1350. *Polyfluorocycloalkenes. Part III.*[1] *Reactions with Alcohols under Ionic Conditions to give Ethers*

By A. B. CLAYTON, J. ROYLANCE, D. R. SAYERS, R. STEPHENS, and J. C. TATLOW

Various polyfluoro-cyclic olefins have been treated with several alcohols in the presence of a base, and the ethers formed fully characterised. Each reaction, with one exception, gave two mono-alkoxy-olefins, one substituted in the vinylic position, the other in the allylic position, by what appears to be an addition–elimination pathway; the ratio of these ethers varied with the alcohol and olefin used. In the characterisation of these olefinic ethers, potassium permanganate oxidation gave a number of new alkoxy-polyfluorodibasic acids.

THE reactions of alcohols with acyclic [2,3] and cyclic [4-11] fluoro-olefins in the presence of bases (ionic conditions) have been studied extensively during a long period. Acyclic

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[1] Part II, P. Robson, J. Roylance, R. Stephens J. C. Tatlow, and R. E. Worthington, *J.*, 1964, 5748.

[2] W. T. Miller, E. W. Fager, and P. H. Griswold, *J. Amer. Chem. Soc.*, 1948, **70**, 431.

[3] J. D. Park, W. M. Sweeney, S. L. Hopwood, and J. A. Lacher, *J. Amer. Chem. Soc.*, 1956, **78**, 1685.

[4] J. D. Park, M. L. Sharrah, and J. R. Lacher, *J. Amer. Chem. Soc.*, 1949, **71**, 2337.

[5] J. T. Barr, K. E. Rapp, R. L. Pruett, C. T. Bahner, J. D. Gibson, and R. H. Lafferty, *J. Amer. Chem. Soc.*, 1950, **72**, 4480.

[6] R. A. Shepard, H. Lessoff, J. D. Domijan, D. B. Hilton, and T. F. Finnegan, *J. Org. Chem.*, 1958, **23**, 2011.

[7] C. O. Parker, *J. Amer. Chem. Soc.*, 1959, **81**, 2183.

[8] R. F. Stockel, M. T. Beachem, and F. M. Megson, *Canad. J. Chem.*, 1964, **42**, 2880.

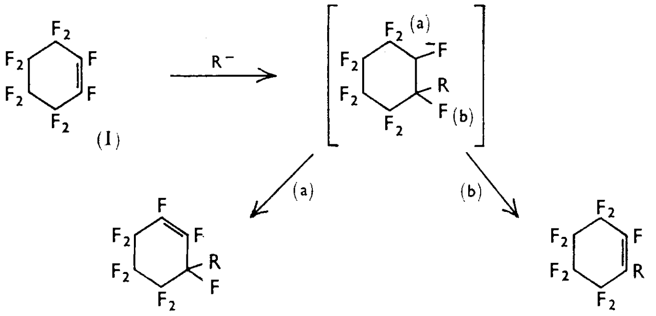
[9] E. T. McBee, D. L. Crain, R. D. Crain, L. R. Belohlav, and H. P. Braendlin, *J. Amer. Chem. Soc.*, 1962, **84**, 3557.

[10] J. D. Park, C. M. Snow, and J. R. Lacher, *J. Amer. Chem. Soc.*, 1951, **73**, 2342.

[11] J. D. Park, J. R. Dick, and J. R. Lacher, *J. Org. Chem.*, 1963, **23**, 1154.

olefins have usually given saturated ethers, *i.e.*, addition products, but in some cases[3] subsequent elimination to olefin ethers occurred. Cyclic olefins have given unsaturated ethers in all cases so far reported. Four different mechanisms have been suggested to explain the various products, *viz.*, direct vinylic substitution,[4] addition to the double bond followed by elimination,[5-9] allylic S_N2[10] and allylic S_N2'.[10,11] The evidence so far available favours the second process in the majority of cases and this is in agreement with analogous reactions of other nucleophils; *e.g.*, ammonia and aliphatic amines,[1,7,12] lithium aluminium hydride,[13] and methyl-lithium.[14] Additional evidence for the operation of this pathway has been obtained in the present work.

Decafluorocyclohexene (1 mol.) (I) reacted exothermically with methanol and potassium hydroxide (1 mol.) to give two main products (II, III) which were separated by preparative gas chromatography. In this and all the subsequent reactions small amounts of polysubstituted ethers were obtained but not examined. Indeed, under the gas chromatographic conditions employed they were not detected. The more shortly retained, minor product (II) was converted by potassium permanganate into a methoxyheptafluoroadipic acid which was characterised as its dianilinium and bis-(*S*-benzylthiuronium) salts.



(II) R = MeO⁻
(IV) R = $C_2H_5O^-$
(VI) R = $CF_3{\cdot}CH_2O^-$
(VIII) R = $(CH_3)_2CHO^-$
(X) R = $CF_2H{\cdot}CF_2{\cdot}CH_2O^-$

(III) R = MeO⁻
(V) R = $C_2H_5O^-$
(VII) R = $CF_3{\cdot}CH_2O^-$
(IX) R = $(CH_3)_2CHO^-$
(XI) R = $CF_2H{\cdot}CF_2CH_2O^-$

Chart 1. (a): loss of F(a) as F⁻; (b): loss of F(b) as F⁻.

