was distilled under reduced pressure to give bromopentafluorobenzene (0.5 g), and unidentified residue (0.8 g).

Fraction II (GLC unit 6, 140°) gave (i) solvent (0.1 g) and (ii) <u>1-bromoheptafluorocyclohexa-1,4-diene</u> (0.6 g), b.p. 110° (Found: C, 25.1; Br, 28.0; F, 47.0. $C_6BrF_7$ requires C, 25.1; Br, 28.0; F, 46.8%). The IR spectrum showed two absorption maxima at 1705 cm$^{-1}$ and 1773 cm$^{-1}$ $({}^{Br}{>}C{=}C{<}^{F}$ and ${}^{F}{>}C{=}C{<}^{F})$ and mass spectrometry gave a top mass peak of 286 with one bromine atom ($C_6BrF_7^+$ requires 286). The $^{19}F$ NMR spectrum had five signals, intensity ratio 2:2:1:1:1, with chemical shifts $\phi$ * 102.0, 112.3, 119.2, 152.0 and 158.0 respectively, in agreement with the proposed structure. Further components obtained from fraction II were (iii) bromopentafluorobenzene (0.6 g), identified by IR spectroscopy and (iv) mixed dibromooctafluorocyclohexene isomers (0.4 g) (Found C, 19.0; Br, 41.8; F, 39.6. $C_6Br_2F_8$ requires C, 18.7; Br, 41.7; F, 39.6%). The IR spectrum showed an absorption maximum at 1680 cm$^{-1}$ $({}^{F}{>}C{=}C{<}^{Br})$, and mass spectrometry a top mass peak of 386, with two bromine atoms ($C_6Br_2F_8^+$ requires 386). The $^{19}F$ NMR spectrum was extremely complex and consistent with the sample being a mixture of isomers.

Fraction III (GLC unit 6, 140°) gave (i) 1-bromoheptafluorocyclohexa-1,4-diene (0.2 g), (ii) the same dibromo olefin mixture as for fraction II (0.5 g) and (iii) bromopentafluorobenzene (1.6 g), all identified by IR spectroscopy.

The reaction was repeated using bromopentafluorobenzene (15 g), bromine (19.8 g), bromine trifluoride (16.7 g) in 1,1,2-trichlorotrifluoroethane (60 cm$^3$) at 0° for 2 h. Work up as above gave a residue (24.0 g), which was fractionally distilled into I, (5.2 g), b.p. 47.5-50°, (solvent); II (0.5 g), b.p. 50-140°, shown by GLC to be a mixture of the dibromooctafluorocyclohexene isomers obtained previously and solvent (ratio 40:60); III (9.3 g), b.p. 140-150° consisting of dibromooctafluorocyclohexene isomers, and a residue (7.9 g). A portion (2.1 g) of this residue (GLC unit 6, 60°) gave (i) the dibromooctafluorocyclohexene isomer mixture (0.3 g) and (ii) tribromononafluorocyclohexane isomers (1.1 g), (Found: C, 14.8; Br, 50.0; F, 35.5. $C_6Br_3F_9$ requires C, 14.9; Br, 49.7; F, 35.4). Mass spectrometry gave a top mass peak (with three bromine atoms) of 486: ($C_6Br_3F_9^+$ requires 486).

## Oxidation of 1-bromoheptafluorocyclohexa-1,4-diene

The diene (0.3 g) was refluxed with $KMnO_4$ (1.0 g) and acetone (20 cm$^3$) for 3 h. Work up in the usual way gave dianilinium difluoromalonate (0.5 g), m.p. 158-60° (cited [21] m.p. 160-161°). The $^{19}F$ NMR spectrum consisted of a single signal $\phi^*$ 110.4, compared with a shift of $\phi^*$ 109.5 for that of an authentic sample [28] .

## Oxidation of the dibromo-octafluorocyclohexene isomer mixture

The olefin mixture (0.4 g) was oxidized by $KMnO_4$/acetone mixture to give dianilinium 3-bromoheptafluoroadipate (0.6 g; 94%), m.p. 207-208°, identical with the product obtained previously from 4-bromononafluorocyclohexene.

