# **626.** *Some Isomeric Hexafluorocyclobutanes and Pentafluorocyclobutenes.*

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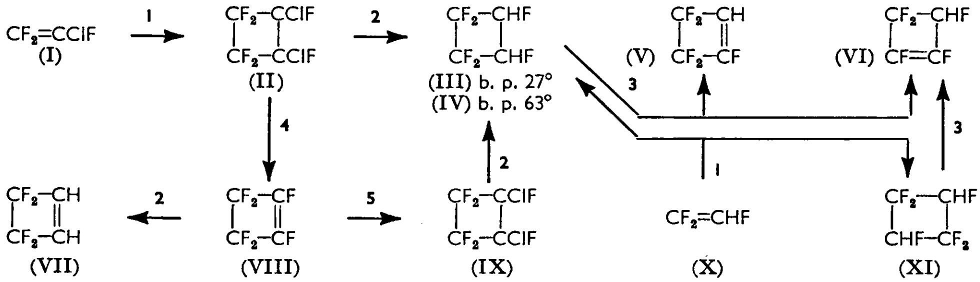
Re-examination of the reaction of lithium aluminium hydride with 1,2-dichlorohexafluorocyclobutane showed that both the known 1*H*,2*H*-hexafluorocyclobutane, b. p. 27°, and a new 1*H*,2*H*-isomer, b. p. 63° were formed. On dehydrofluorination, each 1*H*,2*H*-hexafluorocyclobutane gave principally 1*H*-, and a little 3*H*-pentafluorocyclobutene. High-pressure dimerisation of trifluoroethylene gave a mixture of four products, of which the two 1*H*,2*H*-hexafluorocyclobutanes, and a 1*H*,3*H*-hexafluorocyclobutane, b. p. 38°, have been identified. The last, on dehydrofluorination, gave only 3*H*-pentafluorocyclobut-1-ene which was oxidised to trifluorosuccinic acid. With lithium aluminium hydride, hexafluorocyclobutene gave 3,3,4,4-tetrafluorocyclobut-1-ene.

Thermal dimerisation of fluoroethylenes to give fluorocyclobutanes is well established,[1-5] one of the best known examples [2-5] being the conversion of chlorotrifluoroethylene (I) into 1,2-dichlorohexafluorocyclobutane (II). The latter resembled other chlorofluorocarbons [6,7] in its reaction with lithium aluminium hydride in diethyl ether, the chlorine being completely replaced by hydrogen.[8] Only one fluorohydrocarbon was isolated, a 1*H*,2*H*-hexafluorocyclobutane (III), having b. p. 27°. We now report a re-examination of this reaction which has shown that, besides compound (III), another 1*H*,2*H*-compound (IV), with b. p. 63°, is formed as well. Compound (IV) was isolated by gas chromatography, which was not available when the earlier work [8] was done.



Reagents: 1, Heat and pressure. 2, $LiAlH_4$ in $Et_2O$. 3, Aq. KOH. 4, Zn dust in EtOH. 5, $Cl_2$.

Electron-diffraction studies [9] of octafluorocyclobutane have shown that the ring is puckered. Presumably, however, interconversion of conformations occurs and isomers will arise as from a planar ring. There should be two stereoisomers of a derivative of the type 1,2-$C_4F_6X_2$ and the *trans*-isomer should exist in D- and L-forms. Where the substituents are chlorine or hydrogen, however, no ready means is available for resolving such a racemate. *cis*- and *trans*-Forms of 1,2-dichlorohexafluorocyclobutane have been obtained previously.[10] The usual route to this compound is thermal dimerisation of chlorotrifluoroethylene (I); when this dimer (II) was dechlorinated with zinc dust, and the

