1022. *Fluorocyclohexanes. Part XI.*[1] 1H,3H/2H-, 1H,2H/3H-, and 1H,2H,3H/-*Nonafluorocyclohexane*

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The three 1*H*,2*H*,3*H*-nonafluorocyclohexanes have been prepared from 3*H*-nonafluorocyclohexene by addition of chlorine followed by lithium aluminium hydride reduction. Stereochemical assignments based on fluorine-19 n.m.r. measurements were confirmed by dehydrofluorination studies.

Five nonafluorocyclohexanes have previously been studied;[2-4] and we now report the synthesis and characterisation of the three 1*H*,2*H*,3*H*-nonafluorocyclohexanes which are not formed in the cobaltic fluoride fluorination of benzene.[5]

3*H*-Nonafluorocyclohexene[6] was treated with chlorine under ultraviolet irradiation and the mixture of 1*H*-2,3-dichlorononafluorocyclohexanes obtained reduced with a suspension of lithium aluminium hydride in diethyl ether.[1,2,4] A competing elimination reaction, leading to hydropolyfluorocyclohexenes was found to be dependent on the reagent concentration. Thus, at high concentrations of lithium aluminium hydride, olefin formation occurred to the extent of *ca.* 30%, whereas at low concentrations of this reagent olefin formation was completely absent, and three nonafluorocyclohexanes were obtained. All three were clearly different from the four known 1*H*,2*H*,4*H*-isomers, and the products of dehydrofluorination of each were characteristic of a 1*H*,2*H*,3*H*-system.

As in earlier work[7] the von Auwers–Skita (Isomer Sequence) Rule[8] provided a guide to the stereochemistry of these nonafluorocyclohexanes, *viz.*, 1*H*,3*H*/2*H*- (I) (b. p. 86°), 1*H*,2*H*/3*H*- (II) (b. p. 95°), and 1*H*,2*H*,3*H*/- (III) (b. p. 137°). These allocations were

[1] Part X, J. A. Oliver and R. Stephens, preceding Paper.

[2] D. E. M. Evans, W. J. Feast, R. Stephens, and J. C. Tatlow, *J.*, 1963, 4828.

[3] J. A. Godsell, M. Stacey, and J. C. Tatlow, *Tetrahedron*, 1958, 193.

[4] R. Stephens, J. C. Tatlow, and E. H. Wiseman, *J.*, 1959, 148.

[5] M. Stacey and J. C. Tatlow, *Adv. Fluorine Chem.*, 1960, **1**, 176.

[6] D. E. M. Evans and J. C. Tatlow, *J.*, 1955, 1184; D. E. M. Evans, J. A. Godsell, R. Stephens, J. C. Tatlow, and E. H. Wiseman, *Tetrahedron*, 1958, **2**, 183.

[7] R. J. Heitzman, C. R. Patrick, R. Stephens, and J. C. Tatlow, *J.*, 1963, 281.

[8] K. von Auwers, *Annalen*, 1920, **420**, 84; A. Skita, *Ber.*, 1920, **53**, 1792; N. L. Allinger, *Experientia*, 1954, **10**, 328; H. van Bekkum, A. van Veen, P. E. Verkade, and B. M. Wepster, *Rec. Trav. chim.*, 1961, **80**, 1310.

confirmed by fluorine-19 n.m.r. spectroscopy and a consideration of the spectra of a large number of related compounds.[9]

The dehydrofluorination reactions of the 1*H*,2*H*,3*H*-nonafluorocyclohexanes were consistent with the structures so deduced. The 1*H*,3*H*/2*H*-isomer (I) gave trace amounts of 1*H*-heptafluorocyclohexa-1,3-diene and hexafluorobenzene and unchanged starting material (69%). The 1*H*,2*H*/3*H*-isomer (II) gave trace amounts of 1*H*- and 2*H*-heptafluorocyclohexa-1,3-diene and hexafluorobenzene and 1*H*,6*H*-octafluorocyclohexene (IV). The 1*H*,2*H*,3*H*/-isomer (III) gave trace amounts of 1*H*- and 2*H*-heptafluorocyclohexa-1,3-diene and 1*H*,3*H*-octafluorocyclohexene, 1*H*,6*H*- (IV) and 3*H*,4*H*/-octafluorocyclohexene (V).