Pentafluorobenzene and $BrF_3/Br_2$ –

To pentafluorobenzene (10.0 g) in 1,1,2-trichlorotrifluoroethane (60 $cm^3$) was added bromine (9.6 g) and bromine trifluoride (8.2 g) with stirring, the reaction mixture being kept at 0°. The product (19.8 g) was distilled under reduced pressure through a Vigreux column to give five fractions: I, (6.0 g), b.p. 20-25° [ this gave (GLC unit 7, 92°) (i) solvent (3.0 g) and (ii) 1-bromo-heptafluorocyclohexa-1,4-diene (1.5 g), both identified by IR spectroscopy] ; II, (1.5 g) b.p. 26-42° [ this gave (GLC unit 6, 140°) (i) solvent (0.2 g), (ii) 1-bromo-heptafluorocyclohexa-1, 4-diene (0.8 g), by IR spectroscopy and (iii) a mixture of compounds (0.1 g) not further investigated] ; III (3.8 g), b.p. 42-58° [ by GLC and IR spectroscopy this consisted largely ($>$ 80%) of 1-bromoheptafluorocyclohexa-1, 4-diene] ; IV (1.5 g), b.p. 58-68° [ a complex mixture of compounds which was not treated further] ; V (5.7 g), b.p. 68-82° [ a portion (2.5 g) of this (GLC unit 6, 140°) gave (i) 1-bromocyclohexa-1,4-diene (0.1 g), (ii) the dibromooctafluorocyclohexene mixture obtained previously (0.9 g), (iii) bromopentafluorobenzene (0.3 g) and (iv) the tribromononafluorocyclohexane isomer mixture similar to that obtained from bromopentafluorobenzene (0.2 g) and (v) an inseparable mixture of compounds (0.3 g) ]. All the compounds were identified by IR spectroscopy.

The reaction was repeated at 0° with pentafluorobenzene (15.0 g), bromine (28.8 g) and bromine trifluoride (24.7 g) in 1,1,2-trichlorotrifluoroethane (60 $cm^3$). Separation (GLC unit 8, 150°) gave three components: (I), 1,1,2-trichlorotrifluoroethane (3.6 g), II, a mixture (2.2 g) and III, the tribromononafluorocyclohexane mixture (18.9 g), similar to that obtained from bromopentafluorobenzene. Mixture II (2.2 g) separated (GLC unit 6, 140°) into (i) a liquid (0.5 g) not further investigated and (ii) a dibromononafluorocyclohexane (1.1 g), (Found: C, 17.6; H, 0.5; Br, 39.5; F, 42.1. $C_6HBr_2F_9$ requires C, 17.9; H, 0.2; Br, 39.6; F, 42.4%). The IR spectrum showed an absorption maximum at 2985 (C-H stretch). Mass spectrometry gave a top mass peak of 405 with two bromine atoms ($C_6HBr_2F_9^+$ requires 406).

## 2,3,4,5,6-Pentafluorotoluene and $BrF_3/Br_2$

Pentafluorotoluene (10.0 g) and 1,1,2-trichlorotrifluoroethane (60 $cm^3$) were mixed and cooled to -10°. Bromine (8.8 g) and bromine trifluoride (7.5 g) were added slowly, and the mixture stirred for 1 h. The residue (13.2 g) on fractional distillation gave I (3.1 g), b.p. 47-58°, II, (4.4 g), b.p. 58-110°, III (1.3 g), b.p. 110-114° and IV residue (3.8 g).

I was principally 1,1,2-trichlorotrifluoroethane (IR spectroscopy) II-IV being multicomponent mixtures. II (1.7 g) (GLC unit 6, 80°) gave (i) 1,1,2-trichlorotrifluoroethane (0.1 g) (IR spectroscopy), (ii) 1-methylheptafluorocyclohexa-1,4-diene [29] (0.5 g), (iii) 3-methylheptafluorocyclohexa-1,4-diene [29] (0.3 g) and (iv) a mixture (0.2 g) not further investigated; (ii) and (iii) were identified by IR spectroscopy.

