1351. *Polyfluorocycloalkenes. Part IV.*[1] *1-Bromononafluorocyclohexene and 1-Bromo-2-methoxy- and 1-Bromo-6-methoxy-octafluorocyclohexene*

By S. F. CAMPBELL and R. STEPHENS

Methanolic potassium hydroxide and 1-bromononafluorocyclohexene, prepared by addition of bromine to 1*H*-nonafluorocyclohexene followed by dehydrobromination with aqueous alkali, gave 1-bromo-2-methoxy- and 1-bromo-6-methoxy-octafluorocyclohexene as the sole products; this and the failure to detect liberation of bromide ion is regarded as evidence for the absence of an α-elimination from reactions of this type.

THE reaction of cyclic perfluoro-olefins with alcohols in the presence of potassium hydroxide[1] can be rationalised in terms of the addition of alkoxide ion to the electron-deficient double bond followed by a β-elimination of fluoride ion to give both 1- and 3-alkoxyperfluoro-olefins. However, α-elimination of fluoride ion, although very unlikely with these systems, could operate, at least in part,[2] to produce the same products through rearrangement of a carbene intermediate. Such a process has now been ruled out by treating 1-bromononafluorocyclohexene (III) with methanolic potassium hydroxide, when bromine was completely retained in the unsaturated ethers (VI and VII) produced.

1*H*-Nonafluorocyclohexene (I) was prepared by lithium aluminium hydride reduction of decafluorocyclohexene. The proportion of this olefin in the complex product was considerably increased over that obtained previously.[3] The olefin gave a dibromo-addition product (II) with bromine under ultraviolet irradiation,[4] and both stereoisomers appeared to be present by analytical gas chromatography but could not be separated on a preparative scale. Treatment with aqueous alkali liberated both bromide and fluoride ions from these saturated compounds to give 1-bromononafluorocyclohexene (III) and 1,2- and 1,6-dibromo-octafluorocyclohexenes (IV and V) which were characterised by infrared spectroscopy, mass spectrometry,[5] and oxidation. The monobromide (III) was the predominant product and this would be in agreement with exclusive dehydrobromination of the stereoisomer with a *trans*-disposition of hydrogen and bromine in a chair conformation. Evidence is also available [6] that in the *cis*-isomer dehydrobromination would occur to a substantial extent, *i.e.*, the unfavourable stereochemistry is partly compensated by the easier departure of bromide ion. The 1,2- and 1,6-dibromo-olefins (IV and V) presumably arise from the *trans*-dibromide in *trans*-coplanar eliminations of hydrogen and fluorine at C-2 and C-6, respectively. The larger proportion of the former (IV) would be in agreement with the relative strengths of the C–F bonds at C-2 and C-6.

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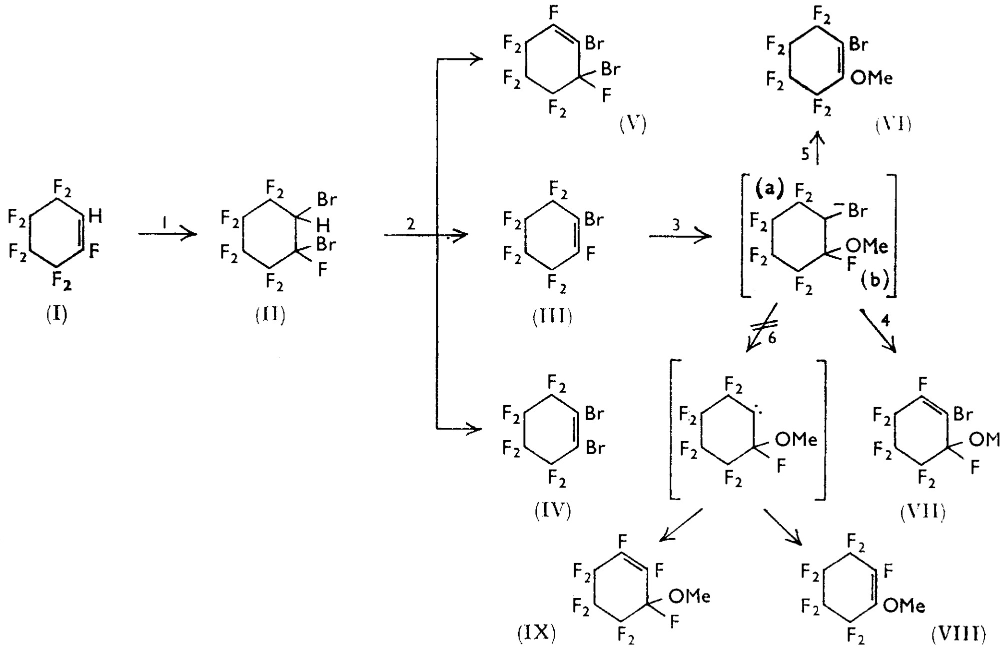
[1] Part III, preceding Paper.
[2] L. Friedman and J. G. Berger, *J. Amer. Chem. Soc.*, 1961, **83**, 492.
[3] D. E. M. Evans, W. J. Feast, R. Stephens, and J. C. Tatlow, *J.*, 1963, 4828.
[4] J. Roylance, J. C. Tatlow, and R. E. Worthington, *J.*, 1954, 4426.
[5] J. R. Majer, unpublished work.
[6] F. Lancashire, D. R. A. Perry, S. F. Campbell, R. Stephens, and J. C. Tatlow, unpublished work.

