37. *Polycyclic Fluoroaromatic Compounds. Part II.* Perfluoromethylnaphthalenes and Derived Compounds.*

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Heptafluoro-1- and -2-trifluoromethylnaphthalene have been prepared by the defluorination of perfluoro-1- and -2-methyldecalin respectively. Among the products of defluorination of perfluoro-1-methyldecalin was undecafluoro-5-trifluoromethyltetralin, and among those of perfluoro-2-methyldecalin was undecafluoro-6-trifluoromethyltetralin. Attempts to hydrolyse the two perfluoromethylnaphthalenes to the corresponding heptafluoronaphthoic acids failed. Heptafluoro-2-trifluoromethylnaphthalene with aluminium chloride gave heptafluoro-2-trichloromethylnaphthalene; this was hydrolysed to heptafluoro-2-naphthoic acid, which gave 2*H*-heptafluoronaphthalene. Heptafluoro-1-trifluoromethylnaphthalene with aluminium chloride gave a pentachloropentafluoro-1-methylnaphthalene and thence a dichloropentafluoro-1-naphthoic acid.

Using our method for the preparation of polyfluoro-aromatic compounds (passage of polyfluoro-alicyclic compounds over a heated metal surface)[1,2] we have prepared heptafluoro-1- and -2-trifluoromethylnaphthalene from perfluoro-1- and -2-methyldecalin,[3] respectively. The yields were, however, disappointingly small and were not improved

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* Part I, preceding paper.

[1] Gething, Patrick, Stacey, and Tatlow, *Nature*, 1959, **183**, 588.
[2] Coe, Patrick, and Tatlow, *Tetrahedron*, 1960, **9**, 240.
[3] Haszeldine and Smith, *J.*, 1950, 3617.

significantly by alteration of such conditions as reactor temperature or contact time. This is difficult to understand in view of the ease of defluorination of perfluorodecalin.[1] Although it might be expected, by analogy with the defluorination of perfluoro-1,2-dimethylcyclohexane and perfluoro-1,4-dimethylcyclohexane,[4] that introduction of a perfluoroalkyl substituent into perfluorodecalin should have no further beneficial effect on the ease of defluorination, we have no previous example of increased difficulty in defluorination of a compound, or of its greater instability than of its analogues containing fewer side-chains under defluorination conditions. The products of defluorination of perfluoro-1-methyldecalin contained material which, from its analysis, appeared to be an undecafluorotrifluoromethyltetralin. That the compound contained an aromatic ring was confirmed by ultraviolet spectroscopy, and the substituent trifluoromethyl group was present in the aromatic ring since oxidation afforded octafluoroadipic acid.[5] With perfluoro-*o*- and -*p*-xylene[4] the sequence of fluorination and defluorination does not involve migration of an alkyl group; it is therefore reasonable to suppose that the partly defluorinated material is undecafluoro-5-trifluoromethyltetralin. A compound isolated from the defluorination products of perfluoro-2-methyldecalin was shown in like manner to be undecafluoro-6-trifluoromethyltetralin.

One of the objectives of the present investigation was the preparation of substituted polyfluoronaphthalenes of known structure for use as reference compounds for the identification of products of attack of nucleophilic reagents on octafluoronaphthalene.[6] It was hoped that hydrolysis of the trifluoromethyl groups in the heptafluorotrifluoromethylnaphthalenes would proceed readily, as for perfluorotoluene[1] and perfluoro-*o*- and -*p*-xylene,[4] and so provide a convenient preparation of the heptafluoronaphthoic acids. However, acidic hydrolysis of each heptafluorotrifluoromethylnaphthalene, even under mild conditions, gave complex coloured mixtures from which none of the desired acid could be obtained. Accordingly, the heptafluorotrifluoromethylnaphthalenes were treated with aluminium chloride in the hope that chlorine would replace fluorine in the trifluoromethyl group, a type of exchange noted before.[7] Heptafluoro-2-trifluoromethylnaphthalene gave heptafluoro-2-trichloromethylnaphthalene, which, on hydrolysis with sulphuric acid, gave heptafluoro-2-naphthoic acid. Under similar conditions, however, heptafluoro-1-trifluoromethylnaphthalene gave a pentachloropentafluoro-1-methylnaphthalene, and variation of reaction conditions did not produce the desired trichloromethyl compound. The pentachloride gave, on hydrolysis, a dichloropentafluoro-1-naphthoic acid of unknown structure. The difference in reactivity of the heptafluorotrifluoromethylnaphthalenes towards aluminium chloride must arise from the differing positions of the trifluoromethyl groups. It is difficult to speculate on the cause of the differing reactivities of the two compounds because the mechanism of the replacement of nuclear fluorine by chlorine is unknown. It is plausible, however, that the availability of a fluorine atom for reaction in the 2-position in heptafluoro-1-trifluoromethylnaphthalene, or the effect of the substituent at the 1-position, may modify the reactivity of the naphthalene toward the reagent.

