

Polyfluorocycloalkenes. Part VIII.¹ The Stereoisomeric 2*H*-Perfluorocyclopentyl and -hexyl Methyl Ethers

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The stereoisomeric 2*H*-octafluorocyclopentyl methyl ethers have been prepared by the lithium aluminium hydride reduction of the stereoisomeric 2-chloro-octafluorocyclopentyl methyl ethers obtained from the cobaltic fluoride fluorination of 2-chlorohexafluorocyclopentenyl methyl ether. Dehydrofluorination of both 2*H*-octafluorocyclopentyl methyl ethers with aqueous base was smooth and gave 1- and 3-methoxyheptafluorocyclopentene. The stereoisomeric 2*H*-decafluorocyclohexyl methyl ethers were obtained from the cobaltic fluoride fluorination of 1*H*-6-methoxy- and 1*H*-2-methoxy-octafluorocyclohexene. The *cis*-2*H*-decafluorocyclohexyl methyl ether and aqueous potassium hydroxide readily gave 1- and 3-methoxynonafluorocyclohexene in the ratio of 17:10, respectively, and the *trans*-isomer gave the same products in the ratio of 2:7, respectively, but much less readily, in agreement with the stereochemistry allocated. The *trans*-isomer was isolated also from the reaction of methanolic potassium hydroxide with decafluorocyclohexene in agreement with an addition-elimination process.

CYCLIC polyfluoro-olefins have given unsaturated ethers in all reactions with alcohols under ionic conditions so far reported.² The process can be rationalised in terms of the *trans*-addition of alkoxide ion to the electron-deficient double-bond followed by a β -elimination of fluoride ion from the carbanionic species produced. The latter might be capable of protonation as well as elimination, however, and if the appropriate saturated ether

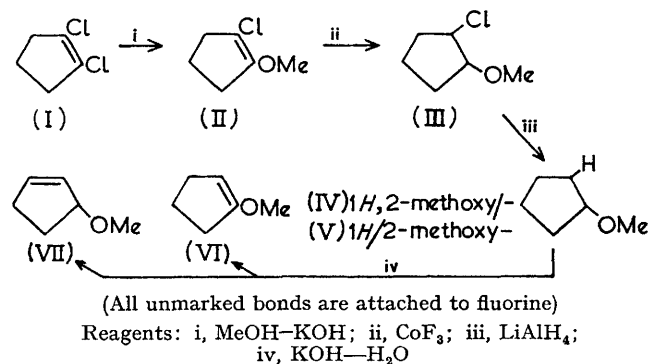
could be found in the reaction products, it would support the proposed pathway. It was of interest, therefore, to examine typical reaction mixtures in more detail than hitherto. To facilitate this study, the stereoisomeric 2*H*-perfluorocyclopentyl and 2*H*-perfluorocyclohexyl methyl ethers were first synthesised unambiguously.

1,2-Dichlorohexafluorocyclopentene (I) reacted exothermically with methanol and potassium hydroxide to

¹ Part VII, J. Riera and R. Stephens, *Tetrahedron*, 1966, **22**, 2555.

² A. B. Clayton, J. Roylance, D. R. Sayers, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 1965, 7358.

give the previously reported,³ but not fully characterised, 2-chlorohexafluorocyclopentenyl methyl ether (II) as the main product. Cobaltic fluoride fluorination of (II) followed the established pattern⁴ of such fluorinations to give *cis*- and *trans*-2-chloro-octafluorocyclopentyl methyl ether (III), and *cis*- and *trans*-2-chloro-octafluorocyclopentyl fluoromethyl ether as the principal products at 80°. The stereoisomeric chloro-fluoro-ethers (III) were not separated but were reduced with lithium aluminium hydride in diethyl ether to a mixture of *cis*- and *trans*-2*H*-octafluorocyclopentyl methyl ether (IV) and (V). The latter isomers were readily separated by g.l.c. and were characterised by their ready dehydrofluorination with aqueous potassium hydroxide to the known² 1- and 3-methoxyheptafluorocyclopentenes (VI) and (VII).



