

36. Polycyclic Fluoroaromatic Compounds. Part I. Some Reactions of Octafluoronaphthalene.

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Octafluoronaphthalene is attacked by a number of nucleophilic reagents in the β -position. The preparation and some simple properties of heptafluoro-2-naphthylhydrazine, 2*H*-heptafluoronaphthalene, 1,3,4,5,6,7,8-heptafluoro-2-methylnaphthalene, heptafluoro-2-naphthol, and heptafluoro-2-naphthyl methyl ether are reported. Defluorination of perfluorodecalin gives a little dodecafluorotetralin in addition to octafluoronaphthalene.

OCTAFLUORONAPHTHALENE has been prepared in good yield by the defluorination of perfluorodecalin over heated nickel or iron.¹ In common with most highly fluorinated aromatic compounds so far obtained, octafluoronaphthalene does not show the extremely limited solubility in, or miscibility with, common organic liquids that are characteristic of aliphatic fluorocarbons. It may be crystallised from solvents that are suitable for the crystallisation of naphthalene. Hexafluorobenzene,² and its derivatives containing simple functional groups,³ are readily attacked by nucleophilic reagents, forming substituted fluoro-aromatic products. This paper reports the beginning of an investigation of the reactions of octafluoronaphthalene with nucleophilic reagents. Two positions (α and β) are available for the first attack, and evidence will be presented to show that the fluorine atom at a β -position is the one replaced preferentially.

Hydrazine in refluxing aqueous ethanol reacted with octafluoronaphthalene as it does³ with hexa- and penta-fluorobenzene. The product was a heptafluoronaphthylhydrazine (I). The best yields were obtained by the use of stoichiometric quantities of the two reactants since the use of an excess of hydrazine gave unidentified polysubstituted

¹ Gething, Patrick, Stacey, and Tatlow, *Nature*, 1959, **183**, 588.

² Godsell, Stacey, and Tatlow, *Nature*, 1956, **178**, 199.

³ Brooke, Burdon, Stacey, and Tatlow, *J.*, 1960, 4754.

material. The product was generally obtained as a brown solid even after repeated recrystallisation from solvents, and was best purified by sublimation. The heptafluoronaphthylhydrazine was converted into a heptafluoronaphthalene (II) by reaction with boiling Fehling's solution. The same heptafluoronaphthalene was obtained directly by the reaction of octafluoronaphthalene with lithium aluminium hydride in refluxing diethyl ether. This compound (II) was shown to be 2*H*-heptafluoronaphthalene since it was identical with a compound obtained⁴ by decarboxylation of heptafluoro-2-naphthoic acid. The structure of this acid was known from its formation by the hydrolysis of heptafluoro-2-trichloromethylnaphthalene obtained from heptafluoro-2-trifluoromethylnaphthalene.⁴ The heptafluoronaphthylhydrazine (I) must therefore be heptafluoro-2-naphthylhydrazine, and the position in octafluoronaphthalene most favoured for reaction with hydrazine and with lithium aluminium hydride is the β -position.

From the reaction of octafluoronaphthalene with methyl-lithium a heptafluoromethylnaphthalene (III) was obtained. Fluorination of this compound over cobaltic fluoride gave the perfluoromethyldecalin obtained also by fluorination of 2-methylnaphthalene. Since there is no evidence of the migration of alkyl groups in these fluorinations, compound (III) must be 1,3,4,5,6,7,8-heptafluoro-2-methylnaphthalene, affording a third example of the preferred reaction of a nucleophilic reagent with the β -position in octafluoronaphthalene. It was hoped to obtain additional evidence for the structure of 1,3,4,5,6,7,8-heptafluoro-2-methylnaphthalene by its conversion into heptafluoro-2-naphthoic acid, but attempts to oxidise it with potassium permanganate or potassium dichromate proved unsuccessful. This experience parallels the difficulty found in the attempted oxidation of 2,3,5,6-tetrafluoro-*p*-xylene,⁵ and since in the latter case the derived dibromide, 2,3,5,6-tetrafluoroxylene dibromide, was oxidised with selenium dioxide to tetrafluoroterephthalic acid it was hoped that 2-bromomethylheptafluoronaphthalene would react in a similar way. This bromide was prepared by the photobromination of 1,3,4,5,6,7,8-heptafluoro-2-methylnaphthalene but was oxidised only with difficulty by selenium dioxide, and the desired heptafluoro-2-naphthoic acid was obtained only in extremely small yield. Its formation, however, supports the assignment of structure to compound (III). As with hexafluorobenzene,⁶ reaction of octafluoronaphthalene with potassium hydroxide in *t*-butyl alcohol gave a hydroxy-derivative which has been assigned the structure heptafluoro-2-naphthol, by analogy with the other replacements described. Reaction of octafluoronaphthalene with sodium methoxide yielded a heptafluoromethyl ether identical with the product of the methylation of the heptafluoronaphthol by diazomethane.

