438. *Fluorocyclopentanes. Part III.*[1] *The Isomeric* 1H:2H:3H- *and* 1H:2H:4H-*Heptafluorocyclopentanes and the* 1H:2H:3H:4H-*Hexafluorocyclopentanes*

By J. Burdon, T. M. Hodgins, R. Stephens, and J. C. Tatlow

The three *1H:2H:3H*- and the three *1H:2H:4H*-heptafluorocyclopentanes have been prepared by addition of chlorine to *2H*- and *3H*-heptafluorocyclopentene, respectively, followed by lithium aluminium hydride reduction. Five of the six *1H:2H:3H:4H*-hexafluorocyclopentanes have been prepared similarly from *3H,4H*/- (VII) and *3H*/*4H*- hexafluorocyclopentene (XII). Stereochemical allocations were determined by mild fluorination with cobalt trifluoride to give the known octafluorocyclopentanes. Dehydrofluorination of the isomers to give fluoro-olefins followed the pattern established in previous work, *i.e.*, that in fluorocyclopentanes elimination can occur when the hydrogen and fluorine are located either *trans* or *cis*. The latter disposition gives rather less ready elimination.

In Part I of this Series[2] we described the fluorination of cyclopentadiene over cobalt trifluoride and the isolation and proof of structure of *1H*/*2H*-, *1H*,/*2H*-, *1H*/*3H*-, and *1H,3H*/-octafluorocyclopentanes. The preparation of all three *1H:2H:3H*-heptafluorocyclopentanes was also described, but only the *1H,3H*/*2H*-isomer (I) was characterised. We have now confirmed that the structures of the other two isomers were, in fact, as allocated in Part I[2] from the Auwers–Skita rule[3] and their relative gas-chromatographic retention times. Further, all the *1H:2H:4H*-hepta- and five of the six *1H:2H:3H:4H*-hexa-fluorocyclopentanes have been prepared and characterised. The synthetic routes were as before,[2] chlorine addition to suitable olefins, followed by reduction with lithium aluminium hydride, as indicated in Figure 1. These polyfluorocyclopentanes were required both for the dehydrofluorination studies reported in this Paper and for reference purposes in relation to the products of fluorination of cyclopentane.

The gross structures of the trihydro-isomers were known from their synthesis, and more information was obtained by mild fluorination[2,4] over cobalt trifluoride to known[2] dihydro-isomers. In this way, the *1H,3H*/*2H*-isomer (I) had been characterised previously[2] by conversion into *1H*/*2H*- and *1H,3H*/-octafluorocyclopentane. However, in the present work, the *1H,2H*/*3H*-isomer (II) gave on fluorination only *1H*/*2H*- and *1H*/*3H*-octafluorocyclopentane; none of the third expected product, the *1H,2H*/-compound, could be detected. Thus, the *1H,3H*/*2H*- and *1H,2H*/*3H*-isomers (I and II) could not be distinguished in this way, and the earlier structure allocations[2] for (I) and for the *1H:3H*-octafluorides were not conclusive. The evidence is, however, sufficient to identity the isomers (I) and (II) as a pair (since these two only can give the known[2] *1H*/*2H*-octafluoride) and hence the remaining *1H:2H:3H*-isomer has to be the all *cis*-compound (III). Fluorination of this isomer (III) gave the known[2] *1H,2H*/-octafluorocyclopentane and a *1H:3H*-isomer, which can therefore only have the *cis*-configuration. This *1H,3H*/-octafluorocyclopentane was identical with the *1H,3H*/-isomer obtained[2] from the fluorination of *1H,3H*/*2H*-heptafluorocyclopentane and hence the previous[2] structure allocations for this isomer (I) and for the *1H:3H*-octafluorides were, in fact, correct.

Also, the *1H,2H*/*3H*-isomer (II) is the only *1H:2H:3H*-compound that can arise from the mild fluorination of both *1H,2H,4H*/*3H*- and *1H,2H,3H*/*4H*-hexafluorocyclopentane (VIII and X). As these compounds were known unambiguously as a pair (see later), this provides further evidence for the structures of the isomers (I) and (II).

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[1] Part II, Burdon, Hodgins, Perry, Stephens, and Tatlow, *J.*, 1965, 808.

[2] Heitzman, Patrick, Stephens, and Tatlow, *J.*, 1963, 281.

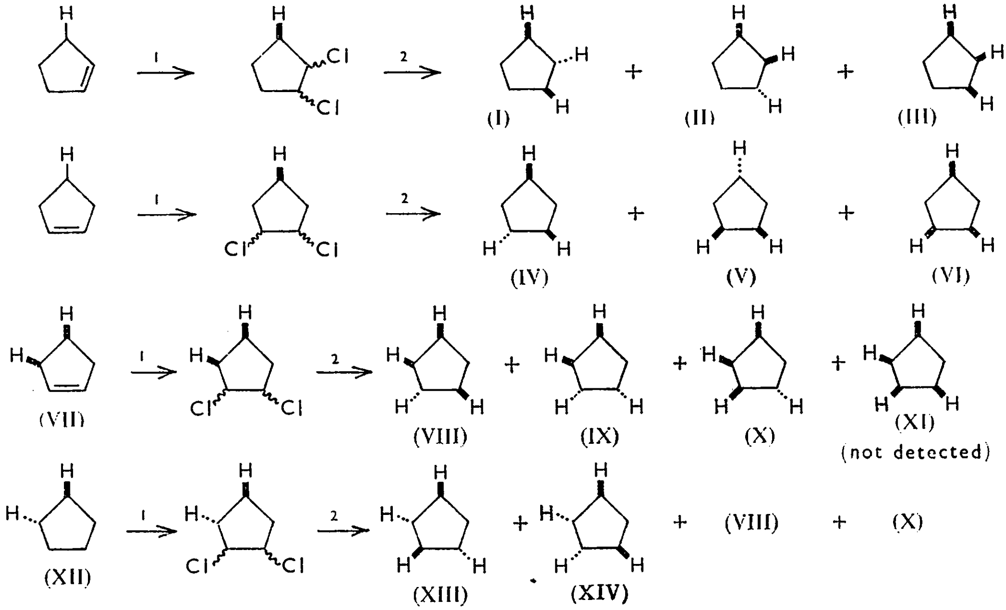
[3] Auwers, *Annalen*, 1920, **420**, 84; Skita, *Ber.*, 1920, **53**, 1792; Allinger, *Experientia*, 1954, **10**, 328; van Bekkum, van Veen, Verkade, and Wepster, *Rec. Trav. Chem.*, 1961, **80**, 1310.