A completely unequivocal differentiation between the *cis*- and *trans*-configuration in the 2*H*-octafluorocyclopentyl methyl ethers was not achieved. It has been shown⁵ that although *trans*-elimination of hydrogen fluoride occurs more readily than *cis*- in polyfluorocyclopentanes, the preference is not as marked as in polyfluorocyclohexanes. On this basis, the isomer of b.p. 94° which dehydrofluorinated slightly faster, is the *cis*-2*H*-octafluorocyclopentyl methyl ether (IV), with a *trans*-vicinal H-F relationship, and that of b.p. 99° the *trans*-isomer (V), with a *cis*-vicinal H-F disposition. However, with heterogeneous reactions such as these, experimental factors (*e.g.* differences in solubility between the stereoisomers) may overshadow the relatively small stereochemical influences in the dehydrofluorinations. The proportions of the products formed with aqueous alkali support the structural allocations made, since it is generally found that *cis*-dehydrofluorination involves more competing elimination of fluorine from a CF₂ group.⁵ Thus, the *cis*-2*H*-octafluorocyclopentyl methyl ether (IV) gave approximately five times as much 1-methoxy-(VI) as 3-methoxy-heptafluorocyclopentene (VII) whereas the *trans*-ether (V) gave approximately equal amounts.

The ¹H and ¹⁹F n.m.r. spectra of the two isomers were

³ A. L. Henne and K. A. Latif, *J. Indian Chem. Soc.*, 1953, **30**, 809.

⁴ A. B. Clayton, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 1965, 7370.

consistent with gross 2*H*-octafluorocyclopentyl methyl ether structures but did not afford a reliable differentiation between the *cis*- and *trans*-configurations.

Neither saturated ether (IV) or (V) could be detected in the products of reaction² of octafluorocyclopentene with methanolic potassium hydroxide. This is not unexpected in view of the ready dehydrofluorination of both the *cis*- and *trans*-ethers (IV) and (V).

The analogous route to stereoisomeric pair of 2*H*-decafluorocyclohexyl methyl ethers gave only one series pure. Thus, 1,2-dichloro-octafluorocyclohexene and methanolic potassium hydroxide gave the known⁶ 2-chloro-octafluorocyclohexenyl methyl ether which, on fluorination over cobaltic fluoride, gave only one of the two 2-chlorodecafluorocyclohexyl methyl ethers in a pure state; the other was admixed with a 2-chlorodecafluorocyclohexyl fluoromethyl ether. Therefore, an alternative route was employed based on 1*H*-6-methoxy- and 1*H*-2-methoxy-octafluorocyclohexene (VIII) and (IX), obtained² from 1*H*-nonafluorocyclohexene (X) and methanolic potassium hydroxide. Cobaltic fluoride fluorination of (VIII) and (IX) gave essentially the same products. Hence, in large-scale experiments the mixture was fluorinated, and it gave the known⁴ methyl undecafluorocyclohexyl ether (XI), *cis*-2*H*-decafluorocyclohexyl methyl ether (XII), a mixture of *trans*-2*H*-decafluorocyclohexyl methyl ether (XIII) and the suspected *cis*-2*H*-decafluorocyclohexyl fluoromethyl ether (XIV), and finally the suspected *trans*-2*H*-decafluorocyclohexyl fluoromethyl ether (XV). The mixed component so obtained was treated with aqueous potassium hydroxide at room temperature. This treatment dehydrofluorinated the suspected *cis*-2*H*-decafluorocyclohexyl fluoromethyl ether (XIV), in agreement with the presence of a favourable vicinal-*trans*-H-F system. The mixture of 1- and 3-fluoromethoxynonafluorocyclohexenes (XVI) and (XVII) so formed, could then be separated from the more alkali-resistant *trans*-2*H*-decafluorocyclohexyl methyl ether (XIII) to give the latter pure.