The ease of reaction of highly fluorinated aromatic compounds with nucleophilic reagents is well established, and is the consequence of the possibility of the displacement of fluorine as its negative ion. It seems that, in general, increasing fluorine content of polyfluoro-aromatic compounds enhances the susceptibility of the carbon-fluorine bonds to nucleophilic attack. Thus a carbon-fluorine bond in hexafluorobenzene is readily attacked by nucleophiles such as the methoxide ion or hydrazine, whereas that in fluorobenzene is not. This behaviour is attributed to the withdrawal of electrons from the aromatic nucleus by the negative inductive effect of the substituent fluorine atoms. In discussing the reaction of aromatic molecules with electrophilic reagents it is supposed that these reagents attack positions that are polarised, or may be polarised by the oncoming reagent, to have the greatest electron density. In a similar way it may be supposed that the attack by nucleophilic reagents will take place at the positions that have, either in the unperturbed state of the molecule or under the influence of the reagent, the greatest deficiency in electron density. If, then, we suppose that in replacing hydrogen by fluorine we do not change the relative polarisation or polarisability of the α - and

⁴ Gething, Patrick, Smith, and Tatlow, following paper.

⁵ Barbour, Buxton, Coe, Stephens, and Tatlow, *J.*, 1961, 808.

⁶ Birchall and Haszeldine, *J.*, 1959, 13.

β -positions in the naphthalene nucleus, we should expect that the position least favoured for electrophilic attack in the hydrocarbon would be that most favoured for nucleophilic attack in the fluorocarbon. Electrophilic attack on naphthalene, such as in nitration, produces under normal conditions, the α -substituted naphthalene. This is consistent with our observation that β -substitution is preferred in nucleophilic attack on octafluoronaphthalene.

The products of defluorination of perfluorodecalin were found to contain, in addition to octafluoronaphthalene and unchanged starting material, <10% of a third component. A quantity of this compound was obtained from the products of a number of experiments by using preparative-scale gas chromatography, and it was shown to be dodecafluorotetralin. That it contains an aromatic nucleus was demonstrated by its showing an ultraviolet spectrum very similar to that of perfluoro-*o*-xylene. Oxidation of the compound with potassium permanganate in acetone solution gave octafluoroadipic acid, demonstrating that one of the rings was saturated.

EXPERIMENTAL

Octafluoronaphthalene.—This was prepared by passing perfluorodecalin over iron gauze at 460–500° as described previously.¹ The solid product recrystallised from benzene to give octafluoronaphthalene, m. p. 87–88°, λ_{\max} (in EtOH; 0.092 g./l.) 2770, 3080, and 3225 Å (ϵ 4650, 1650, and 2060).

Heptafluoro-2-naphthylhydrazine.—Octafluoronaphthalene (2.5 g.), hydrazine hydrate (0.51 g.), and ethanol (12 ml.) were refluxed together for 4 hr., then poured into water and extracted continuously with methylene chloride. The extract was dried (MgSO₄), filtered, and evaporated to leave a brown solid (2.5 g.). Recrystallisation from light petroleum (b. p. 100–120°) followed by sublimation at 110°/0.05 mm. gave *heptafluoro-2-naphthylhydrazine* (1.5 g.), m. p. 118–119° (Found: C, 42.5; H, 1.0. C₁₀H₃F₇N₂ requires C, 42.3; H, 1.1%).