Further, compound (II) was converted by concentrated sulphuric acid into the extremely hygroscopic conjugated octafluorocyclohex-1-en-3-one, showing it to be nonafluoro-3-methoxycyclohexene. Support for this structure was provided by infrared and fluorine-19[15] and proton nuclear magnetic resonance (n.m.r.) spectroscopy and by mass spectrometry.[16] The longer-retained major component (III) was converted by potassium permanganate into octafluoroadipic acid, showing it to be nonafluoro-1-methoxycyclohexene. Again, support for this structure was provided by infrared and fluorine-19[15] and proton n.m.r. spectroscopy and mass spectrometry[16] (these techniques were used throughout this work). The relationship of the ethers (II, III) was confirmed by the isomerisation of nonafluoro-3-methoxycyclohexene (II) into the more stable 1-methoxy-isomer (III), by potassium fluoride in dimethylformamide. The two ethers (II, III) are thought to arise from the two elimination pathways available to the carbanion intermediate depicted in Chart 1, *i.e.*, they arise in an addition–elimination sequence of the type

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[12] T. Mill, J. O. Rodin, R. M. Silverstein, and C. Woolf, *J. Org. Chem.*, 1963, **28**, 836.
[13] D. E. M. Evans, W. J. Feast, R. Stephens, and J. C. Tatlow, *J.*, 1963, 4828.
[14] D. R. Sayers, R. Stephens, and J. C. Tatlow, *J.*, 1964, 3035.
[15] L. F. Thomas, unpublished work.
[16] J. R. Majer, unpublished work.

followed in the reaction of decafluorocyclohexene with lithium aluminium hydride in diethyl ether,[13,17] with methyl-lithium,[14] and with dimethylamine.[18]

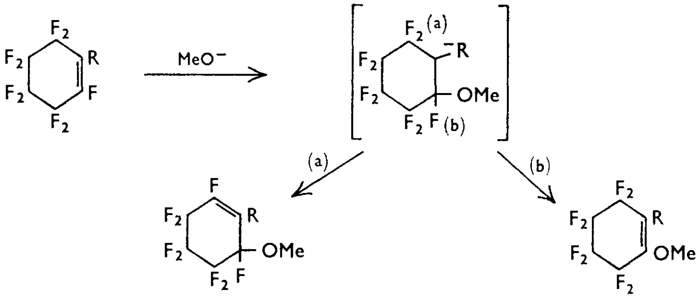
Analogous reactions occurred between decafluorocyclohexene and other alcohols. Thus, under similar conditions, ethanol, 2,2,2-trifluoroethanol, isopropyl alcohol and 2,2,3,3-tetrafluoropropan-1-ol gave the 1- and 3-alkoxy-nonafluorocyclohexenes (IV—IX) as set out in Table 1. These compounds were all fully characterised by oxidation,

TABLE 1

Reaction of alcohols with decafluorocyclohexene (1 mol.) in the presence of base (1 mol.)

Alcohol	3-Alkoxy-isomer as % of total mono-alkoxy-components	1-Alkoxy-isomer as % of total mono-alkoxy-components
Methanol	27·5 (II)	72·5 (III)
2,2,2-Trifluoroethanol	21 (VI)	79 (VII)
Ethanol	15 (IV)	85 (V)
Isopropyl alcohol	10·5 (VIII)	89·5 (IX)
2,2,3,3-Tetrafluoropropan-1-ol ...	31 (X)	69 (XI)

and infrared and fluorine-19[15], and proton n.m.r. spectroscopy and mass spectrometry.[16] Three derivatives of decafluorocyclohexene, *viz.*, 1*H*-, 1-methoxy-, and 1-methyl-nonafluorocyclohexene, were also treated with methanol in the presence of base. Again, the small amounts of polysubstitution products were ignored. In each case a substantial amount of the 6-methoxy-compound was obtained as well as the 1-methoxy-isomer, as depicted in Chart 2. Nonafluoro-1-methylcyclohexene did not react under the standard conditions, and it was necessary to use a refluxing solution of sodium methoxide in methanol to achieve the results described; this is ascribed to deactivation of the double bond by the electron-donating methyl group. The products of these reactions were fully characterised. All had infrared ^{19}F n.m.r. and proton n.m.r. spectra consistent with the proposed structures. Further, 1*H*-octafluoro-6-methoxycyclohexene (XII), the compound of shorter retention time on gas chromatography, was converted by potassium permanganate into heptafluoro-2-methoxy-adipic acid, whilst the isomeric 1*H*-octafluoro-2-methoxycyclohexene (XIII) gave octafluoroadipic acid.



(XII) R = H− (51·5%)
(XIV) R = Me− (46%)
(XVI) R = MeO− (62%)

(XIII) R = H− (48·5%)
(XV) R = Me− (54%)
(XVII) R = MeO− (38%)

Chart 2. (a): loss of F(a) as F−; (b): loss of F(b) as F−.

Octafluoro-6-methoxy-1-methylcyclohexene (XIV), likewise, was oxidised to heptafluoro-2-methoxyadipic acid; octafluoro-1-methoxy-2-methylcyclohexene (XV) giving octafluoroadipic acid. In addition, the first isomer (XIV) on pyrolysis over nickel gauze at 550° gave unchanged material (XIV), the 1,2-disubstituted system (XV) (confirming the vicinal nature of the substituents), and heptafluoro-1-methylcyclohex-1-en-6-one in roughly equal amounts. The latter ketone, arising by elimination of methyl fluoride

[17] E. Nield, R. Stephens, and J. C. Tatlow, *J.*, 1960, 3800.

[18] G. A. Powers, R. Stephens, and J. C. Tatlow, unpublished work.

(cf. α-chloroalkyl ethers[19]), was converted by potassium permanganate into hexafluoroglutaric acid, and displayed consistent ultraviolet infrared and mass spectra.[16] Unsuccessful attempts were made to prepare the 2,4-dinitrophenylhydrazine and semicarbazide derivatives. Pyrolysis of octafluoro-1-methoxy-2-methylcyclohexene (XV) over nickel gave the same ketone but none of the isomeric olefin (XIV), as expected. Octafluoro-1,6-dimethoxycyclohexene (XVI) was converted by potassium permanganate into heptafluoro-2-methoxyadipic acid. The 1,2-isomer (XVII) was oxidised to octafluoroadipic acid. Reaction of methanol–potassium hydroxide with nonafluoro-3-methoxycyclohexene afforded only the 1,6-dimethoxy-compound (XVI).