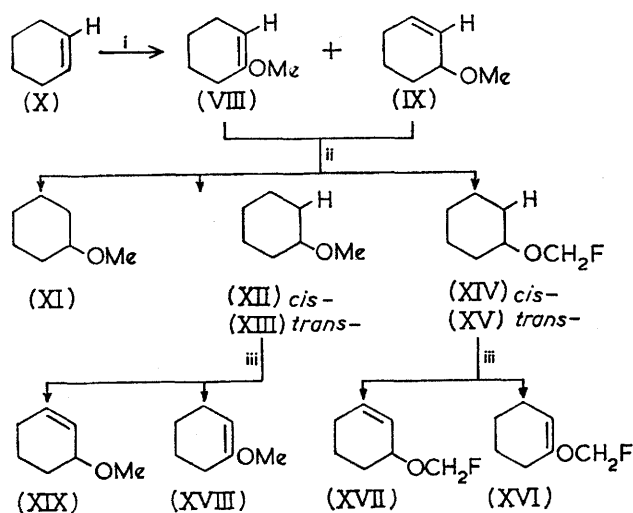
The stereoisomeric 2*H*-decafluorocyclohexyl methyl ethers so obtained were unequivocally identified by dehydrofluorination with aqueous potassium hydroxide. The shorter retained isomer reacted much more readily and was completely dehydrofluorinated to 1- and 3-methoxynonafluorocyclohexenes² (XVIII) and (XIX) after 1 hr. under reflux and hence is *cis*-2*H*-decafluorocyclohexyl methyl ether (XII). The longer retained isomer was much more difficult to dehydrofluorinate, and required 3 hr. under reflux to complete the conversion into 1- and 3-methoxynonafluorocyclohexenes² (XVIII) and (XIX); hence it is *trans*-2*H*-decafluorocyclohexyl methyl ether (XIII). The proportions of the olefins formed in each dehydrofluorination were also consistent with the stereochemistry suggested. Thus, the *cis*-

⁵ J. Burdon, T. M. Hodgins, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 1965, 2382.

⁶ Belg.P. 660,363; U.S.P. 3,354,223 (*Chem. Abs.*, 1968, 21,601r).

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isomer (XII) gave the 1- and 3-methoxy-olefins in the ratio of 17:10 whereas the *trans*-isomer (XIII) gave these olefins in the ratio of 2:7.



(All unmarked bonds are attached to fluorine)

Reagents: i, MeOH-KOH; ii, CoF_3 ; iii, KOH- H_2O

The product of reaction of decafluorocyclohexene with methanolic potassium hydroxide was re-examined to see whether either of the 2*H*-decafluorocyclohexyl methyl ethers was present. The *cis*-isomer (XII) was not detected, but a very minor constituent found was shown, after isolation, to be the *trans*-isomer (XIII). This observation is consistent with an addition-elimination process in which the first step is the *trans*-addition of methoxide ion (*i.e.* attack from above the ring plane) to form a carbanionic species. The exceedingly small yield of the *trans*-2*H*-ether (XIII) however, suggests either that elimination from a carbanionic intermediate of this type is not as sterically dependent as an *E2* dehydrofluorination or that inversion can occur at the carbanion centre. A conformational 'flipping' of the ring would then produce the *cis*-carbanion with its methoxide group equatorial. This should be the arrangement with the least steric interactions but it also has the anti-periplanar stereochemistry favourable to elimination. It is of interest, that the *trans*-2*H*-ether (XIII) was 40% deuteriated by potassium hydroxide in deuterium oxide, whereas, the *cis*-isomer (XII) incorporated no deuterium with this reagent. No inversion of the *trans*- to the *cis*-system could be detected.

The much lower proportion of 3-methoxy-olefin (XIX) produced from the reaction of decafluorocyclohexene with methanolic potassium hydroxide than from the dehydrofluorination reactions of the ethers (XII) and (XIII) is noteworthy. It may, of course, reflect differences between the loss of fluoride ion from preformed carbanions and dehydrofluorination of preformed saturated ethers. Alternatively, the 3-methoxy-olefin (XIX) may be generated initially from the decafluorocyclohexene in just as high proportion, but, having a $\text{CF}=\text{CF}$

double-bond, may then react preferentially with more base.

