584. *Polyfluorocycloalkenes. Part I.* 1-*Methylnonafluorocyclohexene,* 1,2-*Dimethyloctafluorocyclohexene, and Derived Compounds.*

By D. R. Sayers, R. Stephens, and J. C. Tatlow.

Decafluorocyclohexene gave, with methyl-lithium in ether, 1-methylnonafluorocyclohexene and 1,2-dimethyloctafluorocyclohexene, both of which have been fully characterised. The former has been converted by mild oxidation into 2,2,3,3,4,4,5,5-octafluoro-6-oxoheptanoic acid and, by dehydrofluorination, into 3-methyleneoctafluorocyclohex-1-ene, which readily polymerised. 1,2-Dimethyloctafluorocyclohexene reacted with chlorine to give 1,2-dichloro-1,2-dimethyloctafluorocyclohexane and 1-chloromethyl-2-methyloctafluorocyclohex-1-ene, and the latter was dehydrochlorinated to 1,2-dimethyleneoctafluorocyclohexane, which polymerised.

Cyclic fluoro-olefins have been treated with a variety of nucleophiles,[1-4] of which organolithium compounds are among the most reactive.[2] Thus, it is known that methyl-lithium and hexafluorocyclobutene at −78°, interact, apparently by an addition–elimination process, to give [2] 1-methylpentafluoro- and 1,2-dimethyltetrafluoro-cyclobutene, though in fact no rigid proof of structure was provided. We studied the reaction of methyl-lithium with decafluorocyclohexene (I) in ether, and obtained 1-methylnonafluorocyclohexene (II) and 1,2-dimethyloctafluorocyclohexene (III) as the major products, the proportions depending on the ratio of the reactants. Their formation is in agreement with an addition–elimination process (of the type depicted) analogous to that involving lithium aluminium hydride and decafluorocyclohexene in ether.[5]

Use of approximately equimolar amounts of methyl-lithium and decafluorocyclohexene gave a methylnonafluorocyclohexene almost exclusively. This was oxidised by an excess of potassium permanganate in refluxing acetone to octafluoroadipic acid, showing it to be 1-methylnonafluorocyclohexene (II). Several pieces of evidence supported this structural allocation. Thus, permanganate oxidation at room temperature gave a mixture of acids from which octafluoroadipic acid was removed as its ether-insoluble dianilinium salt, to leave 2,2,3,3,4,4,5,5-octafluoro-6-oxoheptanoic acid (V). The formation of this acid would be expected from the mechanism advanced for the permanganate oxidation of fluoro-olefins in acetone.[6] The extremely hygroscopic keto-acid could not be purified but was fully characterised as its *S*-benzylthiouronium salt, methyl ester, and amide. The presence of a ketonic carbonyl group in the methyl ester was demonstrated by the preparation of a 2,4-dinitrophenylhydrazone and by its haloform cleavage with alkali to give the known [7] 5*H*-octafluorovaleric acid (VI). Pyrolytic defluorination [8] of 1-methylnonafluorocyclohexene gave 2,3,4,5,6-pentafluorotoluene (VII) and a trace of pentafluorobenzene, presumably a result of some cleavage [9] of the methyl group. Finally, the mass spectrum [10] and the spectroscopic properties [infrared (i.r.), ^{19}F nuclear magnetic resonance (n.m.r.),[11] and ^{1}H n.m.r.] were entirely consistent with the proposed structure.

A longer-retained component of the original reaction mixture was identified as 3-methyleneoctafluorocyclohexene (VIII) which was also prepared by an alternative procedure. This diene might be formed either by dehydrofluorination of 3-methylnonafluorocyclohexene (IV) with methyl-lithium or by 1,4-dehydrofluorination of the 1-methyl isomer (II)

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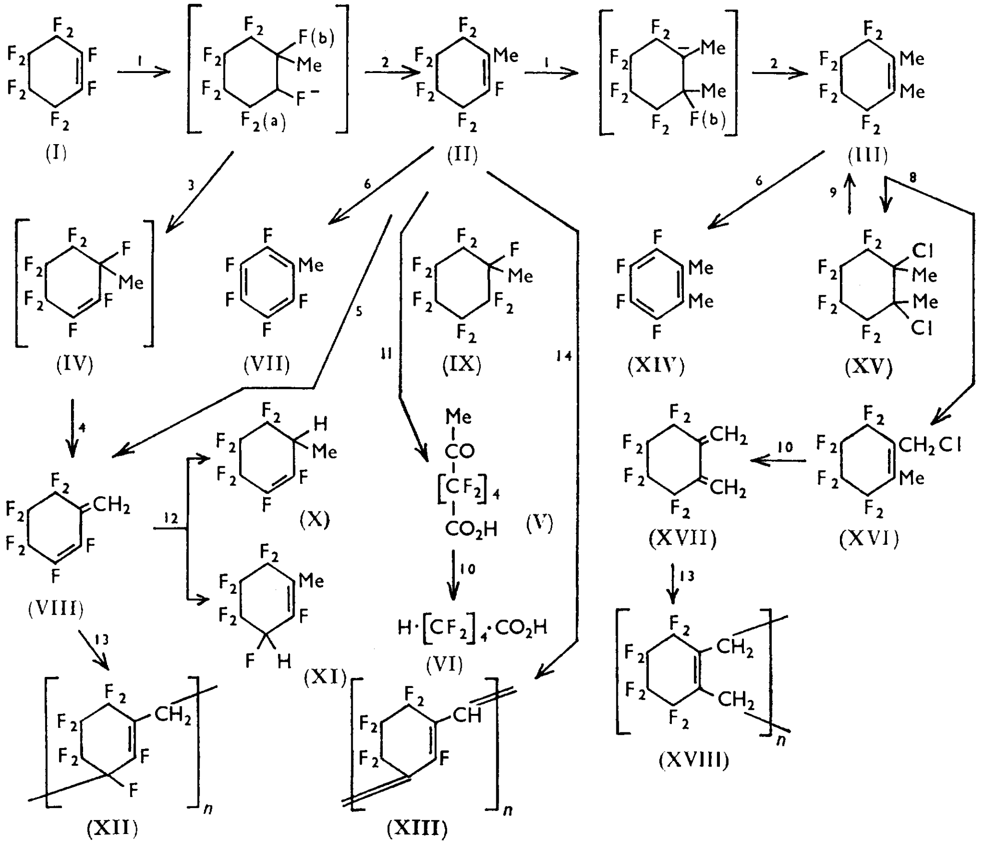
[1] Tarrant and Warner, *J. Amer. Chem. Soc.*, 1954, **76**, 1624.
[2] Dixon, *J. Org. Chem.*, 1956, **21**, 400.
[3] Parker, *J. Amer. Chem. Soc.*, 1959, **81**, 2183.
[4] Rapp, Pruett, Barr, Bahner, Gibson, and Lafferty, *J. Amer. Chem. Soc.*, 1950, **72**, 3646, 4480.
[5] Evans, Feast, Stephens, and Tatlow, *J.*, 1963, 4828.
[6] Burdon and Tatlow, *J. Appl. Chem.*, 1958, **8**, 293.
[7] Sheppard and Muetterties, *J. Org. Chem.*, 1960, **25**, 180.
[8] Coe, Patrick, and Tatlow, *Tetrahedron*, 1960, **9**, 240.
[9] Patrick, Pedler, Seabra, Stephens, and Tatlow, *Chem. and Ind.*, 1963, 1557.
[10] Majer, personal communication.
[11] Thomas and Wyer, unpublished work.

