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POLYCYCLIC FLUOROAROMATIC COMPOUNDS—III[1]

OCTAFLUOROACENAPHTHYLENE, AND DECAFLUORO-INDANE, -ACENAPHTHENE, -ANTHRACENE, AND -PYRENE

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Abstract—Perfluoroperhydro-indane, -fluorene, -acenaphthylene, -phenanthrene, -anthracene and -pyrene have been prepared, by fluorination of the aromatic hydrocarbons with cobaltic fluoride. When defluorinated in the vapour phase over heated metal gauze perfluoro-indane, -acenaphthylene, -acenaphthene, -anthracene and -pyrene were obtained.

A GENERAL method has been developed[2,3] in these laboratories for the preparation of perfluoroaromatic compounds, viz. exhaustive fluorination of an aromatic hydrocarbon to an alicyclic fluorocarbon, followed by defluorination, for example in the vapour phase by passage over a heated metal. It has now been extended from the decalin series[1] to other multiple ring systems, and new aromatic fluorocarbons prepared. The alicyclic fluorocarbon intermediates were all made by fluorination of the analogous aromatic hydrocarbon in the vapour phase using cobaltic fluoride.[4]

Perfluoroperhydroindane[4] was prepared from both indane and indene but the latter was not used extensively because it polymerized in the reactor inlet system. Perfluoroperhydro-fluorene, -acenaphthylene, -phenanthrene and -anthracene were previously prepared in the vapour phase using silver difluoride.[5] In the present work with cobaltic fluoride substantial yields of the fluorocarbons were obtained with physical constants essentially the same as those quoted; small differences may arise from different proportions of stereoisomers. The hitherto unknown perfluoroperhydropyrene was obtained as a waxy solid melting over a wide range, an effect which probably arises from the presence of several stereoisomers; this effect was shown also by perfluoroperhydroanthracene and the much lower melting point quoted[5] previously may result from different stereoisomer ratios. The presence of very small amounts of hydrogen in the fluorocarbons was difficult to assess accurately but none was indicated in the IR spectra of very thick films of the liquids or of dispersions of the solids in 'florube'.

Perfluorodecalin has been separated into *cis*- and *trans*- forms by gas chromatography[6] and similar separations appear possible in the series under discussion. However, with the exception of perfluoroperhydroindane the compounds of these series are capable of existing in several forms though some may be excluded by excessive steric interactions. Gas chromatography was consistent with this in that all of the liquid fluorocarbons gave very broad peaks using dinonyl phthalate as stationary phase. No separations of stereoisomers have been attempted, however.

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[1] Part II; B. Gething, C. R. Patrick, B. J. K. Smith and J. C. Tatlow, *J. Chem. Soc.* 190 (1962).

[2] B. Gething, C. R. Patrick, M. Stacey and J. C. Tatlow, *Nature, Lond.* **183**, 588 (1959).

[3] P. L. Coe, C. R. Patrick and J. C. Tatlow, *Tetrahedron* **9**, 240 (1960).

[4] R. D. Fowler, W. B. Burford, J. M. Hamilton, R. G. Sweet, C. E. Weber, J. S. Kasper and I. Litant, *Ind. Eng. Chem.* **39**, 292 (1947).

[5] E. T. McBee and L. D. Bechtol, *Ind. Eng. Chem.* **39**, 380 (1947).

[6] B. J. K. Smith and C. R. Patrick, *Proc. Chem. Soc.* 138 (1961).

The defluorination studies employed the procedures described in earlier communications[2,3] and involved passing the vapourized fluorocarbon in a stream of nitrogen over a heated metal, usually iron or nickel, contained in a nickel cylinder. In this way perfluoroperhydroindane gave decafluoroindane as the sole defluorination product over a range of temperatures. The indane structure was established by IR and UV spectroscopy (Fig. 1) and confirmed by mass spectroscopy.[7] The absence of octafluoroindene in the products parallels the difficult defluorination of decafluoroethylbenzene to octafluorostyrene[8] and the resistance of octafluorocyclopentene to defluorination.[9]

Perfluoroperhydro- acenaphthylene, -anthracene, and -pyrene were all pyrolysed over nickel turnings and gave perfluoro-acenaphthylene, and -acenaphthene, -anthracene and -pyrene respectively; all were clearly characterized by elemental analysis and by IR and UV spectroscopy. The UV spectra were particularly valuable when comparison was made with the hydrocarbon analogues* (see Figs. 1–6).