Dry hydrogen chloride was passed into a solution of the hydrazine (0.2 g.) in dry ether (5 ml.), and the resultant precipitate was filtered off. Reprecipitation from ethanol by ether afforded *heptafluoro-2-naphthylhydrazine hydrochloride* (0.2 g.), m. p. 211–212° (decomp.) (Found: C, 37.5; H, 1.3. C₁₀H₄ClF₇N₂ requires C, 37.4; H, 1.3%).

Benzaldehyde (0.2 ml.) was added dropwise to a solution of the hydrazine (0.3 g.) in water (1 ml.), and the resulting solution was warmed for 5 min. Recrystallisation of the resultant white precipitate from ethanol gave *benzaldehyde heptafluoro-2-naphthylhydrazone* (0.36 g.), m. p. 196–198° (Found: C, 55.2; H, 1.9. C₁₇H₇F₇N₂ requires C, 54.9; H, 1.9%).

2H-Heptafluoronaphthalene.—(a) *From heptafluoro-2-naphthylhydrazine*. The hydrazine (0.84 g.) and Fehling's solution (40 ml. each of solutions "A" and "B") were refluxed together for 40 min., during which a red precipitate was formed. The product was distilled from the mixture in steam, filtered off from the aqueous distillate, and sublimed at 60°/10 mm., to give *2H-heptafluoronaphthalene* (0.5 g.), m. p. 63–64.5° (Found: C, 47.0; H, 0.5; F, 52.6. C₁₀HF₇ requires C, 47.3; H, 0.4; F, 52.4%), λ_{\max} (in EtOH, 0.0492 g./l.) 2800 (broad), 3180, and 3270 Å (ϵ 4540, 2503, and 3221). Mass spectrometry: principal mass peaks: 254, C₁₀HF₇; 235, C₁₀HF₆; 223, C₉HF₆; 216, C₁₀HF₅. This compound was identical with that obtained by decarboxylation of heptafluoro-2-naphthoic acid⁴ (infrared spectra).

(b) *From octafluoronaphthalene*. A solution of octafluoronaphthalene (3.0 g.) and lithium aluminium hydride (0.115 g.) in dry ether was refluxed for 40 hr., then cooled, dilute sulphuric acid was added, and the organic phase separated. The aqueous phase was extracted with ether (20 ml.), and the ethereal extracts were combined, dried (MgSO₄), filtered, and evaporated to give a solid product (2.7 g.), which was separated by preparative gas chromatography (column 3" diam., 16' length; packing, 1 : 2 silicone elastomer SE 301-kieselguhr; 180°; N₂ 46 l./hr.) to give octafluoronaphthalene (1.1 g.) and *2H-heptafluoronaphthalene* (1.1 g.), m. p. 62–63°, identical with that described above (infrared spectra).

1,3,4,5,6,7,8-Heptafluoro-2-methylnaphthalene.—Methyl-lithium (Li, 0.0073 g./ml.) in dry ether (38 ml.) was added with stirring to a solution of octafluoronaphthalene (10.0 g.) in dry ether (100 ml.). A vigorous reaction took place, and the rate of addition was such that a gentle refluxing was maintained. Stirring was continued for 30 min. after completion of the addition, and the precipitated lithium fluoride was then filtered off. The ether solution was

dried (MgSO_4) and filtered, and the ether removed. The solid (9.5 g.) was separated by preparative-scale chromatography (details as above), into octafluoronaphthalene (2.0 g.) and 1,3,4,5,6,7,8-heptafluoro-2-methylnaphthalene (5.4 g.), m. p. 58° (Found: C, 49.0; H, 1.0; F, 49.7. $\text{C}_{17}\text{F}_7\text{H}_3$ requires C, 49.3; H, 1.1; F, 49.6%); λ_{max} (in EtOH, 0.244 g./l. 2780 (broad), 3115, and 3255 Å (ϵ 4300, 2200, and 2950). Mass spectrometry: principal mass peaks: 268, $\text{C}_{11}\text{H}_3\text{F}_7$; 253, C_{10}F_7 ; 234, C_{10}F_6 .