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

The 1*H*:2*H*:4*H*-compounds (IV—VI) were made from 4*H*-heptafluorocyclopentene, and their stereochemistry was established straightforwardly, since in these cases all the expected dihydroisomers were formed on fluorination, although the amounts of the 1*H*,2*H*/- and 1*H*,3*H*/-isomers, the former particularly, were always much less than the 1*H*/2*H*- and 1*H*/3*H*-compounds. Compound (IV) gave 1*H*/2*H*-, 1*H*/3*H*-, and 1*H*,3*H*/-octafluorides, and was therefore 1*H*,4*H*/2*H*-heptafluorocyclopentane; compound (V) afforded the 1*H*,2*H*/- and 1*H*/3*H*-octafluorides, and was therefore the 1*H*,2*H*/4*H*-heptafluoride; compound (VI) was fluorinated to the 1*H*,2*H*/- and 1*H*,3*H*/-octafluorides and was therefore 1*H*,2*H*,4*H*/-heptafluorocyclopentane. These results are entirely in accord with, and therefore confirm, the previous allocations, *e.g.*, only two trihydro-compounds (VI) and (III) can be fluorinated to the same two dihydro-compounds. Thus, the structure determinations for the whole series of compounds are inter-related, making a self-consistent pattern.

Five 1*H*:2*H*:3*H*:4*H*-hexafluorocyclopentanes (VIII—XIV) were made by the addition of chlorine to 3*H*,4*H*/- (VII) and 3*H*/4*H*-hexafluorocyclopentene (XII) followed by reduction. Olefins (VII) and (XII) were made by dehydrofluorination of suitable heptafluorocyclopentanes (see later). Only three 1*H*:2*H*:3*H*:4*H*-hexafluorides (VIII, X, XIII) were made in quantities sufficient for satisfactory structural investigations. The missing isomer (XI) could have been formed in small amount, since its gas-chromatographic retention time would be expected [2,4,5] to be very long and this was the only isolation technique employed.

(All unmarked bonds are attached to fluorine)



Reagents: 1, $Cl_2/h\nu$; 2, $LiAlH_4$

FIGURE 1*

Only the 1*H*,2*H*,4*H*/3*H*- (VIII) and 1*H*,2*H*,3*H*/4*H*-isomers (X) can be formed from both olefins (VII and XII) (Figure 1); two compounds were, in fact, common to both

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* In all the formulæ in this Paper, only substituents other than fluorine are indicated. The thick lines denote substituents in front of the ring plane, dotted lines those behind it, and wavy lines those of unknown configuration relative to it, as is usual in alicyclic chemistry.

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

routes and they were differentiated by mild fluorination. That they were the pair needed to confirm the structures of the trihydro-compounds (I and II) was established by the number of trihydro-fluorination products isolated (four from one and three from the other); all other 1*H*:2*H*:3*H*:4*H*-hexafluorides can only give two. The fluorination products of compound (VIII) were the 1*H*/2*H*-, 1*H*/3*H*-, and 1*H*,3*H*/-octafluorides and the trihydro-compounds (I), (II), (IV), and (VI), and therefore it could only be 1*H*,2*H*,4*H*/3*H*-hexafluorocyclopentane, even though the 1*H*,2*H*/-octafluoride, also expected, was missing. Compound (X) gave 1*H*/2*H*-, 1*H*/3*H*-, and 1*H*,3*H*/-octafluorocyclopentane and the heptafluorides (II), (IV), and (V); it must therefore be the 1*H*,2*H*,3*H*/4*H*-isomer, although again the expected 1*H*,2*H*/-octafluoride was missing, as was also the 1*H*,2*H*,3*H*/-heptafluoride (III).

One of the other two products of the synthesis from 3*H*/4*H*-hexafluorocyclopentene (XII) was 1*H*,3*H*/2*H*,4*H*-hexafluorocyclopentane (XIII); in this case, all the expected dihydro-(1*H*/2*H*-, 1*H*/3*H*-, and 1*H*,3*H*/-) and trihydro- (I and IV) isomers were formed on mild fluorination. The remaining product from the synthesis from olefin (XII) was present in only trace amounts, but it could only have been 1*H*,4*H*/2*H*,3*H*-hexafluorocyclopentane (XIV). Its gas-chromatographic retention time [greater than (XIII) and less than (VIII)] was consistent [2,4,5] with this structure.

Besides the tetrahydro-isomers (VIII) and (X), only one other compound was isolated from the synthesis from 3*H*,4*H*/-hexafluorocyclopentene (VII). It was present only in trace amounts, and so has been assigned the structure 1*H*,2*H*/3*H*,4*H*-hexafluorocyclopentane (IX) solely on the basis of its gas-chromatographic retention time [greater than (VIII), less than (X)]; the only other possible compound, 1*H*,2*H*,3*H*,4*H*/-hexafluorocyclopentane (XI), would be expected [2,4,5] to have a very much greater retention time.

The syntheses of the hexafluorocyclopentanes differed from those of the heptafluorocyclopentanes in that widely different amounts of the various isomers were formed; in both trihydro-series all the possible isomers were formed in roughly comparable amounts.[2] At this stage, we are not able to explain this; other work has shown that neither chlorine addition [2] to cyclic fluoro-olefins, nor reduction [6] of polyfluorochlorocyclopentanes with lithium aluminium hydride, is stereospecific.