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[1] Coffman, Barrick, Cramer, and Raasch, *J. Amer. Chem. Soc.*, 1949, **71**, 490.
[2] Harmon, U.S.P. 2,404,374/1946.
[3] Henne and Ruh, *J. Amer. Chem. Soc.*, 1947, **69**, 279.
[4] Lacher, Tompkin, and Park, *J. Amer. Chem. Soc.*, 1952, **74**, 1693.
[5] Buxton, Ingram, Smith, Stacey, and Tatlow, *J.*, 1952, 3830.
[6] Tatlow and Worthington, *J.*, 1952, 1251.
[7] Smith and Tatlow, *J.*, 1957, 2505.
[8] Buxton and Tatlow, *J.*, 1954, 1177.
[9] Lemaire and Livingston, *J. Amer. Chem. Soc.*, 1952, **74**, 5732.
[10] Lacher, Büchler, and Park, *J. Chem. Phys.*, 1952, **20**, 1014.

hexafluorocyclobutene (VIII) so formed was treated with chlorine, another sample of dichloride (IX) was obtained. After further purification these dichlorides (II and IX) had slightly different physical properties, the higher-boiling thermal dimer (II) being allocated [10] the *cis*- and the lower-boiling chlorine adduct (IX) the *trans*-structure. Later work [11] has indicated that the crude thermal dimer is a mixture of nearly equal proportions of *cis*- and *trans*-isomers.

In the present work, we repeated the previously reported [8] reaction of 1,2-dichlorohexafluorocyclobutane (II) (prepared by thermal dimerisation of chlorotrifluoroethylene) with lithium aluminium hydride in diethyl ether, using analytical and preparative gas chromatography in the isolation of the products. As before, virtually all the chlorine was removed, and 1*H*,2*H*-hexafluorocyclobutane (III), b. p. 27°, was isolated in about 35% yield. A second product (IV), b. p. 63° (*ca.* 30% yield), was isolated from the high-boiling residues left after distillation of the solvent.

This product (IV) was shown to be a 1*H*,2*H*-hexafluorocyclobutane by dehydrofluorination with aqueous potassium hydroxide. A mixture of two monounsaturated products was obtained; these were separable only with great difficulty by preparative-scale gas chromatography. The major one was 1*H*-pentafluorocyclobutene (V), obtained previously [8] by an analogous reaction with the first hexafluoride (III). The other ($<20\%$) was 3*H*-pentafluorocyclobutene (VI), since it had an infrared band at 1795 cm.$^{-1}$ from a $-CF{=}CF-$ group [cf.[12] the band from hexafluorocyclobutene (VIII) at 1799 cm.$^{-1}$ and that from the $-CH{=}CF-$ group of the 1*H*-isomer (V) at 1685 cm.$^{-1}$]. Infrared spectroscopy showed that the sample of 1*H*-pentafluorocyclobutene (V) obtained in the previous work had contained a little of the new olefin (VI). This was suspected before but could not be proved. Repetition of the dehydrofluorination of compound (III) confirmed that a few percent of compound (VI) was contaminating the major product (V). Mass-spectroscopic investigations were carried out by Dr. J. R. Majer [13] on compounds (III), (IV), and (VI) and supported the structures allocated to them.

The action of ethereal lithium aluminium hydride on 1,2-dichlorohexafluorocyclobutane (IX) prepared by chlorine addition was next studied. A sample was made essentially by the method used by the previous authors; [10] both it (IX) and the thermal dimer (II) had the infrared spectra described.[10] However, with ethereal lithium aluminium hydride the chlorine adduct (IX) gave the two hexafluorocyclobutanes in proportions (III, 31%; IV, 36%) similar to those (III, 37%; IV, 31%) obtained from the dimer (II). In view of the difficulties of isolation little significance can be attached to the small differences in proportions. It seems that some *cis–trans*-interconversion must occur in the reactions of the dichlorocyclobutanes (II and IX) with lithium aluminium hydride. Even if the *cis*- and the *trans*-dichloride were not so pure as was suggested,[10] complete retention or complete inversion of configuration should have given bigger differences in the proportions of the products (III and IV) obtained. It is possible that complete interconversion occurred. In the cyclohexane field, the chlorine adducts of decafluorocyclohexene [7] and of 4*H*-nonafluorocyclohexene [14] were treated with lithium aluminium hydride. In each case, the dichloride was of unknown configuration, but the product contained more *cis*- than *trans*-1*H*,2*H*-compound [(i) 72% 1*H*,2*H*/-, and 28% 1*H*/2*H*-decafluorocyclohexane; [7] (ii) 75% 1*H*,2*H*,4*H*/- + 1*H*,2*H*/4*H*-, and 25% 1*H*,4*H*/2*H*- + 1*H*/2*H*,4*H*-nonafluorocyclohexane [14]].

