45. *Fluorocyclopentanes. Part I. The* 1H,2H- *and* 1H,3H-*Octafluorocyclopentanes, and* 1H,3H/2H-*Heptafluorocyclopentane.*[*]

By R. J. Heitzman, C. R. Patrick, R. Stephens, and J. C. Tatlow.

The vapour-phase fluorination of cyclopentadiene with cobaltic fluoride gave a complex mixture containing 1*H*/2*H*-, 1*H*,2*H*/-, 1*H*/3*H*-, and 1*H*,3*H*/-octafluorocyclopentanes (V—VIII) and 1*H*,3*H*/2*H*-heptafluorocyclopentane (XIII), in addition to the known deca- and nona-fluorocyclopentanes (I, II). Structure allocations were based on dehydrofluorinations, and oxidations of the derived olefins. Characterisation of the 1*H*/2*H*- and 1*H*,2*H*/-octafluorides was facilitated by an alternative synthesis from 1,2-dichlorohexafluorocyclopentene, involving fluorination with cobaltic fluoride and reduction of the derived 1,2-dichloro-octafluorocyclopentanes with lithium aluminium hydride. The stereochemical allocations were based on nuclear magnetic resonance and dipole moment measurements. The structures of the 1*H*,3*H*-octafluorocyclopentanes were based on the established stereochemistry of the 1*H*,2*H*-isomers and their derivation from 1*H*,3*H*/2*H*-heptafluorocyclopentane (XIII) by cobaltic fluoride fluorination. The latter heptafluoride together with its stereoisomers (XIV, XV) were synthesised from 3*H*-heptafluorocyclopentene (X) by chlorination and lithium aluminium hydride reduction. The structural allocations agree with the Auwers–Skita rule.

THE partial fluorination of benzene has recently been studied in detail in this Department,[1] and the techniques used have now been extended to cyclopentane and cyclopentadiene. With cobaltic fluoride at about 200° both give a nearly identical range of polyfluorocyclopentanes. The exhaustive fluorination of cyclopentane with cobalt trifluoride has been reported previously, decafluorocyclopentane (I) [2] and nonafluorocyclopentane (II) [2,3] having been obtained. In the present work, by fractional distillation coupled with preparative scale gas chromatography, several new polyfluorocyclopentanes were isolated.

TABLE 1.

Major products from the fluorination of cyclopentadiene.

Present in distilln. fraction no.	Compound	Retention time * (min.)	B. p.	% of fluorination mixture
(i), (ii)	Decafluorocyclopentane (I)	1·2	22·5° (cited b. p.[2])	10
(xv)	Suspected perfluoro-dimer, $C_{10}F_{16}$ (XVI)	1·5	135	2 †
(iv), (v)	Nonafluorocyclopentane (II)	2·2	38·5 (cited b. p.[2])	22
(vi) (vii)	1*H*/2*H*-Octafluorocyclopentane (V)	3·2	50	9
(viii)	1*H*/3*H*-Octafluorocyclopentane (VII)	5·0	57·5	12
(xi)	1*H*, 3*H*/2*H*-Heptafluorocyclopentane (XIII)	6·2	65	4
(xi)	1*H*, 3*H*/-Octafluorocyclopentane (VIII)	8·0	65	4
(xiii), (xiv)	1*H*, 2*H*, 4*H*-Heptafluorocyclopentane (XVII)	10·2	78	8
(xiii), (xiv)	1*H*, 2*H*/-Octafluorocyclopentane (VI)	13·8	78	1 †

* Stationary phase, dinonyl phthalate; temp. 94°; N_2 flow rate 1·5 l./hr.
† Estimated from area beneath analytical gas chromatography peak.

The lowest-boiling products were the known deca- (I) [2] (b. p. 22·5°) and nona-fluorocyclopentane (II) [3] (b. p. 38·5°). The next fraction gave a compound (V) (b. p. 50°)

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[*] The stereochemical nomenclature used in this and subsequent papers on the polyfluorocyclopentanes is analogous to that used for the polyfluorocyclohexanes.[1]

[1] Stacey and Tatlow in " Advances in Fluorine Chemistry," (ed. Stacey, Tatlow, and Sharpe), Butterworths Scientific Publications, London, 1960, p. 176.

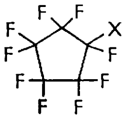
[2] Fowler, Burford, Hamilton, Sweet, Weber, Kasper, and Litant, *Ind. Eng. Chem.*, 1947, **39**, 292.

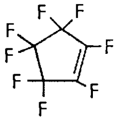
[3] Barber, Burger, and Cady, *J. Amer. Chem. Soc.*, 1951, **73**, 4241.

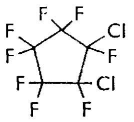
having the correct analysis for an octafluorocyclopentane. The same compound was also obtained, together with an isomeric octafluorocyclopentane (VI) (b. p. 78°), by the reduction with lithium aluminium hydride of 1,2-dichloro-octafluorocyclopentane (IV), prepared by a known route (cobaltic fluoride fluorination) from 1,2-dichlorohexafluorocyclopentene.[4]

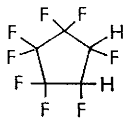
The absence of chlorine migration in the latter fluorination was established by dechlorination with zinc dust of 1,2-dichloro-octafluorocyclopentane (IV) to the known[4] octafluorocyclopentene (III). This was also prepared by the dehydrofluorination of nonafluorocyclopentane (II) with aqueous potassium hydroxide, and its structure was confirmed by oxidation to the known hexafluoroglutaric acid. A useful alternative method of dechlorination of 1,2-dichloro-octafluorocyclopentane (IV) was to pass it over nickel heated to about 500°; this parallels the defluorination reaction that has been applied extensively to the preparation of perfluoroaromatic compounds.[5] It is evident, however, that chlorine is removed more easily than fluorine from a compound by reaction with heated nickel. Hexafluorocyclopentadiene could not be made by defluorination of the fluorocarbons (I) or (III).