1-Bromononafluorocyclohexene (III), methanol, and potassium hydroxide in ether reacted vigorously to give 1-bromo-2-methoxy- and 1-bromo-6-methoxy-octafluorocyclohexene (VI and VII) in agreement with an addition–elimination process.[1] The higher stability of a negative centre on a carbon atom carrying bromine [7] than on one linked to fluorine explains the exclusive attack on the fluoro-substituted carbon of the double bond. The proportion of (VII) was probably much reduced by a higher susceptibility to attack by methoxide ion (disubstituted products were not investigated). The absence of nonafluoro-1- and -3-methoxycyclohexene[1] (VIII and IX) in the ether layer and the absence of bromide ion in the aqueous phase is regarded as conclusive evidence for a purely β-elimination process from the intermediate carbanion.



Reagents: 1, Br_2; 2, KOH, aq.; 3, MeOH–KOH; 4, loss of F(a) as F^-; 5, loss of F(b) as F^-; 6, loss of Br^-.

EXPERIMENTAL

Techniques.—Oxidations, gas chromatography, and infrared measurements were as before.

1H-*Nonafluorocyclohexene*.—A suspension of lithium aluminium hydride (3·0 g.) in diethyl ether (110 c.c.) was added dropwise during 1½ hr. to well stirred decafluorocyclohexene (77·0 g.) at −78°. When the addition was complete the mixture was stirred for ½ hr. at −78°, water (60 c.c.) added, followed by sulphuric acid (100 c.c.; 50% v/v) and the stirred mixture allowed to attain room temperature. The ethereal layer was separated, washed with water, dried ($MgSO_4$), filtered, and fractionally distilled through a vacuum-jacketed column (1 ft. × ½ in.) packed with glass helices to give: (i) ether–decafluorocyclohexene, b. p. 30—31°, from which decafluorocyclohexene (10·0 g.) was separated by gas chromatography (column 488 cm. × 75 mm. diam., packed with dinonyl phthalate–kieselguhr, 1 : 2, 100°; N_2 flow-rate 60 l./hr.); (ii) largely diethyl ether, b. p. 31—40°; (iii) a residue (41·0 g.) which was separated in portions (*ca.* 15 g.) by preparative scale gas chromatography (100°, N_2 flow-rate 60 l./hr.) to give: (i) 1H-nonafluorocyclohexene (30·0 g.) with a correct infrared spectrum; (ii) a mixture (5·0 g.) which was not examined further.

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[7] G. V. D. Tiers, *J. Amer. Chem. Soc.*, 1956, **78**, 2914; J. D. Park, J. R. Dick, and J. H. Adams, *J. Org. Chem.*, 1965, **30**, 400.

1H-1,2-*Dibromononafluorocyclohexane*.—1*H*-Nonafluorocyclohexene (14·0 g.) and bromine (4 c.c.) were kept together in a sealed "Pyrex" tube under ultraviolet irradiation for 96 hr. at *ca.* 15°. Unchanged bromine was then separated and the product (21·0 g.) washed with sodium metabisulphite solution and then water, dried ($MgSO_4$), and filtered and a portion (5·0 g.) separated by gas chromatography (110°; N_2 flow-rate 14 l./hr.) (minor components were not collected) to give 1*H*-1,2-dibromononafluorocyclohexane (4·2 g.), b. p. 151—152° (lit.,[4] 147—150°) (Found: C, 18·1; H, 0·3; Br, 40·0. $C_6HBr_2F_9$ requires C, 17·8; H, 0·3; Br, 39·6%). Gas chromatography indicated the presence of two components which could not be separated on a preparative scale. The proton n.m.r. spectrum was a complex multiplet centred at 4·7 p.p.m. with respect to tetramethyl silane as external reference.

