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PREPARATION OF GEOMETRIC ISOMERS OF SOME POLYFLUORO-2-BUTENES[1]

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Abstract—The preparation of 2*H*-heptafluoro-2-butene from hexachloro-1,3-butadiene and potassium fluoride, using N-methyl-2-pyrrolidone as solvent, has now been found to give the *trans* isomer (>95%). Dehydrohalogenation of pure diastereomeric forms of 2*H*-2,3-dichloroheptafluorobutane and 2*H*-2,3-dibromoheptafluorobutane, formed by the free radical addition of the halogen to 2*H*-heptafluoro-2-butene gives pure *cis* and *trans* isomers of 2-chloroheptafluoro-2-butene and 2-bromoheptafluoro-2-butene. *cis* and *trans*-Octafluoro-2-butene are prepared by dehydrobromination of individual diastereomers of 2*H*-3-bromo-octafluorobutane.

HITHERTO individual geometric isomers of polyfluoro-olefins have not been easily accessible. In some cases, for example 2,3-dichlorohexafluoro-2-butene[2] and octafluoro-2-butene[3], separation of isomers by GLC has been reported but only with very great difficulty in the case of octafluoro-2-butene. Fluoro-olefins are frequently prepared by dehydrohalogenation reactions[4] and we now report that pure geometric isomers of the olefins (IV, V and VI) may be obtained by dehydrohalogenation of the pure diastereomeric forms of 2*H*-2,3-dichloroheptafluorobutane (II), 2*H*-2,3-dibromoheptafluorobutane (III) and 2*H*-3-bromo-octafluorobutane (VII). The diastereomeric forms of the hydro derivatives (II, III and VII) are easily separable by GLC, using a polar column (di-n-decylphthalate). This observation corresponds to other experience in this laboratory, that isomeric halohydrocarbons are generally much more easily resolved on GLC than corresponding derivatives containing chlorine or bromine instead of the hydrogen.

$$CF_3\cdot CH{=}CF\cdot CF_3 + X_2 \xrightarrow{UV} CF_3\cdot CHX\cdot CFX\cdot CF_3 \xrightarrow[(-HX)]{aq.\ KOH} CF_3\cdot CX{=}CF\cdot CF_3$$

I *trans* II: X = Cl IV: X = Cl
III: X = Br V: X = Br
cis or *trans*

$$CF_3\cdot CF{=}CF\cdot CF_3 + \xrightarrow[UV]{HBr} CF_3\cdot CHF\cdot CFBr\cdot CF_3 + CF_3\cdot CFBr\cdot CFBr\cdot CF_3$$

VI VII VIII

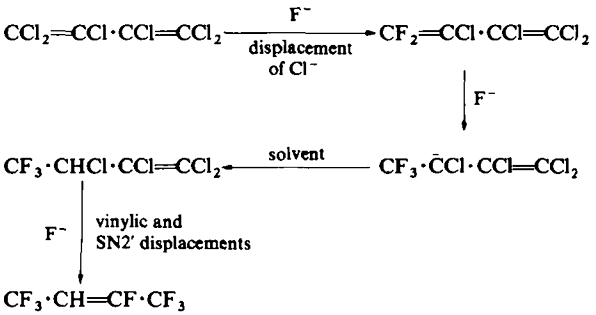
$$\Big\downarrow \begin{array}{l} aq.\ KOH \\ (-HBr) \end{array}$$

$$CF_3\cdot CF{=}CF\cdot CF_3$$

VI: *cis* or *trans*

trans-2H-*Heptafluoro-2-butene.* The preparation of 2*H*-heptafluoro-2-butene by treating hexachlorobuta-1,3-diene with anhydrous potassium fluoride in N-methyl-2-

pyrrolidone solvent at approximately 200° was first reported by Maynard.[5] The reaction was reported to yield a *cis-trans* mixture of the olefin (I). However, under conditions which we have employed only the *trans* isomer ($>95\%$) has been obtained. Although the mechanism of this reaction has not been established it has been proposed[5] that initial 1,2 addition of hydrogen fluoride occurs, although it is more likely that this takes place at some later stage in the reaction sequence. In the subsequent stages we clearly cannot yet distinguish between SN2′, and vinylic displacements, of chloride ion.