III by GLC (unit 6, 80°) consisted largely ($>$ 50% by peak area measurements) of pentafluorotoluene, but contained also traces of the two dienes isolated from II. A portion (1.0 g) of IV (GLC unit 6, 140°) gave (i) pentafluorotoluene (0.2 g), identified by IR spectroscopy, (ii) a mixture of four closely retained components (0.1 g), not further investigated and (iii) a mixture of isomeric methyldibromononafluorocyclohexanes (0.4 g) (Found: C, 19.8; H, 1.0; Br, 38.3; F, 41.0. $C_7H_3Br_2F_9$ requires C, 20.1; H, 0.7; Br, 38.3; F, 40.9%). Mass spectrometry gave a top mass peak of 420 with two bromine atoms ($C_7H_3Br_2F_9$ requires 420). The IR spectrum showed no $>C=C<$ absorption. The $^{19}F$ NMR spectrum was complex and not susceptible to analysis, although the $^1H$ spectrum showed three signals at $\tau$ 7.90, 8.15 and 8.30 corresponding to three different methyl groups.

The reaction was repeated using pentafluorotoluene (9.0 g), bromine (16.0 g) and bromine trifluoride (13.6 g) in 1,1,2-trichlorotrifluoroethane (60 $cm^3$) at 0° for 2 h. Fractional distillation under reduced pressure gave I (5.8 g), identified as solvent, II (2.0 g) b.p. 20-50°, identified by GLC and IR spectroscopy as a mixture of 1-methyl- and 3-methyl-heptafluorocyclohexa-1,4-diene, and III (10.3 g), b.p. 50-70°, identified by IR spectroscopy as the mixed methyldibromononafluorocyclohexane isomers obtained previously.

## 2,3,4,5,6-Pentafluoroanisole and $BrF_3/Br_2$

The title compound (11.0 g), bromine (8.7 g), bromine trifluoride (7.3 g) and 1,1,2-trichlorotrifluoroethane (40 $cm^3$) were reacted at -10° for 1 h. The crude product (19.7 g) fractionally distilled under reduced pressure (100 mm Hg) gave: I (2.7 g) solvent; II (2.6 g), b.p. 20-45°; III (1.0 g) b.p. 45-55°; IV residue (12.2 g). II (GLC unit 9, 100°) gave (i) 1,1,2-trichlorotrifluoroethane (0.1 g), (ii) 3-methoxyheptafluorocyclohexa-1,4-diene (1.4 g), identified [29] by IR spectra and (iii) an inseparable mixture (0.5 g), shown by IR spectroscopy to contain unsaturated compounds. III was a complex mixture which could not be separated: by GLC it contained II(ii) and II(iii) and a longer retained compound. IV was distilled under reduced pressure, and showed only one peak by GLC (unit 10, 100°). It was a mixture of methoxydibromononafluorocyclohexane isomers (Found: C, 19.8; H, 0.8; Br, 36.4; F, 39.7. $C_7H_3Br_2F_9O$ requires C, 19.4; H, 0.7; Br, 36.7; F, 39.7%). IR spectroscopy showed absorption maxima at 2860 $cm^{-1}$, 2970 $cm^{-1}$ and 3020 $cm^{-1}$ ($-OCH_3$). Mass spectrometry gave a top mass peak at 436 with two bromine atoms ($C_7H_3Br_2F_9O^+$ requires 436). The $^1H$ NMR spectrum consisted of a broad peak at $\tau$ 6.1 typical of $-OCH_3$: the $^{19}F$ spectrum was complex and not susceptible to analysis.

