

Polycyclic Fluoro-aromatic Compounds. Part 9.¹ Preparation and Some Reactions of Decafluorofluoranthene

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Fluorinations of fluoranthene with cobalt trifluoride and potassium tetrafluorocobaltate give perfluoroperhydrofluoranthene and perfluorotetradecahydrofluoranthene, respectively. Defluorination of either of these over iron(III) oxide gives decafluorofluoranthene, which is attacked by nucleophiles (OMe^- , H^- , NH_2NH_2) at position 1, and then at 6, 3, and 4. Oxidation of decafluorofluoranthene with nitric acid gives octafluorofluoranthene-2,3-quinone and then heptafluoro-9-oxofluorene-1-carboxylic acid.

OVER the last two decades we, and others, have prepared² a number of perfluoropolynuclear carbocyclic aromatic compounds and have investigated,² in particular, the nucleophilic replacement reactions of most of them. We now report the preparation of decafluorofluoranthene (II) and some of its reactions.

Fluorination of fluoranthene over cobalt trifluoride gave, as expected, perfluoroperhydrofluoranthene (I) (25%), and, on defluorination over iron(III) oxide at

isomers are present as well. Defluorination of (III) gave decafluorofluoranthene (II) in 45% yield.

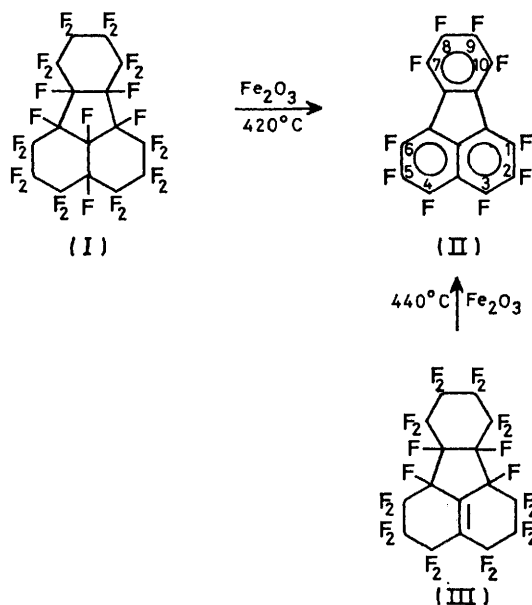
Unlike some^{1,3,5} of the defluorinations of other perfluoro-polycyclics, no partially aromatised products have been detected in the defluorinations reported in this paper. Perfluorodecalin, for example, gives^{5c} a little perfluorotetralin as well as octafluoronaphthalene.

Decafluorofluoranthene is, like its parent hydrocarbon, a pale yellow solid, and the whole of its u.v./visible spectrum strongly resembles that of fluoranthene, a feature commented^{1,4} upon before with other perfluoropolynuclear/aromatic parent hydrocarbon pairs.

Correct analysis of the ^{19}F n.m.r. spectrum of decafluorofluoranthene is crucial for the identification of its nucleophilic replacement products. There were five multiplets of equal intensity (156.7, 153.8, 135.4, 135.0, and 119.2) and two of them (119.2 and 135.4) showed a large coupling constant (38 Hz) which, by analogy with other perfluoropolynuclear aromatics,^{1,3,7} can only be attributed to interaction between F^1 and F^{10} ($\equiv \text{F}_6$ and F_7). The highest field signals (153.8, 156.7) must be due to F_2 ($\equiv \text{F}_5$) and F_8 ($\equiv \text{F}_9$) because only they have two *ortho*-fluorine neighbours: any fluorine in this type of compound possessing only one *ortho*-fluorine would resonate^{1,3,8} below 150. The remaining signal (135.0) must therefore be due to F_3 ($\equiv \text{F}_4$). Decoupling experiments completed the assignments: irradiation of the 119.2 signal caused considerable changes in the 156.7 and 135.0 signals, and collapsed the 38 Hz coupling in that at 135.4, thus allowing the assignments in Table I to be made. Other decoupling studies (irradiating the 153.8 and 156.7 signals) were in agreement.