Fluorination of Heptafluoro-2-methylnaphthalene.—Heptafluoro-2-methylnaphthalene (5.4 g.), in a stream of nitrogen, was passed in 30 min. over cobaltic fluoride contained in a small reactor described previously.⁷ Separation by preparative-scale chromatography (column 3" diam., 16' length; packing, 1:3 dinonyl phthalate-kieselguhr; 100°; N_2 50 l./hr.) gave perfluoro-2-methyldecalin (2.3 g.) having an infrared spectrum identical with that of an authentic specimen and differing from that of perfluoro-1-methyldecalin.

2-Bromomethylheptafluoronaphthalene.—A solution of heptafluoro-2-methylnaphthalene (3.6 g.) and bromine (0.73 ml.) in carbon tetrachloride (5 ml.) was irradiated for 12 hr. with ultraviolet light, then dried (MgSO_4), filtered, and evaporated to leave a solid product (4.5 g.). This solid was sublimed at 80°/0.1 mm. to give a white solid which, on recrystallisation from methanol, gave 2-bromomethylheptafluoronaphthalene (2.0 g.), m. p. 86–87° (Found: C, 37.9; H, 0.3. $\text{C}_{11}\text{H}_2\text{BrF}_7$ requires C, 38.0; H, 0.6%).

A solution of heptafluoronaphthylmethyl bromide (0.255 g.) and thiourea (0.24 g.) was warmed for 5 min. Picric acid (0.25 g.) was added and the solution was warmed for a further 5 min. The precipitate formed on cooling was recrystallised from ethanol, to give the *thiouonium picrate* (0.28 g.), m. p. 206–207° (Found: C, 37.9; H, 1.7. $\text{C}_{18}\text{H}_8\text{F}_7\text{N}_5\text{OS}$ requires C, 37.8; H, 1.4%).

Oxidation of 2-Bromomethylheptafluoronaphthalene with Selenium Dioxide.—A solution of 2-bromomethylheptafluoronaphthalene (1.0 g.) and selenium dioxide (0.52 g.) in ethanol (3 ml.) was heated at 160° for 6 hr. under an air condenser. Water (10 ml.) was added and sulphur dioxide was bubbled through the aqueous mixture to remove the excess of selenium dioxide. The aqueous solution was neutralised and extracted with ether. The solution was then acidified and extracted with ether. This ethereal extract was dried (MgSO_4), filtered, and evaporated to leave a solid product (0.1 g.). Recrystallisation from aqueous methanol gave heptafluoro-2-naphthoic acid (0.05 g.), m. p. 183–185°, having an infrared spectrum identical with that of an authentic specimen⁴ whose m. p. was 188°.

Heptafluoro-2-naphthol.—Octafluoronaphthalene (3.0 g.), potassium hydroxide (1.5 g.), and *t*-butyl alcohol (20 ml.) were heated under reflux for 4 hr. Water (50 ml.) was added to the cooled mixture and the alcohol was distilled off. The aqueous solution was extracted with ether, acidified, and then continuously extracted with ether for 12 hr. The ethereal extract was dried (MgSO_4) and evaporated, to give a solid (2.3 g.), m. p. 116–120°. Recrystallisation from light petroleum (b. p. 100–120°) gave heptafluoro-2-naphthol (1.9 g.), m. p. 120° (Found: C, 44.3; H, 0.3; F, 49.1. $\text{C}_{10}\text{HF}_7\text{O}$ requires C, 44.4; H, 0.4; F, 49.3%).