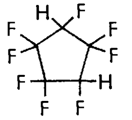
Although the higher boiling of the two isomeric octafluorocyclopentanes (VI) was detected in the fluorination product, it was a minor constituent and could only be prepared practicably by the alternative procedure. This synthesis demonstrated that both compounds are 1*H*,2*H*-octafluorocyclopentanes (V and VI). Support for this was given by the formation of 1*H*- and 3*H*-heptafluorocyclopentene (IX and X) as the sole dehydrofluorination products of each of the isomeric saturated compounds (V) and (VI). The ease of formation and relative amounts of the olefins (IX) and (X) are discussed below. Their structures were established by oxidation to hexafluoro- and 2*H*-pentafluoro-glutaric acid, respectively. The latter acid was identical with that obtained from the pyrolysis of disilver 3*H*-heptafluoroadipate and iodine.[6] Additional evidence for the structure of 3*H*-heptafluorocyclopentene and of the derived acid was provided by the

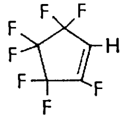

(I: X = F)
(II: X = H)

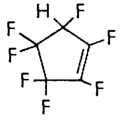

(III)

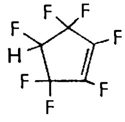

(IV)

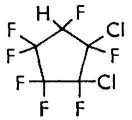

(V) 1*H*/2*H*-(*trans*)
(VI) 1*H*,2*H*/-(*cis*)

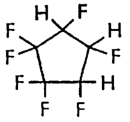

(VII) 1*H*/3*H*-(*trans*)
(VIII) 1*H*,3*H*/-(*cis*)

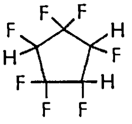

(IX)

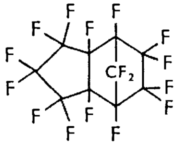

(X)


(XI)


(XII)


(XIII) 1*H*,3*H*/2*H*-
(XIV) 1*H*,2*H*/3*H*-
(XV) 1*H*,2*H*,3*H*/-


(XVII)


(XVI)

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[4] Henne and Latif, *J. Amer. Chem. Soc.*, 1954, **76**, 610.

[5] Gething, Patrick, Stacey, and Tatlow, *Nature*, 1959, **183**, 588.

[6] Barbour, MacKenzie, Stacey, and Tatlow, *J. Appl. Chem.*, 1954, **4**, 341.

formation of tetrafluorosuccinic acid under more strongly oxidising conditions. This is an example of the instability of 2*H*-polyfluoro-acids under oxidising conditions; oxidation of 3*H*-nonafluorocyclohexene is known [7] to give hexafluoroglutaric acid rather than 2*H*-heptafluoroadipic acid unless mild conditions are used.

The Auwers–Skita rule [8] has been clearly demonstrated in the cyclic polyfluorohydrocarbons so far examined; *viz.* in the decafluorocyclohexanes: 1*H*/2*H*- and 1*H*,2*H*/- [9] (b. p.s 70° and 91°, respectively), 1*H*/3*H*- and 1*H*,3*H*/- [10] (b. p.s 78° and 89°, respectively), and 1*H*/4*H*- and 1*H*,4*H*-/ [10] (b. p.s 78° and 86°, respectively). Also, the 1*H*,2*H*-hexafluorocyclobutanes [11] have b. p.s of 27° and 63° although the structural allocations are less certain here. Gas chromatography, with dinonyl phthalate as stationary phase, also shows a stereochemical dependence.[10,11] Thus, the stereoisomer with the hydrogen atoms closer together has a longer retention time. It was, therefore, expected that the 1*H*,2*H*-octafluorocyclopentanes of b. p.s 50° and 78° were the *trans*- and *cis*-isomers (V and VI), respectively. This allocation has been confirmed by measurement of the dipole moments of the two 1*H*,2*H*-octafluorocyclopentanes. The lower-boiling compound has the lower dipole moment, 1·15 D, consistent with experience [9,10] in the cases of stereoisomerism in the polyfluorocyclohexane series, and the higher-boiling compound has a dipole moment of 2·64 D. Thus, the lower-boiling compound has its two hydrogen atoms in the *trans*-configuration, and is (±)-1*H*/2*H*-octafluorocyclopentane (V) (there is at present no available method of resolution for such a racemate), and the higher-boiling compound is the *cis*-1*H*,2*H*/-octafluorocyclopentane (VI). These assignments are supported by nuclear magnetic resonance spectroscopy. The calculated dipole moments of the two isomers, a planar conformation for the cyclopentane ring being assumed, and the observed dipole moment of nonafluorocyclopentane being used, are, 3·05 D for the *cis*-isomer and 1·50 D for the *trans*-isomer. Although there may be doubt about the calculated values for the dipole moments, there can be no question that they will differ markedly for the two isomers, and that the dipole moment of the *cis*-isomer will be the greater.