Analytical GLC of the purified product showed one major component due to the *trans* isomer of I and a very minor component of higher retention time ($\sim 2\%$) corresponding to the *cis* form (see later). The ^{19}F NMR spectrum consisted of three different chemically shifted peaks and was in agreement (after allowing for different referencing conditions) to that attributed to the mixture.[5] In order to confirm the formation of a single isomer, a mixture of *cis* and *trans* isomers of the olefin (I) was prepared by the addition of chlorine to I followed by dechlorination of the resulting 2*H*-2,3-dichloroheptafluorobutane (II). Since neither of these steps is stereospecific this resulted in partial isomerization of the olefin.

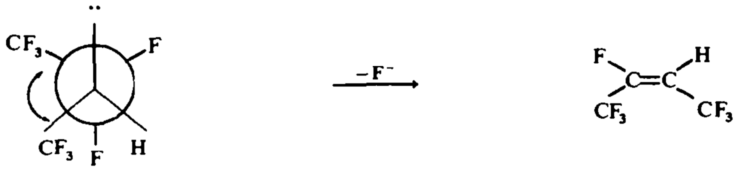
$$\underset{\substack{\textit{trans}\\ \text{I}}}{CF_3\cdot CH{=}CF\cdot CF_3} \xrightarrow[UV]{Cl_2} \underset{\text{II}}{CF_3\cdot CHCl\cdot CFCl\cdot CF_3} \xrightarrow{Zn/EtOH} \underset{\substack{\textit{cis}\text{ and }\textit{trans}\\ \text{I}}}{CF_3\cdot CH{=}CF\cdot CF_3}$$

The ^{19}F NMR spectrum of the product olefin consisted of six peaks and the three new ones may be assigned to the *cis* isomer. The *cis* and *trans* isomers are easily distinguished by comparison of the $J_{CF_3-CF_3}$ values which are 10·2 and 1–2 c/s respectively, since it is known that $J_{trans\,CF_3-CF_3} \ll J_{cis\,CF_3-CF_3}$[6] (Table 2).

We have shown that a mixture of $\sim 27\%$ *cis*- and $\sim 73\%$ *trans*-2*H*-heptafluoro-2-butene (I) is converted to the *trans* isomer only ($>95\%$) by heating a mixture of olefin with potassium fluoride in N-methyl-2-pyrrolidone at 185°. Reactions of fluoride ion with fluoro-olefins are well known and it is also established that nucleophilic attack on fluoro-olefins occurs preferentially at the carbon bearing fluorine.[7] Therefore, the equilibration process may be formulated according to the annexed scheme.

$$\underset{\textit{cis}\text{ and }\textit{trans}}{CF_3\cdot CH{=}CF\cdot CF_3} \xrightleftharpoons{F^-} CF_3\cdot \bar{C}H\cdot CF_2CF_3 \xrightleftharpoons{-F^{\ominus}} \underset{\textit{trans}}{CF_3\cdot CH{=}CF\cdot CF_3}$$

The reaction may be thermodynamically controlled, with the *trans* olefin being the more stable, but kinetic effects probably also favour the *trans* olefin, due to unfavourable interactions between trifluoromethyl groups in the formation of the *cis* isomer.



Surprisingly a mixture of *cis*- and *trans*-octafluoro-2-butene was not converted to the *trans* form under similar conditions. We are unable to account for the different results with these two olefins and the problem is being investigated further.

2-Chloro- and 2-bromoheptafluoro-2-butene. The photochemical addition of chlorine or bromine to 2*H*-heptafluoro-2-butene gave the diastereomeric forms of the adducts (II and III) which were easily separable by GLC, using di-n-decylphthalate as stationary phase. The diastereomers (IIa and IIIa) which gave the *cis* olefin on dehydrohalogenation, and had the longer retention times, constituted 60% and 66% of the products respectively. Results reported for the addition of hydrogen bromide to trifluoroethylene show that the addition of a Br atom takes place at either end of the double bond.[8]