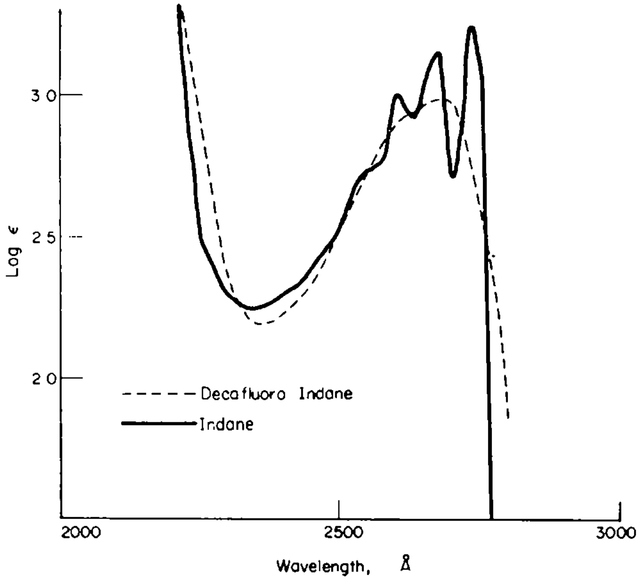

FIG. 1. Indane and decafluoroindane.

Octafluoroacenaphthylene, a yellow crystalline solid, displayed a characteristic UV spectrum similar to that of the hydrocarbon analogue (Fig. 2). Mass spectrometry gave the anticipated total mass peak and fragmentation pattern,[7] and the NMR spectrum contained four peaks of equal intensity. The IR spectrum displayed absorptions associated with fluorinated aromatic nuclei, as indeed did those of all the fluoro-aromatic compounds described in this work. From the combined crude products of about twelve standard defluorinations in the acenaphthylene series a small amount of decafluoroacenaphthene was isolated as a colourless crystalline

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* Friedel and Orchin, *Ultraviolet Spectra of Aromatic Compounds*. New York (1951).

[7] J. R. Majer, private communication.

[8] B. R. Letchford, C. R. Patrick, M. Stacey and J. C. Tatlow, *Chem. & Ind.* 1472 (1962).

[9] R. J. Heitzman, C. R. Patrick, R. Stephens and J. C. Tatlow, *J. Chem. Soc.* 281 (1963).

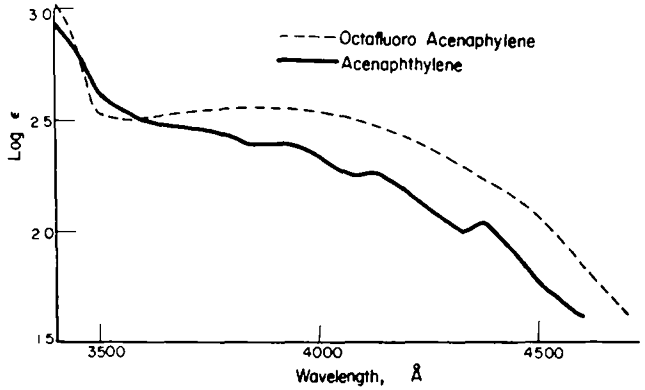

FIG. 2(a). Acenaphthylene and octafluoroacenaphthylene.

