# Polycyclic Fluoro-aromatic Compounds.   Part 7.[1]   Nucleophilic Replacement in Decafluoropyrene

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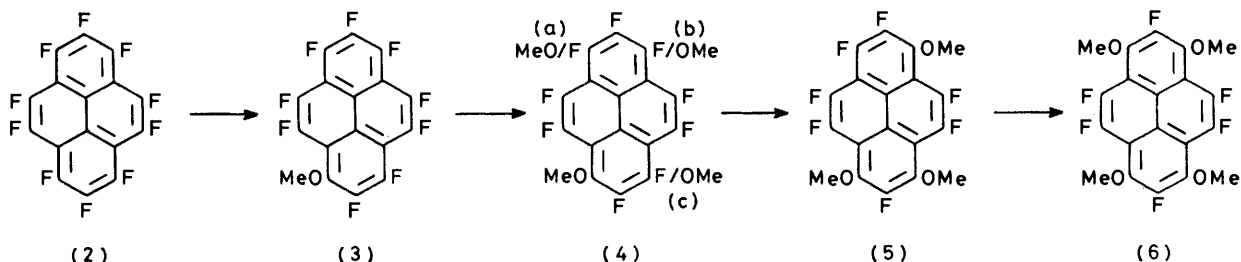
Decafluoropyrene reacts with sodium methoxide with replacement of the fluorine atom at position 1, and then those at 3, 6, and 8.   This has been proved by n.m.r. spectroscopy and by chemical means, and is rationalized by a recently published modification of the I_π repulsion theory.

SIX of the basic perfluoropolynuclear carbocyclic aromatic compounds are known: perfluoro-naphthalene,[2a,3] -acenaphthylene,[4,5] -phenanthrene,[1b,4] -biphenylene,[6] -anthracene,[5] and -pyrene,[5] and the position of attack by nucleophiles is known for all except the last two.   We now report a study of the reaction of methoxide with decafluoropyrene.

Decafluoropyrene has been prepared by the standard Birmingham procedure [2] (defluorination of perfluoroperhydropyrene over a metal [4] or metal oxide [7]) and by exchange of chlorine in decachloropyrene.[8]   We have employed the first method and find that in addition to decafluoropyrene there is a minor product, clearly

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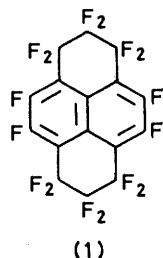
identified by elemental analysis and [19]F n.m.r. spectroscopy as the partially aromatized compound (1).   This parallels the defluorination of perfluorodecalins where

and the tetracarboxylic acid (8) (Scheme 2).   Russian workers [8] have reported the analogous oxidation of decafluoropyrene to give the parent perfluoroquinone and the same acid (8).   Furthermore, elemental analysis of the methoxy-diquinone (7) shows that the methoxy-group is present and hence must be in the lower ring.   [19]F N.m.r. spectroscopy confirmed this: the doublet and triplet (due to *ortho*-F-F coupling) of the parent perfluorodiquinone were replaced, in the methoxy-diquinone (7), by a doublet/triplet pair $(F_8, F_6/F_7)$ and a doublet/doublet pair (F_2/F_3), with one of the latter peaks being shifted *ca.* 5 p.p.m. downfield from its position in the perfluorodiquinone.   Shifts of this magnitude and direction are usual [10] when an *ortho*-fluorine is replaced by a methoxy-group.

The structures of (3)—(6) also followed from their n.m.r. spectra (Table 1).   Decafluoropyrene showed three groups of peaks which were assigned on intensity grounds and by decoupling; a noteworthy feature is the large coupling constant $(J\,^4_{FF} \sim 60\ Hz)$ across the *peri*-positions (*e.g.* F_1—F_{10}), which is similar in magnitude to the *peri*-couplings observed in polyfluoro-naphthalenes [11] and -phenanthrenes.[1b]   On going to the monomethoxy compound (3) from decafluoropyrene, the intensity of the 1,3,6,8-group of signals fell and the triplet (*ortho*-F-F coupling) attributable to F_2 and F_7

SCHEME 1

perfluorotetralins are formed [2a,9] in addition to the major perfluoronaphthalene products; a similar situation arises in the preparation of decafluoro-anthracene.[7]

Treatment of decafluoropyrene with increasing amounts of sodium methoxide in methanol gave the mono-, mixed di- (see later), tri-, and tetra-methoxy compounds (Scheme 1), whose structures followed quite straightforwardly from the chemical and n.m.r. arguments adduced below.