From other fractions of the fluorination product two other octafluorocyclopentanes, b. p.s 58° and 65°, have been isolated. When dehydrofluorinated with aqueous potassium hydroxide both gave the same two products, b. p.s 45° and 51°, shown from elemental analysis to be heptafluorocyclopentenes. One was 3*H*-heptafluorocyclopentene (X), described above. The other, b. p. 45°, on oxidation gave a pentafluoroglutaric acid which, since it was not the 2*H*-isomer, could only be 3*H*-pentafluoroglutaric acid. Support for this allocation lay in the failure to degrade this acid further under more drastic oxidative conditions. Thus, the olefin from which it was derived must be 4*H*-heptafluorocyclopentene (XI). These two olefins, 3*H*- and 4*H*-heptafluorocyclopentene (X, XI), can only be formed simultaneously from the isomeric 1*H*,3*H*-octafluorocyclopentanes. Hexafluorocyclopentadiene was never isolated. However, this compound would be expected to be very susceptible to nucleophilic attack and the dark aqueous phase produced in the dehydrofluorination could have resulted from its reaction with aqueous alkali.

The stereochemistry of the 1*H*,3*H*-octafluorocyclopentanes, expected from gas-chromatographic retention time and b. p.s, has been established by their relationship to a 1*H*,2*H*,3*H*-heptafluorocyclopentane (XIII) found in the polyfluorocyclopentane mixture, and from the known stereochemistry of the 1*H*,2*H*-octafluorocyclopentanes. This heptafluorocyclopentane (XIII) was also prepared from 3*H*-heptafluorocyclopentene (X) by a

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

[8] Auwers, *Annalen*, 1920, **420**, 84; Skita, *Ber.*, 1920, **53**, 1792; Allinger, *Experientia*, 1954, **10**, 328; van Bekkum, van Veen, Verkade, and Wepster, *Rec. Trav. chim.*, 1961, **80**, 1310.

[9] Smith and Tatlow, *J.*, 1957, 2505.

[10] Evans, Godsell, Stephens, Tatlow, and Wiseman, *Tetrahedron*, 1958, **2**, 183.

[11] Fuller and Tatlow, *J.*, 1961, 3198.

route which initially involved addition of chlorine in the presence of ultraviolet light to give a mixture of 1*H*-2,3-dichlorocyclopentanes (XII) which could be separated into three components by gas chromatography. Since four stereoisomers of this compound can be formulated, either the gas-chromatographic separation must have been incomplete or one of the isomers was not formed in the chlorination. Reduction of the mixed 1*H*-2,3-dichloroheptafluorocyclopentanes (XII) with ethereal lithium aluminium hydride gave a mixture of three heptafluorocyclopentanes, b. p.s 65°, 84°, and 135°, which, from their method of preparation, must be 1*H*,2*H*,3*H*-heptafluorocyclopentanes. The first of these, b. p. 65°, was identical with compound (XIII). Fluorination of it under mild conditions [10] with cobaltic fluoride gave four products which were characterised by gas chromatography and infrared spectroscopy as decafluorocyclopentane (I), nonafluorocyclopentane (II), 1*H*/2*H*-octafluorocyclopentane (V), and a 1*H*,3*H*-octafluorocyclopentane (VIII). Since only the *trans*-1*H*/2*H*-octafluorocyclopentane (V), and none of the *cis*-isomer (VI), was found in the fluorination products, the heptafluorocyclopentane (XIII) must have the 1*H*,3*H*/2*H*-configuration. Therefore, the 1*H*,3*H*-octafluorocyclopentane accompanying the *trans*-1*H*/2*H*-isomer must be 1*H*,3*H*/-octafluorocyclopentane (VIII), and the isomer (b. p. 57·5°) must be (±)-1*H*/3*H*-octafluorocyclopentane (VII). These assignments are supported by nuclear magnetic resonance measurements.

Application of the Auwers–Skita rule [8] and consideration of gas-chromatographic retention times indicate that the heptafluorocyclopentanes of b. p.s 84° and 135° have the stereochemistry designated as (±)-1*H*,2*H*/3*H*- and 1*H*,2*H*,3*H*/- (XIV and XV), respectively.

Preparative gas chromatography of the highest-boiling fractions from the fluorination of cyclopentadiene gave a liquid fluorocarbon, b. p. 135°, having a comparatively short retention time, and the approximate analysis for a perfluoroperhydro-4,7-methanoindene (XVI). This could obviously arise from the fluorination of cyclopentadiene dimer, and it was not observed in the product of fluorination of cyclopentane which otherwise gave an identical gas-chromatographic analysis to that obtained from the cyclopentadiene product.

Whereas, in the decafluorocyclohexane series [9,10] comparative qualitative rates of dehydrofluorination with aqueous potash were valuable in providing support for stereochemical assignments based on physical measurements, *e.g.*, 1*H*/2*H*-decafluorocyclohexane lost hydrogen fluoride much more slowly than the 1*H*,2*H*/-stereoisomer, they were of no value in the cyclopentane series. Thus, under identical conditions in aqueous alkali, both 1*H*/2*H*- and 1*H*,2*H*/-octafluorocyclopentane (V, VI) lost hydrogen fluoride at approximately the same rate as did 1*H*,2*H*/-decafluorocyclohexane. Kinetic studies [12] of non-fluorinated cyclopentane systems parallel these observations, though the differences observed would probably be too small to detect by the methods used in the present work. They may in fact be nullified by relative solubility effects, since the dehydrofluorinations are heterogeneous. The increased ease of elimination from a cyclopentane system compared with that from a related cyclohexane has been correlated [12] with the comparative ease of introduction of a double bond into such rings. It seems unlikely, however, that this effect can fully explain the behaviour of the polyfluoro-compounds.