Decarboxylation of heptafluoro-2-naphthoic acid proved difficult. Heating the sodium salt of the acid with soda-lime gave very little of the desired product, but rapid heating of a dry mixture of the acid and sodium hydrogen carbonate did afford 2*H*-heptafluoronaphthalene.

EXPERIMENTAL

Defluorination of Perfluoro-2-methyldecalin.—Perfluoro-2-methyldecalin (10 g.), obtained by fluorination of 2-methylnaphthalene,[3] was volatilised in an inlet tube maintained at 160°

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[4] Gething, Patrick, and Tatlow, *J.*, 1961, 1574.

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

[6] Gething, Patrick, and Tatlow, preceding paper.

[7] Henne and Newman, *J. Amer. Chem. Soc.*, 1938, **60**, 1697.

and passed in nitrogen (3 l./hr.) through a reactor (3″ diam. × 4′ length) at 460° packed with mild steel gauze. The product (5 g.) was condensed in a trap immersed in liquid air. Each run lasted for about 3 hr., and after completion the metal packing was regenerated by passage of hydrogen (20 l./hr.) for about 20 min. The combined products (110 g.) of many such runs were separated by fractional distillation through a 12″ column packed with steel Dixon gauzes. The fractions (i) with b. p. <167·5° (70 g.) were largely starting material, but contained some decomposition products. Fraction (ii) with b. p. 167·5—210° (18 g.) contained starting material together with tetradecafluoromethyltetralin. The dark pasty residue (iii) was distilled further (b. p. 92—94°/15 mm.) to give crude *heptafluoro-2-trifluoromethylnaphthalene* (7·5 g.), m. p. 34—38°. Recrystallisation from benzene gave white needles (3·8 g.), m. p. 42·5—43° (Found: C, 41·0; F, 58·5. $C_{11}F_{10}$ requires C, 41·0; F, 59·0%), $\lambda_{max.}$ (in EtOH; 0·216 g./l.) 3350 and 2765 Å (ε 3585, 3585). Fraction (ii) (18·0 g.) was separated by preparative-scale gas chromatography (column, 3″ diam., length 16′; packing, 1 : 3 silicone elastomer SE 301–kieselguhr; 170°; N_2 40 l./hr.) to give *undecafluoro-6-trifluoromethyltetralin* (8·0 g.) (Found: C, 33·4; F, 67·2. $C_{11}F_{14}$ requires C, 33·2; F, 66·8%), $\lambda_{max.}$ (in EtOH; 0·116 g./l.) 2760 Å (ε 2720), $\nu_{max.}$ 1650 cm.$^{-1}$ (fluorinated aromatic ring).