A complete coupling analysis has not been carried out, because the spectrum was clearly second-order.

We have treated decafluorofluoranthene with three nucleophiles: sodium methoxide, lithium aluminium hydride (this behaves as H^-), and hydrazine. The reactions began by replacement of the fluorine at position 1, and were followed by attack at positions 6, 3, and 4, as shown in Scheme 2. The structures of the methoxide and hydride products have been determined solely, and quite straightforwardly, by ^{19}F n.m.r. spectroscopy. For example, the dimethoxy-compound (V) showed only four signals and so it must be symmetrical: the 119.2 multiplet of decafluorofluoranthene (F_1 , F_6) was com-



SCHEME 1

420 °C, this in turn gave decafluorofluoranthene (II) (30%). This—fluorination then defluorination—is the standard procedure^{1,3-5} by which we have prepared many perfluoropolynuclear aromatics. It is improved by about a two-fold overall increase in yield when potassium tetrafluorocobaltate is used as the fluorinating agent instead of cobalt trifluoride. The fluorination product (40%) here is a mixture of the stereoisomers and double-bond positional isomers of structure (III). The double bond in (III) has no fluorine on it (no i.r. absorption $>1\ 680\ \text{cm}^{-1}$),⁶ but there are too many tertiary C-F signals to be accounted for by stereoisomers of (III) alone, so we conclude that some of its double-bond

pletely absent and the 156.7 (F₂, F₅) had moved downfield by about the usual 3 p.p.m. associated^{3,9} with replacement of an *ortho*-fluorine by a methoxy-group. Similar arguments can be applied to the other methoxy-

pounds [the di- (V) and tetra- (VII) methoxy-compounds and the dihydro-compound (IX)] was the presence of an AA'XX' spectrum due to F₇, F₈, F₉, and F₁₀.