The structural allocations of all the hepta- and hexa-fluorocyclopentanes discussed in this Paper agree with the Auwers–Skita rule [3] and with relative gas-chromatographic retention times.[2,4,5]

If the mild fluorination of a trihydro-isomer were random, then the possible dihydro-compounds would be formed in equal amounts. As mentioned previously, this is clearly not so, and therefore the hydrogens of the trihydro-isomers are fluorinated at different rates. However, since nona- and, in some cases, deca-fluorocyclopentane were also formed, this conclusion is not always clear-cut; the dihydro-compounds might be formed in equal amounts, but be themselves fluorinated further at unequal rates. Thus, no 1*H*,2*H*/-octafluorocyclopentane was formed in the fluorination of 1*H*,2*H*/3*H*-heptafluorocyclopentane (II), but the amounts of nona- and deca-fluorocyclopentane considerably exceeded the combined amounts of 1*H*/2*H*- and 1*H*/3*H*-octafluorocyclopentane; either no 1*H*,2*H*/-isomer was formed, or it was fluorinated much more rapidly than the 1*H*/2*H*- and 1*H*/3*H*-isomers. With 1*H*,2*H*/4*H*-heptafluorocyclopentane (V), however, the ratio of 1*H*/3*H*- to 1*H*,2*H*/-octafluorocyclopentane was 12 : 1, and even if all the nonafluorocyclopentane (there was no decafluorocyclopentane) had come from the 1*H*,2*H*/-compound, the ratio would still be over two. We therefore conclude from these and the other two relevant fluorinations [2] that in the fluorination of 1*H*:2*H*:3*H*- and 1*H*:2*H*:4*H*-heptafluorocyclopentanes, one of the two hydrogens on the same side of the ring is replaced by fluorine in preference to the one on the other side.

With the 1*H*:2*H*:3*H*:4*H*-hexafluorocyclopentanes, the fluorination results are even

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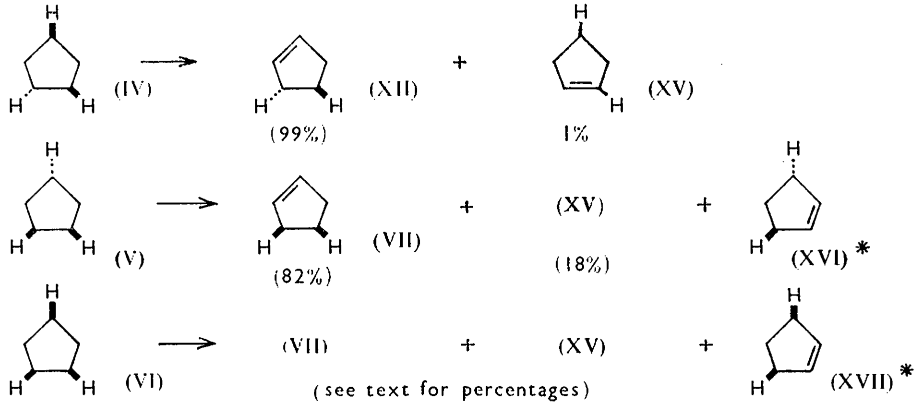
[6] Lancashire, Perry, Stephens, and Tatlow, unpublished work.

more ambiguous. Nevertheless, it is clear that in the two compounds [(VIII) and (X)], in which there are three hydrogens on one side of the ring and one on the other, the fluorinating agent shows more than the statistical three-to-one preference for one of the three.

In previous work on the dehydrofluorinations of polyfluorocyclohexanes with aqueous alkali, three factors have been found to determine which hydrogen and which fluorine are lost [4,7,8] preferentially. They are: (i) the most acidic hydrogen, the one surrounded by most fluorines, is eliminated preferentially; (ii) fluorine is eliminated more readily from $>$CHF groups than from $>CF_2$; and (iii) *trans*-elimination of hydrogen fluoride is much more facile than *cis*. In Part I of this Series [2] we showed that in 1*H*:2*H*-octafluorocyclopentanes the second proviso applied but that the third apparently did not; *cis*- and *trans*-elimination of hydrogen fluoride proceeded at very similar rates. We have now shown that all three factors apply in the polyfluorocyclopentane field, but that *trans*-elimination is preferred to *cis* to only a slight degree. Our results are summarised in Figures 2, 3, and 4.

(All unmarked bonds are attached to fluorine)



(see text for percentages)

* Not proved to be present.

FIGURE 2. Dehydrofluorination of 1*H*:2*H*:4*H*-heptafluorocyclopentanes

The identification of the olefin (XV) from the 1*H*,4*H*/2*H*-isomer (IV) was very tentative. In the dehydrofluorination of the 1*H*,2*H*,4*H*/-compound (VI) an accurate assessment of the relative amounts of the two olefins [(VII) and (XV)] could not be obtained, since the first had the same gas-chomatographic retention time as starting material; more 1*H*:4*H*-hexafluorocyclopentene (XV) was, however, undoubtedly present than in the 1*H*,2*H*/4*H*-case (V).

In each dehydrofluorination there was a clear preference for the most acidic hydrogen to be eliminated; this preference is strongest with compound (IV), where the next most favourable elimination (fluorine from the $>$CHF group) had to be *cis*. *trans*-Elimination is therefore favoured over *cis* in the 1*H*:2*H*:4*H*-compounds. Eliminations in which the least acidic hydrogens and a fluorine from a $>CF_2$ group are removed could not be properly established, although in the dehydrofluorinations of the 1*H*,2*H*/4*H*- and 1*H*,2*H*,4*H*/-isomers trace amounts of two other compounds were detected, and these could have been the olefins (XVI) and (XVII), respectively.

1*H*:4*H*-Hexafluorocyclopentene (XV) gave approximately equal amounts of 1*H*/3*H*- and 1*H*,3*H*/-octafluorocyclopentane on mild fluorination over cobalt trifluoride. Further confirmation of the structure was provided by infrared spectroscopy (CH=CF bond) and by oxidation to the known [2] 3*H*-pentafluoroglutaric acid with permanganate.

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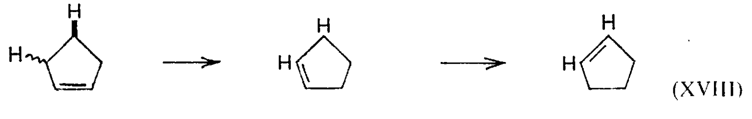
[7] Smith and Tatlow, *J.*, 1957, 2505.
[8] Stephens, Tatlow, and Wiseman, *J.*, 1959, 148.

3H/*4H*- (XII) and *3H*,*4H*/-hexafluorocyclopentene (VII) gave different *2H*:*3H*-tetrafluoroglutaric acids on oxidation with permanganate. On fluorination, however, both 1*H*/2*H*- and 1*H*,2*H*/-octafluorocyclopentane were isolated from each isomer; the *trans*-compound (XII) gave 1*H*:2*H*-octafluorocyclopentene (XVIII)[9] as well, and several more components in amounts too small to be identified were detected from both isomers. This loss of configuration probably occurs through migration of the double bonds around the ring; such migrations have been observed before[8] during the fluorination of polyfluorocyclohexadienes over cobalt trifluoride. Fluorination of either migration product would give both the 1*H*/2*H*- and the 1*H*,2*H*/-isomers.