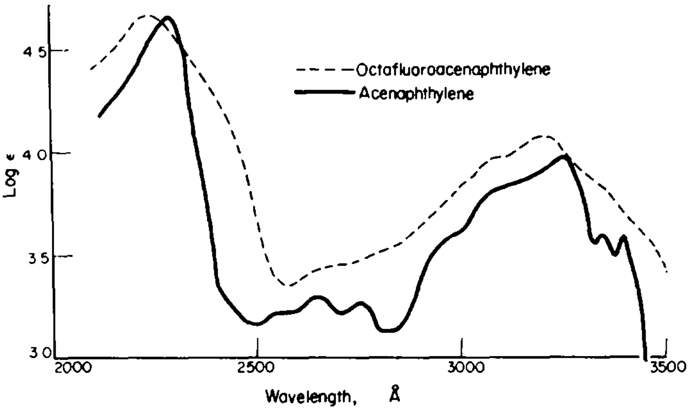

FIG. 2(b). UV and visible of acenaphthylene and octafluoroacenaphthylene.

solid and characterized by elemental analysis and IR and UV spectroscopy (Fig. 3). This compound may well be an intermediate in the formation of octafluoroacenaphthylene.

Decafluoroanthracene was obtained in poor yield but was clearly characterized by its UV absorption spectrum (Fig. 4).

Perfluoroperhydropyrene gave quite good yields of decafluoropyrene considering that sixteen fluorine atoms had to be eliminated. The pyrene system was particularly well characterized by the UV absorption spectrum (Fig. 5) which was almost identical, in the positions of absorption peaks, to that of pyrene, suggesting a coplanar system. It is known[10] that decachloropyrene displays a markedly different UV spectrum and this has been attributed[10] to non-coplanarity arising from interactions of the comparatively bulky chlorine atoms.

Pyrolytic defluorination of samples of perfluoroperhydrophenanthrene, which did not show $\rangle$C—H stretching frequencies in very thick films, did not give pure decafluorophenanthrene. Small amounts of hydrogen were detected both by elemental analysis and IR spectroscopy. The latter indicated that the hydrogen was attached to the carbon of an aromatic ring; this would be consistent with the presence of

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[10] W. L. Mosby, *J. Amer. Chem. Soc.* **77**, 758 (1955).

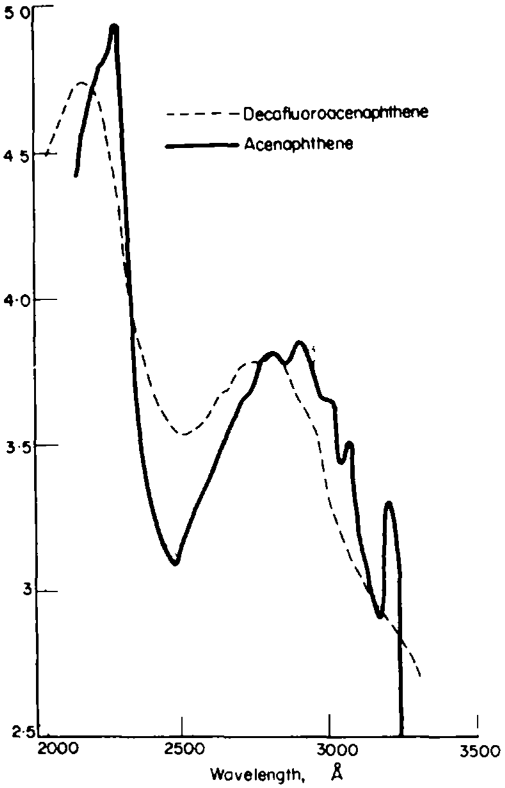

FIG. 3. Acenaphthene and decafluoroacenaphthene.