A coplanar four-atom reaction centre (*e.g.*, H–C–C–F) is the preferred system from which eliminations of this general type proceed, the two pendant groups being *trans*.[13] It seems possible that a second alignment for elimination, less favourable though possible, is that with the groups to be removed *cis* to each other in a coplanar system, those to remain also being *cis*. Then, 1*H*,2*H*/-octafluorocyclopentane could obviously lose hydrogen and fluorine from a *trans* system made coplanar by a slight twisting movement,[14] and the 1*H*/2*H*-analogue could lose hydrogen and fluorine which are *cis* to each other

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[12] Bordwell, Pearson, and Weinstock, *J. Amer. Chem. Soc.*, 1956, **78**, 3468.

[13] Ingold, " Structure and Mechanism in Organic Chemistry," G. Bell, London, 1953, p. 467.

[14] Banthorpe, Hughes, and Ingold, *J.*, 1960, 4054.

in the $>$CHF–CHF$<$ group. A rigid *cis*-elimination of this type from a cyclohexane could not occur without considerable ring deformation, but would be possible in a cyclopentane or a cyclobutane. The two 1*H*,2*H*-hexafluorocyclobutanes [11] lost hydrogen fluoride at roughly the same rates. The resemblance in the behaviour of polyfluorocyclobutanes and -pentanes and the difference from cyclohexanes are noteworthy. If ring system and stability were of over-riding importance, this should not be the case. With both *trans*- and *cis*-elimination from a four-atom centre, the two remaining substituents which will become vinylic are close together and little rotation of each towards the other about the $>$C–C$<$ bond involved is necessary for them to take up the positions they must occupy in the olefinic reaction product. This relatively correct steric alignment of the potential vinylic substituents may be an important feature of a coplanar reaction system.

All this discussion has assumed that the elimination processes are essentially of the synchronous *E*2 type. The possibility that an alternative *E*1*cB* type process, involving a carbanion,[13] may be followed is difficult to rule out. However, no evidence for base-catalysed deuterium exchange could be obtained, using infrared spectroscopy to analyse the reaction products, when 1*H*/2*H*- and 1*H*,2*H*/-decafluorocyclohexane and 1*H*/2*H*- and 1*H*,2*H*/-octafluorocyclopentane were partially dehydrofluorinated with potassium hydroxide in heavy water. Though the expected $\geq$C–H stretching frequencies were observed, no $\geq$C–D stretching frequencies were detected in the region of 2100 cm.$^{-1}$ (the calculated frequency). However, the applicability of the method of exchange was established by using 2-bromo-2-chloro-1,1,1-trifluoroethane which has been shown [15] to undergo deuteration. The product was largely the deuterated compound [15] with a $\geq$C–D stretching frequency of 2255 cm.$^{-1}$ and the $\geq$C–H stretching frequency of the original was just discernible at 2990 cm.$^{-1}$.

Another possible mechanism is the loss of hydrogen and halogen from the same carbon atom to give a carbene intermediate which then rearranges to an olefin. This seems less likely since big variations of reaction rate between stereoisomers would not be expected.[16]

EXPERIMENTAL

Cyclopentadiene was obtained by heating the dicyclic compound (containing a little ferrous sulphate to avoid explosions) and collecting the cyclopentadiene, b. p. 41°, from the top of a vacuum-jacketed column (2′ × ½″) packed with glass helices.

Partial Fluorination of Cyclopentadiene.—Cyclopentadiene (120 g.) was fed (1 c.c./min.) into a reactor of previously described [1] design, containing cobalt trifluoride (6·5 kg.) maintained at 190—250°. The products were collected in a copper trap cooled by solid carbon dioxide and any remaining in the reactor was swept into the trap by a gentle stream of nitrogen. The total product was poured into ice–water (1 l.) and washed with sodium hydrogen carbonate solution. The clear organic layer (200 g.) was separated, and a resin (40 g.) discarded.

The combined products (940 g.) of a number of fluorinations, shown by analytical gas chromatography (1 : 2 dinonyl phthalate–kieselguhr, temp. 100°, N_2 flow-rate 1·5 l./hr.) to contain at least 12 components, were distilled through a vacuum-jacketed column (4′ × 1″) packed with Dixon gauze rings (1/16″ × 1/16″). The distillation was controlled by analytical gas chromatography and the following fractions were collected: (i) b. p. 19—22·8° (62·3 g.) (decafluorocyclopentane and presumably some fragmentation products); (ii) 22·8—25° (28·7 g.) (largely decafluorocyclopentane); (iii) 23—38° (38·6 g.) (intermediate fraction); (iv) 37·8—38·2° (106·3 g.) (large amount of nonafluorocyclopentane); (v) 38·2—38·8° (22·8 g.) (largely C_5F_9H); (vi) 38·2—49° (59·1 g.); (vii) 49·5—56° (62·5 g.); (viii) 56—57° (45·5 g.) (pure 1*H*/3*H*-octafluorocyclopentane); (ix) 57—59·2° (31·1 g.); (x) 59·2—63·7° (34·0 g.); (xi) 63·7—68° (34·3 g.); (xii) 68—75·2° (49·5 g.); (xiii) 75·2—77° (33·1 g.); (xiv) 77—80° (62·5 g.); (xv) >80° (65 g.) (by " flash " distillation).