(Unmarked bonds are joined to flourine)



Since only 1*H*:2*H*-isomers were formed, however, the structure determinations of the two 3*H*:4*H*-olefins [(VII) and (XII)] were not invalidated.

The most favoured aqueous alkaline dehydrofluorination product from all three 1*H*:2*H*:3*H*-heptafluorocyclopentanes is 1*H*:5*H*-hexafluorocyclopentene (XIX); the "outside" hydrogen is the most acidic and the fluorine from the $>$CHF group the most easily

(All unmarked bonds are attached to fluorine)

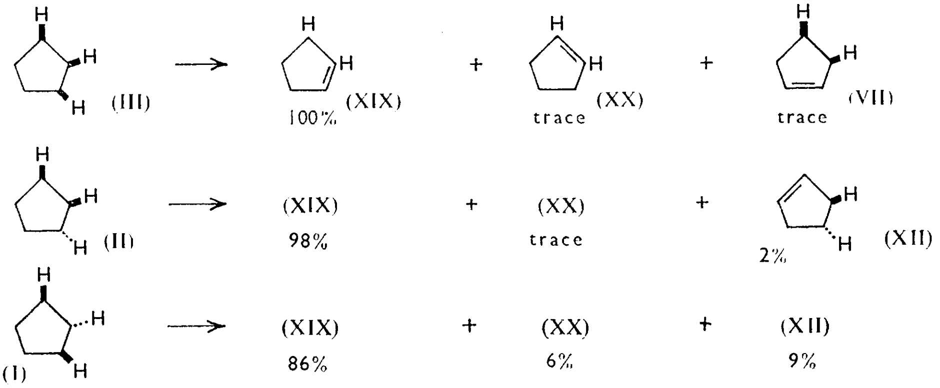


Figure 3. Dehydrofluorination of 1*H*:2*H*:3*H*-heptafluorocyclopentanes

removed. Again, this preference is most marked when this elimination is *trans*; when it is *cis* more elimination of fluorine from the $>CF_2$ group takes place. There is too little of the minor components present for their relative amounts to be discussed, particularly as in each case some (uninvestigated) water-soluble substances must also be formed in order to account for loss of material.

Only one of the two new olefins (XIX and XX) encountered here has been investigated structurally. 1*H*:5*H*-Hexafluorocyclopentene (XIX) gave the known[2,10] 2*H*-pentafluoroglutaric acid on oxidation with permanganate, and both 1*H*/2*H*- and 1*H*,2*H*/-octafluorocyclopentane on mild fluorination with cobalt trifluoride. The identification of the other olefin, 1*H*:3*H*-hexafluorocyclopentane (XX) (there was insufficient material for either an oxidation or a fluorination) rests on elemental analysis, infrared spectroscopic indication of a CH=CF bond, and a mass spectrum consistent with the structure. Further, it is the

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[9] Perry, M.Sc. Thesis, University of Birmingham, 1962.

[10] Barbour, McKenzie, Stacey, and Tatlow, *J. Appl. Chem.*, 1954, **4**, 341.

only olefin, apart from the 1*H*:5*H*-isomer (XIX), that can be formed from all three 1*H*:2*H*:3*H*-compounds.

(All unmarked bonds are attached to fluorine)

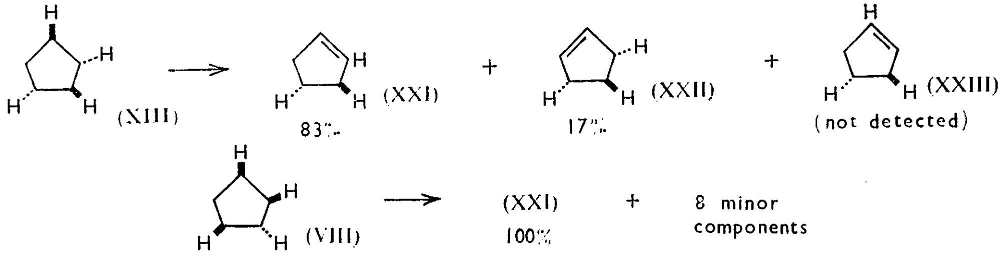

FIGURE 4. Dehydrofluorination of 1*H*:2*H*:3*H*:4*H*-hexafluorocyclopentanes

Only two of the tetrahydro-isomers have been dehydrofluorinated by treatment with aqueous alkali. The structures of the two new olefins obtained have not been established rigidly. Infrared spectroscopy indicated that the major product was the same in each case, and that it contained a CH=CF bond. Only two olefins that contain a CH=CF bond can be formed from both substrates; 1*H*:4*H*/5*H*- (XXI) and 1*H*:3*H*/4*H*-pentafluorocyclopentene (XXIII). We reject the latter, because it would involve the formation of the major product by loss of a less acidic hydrogen, in contradiction of all our previous results. The other new olefin has been assigned the structure 3*H*,5*H*/4*H*-pentafluorocyclopentene (XXII) on the basis of its elemental analysis and infrared spectrum, which indicated a CF=CF bond. It is the only olefin with a CF=CF bond derivable from compound (XIII). If these assignments are correct, then the hexafluorides provide a third set of polyfluorocyclopentanes in which *trans*-elimination of hydrogen fluoride occurs more readily than *cis*. In all three series, however, the preference was not as marked as with the polyfluorocyclohexanes [7,8,11] in accordance with work [12] on non-fluorinated cyclohexanes and cyclopentanes. As we pointed out in Part I,[2] a *cis*-elimination from a cyclopentane means that there is a coplanar arrangement in the H·C–C·F system from which elimination is occurring, and also that the groups to become vinylic are coplanar with the carbons. This cannot happen with a chair form of a cyclohexane but can with a boat form.

In no dehydrofluorination was any polyfluorocyclopentadiene isolated, and in every case there was some loss of fluorohydrocarbon into the aqueous alkali. Cyclopentadienes were probably formed in all the dehydrofluorinations, but, as suggested [2] in Part I, they would be expected to be decomposed by the aqueous alkali to give water-soluble products. The two trace products, both with very short gas-chromatographic retention times, from the dehydrofluorination of 1*H*,3*H*/2*H*-heptafluorocyclopentane (I) might, however, have been cyclopentadienes. Aqueous alkali would, of course, have been a poor choice of reagent had we intended primarily to prepare cyclopentadienes. We have, in fact, shown [1] in Part II that solid potassium hydroxide is a satisfactory reagent for the preparation of hexafluorocyclopentadiene from either 3*H*- or 4*H*-heptafluorocyclohexene; its use could probably be extended to the less highly fluorinated olefins described in this Paper.