$$CF_2{=}CFH \xrightarrow{HBr,\ UV} CF_2BrCFH_2 + CHFBrCF_2H$$

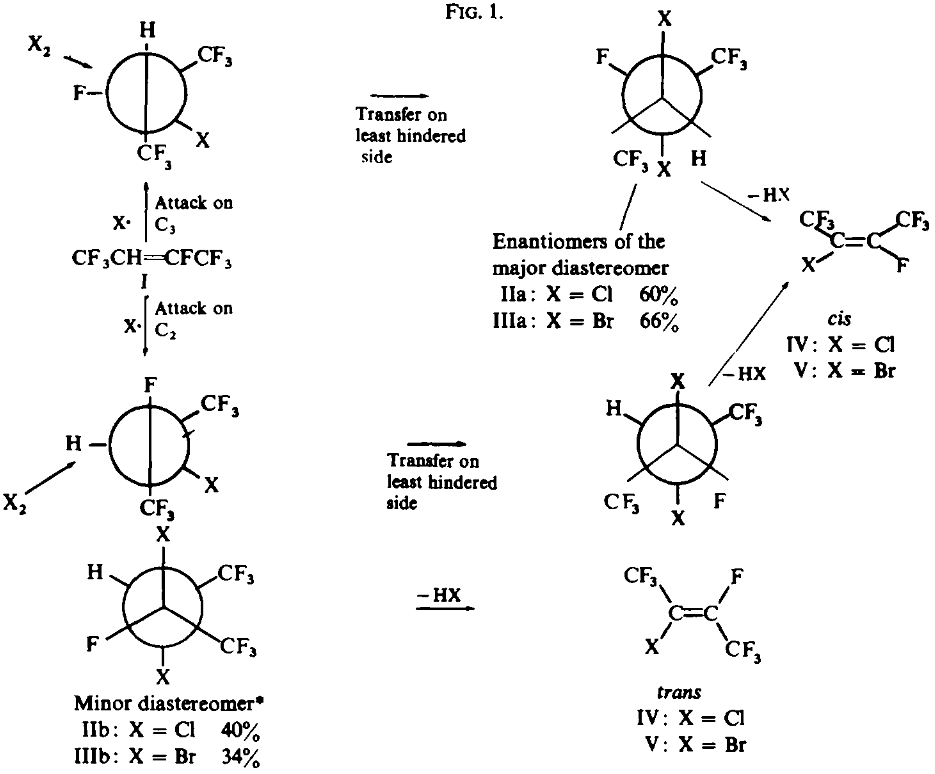
$$43\% \qquad\qquad 57\%$$

It is likely then that initial attack by both Cl and Br atoms on 2*H*-heptafluoro-2-butene (I) occurs at either the 2- or 3-positions, leading to $CF_3\dot{C}HCFXCF_3$ and $CF_3CHX\dot{C}FCF_3$ ($X = Cl$ or Br). It is also apparent that inversion of the intermediate radicals takes place prior to the transfer step, since the diastereomers of 2*H*-2,3-dichloroheptafluorobutane (IIa and IIb) and 2*H*-2,3-dibromoheptafluorobutane (IIIa and IIIb) were produced in the same ratio when either a mixture of *cis*- and *trans*-2*H*-heptafluoro-2-butene, or the *trans* isomer was used. Also, no isomerization of recovered olefin was detected during the addition of either halogen.

Fredricks and Tedder[9] have investigated the halogenation of 2-halobutanes and have explained the preferential formation of *erythro*- over *threo*-2,3-isomers in terms of the halogen approaching a preferred conformation of the intermediate radical, from the least hindered side, in the transfer step. Similar arguments may be used to account for the product ratios reported here (Fig. 1), the preferred conformations of the intermediate radicals having trifluoromethyl groups in *anti* positions. The diastereomeric forms of the adducts have different IR and ^{19}F NMR spectra (see Table 1) and their b.ps differ by 1–2°.

The dehydrohalogenation reactions were carried out using approximately 50% aqueous potassium hydroxide solution at 20–60°, resulting in the expected *trans* elimination. The geometric isomers of the olefins (IV and V) were identified from their ^{19}F NMR spectra, by examination of the coupling constants of the $1{-}CF_3$ group with the 3-F atom, (Table 2). It has been shown that in halogenated propenes J_{CF_3-F} is fairly constant at about 23 c/s when these groups are *cis* to each other, while J_{CF_3-F}

FIG. 1.



