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GEOMETRIC ISOMERS OF FLUORO-OLEFINS

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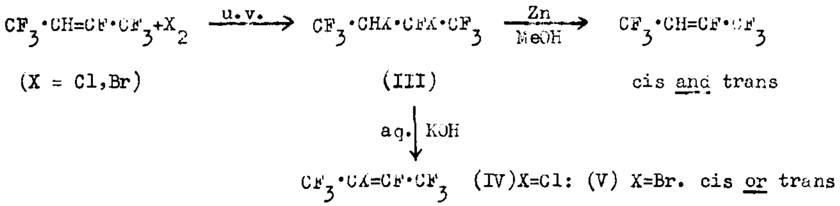
Although the chemistry of fluoro-olefins has been investigated extensively (1,2) the stereochemistry of their reactions has received little attention (3) and this partly arises from the paucity of geometric isomers of fluoro-olefins which can be easily isolated. In the course of attempts to develop methods of obtaining, easily, such isomers we have repeated the reaction of hexachlorobutadiene with potassium fluoride, using N-methyl-2-pyrrolidone as solvent. This reaction was first carried out by Maynard (4) who reported that a mixture of cis and trans isomers of 2-H-heptafluoro-2-butene (II) is produced. However, we have found that, under comparable conditions, only the trans isomer ($>$ 95%) is produced.

$$\underset{}{CCl_2{=}CCl{\cdot}CCl{=}CCl_2} \xrightarrow[200^{\circ}]{KF,N.M.P.} \underset{(I)}{[CF_3{\cdot}\bar{C}H{-}CF_2{\cdot}CF_3]} \underset{-F^-}{\overset{F^-}{\rightleftarrows}} \underset{(II)}{CF_3{\cdot}CH{=}CF{\cdot}CF_3}$$

The ^{19}F - chemical shift data (see Table 1) for the trans isomer (I) is in agreement (after allowing for different referencing conditions) to that attributed to the mixture (4). Therefore, we confirmed the formation of a single isomer by adding chlorine, photochemically, to the olefin (II) and then dehalogenating the resulting mixture of diastereomers (III). Then, a mixture of cis and trans 2H-heptafluoro-2-butene was obtained. The cis and trans olefins



$$\begin{array}{ccccc} CF_3{\cdot}CH{=}CF{\cdot}CF_3{+}X_2 & \xrightarrow{u.v.} & CF_3{\cdot}CHX{\cdot}CFX{\cdot}CF_3 & \xrightarrow[MeOH]{Zn} & CF_3{\cdot}CH{=}CF{\cdot}CF_3 \\ (X = Cl,Br) & & (III) & & \text{cis }\underline{\text{and}}\text{ trans} \\ & & \Big\downarrow{\scriptstyle aq.\ KOH} & & \\ & & CF_3{\cdot}CX{=}CF{\cdot}CF_3 & \text{(IV)X=Cl: (V) X=Br. cis }\underline{\text{or}}\text{ trans} & \end{array}$$

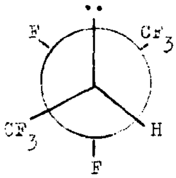
are easily distinguished since it is known (5) that $J^{trans}_{CF_3-CF_3} << J^{cis}_{CF_3-CF_3}$ and the observed values for $J_{CF_3-CF_3}$ for the cis and trans olefins are 10·2 and 1-2 c.p.s. respectively.

Table 1. ^{19}F-Chemical Shifts for Trans- and Cis- 2H-heptafluorobut-2-ene *

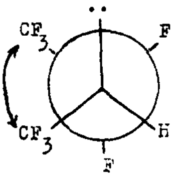
	$1\text{-}CF_3$	$4\text{-}CF_3$	$3\text{-}F$
Trans $CF_3{\cdot}CH{=}CF{\cdot}CF_3$	+60•4	+74•6	+117•2
Cis $CF_3{\cdot}CH{=}CF{\cdot}CF_3$	+56•8	+69•6	+113•2

* Neat liquids. (p.p.m., rel. to $CFCl_3$ as internal ref.)

Therefore, the fluorination reaction leading to olefin (II) involves a highly stereospecific elimination process from an intervening carbanion (I). This indicates either a high configurational stability for the carbanion (I) or, more likely, that elimination from conformer (Ia) is made more favourable than from (Ib) by CF_3-CF_3 interactions during double-bond formation. However, it is of interest to note that the zinc dehalogenation of the individual diastereomers (III), after separation by preparative scale g.l.c., each gave a cis, trans mixture of olefins (II). That is, the dehalogenation, which is often regarded as a carbanionic process (6), is not stereospecific. On the other hand, dehydrohalogenation of individual diastereomers (III), using aqueous potassium hydroxide, was stereospecific giving the corresponding cis or trans isomers of the chloro- or bromo-olefins (IV) and (V), thus providing a convenient route to the latter.



(Ia)



(Ib)

The implications concerning the stereochemistry of these polyfluorocarbanions, and eliminations from them, are being investigated further.

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