(methyl-lithium is known[12] to dehydrofluorinate undecafluorocyclohexane in ether). 3-Methylnonafluorocyclohexene itself was not isolated but would be expected from the alternative " outwards " elimination of fluoride ion from a methyl-lithium–decafluorocyclohexene adduct; its presence was also indicated by the evolution of a little hydrogen fluoride during the distillation. It should be a very minor product since the methyl group will electronically facilitate the " inwards " loss of the tertiary fluorine atom; an effect paralleled in the lithium aluminium hydride reduction of decafluorocyclohexene.[5]

As expected, 1-methylnonafluorocyclohexene displayed a marked decrease in susceptibility to nucleophilic attack. Thus, there was no reaction with ammonia under conditions that rapidly convert decafluorocyclohexene into 1-amino-2,4,4,5,5,6,6-heptafluoro-3-iminocyclohexene[13] in high yield. Some electron deficiency in the double bond, however, was established by further reaction with methyl-lithium to give 1,2-dimethyloctafluorocyclohexene (III). Compatible with this feature of the double-bond character was the failure of 1-methylnonafluorocyclohexene to be epoxidised with trifluoroperacetic acid[14] or to be hydroxylated with hydrogen peroxide in t-butyl alcohol containing catalytic amounts of osmium tetroxide. However, addition of chlorine occurred readily, to give



Reagents: 1, LiMe; 2, loss of F(b) as F^-; 3, loss of F(a) as F^-; 4, loss of HF; 5, NaF; 6, Fe gauze; 7, CoF_3; 8, Cl_2; 9, Zn–EtOH; 10, KOH aq.; 11, $KMnO_4$ in acetone; 12, H_2–Pd; 13, azobisisobutyronitrile; 14, KF in dimethylformamide.

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[12] Smith, Ph.D. Thesis, Birmingham, 1956.

[13] Robson, Roylance, Stephens, and Tatlow, unpublished work.

[14] Emmons and Pagano, *J. Amer. Chem. Soc.*, 1955, **77**, 89.

a crystalline 1,2-dichloro-1-methylnonafluorocyclohexane of unknown stereochemistry. Dechlorination to the original olefin occurred on treatment with zinc dust in ethanol, but there was no reaction with concentrated aqueous potassium hydroxide at 100°. Cobaltic fluoride in the vapour phase at low temperatures gave the waxy methylundecafluorocyclohexane (IX) as the major product, accompanied by a small amount of perfluoromethylcyclohexane; there was no evidence, under these conditions, for partial fluorination of the methyl group. Methylundecafluorocyclohexane was clearly characterised by ^{19}F and ^{1}H n.m.r. spectroscopy;[11] the spectra gave no indication of CH_2F or CHF_2 groups. Attempts to dehydrofluorinate this compound by refluxing with potassium hydroxide in water, liquid paraffin, or sulpholan gave unchanged starting material (100, 100, and 76%, respectively); likewise, passage in nitrogen (1·2 l./hr.) over sodium fluoride at 460° gave only starting material (83%).

However, 1-methylnonafluorocyclohexene (II) was dehydrofluorinated when passed over sodium fluoride, to give 3-methyleneoctafluorocyclohexene; the efficiency of the process appeared to vary with the " age " of the sodium fluoride. The diene is presumably formed by abstraction of a proton by fluoride ion, with synchronous elimination of fluoride ion from C-4. The dehydrofluorination could not be effected by refluxing with crushed potassium hydroxide, or potassium hydroxide in water at 100°, although in sulpholan at 100° a very small amount of the diene, detected by gas chromatography, was formed accompanied by extensive decomposition.