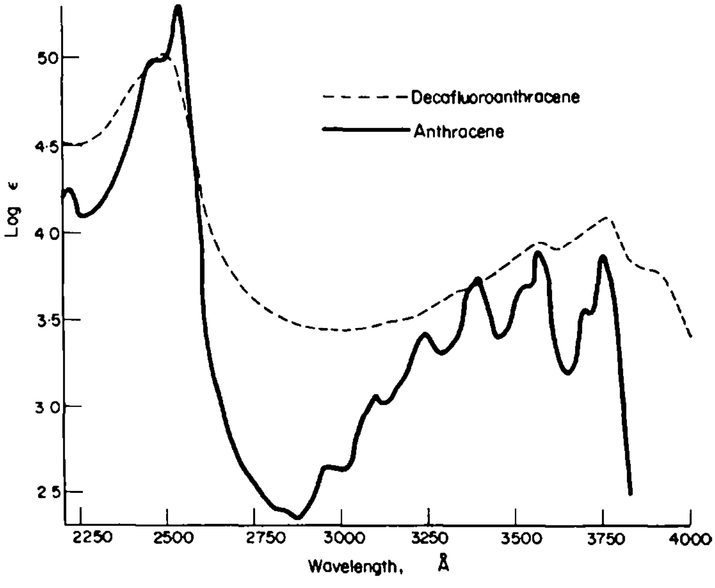

FIG. 4. Anthracene and decafluoroanthracene.

small amounts of nona- and octafluorophenanthrene. The source of the hydrogen may be small amounts of residual hydrogen held by the packing after reduction of the metal fluoride. The nonafluorophenanthrene may then arise from addition of hydrogen across the 9-10 carbon-carbon bond followed by loss of hydrogen fluoride on the metal, and the octafluorophenanthrene by a repetition of this process. Unsuccessful attempts were made to separate the mixture of polyfluorophenanthrenes. The presence of the phenanthrene system was again clearly indicated by the UV absorption spectrum which was closely similar to that of phenanthrene (Fig. 6). Additional

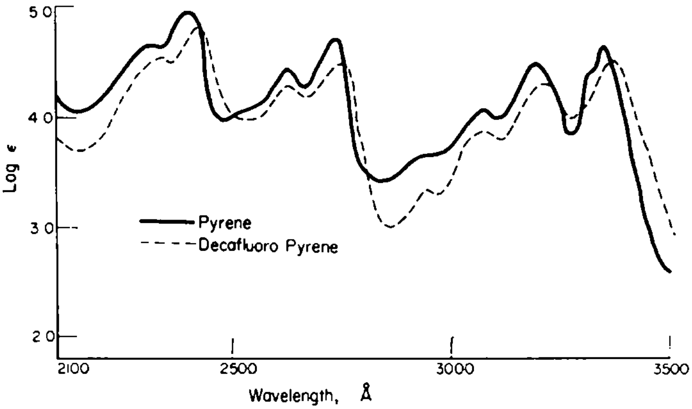

FIG. 5. Pyrene and decafluoropyrene.

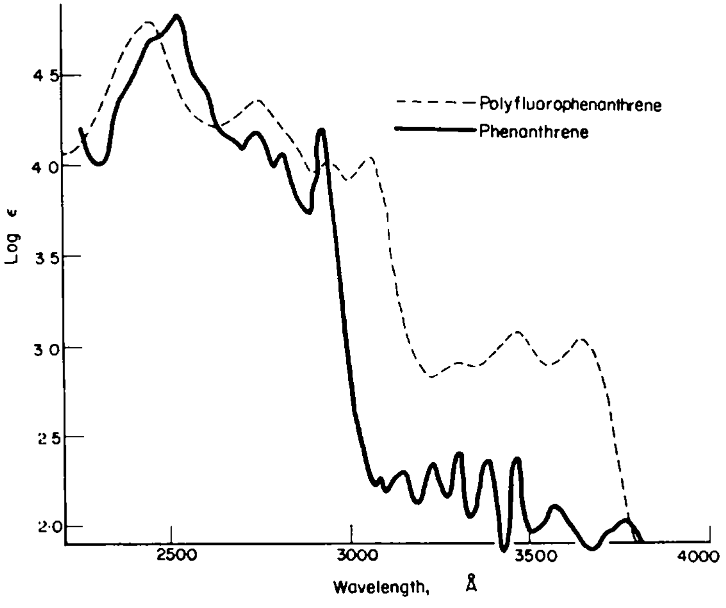

FIG. 6. Phenanthrene and polyfluorophenanthrene.

evidence for the presence of the polyfluorophenanthrene system was provided by its reaction with oleum to give octafluorophenathra-9,10-quinone which readily gave a quinoxaline with *o*-phenylene diamine.