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[15] Hine, Wiesboeck, and Ghirardelli, *J. Amer. Chem. Soc.*, 1961, **83**, 1219; Hine, Wiesboeck, and Ramsay, *ibid.*, p. 1222.

[16] Cristol and Helmreich, *J. Amer. Chem. Soc.*, 1955, **77**, 5034; Cristol and Bly, *ibid.*, 1961, **83**, 4027.

Gas-chromatographic Separation of Distillation Fractions.—Fractions iv, v, vi, vii, xi, xiii, xiv, xv were separated in portions (20—30 g.) by preparative gas chromatography (16′ × 3″ column packed with 1 : 2 dinonyl phthalate–kieselguhr, temp. 60—80°, N_2 flow-rate 40—45 l./hr.). In this way the major products (Table 1) of the fluorination were separated.

Although 1*H*/2*H*-octafluorocyclopentane (V) and the 1*H*,2*H*,4*H*-heptafluorocyclopentane (XVII) were obtained as single components by gas chromatography, nuclear magnetic resonance spectroscopy indicated the presence of a small amount of impurity in the former and elemental analysis revealed an impurity in the latter; this situation might be resolved in future work by using an alternative stationary phase in the gas chromatography column.

Octafluorocyclopentene (III).—(i) *By dehydrofluorination of nonafluorocyclopentane* (II). Nonafluorocyclopentane (9·6 g.), potassium hydroxide (10·4 g.), and water (10 c.c.) were gently refluxed for 3 hr. under both a water and a solid carbon dioxide (−78°) condenser. The product was separated, dried, and distilled to give octafluorocyclopentene (8·1 g.), b. p. 25° (lit.[4] b. p. 25·2°). An absorption peak at 1773 cm.$^{-1}$ in the infrared was ascribed to the –CF=CF– group; there was no absorption characteristic of $\geqslant$CH.

(ii) *By dechlorination of* 1,2-*dichloro-octafluorocyclopentane* (IV). Commercially available 1,2-dichlorohexafluorocyclopentene (200 g.) was fluorinated in the vapour phase over cobalt trifluoride (6·5 kg.) at 180° to give *cis*- and *trans*-1,2-dichloro-octafluorocyclopentane (200 g.), b. p. 85—87° (lit.[4] b. p. 84—85°).

The mixture of *cis*- and *trans*-isomers (2·5 g.) was passed in a stream of nitrogen (1·8 l./hr.) over nickel gauze packed in a nickel tube (1′ × ¾″) maintained at 500°, to give octafluorocyclopentene (1·7 g.). The infrared spectrum was identical with that of the product obtained by dehydrofluorination of nonafluorocyclopentane. No hexafluorocyclopentadiene was detected.

The 1,2-dichloro-octafluorocyclopentanes (90 g.) with zinc dust (100 g.) in ethanol (150 c.c.) under reflux gave octafluorocyclopentene (45·6 g.).

Oxidation of Octafluorocyclopentene (III).—The olefin (2·2 g.), potassium permanganate (5 g.), and water (20 c.c.) were kept in a rocking autoclave at 95° for 17 hr. to give hexafluoroglutaric acid, characterised as the dianilinium salt (2·2 g.), m. p. 219—221° (lit.[7] m. p. 218—220°) (Found: C, 47·6; H, 3·8; F, 26·3. Calc. for $C_{17}H_{16}F_6N_2O_4$: C, 47·9; H, 3·8; F, 26·7%).

1H,2H-*Octafluorocyclopentanes* (V and VI) *from* 1,2-*Dichloro-octafluorocyclopentane* (IV).—1,2-Dichloro-octafluorocyclopentane (105 g.) in ether (50 c.c.) was added during 35 min. to a stirred suspension of lithium aluminium hydride (14 g.) in ether (240 c.c.) at 0°. After 4 hr. the excess of reagent was carefully decomposed with water (50 c.c.) followed by hydrochloric acid (600 c.c., 10% v/v). The ethereal layer was separated and the bulk of the ether removed by fractional distillation (vacuum-jacketed 2′ column packed with glass helices) and the residue (78·4 g.) was shown by analytical gas chromatography to contain three components. The mixture was separated by preparative gas chromatography (nitrogen flow-rate 40 l./hr., temp. 40°) to give (*i*) (±)-1H/2H-*octafluorocyclopentane* (9 g.), b. p. 50° (Found: C, 27·8; H, 0·9. $C_5H_2F_8$ requires C, 28·0; H, 0·9; F, 71·1%); (*ii*) ether; (*iii*) 1H,2H/-*octafluorocyclopentane* (41·6 g.), b. p. 78° (Found: C, 28·0; H, 0·8; F, 70·6%). Compounds (*i*) and (*iii*) were shown to be identical with the 1*H*,2*H*-octafluorocyclopentanes obtained by the cobaltic fluoride fluorination of cyclopentadiene, the first by infrared spectroscopy and analytical gas-chromatographic enrichment and the second by the latter process alone.