3-Methyleneoctafluorocyclohexene (VIII) displayed very strong absorption at 2190 Å, similar to the *trans*-form of an acyclic conjugated diene.[15] The hydrocarbon analogue[16] absorbs at 2310 Å. Oxidation of the diene with potassium permanganate in acetone gave hexafluoroglutaric acid. The diene was rapidly hydrogenated over palladised asbestos at atmospheric pressure, and was allowed to consume one mol. of hydrogen to give roughly equal amounts of 3*H*-3-methyloctafluorocyclohexene (X) and 3*H*-1-methyloctafluorocyclohexene (XI). Both structures were clearly established by i.r. and ^{19}F n.m.r. spectroscopy[11] and mass spectrometry,[10] and are consistent with the anticipated mode of addition of hydrogen, *viz.*, 1,2- and 1,4-addition centred initially at the reactive *exo*-methylene group; hydrogenation of fluorinated double bonds is known to be difficult.[17]

In common with two other highly fluorinated 1,3-dienes containing a terminal methylene group,[18,19] 3-methyleneoctafluorocyclohexene polymerised spontaneously at room temperature, and the process was accelerated by a free-radical initiator. The amorphous colourless polymer was very soluble in acetone, from which it could be cast as a thin transparent film. Such films were flexible but not elastomeric. From both steric and electronic considerations the polymer might be expected to contain a 1,4 " head-to-tail " arrangement of the repeating $C_7H_2F_8$ unit (XII). Confirmation of the structure was obtained from i.r. spectroscopy, which indicated a $CF{=}C{-}CH_2$ system. The polymer developed a red colour at about 150° and gave a black solid at about 300°. A quantitative thermal degradation in oxygen and *in vacuo* revealed a weight loss of about 4% (probably occluded solvent) up to 320°; here sudden decomposition occurred. These thermal effects are thought to involve pyrolytic dehydrofluorination between the methylene group and the adjacent tertiary fluorine atom. It was reported[20] that thermal elimination of hydrogen fluoride from polymers with such structural features can occur as low as 150°, and with striking abruptness,[21] *e.g.*, poly(α-fluorostyrene) at 225—235° gives poly(phenyl acetylene).[21] The production of a deep red, and eventually black, colour presumably

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[15] Woodward, *J. Amer. Chem. Soc.*, 1942, **64**, 72.

[16] Bailey and Gossens, *J. Amer. Chem. Soc.*, 1956, **78**, 2804.

[17] Knunyants, Krasuskaya, Mysov, and Muchtarov, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1962, **12**, 2141; Feast, Stephens, and Tatlow, unpublished work.

[18] Iseron, Hauptschein, and Lawlor, *J. Amer. Chem. Soc.*, 1959, **81**, 2676.

[19] Putnam and Castle, *J. Amer. Chem. Soc.*, 1961, **83**, 389.

[20] Hopkin, Research Report, Imperial Smelting Corpn.

[21] Matsuda, Sedlak, Noland, and Gleckler, *J. Org. Chem.*, 1962, **27**, 4015.

arises from the highly conjugated polyolefin resulting from such a pyrolytic dehydrofluorination.

Additional evidence of such processes was obtained during an attempt to dehydrofluorinate 1-methylnonafluorocyclohexene with potassium fluoride in dimethylformamide. At room temperature a very small amount of 3-methyleneoctafluorocyclohexene was formed, as indicated by gas chromatography. At higher temperatures, however, a black, ether-soluble solid was obtained, but none of the diene was detected. The ultraviolet (u.v.) spectrum of the black solid resembled that reported [22] for polyhepta-1,6-diyne. Further, the very rapid decolourisation of an ether solution of the black solid by chlorine and of an ethyl acetate solution by ozone, strongly suggest that the colour of the polymer is due to a highly conjugated polyolefin (XIII). Such an analogue of polyhepta-1,6-diyne [22] could be produced by 1,4-dehydrofluorination of 1-methylnonafluorocyclohexene (II) to the diene and rapid anionic polymerisation of this to poly-(1-methyleneoctafluorocyclohexene) (XII) with simultaneous dehydrofluorination. However, oxidative degradation of the black solid, with both ozone and potassium permanganate, gave tetrafluorosuccinic acid and a small amount of unidentified acid (difluoromalonic could be expected), as well as the expected hexafluoroglutaric acid, in the approximate ratio 2 : 3. The former acids could arise from the oxidation of alternative structures produced by isomerisations of the type known [23] to occur in polyfluorocyclohexenes [24] under these conditions, but such migrations of double bonds would be expected to eliminate the high degree of conjugation necessary to impart a black colour to the polymer. It is also possible that this highly conjugated polyolefin behaves in an abnormal way on oxidation.

Decafluorocyclohexene and 2 mol. of methyl-lithium in ether gave 1-methylnonafluorocyclohexene (II) (17%) and 1,2-dimethyloctafluorocyclohexene (III) (61%). The latter did not appear to react with potassium permanganate in acetone, and this is thought to reflect the increased electron density of the double bond. Oxidation with potassium permanganate in water at 100°, however, gave octafluoroadipic acid. Pyrolytic defluorination [8] gave 3,4,5,6-tetrafluoroxylene (XIV) with unambiguous i.r., u.v., and ^{19}F n.m.r. spectra,[11] and a consistent mass-spectral fragmentation pattern.[10] This evidence clearly establishes the structure given for the dimethyl-olefin, and it was confirmed by i.r. and ^{1}H and ^{19}F n.m.r. spectroscopy.[11]

1,2-Dimethyloctafluorocyclohexene did not react with trifluoroperacetic acid in the presence of disodium hydrogen phosphate or with hydrogen peroxide in t-butyl alcohol containing catalytic amounts of osmium tetroxide. Presumably the electron-donating character of the methyl groups is still dominated by the perfluorinated " backbone " of the ring. The olefin was also unaffected by sodium fluoride at 420°, and this may well be due to the additional methyl group, which would hinder the removal of a proton in a dehydrofluorination. Cobaltic fluoride at 120—150° gave a very complex mixture which was not separated. Chlorination, however, gave essentially two products, *cis*- and/or *trans*-1,2-dichloro-1,2-dimethyloctafluorocyclohexane (XV) and 1-chloromethyl-2-methyloctafluorocyclohexene (XVI). The former readily gave back 1,2-dimethyloctafluorocyclohexene with zinc dust in ethanol but was unaffected by concentrated aqueous potassium hydroxide at 100°; the latter was characterised by oxidation to octafluoroadipic acid and by dehydrochlorination with aqueous alkali to 1,2-dimethyleneoctafluorocyclohexane (XVII).