Perfluoroperhydrofluorene was exceptional in that under a wide range of defluorination conditions over iron or nickel it gave only very small amounts of mixtures of high melting coloured solids of unknown constitution. There was never any evidence for the formation of decafluorofluorene. This may be a consequence of the known difficulty of formation of a fluorocyclopentadiene system,[9] an instability of decafluorofluorene associated with the difluoromethylene group, or the formation of largely the *trans-anti-trans* fluorocarbon in the fluorination process coupled with difficult defluorination of *trans*-vicinal tertiary fluorine atoms. Indeed, it may involve a combination of all three effects.

The steric effect mentioned above is worthy of more detailed consideration. Evidence is already available that *cis*-perfluorodecalin defluorinates more readily than the *trans*-isomer[11] and the work described here may well be an extension of this. Thus, it seems that defluorination to give aromatic fluorocarbons proceeds best when molecular models* of the alicyclic fluorocarbons can be made with *cis* fusions of the rings. Thus, perfluoroperhydrofluorene can only be constructed in the *trans-anti-trans* form and perfluoroperhydroanthracene can be constructed only with great difficulty in the *cis-anti-cis* and *cis-syn-trans* forms and is impossible in the *cis-syn-cis form*. In contrast, perfluoroperhydro-indane, -acenaphthylene, -phenanthrene and -pyrene readily give structures with *cis*-ring fusions. The last mentioned, which 'aromatizes' with comparative ease, gives space filled models of the *cis-anti-cis*, *cis-anti-trans* and *cis-syn-trans*, -isomers. All of the fluorocarbons considered give rigid but readily constructed "all-*trans*' fused systems.

EXPERIMENTAL

All UV spectra were measured in ethanol, except where otherwise stated, using a CARY 14 recording spectrophotometer.

Apparatus. The cobaltic fluoride fluorination apparatus was the same as that described elsewhere[12] and the reactor vessel was made of Ni (A, 4′ × 4″ contained 2 kg CoF_3, B, 4′ × 6″ contained 6 kg CoF_3). Solid hydrocarbons were introduced either as a molten liquid from a constant feed device or as vapour in a slow stream of N_2.

The defluorination apparatus was of the same design as that described elsewhere[2,3] and consisted of a horizontal Ni tube (4′ × 2½″) packed either with Ni turnings or Fe gauzes and heated along the whole of its length by 5 independently controlled electrically heated fire bricks. The temp. was measured by a thermocouple placed on the surface of the Ni reactor. Fluorocarbons were volatized in an electrically heated glass vessel and the vapour swept into the reactor in a stream of N_2 metered through a rotameter. The products were condensed in a glass trap cooled in liquid air.

Fluorinations. All fluorinations were carried out in the vapour phase over cobaltic fluoride.

Perfluoroperhydroindane

(a) Indene (50 g) was fluorinated in reactor A in the usual manner[12] (input rate 15 g/hr, temp 280° rising to 320° during fluorination) to give a liquid (54 g). Some of the indene polymerized in the inlet system causing repeated blockages.

(b) Indane (123 g) in reactor B (input rate 45 g/hr, temp 390° rising to 430°) gave a liquid (310 g) which was water-washed free of HF, dried ($MgSO_4$) and combined with the product from (a) and several more fluorinations of type (b). The total material (673 g) was fractionally distilled to give perfluoroperhydro-indane (252 g) b.r. 115–117·5° (Found: C, 26·3; H, 0·0; F, 73·8; Mol. wt. 412

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* 'Courtauld' models were used and it is appreciated that these give only an approximate guide to tolerated steric compressions.

[11] C. R. Patrick, B. J. K. Smith and J. C. Tatlow, unpublished work.