The qualitative differences in ease of dehydrofluorination observed are consistent with the preferred coplanar *trans*-1,2-elimination in (I) necessitating loss of fluoride ion from an electronically less favourable $>CF_2$ group, whereas both (II) and (III) can lose fluoride ion from a $>CHF$ group in a coplanar *trans*-1,2-elimination. The 1*H*,2*H*,3*H*/-isomer (III) appeared to dehydrofluorinate most readily and this, together with the structure of the main product (IV), would suggest that elimination occurred in the favourable conformation possessing two axial hydrogen atoms, *i.e.*, *trans*-coplanar elimination between either of the more acidic hydrogen atoms at C-1 and C-3 and the most weakly bonded fluorine atom at C-2. The 1*H*,2*H*/3*H*-isomer (II), however, would be expected to eliminate in an unfavourable conformation with one axial hydrogen atom to give the same olefin (IV).

Catalytic hydrogenation of 3*H*-nonafluorocyclohexene did not afford a practical route to the nonafluorocyclohexanes. As in related work,[1] the palladium catalyst appeared to be rapidly poisoned by hydrogen fluoride arising from dehydrofluorinations on the surface of the catalyst.

EXPERIMENTAL

1H-2,3-*Dichlorononafluorocyclohexanes.*—3*H*-Nonafluorocyclohexene (27·0 g.) and chlorine (*ca.* 12 g.) were kept together in a sealed Pyrex tube (1 ft. × 1 in.) irradiated with ultraviolet light for 48 hr. at 15°. After removal of excess of chlorine, the liquid product (32·0 g.) was separated by gas chromatography [Column A (4·8 m. × 75 mm.; dinonyl phthalate–Celite, 1 : 2), 100°, N_2 60 l./hr.] to give: (i) starting material (a trace), with the expected infrared (i.r.) spectrum; (ii) 1H-2,3-*dichlorononafluorocyclohexane* (13·8 g.), b. p. 125° [Found: C, 23·1; H, 0·4; Cl, 22·6%; *M* (mass spectrometry), 314·92. $C_6HCl_2F_9$ requires C, 22·9; H, 0·3; Cl, 22·5%; *M*, 314·92]; (iii) 1H-2,3-*dichlorononafluorocyclohexane* (10·9 g.), b. p. 130° [Found: C, 22·6; Cl, 22·6%; *M* (mass spectrometry), 314·92].

Lithium Aluminium Hydride Reduction of 1H-2,3-*Dichlorononafluorocyclohexanes.*—(a) A mixture of 1*H*-2,3-dichlorononafluorocyclohexanes (9·9 g.; 0·031 mole) was added over 30 min. to a stirred suspension of lithium aluminium hydride (2·26 g.; 0·060 mole) in dry diethyl ether (150 c.c.) at 0°. After stirring at 18° for a further 30 min., the mixture was cooled to 0° and excess of lithium aluminium hydride destroyed by careful addition of sulphuric acid (50% v/v). When further addition of sulphuric acid gave no reaction, the mixture was stirred at 18° until all solids dissolved. The dried (MgSO₄) ethereal solution was evaporated through a vacuum-jacketed column (1 ft. × ½ in.) packed with glass helices and the residue (b. p. >35°) separated by gas chromatography [Column B (4·8 m. × 35 mm.; dinonylphthalate–Celite, 1 : 2), 100°, N_2 16 l./hr.] to give: (i) ether; (ii) 1H,2H/3H- (II) and 1H,3H/2H-*nonafluorocyclohexane* (I) (0·26 g.) (Found: C, 29·3; H, 1·4. $C_6H_3F_9$ requires C, 29·3; H, 1·3; F, 69·5%); (iii) 1H,2H,3H/-*nonafluorocyclohexane* (III) (1·51 g.), m. p. 32°, b. p. 137° (Found: C, 29·6; H, 1·6; F, 70·2%), the i.r. spectrum was typical of a polyfluorocyclohexane, $v_{max.}$ 2950 cm.⁻¹ ($>C-H$), and 1400—1000 cm.⁻¹ ($>C-F$). The fluorine-19 n.m.r. spectrum [10] of the 1*H*,2*H*,3*H*/-isomer (III) consisted of an AB quadruplet system (total relative intensity 4) centred at 49·2 p.p.m. with separation $\delta = 7$ p.p.m. (assigned to the equivalent fluorine atoms at C-4 and C-6); a broad line (total relative intensity 2) at 54·0 p.p.m. (assigned to the fluorine atoms at C-5) and a broad band (total relative intensity 3) at 142·8 p.p.m. (assigned to the fluorine atoms at