The structure of the the hydrazino-compound (XI),

TABLE I
N.m.r. spectra^a of polyfluorofluoranthenes

Compound (II)	Solvent	Temp. (°C)	1	2	3	4	Chemical shifts ^{b,c}						Coupling constants (Hz) ^{c,d}
	Xylene	35	119.2	156.7	135.0	135.0	5	6	7	8	9	10	
(II)	Xylene	35	119.2	156.7	135.0	135.0	156.7	119.2	135.4	153.8	153.8	135.4	$J_{1,10}$, 38; $J_{1,2}$, 17; $J_{1,3}$, 9.5; $J_{2,3} + J_{2,4}$, 5.5; ^e $J_{7,8} + J_{7,9}$, 16 ^e
(IV) ^f	Xylene	100	4.74	151.1	135.5—137.5		154.7	120.9	135.5— 137.5	158.6	155.9	133.7	$J_{6,7}$, 50; $J_{4,5}$, $J_{5,6}$, $J_{8,9}$, 19; $J_{7,10}$, 15; $J_{9,10}$, 17; $J_{2,OMe}$, 3.0 $J_{2,3} + J_{2,4}$, 5.3 ^h ; $J_{7,8} + J_{7,9}$, 17.2 ^h ; $J_{2,OMe}$, 2.8 $J_{4,5}$, 12 $J_{7,8} + J_{7,9}$, 17.2 ^h
(V)	Xylene	120	4.6	153.4	138.4	138.4	153.4	4.6	134.8 ^g	157.3 ^g	157.3 ^g	134.8 ^g	$J_{2,OMe}$, 3.0 $J_{2,3} + J_{2,4}$, 5.3 ^h ; $J_{7,8} + J_{7,9}$, 17.2 ^h ; $J_{2,OMe}$, 2.8 $J_{4,5}$, 12 $J_{7,8} + J_{7,9}$, 17.2 ^h
(VI)	Xylene	100	4.4	147.6	4.4	137.6	152.6	4.4	134.8	157.3	157.3	134.8	$J_{2,OMe}$, 3.0 $J_{2,3} + J_{2,4}$, 5.3 ^h ; $J_{7,8} + J_{7,9}$, 17.2 ^h ; $J_{2,OMe}$, 2.8 $J_{4,5}$, 12 $J_{7,8} + J_{7,9}$, 17.2 ^h
(VII)	Xylene	130	4.4	147.1	4.4	4.4	147.1	4.4	134.6 ^g	157.3 ^g	157.3 ^g	134.6 ^g	$J_{2,OMe}$, 3.0 $J_{2,3} + J_{2,4}$, 5.3 ^h ; $J_{7,8} + J_{7,9}$, 17.2 ^h ; $J_{2,OMe}$, 2.8 $J_{4,5}$, 12 $J_{7,8} + J_{7,9}$, 17.2 ^h
(VIII)	(CD ₃) ₂ SO	80	8.10	132.8— 133.5	138.8	132.8— 133.5	152.9	119.1	132.8— 133.5	152.0	152.0	139.7	$J_{1,2}$, 9; $J_{1,3}$, 5.5 $J_{1,2}$, 7.8; $J_{7,8}$, 20.3 ⁱ ; $J_{7,9}$, -3.1 ⁱ ; $J_{7,10}$, 13.9 ⁱ ; $J_{8,9}$, 16.3 ⁱ
(IX) ^f	(CD ₃) ₂ SO	100	7.98	132.1	139.1	139.1	132.1	7.98	139.5 ^g	152.8 ^g	152.8 ^g	130.5	$J_{1,2}$, 7.8; $J_{7,8}$, 20.3 ⁱ ; $J_{7,9}$, -3.1 ⁱ ; $J_{7,10}$, 13.9 ⁱ ; $J_{8,9}$, 16.3 ⁱ
(X)	(CD ₃) ₂ SO	100	7.6	106.4	7.6	143.2	135.0	7.6	140.1 ^j	153.4	154.9	141.1 ^j	$J_{1,2}$, 7.5; $J_{4,5}$, 12.5; $J_{6,8}$, 8.5; $J_{7,8}$, $J_{8,9}$, $J_{9,10}$, 18 $J_{4,5}$, $J_{5,6}$, 20.5; $J_{6,7}$, 50; $J_{7,8}$, $J_{8,9}$, $J_{9,10}$, 19 $J_{1,5}$, $J_{1,8}$, 7; $J_{1,10}$, 53; $J_{4,5}$, 19.6; $J_{4,6}$, 15.0; $J_{5,6}$, 19.9; $J_{6,7}$, 54; $J_{7,8}$, 21.2; $J_{7,9}$, 6.5; $J_{7,10}$, 14.4; $J_{8,9}$, 19.5; $J_{8,10}$, 7.0; $J_{9,10}$, 20.5
(XI)	C ₆ D ₆	55	7.99 ^k 8.21 ^l	143.8	137.1 137.9	134.8— 136.6	156.3	122.1	134.8— 136.6	162.1	157.8	137.1— 137.9	$J_{7,8}$, $J_{8,9}$, $J_{9,10}$, 18 $J_{4,5}$, $J_{5,6}$, 20.5; $J_{6,7}$, 50; $J_{7,8}$, $J_{8,9}$, $J_{9,10}$, 19 $J_{1,5}$, $J_{1,8}$, 7; $J_{1,10}$, 53; $J_{4,5}$, 19.6; $J_{4,6}$, 15.0; $J_{5,6}$, 19.9; $J_{6,7}$, 54; $J_{7,8}$, 21.2; $J_{7,9}$, 6.5; $J_{7,10}$, 14.4; $J_{8,9}$, 19.5; $J_{8,10}$, 7.0; $J_{9,10}$, 20.5
(XII) ^f	(CD ₃) ₂ SO	35	107.0			133.6	156.3	121.1	134.8	148.0	153.2	130.4	$J_{7,8}$, $J_{8,9}$, $J_{9,10}$, 19 $J_{1,5}$, $J_{1,8}$, 7; $J_{1,10}$, 53; $J_{4,5}$, 19.6; $J_{4,6}$, 15.0; $J_{5,6}$, 19.9; $J_{6,7}$, 54; $J_{7,8}$, 21.2; $J_{7,9}$, 6.5; $J_{7,10}$, 14.4; $J_{8,9}$, 19.5; $J_{8,10}$, 7.0; $J_{9,10}$, 20.5