The reactions of octafluorocyclopentene (XVIII) and hexafluorocyclobutene (XIX) with methanol in the presence of base were also studied. With octafluorocyclopentene (XVIII) only 4% of the total monomethoxy-material was heptafluoro-3-methoxycyclopentene (XX), the rest was the 1-methoxy-isomer (XXI). This reaction has been described recently,[8] but the minor component (XX) was not reported. With hexafluorocyclobutene (XIX) only pentafluoro-1-methoxycyclobutene (XXII) was isolated; a second, trace component was believed to be the 3-methoxy-isomer (XXIII), but was not present in sufficient quantity to isolate. Oxidations of these products gave the expected acids (Table 2).

A reasonable explanation of all these observations can be based on an addition–elimination process if it is assumed that the addition step is *trans* and that the carbanion retains its configuration during its short life-time. Then, the stereochemistry of an anion formed from decafluorocyclohexene would favour an " outwards " elimination, that is loss of F from $>CF_2$, if the expected *trans*-coplanar elimination pathway is followed. However, this is electronically unfavourable, involving loss of fluorine from the more stable type of grouping. The more electronically-favourable " inwards " elimination (loss of F from $>C(F)OR$) would involve a *cis*-non-coplanar system.[13] The situations resemble those in the dehydrofluorinations of 1*H*/2*H*- and 1*H*,2*H*/-decafluorocyclohexane,[20] though the latter reactions are probably synchronous and do not involve free anionic intermediates. If all anionic additions to decafluorocyclohexene follow the same pathway, as seems likely, then the proportions of " inwards " and " outwards " elimination vary with the incoming group. Attack by methyl-lithium[14] and by dimethylamine[18] gives only 1-substituted products, and by lithium aluminium hydride[13] gives a ratio 1*H*- to 3*H*-nonafluorocyclohexene of 50 to 1. The true ratio may be rather lower, however, since the reaction is difficult to stop at this stage, and the 3*H*-olefin may undergo further attack more rapidly than its isomer. All the alkoxides used in the present work have given a higher proportion of the 3-substituted products (Table 1); this also may be falsified by a higher rate of reaction of the latter products with alkoxides. However, the general trend follows the electronic character of the group R (Chart 1), *i.e.*, the more the inductive electron-attracting power of R the less readily is the fluorine marked (b) lost and the higher the proportion of 3-substituted product arising from pathway (a).

In the reactions of methanol with perfluorocyclo-pentene and -butene, low proportions of 3-methoxy-products were isolated. It is known that stereochemical opposition to *cis*-coplanar eliminations is much less in fluorocyclo-pentanes[21] and -butanes[22] than in cyclohexanes (cf. the dehydrofluorinations of 1*H*/2*H*- and 1*H*,2*H*/-octafluorocyclopentane and of 1*H*/2*H*- and 1*H*,2*H*/-hexafluorocyclobutane). Thus, if similar effects apply for these anionic intermediates, the *cis*-coplanar elimination pathway would be available and less " outwards " elimination would be expected, as is found experimentally.

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[19] M. F. Shostakovskiĭ and A. V. Bogdanova, *Izvst. Akad. Nauk. S.S.S.R. Otdel. khim. Nauk.*, 1950, 321.

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

[21] C. H. DePuy, R. D. Thurn, and G. F. Morris, *J. Amer. Chem. Soc.*, 1962, **84**, 1314; R. J. Heitzman, C. R. Patrick, R. Stephens, and J. C. Tatlow, *J.*, 1963, 281; N. A. Le Bel, P. D. Beirne, E. R. Karger, J. C. Powers, and P. M. Subramanian, *J. Amer. Chem. Soc.*, 1963, **85**, 3199; R. Stephens and E. H. Wiseman, *J.*, 1963, 2083.

[22] G. Fuller and J. C. Tatlow, *J.*, 1961, 3198.

TABLE 2

Products of oxidation of fluoro-olefins

Olefin oxidised	Wt. of olefin oxidised	Acid produced	Yield as dianilinium salt (%)
Nonafluorocyclohexenes			
3-Methoxy	1·0 g.	Heptafluoro-2-methoxyadipic	79
1-Methoxy-	1·0 g.	Octafluoroadipic	63
3-Ethoxy-	0·6 g.	*2-Ethoxyheptafluoroadipic*	57
1-Ethoxy-	1·0 g.	Octafluoroadipic	61
3-(2′,2′,2′-Trifluoroethoxy)-	0·6 g.	*Heptafluoro-2-(2′,2′,2′-trifluoroethoxy)adipic*	60
1-(2′,2′,2′-Trifluoroethoxy)-	0·6 g.	Octafluoroadipic	72
3-Isopropoxy-	0·5 g.	*Heptafluoro-2-isopropoxyadipic*	56
1-Isopropoxy-	1·0 g.	Octafluoroadipic	73
3-(2′,2′,3′,3′-Tetrafluoro-n-propoxy)	1·0 g.	Heptafluoro-2-(2′,2′,3′,3′-tetrafluoro-n-propoxy)adipic	70
1-(2′,2′,3′,3′-Tetrafluoro-n-propoxy)	1·0 g.	Octafluoroadipic	76
Octafluorocyclohexenes			
1*H*-2-Methoxy	1·0 g.	Octafluoroadipic	53
1*H*-6-Methoxy-	1·0 g.	Heptafluoro-2-methoxyadipic	58
* 1,2-Dimethoxy-	0·5 g.	Octafluoroadipic	67
* 1,6-Dimethoxy-	0·5 g.	Heptafluoro-2-methoxyadipic	81
† 6-Methoxy-1-methyl-	0·9 g.	Heptafluoro-2-methoxyadipic	72
† 2-Methoxy-1-methyl-	0·2 g.	Octafluoroadipic	81
Heptafluorocyclopentenes			
3-Methoxy-	0·3 g.	*Pentafluoro-2-methoxyglutaric*	42·5
1-Methoxy-	2·0 g.	Hexafluoroglutaric	69
Others			
Pentafluoro-1-methoxycyclobut-1-ene	0·6 g.	Tetrafluorosuccinic	53
Octafluorocyclohex-1-en-3-one	0·6 g.	Hexafluoroglutaric	81
Heptafluoro-1-methylcyclohex-1-en-3-one	0·2 g.	Hexafluoroglutaric	42

* Refluxed for 1 hr. † Using aqueous potassium permanganate in a sealed tube at 100° for 1 hr.

