# *The Reactions of Highly Fluorinated Organic Compounds. Part VI.** *Octafluoro*cyclo*hexa-*1 : 3- *and* -1 : 4-*diene and Difluoromalonic Acid.*

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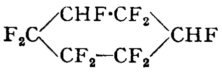
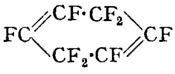
Dehydrofluorination of 1*H* : 3*H*-decafluoro*cyclo*hexane † affords both octafluoro*cyclo*hexa-1 : 3- and -1 : 4-diene. The former is oxidised to tetrafluorosuccinic acid, and the latter to difluoromalonic acid which is a comparatively stable acid.

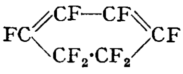
In a recent communication (Barbour, Mackenzie, Stacey, and Tatlow, *J. Appl. Chem.*, 1954, **4**, 347) the fluorination of benzene, with cobaltic fluoride at 150°, was described. Among the products was a decafluoro*cyclo*hexane (b. p. 78°) which was identified tentatively as having a 1*H* : 3*H*-structure (I). We now report further investigations on the exhaustive dehydrofluorination of this compound. Refluxing with concentrated aqueous potassium hydroxide eliminated 2 mols. of hydrogen fluoride and gave material of molecular formula $C_6F_8$, separated by fractional distillation into two octafluoro*cyclo*hexadienes. One of these (b. p. 57—58°) was the 1 : 4-diene (II), since with permanganate it gave difluoromalonic acid, identified as the free acid, organic salts, and the diamide. Addition of bromine to the 1 : 4-diene (II) gave, first, 4 : 5-dibromo-octafluoro*cyclo*hex-1-ene, and then 1 : 2 : 4 : 5-tetrabromo-octafluoro*cyclo*hexane. The diene and its dibromide both gave characteristic infra-red C=C bands, the intensity of that from the former being about twice those of analogous mono-olefins (including the latter). The 1 : 4-diene (II) appears to be the same compound as that obtained by McBee, Lindgren, and Ligett (*Ind. Eng. Chem.*, 1947, **39**, 378; U.S.P. 2,432,997, 2,586,364; *Chem. Abs.*, 1948, **42**, 2618; 1952, **46**, 8675) by fluorination of hexachlorobenzene (using $BrF_3$ and then $SbF_5$), followed by dehalogenation. These authors, however, did not work out its structure.



(I)



(II)



(III)

The second diolefin from the original dehydrofluorination reaction had b. p. 63—64° and was rather unstable (see p. 3780). It was shown to be octafluoro*cyclo*hexa-1 : 3-diene (III) as follows. Permanganate oxidation afforded tetrafluorosuccinic acid, identified as two well-characterised derivatives. Bromine addition gave a dibromo-octafluoro*cyclo*hexene fraction, probably a mixture, and then 1 : 2 : 3 : 4-tetrabromo-octafluoro*cyclo*hexane, and addition of chlorine gave the analogous 1 : 2 : 3 : 4-tetrachloro-compound. In infra-red spectroscopic measurements, the conjugated diene (III) showed two distinct C=C bands, the sum of their intensities being approximately equal to the intensity of the one band given by the 1 : 4-diene (II). The dibromo-addition product of (III) gave a broad C=C band, of lower intensity; this may have been due to the presence of isomers.

All these observations confirm that the decafluoro*cyclo*hexane (b. p. 78°) is in fact a 1*H* : 3*H* compound (I), if it is assumed that migration of fluorine cannot occur in the types of reaction used. The earlier work (Barbour *et al.*, *loc. cit.*) showed that the compound could not have a 1*H* : 4*H*-structure, whilst the isolation of the two dienes (II) and (III) rules out the possibility that it might be a 1*H* : 2*H*-compound. It seems that in a 1*H* : 3*H*-compound (I) fluorine can be removed from either of the $\cdot CF_2\cdot$ groups flanking a CHF group. The mode of elimination from the isomeric 1*H* : 2*H*-type of structure is described by Roylance, Tatlow, and Worthington (*J.*, in the press).

There seems to be only one previous reference to difluoromalonic acid. Henne and DeWitt (*J. Amer. Chem. Soc.*, 1948, **70**, 1548) oxidised 3 : 3-difluoropenta-1 : 4-diene and

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* Part V, *J.*, 1954, 1177.

† For this use of *H*, see *Chem. Eng. News*, 1952, **30**, 4515, and *J.*, 1952, 5059.

3 : 3-difluorohexachloropenta-1 : 4-diene with alkaline permanganate. They did not purify the acid but obtained the dimethyl ester and the diamide. The melting points of their amide and of ours agree well. Henne and DeWitt implied that free difluoromalonic acid was decarboxylated readily even in the cold. However, the acid isolated in the present work, though very deliquescent, was quite stable under normal conditions. It was best purified by distillation *in vacuo* and was recovered after being heated at 200°. After 20 hr. at 10—15° with 2N-sodium hydroxide negligible amounts of fluorine had been removed, and only 10% or so was hydrolysed after 3 hr. at 100° with 5N-alkali. Though perhaps rather less stable than the higher members of the homologous perfluorodicarboxylic acid series, difluoromalonic acid appears to be similar to them in many respects.

