1021. *Fluorocyclohexanes. Part X.*[1] 1H,2H,4H,5H/-*Octafluorocyclohexane*

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Four stereoisomeric 1*H*,2*H*,4*H*,5*H*-octafluorocyclohexanes have been described.[2] The remaining stereoisomer has now been isolated, firstly from a synthesis which gives a mixture of stereoisomeric octafluorocyclohexanes, and secondly from the products obtained by the cobaltic fluoride fluorination of benzene.

OCTAFLUOROCYCLOHEXA-1,4-DIENE was treated with chlorine under ultraviolet irradiation. The adduct was reduced directly with lithium aluminium hydride in diethyl ether, which normally[3] readily replaces chlorine in a chlorofluorocarbon by hydrogen. However, in addition to the octafluorocyclohexanes, minor products were obtained containing –CH=CF– groups, as indicated by infrared (i.r.) spectroscopy, presumed to arise from dechlorination[4] followed by reduction[5] of the derived olefins. Two of the three major products were tentatively identified from gas-chromatographic retention volumes as 1*H*,2*H*/4*H*,5*H*- and 1*H*,2*H*,4*H*/5*H*-octafluorocyclohexane[2] (16 and 59% of total product, respectively, by peak area). The third major component (25% by peak area) was of very long retention time [this was expected[2] for 1*H*,2*H*,4*H*,5*H*/-octafluorocyclohexane, since it contains the structural features of the three highest-boiling (*cis*) decafluorocyclohexanes], and a short preparative gas chromatography column was used to facilitate its separation. The highly crystalline octafluorocyclohexane so obtained was characterised by cobaltic fluoride

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[1] Part IX, W. J. Feast and R. Stephens, *J.*, 1965, 3502.

[2] E. Nield, R. Stephens, and J. C. Tatlow, *J.*, 1959, 159.

[3] J. C. Tatlow and R. E. Worthington, *J.*, 1952, 1251; J. Roylance, J. C. Tatlow, and R. E. Worthington, *J.*, 1954, 4426.

[4] J. F. King and R. G. Pews, *Canad. J. Chem.*, 1964, **42**, 1294.

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

fluorination in the usual way,[2] which gave, as the major product (90%), only one nonafluorocyclohexane, *viz.*, 1*H*,2*H*,4*H*/-nonafluorocyclohexane.[6] The other products of the fluorination were tentatively identified by gas-chromatographic retention times as perfluoro-, undecafluoro-, and 1*H*,4*H*/-, 1*H*,2*H*/-, and 1*H*,3*H*/-decafluoro-cyclohexane.

1*H*,2*H*,4*H*,5*H*/-Octafluorocyclohexane was prepared also by a similar route based on 4*H*,5*H*/-octafluorocyclohexene.[6] The latter olefin was chlorinated, and the chloro-adduct reduced with lithium aluminium hydride in diethyl ether, to give, after the above isolation procedure, the same crystalline 1*H*,2*H*,4*H*,5*H*/-octafluorocyclohexane. The very slightly improved yield is offset by the readier availability of octafluorocyclohexa-1,4-diene.

Catalytic hydrogenation of octafluorocyclohexa-1,4-diene did not give the octafluorocyclohexanes. Palladised charcoal appeared to be rapidly poisoned, presumably by hydrogen fluoride, and Adams catalyst gave an extremely complex reaction product which evolved a considerable amount of hydrogen fluoride. These effects presumably arise from facile dehydrofluorinations on the surface of the catalysts, and are similar to those observed with other perfluoro-olefins.[7]

Analytical gas chromatography of the residue (b. p. >136°) remaining after removal of the four known octafluorocyclohexanes [2] from the mixture obtained on cobaltic fluoride fluorination of benzene revealed a very minor component (0·05% of the total fluorination product), which was separated by preparative gas chromatography on a short column to give 1*H*,2*H*,4*H*,5*H*/-octafluorocyclohexane.