[12] M. Stacey and J. C. Tatlow in *Advances in Fluorine Chemistry* (Edited by M. Stacey, J. C. Tatlow and A. G. Sharpe) Butterworths, p. 176. London (1960).

by mass spectrometry. Calc. for C_9F_{16}: C, 26·2; F, 73·8%; M, 412). No $\geqslant$C—H stretching frequency was observed in the IR spectrum of a 1·3 mm thick film of the liquid fluorocarbon. Quoted[4] b.p. 116–117°.

Perfluoroperhydrofluorene

Fluorene (148 g) was fluorinated as described (reactor B, throughput rate 35 g/hr, temp 390° rising to 420°). The product (837 g) of several fluorinations was fractionally distilled from phosphoric oxide through a vacuum jacketed column (1′ × $\frac{1}{2}$″) packed with Dixon gauze rings ($\frac{1}{16}$″ × $\frac{1}{16}$″) to give perfluoroperhydrofluorene (417 g) b.r. 190–192° (Found: C, 27·6; H, 0·0; F, 71·1. Calc. for $C_{13}F_{22}$: C, 27·2; F, 72·8%). No $\geqslant$CH stretching frequency in IR spectrum of 1·3 mm thick film. Quoted[5] b.p. 190°.

Perfluoroperhydroacenaphthylene

Acenaphthene (156 g) was fluorinated in the usual way (reactor B, input rate 35 g/hr, temp 400°) to give the crude fluorocarbon (390 g). The combined products of several runs were refluorinated in the same reactor to remove any remaining hydrogen and the resulting liquid (1020 g) fractionally distilled from phosphoric oxide to give perfluoroperhydroacenaphthylene (649·5 g) b.r. 175·5–176° (Found: C, 26·1; H, 0·0; F, 70·9. Calc. for $C_{12}F_{20}$: C, 27·5; F, 72·5%). No $\geqslant$CH stretching frequency was detected in the IR spectrum of a 1·3 mm thick film. Quoted[5] b.p. 173°.

Perfluoroperhydrophenanthrene

Phenanthrene (80 g) was fluorinated in the usual way (reactor B, input rate 36 g/hr, temp 440°) to give a crude liquid fluorocarbon (193 g). The combined products of several runs were refluorinated under the same conditions to give a liquid fluorocarbon (927 g) which was fractionally distilled from phosphoric oxide to give perfluoroperhydrophenanthrene (579 g) b.r. 214·5–216° (Found: C, 26·8; H, 0·0; F, 72·7. Calc. for $C_{14}F_{24}$: C, 26·9; F, 73·0%). There were no IR $\geqslant$CH stretching frequencies in a 1·3 mm thick film. Quoted[6] b.p. 205–206°.

Perfluoroperhydroanthracene

Anthracene (125 g) was fluorinated (reactor B, input rate 30 g/hr temp 440°) to give a white solid (253 g) m.p. 70–100°. The combined products (530 g) were refluorinated under the same conditions and a portion (10·0 g) of the product (450 g) recrystallized from perfluoro-1,4-dimethylcyclohexane to give perfluoroperhydroanthracene (6·0 g) m.p. 140–150° (Found: C, 26·7; H, 0·0; Calc. for $C_{14}F_{24}$: C, 26·9%). No $\geqslant$CH IR stretching frequency was observed in a thick film of a dispersion in 'florube'. Quoted[6] m.p. 76–81°.

Perfluoroperhydropyrene

Pyrene (60 g) was fluorinated (Reactor A, input rate 12 g/hr, temp 410°) to give a white solid (116 g) m.p. 60–109° which was refluorinated under the same conditions and a portion (1·45 g) of the product (85 g) recrystallized from perfluoro-1,4-dimethylcyclohexane to give *perfluoroperhydropyrene* (1·0 g) m.p. 90–133° (Found: C, 28·2; H, 0·0; F, 72·0. $C_{16}F_{26}$ requires: C, 28·0; F, 72·0%); this analysis had to be carried out at 950° to obtain complete combustion to CO_2.[13] There was no IR $\geqslant$CH stretching frequency in a thick film of a dispersion in 'florube'.