EXPERIMENTAL

Techniques.—Oxidations, gas chromatography, and the spectroscopic measurements were carried out as before,² unless otherwise stated. Known acids were characterised by two derivatives which had correct elemental analyses.

1-Chloro-2-methoxyhexafluorocyclopentene.—1,2-Dichloro-hexafluorocyclopentene (100 g.) was treated with methanol and potassium hydroxide, in the manner described previously,³ to give a liquid product (93.4 g.) which was shown by gas chromatography to contain two principal components. Fractional distillation through a vacuum-jacketed column (1 ft \times $\frac{1}{2}$ in. diam.) packed with glass helices gave: (i) 1,2-dichlorohexafluorocyclopentene (44 g.), b.p. 90–91°, with a correct i.r. spectrum; (ii) a mixture of (i) and (iii) (5.0 g.) b.p. 90–129°, (iii) 1-chloro-2-methoxyhexafluorocyclopentene (33 g.), b.p. 129–131° (lit.,³ b.p. 130°/742 mm.) (Found: C, 29.7; H, 1.2. Calc. for $\text{C}_6\text{H}_3\text{ClF}_6\text{O}$: C, 29.9; H, 1.2%), ν_{max} 1655 cm^{-1} [$\text{C}=\text{C}(\text{OMe})$], the ^1H n.m.r. consisted of a broad band at 4.05, whilst the ^{19}F n.m.r. spectrum consisted of three bands of equal intensity: 34.2, 37.2, 37.5, and 52.4; (iv) a residue (13.5 g.) was not examined. Component (iii) (1.0 g.) was oxidised by potassium permanganate in acetone to hexafluoroglutaric acid (85%).

1-Chloro-2-methoxyoctafluorocyclohexene.—1,2-Dichloro-octafluorocyclohexene (29.0 g.), treated in the same way as in the preceding reaction gave a liquid product (28.0 g.) which was shown by gas chromatography to contain two components which were separated by gas chromatography (100°; N_2 , 60 l./hr.) to give: (i) 1,2-dichloro-octafluorocyclohexene (13.5 g.) with a correct i.r. spectrum; (ii) 1-chloro-2-methoxyoctafluorocyclohexene (6.5 g.), b.p. 133–134° (lit.,⁶ b.p. 135–136°) (Found: C, 29.0; H, 1.1. Calc. for $\text{C}_7\text{H}_3\text{ClF}_8\text{O}$: C, 28.9; H, 1.0%), ν_{max} 1635 cm^{-1} [$-\text{CCl}=\text{C}(\text{OMe})-$], the ^1H n.m.r. consisted of a triplet centred at 3.9 (J_{HF} ca. 0.8 c./sec.), whilst the ^{19}F n.m.r. spectrum consisted of four bands of equal intensity at 33.8, 38.4, 57.9, and 58.9; the compound was oxidised with potassium permanganate in acetone to octafluoroadipic acid (67%).

Fluorination of 1-Chloro-2-methoxyhexafluorocyclopentene.—This olefin (90.0 g.) was fluorinated in a stream of nitrogen (10 l./hr.) at 80° in a small, stirred cobaltic fluoride reactor,⁴ to give a liquid product (72.0 g.) which was separated by gas chromatography (80°; N_2 , 60 l./hr.) to give: (i) very volatile material (0.3 g.) (ii) *cis*- and *trans*-2-chloro-octafluorocyclopentyl methyl ether (28.0 g.), b.p. 107–108° (Found: C, 25.9; H, 0.9. $\text{C}_6\text{H}_3\text{ClF}_8\text{O}$ requires C, 25.9; H, 1.1%), ν_{max} 2960 cm^{-1} (C-H), the ^1H n.m.r. spectrum consisted of a single peak at 3.55 whilst the ^{19}F n.m.r. spectrum had a total relative intensity ratio of 8, with bands at 55.1 and 63.9 (each of intensity ratio 1) (tertiary fluorine atoms at C-1 and C-2) and two complex bands (total intensity ratio 6) at 47.4 and 50.2 (fluorine atoms at C-3, C-4 and C-5); (ii) *cis*- and *trans*-2-chloro-octafluorocyclopentyl fluoromethyl ether (8.5 g.), b.p. 109° (Found: C, 24.5; H, 0.9. $\text{C}_6\text{H}_2\text{ClF}_9\text{O}$ requires C, 24.3; H, 0.7%), ν_{max} 2960 cm^{-1} (C-H), the ^1H n.m.r. spectrum consisted of a doublet centred at 5.4 (J_{HF} ca. 50 c./sec.), each line of which showed slight coupling, whilst the ^{19}F n.m.r. spectrum had a total intensity ratio of 9 and displayed a triplet at 55.7 (intensity ratio 1) (OCH_2F), two bands at 58.4 and 66.7 (each of intensity