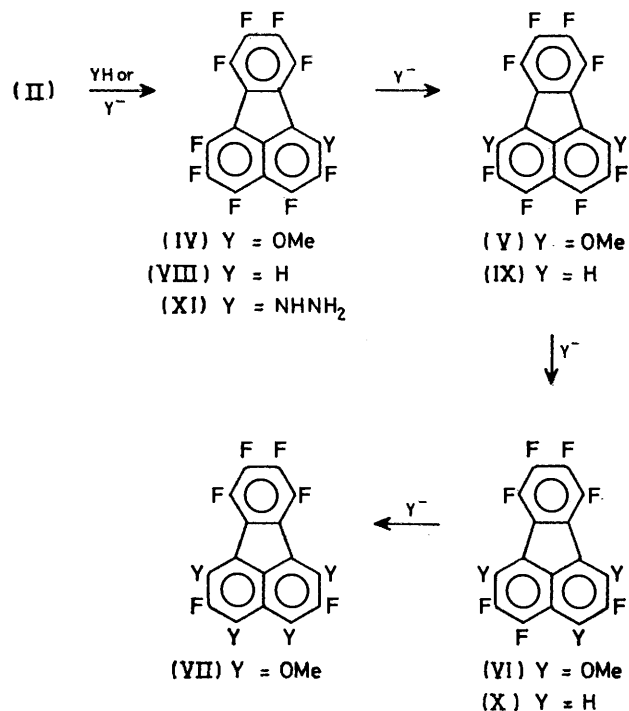
^a Run on a Varian XL 100 instrument operating at 100.1 MHz (¹H) and 94.1 MHz (¹⁹F). ^b ¹⁹F shifts in this Table and in the body of the paper are in p.p.m. upfield from external CFCl₃; ¹H shifts in p.p.m. downfield from external SiMe₄. ^c See compound (II), Scheme 1, for numbering. ^d Constants only approximate. Most ¹⁹F signals were more highly coupled than the listed constants imply: only the clearly discernible values are listed. Many signals were also part of a second-order system: this has been ignored unless otherwise noted. ^e Obtained from AA'XX' system left after irradiating 119.2 signal. ^f Assignments and couplings confirmed by double irradiation studies. ^g These signals formed a typical AA'XX' pattern. ^h Directly observable as a sum from AA'XX' spectrum. ⁱ Obtained by complete analysis of AA'XX' spectrum. ^j Or *vice-versa*. ^k NH₂. ^l NH.

compounds and also to the hydride replacement products, noting that the downfield shift produced by an *ortho*-H replacing an *ortho*-F is *ca.*¹⁰ 20—25 p.p.m. The full assignments are given in Table I. A feature of the ¹⁹F n.m.r. spectra of the symmetrically substituted com-

which was, like ^{5c} heptafluoronaphthylhydrazine, not very stable, was confirmed by treatment with aqueous copper sulphate,¹¹ which converted it into the mono-hydro-compound (VIII).