DEFLUORINATIONS

Perfluoroperhydroindane

In a typical experiment (see Table 1) this compound (8·8 g) was passed over Ni turnings (temp 490°; N_2 flow-rate 3·4 l./hr). The combined products (20·7 g) of 4 defluorinations were separated by gas chromatography (column 16′ × 3″, silicone gum/Kieselguhr, 1:2, temp 130° N_2 flow-rate 60 l./hr) to give unchanged fluorocarbon (12·9 g) and *decafluoroindane* (2·3 g) b.p. 136° n_D^{25} 1·3775 (Found: C, 36·2; H, 0·0; F, 63·4. C_9F_{10} requires: C, 36·3; F, 63·7%). Mass spectral breakdown gave principal peaks at 298 (C_9F_{10}), 279 and 248 and the anticipated fragmentation pattern.[7] UV spectrum shown in Fig. 1. ν_{max} 1655 and 1540 cm^{-1} (fluorinated benzene ring).

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[13] A. D. Campbell and A. M. G. Macdonald, *Anal. Chim. Acta* **26,** 275 (1962).

Perfluoroperhydroacenaphthylene

This compound (39 g) was passed over Ni turnings (temp 500°, N_2 flow-rate 8 l./hr). The yellow solid (8·1 g) obtained was filtered off from unchanged fluorocarbon (13·3 g) and the combined products (110 g) of several such defluorinations were recrystallized from ethanol to give yellow plates of *octafluoroacenaphthylene* (61·0 g) m.p. 149° (Found: C, 48·7; F, 51·4. $C_{12}F_8$ requires: C, 48·7; F, 51·3%). Mass spectral breakdown: total mass peak 296 ($C_{12}F_8$) and consistent fragmentation pattern.[7] The ^{19}F NMR spectrum of a 1·2M solution in acetone displayed 4 peaks of equal intensity. UV spectrum shown in Fig. 2 ν_{max} 1655, 1620 and 1485 cm^{-1} (fluorinated aromatic nucleus).

TABLE 1. EFFECT OF TEMPERATURE ON THE DEFLUORINATION OF PERFLUOROPERHYDROINDANE (charge of 8·8 g in each case; N_2 flow-rate 3·4 l./hr).

Temp (°C)	Wt of starting material recovered (g)	Wt of decafluoroindane (g)
405	7·0	—
425	7·3	—
445	6·3	—
470	4·2	0·2
490	4·25	0·75
500	4·2	0·75
510	2·7	0·45

The crude solid product (110 g) from several defluorinations were combined and fractionally crystallized from ethanol. The final mother-liquor was divided into 4 parts and subjected to adsorption chromatography on alumina (20″ × 1½″) using petrol (60–80°) as eluent. In each case a strong yellow band was followed by a progressively weaker yellow tail and, by repeating the process on the combined appropriate fractions, a very pale yellow solid (7 g) was isolated which recrystallized from ethanol to give *decafluoroacenaphthene* (5 g) m.p. 68–70° (Found: C, 43·2, F, 56·1. $C_{12}F_{10}$ requires: C, 43·2; F, 56·8%). UV spectrum shown in Fig. 3 ν_{max} 1640 and 1520 cm^{-1} (fluorinated aromatic nucleus).

Perfluoroperhydroanthracene

This compound (11·2 g) was passed over Ni turnings (temp 420°, N_2 flow-rate 9 l./hr) to give a pale yellow solid (8·8 g) which was fractionally sublimed to give unchanged fluorocarbon (6·0 g) and *decafluoroanthracene* (0·25 g) m.p. 196–197° (Found: C, 46·7. $C_{14}F_{10}$ requires: C, 47·0%). ν_{max} 1675, 1600, 1570, 1510 and 1495 cm^{-1} were ascribed to fluorinated aromatic nuclei, no $\geqslant$C—H stretching frequencies were detected. UV spectrum shown in Fig. 4.