## EXPERIMENTAL

*Dehydrofluorination of* 1H : 3H-*Decafluoro*cyclo*hexane*.—The decafluoro-compound (120 g.; b. p. 78°, m. p. 39°; Barbour *et al.*, *loc. cit.*) was boiled for 6 hr. with potassium hydroxide (200 g.) in water (200 c.c.). The organic phase was separated, washed with water, dried ($MgSO_4$), and fractionated through a 2′ column. The fractions obtained, all colourless mobile liquids, were: (i) octafluoro*cyclo*hexa-1 : 4-diene (25·6 g.), b. p. 57—58°, $n_D^{18}$ 1·318 (Found: C, 32·3; F, 67·4. Calc. for $C_6F_8$: C, 32·2; F, 67·8%); (ii) mixed dienes (17·5 g.), b. p. 58—63°; (iii), *octafluoro*cyclo*hexa*-1 : 3-*diene* (14·4 g.), b. p. 63—64°, $n_D^{18}$ 1·329 (Found: C, 31·9; F, 68·0%); and (iv) residue (16·0 g.), b. p. above 64°. McBee, Lindgren, and Ligett (*loc. cit.*) gave b. p. 56—57°, $n_D^{20}$ 1·3149, for perfluoro*cyclo*hexadiene.

The 1 : 3-diene is apparently unstable and decomposed slowly at room temperature. After 1—2 days the sample was turbid, hydrogen fluoride appeared to be present, and analysis gave carbon figures 1—2% low with a little hydrogen (*ca.* 0·5%) then appearing as well.

Infra-red spectroscopic examination of the 1 : 4-diene showed the presence of a C=C band at 1739 cm.$^{-1}$ of which the intensity was about twice that of the bands, also at 1739 cm.$^{-1}$, given by decafluoro*cyclo*hexene, or the nonafluoro*cyclo*hexene obtained from the 1*H* : 3*H*-decafluoro-compound (Barbour *et al.*, *loc. cit.*). The 1 : 3-diene showed two bands, at 1713 and 1753 cm.$^{-1}$, with a total optical density approximately equal to that of the one band given by the 1 : 4-diene. The measurements were made on carbon tetrachloride solutions (0·1—0·2M) with a Grubb-Parsons spectrometer with a rock-salt prism.

The 1 : 3-diene gave a band in the ultra-violet at (max.) λ 2560 Å, ε approx. 3160 (*c* 0·10 g./l. in diethyl ether). The 1 : 4-diene showed no selective absorption in this region. No great accuracy is claimed for these figures because of the instability of the diene and the volatility of the solution.

*Addition of Bromine to the* 1 : 4-*Diene*.—(*a*) The olefin (4·0 g.; b. p. 57°) and bromine (12·0 g.), in a hard-glass flask, were irradiated with ultra-violet light for 17 hr., the heat from the lamp causing gentle reflux. After being washed with aqueous sodium pyrosulphite and dried ($P_2O_5$), the organic phase was distilled, to give 4 : 5-*dibromo-octafluoro*cyclo*hex*-1-*ene* (3·5 g.), b. p. 40°/13 mm., 50°/20 mm. (Found: C, 19·0; F, 39·5. $C_6Br_2F_8$ requires C, 18·8; F, 39·6%), and 1 : 2 : 4 : 5-*tetrabromo-octafluoro*cyclo*hexane* (0·5 g.), b. p. 99°/20 mm., m. p. 40—42° (Found: C, 13·0; F, 28·0. $C_6Br_4F_8$ requires C, 13·25; F, 28·0%). 4 : 5-Dibromo-octafluoro*cyclo*hex-1-ene gave a C=C band in the infra-red at 1754 cm.$^{-1}$.

(*b*) When the experiment was carried out for 48 hr., the dibromide (1·0 g.) and the tetrabromide (3·1 g.) were obtained. Re-treatment of the dibromide and intermediate fractions (1·6 g.) for 24 hr. gave the tetrabromide (1·2 g.), m. p. 42°.

*Additions of Bromine and Chlorine to the* 1 : 3-*Diene*.—(*a*) The olefin (1·70 g.; b. p. 63°) and bromine (2·7 g.) were treated as in the case of the isomeric diene to give dibromo-octafluoro*cyclo*hexenes (1·00 g.), b. p. 54—56°/20 mm., 74°/100 mm. (Found: C, 19·0; F, 39·7%), and 1 : 2 : 3 : 4-*tetrabromo-octafluoro*cyclo*hexane* (1·10 g.), b. p. 105°/20 mm., m. p. 42—43° (Found: C, 13·3; F, 28·1%).

(*b*) The olefin (2·3 g.) and chlorine (4·0 g.) were sealed in a hard-glass tube which was irradiated with ultra-violet light for 24 hr. Isolation as usual afforded 1 : 2 : 3 : 4-*tetrachloro-octafluoro*cyclo*hexane* (2·80 g.), b. p. 49—50°/20 mm., m. p. 59—60° (Found: C, 19·9; F, 41·2. $C_6Cl_4F_8$ requires C, 19·7; F, 41·5%).