Unequivocal allocation of structure to compounds (III) and (IV) is not yet possible. The difference in boiling points (36°) between them is considerable; for the analogous 1*H*,2*H*-decafluorocyclohexanes [7] it is 21°. In the cyclohexane series it seems that a stereoisomer with hydrogen atoms close together in space has a higher boiling point and a longer retention time in gas chromatography than one where they are further apart. On

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[11] Park, Holler, and Lacher, *J. Org. Chem.*, 1960, **25**, 990.
[12] Burdon and Whiffen, *Spectrochim. Acta*, 1958, **12**, 139.
[13] Majer, " Advances in Fluorine Chemistry," Butterworths, London, 1961, Vol. II, p. 55.
[14] Stephens, Tatlow, and Wiseman, *J.*, 1959, 148.

this basis, compound (III) should be the *trans*- and compound (IV) the *cis*-isomer. In contrast, from the arguments on dehydrofluorination developed in the cyclohexane series,[7,14] it might be expected that the *cis*- would give less 3*H*-pentafluorocyclobutene (VI) than the *trans*-isomer. Experimentally, the higher-boiling hexafluoride (IV) gave rather more than the other (III). However, qualitatively there appeared to be a much smaller difference between the rates of elimination of these stereoisomers (III and IV) than there was with the analogous [7] cyclohexanes, 1*H*/2*H*- and 1*H*,2*H*/-decafluorocyclohexane. Compound (IV) appeared to be more reactive, but both were dehydrofluorinated completely at room temperature with no starting material left (cf. *trans*-1*H*,2*H*-decafluorocyclohexane [7]). The geometry of the cyclobutane ring will make the operation of a rigid planar *trans*-elimination mechanism more difficult for this ring system than for cyclohexanes. Nevertheless, elimination occurs quite readily. It is possible that because of the strain in the cyclobutane ring system, elimination processes not normally favoured, for example involving carbanions, can operate. If the allocation of structure [10] to the 1,2-dichlorohexafluorocyclobutanes is correct, then the higher-boiling stereoisomer (the thermal dimer II) is *cis*, and the lower-boiling one (IX) is *trans*. The former gave slightly more of the lower-boiling 1*H*,2*H*-compound (III), and the latter (IX) gave slightly more of the other isomer (IV). If these proportions of products are significant then there is a discrepancy, but it seems much more probable that *cis–trans*-interconversion occurred and that equal amounts of the two dihydro-compounds were formed in each case. Thus, though compound (III) is most likely to be *trans*, and compound (IV) *cis*, a final decision must await measurements of dipole moments.

The isolation of two compounds (III and IV) after reaction of lithium aluminium hydride with the dichlorides (II and IX) has possible repercussions on other work. Perfluorocyclobutene (VIII) has been treated [15] with bromine, chlorine, iodine chloride, and hydrogen bromide. In each case the addition product was reduced with ethereal lithium aluminium hydride to give compound (III) in yields varying from 51% to 74%, which were stated to be low owing to difficulties of isolation. As in our earlier work,[8] the isomer (IV) was not detected, but it seems very likely that some was present. When the fluorocarbon (VIII) was treated [16] with hydrogen iodide, a compound of b. p. 63—65° was formed to which the structure 1,1,2,3,4,4-hexafluorobutane was allocated. The authors stated that the product expected by hydrogen addition (*i.e.*, III) was not produced, but the new compound (IV) with very similar properties to those of the material isolated could have been, and could have contaminated the product.