* For conciseness, only one enantiomer is shown in this case.

TABLE 1. FLUORINE-19 CHEMICAL SHIFTS OF POLYFLUOROBUTANES

Compound	Chemical shift	Group
$CF_3CHClCFClCF_3$ (IIa)	−94·3, −84·4 −38·3	CF_3 CF_3 CFCl
$CF_3CHClCFClCF_3$ (IIb)	−94·0, −82·6 −38·0	CF_3, CF_3 CFCl
$CF_3CHBrCFBrCF_3$ (IIIa)[a]	−97·5, 87·2 −45·4	CF_3, CF_3 CFBr
$CF_3CHBrCFBrCF_3$ (IIIb)	−97·0, −84·9 −41·3	CF_3, CF_3 CFBr
$CF_3CHFCFBrCF_3$ (VIIa)	−91·0, −84·0 −23·3 33·4	CF_3, CF_3 CFBr CHF
$CF_3CHFCFBrCF_3$ (VIIb)	−91·6, −85·8 −18·7 32·6	CF_3, CF_3 CFBr CHF
$CF_3CFBrCFBrCF_3$[b] (VIII)	−89·6, −89·3 −34·4, −33·1	CF_3, CF_3 CFBr, CFBr

[a] Neat liquid.

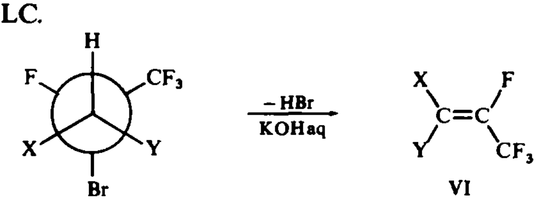
[b] Two diastereomers.

TABLE 2. FLUORINE-19 CHEMICAL SHIFTS OF POLYFLUORO-2-BUTENES
(Neat liquids, ppm rel. to $CFCl_3$ as internal ref, +ve shifts are measured to a higher field)

Olefin	Chemical shift (p.p.m.)	Coupling Constants (c/s)	Group
trans-$CF_3CH{=}CFCF_3$	60·4	$J_{14} = 1–2$	1-CF_3
	74·6		4-CF_3
	117·2		3-F
cis-$CF_3CH{=}CFCF_3$	56·8		1-CF_3
	69·6	$J_{41} = 10·2$	4-CF_3
	113·2		3-F
trans-$CF_3CBr{=}CFCF_3$	62·6	$J_{13} = 25·5$	1-CF
	68·1		4-CF_3
	102·4		3-F
cis-$CF_3CBr{=}CFCF_3$	59·8	$J_{13} = 9·0$	1-CF_3
	66·2		4-CF_3
	95·6		3-F
trans-$CF_3CF{=}CFCF_3$	69·9		CF_3
	160·9		F
cis-$CF_3CF{=}CFCF_3$	67·2		CF_3
	143·7		F

is about 9·5 c/s when the groups are *trans*.[10] The spectra of *cis*- and *trans*-2-chloroheptafluoro-2-butene (IV) have been analysed by Tiers.[11]

Separation of cis- *and* trans-*octafluoro-2-butene.* The photolytic addition of hydrogen bromide to octafluoro-2-butene (VI) giving 2*H*-3-bromo-octafluorobutane (VII) and 2,3-dibromo-octafluorobutane (VIII) was first reported by Haszeldine and Osborne.[12] We have found that elimination of hydrogen bromide from diastereomer VIIa which was produced in the greater amount (~65%), gave the *trans* olefin (VI) while the *cis* isomer was obtained from the minor diastereomer (VIIb). The preponderance of VIIa can be accounted for by considering the stereochemistry of attack on the intermediate radical, in arguments similar to those described earlier. Olefin recovered from a reaction starting with the *trans* isomer was partly isomerized. It is deduced that both diastereomers of the dibromo-compound (VIII) were produced, since the ^{19}F NMR spectrum showed four different chemically shifted peaks, but these were not separable on GLC.