The positions of attack of the nucleophiles on deca-

fluorofluoranthene can be rationalized by the amplified I_{π} repulsion theory,¹² as recently applied³ to nucleophilic replacement in decafluoropyrene. This consists in summing HOMO charge densities on the carbons which

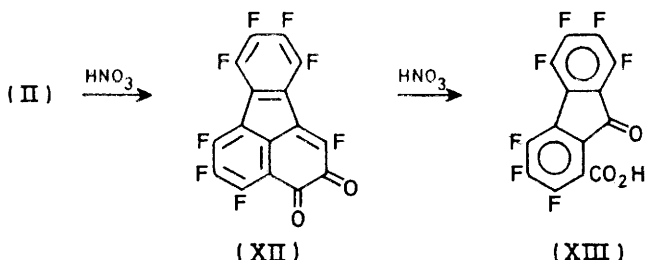


SCHEME 2

bear fluorines in each possible anionic Wheland intermediate: these charges are taken from tables of Hückel

C_1 ($\equiv C_6$) attack, followed by C_3 ($\equiv C_4$)—as it does for other perfluoro-polynuclear aromatics.^{3,12}

Oxidation of fluoranthene is stated¹³ to give the 2,3-quinone and 2-oxofluorene-1-carboxylic acid. Decafluorofluoranthene behaves similarly (Scheme 3). Nitric acid treatment gave a mono-quinone which must be the 2,3-isomer (XII) from its ¹⁹F n.m.r. spectrum: the leading features were the eight equal signals, showing the molecule to be asymmetric; two pairs of signals were strongly



SCHEME 3

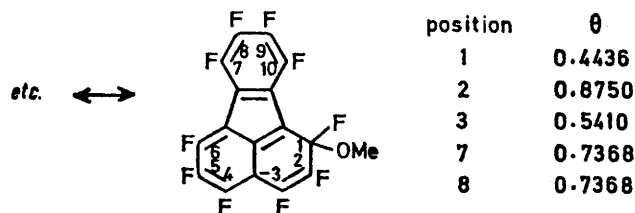
coupled (53 and 54 Hz), showing that there were fluorines on carbons 1, 6, 7, and 10. Stronger oxidation gave the 9-oxofluorene-1-carboxylic acid (XIII). Polyfluoropyrenes behave similarly^{3,14} in giving quinones and carboxylic acids by oxidation with nitric acid.

EXPERIMENTAL

Fluorination of Fluoranthene—(a) *Over cobalt trifluoride.* Fluoranthene (10 g) was introduced during 2½ h, in a stream of nitrogen (3 dm³ h⁻¹), into a heated (410–470 °C) and stirred reactor of the type described previously¹⁵ (containing 2 kg of cobalt trifluoride). Products were swept from the reactor with nitrogen (25 dm³ h⁻¹) and collected in a

TABLE 2

Carbon atom	HOMO Coefficients for the 1-fluoranthenium anion								
Coefficient * (c_i)	2	3	4	5	6	7	8	9	10
	0.3165	0.0517	-0.1360	0.2859	0.1827	0.1547	0.2838	-0.1083	-0.3015



* A. Streitwieser *et al.*, 'Supplemental Tables of Molecular Orbital Calculations,' Pergamon, London, 1965, vol. 1. The relevant figures are listed on pp. 348–370.

HOMOs of the parent hydrocarbons. The procedure is summarized for attack at position 1 in decafluorofluoranthene in Table 2, where values of Σc_i^2 [$=\theta$; summation over all carbons which bear fluorines (C_2 – C_{10} for attack at C_1)] are listed for attack at all positions. The I_{π} repulsion theory argues¹² that the most stable anionic Wheland intermediate is that which has least charge on the carbons which bear fluorines; therefore, the smaller the value of θ , the more likely the attack. This turns out correctly for decafluorofluoranthene— θ is lowest for

cooled (–78 °C) trap. After being washed with water and aqueous sodium hydrogen carbonate, the combined products (125.1 g) from six such runs were distilled at 1 mmHg from phosphoric oxide through a vacuum-jacketted glass column (10 cm \times 1 cm) packed with Dixon gauze rings to give (i) a forerun (60.1 g), b.p. 20–65 °C/1 mmHg; and (ii) b.p. 65–73 °C/1 mmHg which was perfluoroperhydrofluoranthene (I) (51.9 g), b.p. 248 °C (lit.,¹⁶ 235–239 °C) (Found: C, 28.2; F, 71.7. Calc. for $C_{16}F_{26}$: C, 28.0; F, 72.0%). The ¹⁹F n.m.r. spectrum showed large numbers of overlapping peaks in the 104–155 (CF_2) and 174–201 (CF)

regions in intensity ratio 10 : 3; this clearly indicates a mixture of stereoisomers.