[9] J. Homer and L. F. Thomas, *Trans. Faraday Soc.*, 1963, **59**, 2431.
[10] L. F. Thomas, personal communication.

C-1, C-2, and C-3); these assignments were made from published [9] correlation rules for a series of polyfluorocyclohexanes.

(*b*) Using the same procedure as in (*a*), the 1*H*-2,3-dichlorononafluorocyclohexanes (68·4 g., 0·217 mole) were treated with lithium aluminium hydride (17·6 g., 0·464 mole) in diethyl ether (200 c.c.). Analytical gas chromatography indicated substantially the same product as in (*a*) but with nine additional components in trace amounts. The i.r. spectrum of the mixture of minor components showed a series of absorption peaks between 1700 and 1770 cm.$^{-1}$ (ascribed to polyfluorocycloalkenes).

(*c*) Using the same procedure as in (*a*), the 1*H*-2,3-dichlorononafluorocyclohexanes (223·6 g., 0·71 mole) were treated with lithium aluminium hydride (52 g., 1·37 mole) in diethyl ether (250 c.c.). A violent reaction occurred on cautious addition of sulphuric acid which resulted in loss of material. Analytical gas chromatography and i.r. spectroscopy of the dried (MgSO$_4$), total product (146·4 g.) indicated a complex mixture of chlorofluorocyclo-hexenes and -hexanes; this material was treated with lithium aluminium hydride (26·1 g.) in diethyl ether (800 c.c.) and the usual isolation procedure using gas chromatography (Column A, 100°, N$_2$ 60 l./hr.) gave: (i) 1*H*,2*H*/3*H*- and 1*H*,3*H*/2*H*-nonafluorocyclohexanes (13·1 g.); (ii) a complex mixture (at least seven components) of hydrofluoro- and hydrochlorofluoro-cyclohexenes (5·9 g.), the i.r. spectrum, which was typical of a mixture, had $\nu_{max.}$ 1660 (–CH=CCl–²), 1710 (–CH=CF–), and 1750 cm.$^{-1}$ (–CF=CF–); (iii) 1*H*,5*H*,6*H*,6*H*-hexafluorocyclohexene (12·9 g.), with the expected i.r. spectrum;[11] (iv) 1*H*,2*H*,3*H*/-nonafluorocyclohexane (29·0 g.), with the expected i.r. spectrum.