Defluorination of Perfluoro-1-methyldecalin.—Perfluoro-1-methyldecalin (10 g.) was defluorinated as above, giving a mixture of products (6·7 g.). The combined products (217 g.) from many runs were fractionated to give fractions (i) (194 g.), b. p. <164·5° (starting material together with breakdown products), (ii) (10 g.), b. p. 164·5—173° (starting material and undecafluoro-1-trifluoromethyltetralin), and (iii) a residue which was separated by preparative-scale gas chromatography (column 3″ diam., length 16′; packing, 1 : 3 silicone elastomer SE 301–kieselguhr; 180°; N_2 46 l./hr.). This afforded *heptafluoro-1-trifluoromethylnaphthalene* (3·4 g.) (Found: C, 41·3; F, 59·0. $C_{11}F_{10}$ requires C, 41·0; F, 59·0%), $\lambda_{max.}$ (in EtOH, 0·126 g./l.) 2780, 3180, and 3340 Å (ε 3950, 1050, and 875), and *undecafluoro-5-trifluoromethyltetralin* (7·3 g.) (Found: C, 33·4; F, 66·5. $C_{11}F_{14}$ requires C, 33·2; F, 66·8%), $\lambda_{max.}$ (in EtOH, 0·254 g./l.) 2640 Å (ε 1120), $\nu_{max.}$ 1645 cm.$^{-1}$ (fluorinated aromatic ring). Mass spectrometry, principal mass peaks: 398, $C_{11}F_{14}$; 379, $C_{11}F_{13}$; 348, $C_{10}F_{12}$.

Oxidation of the Perfluoromethyltetralins.—Heptafluoro-6-trifluoromethyltetralin (1·0 g.) was shaken with potassium permanganate (3·0 g.) in acetone (300 ml.) for 15 hr. at room temperature. After a further 30 hr. the solution was diluted with water (300 ml.), and the acetone removed by evaporation. The resulting solution was decolorised with sulphur dioxide, made alkaline with sodium carbonate, and extracted in the usual way to give octafluoroadipic acid (0·91 g.), which formed dianilinium octafluoroadipate (0·78 g.), m. p. 192—202°. Recrystallisation from chloroform and acetone gave crystals (60% recovery), m. p. and mixed m. p. 209—211° (Found: C, 45·4; H, 3·4. $C_{18}H_{16}F_8N_2O_4$ requires C, 45·5; H, 3·3%).

Undecafluoro-5-trifluoromethyltetralin (1·0 g.) was oxidised in a similar way to give the crude dianilinium salt (0·7 g.). A portion of this (0·35 g.) was dissolved in water (5 ml.), and a saturated solution of *S*-benzylthiouronium chloride was added. The resultant precipitate was filtered off and recrystallised from water, to give di-*S*-benzylthiouronium octafluoroadipate (0·2 g.), m. p. 243° (Found: C, 42·2; H, 3·5%). Cited values[5] are: dianilinium salt, m. p. 210—211°; di-*S*-benzylthiouronium salt, m. p. 244°.

Attempted Hydrolysis of the Heptafluorotrifluoromethylnaphthalenes.—Fuming sulphuric acid (1·0 ml.) and heptafluoro-2-trifluoromethylnaphthalene were heated in a sealed tube at 170° for 15 hr., then poured into water. Extraction with ether yielded a sticky red solid which gave, on recrystallisation, two crops of crystals both of which melted over a very wide temperature range (200—250°).

Concentrated sulphuric acid (1·0 ml.), diluted with water (1·0 ml.), was refluxed for 3 hr. with heptafluoro-2-trifluoromethylnaphthalene (1·0 g.). The product was mixed with water and made alkaline. Extraction of this mixture with ether gave starting material (0·66 g.). Extraction, with ether, of the acidified mixture of products gave only a negligible amount of material.

Heptafluoro-1-trifluoromethylnaphthalene reacted similarly.

Preparation of Heptafluoro-2-trichloromethylnaphthalene.—Heptafluoro-2-trifluoromethylnaphthalene (4·6 g.) was dissolved in redistilled acetyl chloride (7·5 ml.), and resublimed aluminium chloride (2·1 g., 1·0 mole) was added during 20 min. while the mixture was cooled in ice. The solution assumed a deep green colour. The mixture was then heated at 30° for 30 min. and refluxed for a further 30 min., by which time it had become pasty, then allowed to cool and poured into ice-cold water which was next made slightly alkaline and extracted with ether (3 × 50 ml.). The ethereal solution was washed, dried ($MgSO_4$), and evaporated to dryness, giving a sticky orange solid (4·5 g.). This crystallised from methanol to give cream-coloured *heptafluoro*-2-*trichloromethylnaphthalene* (2·0 g.), m. p. 74·5—77·0°. Recrystallisation from methanol gave white crystals, m. p. 80·0—80·5° (Found: C, 35·7; F, 36·2; Cl, 28·5. $C_{11}Cl_3F_7$ requires C, 35·6; F, 35·8; Cl, 28·7%).