The experiment was repeated using 2,3,4,5,6-pentafluoroanisole (8.0 g), bromine (13.0 g) and bromine trifluoride (11.2 g), in 1,1,2-trichlorotrifluoroethane (60 $cm^3$) at 0° for 2 h. The reaction product was treated as before and the solvent evaporated to give a residue (17.1 g) which was separated by vacuum distillation (96°/100 mm Hg) into (i) solvent (3.6 g) and (ii) the mixture of methoxydibromononafluorocyclohexane isomers (12.4 g).

## Hexafluorobenzene and $BrF_3$ alone

(a) Hexafluorobenzene (10.0 g) was stirred with 1,1,2-trichlorotrifluoroethane (60 $cm^3$) and bromine trifluoride (7.4 g) added slowly, and the mixture stirred for 1 h. Isolation (GLC unit 3, 80°) gave (i) 1,1,2-trichlorotrifluoroethane (3.4 g) and (ii) hexafluorobenzene (6.5 g), both identified by IR spectroscopy.

(b) The reaction as in (a) was repeated but with the addition of bromine (0.43 g). The residue (11.9 g) (GLC unit 3, 80°) gave (i) 1,1,2-trichlorotrifluoroethane (3.7 g) and (ii) 4-bromononafluorocyclohexene (8.2 g), both identified by IR spectroscopy.

## Pentafluorobenzene and $BrF_3$ alone

Pentafluorobenzene (10.0 g), 1,1,2-trichlorotrifluoroethane (60 $cm^3$) and bromine trifluoride (8.2 g) at 0° for 2 h gave a residue (15.2 g) which fractionally distilled into I (5.0 g), b.p. 47.5°, (by IR spectroscopy 1,1,2-trichlorotrifluoroethane); II (1.2 g), b.p. 47.5-86°; III (2.7 g), b.p. 86-110°, IV (2.1 g), b.p. 110-125° and V residue (2.5 g).

II (GLC unit 6, 140°) gave (i) 1,1,2-trichlorotrifluoroethane (0.3 g), (ii) 1-bromoheptafluorocyclohexa-1,4-diene (0.2 g), (iii) pentafluorobenzene (0.2 g), (iv) a mixture of the dibromooctafluorocyclohexene isomers (0.1 g) and (v) bromopentafluorobenzene (0.1 g). III (GLC unit 6, 140°) gave (i) 1-bromoheptafluorocyclohexa-1,4-diene (0.5 g), (ii) the mixture of dibromooctafluorocyclohexene isomers (0.8 g) and (iii) bromopentafluorobenzene (0.6 g). IV (1.1 g) (GLC unit 6, 140°) gave (i) the mixture of dibromooctafluorocyclohexene isomers (0.1 g) and (ii) bromopentafluorobenzene (0.7 g). V (2.5 g) was distilled under reduced pressure to give bromopentafluorobenzene (2.1 g). All the components obtained from these fractions were identified by IR spectroscopy.

## 2,3,4,5,6-Pentafluoroanisole and $BrF_3$ alone

Pentafluoroanisole (7.4 g) 1,1,2-trichlorotrifluoroethane (60 $cm^3$) and bromine trifluoride (4.9 g) were stirred together at 0° for 2 h. Fractional distillation gave I (5.5 g), b.p. 47.5-90°, 1,1,2-trichlorotrifluoroethane; II (1.7 g) b.p. 90-110°; III (2.1 g), b.p. 110-130° and IV residue (3.6 g).

II gave (GLC unit 6, 140°) (i) 1,1,2-trichlorotrifluoroethane (0.3 g), (ii) 3-methoxyheptafluorocyclohexa-1,4-diene (0.8 g) and (iii) an unknown mixture (0.2 g); III (GLC unit 6, 140°) gave (i) 3-methoxyheptafluorocyclohexa-1,4-diene (0.3 g), (ii) a mixture identical to II (iii) (0.1 g) and (iii) the mixture of methoxydibromononafluorocyclohexane isomers (0.3 g): IV also was methoxydibromononafluorocyclohexane isomers. All of the components from the fractions were identified by IR spectroscopy.

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