The monomethoxy compound (3), on treatment with concentrated nitric acid, gave the methoxy-diquinone (7)

split into a triplet and doublet of equal intensity, with the latter *ca.* 5 p.p.m. downfield from the former which was in about the same place as the F_2/F_7 signal of decafluoropyrene; as mentioned, this downfield shift is in line with expectation.   The spectra of the tri(5)- and tetra(6)-methoxy compounds can be interpreted similarly; each methoxy-group reduces the intensity of the F_1, F_3, F_6, F_8 group of signals and alters the coupling on the neighbouring 2- or 7-fluorine while shifting it downfield by *ca.* 5 p.p.m.

The dimethoxy-compounds (4) were clearly a mixture.

Weak triplet and singlet ^{19}F n.m.r. signals at approximately the expected positions suggest the presence of some 5—10% of the 1,3-dimethoxy-compound (4c),

Detailed analyses of the n.m.r. spectra of the methoxylated polyfluoropyrenes were not possible because the spectra were relatively weak owing to low solubilities,
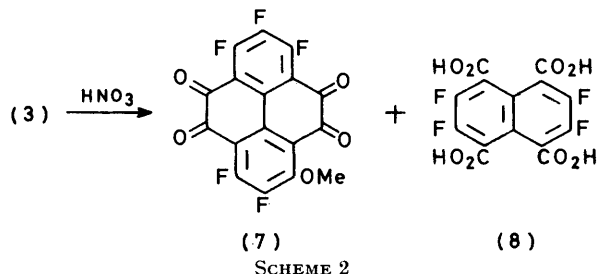
TABLE 1

N.m.r. spectra of polyfluoropyrene
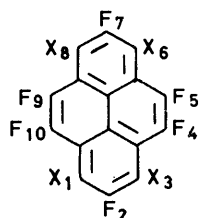
(2) $X_1 = X_3 = X_6 = X_8 = F$ (4c) $X_6 = X_8 = F$, $X_1 = X_3 = OMe$
(3) $X_1 = X_6 = X_8 = F$, $X_3 = OMe$ (5) $X_6 = F$, $X_1 = X_3 = X_8 = OMe$
(4a) $X_1 = X_6 = F$, $X_3 = X_8 = OMe$ (6) $X_1 = X_3 = X_6 = X_8 = OMe$
(4b) $X_3 = X_6 = F$, $X_1 = X_8 = OMe$

Compound	Solvent	$T/°C$	Chemical shifts (multiplicity) ^{a}										Coupling constants ^{b}
			X_1	F_2	X_3	F_4	F_5	X_6	F_7	X_8	F_9	F_{10}	
(2) ^{c}	Acetone	34	137.1 (br d)	155.8 (t)	137.1 (br d)	146.7 (br d)	146.7 (br d)	137.1 (br d)	155.8 (t)	137.1 (br d)	146.7 (br d)	146.7 (br d)	$J_{F_1F_2} = 21.2$, $J_{F_1F_{10}} \sim$ 70
(3) ^{c}	Xylene	34	138.5—139.5 (m)	150.8 (br d)	4.09 (dd)	147.0—148.5 (m)		138.5—139.5 (m)	157.2 (br t)	138.5—139.5 (m)	147.0—148.5 (m)		$J_{F_6F_7} = J_{F_7F_8} = 19.2$, $J_{F_1F_2} = 19.0$ $J_{F_2OMe} = 1.5$, $J_{F_4OMe} \sim$ 0.2 e
(4a,b)	Xylene	90	4.07 f 139.1—140.1 f (br d)	151.7 (d)	4.09 139.1—140.1 (br d)	146.9—149.7 (m)		139.1—140.1 (br d)	151.7 (d)	4.07—4.09 (2 × d)	146.9—149.7 (m)		$J_{F_5F_6} \sim$ 60, $J_{F_6F_7} \sim$ 18 $J_{F_7OMe} = 1.4$ and 1.8 f
(4c)	Xylene	90		144.4 g (s)					158.1 g (t)				$J_{F_6F_7} = 18.0$
(5)	Xylene	135	3.98 (m)	143.7 (s)	3.98 (m)	146.5—148.0 (m)		139.1 (dd)	150.8 (d)	3.98 (m)	146.5—148.0 (m)		$J_{F_5F_6} \sim$ 60, $J_{F_6F_7} \sim$ 20
(5)	Mesitylene	160		144.5 (s)		147.7 (s)			144.5 (s)		147.7 (s)		