ratio 1) (tertiary fluorine atoms at C-1 and C-2), bands between 32.5 and 48.7 (total intensity ratio 6) appeared to be three overlapping AB quadruplets (fluorine atoms at C-3, C-4, and C-5); (iii) 1-chloro-2-methoxyhexafluorocyclopentene (20.5 g.) with a correct i.r. spectrum.

Fluorination of 1-Chloro-2-methoxyoctafluorocyclohexene.—This olefin (17.0 g.) when fluorinated, by the standard procedure,⁴ at 100° and with a nitrogen flow-rate of 12 l./hr. gave a liquid product (15.0 g.) which was separated by gas chromatography (100°; N₂, 60 l./hr.) to give (i) a 2-chlorodecafluorocyclohexyl methyl ether (3.0 g.), b.p. 121–122° (Found: C, 25.7; H, 0.9. C₇H₂ClF₁₀O requires C, 25.6; H, 0.9%), ν_{\max} 2960 cm.⁻¹ (C-H), the ¹H n.m.r. spectrum consisted of a broad singlet at 3.7 whilst the ¹⁹F n.m.r. spectrum had a total intensity ratio of 10 with bands at 43.7 and 59.6, each of intensity ratio 1 (tertiary fluorine atoms at C-1 and C-2), bands at 36.2, 38.0, 42.2, 42.9, and 43.7, each of intensity ratio 1, and a band at 41.5 (intensity ratio 3) were too complex to be analysed; (ii) a mixture of (2.3 g.) which was shown by ¹H n.m.r. spectroscopy and analytical gas chromatography to be a mixture of a 2-chlorodecafluorocyclohexyl methyl ether and a 2-chlorodecafluorocyclohexyl fluoromethyl ether; (iii) 1-chloro-2-methoxyoctafluorocyclohexene (5.0 g.) with a correct i.r. spectrum.

cis- and trans-2H-Octafluorocyclopentyl Methyl Ether.—The mixed *cis-* and *trans-*2-chloro-octafluorocyclopentyl methyl ether (25.0 g.) in diethyl ether (30 c.c.) was added dropwise to a stirred suspension of lithium aluminium hydride (18.0 g.) in diethyl ether at 0°. After the addition was complete the mixture was stirred for a further 2 hr. at 0°, 50% (v/v) hydrochloric acid (200 c.c.) was then added and the stirring was continued at *ca.* 18° until all the solid had dissolved. The ether layer was washed with water, dried (Na₂SO₄), filtered; most of the ether was then removed under reduced pressure to leave a liquid (25.0 g.). The latter was shown by gas chromatography (100°; N₂, 1 l./hr.) to contain ether and two other components; these were separated by gas chromatography (70°; N₂, 60 l./hr.) to give: (i) diethyl ether (16.5 g.); (ii) *trans-2H-octafluorocyclopentyl methyl ether* (2.8 g.), b.p. 99° (Found: C, 29.4; H, 1.6. C₆H₄F₈O requires C, 29.5; H, 1.6%); (iii) *cis-2H-octafluorocyclopentyl methyl ether* (3.3 g.), b.p. 94° (Found: C, 29.4; H, 1.6%).

