

The Acidity of Hydrogen in Fluorohydrocarbons: A Bridgehead Perfluorocarbanion

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THROUGHOUT an extensive study of polyfluorocycloalkanes,^{1,2} the most important general reaction found has been heterogeneous dehydrofluorination with aqueous potassium hydroxide to give fluorocycloalkenes. With cyclohexanes a *trans*-coplanar arrangement of the hydrogen and fluorine atoms to be eliminated is necessary for rapid reaction¹; with cyclopentanes though a *trans*-coplanar arrangement gives the easiest elimination, a *cis*-coplanar system also gives a double bond fairly readily.^{2,3} These reactions probably proceed by a concerted *E2* mechanism. The possibility that an alternative *E1_cB* type process may be

followed is, however, difficult to rule out. When *1H/2H*- and *1H,2H*-decafluorocyclohexane and *1H/2H*- and *1H,2H*-octafluorocyclopentane were treated² with potassium hydroxide in deuterium oxide no deuteration could be detected though it did occur with 1-bromo-1-chloro-2,2,2-trifluoroethane. Thus, if carbanions are formed from these alicyclic fluorides they must eliminate fluoride ion faster than they reprotonate.

In support of this, we have now found that fluorohydrocarbons with no easy dehydrofluorination pathway available readily undergo deuteration under similar heterogeneous conditions (*cf.*

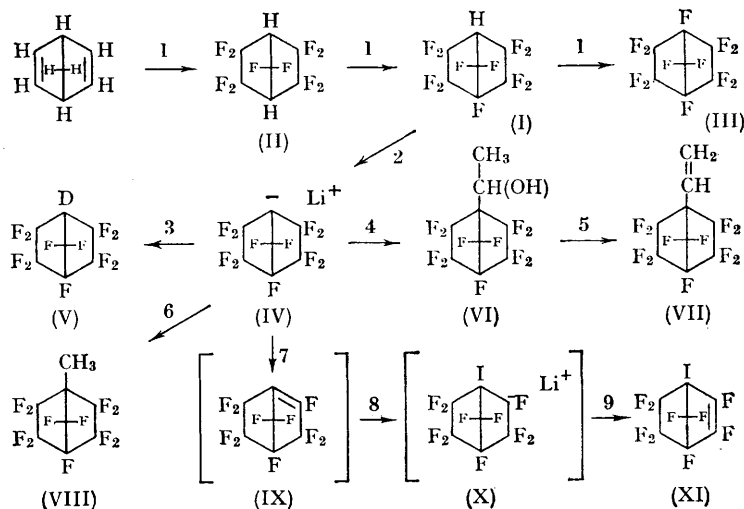
¹ D. E. M. Evans, W. J. Feast, R. Stephens and J. C. Tatlow, *J. Chem. Soc.*, 1963, 4828, and earlier references cited.

² R. J. Heitzman, C. R. Patrick, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 1963, 281; J. Burdon, T. M. Hodgins, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 1965, 2382.

³ C. H. DePuy, R. D. Thurn and G. F. Morris, *J. Amer. Chem. Soc.*, 1962, **84**, 1314.

$\text{CF}_3\cdot\text{CF}_2\text{H}$ and $\text{CF}_3\cdot\text{CF}_2\cdot\text{CF}_2\text{H}^4$). Thus, pentafluorobenzene (cf. fluorobenzene⁵), 1H-nonafluorocyclohexene (cf. $\text{CClH} = \text{CClH}^6$ and $\text{CCl}_2 = \text{CClH}^7$), 1H-undecafluorobicyclo[2,2,1]heptane (I), and 1H,4H-decafluorobicyclo[2,2,1]heptane (II) undergo exchange on being heated in a sealed tube with potassium hydroxide in deuterium oxide (1:1, w/v) at 100° for 3 hr. The respective products contained C_6DF_5 (70%), C_6DF_9 (65%), C_7DF_{11} (80%) and, from (II), $\text{C}_7\text{D}_2\text{F}_{10}$ (57%) and

further by treatment with methyl-lithium, prepared from methyl iodide, in diethyl ether at -50°. Methane was rapidly evolved and undecafluorobicyclo[2,2,1]heptyl-lithium (IV) formed. This was proved by the addition (at -50°) of deuterium oxide, which gave pure 1-deutero-undecafluorobicyclo[2,2,1]heptane (V) in 60% yield, whilst acetaldehyde afforded 1-(undecafluorobicyclo[2,2,1]heptan-1-yl)ethanol (VI) in 44% yield, m.p. 99–100°; with phosphoric oxide it gave



Reagents: 1, CoF_3 ; 2, CH_3Li ; 3, D_2O ; 4, $\text{CH}_3\cdot\text{CHO}$; 5, P_2O_5 ; 6, CH_3Br ; 7, above 15°, loss of F^- ; 8, LiI ; 9, loss of F^- .