Perfluoroperhydropyrene

This compound (10 g) was passed over Ni turnings (temp 450°, N_2 flow-rate 8 l./hr) to give a crystalline solid (3 g) which was recrystallized from benzene to give *decafluoropyrene* (1·8 g) m.p. 225–226° (Found: C, 50·3; F, 50·0. $C_{16}F_{10}$ requires: C, 50·3; F, 49·7%). ν_{max} 1660, 1630, 1510 and 1495 cm^{-1} (fluorinated aromatic nuclei). UV spectrum shown in Fig. 5.

Perfluoroperhydrophenanthrene

This compound (20 g) was passed over Fe gauze (temp 410°, N_2 flow-rate 10 l./hr) and the solid product (3·3 g) separated from unchanged fluorocarbon (9·2 g) by filtration. Recrystallization from benzene gave a polyfluorophenanthrene (2·0 g) m.p. 55–58° (Found: C, 49·6; F, 51·3%). A similar pyrolysis product (4·5 g) was recrystallized from perfluoro-1,4-dimethylcyclohexane to give a highly crystalline solid (2·0 g) m.p. 53–54·5° (Found: C, 48·1; H, 0·5. $C_{14}F_{10}$ requires: C, 47·0; F, 53·0%; $C_{14}F_9H$ requires: C, 49·4; H, 0·3; F, 50·3%; $C_{14}F_8H_2$ requires: C, 52·2; H, 0·6; F, 47·2%). ν_{max} 1675, 1650, 1525 and 1500 cm^{-1} (fluorinated aromatic nucleus) and 3080 cm^{-1} (dispersion in 'florube') ($\geqslant$C—H). UV spectrum shown in Fig. 6.

The crystalline polyfluorophenanthrene (1·15 g) and oleum (20% SO_3; 15 ml) were kept at 100° for 3 hr and the yellow homogeneous solution so obtained poured into iced-water (500 ml). The yellow precipitate was dissolved in ether and the cloudy aqueous phase extracted with ether. The dried ($MgSO_4$) ethereal extracts were filtered and evaporated to leave a brown solid (0·7 g) which was recrystallized from benzene–petrol (b.p. 60–80°) to give yellow needles of *octafluorophenanthra-9,10-quinone* (0·35 g) m.p. 123–124° (Found: C, 48·0; H, 0·0; F, 43·1. $C_{14}F_8O_2$ requires: C, 47·8; F, 43·2%). ν_{max} 1705 cm^{-1} (>C═O), 1660, 1620, 1510 cm^{-1} (fluorinated aromatic nucleus); the UV spectrum in diethyl ether, λ_{max} 2425, 3150, 3630 Å ($\log_{10} \epsilon$ 4·5, 3·85, 3·45, respectively), was similar to that of phenanthra-9,10-quinone.

When the quinone (0·04 g) and *o*-phenylenediamine (0·02 g) in ethanol (10 ml) was refluxed for 5 min and then cooled to room temp, a yellow precipitate, m.p. 181–183°, was obtained which was recrystallized from ethanol to give pale yellow crystals of the *quinoxaline* (0·02 g) m.p. 183° (Found: C, 56·9; H, 0·7. $C_{20}H_4F_8N_2$ requires: C, 56·6; H, 0·9%).

Perfluoroperhydrofluorene

This compound was difficult to defluorinate under all conditions tried as Table 2 shows.

TABLE 2. EFFECT OF TEMPERATURE ON THE DEFLUORINATION OF PERFLUOROPERHYDROFLUORENE (charge 9·9 g, over nickel turnings)

Temp (°C)	N_2 flow-rate (l./hr)	Wt of starting material recovered (g)	Product (g) (complex) (m.p. 250°)
445	8	8·3	—
450	8·2	7·45	0·02
475	8	8·0	—
500	8	8·0	—
500	8	5·0	0·06
510	7·6	6·5	0·01
540	8	6·1	—
560	3	—	—
570	8	4·4	—

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