Characterisation of trans-2H-Octafluorocyclopentyl Methyl Ether.—(a) *Spectroscopy.* The i.r. spectrum showed a multiple absorption band near 2960 cm.⁻¹ (CH) but no bands in the range 2960–1460 cm.⁻¹ (saturated system). The ¹H n.m.r. spectrum consisted of a broad singlet at 3.45 (intensity ratio 3) and a doublet (J_{HF} *ca.* 50 c./sec.) centred at 4.55 (relative intensity ratio 1) each band of which showed slight coupling of small *J*. The ¹⁹F n.m.r. spectrum had a total intensity ratio of 8, with a band (intensity ratio 1) at 62.9 (tertiary fluorine atom at C-1), a band (intensity ratio 1) at 133.9 (tertiary fluorine at C-2), a group of bands at 36.7, 39.9, 51.0, 54.2 (total intensity ratio 2; an AB quadruplet arising from the fluorines at C-3), a group of bands at 44.6, 47.0, 49.4, 51.8 (total intensity ratio 2; an AB quadruplet arising from the fluorines at C-4) and a group of bands at 49.4, 51.8, and 54.2 (total intensity ratio 2; an AB quadruplet arising from the fluorines at C-5).

(b) *Dehydrofluorination.* The ether (2.0 g.), potassium hydroxide (3 g.), and water (3 c.c.) were shaken together at *ca.* 18°. As before, samples of the lower layer were examined periodically by ¹H n.m.r. spectroscopy and gas

chromatography; this revealed 15% reaction after 10 min. and 75% reaction after 40 min. The mixture was then heated under reflux for 90 min. after which the lower layer was washed with water, dried (Na₂SO₄), and filtered to give a liquid (1.8 g.) which was shown by g.l.c. and n.m.r. spectroscopy to contain only 1- and 3-methoxyheptafluorocyclopentene² in the ratio of 16 : 13.

Characterisation of cis-2H-Octafluorocyclopentyl Methyl Ether.—(a) *Spectroscopy.* The i.r. spectrum showed a multiple absorption band near 2960 cm.⁻¹ (CH) and no absorption ascribable to a double bond. The ¹H n.m.r. spectrum consisted of a broad singlet at 3.5 (intensity ratio 3) and a doublet (J_{HF} *ca.* 50 c./sec.; intensity ratio 1) centred at 4.7, each broad line of which showed slight coupling. The ¹⁹F n.m.r. spectrum had a total intensity ratio of 8 and displayed a band at 121.9 (intensity ratio 1, tertiary fluorine at C-2), four bands at 38.3, 40.6, 47.1, and 49.4, thought to constitute an AB quadruplet, bands at 44.6, 47.8, and 52.6, which taken together with the band at 49.4 (tertiary fluorine at C-1) are part of a suspected AB quadruplet, bands at 45.4, 47.8, 51.8, and 54.2 are thought to be another AB quadruplet; the total intensity ratio of the three AB quadruplets was 7.

(b) *Dehydrofluorination.*—The ether (2.0 g.), potassium hydroxide (3 g.), and water (3 c.c.) were shaken together at *ca.* 18°. As before, samples of the lower layer were examined periodically by ¹H n.m.r. spectroscopy and gas chromatography and this revealed 35% reaction after 10 min. and 90% reaction after 40 min. The mixture was then heated under reflux for 90 min.; the lower layer was washed with water, dried (Na₂SO₄), and filtered to give a liquid (1.8 g.) which was shown by the above techniques to contain only 1- and 3-methoxyheptafluorocyclopentene in the ratio of 26 : 5; this was confirmed by comparison with a synthetic mixture of these olefins in the same ratio.

Fluorination of 1H-6-Methoxy- and 1H-2-Methoxy-octafluorocyclohexene.—1H-6-Methoxyoctafluorocyclohexene (5.0 g.) gave a liquid product (2.8 g.) when fluorinated by the standard procedure⁴ at 100° and with a nitrogen flow-rate of 10 l./hr. Likewise, 1H-2-methoxyoctafluorocyclohexene (4.0 g.) gave a liquid product (2.0 g.). Both products were shown by gas chromatography and i.r. spectroscopy to be almost identical (there was a small variation in relative peak heights).