VI

VIIa: X = CF_3, Y = F
VIIb: X = F, Y = CF_3

EXPERIMENTAL

The addition reactions were initiated using a 500 w. Hanovia UV lamp. Analytical-scale GLC was carried out using a Perkin-Elmer Model 451 Fractomer with di-isodecylphthalate as stationary phase. An Aerograph A700 'Autoprep' with di-n-decylphthalate as stationary phase was used for preparative-scale GLC. Diastereomeric forms of compounds are listed in their order of appearance from these columns.

B. ps were determined by Siwoloboff's method and are uncorrected. NMR spectra were determined using a Perkin-Elmer R10 spectrometer operating at 56·46 Mc/s.

trans-2H-*Heptafluoro-2-butene*

Hexachloro-1,3-butadiene (133 g, 0·510 mole) was added over a period of 3 hr, to a mixture of N-methyl-2-pyrrolidone (750 ml), purified by distillation, and anhyd KF (270 g, 4·65 moles) contained in a flask at 200° which was fitted with a stirrer and reflux condenser also connected to a trap at −183°. The temp was maintained for a further 3 hr while the product (56·7 g) collected in the trap. Fractional distillation of the product gave *trans*-2*H*-heptafluoro-2-butene (55 g, 59%) containing a trace of impurity corresponding to the *cis* isomer (~2%).

Additions to 2H-*heptafluoro-2-butene*

(a) *Chlorine.* (i) *trans*-2*H*-heptafluoro-2-butene (177 g, 97·3 mmoles) and Cl_2 (6·7 g, 94·5 mmoles) were sealed in a silica tube and irradiated at a distance of 25 cm for 17·25 hr. The tube was then opened and low boiling material allowed to evaporate off. The product was then distilled giving a colourless liquid (21·5 g). Analytical-scale GLC showed two separable major components and a trace of material of lower retention time. Separation of the major components by preparative scale GLC gave: the diastereomer (IIb) of 2H-2,3-*dichloroheptafluorobutane* b.p. 73°/763 mm. (Found: C, 18·9; H, 0·4; Cl, 28·4; F, 51·9. $C_4HCl_2F_7$ requires: C, 19·0; H, 0·4; Cl, 28·0; F, 52·6%); and the diastereomer (IIa) of 2H-2,3-*dichloroheptafluorobutane* b.p. 74–75°/763 mm. (Found: C, 18·9; H, 0·4; F, 52·8%). The overall yield of the mixture (II) was essentially quantitative. Analytical-scale GLC of a sample of the undistilled product showed the composition to be IIb 41% and IIa 59%.

(ii) Irradiation of a mixture of 2*H*-heptafluoro-2-butene (5·4 g, 29·7 mmoles) (*cis*: *trans* ratio 27:73 approx) and Cl_2 (1·95 g, 27·5 mmoles) in a pyrex tube at a distance of 15 cm, for 15 hr gave 2*H*-2,3-dichloroheptafluorobutane (5·5 g) plus a trace of material of higher retention time. The composition of the diastereomers was IIb 39% and IIa 61%, (from analytical-scale GLC).

(iii) Irradiation of *trans*-2*H*-heptafluoro-2-butene (4·85 g, 26·7 mmoles) and Cl_2 (1·15 g, 16·2 mmoles) under the same conditions as in (ii) gave 2*H*-2,3-dichloroheptafluorobutane (3·6 g) and the recovered olefin (1·9 g) was shown to be the *trans* isomer (>95%, by ^{19}F NMR and IR spectroscopy).

In some reactions analytical GLC showed a small peak of higher retention time, which may have been due to 2,2,3-trichloroheptafluorobutane but this was not confirmed. In general, liquid phase chlorination of F-containing olefins takes place without substitution but in the vapour phase some substitution may occur.[13].