^{a} ^{1}H shifts on δ-scale from external Me$_4$Si. ^{19}F shifts in p.p.m. upfield from external CFCl$_3$; br = broad, d = doublet, t = triplet, m = complex set of peaks. ^{b} In Hz; most peaks showed further, incompletely resolved, coupling. ^{c} Internal references used. ^{d} Spectrum clearly second-order; coupling constant approximate. ^{e} The splitting of the multiplets due to F$_4$, F$_5$, F$_6$ etc. was consistent with the presence of a further coupling of ca. 60 Hz. ^{f} One peak or coupling from (4a) and one from (4b); assignment unknown. ^{g} Only peaks attributable to (4c) in spectrum of mixed (4a, b, and c).

although this is far from certain. Two separate doublets in the OMe region of the ^{1}H n.m.r. spectrum imply that

SCHEME 2

both the 1,6(4a)- and 1,8(4b)-dimethoxyoctafluoropyrenes were present in comparable amounts. The

particularly in the cases of the tri(5)- and tetra(6)-methoxy compounds. We have therefore reported (Table 1) mainly the larger coupling constants (J_{FF} ortho $\sim$ 20 Hz, and J_{FF} peri $\sim$ 60 Hz).

The position of attack of methoxide on decafluoropyrene can be rationalized by our recent [12] amplification of the older [13] I_π repulsion theory. Briefly, this consists in summing the charge densities on the carbons which carry fluorine in each possible anionic Wheland-type intermediate. These charges are taken from the Hückel HOMO *of the parent hydrocarbon.* For example, consider replacement at the 4-position of decafluoropyrene. The HOMO coefficients for the hydrocarbon pyrenium anion are shown in Table 2. ΣC_i^2 ($= θ$) over the carbon atoms which bear fluorines (C_1—C_3 and

TABLE 2

HOMO coefficients for the 4-pyrenium and 4-methoxydecafluoropyrenium anions

Carbon atom	1	2	3	5	6	7	8	9	10
Coefficient (C_i)	0.0	0.1400	0.0	0.7001	0.4201	0.0	0.4201	0.1400	0.0

Position	θ
C$_4$	0.9923
C$_1$	0.7123
C$_2$	0.7777

complexity of the signals in the 4,5,9,10-fluorine region of the ^{19}F spectrum is in accord with this; (4a) or (4b), *alone,* would be expected to give a relatively simple spectrum.

C_5—C_{10}) in the 4-methoxydecafluoropyrenium ion is also shown in Table 2, together with values for attack at C_6 and C_7. If the I_π repulsion argument [13] is correct (that the predominant feature in polyfluoroarenium

anions is a destabilizing repulsion between π-electron charge on a carbon atom and the lone pair on the attached fluorine) then replacement would be expected to occur at that position which gives the least value for θ. With decafluoropyrene this is position 6 ($\equiv$ **3**) which agrees with our results. This type of argument also [12] rationalizes the position of attack in other perfluoropoly-nuclear aromatics.

EXPERIMENTAL

[19]F N.m.r. chemical shifts are given in p.p.m. upfield from $CFCl_3$ and ^{1}H shifts on the δ-scale. References are internal for spectra run at 34 °C and external otherwise; a Varian XL100 instrument was used.

Defluorination of Perfluoroperhydropyrene.—Perfluoroper-hydropyrene [4] (4.00 g) was passed for 4 h in a stream of nitrogen (0.2 dm^3/h) over iron(III) oxide powder in a steel tube (45 × 2.5 cm). The products were collected in a trap cooled in liquid air. Volatile products (b.p. <15 °C) were allowed to escape and the pale yellow residue (2.18 g) was crystallized from benzene to give decafluoro-pyrene (1.50 g), m.p. 224—225 °C (lit.,[4] 225—226 °C). The mother liquors were evaporated and 0.5 g of the residue was separated by g.l.c. (Pye 104 instrument; silicone gum on Celite; temperature programmed from 190—270 °C; N_2 carrier gas pressure, 25 p.s.i.) to give (i) *perfluoro*-1,2,3,6,7,8-*hexahydropyrene* (**1**) (0.36 g), m.p. 154—155 °C (purified by sublimation) (Found: C, 38.8; H, 0.0. $C_{16}F_{16}$ requires C, 38.7%); δ$_F$ (CD_3COCD_3) 112.2 (F_1, F_3, F_6, F_8), 125.9 (F_4, F_5, F_9, F_{10}), and 138.0 (F_2, F_7); *m/e* 496 ($C_{16}F_{16}{}^+$), 477 ($C_{16}F_{15}{}^+$), 427 ($C_{15}F_{13}{}^+$), and 377 ($C_{14}F_{11}{}^+$); and (ii) deca-fluoropyrene (0.06 g), identified by its i.r. spectrum.