A mixture of the above olefins (14.0 g.; 1 : 1) fluorinated, in the above way, at 80° and with a nitrogen flow-rate of 20 l./hr., gave a liquid product (13.0 g.) shown by gas chromatography (100°; N₂ 1 l./hr.) to be nearly identical with the above, which was separated (65°; N₂ 60 l./hr.) to give: (i) methyl undecafluorocyclohexyl ether (2.7 g.), with a correct i.r. spectrum;⁴ (ii) *cis-2H-decafluorocyclohexyl methyl ether* (2.7 g.), b.p. 115° (Found: C, 28.8; H, 1.6. C₇H₄F₁₀O requires C, 28.6; H, 1.4%); (iii) *trans-2H-decafluorocyclohexyl methyl ether* (4.2 g.) containing the suspected *cis-2H-decafluorocyclohexyl fluoromethyl ether*; (iv) suspected *trans-2H-decafluorocyclohexyl fluoromethyl ether* (0.5 g.) which was not examined further.

Fraction (iii), potassium hydroxide (3.0 g.) and water (3 c.c.) were shaken together at *ca.* 18° for 2 hr. The lower layer was washed with water, dried (Na₂SO₄), and the resultant liquid (4.0 g.) was separated (90°; N₂, 15 l./hr.) to give: (i) a mixture of the suspected 1- and 3-fluoromethoxy-nonafluorocyclohexenes (0.9 g.), which were not examined further; (ii) *trans-2H-decafluorocyclohexyl methyl ether* (1.4 g.) b.p. 111° (Found: C, 28.5; H, 1.3%).

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Characterisation of cis-2H-Decafluorocyclohexyl methyl ether.—(a) *Spectroscopy.* The i.r. spectrum showed a multiple absorption band centred at 2960 cm^{-1} (CH) but none between this and 1460 cm^{-1} (saturated system). The ^1H n.m.r. spectrum consisted of a broad singlet at 3.55 (relative intensity ratio 3; OMe) and a doublet (J_{HF} ca. 45 c./sec.), centred at 4.65 (relative intensity ratio 1; CHF), each broad band of which showed slight coupling. The ^{19}F n.m.r. spectrum had a total intensity ratio of 10, with a band at 154.5 (intensity ratio 1) ascribable to the tertiary fluorine atom at C-2, a band at 70.7 (intensity ratio 1, tertiary fluorine atom at C-1) and four overlapping AB quadruplets between 47 and 66 (total intensity ratio 8).

(b) *Dehydrofluorination.* The ether (1.7 g.), potassium hydroxide (3 g.), and water (3 c.c.) were vigorously shaken together at ca. 18°. After 10 min. of this treatment a sample of the lower layer was shown by ^1H n.m.r. spectroscopy and gas chromatography to have reacted to the extent of ca. 5%. Further assays were made in this way after 40 min. (15%) and 105 min. (40%). Finally, the mixture was heated under reflux for 1 hr.; the lower layer was washed with water, dried (Na_2SO_4), and filtered. The liquid (1.5 g.) so obtained was shown by gas chromatography (enrichment technique) and ^1H n.m.r.- and i.r.-spectroscopy to contain 1- and 3-methoxynonafluorocyclohexene in the ratio of 17 : 10; this was confirmed by a comparison with a synthetic mixture of these compounds in the same proportions.

Characterisation of trans-2H-Decafluorocyclohexyl Methyl Ether.—(a) *Spectroscopy.* The i.r. spectrum showed a multiple absorption band centred at 2960 cm^{-1} (CH); there were no bands however in the range 2960—1465 cm^{-1} (saturated system). The ^1H n.m.r. spectrum consisted of a broad singlet at 3.55 (intensity ratio 3, OMe) and a doublet (J_{HF} ca. 45 c./sec.) centred at 4.8 (relative intensity ratio 1, CHF), each broad band of which showed slight coupling of smaller coupling constant than that of the *cis*-isomer. The ^{19}F n.m.r. spectrum had a total intensity ratio of 10, with a band at 145.7 (intensity ratio 1, tertiary fluorine at C-2), a band at 60.4 (intensity ratio 1, tertiary fluorine at C-1) and four overlapping AB quadruplets between 43 and 63 (total intensity ratio 8).