EXPERIMENTAL

Reduction of the 1H-3,4-*Dichloroheptafluorocyclopentanes*.—The mixed cyclopentanes [1] (13·0 g.) in dry ether (100 ml.) were added over 2 hr. to a stirred solution of lithium aluminium hydride (2·0 g.) in dry ether (200 ml.) at 0°. The reaction mixture was stirred for a further 2 hr., and then the excess of lithium aluminium hydride was destroyed in the usual way with 50% sulphuric acid. Distillation of the dried ($MgSO_4$) ether layer through a 6 in. column

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[11] Godsell, Stacey, and Tatlow, *Tetrahedron*, 1958, **2**, 193; Nield, Stephens, and Tatlow, *J.*, 1959, 159.

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

packed with glass helices left a residue, which was shown by gas chromatography to contain four peaks that were separated by this technique on a preparative scale [column 4·8 m. × 35 mm. diam., packed with dinonyl phthalate–kieselguhr (1 : 2); temp. 98° N_2 flow-rate 11 l./hr.] to give (i) ether; (ii) 1H,4H/2H-*heptafluorocyclopentane* (IV) (2·3 g.), b. p. 78° (Found: C, 30·4; H, 1·3. $C_5H_3F_7$ requires C, 30·6; H, 1·5%); (iii) 1H,2H/4H-*heptafluorocyclopentane* (V) (1·9 g.), b. p. 94° (Found: C, 30·5; H, 1·4%); and (iv) 1H,2H,4H/-*heptafluorocyclopentane* (VI) (2·3 g.), b. p. 115° (Found: C, 30·7; H, 1·7%).

Fluorination of the Isomeric Heptafluorocyclopentanes.—Each compound was fluorinated by introducing it during *ca.* 10 min. in a stream of nitrogen (2—3 l./hr.) into a small static cobalt trifluoride reactor [4] at 180°. The products were flushed out of the reactor for *ca.* 3 hr. with nitrogen (2—3 l./hr.) and collected in a cooled (−78°) trap. The contents of the trap were poured into ice–water and the fluorohydrocarbon layer was separated into its components by preparative-scale gas chromatography (same column as in the previous experiment; temp. and flow-rate stated in each case). All the components were identified by comparison of their infrared spectra with those of authentic specimens.[2]

(*a*) 1H,4H/2H-*Heptafluorocyclopentane* (IV). This compound (2·0 g.) gave mixed fluorohydrocarbons (1·6 g.), which were separated into (temp. 96°; N_2 flow-rate 16 l./hr.) perfluorocyclopentane (trace), nonafluorocyclopentane (0·3 g.), 1*H*/2*H*-octafluorocyclopentane (0·2 g.), 1*H*/3*H*-octafluorocyclopentane (0·4 g.), 1*H*,3*H*/-octafluorocyclopentane (0·1 g.), and unchanged 1*H*,4*H*/2*H*-heptafluorocyclopentane (IV) (0·2 g.).

(*b*) 1H,2H/4H-*Heptafluorocyclopentane* (V). This compound (2·0 g.) yielded mixed fluorocarbons (1·3 g.) which were separated (temp. 98°; N_2 flow-rate 16 l./hr.) into nonafluorocyclopentane (0·2 g.), 1*H*/3*H*-octafluorocyclopentane (0·6 g.), 1*H*,2*H*/-octafluorocyclopentane (*ca.* 0·05 g.), and unchanged 1*H*,2*H*/4*H*-heptafluorocyclopentane (V) (*ca.* 0·1 g.).

(*c*) 1H,2H,4H/-*Heptafluorocyclopentane* (VI). Mixed fluorohydrocarbons (0·5 g.) were obtained by fluorination of this compound (1·0 g.). They were separated (temp. 100°; N_2 flow-rate 12 l./hr.) into nonafluorocyclopentane (0·2 g.) and 1*H*,3*H*/-octafluorocyclopentane (0·1 g.): 1*H*,2*H*/-octafluorocyclopentane and the starting material were also indicated by analytical gas chromatography, but only in trace amounts, and they were not isolated.

(*d*) 1H,2H/3H-*Heptafluorocyclopentane* (II). Separation (temp. 102°; N_2 flow-rate 19 l./hr.) of the mixed fluorohydrocarbons (1·3 g.) from the fluorination of this compound (2·0 g.) gave perfluorocyclopentane (0·1 g.), nonafluorocyclopentane (0·6 g.), 1*H*/2*H*-octafluorocyclopentane (0·1 g.) and 1*H*/3*H*-octafluorocyclopentane (0·2 g.).

(*e*) 1H,2H,3H/-*Heptafluorocyclopentane* (III) [With A. Bergomi]. This compound (3·0 g.) yielded mixed fluorohydrocarbons (1·8 g.) which were separated (temp. 90°; N_2 flow-rate 19 l./hr.) into nonafluorocyclopentane (0·2 g.), 1*H*,3*H*/-octafluorocyclopentane (0·5 g.) and 1*H*,2*H*/-octafluorocyclopentane (0·3 g.).

Dehydrofluorination of 1H,4H/2H-*Heptafluorocyclopentane* (IV).—The trihydro-compound (52·2 g.) was refluxed with a solution of potassium hydroxide (64·5 g.) in water (120 ml.) for 50 min. Analytical gas chromatography indicated that the organic phase (46·3 g.) contained two components, which were separated by preparative gas chromatography [column 4·8 m. × 75 mm. dia., packed with dinonyl phthalate–kieselguhr (1 : 2); temp. 100°; N_2 flow-rate 50 l./hr.]. They were (i) 3H/4H-*hexafluorocyclopentene* (XII) (27·4 g.), b. p. 68° (Found: C, 34·2; H, 1·2. $C_5H_2F_6$ requires C, 34·1; H, 1·1%), $\nu_{max.}$ at 1760 cm.$^{-1}$ (CF=CF); [13] and (ii) unchanged 1*H*,4*H*/2*H*-heptafluorocyclopentane (IV) (6·0 g.). Infrared spectroscopy indicated that the latter compound was contaminated with a small amount (<5%) of an unsaturated impurity [$\nu_{max.}$ at 1705 cm.$^{-1}$ (CH=CF) [13]].