1,2-Dimethyleneoctafluorocyclohexane was oxidised to octafluoroadipic acid, and had characteristic i.r. and u.v. spectra, and mass spectrometry gave the anticipated breakdown pattern.[10] It did not react with maleic anhydride, presumably because of the effect of the fluorinated " backbone " on the electron density of the diene system. It did, however,

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[22] Stille and Frey, *J. Amer. Chem. Soc.*, 1961, **83**, 1697.
[23] Miller, Fried, and Goldwhite, *J. Amer. Chem. Soc.*, 1960, **82**, 3091.
[24] Rimmington, M.Sc. Thesis, Birmingham, 1962.

appear to polymerise, with azobisisobutyronitrile as initiator. The suspected poly-(1,2-dimethyleneoctafluorocyclohexane) (XVIII) possessed physical properties similar to those of poly-(1,2-dimethylenecyclohexane),[25] *viz.*, a hard, highly crystalline, inelastic substance.

EXPERIMENTAL

Gas Chromatography.—Analytical work was carried out using columns 2 m. long × 4 mm. diameter packed with dinonyl phthalate–kieselguhr (1 : 2) used at 100° and N_2 *ca.* 1·0 l./hr. (unit A), and a column 1 m. × 4 mm. packed with silicon gum–kieselguhr (1 : 2) used at 130° and N_2 *ca.* 0·3 l./hr. (unit B). For preparative-scale work three columns were used. Column A was 488 cm. × 75 mm. and column B was 488 cm. × 35 mm., both with the same packing as unit A. Column C was 488 cm. × 75 mm. with the same packing as unit B.

N.m.r. Spectroscopy.—The ^{19}F spectra were measured on a Mullard SL 44 Mark 1 instrument at 30·107 Mc./sec., and the ^{1}H spectra were measured on a Varian instrument at 60 Mc./sec.

1-*Methylnonafluorocyclohexene.*—Methyl-lithium (0·42 mole) in ether (350 c.c.) was added dropwise to a stirred solution of decafluorocyclohexene (100 g., 0·38 mole) in ether (240 c.c.) at −78°. After the addition was complete the mixture was allowed to attain room temperature and shaken with dilute hydrochloric acid until two clear layers separated. The ether layer was combined with ether extracts of the aqueous phase, dried (P_2O_5), filtered, and distilled, to give (*a*) ether–decafluorocyclohexene azeotrope which was separated by preparative-scale gas chromatography (column A, 100°, 50 l./hr.), to give pure decafluorocyclohexene (10·0 g.), and (*b*) a liquid residue which was separated by preparative-scale gas chromatogrphy (column A, 100°, 50 l./hr.) (in four portions), to give (i) diethyl ether (10·0 g.), (ii) 1-*methylnonafluorocyclohexene* (80·1 g.), b. p. 89·5°, $n_D^{21\cdot5}$ 1·3216 (Found: C, 32·9; H, 1·3; F, 66·0. $C_7H_3F_9$ requires C, 32·6; H, 1·2; F, 66·2%), (iii) 3-methyleneoctafluorocyclohexene (0·08 g.), identical with material prepared by an alternative route.

Characterisation of 1-*Methylnonafluorocyclohexene.*—(*a*) The olefin (7·5 g.) was passed over iron gauze at 470° in a stream of nitrogen (6·0 l./hr.), and the liquid product (5·5 g.) separated by preparative-scale gas chromatography (column A, 100°, 65 l./hr.), to give (i) 1-methylnonafluorocyclohexene (3·8 g.), (ii) pentafluorobenzene (trace), and (iii) 2,3,4,5,6-pentafluorotoluene (1·0 g.). All displayed correct i.r. spectra.

(*b*) The olefin showed an absorption band at 1725 cm.$^{-1}$ (CF=CMe). The ^{19}F (ref. 10) and ^{1}H n.m.r. spectra were consistent with the proposed structure; the former consisted of four signals centred at 39·6 (unequal doublet of small coupling constant), 42·9 (unequal doublet of small coupling constant), 53·8, and 57·8 p.p.m., with respect to trifluoroacetic acid, of intensity ratio 2 : 2 : 1 : 4, corresponding to the fluorine atoms on C-6, C-3, C-2, and C-4 and C-5, respectively; the latter consisted of a doublet of triplets (J = 1·6 c./sec.) centred at 1·67 p.p.m. downfield from tetramethylsilane as external reference.

(*c*) The olefin (2·5 g.) was added to potassium permanganate (7·5 g.) in dry acetone (375 c.c.) and refluxed for 30 min. Water (50 c.c.) was added, and working up in the usual way gave dianilinium octafluoroadipate (2·71 g., 59%), m. p. 211—212°; a portion (0·75 g.) of this was converted into the di-(*S*-benzylthiouronium) salt (0·58 g.), m. p. 244°.