Other possible routes to unsaturated derivatives of cyclobutane were investigated in the present work. On further treatment of the cyclobutene (VI) with alkali, there was no evidence of the formation of a cyclobutadiene derivative. Passage of hexafluorocyclobutene (VIII) over heated metal gauze in the apparatus used [17] for the defluorination of fluoro-cyclohexenes and -cyclohexanes to aromatic fluoro-compounds also failed to give a cyclobutadiene, no reaction or complete degradation resulting. The perfluoro-compound (VIII) reacted with ethereal lithium aluminium hydride in the same way as fluorocyclohexenes do.[18] The product was 3,3,4,4-tetrafluorocyclobutene (VII), as shown by oxidation to tetrafluorosuccinic acid and by addition of bromine to give a 1,2-dibromo-adduct. The $-CH=CH-$ group had a characteristically [12] very weak infrared band; it is possible to overlook, in the spectrum of a fluoro-olefin, absorption due to a double bond of this type. A two-fold addition–elimination process of the type postulated before [18] appears to explain this reaction of olefin (VIII). Under the conditions used the supposed primary product 1*H*-pentafluorocyclobutene (V) must itself be sufficiently reactive to give the dihydro-compound (VII). This, however, would be appreciably less reactive towards

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[15] Haszeldine and Osborne, *J.*, 1956, 61.
[16] Haszeldine and Osborne, *J.*, 1955, 3880.
[17] Gething, Patrick, Stacey, and Tatlow, *Nature*, 1959, **183**, 588.
[18] Nield, Stephens, and Tatlow, *J.*, 1960, 3800.

lithium aluminium hydride, as happens in other series[18] with increasing numbers of hydrogen atoms on the vinylic or α-carbon atoms. Since this work was done the preparation of 3,3,4,4-tetrafluorocyclobutene (VII) by dehydrobromination of 3-bromo-1,1,2,2-tetrafluorocyclobutane (made from tetrafluoroethylene and vinyl bromide) has been described.[11]

Thermal dimerisation of trifluoroethylene (X) is another route to polyfluorocyclobutanes; it has been attempted before[11] but without success. Trifluoroethylene (X) was prepared[19] from chlorotrifluoroethylene (I). It was very resistant to cyclo-dimerisation, but after being heated in an autoclave at 260° for 23 hr., it had formed a liquid product. This was shown by gas chromatography to contain 4 components, which were separated by preparative-scale gas chromatography. The first was a trace of unchanged olefin (X) and the second had an infrared spectrum identical with that of 1*H*,2*H*-hexafluorocyclobutane (III). The third was a new compound (XI), and the fourth was shown by infrared spectroscopy to be a mixture of roughly equal proportions of the 1*H*,2*H*-isomer (IV) and a second new compound. Analysis, mass spectrometry, and infrared spectroscopy suggested that compound (XI) was a 1*H*,3*H*-hexafluorocyclobutane. This was confirmed by dehydrofluorination with aqueous potassium hydroxide, the sole product being 3*H*-pentafluorocyclobutene (VI), identical with the material obtained previously. This product (VI) should also be a racemic mixture, but resolution would be difficult. Isolation of the cyclobutene (VI) on a larger scale than hitherto enabled its structure to be confirmed. With bromine, a dibromo-adduct was formed, and oxidation with potassium permanganate in acetone gave trifluorosuccinic acid. This was identified as its dianilinium salt which has been made recently[20] from acid obtained by reduction of chlorotrifluorosuccinic acid with zinc. The second new compound could not be separated from compound (IV). It was probably the other stereoisomer of 1*H*,3*H*-hexafluorocyclobutane (XI); the infrared spectrum was in accord with this, but proof must await its separation. Thus it appeared that cyclo-dimerisation of trifluoroethylene gives all four possible products, and in roughly comparable amounts. It is now apparent that additions to unsymmetrical fluoro-olefins do not always proceed exclusively in one direction, and trifluoroethylene gives[21] both products from free-radical addition reactions. It was shown recently[22] that hexafluoropropene can be cyclo-dimerised under drastic conditions, three perfluoro(dimethylcyclobutanes) being isolated. So far as we are aware, homo-dimerisation of a fluoro-olefin to a cyclobutane has been reported only for compounds containing a $>CF_2$ group, and it now appears that these groups in the two reactant molecules do not in all cases have to join up to give a product containing a $-CF_2-CF_2-$ residue.