(b) *Bromine.* (i) *trans*-2*H*-heptafluoro-2-butene (5·0 g, 27 mmoles) and BR_2 (5·4 g, 34 mmoles) were sealed in a pyrex tube and irradiated at a distance of 25 cm for 37·25 hr. The tube was then opened and the liquid product shaken with sodium metabisulphite soln and separated (8·55 g). Analytical-scale GLC showed the presence of two major components separation of which by preparative-scale GLC gave: the diastereomer (IIIb) of 2H-2,3-*dibromoheptafluorobutane* b.p. 108°/765 mm. (Found: C, 14·2; H, 0·2; Br, 46·3; F, 38·7. $C_4HBr_2F_7$ requires: C, 14·1; H, 0·3; Br, 46·7; F, 38·9%); and the diastereomer (IIIa) of 2H-2,3-*dibromoheptafluorobutane* b.p. 110–111°/765 mm. (Found: C, 13·9; H, 0·4; Br, 46·7; F, 38·4%). The overall yield of the mixture (III) was 91%. Analytical-scale GLC of a sample of the undistilled product showed the diastereomer composition to be IIIb 34% and IIIa 66%.

(ii) Irradiation of 2*H*-heptafluoro-2-butene (4·3 g, 24 mmoles) (*cis*:*trans* ratio 27:73 approx) and Br_2 (4·5 g, 28 mmoles) in a pyrex tube for 15·5 hr gave 2*H*-2,3-dibromoheptafluorobutane (6·8 g, 84%). The diastereomer composition was IIIb 34% and IIIa 66%.

(iii) Irradiation of *trans*-2*H*-heptafluoro-2-butene (4·0 g, 22 mmoles) and Br_2 (0·5 g, 3·1 mmoles) under the same conditions as in (ii) gave 2*H*-2,3-dibromoheptafluorobutane (0·6 g). No isomerization of the recovered olefin was detected by comparison of its IR spectrum with that of the starting olefin.

Addition of hydrogen bromide to octafluoro-2-butene

The addition of HBr to a mixture of *cis*- and *trans*-octafluoro-2-butene was carried out using the procedure reported by Haszeldine and Osborne.[11] The diastereomeric forms of 2*H*-3-bromo-octafluorobutane (VII); and 2,3-dibromo-octafluorobutane (VIII) were separated by preparative-scale GLC.

Additions to pure geometric isomers. (i) When *trans*-octafluoro-2-butene (0·6 g, 3 mmoles) and HBr (0·55 g, 6·8 mmoles) were irradiated in a silica tube at a distance of 15 cm for 11 hr the composition of the diastereomers of a 2*H*-3-bromo-octafluorobutane obtained was VIIa 68% and VIIb 32%, with a little 2,3-dibromo-octafluorobutane present, (from analytical scale GLC).

(ii) Similarly when *cis*-octafluoro-2-butene (0·6 g, 3 mmoles) and HBr (0·55 g, 6·8 mmoles were irradiated under the same conditions as in (i) the composition of the diastereomers was VIIa 62% and VIIb 38%, also with a little 2,3-dibromo-octafluorobutane present.

(iii) *trans*-Octafluoro-2-butene (1·45 g, 7·25 mmoles) and HBr (0·24 g, 2·97 mmoles) were similarly irradiated for 15·5 hr. The recovered octafluoro-2-butene (0·8 g, 4 mmoles) was shown to consist of ~17% *cis* and ~83% *trans* isomer by ^{19}F NMR spectroscopy. The liquid remaining in the tube (~0·1 g) was a mixture of VII and VIII (from analytical scale GLC).

Dehydrohalogenation reactions

The reactions were carried out in a 3-necked flask (250 ml) fitted with a N_2 inlet, dropping funnel, magnetic stirrer, and a reflux condenser leading to a trap at −183°. N_2 was passed through the apparatus during reaction.

(a) trans-2-*Chloroheptafluoro-2-butene*. The diastereomer (IIb) of 2*H*-2,3-dichloroheptafluorobutane (2·45 g, 9·69 mmoles) was run into a soln of KOH (17·5 g, 0·312 mole) in water (20 ml) with stirring. The flask was warmed on a water bath to about 60° and the lower organic layer slowly disappeared. The gas collected in the trap was identified as *trans*-2-chloroheptafluoro-2-butene (1·6 g, 76%) by its ^{19}F NMR spectrum.

(b) cis-2-*Chloroheptafluoro-2-butene*. Similarly the diastereomer (IIa) of 2*H*-2,3-dichloroheptafluorobutane (3·75 g, 14·8 mmoles) and KOH (19·8 g, 0·353 mole) in water (20 ml) gave *cis*-2-chloroheptafluoro-2-butene (1·95 g, 61%) again identified by ^{19}F NMR spectroscopy.