The olefin (25·0 g.) was added to potassium permanganate (15·8 g.) in dry acetone (1 l.), and the mixture shaken for 30 min. at room temperature. Water (100 c.c.) was added and the usual isolation procedure followed, to give a syrupy acid (15·1 g.); this was dissolved in ether (10 c.c.), and aniline (10 g.) was added to give a precipitate of dianilinium octafluoroadipate (2·80 g., 6·1%), m. p. 211—211·5°. The remaining ether solution was shaken with 10% (w/v) aqueous sodium hydrogen carbonate (100 c.c.), and the two layers were separated. The aqueous layer was acidified with concentrated hydrochloric acid (100 c.c.) and continuously extracted with ether for 24 hr. The extract was dried ($MgSO_4$), filtered, and distilled, to leave a syrup (13·3 g., 47%) which could not be crystallised and would not distil. A portion (1·2 g.) of the suspected 2,2,3,3,4,4,5,5-octafluoro-6-oxoheptanoic acid was converted into its S-*benzylthiouronium salt* (1·32 g.), m. p. 158—159° (Found: C, 40·0; H, 3·3. $C_{15}H_{14}F_8N_2O_3S$ requires C, 39·6; H, 3·1%), $\nu_{max.}$ 1760 cm.$^{-1}$ (C=O in $CF_2{\cdot}CO{\cdot}CH_3$).

The heptanoic acid (11·1 g.), methanol (6 c.c.), and fluorosulphonic acid (1 c.c.) gave, in the normal way, *methyl* 2,2,3,3,4,4,5,5-*octafluoro*-6-*oxoheptanoate* (9·3 g.), b. p. 87—89°/10 mm.

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[25] Bailey and Golden, *J. Amer. Chem. Soc.*, 1954, **76**, 5418.

(Found: C, 31·9; H, 2·0. $C_8H_6F_8O_3$ requires C, 31·8; H, 2·0%), $\nu_{max.}$ 1787 (CO in $CF_2{\cdot}CO_2Me$) and 1768 cm.$^{-1}$ (CO in $-CF_2{\cdot}CO{\cdot}CH_3$).

Ammonia gas was passed through a solution of the methyl ester (0·96 g.) in ether (10 c.c.) for 10 min. The ether was evaporated, to leave 2,2,3,3,4,4,5,5-*octafluoro*-6-*oxoheptanamide* (0·95 g.), m. p. 92—93° (from ethanol) (Found: C, 29·4; H, 2·0. $C_7H_5F_8NO$ requires C, 29·3; H, 1·7%), $\nu_{max.}$ 1760 (CO in $CF_2{\cdot}CO{\cdot}CH_3$) and 1712 cm.$^{-1}$ (CO in $CF_2{\cdot}CONH_2$).

The methyl ester (0·30 g.) and 2,4-dinitrophenylhydrazine in aqueous methanol gave the *hydrazone* (0·40 g.), m. p. 88—89° (from ethanol) (Found: C, 34·9; H, 2·2. $C_{14}H_{10}F_8N_4O_6$ requires C, 34·9; H, 2·1%).

The methyl ester (1·00 g.) and 10% (w/w) aqueous sodium hydroxide were kept at 100° for 4 hr., cooled, acidified with concentrated hydrochloric acid (25 c.c.), and continuously extracted with ether for 24 hr. The dried ($MgSO_4$) extract was filtered and evaporated, and the acidic residue chromatographed on paper [26] (Whatman No. 1) using ethanol–aqueous ammonia (1·5N)–ammonium carbonate (1·5N) (1 : 1 : 1 v/v) containing 0·03% (v/v) Chlorophenol Red as indicator; this indicated the presence of two acids (R_F 0·87 and 0·78) (acetic acid gave R_F 0·87 under identical conditions). Fractional distillation *in vacuo* of the acid mixture gave a residue of impure 5*H*-octafluorovaleric acid [7] which was converted in the usual way into S-*benzylthiouronium* 5H-*octafluorovalerate* (0·25 g.), m. p. 172—173° (Found: C, 38·1; H, 2·9. $C_{13}H_{12}F_8N_2O_2S$ requires C, 37·9; H, 2·9%).

Chlorination of 1-*Methylnonafluorocyclohexene*.—Dry chlorine was passed for 2 hr. through the olefin (5·5 g.) in an irradiated (u.v.) quartz flask surmounted by a condenser at −78°. The liquid product (6·9 g.) was separated by preparative gas chromatography (column A, 100°, 70 l./hr.), to give (i) 1-methylnonafluorocyclohexene (0·2 g.), with a correct i.r. spectrum, (ii) *cis*- and/or *trans*-1,2-dichloro-1-methylnonafluorocyclohexane (5·6 g., 80%), m. p. 91° (sealed tube) (Found: C, 25·3; H, 0·9; F, 52·2. Calc. for $C_7H_3Cl_2F_9$: C, 25·5; H, 0·9; F, 51·6%).

The dichloro compound (1·6 g.) was added to a slurry of zinc dust (4·0 g.) in ethanol (10 c.c.), refluxed for 4 hr., cooled, and filtered, and water (50 c.c.) was added. The liquid hydrofluorocarbon so obtained was dried (P_2O_5) and distilled, to give 1-methylnonafluorocyclohexene (0·80 g.), b. p. 89—90·5° with a correct i.r. spectrum.

The dichloro-compound (1·7 g.), potassium hydroxide (5·0 g.), and water (5 c.c.) were shaken together in a sealed tube at 100° for 2 hr. The solid product (1·6 g.) was unchanged dichloro-1-methylnonafluorocyclohexane with a correct gas-chromatographic retention time and i.r. spectrum.