Further additions to 1-substituted nonafluorocyclohexenes gave much more " outwards " elimination (Chart 2) than any reaction of decafluorocyclohexene itself studied so far. The same effect was noted when 1*H*-nonafluorocyclohexene was treated[13] with lithium aluminium hydride (25% " outwards " elimination). The reasons for this are uncertain at present.

The products obtained from these various reactions offer no support for either direct vinylic substitution or allylic S_N2 mechanisms. If the latter were operating, more isomers would be expected in some cases (Chart 2). Also, nonafluoro-3-methoxycyclohexene should give some octafluoro-3,3-dimethoxycyclohexene, whereas the 1,6-dimethoxyisomer was the only product isolated (cf. also 3*H*-nonafluorocyclohexene and lithium aluminium hydride[13]). Finally, it is not apparent why smaller proportions of 3-methoxy-products should arise in the cyclopentene and cyclobutene series.

It is much more difficult to rule out an S_N2' process, particularly since addition followed by " outward " elimination and the S_N2' routes can be considered as extreme forms of the same general process, the lifetime of the anion being the significant factor. This has been pointed out,[23] and it also appears that our cases are not particularly favourable ones for the generally accepted type of S_N2' transition state.[24] The possible operation of a carbene process by α-elimination from the intermediate carbanion, which is unlikely in these systems, has been ruled out (see following Paper). For the present, therefore,

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[23] W. T. Miller and A. H. Fainberg, *J. Amer. Chem. Soc.*, 1957, **79**, 4164.
[24] R. H. Dewolfe and W. G. Young, *Chem. Rev.*, 1956, **56**, 781.

since the addition–elimination route can explain all the products obtained quite well we see no need to invoke a simultaneous S_N2' process which can only give rise to some of them.

TABLE 3

Characterisation of salts from oxidation of fluoro-olefins

	Dianilinium salt					Di-(*S*-benzylthiuronium) salt				
		Found (%)		Reqd. (%)			Found (%)		Reqd. (%)	
	M. p.	C	H	C	H	M. p.	C	H	C	H
Heptafluoro-2-methoxyadipic acid	188°	47·1	4·0	46·7	3·9	194—195°	43·7	4·2	43·5	4·0
Octafluoroadipic acid	210—211	—	—	—	—	243—244	—	—	—	—
2-*Ethoxyheptafluoroadipic acid*	168—169	47·5	4·4	47·8	4·2	182—183	44·4	4·1	44·4	4·2
Heptafluoro-2-(2′,2′,2′-*trifluoroethoxy*)*adipic acid*	204	43·1	3·2	43·2	3·3	182	—	—	—	—
Heptafluoro-2-isopropoxyadipic acid	161—162	49·1	4·5	48·9	4·5	156	45·4	4·5	45·3	4·4
Pentafluoro-2-methoxyglutaric acid	170—171	—	—	—	—	166—167	45·5	4·7	45·2	4·3
Hexafluoroglutaric acid	220	—	—	—	—	189—190	—	—	—	—
Tetrafluorosuccinic acid	222—223	—	—	—	—	190	—	—	—	—
Heptafluoro-2-(2′,2′,3′,3′-*tetrafluoro-n-propoxy*)*adipic acid*	204—205	42·6	3·2	42·8	3·2	145—147	41·0	3·5	40·8	3·4

EXPERIMENTAL

Techniques.—Analytical gas chromatography was carried out in glass columns (2 m. long × 4 mm. diameter) packed with dinonyl phthalate–kieselguhr (1 : 2) and run at 100° with a nitrogen flow-rate of *ca.* 1 l./hr. In preparative scale work a copper column (4·88 m. long × 75 mm. diameter) was used packed with dinonyl phthalate–kieselguhr (1 : 2) and run at 100° with a nitrogen flow-rate of *ca.* 60 l./hr. Fluorine-19 nuclear magnetic resonance (n.m.r.) spectra were measured [15] on a Mullard S.L.44 Mk. 1 instrument at 30·107Mc./sec. and the figures quoted are fluorine chemical shifts and are in p.p.m. from trifluoroacetic acid as external reference. Proton n.m.r. spectra were measured with a Varian instrument at 60 Mc./sec., and the figures quoted are chemical shifts in p.p.m. from tetramethylsilane as external reference. Mass spectra were measured on a Metropolitan Vickers M.S.2 instrument.[16]

General Procedure used in the Reaction of an Alcohol with a Polyfluorocycloalkene.—The dry alcohol (1·1 mol.) was added dropwise to a stirred mixture of the olefin (1·0 mol.) and potassium hydroxide pellets (1·0 mol.) at room temperature; heat was evolved and potassium fluoride precipitated. After the addition was completed stirring was continued for a further 1 hr. at room temperature, excess of water was then added, the lower layer separated, washed with water, and dried (Na_2SO_4).