EXPERIMENTAL

1H,2H,4H,5H/-*Octafluorocyclohexane.* (a) *From octafluorocyclohexa*-1,4-*diene.* This compound [8] (12·8 g.) and chlorine (*ca.* 10 g.) were sealed together in a Pyrex tube which was irradiated with u.v. light for 16 hr. to give a waxy solid (20·5 g.). The latter solid (20·0 g.) in dry ether (50 c.c.) was added during 45 min. to a stirred suspension of lithium aluminium hydride (10·0 g.) in dry ether (200 c.c.) at 0°. After 6 hr. at 0° and 16 hr. at room temperature, sulphuric acid (150 c.c.; 65% v/v) was added cautiously, followed by water (200 c.c.), the ethereal layer was separated, and the aqueous layer extracted four times with ether (100 c.c.). The combined extracts were washed with water, dried ($MgSO_4$), and filtered. The bulk of the ether was removed by fractional distillation (1 ft. column packed with glass helices), and the residue (13·3 g.) was shown by analytical gas chromatography [dinonyl phthalate–Celite, 1 : 4; 56 cm. tube, 3 mm. i.d. (column A); 100°; N_2 flow-rate 6·3 l./hr. at 7 p.s.i.] to contain three major components in addition to diethyl ether. The mixture was separated (in two equal portions) using preparative gas chromatography [dinonyl phthalate–coarse Celite, 1 : 4; 90 cm. × 3 cm. i.d. (column B); 100°; N_2 flow-rate 20 l./hr.] to give (in total): (i) a mixture (10 g.); (ii) (after 5½ hr.) 1H,2H,4H,5H-*octafluorocyclohexane* (2·45 g.), m. p. 98—98·5° (with sublimation), b. p. 176—177°/751 mm. (Found: C, 31·5; H, 1·8. $C_6H_4F_8$ requires C, 31·6; H, 1·8%), the ^{19}F n.m.r. spectrum was consistent with the proposed structure.[9]

(b) *From* 4H,5H/-*octafluorocyclohexene.* This olefin [6] (5·7 g.) and chlorine (*ca.* 3 g.) were sealed together in a Pyrex tube, which was irradiated with u.v. light for 17 hr. to give a liquid product (9·2 g.). The latter material (5·7 g.) in ether (50 c.c.) was treated with lithium aluminium hydride (6·0 g.) in ether (250 c.c.) in the manner described previously. The usual procedure gave 1*H*,2*H*,4*H*,5*H*/-octafluorocyclohexane (0·95 g.), m. p. 98°, with a correct i.r. spectrum.

(c) *From the cobaltic fluoride fluorination of benzene.* Benzene (8·2 l.) was fluorinated in the usual way [10] at 140—180° to give a mixture of polyfluorocyclohexanes (13·3 kg.) which was fractionally distilled, and the residue (25 g.) separated in three portions by preparative gas chromatography (column B; 100°; N_2 flow-rate 20 l./hr.) to give 1*H*,2*H*,4*H*,5*H*/-octafluorocyclohexane (6·7 g.) with a correct i.r. spectrum.

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

[7] I. L. Knunyants, E. I. Mysov, and M. P. Krasuskaya, *Izvest. Akad. Nauk S.S.S.R.*, 1958, 906; W. J. Feast, R. Stephens, and J. C. Tatlow, unpublished work.

[8] D. E. M. Evans and J. C. Tatlow, *J.*, 1954, 3779.

[9] L. F. Thomas, unpublished work; J. Homer and L. F. Thomas, *Trans. Faraday Soc.*, 1963, **59**, 2431.

[10] R. P. Smith and J. C. Tatlow, *J.*, 1957, 2505.

Fluorination of 1H,2H,4H,5H/-*octafluorocyclohexane.*—The octafluorocyclohexane (1·0 g.) was sublimed into a stream of nitrogen (7·5 l./hr.) passing over cobaltic fluoride at 140° in the vessel described before.[11] Analytical gas chromatography (dinonyl phthalate–Celite, 1 : 4; 170 cm. tube; 100°; N_2 flow-rate 6 l./hr.) indicated that the product (0·8 g.) contained (in order of increasing retention time): (i) perfluorocyclohexane; (ii) undecafluorocyclohexane; (iii) 1*H*,4*H*/-decafluorocyclohexane; (iv) 1*H*,2*H*/-decafluorocyclohexane; (v) 1*H*,3*H*/-decafluorocyclohexane [(i)—(v) amounted in all to 5% of the total product, as measured by peak areas]; (vi) 1*H*,2*H*,4*H*/-nonafluorocyclohexane (90% of the total product by peak area); (vii) 1*H*,2*H*,4*H*,5*H*/-octafluorocyclohexane (5% of total product by peak area). Separation of a portion (40 μl.) of this mixture by gas chromatography (column A; 100°; N_2 flow-rate 6·3 l./hr. at 7 p.s.i.) gave 1*H*,2*H*,4*H*/-nonafluorocyclohexane with a correct i.r. spectrum.

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