Fluorination of 1-*Methylnonafluorocyclohexene*.—The olefin (42·0 g.; 18·0 g./hr.) was passed through a static cobaltic fluoride reactor at 150° and the product separated by preparative gas chromatography (column A, 150°, 60 l./hr.), to give (i) perfluoromethylcyclohexane (0·8 g., 1·5%) with a correct i.r. spectrum, (ii) *methylundecafluorocyclohexane* (22·1 g., 46%), m. p. 34°, b. p. 84·5° (Found: C, 28·1; H, 1·1; F, 70·3. $C_7H_3F_{11}$ requires C, 28·3; H, 1·0; F, 70·6%), $\nu_{max.}$ 2900—3000 cm.$^{-1}$ (CH_3); ^{19}F (ref. 10) and ^1H n.m.r. spectra were consistent with the assigned structure, the proton spectrum consisting of a doublet (J = 23 c./sec.) centred at 1·5 p.p.m. downfield from tetramethylsilane as external reference, very weak coupling with other ring fluorines being indicated by the width of the signals, and (iii) 1-methylnonafluorocyclohexene (19·1 g.) with a correct i.r. spectrum.

Attempted Dehydrofluorination of Methylundecafluorocyclohexane.—This compound was unaffected by refluxing for 4 hr. with 50% w/v aqueous potassium hydroxide or with powdered potassium hydroxide in Nujol, or by passage in nitrogen (1·2 l./hr.) over sodium fluoride at 460° (83% recovery). When refluxed with potassium hydroxide in sulpholan for 1 hr. some decomposition occurred and 76% of the starting material was recovered.

Dehydrofluorination of 1-*Methylnonafluorocyclohexene*.—The olefin was passed over heated sodium fluoride in a stream of nitrogen (see Table 1). The products were separated by preparative gas chromatography (column B, 100°, 14 l./hr.), to give (i) 1-methylnonafluorocyclohexene, with a correct i.r. spectrum, and (ii) 3-*methyleneoctafluorocyclohexene*, b. p. 98°, n_D^{25} 1·3502 (Found: C, 35·3; H, 1·0. $C_7H_2F_8$ requires C, 35·3; H, 0·8%), $\nu_{max.}$ 3070 (=CH_2), 1720, and 1637 cm.$^{-1}$ (conjugated double-bond system), $\lambda_{max.}$ (in n-hexane) 2190 Å (ε 1·42 × 10^4).

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[26] Hartley and Lawson, *J. Chromatog.*, **1960**, **4**, **410**.

The diene (0·084 g.), potassium permanganate (0·50 g.), and dry acetone (30 c.c.) were refluxed for 30 min., and the usual isolation procedure gave hexafluoroglutaric acid (53%), identified as the dianilinium and bis-(*S*-benzylthiouronium) salts, m. p. 216—218° (lit.,[27] 218—220°) and 189—190° (lit.,[28] 189—190°) respectively, both with correct i.r. spectra.

TABLE 1.

Reaction of 1-methylnonafluorocyclohexene with sodium fluoride.

Temp.	N_2 (l./hr.)	Olefin (g.)	Recovered olefin (g.)	Diene (g.)	Temp.	N_2 (l./hr.)	Olefin (g.)	Recovered olefin (g.)	Diene (g.)
380°	1·2	12·0	10·5	0·21	465°	1·5	7·5	4·2	0·33
420	1·2	12·0	8·0	0·90	465	3·0	7·5	5·4	0·40
425	1·5	7·5	5·8	0·07	465	6·0	7·5	5·6	0·35
425	3·0	7·5	6·5	0·16	490	1·5	7·5	2·8	0·65
425	6·0	7·5	6·7	0·11	490	3·0	7·5	4·0	0·72
460	1·2	12·0	4·5	0·72	490	6·0	7·5	4·8	0·56

Hydrogenation of 3-*Methyleneoctafluorocyclohexene.*—The diene (1·20 g., 0·005 mole) in ether (5 c.c.) was hydrogenated at 25°/745 mm. using palladised asbestos (0·05 g.) as catalyst. When the desired uptake of hydrogen (150 c.c., 0·006 mole) was attained, the filtered ether solution was examined by gas chromatography (column A, 100°, 1·0 l./hr.), which revealed two components in addition to ether and starting material (trace amount). The mixture was separated by preparative gas chromatography (column A, 100°, 60 l./hr.) into: (i) ether (1·9 g.); (ii) 3H-3-*methyloctafluorocyclohexene* (0·33 g.), b. p. 106° n_D^{21} 1·3389 (Found: C, 35·0; H, 1·9. $C_7H_4F_8$ requires C, 35·0; H, 1·7%), $\nu_{max.}$ 1747 cm.$^{-1}$ (CF=CF double bond); the ^{19}F n.m.r. spectrum was consistent with the proposed structure,[11] in particular there being no high-field signal assignable to a >CHF group. There were two absorptions assignable to the olefinic fluorine nuclei, one deshielded by the adjacent substituents. Mass spectrometry gave $M = 240$ ($C_7H_4F_8$) and the anticipated fragmentation pattern;[10] (iii) 3H-1-*methyloctafluorocyclohexene* (0·36 g.), b. p. 107°, n_D^{21} 1·3421 (Found: C, 35·0; H, 1·6%), $\nu_{max.}$ 1720 cm.$^{-1}$ (CF=C–CH_3 double bond); the ^{19}F n.m.r. spectrum was consistent with the proposed structure, and was separable into three parts of relative intensity ratio 3 : 4 : 1. The highest field signal (relative intensity 1) was of the chemical shift for a >CHF type absorption (120 p.p.m. with respect to trifluoroacetic acid).[11] Mass spectrometry gave $M = 240$ ($C_7H_4F_8$), and a consistent fragmentation pattern,[10] in particular a fragment of mass 158 (CH_3–C=CF·CF_2·CF_2^+).

Polymerisation of 3-*Methyleneoctafluorocyclohexene.*—The diene was polymerised in sealed tubes under nitrogen (see Table 2). Residual diene was removed by vacuum distillation, to leave *poly*-(3-*methyleneoctafluorocyclohexene*) [Found: C, 35·3; H, 1·1; F, 63·5. $(C_7H_2F_8)_n$ requires C, 35·3; H, 0·8; F, 63·9%], $\nu_{max.}$ 1690 cm.$^{-1}$ (CF=C–CH_2 double bond). The polymer dissolved readily in acetone, and on evaporation gave the polymer as a flexible, but inelastic, transparent film.

