387. *Fluorocyclohexanes. Part VII.*[1] *Prototropic Migration in* 3H,4H/-*Octafluorocyclohexene.*

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1H,2H/4H-NONAFLUOROCYCLOHEXANE with aqueous potassium hydroxide gave[2] six unsaturated products, including 3H,4H/-octafluorocyclohexene, which in turn with aqueous potassium hydroxide gave four compounds. Three of these last four were expected[2] dehydrofluorination products, 1H- and 2H-heptafluorocyclohexa-1,3-diene and hexafluorobenzene. The fourth was found in very small yield and appeared to be 3H,6H-octafluorocyclohexene an isomer of the starting cyclohexene derivative. Evidence is presented here substantiating this rearrangement which is the first in the polyfluorocyclohexane series.

When 3H,4H/-octafluorocyclohexene was boiled with aqueous potassium hydroxide, the 3H,6H-isomer was separated from the dehydrofluorination products as a single component by gas chromatography over dinonyl phthalate–kieselguhr. However, using an analytical column packed with trifluoroacetic acid on Carbowax–kieselguhr resolved this cyclohexene into two components, presumably the *cis*- and *trans*-forms. If we assume a close similarity in specific peak heights, the ratio of components is ~5 : 1. Separation of the pure isomers was, however, not effected since there was no appropriate preparative-scale column available.

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[1] Part VI, Nield, Stephens, and Tatlow, *J.*, 1960, 3800.

[2] Stephens, Tatlow, and Wiseman, *J.*, 1959, 148.

Treatment of the mixed stereoisomers with potassium hydroxide gave a mixture of 1H-heptafluorocyclohexa-1,3-diene and hexafluorobenzene. The diene arises by a 1,4-elimination, and the low yield and dark brown aqueous phase are analogous to occurrences in other dehydrofluorinations where a diene is formed. They are in contrast with those where no stable diene is possible, when high yields of aromatic fluoro-compounds are produced together with a colourless aqueous phase.

Treatment[1] of the mixed stereoisomers with cobaltic fluoride gave, in addition to unchanged starting material, 1H/4H- and 1H,4H/-decafluorocyclohexane by saturation of the double bond. It is significant that there was approximately five times as much *trans*- as *cis*-1H/4H-decafluoride; this, coupled with the gas chromatogram of the mixed stereoisomers, suggests that the 3H/6H-octafluorocyclohexene is the major isomerised component.

The infrared spectrum of the mixed isomers displayed absorptions characteristic of the stretching frequency of a C–H "α" to a double bond[3] and a –CF=CF– system.[4] Further, the mass spectrum contained peaks of mass numbers entirely consistent with those derivable from a 3H,6H-octafluorocyclohexene.[5]

Only the 3H,4H/-octafluorocyclohexene gives a rearrangement product with alkali, not the 3H/4H-isomer. The reaction is presumably a prototropic migration[6] which is favoured by the stereochemistry of the system. The proportions of the dehydrofluorination products from it indicate that the predominant conformer is that where the 3-hydrogen atom occupies a pseudo-equatorial position. The 3H,6H-octafluorocyclohexenes could thus arise from the enhanced reactivity of an allylic hydrogen towards base, even when in the pseudo-equatorial position, coupled with the absence of an easy elimination process. Synchronous rearrangement and solvent protonation intervene to produce the 3H,6H-olefin, a system of greater symmetry and lower dipole moment. A carbanion intermediate could be involved[7] but is not considered essential to the rearrangement.

3H/4H-Octafluorocyclohexene[8] gives 1H- and 2H-heptafluorocyclohexa-1,3-diene and hexafluorobenzene (64, 23, and 13%, respectively) but no isomeric olefin. However, the predominant conformation of the 3H/4H-olefin will be such that the hydrogen atoms occupy axial positions and sterically favourable synchronous eliminations of hydrogen fluoride can occur, *viz.*, coplanar *trans*-1,4-, to give hexafluorobenzene, and the recently proposed[9] coplanar *cis*-1,2-, to give the dienes. It is significant that the latter predominate.

The 3H,6H-olefins give, on dehydrofluorination, hexafluorobenzene and, by a 1,4-elimination, 1H-heptafluorocyclohexa-1,3-diene. The latter elimination may account for the presence of five times as much of the *trans*-3H/6H-olefin as of the *cis*-isomer. The former, possessing a *cis*-disposition of hydrogen and fluorine between C-3 and C-6, probably undergoes 1,4-elimination less readily than its isomer.

Experimental.—3H,4H/-*Octafluorocyclohexene.* In a typical experiment 1H,2H/4H-nonafluorocyclohexane (50·0 g.; b. p. 107°) was dehydrofluorinated as described previously[2] to a mixture of seven compounds from which was separated 3H,4H/-octafluorocyclohexene (6·0 g.; b. p. 116°, n_D^{21} 1·3390).