Reaction of Methanol with Decafluorocyclohexene.—This olefin (91 g.) gave a liquid product (89·1 g.) under the standard conditions. Analytical gas chromatography showed three components which were separated on a preparative scale to give: (i) decafluorocyclohexene (16·0 g.) with a correct infrared spectrum; (ii) *nonafluoro-3-methoxycyclohexene* (14·6 g.), b. p. 105—106° (Found: C, 30·6; H, 1·2. $C_7H_3F_9O$ requires C, 30·7; H, 1·1%); $\nu_{max.}$ 2,960 ($\geqslant$C–H) and 1742 cm.$^{-1}$ (–CF=CF–); the fluorine-19 n.m.r. spectrum [15] had a total intensity ratio of 9, with a doublet (intensity ratio 3) at 42·3 (fluorine atoms at C_3 and C_6), a single peak (intensity ratio 2) at 52·4 (fluorine atoms at C-4), a doublet (intensity ratio 2) at 55·7 (fluorine atoms at C-5) and two single peaks (each of intensity ratio 1) at 69 and 82 (fluorines at C-1 and C-2); the proton n.m.r. spectrum consisted of a single, broad band at 3·4; mass spectrometry gave a top mass peak of 274 ($C_7H_3F_9O$) and a consistent fragmentation pattern; [16] (iii) *nonafluoro-1-methoxycyclohexene* (34·5 g.), b. p. 110—111° (Found: C, 30·7; H, 1·0%); $\nu_{max.}$ 2960 ($\geqslant$C–H) and 1705 cm.$^{-1}$ [–CF=C(OCH_3)–]; the fluorine-19 n.m.r. spectrum [15] had a total intensity ratio of 9 and consisted of a doublet (intensity ratio 4) at 40 (fluorine atoms at C-3 and C-6), a single band (intensity ratio 4) at 57·2 (fluorine atoms at C-4 and C-5) and a single band (intensity ratio 1) at 84 (fluorine atom at C-2); the proton n.m.r. spectrum consisted of a doublet (J_{HF} = 4 c.p.s.) centred at 3·8; mass spectrometry gave a top mass peak at 274 ($C_7H_3F_9O$) and a consistent fragmentation pattern.[16]

Demethylation of Nonafluoro-3-methoxycyclohexene.—This compound (5·0 g.) and concentrated sulphuric acid (20 c.c.) were refluxed fo 30 min. Then the dark homogeneous solution was distilled to give *octafluorocyclohex*-1-*en*-3-*one* (3·2 g.), b. p. 160°, $\lambda_{max.}$ 3000 Å (ε 16·8 × 10^3) (in ethanol). When this compound was exposed to the atmosphere colourless crystals of a hydrate quickly formed which was dried (P_2O_5) *in vacuo* at room temperature to give the *trihydrate* (3·8 g.), m. p. 79—80° (Found: C, 24·6; H, 2·3. $C_6F_8O,3H_2O$ requires C, 24·5; H, 2·0%), $\nu_{max.}$ 3450 ("bound" water), 1730 (–CF=CF–), and 1640 cm.$^{-1}$ ($>$C=O and/or "bound" water), $\lambda_{max.}$ 3000 Å (ε 2·67 × 10^3) (in ethanol).

Isomerisation of Nonafluoro-3-methoxycyclohexene.—This compound (1·0 g.), potassium fluoride (0·5 g.), and dimethylformamide (2 c.c.) were refluxed for 4 hr. After cooling, excess of water was added and the lower layer separated, washed with water, and dried ($MgSO_4$). The liquid product (0·7 g.) was shown by analytical gas chromatography to contain starting material and nonafluoro-1-methoxycyclohexene in the ratio of 4 : 1.

Reaction of Ethanol with Decafluorocyclohexene.—This olefin (25·0 g.) in the usual way gave a liquid product (29·7 g.) which was shown by analytical gas chromatography to contain three components which were separated on a preparative scale to give: (i) decafluorocyclohexene (14·5 g.) with a correct infrared spectrum; (ii) 3-*ethoxynonafluorocyclohexene* (2·0 g.), b. p. 109—110° (Found: C, 33·4; H, 1·7. $C_8H_5F_9O$ requires C, 33·4; H, 1·7%); $\nu_{max.}$ 2990 ($\geq$C–H) and 1735 cm.$^{-1}$ (–CF=CF–); the fluorine-19 n.m.r. spectrum[15] had a total intensity ratio of 9 and was similar to that of nonafluoro-3-methoxycyclohexene; the proton n.m.r. spectrum consisted of a triplet (J = 7 c.p.s.) centred at 1·1 and a quartet (J = 7 c.p.s.) centred at 3·9 in the intensity ratio 3 : 2; mass spectrometry gave a top mass peak of 288 ($C_8H_5F_9O$) and a consistent fragmentation pattern;[16] (iii) 1-*ethoxynonafluorocyclohexene* (11·4 g.), b. p. 108—109° (Found: C, 33·6; H, 1·6%); $\nu_{max.}$ 2990 ($\geq$C–H) and 1704 cm.$^{-1}$ [–CF=C(OC_2H_5)]; the fluorine-19 n.m.r. spectrum[15] had a total intensity ratio of 9 and was similar to that of nonafluoro-1-methoxycyclohexene; the proton n.m.r. spectrum consisted of a triplet of doublets (J = 7 c.p.s. and $J \sim$ 0·5 c.p.s.) centred at 1·1 (intensity ratio 3) and a quartet of doublets (J = 7 c.p.s. and J = 2·5 c.p.s.) centred at 4·1 (intensity ratio 2); mass spectrometry gave a top mass peak of 288 ($C_8H_5F_9O$) and a consistent fragmentation pattern.[16]

Reaction of 2,2,2-*Trifluoroethanol with Decafluorocyclohexene.*—In the usual way decafluorocyclohexene (25·0 g.) gave a liquid product (28·0 g.) which was shown by gas chromatography to contain three components which were separated by this technique to give: (i) decafluorocyclohexene (2·4 g.) with a correct infrared spectrum; (ii) *nonafluoro*-3-(2′,2′,2′-*trifluoroethoxy*)-*cyclohexene* (3·4 g.), b. p. 114—115° (Found: C, 28·2; H, 0·7. $C_8H_2F_{12}O$ requires C, 28·1; H, 0·6%); $\nu_{max.}$ 1740 cm.$^{-1}$ (–CF=CF–); the fluorine-19 n.m.r. spectrum[15] had a total intensity ratio of 12 with a band (intensity ratio 3) at −1·1 (–CF_3), a band (intensity ratio 2) at 41·2 (fluorine atoms at C-6), a band (intensity ratio 3) at 52·5 (fluorine atoms at C-3 and C-4), a band (intensity ratio 2) at 55·1 (fluorine atoms at C-5), a band (intensity ratio 1) at 73·4 (fluorine atom at C-2) and a band (intensity ratio 1) at 80·4 (fluorine atom at C-1); mass spectrometry gave a top mass peak of 342 ($C_8H_2F_{12}O$) and a consistent fragmentation pattern;[16] (iii) *nonafluoro*-1-(2′,2′,2′-*trifluoroethoxy*)*cyclohexene* (12·2 g.), b. p. 108—109° (Found: C, 28·0; H, 0·5%); $\nu_{max.}$ 1725 cm.$^{-1}$ [–CF=C(OCH_2CF_3)–]; the fluorine-19 n.m.r. spectrum[15] had a total intensity ratio of 12 with a band (of intensity ratio 3) at −8·3 (–CF_3), three signals (intensity ratios 2, 1, and 1) centred at 40 (fluorine atoms at C-3 and C-6), a band (intensity ratio 4) at 55 (fluorine atoms at C-4 and C-5), and a band (intensity ratio 1) at 79 (fluorine atom at C-2); mass spectrometry gave a top mass peak of 342 ($C_8H_2F_{12}O$) and a consistent fragmentation pattern.[16]