(b) *Over potassium tetrafluorocobaltate(III)*. This reaction was carried out as in (a) but at 390—420 °C with 75—80 g of fluoranthene being used in each run in a reactor containing 6 kg of KCoF_4 ; yields were in the range 147—160 g. Distillation of 659 g of such a product gave a fraction (395 g), b.p. 77—81 °C/2 mmHg which was *perfluorotetradecafluoranthene* (III), b.p. 224—225 °C (Found: C, 29.2; F, 70.8; top mass peak 648. $\text{C}_{16}\text{F}_{24}$ requires C, 29.6; F, 70.4%; M^+ 648). The ^{19}F n.m.r. spectrum showed complex patterns of peaks in the ranges 110—145 (CF_2) and 150—190 (CF) in the ratio 5 : 1, consistent with a mixture of stereo- and double-bond-isomers.

Preparation of Decafluorofluoranthene (II).—(a) *From perfluoroperhydrofluoranthene (I)*. This compound (I) (6.0 g) was passed, in a stream of nitrogen ($0.8 \text{ dm}^3 \text{ h}^{-1}$), down a heated (420 °C) vertical nickel tube ($45 \times 2.5 \text{ cm}$) packed with iron(III) oxide. The product (1.36 g) was collected in a liquid-air cooled trap. Addition of acetone gave two layers: the lower one was the starting material, and the upper one was evaporated to leave a reddish yellow solid which was sublimed *in vacuo* and recrystallized from cyclohexane to give yellow crystals of *decafluorofluoranthene* (II) (1.0 g), m.p. 138 °C (Found: C, 50.1; F, 49.8. $\text{C}_{16}\text{F}_{10}$ requires C, 50.3; F, 49.7%). This compound displayed a top mass peak at 381.985 ($\text{C}_{16}\text{F}_{10}$ requires 381.984) and major mass peaks at 363 (C_{16}F_9), 351 (C_{15}F_9), 344 (C_{16}F_8), 332 (C_{15}F_8), and 313 (C_{15}F_7); λ_{max} (ϵ , 0.018 g dm^{-3} in EtOH) at 210 (ϵ 31 000), 235 (35 200), 254 (14 400), 271 (8 910), 282 (7 430), 305 (3 400), 318 (6 790), 353 (10 600), and 370 nm (8 490); and ν_{max} at 1 500, 1 518, 1 602, 1 620, and $1\ 660 \text{ cm}^{-1}$.

(b) *From perfluorotetradecafluoranthene (III)*. This compound (III) (5.6 g) was defluorinated as in (a), but at 440 °C to give crude product (2.0 g) and pure *decafluorofluoranthene* (II) (1.5 g).

Reaction of Decafluorofluoranthene (II) with Sodium Methoxide.—Sodium methoxide in methanol (6 cm^3 ; 0.22M), *decafluorofluoranthene* (0.50 g), and methanol (40 cm^3) were refluxed for 2 h; the bulk of the methanol was then evaporated and the residue added to water (200 cm^3). The precipitate (0.49 g) was filtered off, dried, and separated on a column (45 $\text{cm} \times 2.5 \text{ cm}$) of silica gel with light petroleum (b.p. 40—60 °C)—benzene (4 : 1) as eluant. The first fraction contained *decafluorofluoranthene* (0.01 g), the second *nonafluoro-1-methoxyfluoranthene* (IV) (0.34 g), m.p. 208—208.5 °C [from light petroleum (b.p. 60—80 °C)] (Found: C, 51.8; H, 0.6. $\text{C}_{17}\text{H}_3\text{F}_9\text{O}$ requires C, 51.8; H, 0.8%), and the third *octafluoro-1,6-dimethoxyfluoranthene* (V) (0.10 g).