## EXPERIMENTAL

*Reduction of* 1,2-*Dichlorohexafluorocyclobutane* (II) (*Thermal Dimer*).—The dichloride was prepared from chlorotrifluoroethylene in an autoclave as before;[5] the infrared spectrum was the same as that published.[10] The compound (II) (30·0 g.) was added during 25 min. to a stirred suspension of lithium aluminium hydride (7·9 g.) in diethyl ether (200 c.c.), cooled by ice, under a reflux condenser cooled in solid carbon dioxide–ethanol. After 1¾ hr. at 0°, water (20 c.c.) was added, followed by 12N-sulphuric acid (75 c.c.) and more water (150 c.c.). The aqueous phase contained chloride ion corresponding to 94% of the original organic chlorine. The ether layer and ethereal extracts of the aqueous phase were dried ($MgSO_4$) and fractionally distilled (4′ column packed with nickel gauzes) to give fractions (i) (11·0 g.), b. p. 27·5—32°, (ii) (14·5 g.), b. p. 33·0—33·5°, and (iii) (15·0 g.), b. p. 33·5°. Distillation was continued through a 1′ column to give (iv) b. p. 33·9°, and (v) (13·5 g.), the still residue. Fraction (iv) was ether and (iii) was ether containing only a trace of product.

Fractions (i) and (ii) were separated by preparative-scale gas chromatography (column A

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[19] Park, Sharrah, and Lacher, *J. Amer. Chem. Soc.*, 1949, **71**, 2339; Park, Lycan, and Lacher, *J. Amer. Chem. Soc.*, 1951, **73**, 711.

[20] Raasch, Miegel, and Castle, *J. Amer. Chem. Soc.*, 1959, **81**, 2678.

[21] Haszeldine and Steele, *J.*, 1957, 2800.

[22] Hauptschein, Fainberg, and Braid, *J. Amer. Chem. Soc.*, 1958, **80**, 842.

of ref. 14, temp. 58°, $N_2$ flow rate 8·3 l./hr., 3 portions) to give 1*H*,2*H*-hexafluorocyclobutane (III) (7·7 g.) and ether. Compound (III) had b. p. 27°, $\nu_{max.}$ 2986 cm.$^{-1}$ ($\geqslant$C–H); mass spectrometry gave principal mass peaks 164 very small ($C_4H_2F_6$), 100 ($C_2F_4$), 95 ($C_3H_2F_3$), 82 ($C_2HF_3$), 64 ($C_2H_2F_2$). The compound was identical with that isolated before.[8] The still residue (v) was separated by gas chromatography (column A, temp. 86°, $N_2$ flow rate 8·5 l./hr., 2 portions) into ether and 1H,2H-*hexafluorocyclobutane* (IV) (6·5 g.), b. p. 62·5—63·5°, $n_D^{19}$ 1·2974, $\nu_{max.}$ 3012, 2973 cm.$^{-1}$ ($\geqslant$C–H) (Found: C, 28·9; H, 1·3; F, 69·0. $C_4H_2F_6$ requires C, 29·3; H, 1·2; F, 69·5%). Mass spectrometry gave principal mass peaks 164 vanishingly small ($C_4H_2F_6$), 144 small ($C_4HF_5$), 131 small ($C_3F_5$), 126 small ($C_4H_2F_4$), 100 ($C_2F_4$), 95 ($C_3H_2F_3$), 82 ($C_2HF_3$), 64 ($C_2H_2F_2$).