Fluorination of 3H/4H-*Hexafluorocyclopentene* (XII).—This olefin (1·0 g.) was fluorinated in the small static cobalt trifluoride reactor at 200°, as described before, to give a product mixture (0·8 g.), which was separated by gas chromatography (35 mm. dia. column; temp. 100°; N_2 flow-rate 15 l./hr.) into nonafluorocyclopentane (0·1 g.), 1*H*/2*H*-octafluorocyclopentane (0·4 g.), 1*H*:2*H*-hexafluorocyclopentene [9] (trace), and 1*H*,2*H*/-octafluorocyclopentane (0·1 g.). The saturated compounds [2] were identified by infrared spectroscopy and the olefin by comparison of its gas-chromatographic retention time with that of an authentic specimen.[7] Two other components were also present but in amounts too small to be isolated.

Oxidation of 3H/4H-*Hexafluorocyclopentene* (XII).—Aqueous potassium permanganate

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

(250 ml., 4·5% w/w) was added to a rapidly stirred suspension of the olefin (6·4 g.) in 0·8N-sulphuric acid (375 ml.) at *ca.* 18°. An exothermic reaction occurred and, after 2 hr. stirring, the reaction mixture was decolourised with sulphur dioxide and the acid product isolated by ether extraction. The crude acid in ether was treated with aniline to give *dianilinium* (±)-threo-2H,3H-*tetrafluoroglutarate* (9·1 g.) m. p. 160°. The pure salt had m. p. 163—164° (from acetone–chloroform) (Found: C, 52·6; H, 4·5. $C_{17}H_{18}F_4N_2O_4$ requires C, 52·3; H, 4·6%). The dianilinium salt (1·0 g.) in water with *S*-benzylthiuronium chloride gave *bis*-S-*benzylthiuronium* (±)-threo-2H,3H-*tetrafluoroglutarate* (0·3 g.) (from water), m. p. 180° (Found: C, 47·4; H, 4·5. $C_{21}H_{24}F_4N_4O_4S_2$ requires C, 47·0; H, 4·5%).

Dehydrofluorination of 1H,2H/4H-*Heptafluorocyclopentane* (V).—The trihydro-compound (3·9 g.) was shaken at *ca.* 18° with a solution of potassium hydroxide (2·7 g.) in water (50 ml.) for 130 min. Analytical gas chromatography indicated that the organic phase (2·8 g.) contained three major and one minor component; these were separated by gas chromatography (35 mm. dia. column; temp. 103°; N_2 flow-rate 18 l./hr.) and were (i) 1H:4H-*hexafluorocyclopentene* (XV) (0·2 g.), b. p. 66° (Found: C, 33·8; H, 1·4. $C_5H_2F_6$ requires C, 34·1; H, 1·1%), $\nu_{max.}$ at 1700 cm.$^{-1}$ (CH=CF);[13] (ii) unknown substance (trace); (iii) unchanged 1*H*,2*H*/4*H*-heptafluorocyclopentane (V) (0·2 g.), identified by infrared spectroscopy; and (iv) 3H,4H/-*hexafluorocyclopentene* (VII) (0·9 g.), b. p. 104° (Found: C, 34·2; H, 1·2%), $\nu_{max.}$ at 1780 cm.$^{-1}$ (CF=CF).[13]

Fluorination of 1H:4H-*Hexafluorocyclopentene* (XV).—This olefin (1·0 g.) was fluorinated in a stream of nitrogen at 120° in a small stirred cobalt trifluoride reactor (48 cm. long × 5 cm. diam., containing *ca.* 150 g. of cobalt trifluoride) in the usual way. Separation of the product mixture (0·8 g.) by gas chromatography (35 mm. dia. column; temp. 100°; N_2 flow-rate 13 l./hr.) yielded nonafluorocyclopentane (trace), 1*H*/3*H*-octafluorocyclopentane (0·2 g.), and 1*H*,3*H*/-octafluorocyclopentane (0·15 g.), all identified by infrared spectroscopy.[2]

Oxidation 1H:4H-*Hexafluorocyclopentene* (XV).—The olefin (0·2 g.) was oxidised [14] with potassium permanganate (0·5 g.) in acetone (50 ml.) and the product acid isolated as its dianilinium salt. It was dianilinium 3*H*-pentafluoroglutarate (0·11 g.), m. p. 200° (lit.,[2] m. p. 203—204°), identified by infrared spectroscopy. This dianilinium salt was converted into bis-*S*-benzylthiuronium 3*H*-pentafluoroglutarate, m. p. 196° (from water) (lit.,[2] m. p. 200—201°) (Found: C, 45·6; H, 3·9. Calc. for $C_{21}H_{23}F_5N_4O_4S_2$: C, 45·5; H, 4·2%).

Fluorination of 3H,4H/-*Hexafluorocyclopentene* (VII).—Fluorination of the olefin (1·0 g.) in the small stirred cobalt trifluoride reactor at 130° gave, after gas-chromatographic separation (35 mm. dia. column; temp. 100°; N_2 flow-rate 15 l./hr.) of the product (0·8 g.), nonafluorocyclopentane (0·3 g.), 1*H*/2*H*-octafluorocyclopentane (0·1 g.), and 1*H*,2*H*/-octafluorocyclopentane (0·1 g.), all identified by infrared spectroscopy.[2] Analytical gas chromatography showed the presence of seven other components, but their amounts were too small to be isolated by the preparative technique.

Oxidation of 3H,4H/-*Hexafluorocyclopentene* (VII).—This olefin (3·1 g.) was oxidised by the permangante (200 ml., 3% w/w)/sulphuric acid (200 ml., 2N) procedure as described for 3*H*/4*H*-hexafluorocyclopentene (XII). The crude dianilinium salt (4·8 g.) had m. p. 158—160°; recrystallisation from acetone–chloroform gave pure *dianilinium* (±)-erythro-2H,3H-*tetrafluoroglutarate*, m. p. 164—165° (Found: C, 52·4; H, 4·4. $C_{17}H_{18}F_4N_2O_4$ requires C, 52·3; H, 4·6%). The crude dianilinium salt was converted into *bis*-S-*benzylthiuronium* (±)-erythro-2H,3H-*tetrafluoroglutarate*, m. p. 191° (from water) (Found: C, 46·9; H, 4·4. $C_{21}H_{24}F_4N_4O_4S_2$ requires C, 47·0; H, 4·5%).