Reaction of Isopropyl Alcohol with Decafluorocyclohexene.—In the usual way this olefin (34·0 g.) gave a liquid product (25·7 g.) which was separated by gas chromatography to give: (i) decafluorocyclohexene (4·3 g.) with a correct infrared spectrum; (ii) *nonafluoro*-3-*isopropoxycyclohexene* (1·0 g.), b. p. 104—105° (Found: C, 36·0; H, 2·2. $C_9H_7F_9O$ requires C, 35·8; H, 2·3%); $\nu_{max.}$ 3000 ($\geq$C–H) and 1740 cm.$^{-1}$ (–CF=CF–); the proton n.m.r. spectrum consisted of a doublet of doublets (J = 6 c.p.s. and 1 c.p.s.) centred at 1·0 (intensity ratio 6) and a septet (J = 6 c.p.s.) centred at 4·3 (intensity ratio 1); (iii) *nonafluoro*-1-*isopropoxycyclohexene* (7·4 g.), b. p. 118—119° (Found: C, 36·1; H, 2·3%); $\nu_{max.}$ 3000 ($\geq$C–H) and 1700 cm.$^{-1}$ [–CF=C(OC_3H_7)–]; the proton n.m.r. spectrum consisted of a doublet of doublets (J = 6 c.p.s. and 1 c.p.s.) centred at 1·0 (intensity ratio 6) and a septet of doublets (J = 6 and 1·5 c.p.s.) centred at 4·5 (intensity ratio 1).

Reaction of 2,2,3,3-*Tetrafluoropropan*-1-*ol with Decafluorocyclohexene.*—In the usual way decafluorocyclohexene (20·0 g.) gave a liquid product (25 g.) which was separated by gas chromatography to give: (i) decafluorocyclohexene (2·5 g.) with a correct infrared spectrum; (ii) *nonafluoro*-3-(2′2′3′3′-*tetrafluoro*-n-*propoxy*)*cyclohexene* (2·4 g.), b. p. 139° (Found: C, 29·2; H, 1·0. $C_9H_3F_{13}O$ requires C, 28·9; H, 0·8%); $\nu_{max.}$ 2960 ($\geq$C–H) and 1742 cm.$^{-1}$ (–CF=CF–); the fluorine-19 n.m.r. spectrum[15] had a total intensity ratio of 13, with a band (intensity ratio 2) at 41 (fluorine atoms at C-6), a triplet (intensity ratio 2; J_{HF} = 15 c.p.s.) centred at 48 (–CH_2–CF_2–), a band (intensity ratio 3) at 52 (fluorine atoms at C-3 and C-4), a band (intensity ratio 2) at 56, (fluorine atoms at C-5), a doublet (intensity ratio 2; J_{HF} = 50 c.p.s.) centred at 61·5 (–CF_2H), a band (intensity ratio 1) at 71 (fluorine atom at C-2) and a band (intensity ratio 1) at 78 (fluorine atom at C-1); the proton n.m.r. spectrum consisted of a triplet (J_{HF} = 12·5 c.p.s.) centred at 4·0 (–CH_2CF_2–) and a triplet of triplets ($J_{HF\,gem.}$ = 50 c.p.s., $J_{HF\,vic.}$ = 4 c.p.s.) centred at 5·4 (–CF_2CF_2H); (iii) *nonafluoro*-1-(2′2′3′3′-*tetrafluoro*-n-*propoxy*)*cyclohexene* (5·5 g.), b. p. 142° (Found: C, 28·6; H, 0·9%); $\nu_{max.}$ 2960 ($\geq$C–H) and 1705 cm.$^{-1}$ [–CF=C($OC_3H_3F_4$)–]; the fluorine-19 n.m.r. spectrum [15] had a total intensity ratio of 13, with a split band (intensity ratio 4) at 40 (fluorine atoms at C-3 and C-6), a triplet (intensity ratio 2; J_{HF} = 13·5 c.p.s.) centred at 49 (–CH_2·CF_2–), a band (intensity ratio 4) at 57 (fluorine atoms at C-4 and C-5), a doublet (intensity ratio 2; J_{HF} = 63 c.p.s.) centred at 62·5 (–CF_2H) and a band (intensity ratio 1) at 77 (fluorine atom at C-2); the proton n.m.r. spectrum consisted of a triplet (J_{HF} = 10 c.p.s.) centred at 4·2 (–CH_2·CF_2–) and a triplet of triplets ($J_{HF\,gem.}$ = 50 c.p.s., $J_{HF\,vic.}$ = 4 c.p.s.) at 5·45 (–CF_2·CF_2H).