Dehydrofluorination of 1H,2H/-*Octafluorocyclopentane* (VI).—The octafluoride, b. p. 78° (16·3 g.), potassium hydroxide (19 g.), and water (20 c.c.) were refluxed for 1 hr. The organic layer (12·4 g.) was separated and analytical gas chromatography indicated 2 components which were separated by preparative gas chromatography (temp. 70°, N_2 flow-rate 44 l./hr.) to give: (*i*) 1H-*heptafluorocyclopentene* (8·5 g.), b. p. 46° (Found: C, 31·4; H, 0·6; F, 69·1. C_5HF_7 requires C, 30·9; H, 0·5; F, 68·6%), $\nu_{max.}$ at 1696 (–CF=CH–) and 3120 cm.$^{-1}$ ($\geqslant$C–H); (*ii*) 3H-*heptafluorocyclopentene* (1·0 g.), b. p. 51° (Found: C, 31·0; H, 0·5; F, 68·4%), $\nu_{max.}$ at 1765 (–CF=CF–) and 2975 cm.$^{-1}$ ($\geqslant$C–H).

Dehydrofluorination of (±)-1H/2H-*Octafluorocyclopentane* (V).—This compound (7 g.) under similar conditions to those used with the 1*H*,2*H*/-isomer gave the same products, *viz.*, 1*H*-heptafluorocyclopentene (4 g.) and 3*H*-heptafluorocyclopentene (0·3 g.); both displayed correct infrared spectra.

Comparative Studies of the Dehydrofluorinations of the 1H,2H-*Octafluorocyclopentanes and the*

1H,2H-*Decafluorocyclohexanes.*—1*H*/2*H*- and 1*H*,2*H*/-Decafluorocyclohexane were prepared by the lithium aluminium hydride reduction of the 1,2-dichlorodecafluorocyclohexanes (75 g.).[9]

The four compounds under examination were each covered with aqueous potassium hydroxide solution (10 c.c.; 10% w/v) at 0° and the mixtures kept under reflux for 20 min. and then rapidly cooled to 0°. The organic layers were then analysed qualitatively by gas chromatography (1 : 2 dinonyl phthalate–kieselguhr, temp. 84°, nitrogen flow-rate 1·45 l./hr.).

1*H*/2*H*-Octafluorocyclopentane and the derived 1*H*-heptafluorocyclopentene had very similar retention times. Infrared analysis of the products was based on the absorption peaks for –CH=CF– (*ca.* 1700 cm.$^{-1}$ in a cyclopentene, *ca.* 1720 cm.$^{-1}$ in a cyclohexene) and for –CF=CF– (*ca.* 1760 cm.$^{-1}$ in a cyclopentene and *ca.* 1750 cm.$^{-1}$ in a cyclohexene). A gas-cell of 10 cm. path-length filled to a pressure of 25 mm. was used. Approximately equal amounts of dehydrofluorination of 1*H*/2*H*- and 1*H*,2*H*/-octafluorocyclopentane and 1*H*,2*H*/-decafluorocyclohexane, and appreciably less with 1*H*/2*H*-decafluorocyclohexane, were observed.

Dehydrofluorinations in Heavy Water.—(i) 1H/2H-*Decafluorocyclohexane.*—This compound (2·8 g.), deuterium oxide (10 g.), and potassium hydroxide (1 g.) were refluxed for 5 min. The mixture was then rapidly cooled to 0° and a vapour sample of the organic phase examined by infrared spectroscopy; this revealed a ⩾C–H stretching frequency at 2975 cm.$^{-1}$ of medium intensity and no peak in the region 2100—2200 cm.$^{-1}$; weak absorptions at 1720 and 1750 cm.$^{-1}$ were ascribed to the fluoro-olefins[17] produced by dehydrofluorination. The mixture was refluxed for a further 15 min. and the measurement repeated but the infrared spectrum was essentially unchanged. A similar result was obtained with the 1*H*,2*H*/-isomer, except that more dehydrofluorination (about 50%) occurred.

(ii) 1H/2H-*Octafluorocyclopentane.* This compound (1·7 g.), deuterium oxide (10 g.), and potassium hydroxide (1 g.) were refluxed for 2·5 min. and then cooled rapidly to 0°. A gas sample of the organic phase displayed infrared absorption of medium intensity at 2970 cm.$^{-1}$ (⩾C–H stretching) and no absorption ascribable to a ⩾C–D stretching between 2000 and 2500 cm.$^{-1}$ Absorptions at 1765 and 1696 cm.$^{-1}$ were produced by fluoro-olefins arising from dehydrofluorination. A completely similar result was given by 1*H*,2*H*/-octafluorocyclopentane.

(iii) 2-*Bromo*-2-*chloro*-1,1,1-*trifluoroethane.* This compound (2 g.), deuterium oxide (10 g.), and potassium hydroxide (1 g.) were refluxed together for 2 hr. and cooled to 0°. A gas sample of the organic phase displayed an infrared absorption peak at 2250 cm.$^{-1}$ (⩾C–D stretching) of medium strength (not present in the starting material) and a very weak absorption at 2990 cm.$^{-1}$ (⩾C–H stretching) present as a peak of medium strength in the starting material.