Dehydrohalogenation of the 1H-1,2-*Dibromononafluorocyclohexanes*.—The dibromide (50·0 g.) and aqueous potassium hydroxide (50 c.c.; 18N) were shaken together for 20 hr. at 15°. The halogenocarbon layer was separated, washed with water, dried ($MgSO_4$), and separated by gas chromatography (92°; N_2 flow-rate 38 l./hr.) to give (i) 1-*bromononafluorocyclohexene* (24·6 g.), b. p. 95—96° (Found: C, 22·6; H, 0·1; Br, 24·1. C_6BrF_9 requires C, 22·3; H, 0; Br, 24·8%), $\nu_{max.}$ 1695 cm.$^{-1}$ (–CF=CBr–), mass spectrometry[5] gave a top mass peak of 303 ($C_6BrF_8^+$), the fluorine-19 n.m.r. spectrum consisted of five bands in the intensity ratio of 2 : 1 : 2 : 2 : 2, oxidation with potassium permanganate in acetone gave octafluoroadipic acid which was characterised as its dianilinium salt (50%); (ii) a mixture (7·1 g.) of two components which were separated by further gas chromatography (102°; N_2 flow-rate 16 l./hr.) to give: (a) 1,6-*dibromo-octafluorocyclohexene* (0·8 g.), b. p. 145° (Found: C, 19·0; H, 0·1. $C_6Br_2F_8$ requires C, 18·8%), $\nu_{max.}$ 1690 cm.$^{-1}$ (–CF=CBr–); mass spectrometry gave a top mass peak of 382 ($C_6Br_2F_8$) and a consistent fragmentation pattern;[5] oxidation with potassium permanganate in acetone gave 1-bromoheptafluoroadipic acid which was characterised as its *dianilinium salt* (70%), m. p. 195—196° (decomp.) (Found: C, 39·8; H, 2·9. $C_{18}H_{16}BrF_9N_2O_4$ requires C, 40·2; H, 3·0%); (b) 1,2-*dibromo-octafluorocyclohexene* (3·0 g.), b. p. 149—150° (Found: C, 19·1; H, 0·1; Br, 41·6. $C_6Br_2F_8$ requires C, 18·8; Br, 41·7%), $\nu_{max.}$ 1610 cm.$^{-1}$ (–CBr=CBr–); mass spectrometry gave a top mass peak of 382 ($C_6Br_2F_8$) and a consistent fragmentation pattern;[5] oxidation with potassium permanganate in acetone gave octafluoroadipic acid which was characterised as its dianilinium salt (80%).

Reaction of 1-*Bromononafluorocyclohexene with Methanol*.—1-Bromononafluorocyclohexene (5·0 g.), potassium hydroxide (0·87 g.), and dry diethyl ether (10 c.c.) were stirred vigorously together at 15° and dry methanol (1·4 c.c.) added dropwise, whereupon a vigorous reaction occurred. The stirring was continued for 2 hr. at 15°, water was then added, and the aqueous phase shown to be free from bromide ion; the organic layer was separated, dried ($MgSO_4$), and filtered and most of the ether distilled off. The residue (4·8 g.) was separated by gas chromatography (105°; N_2 flow-rate 10 l./hr.) to give: (i) ether; (ii) 1-bromononafluorocyclohexene (0·3 g.), with a correct infrared spectrum; (iii) 1-*bromo-octafluoro*-6-*methoxycyclohexene* (0·3 g.), b. p. 147° (Found: C, 24·8; H, 1·1. $C_7H_3BrF_8O$ requires C, 25·1; H, 0·9%), $\nu_{max.}$ 1693 cm.$^{-1}$ (–CF=CBr–); the proton n.m.r. spectrum consisted of a multiplet centred at 3·7 p.p.m. with respect to tetramethylsilane as external reference; oxidation of this olefin with potassium permanganate in acetone gave heptafluoro-3-methoxyadipic acid which was characterised as its dianilinium salt (73%), m. p. 188—190° (lit.,[1] m. p. 188°), with a correct infrared spectrum; (iii) 1-*bromo-octafluoro*-2-*methoxycyclohexene* (2·0 g.), b. p. 151—152° (Found: C, 24·7; H, 0·8; Br, 23·5. $C_7H_3BrF_8O$ requires Br, 23·9%), $\nu_{max.}$ 1655 cm.$^{-1}$ [–CBr=C(OCH_3)–], the proton n.m.r. spectrum consisted of a singlet at 3·95 p.p.m. and the fluorine-19 n.m.r. spectrum consisted of four bands of equal intensities; oxidation of this olefin, in the usual way, gave octafluoroadipic acid (70%).

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