Reaction of Methanol with 1H-*Nonafluorocyclohexene*.—In the usual way 1*H*-nonafluorocyclohexene [13] (23·0 g.) gave a liquid product (24·0 g.) which was separated by gas chromatography to give: (i) 1*H*-nonafluorocyclohexene (4·0 g.) with a correct infrared spectrum; (ii) 1H-*octafluoro*-6-*methoxycyclohexene* (8·5 g.), b. p. 110° (Found: C, 32·6; H, 1·7. $C_7H_4F_8O$ requires C, 32·8; H, 1·6%); $\nu_{max.}$ 1717 cm.$^{-1}$ (–CF=CH–); the proton n.m.r. spectrum consisted of a broad singlet at 3·4 (intensity ratio 3) and a multiplet centred at 5·7 (intensity ratio 1); (iii) 1H-*octafluoro*-2-*methoxycyclohexene* (8·0 g.), b. p. 143° (Found: C, 32·8; H, 1·6%); $\nu_{max.}$ 1675 cm.$^{-1}$ [–CH=C(OCH_3)–]; the proton n.m.r. spectrum consisted of a broad singlet at 3·5 (intensity ratio 3) and a multiplet centred at 5·0 (intensity ratio 1).

Reaction of Methanol with Nonafluoro-1-*methylcyclohexene*.—The olefin [14] (81·0 g.) in methanol (150 c.c.) was added to a solution of sodium (7·5 g.) in methanol (150 c.c.) at room temperature. The mixture was homogeneous and a slight increase in temperature was noted. After refluxing the solution for 6 hr., water (1 l.) was added and the lower layer separated and dried ($MgSO_4$). Analytical gas chromatography indicated three components. Unchanged starting material (35 g.) b. p. 89·5—90° was removed by fractional distillation and the residue was separated by gas chromatography to give: (i) nonafluoro-1-methylcyclohexene (10·8 g.) with a correct infrared spectrum; (ii) *octafluoro*-6-*methoxy*-1-*methylcyclohexene* (15·0 g.), b. p. 134°, n_D^{23} 1·3532 (Found: C, 35·7; H, 2·3. $C_8H_6F_8O$ requires C, 35·6; H, 2·2%); $\nu_{max.}$ 3025, 2980, and 2860 ($\geq$C–H) and 1720 cm.$^{-1}$ [–CF=C·(CH_3)–]; the proton n.m.r. spectrum consisted of a complex multiplet centred at 1·8 (intensity ratio 1) and a complex multiplet centred at 3·6 (intensity ratio 1); (iii) *octafluoro*-1-*methoxy*-2-*methylcyclohexene* (17·5 g.), b. p. 138°, n_D^{23} 1·3532 (Found: C, 35·6; H, 2·3%); $\nu_{max.}$ 3020, 2965, and 2860 ($\geq$C–H) and 1685 cm.$^{-1}$ [–C(CH_3)=C(OCH_3)–]; the proton n.m.r. spectrum consisted of a triplet (J_{HF} = 1·5 c.p.s.) centred at 1·7 (intensity ratio 1) and a triplet (J_{HF} = 0·5 c.p.s.) centred at 3·6 (intensity ratio 1).

Pyrolytic Isomerisation of Octafluoro-6-*methoxy*-1-*methylcyclohexene*.—This olefin (3·0 g.) was passed in a stream of nitrogen (1 l./hr.) over nickel gauze contained in a nickel cylinder at 550°. The liquid product (1·3 g.) was shown by gas chromatography to contain three components which were separated by this technique to give: (i) *heptafluoro*-1-*methylcyclohex*-1-*en*-6-*one* (0·31 g.), b. p. 110°, n_D^{21} 1·3563 (Found: C, 35·6; H, 1·5. $C_7H_3F_7O$ requires C, 35·6; H, 1·3%); $\nu_{max.}$ 1745 ($>$C=O) and 1687 cm.$^{-1}$ [–CF=C(CH_3)–], $\lambda_{max.}$ 2655 and 2985 Å (ε 8·5 × 10^3 and 9·2 × 10^3, respectively; in ethanol); mass spectrometry revealed a total mass peak of 236 ($C_7H_3F_7O$); oxidation gave hexafluoroglutaric acid (42%); (ii) octafluoro-6-methoxy-1-methylcyclohexene (0·35 g.), with a correct infrared spectrum; (iii) octafluoro-1-methoxy-2-methylcyclohexene (0·4 g.) with a correct infrared spectrum.

Pyrolysis of Octafluoro-1-*methoxy*-2-*methylcyclohexene*.—This olefin (3·0 g.) was treated in exactly the manner described previously and in the same way gave: (i) *heptafluoro*-1-*methylcyclohex*-1-*en*-6-*one* (0·53 g.) and (ii) octafluoro-1-methoxy-2-methylcyclohexene (0·1 g.); both had correct infrared spectra.

*Reaction of Methanol with Nonafluoro-*1*-methoxycyclohexene*.—Dry methanol (5 c.c.), this olefin (15 g.), and potassium hydroxide (3·5 g.) gave, in the usual way, a liquid product (15·0 g.) which was shown by analytical gas chromatography (90 mm. column of silicone gum–kieselguhr (1 : 2), 100°, N_2 flow-rate 0·3 l./hr.) to contain two components which were separated on a preparative scale (silicone gum–kieselguhr; 80°, N_2 flow-rate, 60 l./hr.) to give: (i) *octafluoro-*1,2*-dimethoxycyclohexene* (4·0 g.), b. p. 145° (Found: C, 33·6; H, 2·0. $C_8H_6F_8O_2$ requires C, 33·6; H, 2·1%); $\nu_{max.}$ 2980 ($\geq$C–H) and 1675 cm.$^{-1}$ [–C(OCH_3)=C(OCH_3)–]; the fluorine-19 n.m.r. spectrum[15] had a total intensity ratio of 8 and consisted of two bands of equal intensity at 36·9 (fluorine atoms at C-4 and C-5) and 56·2 (fluorine atoms at C-3 and C-6); the proton n.m.r. spectrum consisted of a broad singlet at 3·65; (ii) *octafluoro-*1,6*-dimethoxycyclohexene* (6·5 g.), b. p. 155° (Found: C, 33·8; H, 2·3%); $\nu_{max.}$ 2980 ($\geq$C–H) and 1700 cm.$^{-1}$ [–CF=C(OCH_3)–]; the fluorine-19 n.m.r. spectrum[15] had a total intensity ratio of 8 with a doublet (intensity ratio 2) at 39 (fluorine atoms at C-4), a band (intensity ratio 5) at 55 (fluorine atoms at C-3, C-5, and C-6) and a band (intensity ratio 1) at 88 (fluorine atom at C-2); the proton n.m.r. spectrum consisted of a broad singlet at 3·45 [$>$CF(OCH_3)] and a doublet (J_{HF} = 4 c.p.s.) centred at 3·8 [–CF=C(OCH_3)–].