TABLE 2.

Polymerisation of 3-methyleneoctafluorocylohexene.

Temp.	Time	Diene (g.)	Polymer (g.)	Polymer (%)
ca. 20°	42 days	0·616	0·170	26·6
80	28 hr.	0·481	0·078	16·4
80 *	6 hr.	0·458	0·300	66·0

* With 0·0015 g. αα′-azobisisobutyronitrile as initiator.

Reaction of 1-*Methylnonafluorocyclohexene with Potassium Fluoride.*—The olefin (5·0 g.), anhydrous potassium fluoride (5·0 g.), and dimethylformamide (25 c.c.) were kept at 85° for 12 hr. The mixture was poured into water (100 c.c.) and extracted with ether (3 × 50 c.c.). The ether solution was dried ($MgSO_4$), filtered, and distilled, to leave a brittle black solid (1·1 g.), $\nu_{max.}$ 1700—1600 cm.$^{-1}$ (double bond), $\lambda_{max.}$ (in ethanol) 2000—7000 Å. The distillate was separated by preparative gas chromatography, to give ether, and 1-methylnonafluorocyclohexene (1·6 g.) with a correct i.r. spectrum. A solution of the black polymer in ether was instantly decolourised by gaseous chlorine.

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[27] Evans and Tatlow, *J.*, 1955, 1184.

[28] Dobinson, Lawson, and Ward, *Fuel*, 1956, **35**, No. 4, 406.

The black polymer (0·5 g.) and potassium permanganate (5·0 g.) in dry acetone (250 c.c.) were refluxed for 1 hr. and filtered, and water was added. Acetone was distilled off and potassium permanganate (2·0 g.) added to complete the oxidation. The aqueous solution was then treated in the usual way, and the concentrated ether solution (1·0 c.c.) was treated with aniline to give a precipitate of dianilinium salts (0·46 g.). Fractional crystallisation from acetone–chloroform gave dianilinium hexafluoroglutarate and tetrafluorosuccinate with correct i.r. spectra; the i.r. spectrum of the crude mixture of acids indicated a ratio of 3 : 2, respectively. A small proportion ($<10\%$) of unidentified acid product was also present.

Ozone was passed through a solution of the polymer (0·20 g.) in dry ethyl acetate (40 c.c.) for 3 hr. in a cyclic ozonisation apparatus,[28] the solution being rapidly decolourised. It was evaporated to small volume (*ca.* 0·5 c.c.) and 5% (w/v) hydrogen peroxide in 5% (w/v) sodium hydroxide (10 c.c.) was added. The mixture was refluxed for ½ hr. and cooled, and potassium permanganate (2·0 g.) in water (20 c.c.) added to complete the oxidation. The resultant mixture was treated in the usual way, to give an ether solution of acid products which was evaporated to small volume (*ca.* 0·5 c.c.). Aniline was added, to give a precipitate of dianilinium salts (0·20 g.) with an i.r. spectrum identical with that of the mixture obtained in the analogous permanganate oxidation.

1,2-*Dimethyloctafluorocyclohexene.*—Methyl-lithium (0·91 mole) in ether (600 c.c.) was added dropwise to a stirred solution of decafluorocyclohexene (100·0 g., 0·38 mole) in ether (250 c.c.) at −78°. The usual isolation procedure gave a liquid which was separated by gas chromatography (column A, 100°, 70 l./hr.) into: (i) ether (9·0 g.), with a correct i.r. spectrum; (ii) 1-methylnonafluorocyclohexene (17·4 g., 17·5%), with a correct i.r. spectrum; (iii) a mixture of four unidentified compounds (1·1 g.); (iv) 1,2-*dimethyloctafluorocyclohexene* (60·4 g., 61·5%), b. p. 135·5—136°, $n_D^{21\cdot5}$ 1·3518 (Found: C, 38·0; H, 2·4. $C_8H_6F_8$ requires C, 37·8; H, 2·4%).

Characterisation of 1,2-*Dimethyloctafluorocyclohexene.*—(*a*) The olefin (15·0 g.) was passed over iron gauze at 340° in a stream of nitrogen (4·5 l./hr.). Inspection of the product (11·4 g.) by analytical gas chromatography (unit A, 100°, 1 l./hr.) indicated the presence of starting material and one product, and these were separated by gas chromatography (column A 100°, 70 l./hr.), to give: (i) 1,2-dimethyloctafluorocyclohexene (7·1 g.) with a correct i.r. spectrum; (ii) 3,4,5,6-*tetrafluoro*-o-*xylene* (3·1 g., 29·5%), m. p. 34°, b. p. 153° (Found: C, 55·4; 52·8; H, 3·7; 3·2. $C_8H_6F_4$ requires C, 53·9; H, 3·4%), $\nu_{max.}$ 3083, 3002, and 2935 (CH_3), 1525 and 1505 cm.$^{-1}$ (aromatic ring), $\lambda_{max.}$ (in n-hexane) 2620 Å (ε 470); the ^{19}F n.m.r. spectrum[11] contained two signals of equal intensity; the mass spectrum contained a top-mass peak of 178 ($C_8H_6F_4$) and a consistent fragmentation pattern.[10]

(*b*) The olefin showed absorption bands at 3038, 2963, and 2890 cm.$^{-1}$ ($\vdots$CH) and a weak band at 1683 cm.$^{-1}$ [$C-(CH_3)=C(CH_3)$]. The ^{19}F (ref. 10) and ^1H n.m.r. spectra were entirely consistent with the proposed structure. The former consisted of two signals of equal intensity at 35·49 and 57·9 p.p.m. with respect to trifluoroacetic acid, assignable to the fluorine nuclei at C-3 and C-6, and C-4 and C-5, respectively. The latter consisted of a triplet (J = 1·3 c./sec.) centred at 1·68 p.p.m. downfield from tetramethylsilane as external reference.