(c) cis- *and* trans-2-*Bromoheptafluoro-2-butene*. 2*H*-2,3-Dibromoheptafluorobutane (51·6 g, 0·151 mole) was run into a stirred soln of KOH (35·5 g, 0·633 mole) in water (55 ml) over a period of 30 min. A little material condensed in the trap (at −78°) above the reflux condenser and after 1 hr the flask was warmed to ~50°. Analytical-scale GLC of the combined lower organic layer in the flask (19·0 g) and the material in the cold trap (8·8 g) showed two overlapping peaks, and the product (27·8 g, 71%) was identified from its ^{19}F NMR spectrum as cis- *and* trans-2-*bromoheptafluoro-2-butene* b.p. 50–51°/760 mm (micro distillation). (Found: Br, 31·0%; M.W. 258 (Regnault); $m/e = 260$ (P), 262 (P + 2). C_4BrF_7 requires: Br, 30·6%; M.W. 261; $m/e = 260$ (P), 262 (P + 2)).

(d) trans-2-*Bromoheptafluoro-2-butene*. Using the same procedure as above the diastereomer (IIIb) of 2*H*-2,3-dibromoheptafluorobutane (1·0 g, 2·9 mmoles) and KOH (19·5 g, 0·347 mole) in water (20 ml) gave *trans*-2-bromoheptafluoro-2-butene (0·65 g, 85%) identified by its ^{19}F NMR spectrum.

(e) cis-2-*Bromoheptafluoro-2-butene*. Similarly the diastereomer (IIIa) of 2*H*-2,3-dibromoheptafluorobutane (3·1 g, 9·1 mmoles) and KOH (12·5 g, 0·223 mole) in water (20 ml) gave *cis*-2-bromoheptafluoro-2-butene (1·5 g, 63%) identified by its ^{19}F NMR spectrum.

(f) trans-*Octafluoro-2-butene*. The diastereomer (VIIa) of 2*H*-3-bromo-octafluorobutane (7·2 g, 26 mmoles) was run into a stirred soln of KOH (20·0 g, 0·357 mole) in water (20 ml) over a period of 30 min. After a further 30 min the flask was warmed to ~50° and the material in the trap was identified as *trans*-octafluoro-2-butene (3·7 g, 72%) from its IR and ^{19}F NMR spectra (two peaks present, indicating a single geometric isomer).

(g) cis-*Octafluoro-2-butene*. By the same procedure the diastereomer (VIIb) of 2*H*-3-bromo-octafluorobutane (6·2 g, 22 mmoles) and KOH (20·2 g, 0·360 mole) in water (20 ml) gave *cis*-octafluoro-2-butene (3·5 g, 79%) identified by its IR (C═C stretching vibration at ~5·8 μ) and ^{19}F NMR spectra (two peaks).

Dechlorination of 2H-2,3-*dichloroheptafluorobutane*

The apparatus was the same as that used for the dehydrohalogenation reactions and N_2 was passed through. The flask was charged with Zn dust (9·3 g, 0·142 mole) and EtOH (50 ml), and a few drops of glacial AcOH were added to activate the Zn. Stirring was commenced and II (4·75 g, 18·8 mmoles) was run in over a period of 10 min. The EtOH was then refluxed on a water bath for 1 hr and a mixture of ~27 *cis*- and ~73% *trans*-2*H*-heptafluoro-2-butene (2·9 g, 85%) was collected in the trap, identified by ^{19}F NMR spectroscopy.

cis-trans *Isomerization of* 2H-*heptafluoro-2-butene*

A Carius tube was charged with redistilled N-methyl-2-pyrrolidone (20 ml), anhyd KF (4·3 g, 74 mmoles) and a mixture of ~27 *cis*- and ~73% *trans*-2*H*-heptafluoro-2-butene (3·5 g, 19 mmoles). The tube was then sealed under vacuum and heated at 185° for 9 hr. After cooling, the gaseous material (2·8 g) was vented to a vacuum system and identified as *trans*-2*H*-heptafluoro-2-butene (>95%) from its IR and ^{19}F NMR spectra.

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