The following compounds were prepared similarly by using two, three, and four molar proportions of sodium methoxide in methanol [reflux time (h), light petroleum (b.p. 40—60 °C)—benzene eluant composition, and % yield are given in parentheses]: *octafluoro-1,6-dimethoxyfluoranthene* (V) (5, 4 : 1, 38), m.p. 261 °C [from light petroleum (b.p. 60—80 °C)] (Found: C, 53.1; H, 1.7. $\text{C}_{18}\text{H}_6\text{F}_8\text{O}_2$ requires C, 53.2; H, 1.5%); *heptafluoro-1,3,6-trimethoxyfluoranthene* (VI) (8, 2 : 1, 57), m.p. 284—285 °C [from light petroleum (b.p. 60—80 °C) containing a little benzene] (Found: C, 54.4; H, 2.3. $\text{C}_{19}\text{H}_9\text{F}_7\text{O}_3$ requires C, 54.6; H, 2.2%); *hexafluoro-1,3,4,6-tetramethoxyfluoranthene* (VII) (92, 1 : 2, 57), m.p. 258 °C [from light petroleum (b.p. 60—80 °C)—benzene] (Found: C, 55.5; H, 2.7. $\text{C}_{20}\text{H}_{12}\text{F}_6\text{O}_4$ requires C, 55.8; H, 2.8%).

All four methoxy-compounds showed strong molecular ion peaks and fragments due to loss of methyl and methoxy-groups.

Reaction of Decafluorofluoranthene (II) with Lithium Aluminium Hydride.—Decafluorofluoranthene (0.6 g), lithium aluminium hydride (0.08 g), and dry ether (100 cm^3) were refluxed together under nitrogen. Sulphuric acid (15 cm^3 ; 6M) was then added to the green reaction mixture and the ether layer was separated, dried (MgSO_4), and evaporated to leave a residue (0.58 g) which was separated (from the 1H, 6H-compound) as described in the previous experiment to give *nonafluoro-1H-fluoranthene* (VIII) (88, 1 : 1, 45), m.p. 155—156 °C (from cyclohexane followed by sublimation *in vacuo*) (Found: C, 52.9; H, 0.5; F, 47.2. C_{16}HF_9 requires C, 52.8; H, 0.3; F, 47.0%). It was necessary to use an excess of hydride to avoid leaving any unchanged *decafluorofluoranthene* since this could not be separated from the 1H-compound.

The following compounds were prepared similarly using two and three molecular proportions of lithium aluminium hydride (the trihydro-compound was least strongly adsorbed on the column, then the di-, and finally the mono- and the starting material): *octafluoro-1H, 6H-fluoranthene* (IX) (18, 1 : 1, 64), m.p. 172—173 °C [from light petroleum (b.p. 60—80 °C), then sublimation *in vacuo*] (Found: C, 55.8; H, 0.5. $\text{C}_{16}\text{H}_2\text{F}_8$ requires C, 55.5; H, 0.6%); *heptafluoro-1H, 3H, 6H-fluoranthene* (X) (19, 1 : 0, 54), m.p. 187 °C [from light petroleum (b.p. 60—80 °C), then sublimation *in vacuo*] (Found: C, 59.2; H, 1.0. $\text{C}_{16}\text{H}_3\text{F}_7$ requires C, 58.6; H, 0.9%). The three hydro-compounds were all pale green and fluoresced (under a u.v. lamp) either blue (1H-compound) or green (1H, 6H- and 1H, 3H, 6H-compounds).