(*c*) The olefin (1·0 g.), potassium permanganate (5·0 g.), and water (20 c.c.) were shaken vigorously in a sealed tube at 100° for 2 hr. The usual procedure gave dianilinium octafluoroadipate (1·11 g., 59%), m. p. 209—210° (from acetone–chloroform) with a correct i.r. spectrum. A portion (0·70 g.) of the dianilinium salt was converted into the bis-(*S*-benzylthiouronium) salt (0·81 g.), m. p. 243·5—244° (from water), with a correct i.r. spectrum.

Chlorination of 1,2-*Dimethyloctafluorocyclohexene.*—The olefin (52·5 g.) and chlorine (12·8 g.) were irradiated with u.v. light in a sealed tube until the solution became colourless (*ca.* 4 hr.). The tube was cooled in liquid air and opened. On warming, hydrogen chloride was evolved, and the product was neutralised with dilute sodium hydrogen carbonate solution. The organic layer was separated (in four portions) by preparative gas chromatography (column C, 150°, 70 l./hr.) into: (i) 1,2-dimethylcyclohexene (17·1 g.) with a correct i.r. spectrum; (ii) 1-*methyl*-2-*chloromethyloctafluorocyclohexene* (15·6 g., 26%), b. p. 162°, n_D^{20} 1·3753 (Found: C, 33·3; H, 1·6. $C_8H_5ClF_8$ requires C, 33·3; H, 1·7%), $\nu_{max.}$ 1675 cm.$^{-1}$ (w) ($C{\cdot}CH_3{=}C{\cdot}CH_2Cl$ group); (iii) *cis*- and/or *trans*-1,2-dichloro-1,2-dimethyloctafluorocyclohexane (12·4 g., 18·5%), m. p. 132—133° (sealed tube) (Found: C, 29·5; H, 1·9. Calc. for $C_8H_6Cl_2F_8$: C, 29·5; H, 1·9%); (iv) minor products (10·0 g.) which could not be separated. 1,2-Dichloro-1,2-dimethyloctafluorocyclohexane (2·0 g.), zinc dust (3·0 g.), and ethanol (10 c.c.) were refluxed together for 4 hr., cooled, filtered, and poured into water (100 c.c.). The organic layer was separated by preparative gas chromatography (column C, 150°, 70 l./hr.), to give (i) 1,2-dimethyloctafluorocyclohexene (0·95 g., 61%), and (ii) starting material (0·21 g.); both had correct i.r. spectra.

Characterisation of 1-*Methyl*-2-*chloromethyloctafluorocyclohexene*.—(*a*) The olefin (1·0 g.), potassium permanganate (2·5 g.), and water (20 c.c.) were shaken vigorously in a sealed tube at 100° for 2 hr. The usual procedure gave dianilinium octafluoroadipate (1·0 g.), m. p. 210° (from acetone–chloroform), with a correct i.r. spectrum. A portion (0·1 g.) of the dianilinium salt was converted into bis-(*S*-benzylthiouronium) octafluoroadipate (0·11 g.), m. p. 243°, with a correct i.r. spectrum.

(*b*) The olefin (6·7 g.), potassium hydroxide (6·7 g.), and water (6·7 c.c.) were shaken vigorously in a sealed tube at 100° for 1 hr. Considerable charring occurred, and ether (5 c.c.) was added. The ether solution was separated by gas chromatography (column C, 130°, 60 l./hr.), to give: (i) ether (2·5 g.); (ii) 1,2-*dimethyleneoctafluorocyclohexane* (1·64 g., 28%), b. p. 124—125°, $n_D^{18\cdot5}$ 1·3567 (Found: C, 37·9; H, 2·0. $C_8H_4F_8$ requires C, 38·1; H, 1·6%), $\nu_{max.}$ 1920 cm.$^{-1}$ (w) (overtone of CH deformation in $=CH_2$), $\lambda_{max.}$ (in ethanol) 2080 Å (ε 6·3 × 10^3). Mass spectrometry gave a molecule ion at 252 ($C_8H_4F_8$) and a consistent fragmentation pattern.[10]

The diene (0·09 g.), potassium permanganate (0·55 g.), and water (5 c.c.) were shaken together in a sealed tube at 100° for 2 hr. The usual isolation procedure gave dianilinium octafluoroadipate (0·10 g., 55·5%), m. p. 209—210°, with a correct i.r. spectrum. A portion (0·03 g.) was converted into bis-(*S*-benzylthiouronium) octafluoroadipate (0·03 g.), m. p. 244°, with a correct i.r. spectrum.

Polymerisation of 1,2-*Dimethyleneoctafluorocyclohexane*.—The diene (0·43 g.) was kept with azobisisobutyronitrile (0·0005 g.) under nitrogen in a sealed tube at 60° for 50 hr. A precipitate formed, and unchanged diene (0·19 g.) was removed by evaporation *in vacuo*, to leave a white solid (0·24 g.) which was reprecipitated from acetone to give the suspected *poly*-(1,2-*dimethyleneoctafluorocyclohexane*), m. p. 221—222° (Found: C, 37·8; H, 1·7; F, 60·5. $[C_8H_4F_8]_n$ requires C, 38·1; H, 1·6; F, 60·3%), sharp rings were observed in its *X*-ray powder photograph.

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CHEMISTRY DEPARTMENT, THE UNIVERSITY,
EDGBASTON, BIRMINGHAM 15.

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