Reduction of *gem*-Bromofluorocyclopropanes with Lithium Aluminium Hydride

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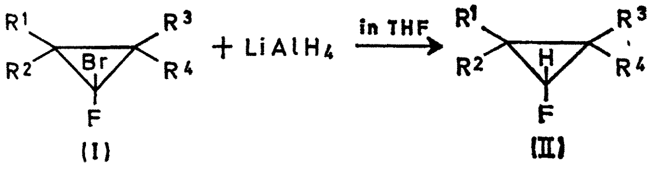
Summary The reduction of *gem*-bromofluorocyclopropanes with lithium aluminium hydride in tetrahydrofuran proceeds stereospecifically, *i.e.*, with retention of configuration, presumably *via* a four-centre mechanism.

LITHIUM aluminium hydride is known to reduce organic halogen compounds to the corresponding hydrocarbons. Two mechanisms have been suggested for this reaction: Eliel[1] and Cram and Rickborn[2] claimed it proceeded by an S_N2 mechanism because the reduction of optically-active compounds afforded the inversion products, while Brown and Krishnamurthy[3] suggested the possibility of a four-centre-type mechanism for the reduction of aryl halides.

We report evidence that the reduction of halogenocyclopropanes with lithium aluminium hydride occurs by a four-centre-type mechanism. The halogen compounds employed, 7-bromo-7-fluorobicyclo[4,1,0]heptane (Ia and b) and 1-bromo-1-fluoro-2-phenylcyclopropane (Ic and d), were prepared by the reaction of bromofluorocarbene with cyclohexene and styrene, respectively.[4] These cyclopropanes were obtained as a mixture of two geometrical isomers.†



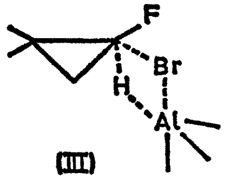
a; $R^1 = R^3 = H, R^2, R^4 = -(CH_2)_4-$
b; $R^1, R^3 = -(CH_2)_4-, R^2 = R^4 = H$
c; $R^1 = R^3 = R^4 = H, R^2 = Ph$
d; $R^1 = Ph, R^2 = R^3 = R^4 = H$

The reduction of 7-bromo-7-fluorobicyclo[4,1,0]heptane [an isomeric mixture, (Ia) : (Ib) 36 : 64] was carried out in tetrahydrofuran under reflux for 4—5 h to give an isomeric mixture of 7-fluorobicyclo[4,1,0]heptane [(IIa) : (IIb) 39 : 61] in 65% yield, together with a small amount of the dihydro-product, bicyclo[4,1,0]heptane. Under the same conditions, 1-bromo-1-fluoro-2-phenylcyclopropane [(Ic) : (Id) 53 : 47] was reduced to 1-fluoro-2-phenylcyclopropane [60% yield, (IIc) : (IId) 55 : 45] and a small amount of 1-phenylcyclopropane. No bromocyclopropanes were formed in either reaction. The structures of the products were determined by their i.r. and n.m.r. spectra.[5]

The fact that the isomer ratio of the reduction product was nearly the same as that of the starting material suggests that this reduction proceeds stereospecifically, *i.e.*, with retention of configuration. This was verified by reducing (Ia and b) and (Ic and d), separated by preparative g.l.c., with $LiAlH_4$ under the same conditions as described above. Chromatography of the products showed that only one isomer (IIa) of 7-fluorobicyclo[4,1,0]heptane was formed from (Ia), and the other isomer (IIb), from (Ib).

A similar stereospecificity was observed also in the reduction of (Ic and d); (Ic) was converted exclusively into (IIc), and (Id) into (IId).

These results cannot be explained by either the S_N2 or the S_N1 mechanism. If the reduction proceeds by an S_N2 mechanism (Ia) should give the inversion product (IIb) and (Ib) should give (IIa), and if an S_N1-type reaction occurs, a mixture of the two isomeric fluorocyclopropanes should be formed from either of the starting materials. The most plausible mechanism that can explain the present results is, therefore, the four-centre mechanism *via* the transition state (III).



(III)

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† The structure assignments for the geometrical isomers were made by their ^1H and ^{19}F n.m.r. spectra, based on the generalizations that in fluorocyclopropanes the ring hydrogen[6] and fluorine[7] are more strongly coupled with *cis*-hydrogen than with *trans*-hydrogen, and that in alkyl- or aryl-substituted cyclopropanes the ring hydrogen[6] and fluorine[8] are shielded by *cis*- and deshielded by *trans*-substituents. N.m.r. data: (Ia), δ_F 76 p.p.m. (upfield from CF_3CO_2H as external reference), J_{HF}^{VIC} 13Hz; (Ib), δ_F 41 p.p.m., J_{HF}^{VIC} 21Hz; (Ic), δ_F 65 p.p.m., $J_{H'F}^{VIC}$ 3Hz; (Id), δ_F 44 p.p.m., $J_{H'F}^{VIC}$ 17Hz (H′ denotes the hydrogen bonded to the carbon atom substituted by the phenyl group).

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