Dehydrofluorination of 3H,4H/-*octafluorocyclohexene.* In a typical experiment the cyclohexene (40·4 g.) was dehydrofluorinated as described previously,[2] and from the five-component mixture the mixed 3H/6H- and 3H,6H/-octafluorocyclohexene (0·1 g.), b. p. 101° (Siwoloboff), n_D^{18} 1·3367 (Found: C, 32·0; H, 0·9. Calc. for $C_6H_2F_8$: C, 31·9; H, 0·9%) was isolated.

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[3] Steele and Whiffen, *Tetrahedron*, 1958, **3**, 181.

[4] Burdon and Whiffen, *Spectrochim. Acta*, 1958, **12**, 139.

[5] Majer, personal communication.

[6] Lowry, *J.*, 1927, 2554.

[7] Orloff and Kolka, *J. Amer. Chem. Soc.*, 1954, **76**, 5484.

[8] Godsell, Stacey, and Tatlow, *Tetrahedron*, 1958, **2**, 193.

[9] Morris, DePuy, and Thurn, *J. Amer. Chem. Soc.*, 1962, 1314; Heitzman, Patrick, Stephens, and Tatlow, *J.*, 1963, 281; Le Bel, Karger, Powers, and Subramanian, 142nd Meeting Amer. Chem. Soc., Sept. 1962, 101Q.

Under the conditions of the gas-chromatographic analysis normally used, the latter olefins were detected as one component; a single peak was obtained on a variety of stationary phases, *viz.*, dinonyl phthalate–kieselguhr (1 : 2), tritolyl phosphate–kieselguhr (1 : 3), silicone oil–silicone rubber (1 : 10), and various borate esters–kieselguhr (1 : 10). However, with a column packing of trifluoroacetic acid (1 pt.) on Carbowax–kieselguhr (3 : 1; 10 pts.) (temp. 70°; N_2 flow-rate 0·5 l./hr.) the olefins were resolved into two peaks with retention times of 38·0 and 50·5 min., respectively the former having a peak area five times that of the latter.

Characterisation of the mixed 3H/6H- and 3H,6H*/-octafluorocyclohexenes.* (*a*) Fluorination. The fluorination apparatus [1] consisted of a copper tube (13″ × ¼″) completely packed with a mixture of cobaltic fluoride (*ca.* 7 g.) and nickel gauze cylinders ($\frac{1}{16}$″ × $\frac{1}{16}$″). The tube was heated electrically and the temperature measured by a thermometer in contact with the reactor tube. The mixed cyclohexenes (0·81 g.) were passed through the reactor at 50° in a stream of nitrogen (*ca.* 1 l./hr.), and the products were collected in a glass trap cooled by liquid oxygen. Gas-chromatographic analysis of the product (dinonyl phthalate–kieselguhr 1 : 2; temp. 110°; N_2 flow-rate 1·2 l./hr. revealed a large amount of unchanged starting material. The latter product was, therefore, twice recycled through the cobaltic fluoride at 100°; gas chromatography then showed the presence of three components; this mixture (1·40 g.) was separated by preparative-scale gas chromatography (16′ × 3 cm., dinonyl phthalate–kieselguhr 1 : 2; temp. 95°; N_2 flow-rate 10 l./hr.) to give: (i) 1H/4H-decafluorocyclohexane (0·88 g.); (ii) 1H,4H/-decafluorocyclohexane (0·18 g.); and (iii) unchanged mixed 3H,6H-octafluorocyclohexenes (0·12 g.). Fractions (i) and (ii) had correct infrared spectra over the range 650—3500 cm.$^{-1}$.

(*b*) Dehydrofluorination. The mixed cyclohexenes (1·31 g.), potassium hydroxide (1·50 g.), and water (3 c.c.) were shaken together for 2¼ hr. in a sealed tube at 100°. The fluorocarbon layer (0·58 g.) was separated from the dark brown aqueous layer, and gas chromatography indicated the presence of three components in the former which were separated by preparative-scale gas chromatography to give (i) 1H-heptafluorocyclohexa-1,3-diene (0·32 g.) and (ii) hexafluorobenzene (0·18 g.); the small amount of starting material was not collected but identified from its retention time. Fractions (i) and (ii) had correct infrared spectra over the range 650—3500 cm.$^{-1}$.

(*c*) Spectroscopy. The mixture displayed absorption peaks in the infrared at 1750 and 2960 cm.$^{-1}$ characteristic of a –CF=CF– group [4] and a hydrogen atom " α " to the double bond,[3] respectively. The olefins showed no selective absorption over the ultraviolet range 2400—3000 Å.

When subjected to fragmentation in a mass spectrometer the olefins showed intense peaks at mass numbers 226, 207, 157, 144, 137, 126, 119, 113, and 107 (*M*, 226).[5]

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