Dehydrofluorination of 1H,2H,4H/-*Heptafluorocyclopentane* (VI).—The trihydro-compound (7·7 g.) was shaken with aqueous potassium hydroxide (5 g. in 25 ml.) at *ca.* 18° for 3 hr. Analytical gas chromatography indicated that the product (5·3 g.) contained two major components and one minor. Separation by the same technique (35 mm. dia. column; temp. 100°; N_2 flow-rate 15 l./hr.) gave 1*H*:4*H*-hexafluorocyclopentene (XV) (2·0 g.), identified by infrared spectroscopy. The major component that was retained longer had a retention time identical to that of the starting material and 3*H*,4*H*/-hexafluorocyclopentene (VI); infrared spectroscopy confirmed that both components were present. The minor component was present in an amount too small to be isolated.

Dehydrofluorination of the Isomeric 1H:2H:3H-*Heptafluorocyclopentanes*.—Each of these olefins was shaken with aqueous potassium hydroxide at *ca.* 18° for the specified time. The

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[14] Burdon and Tatlow, *J. Appl. Chem.*, 1958, **8**, 293.

products were separated by gas chromatography (35 mm. diam. column; temp. 98—102°; N_2 flow-rate 14—16 l./hr.) and, where known, identified by infrared spectroscopy.

(*a*) 1H,3H/2H-*Heptafluorocyclopentane* (I). Treatment of this component (4·7 g.) with 13N-potassium hydroxide (130 ml.) for 5 hr. gave (i) unknown (trace); (ii) unknown (trace); (iii) 3*H*/4*H*-hexafluorocyclopentene (XII) (*ca.* 0·05 g.); (iv) unchanged 1*H*,3*H*/2*H*-heptafluorocyclopentane (I) (0·7 g.); (v) 1H:3H-*hexafluorocyclopentene* (XX) (*ca.* 0·03 g.), b. p. 68—69° (Found: C, 33·8; H, 1·1. $C_5H_2F_6$ requires C, 34·1; H, 1·1%), $\nu_{max.}$ at 1700 cm.$^{-1}$ (CH=CF);[13] the mass spectrum was consistent with this structure and contained a major peak at 176 corresponding to the molecular ion $C_5H_2F_6$; and (vi) 1H:5H-*hexafluorocyclopentene* (XIX) (0·5 g.), b. p. 74° (Found: C, 34·3; H, 1·4%), $\nu_{max.}$ at 1700 cm.$^{-1}$ (CH=CF).[13]

(*b*) 1H,2H/3H-*Heptafluorocyclopentane* (II). This compound (11·6 g.) was treated for 43 hr. with aqueous potassium hydroxide (10 g. in 25 ml.) to give 3*H*/4*H*-hexafluorocyclopentene (XII) (0·1 g.) and 1*H*:5*H*-hexafluorocyclopentene (XIX) (5·5 g.). There was another minor component present, in an amount too small to be isolated, which had the same retention time as 1*H*:3*H*-hexafluorocyclopentene (XX).

(*c*) 1H,2H,3H/-*Heptafluorocyclopentane* (III). On treatment for 16 hr. with aqueous potassium hydroxide (2 g. in 5 ml.), this compound (0·5 g.) gave 1*H*:5*H*-hexafluorocyclopentane (XIX) (0·3 g.) and three other components, two of which had retention times corresponding to 1*H*:3*H*- (XX) and 3*H*,4*H*/- (VII) hexafluorocyclopentene; all three were present in amounts too small to be isolated.

Fluorination of 1H:5H-*Hexafluorocyclopentene* (XIX).—The olefin (1·0 g.) was fluorinated in the usual way in the small static cobalt trifluoride reactor at 160°. Gas chromatographic separation (35 mm. dia. column) of the product (0·6 g.) gave perfluorocyclopentane (trace), nonafluorocyclopentane (0·3 g.) 1*H*/2*H*-octafluorocyclopentane (0·2 g.), and 1*H*,2*H*/-octafluorocyclopentane (trace), all identified by infrared spectroscopy.[2]

Oxidation of 1H:5H-*Hexafluorocyclopentene* (XIX).—Oxidation of the olefin (7·5 g.) by the permanganate (300 ml.; 4·5% w/w)–sulphuric acid (200 ml., 2N) procedure gave dianilinium 2*H*-pentafluoroglutarate (5·4 g.), m. p. 183° (from acetone–chloroform) (lit.,[10] m. p. 183—184°) (Found: C, 49·9; H, 4·6. Calc. for $C_{17}H_{17}F_5N_2O_4$: C, 50·0; H, 4·2%), which was converted into bis-*S*-benzylthiuronium 2*H*-pentafluoroglutarate, m. p. 178° (from water) (lit.,[2] m. p. 176—177°) (Found: C, 45·5; H, 4·5. Calc. for $C_{21}H_{23}F_5N_5O_4S_2$: C, 45·5; H, 4·2%).

Addition of Chlorine to 3H/4H-*Hexafluorocyclopentene* (XII).—Chlorination of the olefin (21·7 g.) for 90 min. under ultraviolet irradiation as described [1] for 4*H*-heptafluorocyclopentene gave the mixed 1H/2H-3,4-*dichlorohexafluorocyclopentanes* (24·8 g.), b. p. 118° (Found: C, 24·4; H, 0·8. $C_5H_2Cl_2F_6$ requires C, 24·3; H, 0·8%).

Addition of Chlorine to 3H,4H/-*Hexafluorocyclopentene* (VII).—The olefin (5·0 g.) and excess of chlorine gave, after 6 hr. irradiation, the mixed 1H,2H/-3,4-*dichlorohexafluorocyclopentanes* (3·8 g.), b. p. 136° (Found: C, 24·2; H, 0·8%).