*Difluoromalonic Acid*.—Octafluoro*cyclo*hexa-1 : 4-diene (10·0 g.), potassium permanganate (60 g.), and water (60 c.c.) were shaken together for 17 hr. at 95° in a rocking autoclave. The acidic product, after isolation and extraction as described in earlier papers, was heated at 100°/15 mm. for 5 min. and then taken up in dry ether, the small inorganic impurity filtered off, and the solvent evaporated. The residue, after being dried *in vacuo* as before, was a deliquescent acidic solid (8·4 g.), m. p. 115°. By distillation of this solid (1 g.) at 135° (bath-temp.)/15 mm. on to a cold finger, there was obtained *difluoromalonic acid* (0·9 g.), m. p. 117—118° (Found : C, 25·8; H, 1·6%; equiv. 69·6. $C_3H_2O_4F_2$ requires C, 25·7; H, 1·4%; equiv. 70·0). No fluoride ion was detected in the titration liquors.

The acid may be recrystallised from dry benzene but the above method of purification is preferable.

To the crude acid (1·00 g.) in ether (5 c.c.), aniline was added dropwise until precipitation was complete. The solid was filtered off and recrystallised twice from acetone–chloroform, to give the *dianilinium* salt (1·50 g.), m. p. 160—161° (Found : C, 55·5; H, 4·9; F, 11·5%; equiv. 165. $C_{15}H_{16}O_4N_2F_2$ requires C, 55·2; H, 4·9; F, 11·6%; equiv., 163).

The crude acid (0·30 g.) was dissolved in aqueous sodium hydroxide, the pH adjusted to *ca.* 4 with hydrochloric acid, and aqueous *S*-benzylthiuronium chloride added. The precipitate was recrystallised from water to give *di-*(S-*benzylthiuronium*) *difluoromalonate* (0·80 g.), m. p. 180—182° (Found : C, 48·3; H, 4·8. $C_{19}H_{22}O_4N_4S_2F_2$ requires C, 48·3; H, 4·7%).

Fluorosulphonic acid (0·5 c.c.) was added to the crude acid (1·00 g.) in ethyl alcohol (8·0 c.c.). After the initial vigorous reaction, the mixture was refluxed for 15 min. Water was added, the residual oil was extracted with ether, the extracts were dried ($MgSO_4$) and filtered, and ammonia gas was passed through. After 17 hr. at 10—15°, the solvent was evaporated and the residue was recrystallised from water to give difluoromalondiamide (0·64 g.), m. p. 206—207° (Found : C, 25·9; H, 2·8; F, 27·5. Calc. for $C_3H_4O_2N_2F_2$ : C, 26·1; H, 2·9; F, 27·5%). Henne and DeWitt (*loc. cit.*) cited m. p. 206·4° ± 0·2°.

When pure difluoromalonic acid was heated to 200° for 20 min., no evolution of carbon dioxide was detected. The recovered acid had m. p. 115—116° and gave a dianilinium salt, m. p. 160—161°.

The pure acid was heated for 3 hr. at 100° with 5N-sodium hydroxide. Determination of the fluoride ion content of the solution showed that about 10% of that present in the original acid had been removed. After treatment of the aqueous solution by acidification, extraction, etc., as before, only difluoromalonic acid (80% recovery), m. p. 112—114°, was obtained. This gave the dianilinium salt, m. p. 160—161° (Found : equiv., 164). When the acid was kept for 20 hr. at 10—15° in 2N-sodium hydroxide, less than 1% of the fluorine was removed as ionic fluoride.

*Tetrafluorosuccinic Acid Derivatives.*—Octafluoro*cyclo*hexa-1 : 3-diene (5·5 g.) was oxidised with potassium permanganate (40 g.) in water (60 c.c.), in a rocking autoclave at 100° for 24 hr. After isolation as previously described (Buxton and Tatlow, *J.*, 1954, 1177) there was obtained crude tetrafluorosuccinic acid (3·8 g.), m. p. 115—116°, which was converted into the dianilinium salt (60% based on acid), m. p. 224—225° (Found : C, 51·1; H, 4·3; F, 19·7%; equiv., 189. Calc. for $C_{16}H_{16}O_4N_2F_4$ : C, 51·1; H, 4·3; F, 20·2%; equiv., 188), and into the diamide (67% based on acid), m. p. 258—259° (Found : C, 25·7; H, 2·1; F, 40·0. Calc. for $C_4H_4O_2N_2F_4$ : C, 25·5; H, 2·1; F, 40·4%). Reported values (*idem, loc. cit.*) are m. p. 224—225° (salt) and m. p. 259° (amide).

The acid gave a *di-*(S-*benzylthiuronium*) salt (60%; from water), m. p. 189—190° (Found : C, 46·3; H, 4·0. $C_{20}H_{22}O_4N_4S_2F_4$ requires C, 46·0; H, 4·2%).

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