*Preparation and Reduction of* 1,2-*Dichlorohexafluorocyclobutane* (IX) (*Photochemical Adduct*).—Hexafluorocyclobutene [5] (23·0 g.) and chlorine (22·0 g.) in a hard-glass tube surmounted by a reflux condenser cooled in solid carbon dioxide–ethanol were irradiated with light from a high-pressure mercury lamp (G.E.C. " Osram," 125 w, black glass). After 6 hr., the residual liquid was washed with 10% aqueous sodium hydrogen carbonate and dried ($MgSO_4$). It was combined with the product from a similar experiment on hexafluorocyclobutene (16·0 g.) and fractionally distilled (6" column) to give 1,2-dichlorohexafluorocyclobutane (IX) (32·0 g.), b. p. 58·5—59·3°, $n_D^{21}$ 1·3330. The infrared spectrum was similar to that given previously.[10] The band at 1021 cm.$^{-1}$ was stronger and those at 1050 and 890 cm.$^{-1}$ much weaker than those from the thermal dimer.

This dichloride (IX) (30 g.) was treated with lithium aluminium hydride in diethyl ether under conditions identical with those described for the reduction of the thermal dimer (II). Isolation as before gave 1*H*,2*H*-hexafluorocyclobutane (III), b. p. 27° (6·6 g.), and the stereoisomer (IV), b. p. 63° (7·6 g.), having infrared spectra identical with those of the corresponding samples from the previous experiment.

*Dehydrofluorination of* 1H,2H-*Hexafluorocyclobutane* (IV).—Compound (IV) (35·0 g.) and potassium hydroxide (70 g.) in water (50 c.c.) at 19° were stirred for 3¾ hr. (after 30 min. the temperature of the mixture exceeded 30° and intermittent cooling was necessary to control the refluxing). The mixture was cooled, and then separated in an ice-cold funnel, and the organic layer (20·6 g.) was washed quickly with ice-cold water. Analytical gas chromatography showed virtually no starting material, but the peak due to the known [8] 1*H*-pentafluorocyclobutene (V) had an inflexion on its leading edge. Preparative-scale gas chromatography [14] (column B, temp. 27°, $N_2$ flow rate 56 l./hr.) gave three fractions, (*a*) (2·0 g.), (*b*) (8·2 g.), and (*c*) (6·4 g.). Further preparative-scale gas chromatography on fraction (*a*) (column A, temp. 34°, $N_2$ flow rate 5·8 l./hr.) gave a sample (0·8 g.) of 3H-*pentafluorocyclobutene* (VI) [Found: *M*, 144 (by mass spectrometry). $C_4HF_5$ requires *M*, 144], $\nu_{max.}$ 1795 (–CF=CF–) and 2988 cm.$^{-1}$ ($\geqslant$C–H). Mass spectrometry gave principal mass peaks 144 ($C_4HF_5$), 125 ($C_4HF_4$), 94 ($C_3HF_3$), 93 ($C_3F_3$), 82 small ($C_2HF_3$) and 62 small ($C_2F_2$); the stable peak at 100 ($C_2F_4$) was virtually absent.

Further purification (column B, temp. 32°, $N_2$ flow rate 46 l./hr.), was carried out on fraction (*c*). The final part of the material was 1*H*-pentafluorocyclobutene (V) which had $\nu_{max.}$ 1673 (–CF=CH–) and 3143 cm.$^{-1}$ ($\geqslant$C–H) with no detectable bands due to the 3*H*-isomer (VI).

Infrared measurements on the original mixture showed the presence of 15—20% of the 3*H*-cyclobutene (VI).