1H,2H/3H- *and* 1H,3H/2H-*Nonafluorocyclohexanes.*—The mixture (15·4 g.) of these compounds obtained in the above experiments was separated by gas chromatography [Column C (4·8 m. × 75 mm.; Silicone elastomer 301–Celite, 1 : 5), 65°, N$_2$ 59 l./hr.] to give: (i) 1*H*,3*H*/2*H*-nonafluorocyclohexane (2·3 g.), b. p. 86°, $\nu_{max.}$ 2950 (⊃C–H) and 1400—1000 cm.$^{-1}$ (⊃C–F). The fluorine-19 n.m.r. spectrum [10] consisted of a single line (total relative intensity 4) at 52·9 p.p.m. (assigned to the two equivalent –CF$_2$– groups at C-4 and C-6), an AB quadruplet system (total relative intensity 2) centred at 57·8 p.p.m. with separation $\delta = 20$ p.p.m. (fluorine atoms at C-5), a broad band (total relative intensity 2) at 144 p.p.m. (equivalent fluorine atoms at C-1 and C-3), and a broad band (total relative intensity 1) at 129·9 p.p.m. (fluorine atom at C-2); (ii) 1*H*,2*H*/3*H*-nonafluorocyclohexane (6·7 g.), b. p. 95°, $\nu_{max.}$ 2950 (⊃C–H) and 1400—1000 cm.$^{-1}$ (⊃C–F). The fluorine-19 n.m.r. spectrum [10] consisted of a broad line (total relative intensity 2) centred at 51·9 p.p.m. (fluorine atoms at C-4), two AB quadruplets of equal intensity (total relative intensity 4) centred at 49·8 and 56·2 p.p.m. with separations $\delta = 9·6$ and 16·2 p.p.m., respectively (fluorine atoms at C-6 and C-5), a broad band (total relative intensity 1) at 45 p.p.m. (fluorine atom at C-3) and a broad band (total relative intensity 2) at 38 p.p.m. (fluorine atoms at C-1 and C-2).

Dehydrofluorination of 1H,3H/2H-*nonafluorocyclohexane* (I).—This compound (1·6 g.), potassium hydroxide (3·0 g.), and water (10 c.c.) were shaken together in a sealed Pyrex tube (1 ft. × 1 in.) at *ca.* 80° for 1 hr. The colourless organic product was separated from the deep yellow aqueous layer and on gas chromatography (Column B, 100°, N$_2$ 16 l./hr.) gave: (i) 1*H*-heptafluorocyclohexa-1,3-diene (trace); (ii) hexafluorobenzene (trace); (iii) 1*H*,3*H*/2*H*-nonafluorocyclohexane (1·1 g., 69%); all with the expected i.r. spectra.

Dehydrofluorination of 1H,2H/3H-*nonafluorocyclohexane* (II).—This compound (4·5 g.), potassium hydroxide (4·5 g.), and water (15 c.c.) were shaken together in a sealed Pyrex tube (1 ft. × 1 in.) at *ca.* 80° for 1¼ hr. The colourless organic product (1·0 g.) was separated from the black aqueous phase and on gas chromatography (Column B, 100°, N$_2$ 16 l./hr.) gave: (i) 1*H*-heptafluorocyclohexa-1,3-diene (trace); (ii) 2*H*-heptafluorocyclohexa-1,3-diene (trace); (iii) hexafluorobenzene (trace); (iv) 1*H*,6*H*-octafluorocyclohexene (0·8 g.); all with the expected i.r. spectra.

Dehydrofluorination of 1H,2H,3H/-*nonafluorocyclohexane* (III).—This compound (11·9 g.), potassium hydroxide (10 g.), and water (60 c.c.) were refluxed together for ½ hr. The colourless organic product was separated from the black aqueous layer and on gas chromatography (Column B, 100°, N$_2$ 16 l./hr.) gave: (i) 1*H*-heptafluorocyclohexa-1,3-diene (trace); (ii) 2*H*-heptafluorocyclohexa-1,3-diene (trace); (iii) 1*H*,3*H*-octafluorocyclohexene (trace); (iv) 1*H*,6*H*-octafluorocyclohexene (6·0 g.); (v) 3*H*,4*H*/-octafluorocyclohexene (0·5 g.); all with the expected i.r. spectra.

[11] W. F. Feast and R. Stephens, *J.*, 1965, 3502.

N.m.r. Spectroscopy.—The fluorine-19 spectra were measured on a Mullard SL44 Mark 1 instrument at 30·107 Mc./sec.   The figures quoted are chemical shifts (δ) and are in p.p.m. from trifluoroacetic acid as external reference.

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