Reduction of the 1H/2H-3,4-*Dichlorohexafluorocyclopentanes.*—The mixed dichlorides (15·4 g.) in dry ether (100 ml.) were reduced with lithium aluminium hydride (4·5 g.) in dry ether (200 ml.) as described for the 1*H*-3,4-dichloroheptafluorocyclopentanes. After removal of the ether, the residue was separated by gas chromatography (35 mm. diam. column; temp. 100°; N_2 flow-rate 14 l./hr.) to give (i) ether; (ii) 1H,3H/2H,4H-*hexafluorocyclopentane* (XIII) (1·4 g.), b. p. 82° (Found: C, 34·0; H, 2·1. $C_5H_4F_6$ requires C, 33·7; H, 2·3%); (iii) 1*H*,4*H*/2*H*,3*H*-hexafluorocyclopentane (XIV) (trace); (iv) 1H,2H,4H/3H-*hexafluorocyclopentane* (VIII) (2·8 g.), b. p. 108° (Found: C, 33·9; H, 2·3%); and (v) 1H,2H,3H/4H-*hexafluorocyclopentane* (X) (4·2 g.), b. p. 134° (Found: C, 34·1; H, 2·2%).

Reduction of the Isomeric 1H,2H/-3,4-*Dichlorohexafluorocyclopentanes.*—Reduction of the dichlorides (3·8 g.) in dry ether (40 ml.) with lithium aluminium hydride (1·0 g.) in dry ether (50 ml.) gave (separation on the 35 mm. diam. column; temp. 93°; N_2 flow-rate 15 l./hr.) (i) ether; (ii) 1*H*,2*H*,4*H*/3*H*-hexafluorocyclopentane (VIII) (trace); (iii) 1*H*,2*H*/3*H*,4*H*-hexafluorocyclopentane (IX) (trace); and (iv) 1*H*,2*H*,3*H*/4*H*-hexafluorocyclopentane (X) (0·8 g.). Components (ii) and (iv) were identified by comparison of their infrared spectra with those of the compounds obtained in the previous experiment.

Fluorination of 1H:2H:3H:4H-*Hexafluorocyclopentanes.*—All three compounds were fluorinated in the small stirred cobalt trifluoride reactor at 120° in a stream of nitrogen (1·5—2 l./hr.) by introducing them into the reactor over about 1 hr. and then flushing the products out for a further 3 hr. The products in each case were washed with water, and separated by gas chromatography (35 mm. diam. column; temp. 95—100°; N_2 flow-rate 14—15 l./hr.) and were identified by infrared spectroscopy.

(*a*) 1H,3H/2H,4H-*Hexafluorocyclopentane* (XIII). This compound (2·7 g.) gave mixed fluorohydrocarbons (2·5 g.) which were separated into 1*H*/2*H*-octafluorocyclopentane (trace); 1*H*/3*H*-octafluorocyclopentane (0·1 g.); 1*H*,3*H*/2*H*-heptafluorocyclopentane (I) (0·1 g.), 1*H*,3*H*/-octafluorocyclopentane (*ca.* 0·05 g.), and a mixture of 1*H*,4*H*/2*H*-heptafluorocyclopentane (IV) and unchanged 1*H*,3*H*/2*H*,4*H*-hexafluorocyclopentane (XIII) (0·2 g.).

(*b*) 1H,2H,4H/3H-*Hexafluorocyclopentane* (VIII). This isomer (2·3 g.) gave a product (2·1 g.) that was nonafluorocyclopentane (*ca.* 0·05 g.), 1*H*/2*H*-octafluorocyclopentane (*ca.* 0·05 g.), 1*H*/3*H*-octafluorocyclopentane (0·1 g.), 1*H*,3*H*/2*H*-heptafluorocyclopentane (I) (0·1 g.), 1*H*,3*H*/-octafluorocyclopentane (0·1 g.), 1*H*,4*H*/2*H*-heptafluorocyclopentane (IV) (0·5 g.), 1*H*,2*H*/3*H*-heptafluorocyclopentane (II) (0·2 g.), unchanged 1*H*,2*H*,4*H*/3*H*-hexafluorocyclopentane (VIII) (0·1 g.), and 1*H*,2*H*,4*H*/-heptafluorocyclopentane (VI) (0·1 g.).

(*c*) 1H,2H,3H/4H-*Hexafluorocyclopentane* (X). The products (3·2 g.) from this isomer (3·5 g.) were separated into nonafluorocyclopentane (*ca.* 0·05 g.), 1*H*/2*H*-octafluorocyclopentane (*ca.* 0·05 g.), 1*H*/3*H*-octafluorocyclopentane (0·26 g.), 1*H*,3*H*/-octafluorocyclopentane (0·1 g.), 1*H*,4*H*/2*H*-heptafluorocyclopentane (IV) (0·24 g.), 1*H*,2*H*/3*H*-heptafluorocyclopentane (II) (0·1 g.), and 1*H*,2*H*/4*H*-heptafluorocyclopentane (V) (0·33 g.).

Dehydrofluorination of 1H,3H/2H,4H-*Hexafluorocylopentane* (XIII).—The tetrahydro-compound (2·3 g.) was shaken at *ca.* 18° with aqueous potassium hydroxide (11·0 g. in 30 ml.) for 5 hr. The non-aqueous product (0·9 g.) was separated by gas chromatography (35 mm. diam. column; temp. 100°; N_2 flow-rate 15 l./hr.) into (i) 1H:4H/5H-*pentafluorocyclopentene* (XXI) (0·5 g.), b. p. 79° (Found: C, 37·9; H, 1·9. $C_5H_3F_5$ requires C, 38·0; H, 1·9%), $\nu_{max.}$ at 1690 cm.$^{-1}$. (CH=CF); [13] and (ii) 3H,5H/4H-*pentafluorocyclopentene* (XXII) (0·1 g.), b. p. 79° (Found: C, 36·2; H, 1·7%), $\nu_{max.}$ at 1790 cm.$^{-1}$ (CF=CF).[13]

Dehydrofluorination of 1H,2H,4H/3H-*Hexafluorocyclopentane* (VIII).—The non-aqueous products (25·4 g.) from the treatment of this isomer (30·4 g.) with aqueous potassium hydroxide (16·0 g. in 50 ml.) at *ca.* 18° for 22 hr. were separated by gas chromatography (70 mm. diam. column; temp. 104°; N_2 flow-rate 55 l./hr.) to give 1*H*:4*H*/5*H*-pentafluorocyclopentene (XXI) (18·0 g.), which was identified by comparison of its infrared spectrum with that of the compound obtained in the previous experiment. Eight other minor components were also indicated by analytical gas chromatography, but none was present in sufficient amount for isolation.

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