Oxidation of 1H-*Heptafluorocyclopentene* (IX).—The olefin (0·8 g.), potassium permanganate (1·5 g.), sodium hydrogen carbonate (3·0 g.), and water (100 c.c.) were heated together at 80° for 2 hr. to give hexafluoroglutaric acid which was characterised as the dianilinium salt (0·3 g.), m. p. and mixed m. p. 221° (lit.[7] m. p. 218—220°) (Found: C, 48·0; H, 4·0. Calc. for $C_{17}H_{16}F_6N_2O_4$: C, 47·9; H, 3·8%).

Oxidation of 3H-*Heptafluorocyclopentene* (X).—(a) *Mild conditions.* The olefin (0·5 g.), potassium permanganate (1 g.), sodium hydrogen carbonate (2 g.), and water (40 c.c.) were gently refluxed together for 75 min. to give 2*H*-pentafluoroglutaric acid, characterised as the dianilinium salt, m. p. 183—184° alone and in admixture with a specimen obtained by another route.[6]

The dianilinium salt (0·6 g.) in water with *S*-benzylthiouronium chloride gave ***bis*-S-*benzylthiouronium* 2H-*pentafluoroglutarate*** (0·5 g.), m. p. 176—177° (from water) (Found: C, 45·8; H, 4·2. $C_{21}H_{23}F_5N_4O_4S_2$ requires C, 45·5; H, 4·2%).

(b) *Drastic conditions.* The olefin (1·9 g.), potassium permanganate (15 g.), and water (35 c.c.) were refluxed for 88 hr. to give tetrafluorosuccinic acid. The crude acid in ether was treated with aniline to give dianilinium tetrafluorosuccinate (1·94 g.), m. p. 218—220° (lit.[18] m. p. 224—225°).

The dianilinium salt (2·43 g.) in water with *S*-benzylthiouronium chloride gave bis-*S*-benzylthiouronium tetrafluorosuccinate (0·34 g.), m. p. 188—189° (from water) (lit.[18] m. p. 189—190°) (Found: C, 45·6; H, 4·2. Calc. for $C_{20}H_{22}F_4N_4O_4S_2$: C, 46·0; H, 4·2%).

Dipole-moment Measurements on 1H/2H- *and* 1H,2H/-*Octafluorocyclopentane* (V *and* VI).—These were determined by the standard method from measurements of the dielectric constants of dilute solutions of the compounds in benzene, with correction for the refractive indices of

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[17] Burdon and Whiffen, *Spectrochim. Acta*, 1958, **12**, 139.

[18] Evans and Tatlow, *J.*, 1954, 3779.

the solutions. Dielectric constants were measured by the "Resonance" method in an apparatus similar to that of Bender;[19] the refractive indices were measured by using an Abbé refractometer at 22°. The calculations were carried out by Guggenheim's method.[20] Measurements on the *trans*-octafluoride (b. p. 50°) were made with 6 solutions (1·8—9% by wt.), and for the *cis*-octafluoride (b. p. 78°) with 5 solutions (2·6—8·6%). The dipole moment of the *trans*-octafluoride was 1·15 D, and of the *cis*-octafluoride 2·64 D. Though no great accuracy can be claimed, the results show a clear distinction between the *cis*- and the *trans*-form.

Isolation of the 1H,3H-*Octafluorocyclopentanes* (VII *and* VIII).—Fraction (viii), b. p. 56—57°, from the distillation of the fluorinated cyclopentadiene was (±)-1H/3H-*octafluorocyclopentane* (Found: C, 28·3; H, 0·9; F, 71·1. $C_5H_2F_8$ requires C, 28·0; H, 0·9; F, 71·1%). Fraction (xi), b. p. 63·7—68°, was separated by preparative gas-phase chromatography as mentioned earlier, and gave a heptafluorocyclopentane, b. p. 65° (see later), and 1H,3H/-*octafluorocyclopentane*, b. p. 65° (Found: C, 27·9; H, 1·0%).

Dehydrofluorination of (±)-1H/3H-*Octafluorocyclopentane* (VII).—The octafluoride, b. p. 57·5° (61 g.), potassium hydroxide (70 g.), and water (80 g.) were refluxed for 2·5 hr. The organic product (50 g.) was separated and shown by analytical gas chromatography to contain two components. Separation of the product (29·3 g.) by preparative-scale gas chromatography (temp. 62°, nitrogen flow-rate 44 l./hr.) gave 4H-*heptafluorocyclopentene* (11·8 g.), b. p. 45° (Found: C, 30·8; H, 0·8; F, 68·4. C_5HF_7 requires C, 30·9; H, 0·5; F, 68·6%), and 3*H*-heptafluorocyclopentene (12·5 g.), b. p. 51° (Found: C, 31·0; H, 0·6%); this was identical with the 3*H*-heptafluorocyclopentene, b. p. 51° obtained from the 1*H*,2*H*-octafluorocyclopentanes.

Dehydrofluorination of 1H,3H/-*Octafluorocyclopentane* (VIII).—The octafluoride, b. p. 65° (28 g.), potassium hydroxide (30 g.), and water (30 c.c.) were refluxed together for 2·5 hr. The organic product (24 g.) was separated by preparative gas chromatography (temp. 60°, N_2 flow-rate 45 l./hr.) to give 4*H*-heptafluorocyclopentene (10·1 g.), b. p. 45°, and 3*H*-heptafluorocyclopentene (10·3 g.), b. p. 51°; both displayed correct infrared spectra.