Reaction of Decafluoropyrene with Sodium Methoxide.—The pyrene (2.00 g) in dry methanol (20 cm^3) was refluxed for 4 h with sodium methoxide in methanol (53 cm^3; 0.11 M). The reaction mixture was poured into water and the precipitate (1.70 g) was filtered off and dried. Separation on a column (50 × 2.5 cm) of silica gel with light petroleum (b.p. 40—60 °C)–benzene as eluant (4 : 1 ratio at start, 3 : 7 at finish) gave: (i) decafluoropyrene (0.12 g, identified by i.r.); (ii) *nonafluoro*-1-*methoxypyrene* (**3**) (0.81 g), m.p. 164—165 °C [from light petroleum (b.p. 60—80 °C)–benzene] (Found: C, 51.5; H, 0.8. $C_{17}H_3F_9O$ requires C, 51.8; H, 0.8%); and (iii) mixed octafluorodimethoxypyrenes (0.47 g).

The following were obtained as major products when decafluoropyrene was treated in a similar way with 2 (4 h reflux), 4 (24 h), and 4.5 (94 h) molecular proportions of sodium methoxide in methanol, respectively: mixed octa-fluorodimethoxypyrenes (**4**) (see Discussion section for composition), yield 39%, m.p. 223—224 °C (Found: C, 52.8; H, 1.5. Calc. for $C_{18}H_6F_8O_2$: C, 53.2; H, 1.5%); *heptafluoro*-1,3,6-*trimethoxypyrene* (**5**) (56%), m.p. 281—282 °C [from light petroleum (b.p. 60—80 °C)–benzene]

(Found: C, 54.6; H, 2.2. $C_{19}H_9F_7O_3$ requires C, 54.6; H, 2.2%); and *hexafluoro*-1,3,6,8-*tetramethoxypyrene* (**6**) (47%), m.p. 341—342 °C (from benzene) (Found: C, 55.5; H, 2.8. $C_{20}H_{12}F_6O_4$ requires C, 55.8; H, 2.8%).

Oxidation of Nonafluoro-1-*methoxypyrene* (**3**) *with Nitric Acid.*—The pyrene (0.30 g) in nitric acid (*d* 1.5; 2 cm^3) was kept at 80 °C for 1 h and then poured into water (300 cm^3). The yellow precipitate was filtered off and crystallized from light petroleum (b.p. 60—80 °C) containing a small amount of acetone to give *pentafluoro*-1-*methoxypyrene*-4,5,9,10-*diquinone* (**7**) (0.15 g), m.p. >400 °C (Found: C, 53.5; H, 0.9; M^+, 381.985. $C_{17}H_3F_5O_5$ requires C, 53.4; H, 0.8%; M^+, 381.990); ν$_{max.}$ 1730, 1 670, 1 585, and 1 560 cm^{-1}; λ$_{max.}$ 227 (ε 25 900), 255 (15 700), and 295 nm (9 385); δ$_F$ (DMSO; 34 °C) 124.4 (F_8), 155.2 (F_7), 124.3 (F_6) 126.2 (F_3), and 149.6 (F_2) (J_{F7F8} 20.7, J_{F6F7} 20.3, and J_{F2F3} 19.5 Hz); δ$_H$ 4.13 (d, *J* 2.9 Hz, coupled to F_2). Hexafluoropyrene-4,5,9,10-diquinone showed δ$_F$ (DMSO; 34 °C) 124.2 (d, F_1, F_3, F_6, F_8) and 154.6 (t, F_2, F_7) (*J* 20.5 Hz).

The original yellow filtrate was extracted continuously with ether and the extracts were dried (MgSO$_4$) and eva-porated to leave a sticky solid (0.1 g). This was taken up in 10% aqueous sodium carbonate and the solution extracted with ether. Acidification of the aqueous solution, followed by extraction with ether, gave, after crystallization from acetone–light petroleum (b.p. 60—80 °C), tetrafluoro-naphthalene-1,4,5,8-tetracarboxylic acid (**8**) (0.05 g), m.p. >360 °C (Found: C, 44.4; H, 1.1. Calc. for $C_{14}H_4O_8$: C, 44.7; H, 1.1%); *m/e* 339.966 (Calc. for $M - 2H_2O$, 339.963); δ$_F$ (DMSO) 131.6(s); δ$_H$ 8.4(s).

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