*Dehydrofluorination of* 1H,2H-*Hexafluorocyclobutane* (III).—Compound (III) (15·2 g.) was dehydrofluorinated as described before.[8] Infrared spectroscopy and analytical gas chromatography of the product (9·5 g.) revealed 1*H*-pentafluorocyclobutene (V) containing the 3*H*-isomer (VI) (<10%).

*Dimerisation of Trifluoroethylene.*—This olefin (14·5 g.) was condensed in a test-tube cooled by liquid air. The tube was then rapidly put into an autoclave (120 c.c. capacity) which was assembled quickly. After being heated at 260° for 23 hr. (50—60 atm.), the vessel was cooled and opened, volatile material (6·5 g.) escaping. The liquid residue (7·5 g.) showed 4 peaks on analytical gas chromatography over 1 : 2 dinonyl phthalate–kieselguhr (temp. 82°, $N_2$ flow rate 0·8 l./hr.), but over trifluoroacetic acid–Carbowax–kieselguhr at 75° the fourth peak was partly resolved and showed two components. Separation of part (2·8 g.) by preparative-scale gas chromatography (column A, temp. 68°, $N_2$ flow rate 8·4 l./hr.) gave four fractions: (i) trifluoroethylene (trace); (ii) 1*H*,2*H*-hexafluorocyclobutane (III), b. p. 27° (0·6 g.); (iii) 1*H*,3*H*-hexafluorocyclobutane (XI) (1·0 g.); (iv) mixed fraction (1·2 g.). Fraction (iv) was shown to be 1*H*,2*H*-hexafluorocyclobutane (IV), b. p. 63°, and a new compound, in approximately equal proportion; the last had additional infrared peaks at 1330, 1237, 1065, 1025, 885 and 834 cm.$^{-1}$ but none ascribable to –CF=CF– or –CF=CH– groups. Aliphatic hydrogen was present and the molecule appeared to be broadly similar to compound (IV).

Repetition of the experiment at 300—320° for 17 hr. gave the same products, from which 1H,3H-*hexafluorocyclobutane* (XI) (fraction ii) was isolated (yield *ca.* 15% on unrecovered olefin), with b. p. 38—39°, $n_D^{25}$ 1·2850 (Found: C, 29·0; H, 1·2%), $\nu_{max.}$ 3009, 2974 cm.$^{-1}$ ($\geqslant$C–H). Mass spectrometry gave principal mass peaks 95 ($C_3H_2F_3$), 82 ($C_2HF_3$); the peak at 100 ($C_2F_4$) was virtually absent.

*Dehydrofluorination of* 1H,3H-*Hexafluorocyclobutane* (XI).—The compound (5·4 g.) and potassium hydroxide (20 g.) in water (15 c.c.) were stirred at 15°. After 5 min., spontaneous refluxing started. After 2½ hr., water (10 c.c.) was added, the mixture was cooled in an ice-bath, and the organic layer was separated quickly and dried, to give 3*H*-pentafluorocyclobutene (VI) (3·3 g.), b. p. 25—26°, having an infrared spectrum identical with that of the sample mentioned above.

*Characterisation of* 3H-*Pentafluorocyclobutene* (VI).—(a) *Bromine addition.* Compound (VI) (0·9 g.) and bromine (1·0 c.c.) were shaken for 2½ hr. in a sealed hard-glass tube which was irradiated with ultraviolet light. The product was washed with 10% sodium hydrogen carbonate solution, dried, and distilled, to give 3H-1,2-*dibromopentafluorocyclobutane* (0·95 g.), b. p. 114—115°/743 mm., $n_D^{22}$ 1·4107 (Found: C, 15·9; H, 0·3; F, 30·7. $C_4HBr_2F_5$ requires C, 15·8; H, 0·3; F, 31·3%).