Preparation of Dichloropentafluoro-1-*trichloromethylnaphthalene*.—In a similar way, heptafluoro-1-trifluoromethylnaphthalene (3·0 g.) was treated with aluminium chloride (1·4 g.) in acetyl chloride (5 ml.). The ethereal extracts from the reaction mixture gave, on evaporation, a solid (2·5 g.) which on recrystallisation from ethanol gave a 1-*trichloromethyl-dichloropentafluoronaphthalene* (1·5 g.), m. p. 124—125° (Found: C, 32·9; F, 23·5. $C_{11}Cl_5F_5$ requires C, 32·6; F, 23·5%).

Hydrolysis of Heptafluoro-2-*trichloromethylnaphthalene*.—Heptafluoro-2-trichloromethylnaphthalene (0·74 g.) was added to concentrated sulphuric acid (3·0 ml.) in a Carius tube, a transient mauve colour appearing. The tube was sealed and heated at 100° for 30 min. The tube was then opened, and the products, by this time a dark green, were poured into iced water, whereupon a white precipitate was formed. The mixture was made alkaline with sodium carbonate, extracted with ether (2 × 50 ml.), then acidified and extracted continuously with ether for 18 hr. The ethereal solution was dried ($MgSO_4$) and evaporated, to give a cream solid (0·52 g.). Recrystallisation from aqueous ethanol yielded *heptafluoro*-2-*naphthoic acid* (0·33 g.), m. p. 188—189° (Found: C, 44·5; H, 0·5; F, 44·7. $C_{11}HF_7O_2$ requires C, 44·3; H, 0·3; F, 44·6%).

This acid (0·10 g.), in dry ether, with aniline gave *anilinium heptafluoro*-2-*naphthoate* (0·058 g.), m. p. 192—194° (from acetone–chloroform) (Found: C, 52·0; H, 2·2. $C_{17}H_8F_7NO_2$ requires C, 52·2; H, 2·05%).

Hydrolysis of 1-*Trichloromethyl-dichloropentafluoronaphthalene*.—This compound (0·5 g.) was hydrolysed as described above with concentrated sulphuric acid (2 ml.), to give a *dichloropentafluoro*-1-*naphthoic acid*, m. p. 157—158° (from aqueous acetic acid) (0·2 g.) (Found: C, 40·1; H, 0·2. $C_{11}HCl_2F_5O_2$ requires C, 39·9; H, 0·3%). It gave an *anilinium salt*, m. p. 191—192° (from acetone–chloroform) (Found: C, 47·8; H, 1·8. $C_{17}H_8Cl_2F_5NO_2$ requires C, 48·1; H, 1·9%).

Decarboxylation of Heptafluoro-2-*naphthoic Acid*.—The acid (0·316 g.) and sodium hydrogen carbonate (1·13 g.) were mixed, crushed, and dried for 1 hr. under reduced pressure at 20° before being strongly heated. A grey solid (0·236 g.) distilled and was sublimed (85°/15 mm.) to give white crystals of 2H-*heptafluoronaphthalene* (0·119 g.), m. p. 62—63° (Found: C, 47·5; H, 0·6; F, 52·3. $C_{10}HF_7$ requires C, 47·3; H, 0·4; F, 52·35%). The residue from the decarboxylation (0·09 g.) was mixed with sodium hydrogen carbonate (0·360 g.), dried as above, and heated, but no further material distilled.

The authors thank the Department of Industrial and Scientific Research and the Imperial Smelting Corporation for maintenance grants (to B. G. and B. J. K. S., respectively), and Dr. J. R. Majer for mass spectrometry.

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[*Received, August* 30*th*, 1961.]