*Reaction of Methanol with Nonafluoro-*3*-methoxycyclohexene*.—Dry methanol (7 c.c.), nonafluoro-3-methoxycyclohexene (20 g.), and potassium hydroxide (4·5 g.) in the usual way gave a liquid product (20·0 g.) which was separated by gas chromatography (silicone gum–kieselguhr; 90°; N_2 flow-rate 6 l./hr.) to give *octafluoro-*1,6*-dimethoxycyclohexene* (13·0 g.), b. p. 154° with a correct infrared spectrum.

Reaction of Methanol with Octafluorocyclopentene.—In the usual way octafluorocyclopentene (33·3 g.) gave a liquid product (32·4 g.) which was separated by gas chromatography to give: (i) octafluorocyclopentene (4·0 g.) with a correct infrared spectrum; (ii) *heptafluoro-*3*-methoxycyclopentene* (0·8 g.), b. p. 80° (Found: C, 32·2; H, 1·5. $C_6H_3F_7O$ requires C, 32·2; H, 1·3%); $\nu_{max.}$ 2960 ($\geq$C–H) and 1765 cm.$^{-1}$ (–CF=CF–); the fluorine-19 n.m.r. spectrum[15] had a total intensity ratio of 7, with bands at 42 and 45 (both of intensity ratio 1; probably part of an A–B quadruplet from the fluorine atoms at C-5), a band (intensity ratio 1) at 51 (fluorine atom at C-3), a band (of intensity ratio 2) at 53 (collapsed signal from fluorine atoms at C-4), bands at 74 and 84 (each of intensity ratio 1; fluorine atoms at C-2 and C-1, respectively); the proton n.m.r. spectrum consisted of a broad singlet centred at 3·3; mass spectrometry gave a top mass peak at 224 ($C_6H_3F_7O$) and a consistent fragmentation pattern;[16] (iii) *heptafluoro-*1*-methoxycyclopentene* (22 g.), b. p. 103—104° (Found: C, 32·5; H, 1·6%); $\nu_{max.}$ 2960 ($\geq$C–H) and 1728 cm.$^{-1}$ [–CF=C(OCH_3)–]; the fluorine-19 n.m.r. spectrum[15] had a total intensity ratio of 7, with bands at 43 and 44 (each of intensity ratio 2; fluorine atoms at C-3 and C-5), a band at 58 (intensity ratio 2; fluorine atoms at C-4) and a band at 92·6 (intensity ratio 1; fluorine atoms at C-2); the proton n.m.r. spectrum consisted of a doublet (J_{HF} = 3·5 c.p.s.) centred at 3·8; mass spectrometry gave a top mass peak of 224 ($C_6H_3F_7O$) and a consistent pattern.[16]

Reaction of Methanol with Hexafluorocyclobutene.—In the usual way, but at 4°, hexafluorocyclobutene (39·0 g.) gave a liquid product (36·5 g.) which was shown by analytical gas chromatography to contain one main component and one in trace amount. The former was separated by gas chromatography to give: (i) Hexafluorocyclobutene (12·0 g.) with a correct infrared spectrum; (ii) pentafluoro-1-methoxycyclobutene (14·7 g.), b. p. 89° (lit.,[4] 87°) (Found: C, 34·5; H, 1·8. Calc. for $C_5H_3F_9O$: C, 34·5; H, 1·7%); $\nu_{max.}$ 2960 ($\geq$C–H) and 1765 cm.$^{-1}$ [–CF=C(OCH_3)–]; the fluorine-19 n.m.r. spectrum[15] had a total intensity ratio of 5, with two bands at 38 and 41 (each of intensity ratio 2; fluorine atoms at C-3 and C-4) and a band at 65 (intensity ratio 1; fluorine atom at C-2); the proton n.m.r. spectrum consisted of a doublet (J_{HF} = 1·2 c.p.s.) centred at 3·6; mass spectrometry gave a top mass peak of 174 ($C_5H_3F_5O$) and a consistent fragmentation pattern.[16]

General Procedure used in Olefin Characterisations by Potassium Permanganate Oxidation.—The olefin (1 mol.) was added to a mixture of potassium permanganate (4 mol.) in dry ($MgSO_4$) acetone (200 c.c. per g. of olefin) and the mixture shaken mechanically for ½ hr. An exothermic reaction usually occurred with the formation of a brown precipitate of manganese dioxide. Water (200 c.c. per g. of olefin) was added, the mixture shaken for ½ hr., excess of sodium hydrogen carbonate added and the acetone removed at a reduced pressure. The remaining aqueous suspension was acidified with 2N-sulphuric acid, decolourised with sodium metabisulphite, and extracted with ether continuously for 18 hr. The dried ($MgSO_4$), filtered, ether extract was evaporated to leave the acid as a partly crystalline solid which was dissolved in dry ether (25 c.c. per g.) and a slight excess of redistilled aniline added dropwise until precipitation of the crude dianilium salt was complete. One half of the latter was recrystallised from acetone–chloroform and the other half was converted into the bis-*S*-benzylthiuronium salt by mixing aqueous solutions of the aniline salt and *S*-benzylthiuronium chloride, followed by two recrystallisations of the precipitate from water.

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CHEMISTRY DEPARTMENT, THE UNIVERSITY,
EDGBASTON, BIRMINGHAM 15.

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