(b) *Dehydrofluorination.* This ether (1.0 g.), potassium hydroxide (3.0 g.), and water (3 c.c.) were vigorously shaken together at ca. 18°. As before, samples of the lower layer were examined periodically by ^1H n.m.r. spectroscopy and gas chromatography. No detectable reaction was observed after 105 min. The mixture was then heated under reflux; a sample taken after 1 hr. revealed that reaction had occurred to the extent of 25%. After a further 2 hr. under reflux, the lower layer was separated, washed with water, dried (Na_2SO_4), and filtered. The liquid (0.8 g.) so

obtained was shown by ^1H n.m.r. and i.r. spectroscopy and gas chromatography to contain only 1- and 3-methoxynonafluorocyclohexene in the ratio of 2 : 7; this was confirmed by a comparison with a synthetic mixture of these compounds in the same proportions.

Isolation of trans-2H-Decafluorocyclohexyl Methyl Ether from the Reaction of Decafluorocyclohexene with Methanol.—Methanol (1.1 mol.) was added dropwise to a stirred mixture of decafluorocyclohexene (176 g.) and potassium hydroxide pellets (1.0 mol.) at room temperature; heat was evolved and potassium fluoride was precipitated. After the addition was completed stirring was continued for a further 1 hr. at room temperature; an excess of water was then added and the lower layer was separated, washed with water, dried (Na_2SO_4), and filtered. The filtrate (175 g.) was shown by gas chromatography (100°; N_2 , 1 l./hr.) to contain two major products and one trace component with retention times identical to those of 1- and 3-methoxynonafluorocyclohexene and *trans*-2H-decafluorocyclohexyl methyl ether. Fractional distillation through a vacuum-jacketed column (1 ft. \times $\frac{1}{2}$ in. diam.) packed with Dixon gauge rings gave: (i) decafluorocyclohexene (38 g.), b.p. 52—53° with a correct i.r. spectrum; (ii) a mixture of 1- and 3-methoxynonafluorocyclohexene (90 g.) b.p. 53—110°; (iii) a residue (47 g.) b.p. 110°. A portion (3.0 g.) of the last was separated by gas chromatography (60°; N_2 , 60 l./hr.) to give: (i) 3-methoxynonafluorocyclohexene (0.3 g.) with a correct i.r. spectrum; (ii) 1-methoxynonafluorocyclohexene (14 g.) with a correct i.r. spectrum; (iii) a mixture of (ii) and *trans*-2H-decafluorocyclohexyl methyl ether (1.9 g.); (iv) a mixture of 1,2- and 1,6-dimethoxyoctafluorocyclohexene (2.0 g.). Fraction (iii) was re-separated by gas chromatography (75°; N_2 , 15 l./hr.) to give: (i) 1-methoxynonafluorocyclohexene (0.6 g.) with a correct i.r. spectrum; (ii) *trans*-2H-decafluorocyclohexyl methyl ether (0.6 g.) with correct i.r. and ^1H n.m.r. spectra.

Deuteration of trans-2H-Decafluorocyclohexyl Methyl Ether.—The ether (1.0 g.), potassium hydroxide (2.0 g.), and deuterium oxide (2 c.c.) were shaken together for 2 hr.; the lower layer was shown by ^1H n.m.r. spectroscopy and gas chromatography to have reacted to the extent of ca. 10%. The dried (P_2O_5) reaction product was separated by gas chromatography (80°; N_2 , 15 l./hr.) to give a mixture (0.5 g.) of *trans*-2H- and *trans*-2D-decafluorocyclohexyl methyl ether in the ratio 9 : 11 by mass spectrometry.

cis-2H-Decafluorocyclohexyl methyl ether (1.0 g.), potassium hydroxide (2.0 g.), and deuterium oxide (2 c.c.) were shaken together for 20 min.; the lower layer was dried (P_2O_5) and shown by ^1H n.m.r. spectroscopy and gas chromatography to have reacted to the extent of ca. 10% and by mass spectrometry to be free of deuterium.

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