(b) *Oxidation.* A small tube containing compound (VI) (1·1 g.) was dropped into a flask containing potassium permanganate (1·32 g.) in dry acetone (200 c.c.), which was then shaken and cooled in running water for 5 min. The flask was shaken at 10—15° for 30 min., and water (200 c.c.) then added. Most of the acetone was distilled off and the residue acidified with sulphuric acid, treated with aqueous sodium hydrogen sulphite to remove the precipitate, and extracted exhaustively with ether. The extract was dried ($MgSO_4$), evaporated, and dissolved in a little ether; aniline in ether was added to give a precipitate (1·88 g.), m. p. 180—182° (decomp.). Recrystallisation from acetone–chloroform gave dianilinium trifluorosuccinate, m. p. 181—182° (decomp.) (Found: C, 53·3; H, 4·6%; equiv., 177. Calc. for $C_{16}H_{17}F_3N_2O_4$: C, 53·6; H, 4·8%; equiv., 179) [cited,[20] m. p. 181—186° (decomp.)].

3,3,4,4-*Tetrafluorocyclobutene* (VII).—A solution of hexafluorocyclobutene (16 g.) in dry diethyl ether (20 c.c.) at –78° was added during 5 min. to a stirred suspension of lithium aluminium hydride (4·5 g.) in diethyl ether (100 c.c.) at –78°. After 5 min. further water (20 c.c.) was added cautiously, followed by 12N-sulphuric acid (50 c.c.) and more water (100 c.c.). The ether layer and ethereal extracts of the aqueous phase were dried ($MgSO_4$) and fractionally distilled through a 3′ column packed with Dixon gauzes. The distillate had b. p. 34° and was ether; a residue (36 g.) which remained was separated by preparative-scale gas chromatography (column B, temp. 48°, $N_2$ flow rate 48 l./hr., 2 portions) to give ether, and 3,3,4,4-tetrafluorocyclobutene (4·65 g.), b. p. 53·9—54·8°/738 mm., $n_D^{20}$ 1·3102 (Found: C, 38·2; H, 1·6; F, 59·9. Calc. for $C_4H_2F_4$: C, 38·1; H, 1·6; F, 60·3%), for which cited values [11] were b. p. 50·4—50·5°/634 mm., $n_D^{20}$ 1·3114. In the infrared there were bands at 1565 (–CH=CH–, very weak) and 3111 cm.$^{-1}$ ($\geqslant$C–H, weak). Mass spectrometry gave principal mass peaks, 126 ($C_4H_2F_4$), 107 ($C_4H_2F_3$), 100 ($C_2F_4$), 76 ($C_3H_2F_2$), 26 ($C_2H_2$).

*Characterisation of* 3,3,4,4-*Tetrafluorocyclobutene* (VII).—(a) *Bromine addition.* Compound (VII) (2·5 g.) was treated for 8 hr. with bromine (5·8 g.), as for compound (VI), to give 3,4-dibromo-1,1,2,2-tetrafluorocyclobutane (4·0 g.), b. p. 114—115°/750 mm., $n_D^{21}$ 1·4229 (Found: C, 16·9; H, 0·7; Br, 55·5; F, 26·4. Calc. for $C_4H_2Br_2F_4$: C, 16·8; H, 0·7; Br, 55·9; F, 26·6%), for which b. p. 63—64°/79 mm. and $n_D^{20}$ 1·4220 have been cited.[11] (b) *Oxidation.* Compound (VII) (1·5 g.), potassium permanganate (10 g.), and water (50 c.c.) were heated at 80° for 14 hr. in a rocking autoclave. Isolation as usual gave tetrafluorosuccinic acid (45%), m. p. 114—118°, identified as its dianilinium (m. p. 220—222°) and di-*S*-benzylthiouronium salt (m. p. 190—191°); both had correct analyses.

The authors thank Professor M. Stacey, F.R.S., for his interest, Dr. D. H. Whiffen for the infrared spectroscopy, Dr. J. R. Majer for the mass spectrometry, and the Medical Research Council for a Fellowship (to G. F.).

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[*Received, January 23rd*, 1961.]