$\text{C}_7\text{HDF}_{10}$ (38%), as determined by proton n.m.r. spectroscopy and mass spectrometry.⁸

The hitherto unknown compounds (I), m.p. 94–96° (sealed tube), and (II), m.p. 92–93° (sealed tube), were isolated in good yield from the complex mixture obtained by cobaltic fluoride fluorination of bicyclo[2,2,1]heptadiene at 250–300°. Cobaltic fluoride fluorination converted (I) into dodecafluorobicyclo[2,2,1]heptane (III), and (II) into a mixture of (I) and (III).

That a carbanion must be formed by the action of strong bases on compound (I) was confirmed

1-vinylundecafluorobicyclo[2,2,1]heptane (VII) m.p. 49–50° (sealed tube) and with methyl bromide it gave 1-methylundecafluorobicyclo[2,2,1]heptane (VIII) (50%) m.p. 125–126° (sealed tube).

The deuteration of (I) and (II) and the reaction of (I) with methyl-lithium clearly indicate that purely inductive effects can give rise to a carbanion. The inductive influence of three $>\text{CF}_2$ groups suffices in these cases without resonance stabilisation of the anion by neighbouring unsaturated groups. This last effect appears to be involved with bicyclo[2,2,2]octane-2,6-dione,⁹ but it now

⁴ L. H. Slaugh and E. Bergman, *J. Org. Chem.*, 1961, **26**, 3158.

⁵ J. D. Roberts, D. A. Semenov, H. E. Simmons, and L. A. Carlsmith, *J. Amer. Chem. Soc.*, 1956, **78**, 601.

⁶ S. I. Miller, and W. G. Lee, *J. Amer. Chem. Soc.*, 1959, **81**, 6313.

⁷ L. C. Leitch and H. J. Bernstein, *Canad. J. Res.*, 1950, **28B**, 35.

⁸ J. R. Majer, unpublished work.

⁹ P. D. Bartlett and G. F. Woods, *J. Amer. Chem. Soc.*, 1940, **62**, 2933.

seems that carbanion formation by the bicyclic trisulphone of Doering and Levy¹⁰ may arise from inductive effects alone.

The stability of compounds (I) and (II) to strong aqueous alkali at 100° is in agreement with the absence of an easy dehydrofluorination process. Elimination would not be coplanar and also, and more important, would violate Bredt's rule. The rapid reprotonation of the anions resulting from the large excess of water present is not therefore surprising. Likewise, when formed from methyl-lithium in diethyl ether, the anion from (I) is much more stable than any perhalogenocarbanion so far reported; *e.g.*, the primary, secondary, and tertiary perfluorocarbanions described by Andreades¹¹ lose fluoride ion at -70°. However, reprotonation of the anion is impossible in ether, and at about 15° elimination of fluoride ion sets in

and lithium fluoride is precipitated. The organic product appears to be a transient bridgehead olefin (IX), or diradical. Lithium iodide present in the system adds rapidly to this giving, presumably, the 1-iodoundecafluorobicyclo[2,2,1]heptan-2-yl anion (X). This should instantly undergo a *cis*-coplanar β -elimination¹² to give the product actually isolated, 1-iodononafluorobicyclo[2,2,1]-hept-2-ene, b.p. 124°. From reactions in the presence of other addends we have isolated analogous products, indicating that a bridgehead olefin has been formed, at least as a transient intermediate, from this fluoronorbornane system.

Compounds (I)—(III), (VI)—(VIII), and (XI) had correct elemental analyses and consistent i.r., n.m.r., and mass spectra.

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¹⁰ W. v. E. Doering and L. K. Levy, *J. Amer. Chem. Soc.*, 1955, **77**, 509.

¹¹ S. Andreades, *J. Amer. Chem. Soc.*, 1964, **86**, 2003.

¹² N. A. LeBel, P. D. Beirne, E. R. Karger, J. C. Powers, and P. M. Subramanian, *J. Amer. Chem. Soc.*, 1963, **85**, 3199.