Reaction of Decafluorofluoranthene (II) with Hydrazine.—Decafluorofluoranthene (0.50 g) in ethanol (10 cm^3) was refluxed with hydrazine hydrate (0.07 g) for 4 h. The reaction mixture was then poured into water, and the precipitate filtered off and dried (0.48 g). Separation on a column (25 \times 2.5 cm) of silica gel gave: (i) (carbon tetrachloride as eluant) *decafluorofluoranthene* (0.02 g); (ii) [light petroleum (b.p. 60—80 °C)—benzene (1 : 1)] unknown (0.01 g); and (iii) (benzene) *nonafluoro-1-ylhydrazine* (XI) (0.36 g), m.p. 222—223 °C (decomp.) (from cyclohexane). This compound could not be purified sufficiently for a correct elemental analysis to be obtained; it did give an acceptable ^{19}F n.m.r. spectrum (Table I) and i.r. showed a strong peak at $3\ 415 \text{ cm}^{-1}$, attributable to NH stretching.

The fluoranthenylydrazine (XI) (0.15 g) was refluxed with a concentrated aqueous solution of copper sulphate (6 cm^3) for 6 h. The green solid which had collected in the condenser was dissolved in ether, and the ethereal solution was dried (MgSO_4) and evaporated to leave a solid which was crystallized from cyclohexane to give *nonafluoro-1H-fluoranthene* (VIII) (0.10 g), m.p. 155 °C, identified by i.r.

Oxidation of Decafluorofluoranthene (II) with Nitric Acid.—(a) At 23 °C. The fluoranthene (0.50 g) and nitric acid (3.0 cm^3 ; d 1.5) were stirred at 23 °C for 55 min. The homogeneous red solution was poured into iced water (300 cm^3) and the precipitate was filtered off, dried, and sublimed *in vacuo* to give an orange solid (0.31 g). Crystallisation from benzene gave the bright red *octafluorofluoranthene-2,3-quinone* (XII) (0.24 g), m.p. 173—174 °C (Found: C, 50.8%; top mass peak 375.981. $\text{C}_{16}\text{F}_8\text{O}_2$ requires C, 51.1%; M^+ , 375.977); strong fragment ions were displayed

at 348 ($M - CO$) and 320 ($M - 2CO$); λ_{\max} (c , 0.02 g dm⁻³ in ethanol) at 232 (ϵ 29 000), 262 (18 400), 340 (5 260), and 376 nm (3 010); ν_{\max} 1 710, 1 690, 1 630, 1 512, 1 500, and 1 485 cm⁻¹.

(b) At 70—80 °C. The fluoranthene (0.50 g) and nitric acid (3.5 cm³; d 1.5) were stirred at 70—80 °C for 5 h. Work-up as in (a) gave the yellow heptafluoro-9-oxofluoranthene-1-carboxylic acid (XIII) (0.14 g), m.p. 241 °C (from benzene, followed by sublimation *in vacuo*) (Found: C, 48.3; H, 0.4. C₁₄HF₇O₃ requires C, 48.0; H, 0.3%); top mass peak 349 ($M - H$) and fragment ion at 306 ($M - CO_2$); λ_{\max} (c , 0.012 g dm⁻³ in ethanol) at 206 (ϵ 18 600), 247 (40 100), 302 (3 110), 315 (3 110), 330 (2 960), and 380 nm (1 410); ν_{\max} 1 730, 1 710, 1 658, 1 625, 1 505, and 1 488 cm⁻¹ and a broad peak between 3 100 and 2 500 cm⁻¹; the ¹H n.m.r. spectrum showed a broad singlet at δ 10.4. The ¹⁹F n.m.r. spectrum [in (CD₃)₂CO] showed seven peaks of equal intensity at (assignment in parentheses) 128.4 (F⁴), 133.9 (F⁵), 135.3 (F²), 138.8 (F⁸), 143.5 (F⁶), 147.1 (F³), and 151.6 (F⁷) from which the following coupling constants (in Hz) were obtained: J_{23} , 19.8; J_{24} , 8.6; J_{34} , 19.8; J_{45} , 68; J_{56} , 20.6; J_{57} , ~2.0; J_{58} , 15.0; J_{67} , 18.3; J_{68} , 9.6; J_{78} , 21.4.

[9/1625 Received, 15th October, 1979]

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