Heptafluoro-2-naphthol (0.23 g.), toluene-*p*-sulphonyl chloride (0.4 g.), and pyridine (1 ml.) were heated on a water bath for 2 min. The mixture was poured into water, and the precipitated solid was filtered off and washed with dilute sodium carbonate solution and with water. Recrystallisation from ethanol gave heptafluoro-2-naphthyl toluene-*p*-sulphonate (0.15 g.), m. p. 117–118° (Found: C, 48.1; H, 1.6. $\text{C}_{17}\text{H}_7\text{F}_7\text{O}_3\text{S}$ requires C, 48.1; H, 1.7%).

Heptafluoro-2-naphthol (0.54 g.), benzoyl chloride (0.5 g.), and pyridine (2 ml.) were heated on a water bath for 15 min. This gave heptafluoro-2-naphthyl benzoate (0.30 g.), m. p. 134° (from ethanol) (Found: C, 54.2; H, 1.4. $\text{C}_{17}\text{H}_5\text{F}_7\text{O}_2$ requires C, 54.5; H, 1.3%).

Heptafluoro-2-naphthyl Methyl Ether.—(a) Octafluoronaphthalene (3.0 g.) and sodium methoxide in methanol (0.44N; 35 ml.) were heated under reflux for 3 hr. The mixture was poured into a large volume of water and the product extracted with ether. The ethereal extract was dried (MgSO_4), filtered, and evaporated to give a solid product (2.7 g.). Recrystallisation from aqueous methanol gave heptafluoro-2-naphthyl methyl ether (1.7 g.), m. p. 40–41° (Found: C, 46.7; H, 1.2; F, 47.1. $\text{C}_{11}\text{H}_3\text{F}_7\text{O}$ requires C, 46.5; H, 1.1; F, 46.8%).

(b) Ethereal diazomethane, prepared from nitrosomethylurea (10.0 g.), was added slowly to an ice-cold solution of heptafluoro-2-naphthol (1.7 g.) in ether until no more nitrogen was evolved. The resulting solution was dried (MgSO_4), filtered, and evaporated to leave a solid

⁷ Evans, Godsell, Stephens, Tatlow, and Wiseman, *Tetrahedron*, 1958, 2, 183.

(1.65 g.), m. p. 33—35°. Sublimation of this at 70°/0.1 mm. gave the ether (1.3 g.), m. p. 39—40.5° with an infrared spectrum identical with that from (a).

Dodecafluorotetralin.—The liquid residue, obtained after the separation of the crude solid octafluoronaphthalene from the products of defluorination of perfluorodecalin, (13.4 g.), collected from several defluorination experiments, were separated by preparative-scale chromatography (packing, 1 : 3 silicone elastomer SE301-kieselguhr; 150°; N₂ 50 l./hr.) to give perfluorodecalin (8.6 g.) and *perfluorotetralin* (2.3 g.) (Found: C, 34.6; F, 65.3. C₁₀F₁₂ requires C, 34.5; F, 65.5%), λ_{max} . (in EtOH, 0.23 g./l) 2730 Å (ϵ 1885). Mass spectrometry: principal mass peaks: 329, C₁₀F₁₁; 310, C₁₀F₁₀.

Oxidation of Perfluorotetralin.—Perfluorotetralin (1.0 g.) was added to a solution of potassium permanganate (2.7 g.) in acetone (200 ml., previously dried over MgSO₄) and the mixture was shaken overnight. Water (200 ml.) was then added and the acetone was removed by distillation. The resulting aqueous suspension was acidified with sulphuric acid, decolorised with sulphur dioxide, and continuously extracted with ether for 12 hr. Addition of aniline to the dried (MgSO₄) ether extracts gave a precipitate of crude dianilinium octafluoroadipate (0.74 g.). Of this a quantity (0.25 g.) was dissolved in water (5 ml.), and a saturated solution of *S*-benzylthiuronium chloride was added. The white precipitate produced (0.36 g.) was recrystallised from water, to give di-(*S*-benzylthiuronium) octafluoroadipate (0.2 g.), m. p. 240° (Found: C, 42.8; H, 3.7. Calc. for C₂₂H₂₂F₈N₄O₄S₂: C, 42.4; H, 3.5%). (Cited ⁸ m. p. 244°).

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