Oxidation of 4H-*Heptafluorocyclopentene* (XI).—The olefin (4 g.), potassium permanganate (7 g.), sodium hydrogen carbonate (15 g.), and water (250 c.c.) were gently refluxed for 75 min. to give a pentafluoroglutaric acid. The crude acid in ether was treated with aniline to give *dianilinium* 3H-*pentafluoroglutarate* (1·8 g.), m. p. 203—204° (from acetone–chloroform) (Found: C, 49·8; H, 4·2; F, 22·75. $C_{17}H_{17}F_5N_2O_4$ requires C, 50·0; H, 4·2; F, 23·3%). The dianilinium salt (0·6 g.) in water with *S*-benzylthiouronium chloride gave *bis*-S-*benzylthiouronium* 3H-*heptafluoroglutarate* (0·55 g.), m. p. 200—201° (from water) (Found: C, 45·3; H, 4·1; F, 17·5. $C_{21}H_{23}F_5N_4O_4S_2$ requires C, 45·5; H, 4·2; F, 17·1%).

When the olefin (1·3 g.), potassium permanganate (10 g.), and water (40 c.c.) were refluxed for 40 hr., 3*H*-pentafluoroglutaric acid was obtained, and identified as the dianilinium salt (0·7 g.), m. p. and mixed m. p. 200—202°.

Synthesis of the 1H,2H,3H-*Heptafluorocyclopentanes* (XIII—XV) *from* 3H-*Heptafluorocyclopentene* (X).—*Chlorination of* 3H-*heptafluorocyclopentene*. The olefin (19·3 g.) and liquid chlorine (25 g.) were irradiated with ultraviolet light for 4 hr. in a quartz flask fitted with a condenser at −78°. The excess of chlorine was removed by washing the products with aqueous sodium hydrogen carbonate (10% w/v). The product (24·5 g.) was dried (P_2O_5) and distilled. Analytical gas chromatography of the distillate showed 3 components none of which was starting material. The infrared spectrum showed no absorption for –C=C– groups.

Reduction of the 1H-2,3-*Dichloroheptafluorocyclopentanes* (XII). This mixture (24 g.) in dry ether (20 c.c.) was added to a stirred suspension of lithium aluminium hydride (5 g.) in dry ether (100 c.c.) at 0°. The apparatus was fitted with a condenser cooled to −78°. After 5 hours' stirring at 15°, unchanged lithium aluminium hydride was destroyed at 0° by the careful addition of water (15 c.c.) followed by hydrochloric acid (300 c.c., 10% v/v) to dissolve the solid. The ethereal layer (68 g.) was distilled through a column (2′ × ¼″) and the residue was shown by gas chromatography to contain four peaks which were separated by using this technique on a preparative scale (temp. 70°, N_2 flow-rate 44 l./hr.) to give: (i) ether; (ii) 1H,3H/2H-*heptafluorocyclopentane* (1·7 g.), b. p. 65°; (iii) (±)-1H,2H/3H-*heptafluorocyclopentane* (2·4 g.), b. p. 84° (Found: C, 30·4; H, 1·7. $C_5H_3F_7$ requires C, 30·6; H, 1·5%); (iv) 1H,2H,3H/-*heptafluorocyclopentane* (5·9 g.), b. p. 135° (Found: C, 31·0; H, 1·7%). The b. p.s were measured by "flash" distillation. The product (ii) displayed an infrared spectrum

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[19] Bender, *J. Chem. Educ.*, 1946, **23**, 179.

[20] Guggenheim, *Trans. Faraday Soc.*, 1951, **47**, 573.

identical with that of the heptafluorocyclopentane, b. p. 65°, isolated previously from the cobalt trifluoride fluorination of cyclopentadiene (Found: C, 30·7; H, 1·5; F, 68·3. $C_5H_3F_7$ requires C, 30·6; H, 1·5; F, 67·9%).

Fluorination of 1H,3H/2H-*Heptafluorocyclopentane* (XIII).—1*H*,3*H*/2*H*-Heptafluorocyclopentane (7 g.) was added during 7 min. into a small static cobalt trifluoride reactor[10] at 180°. After a further 10 min. the reactor was flushed with nitrogen (2 l./hr.). The products were collected in a copper trap at −78°. The contents of the trap were poured into ice–water and washed with a solution of sodium hydrogen carbonate to give a clear liquid (4·5 g.) which was shown by analytical gas chromatography to contain 5 components which were identified, by enrichment of the mixture with authentic specimens, as decafluorocyclopentane, nonafluorocyclopentane, 1*H*/2*H*-octafluorocyclopentane, 1*H*,3*H*/2*H*-heptafluorocyclopentane, and 1*H*,3*H*/octafluorocyclopentane. A portion (7·5 μl.) of the latter mixture was separated by gas chromatography (6′ × ½″ column packed with dinonyl phthalate–Celite at 92°, N_2 flow-rate 1·2 l./hr.) and the above components were collected in small glass traps at −180°; they all displayed the correct infrared spectra.

The authors thank Professor M. Stacey, F.R.S., for his interest, Dr. L. F. Thomas for nuclear magnetic resonance spectroscopy measurements, and British Nylon Spinners for a scholarship (to R. J. H.).

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[*Received, March* 29*th*, 1962.]