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FLUORINATIONS WITH POTASSIUM TETRAFLUOROCOBALTATE(III)—V[1]

THE FLUORINATIONS OF SOME POLYCYCLIC AROMATIC HYDROCARBONS OVER POTASSIUM TETRAFLUOROCOBALTATE(III) AND AN IMPROVED SYNTHESIS OF PERFLUORO-PHENANTHRENE AND -PYRENE

J. BURDON, J. R. KNIGHTS, I. W. PARSONS* and J. C. TATLOW
Department of Chemistry, University of Birmingham, P.O. Box 363, Birmingham B15 2TT, U.K.

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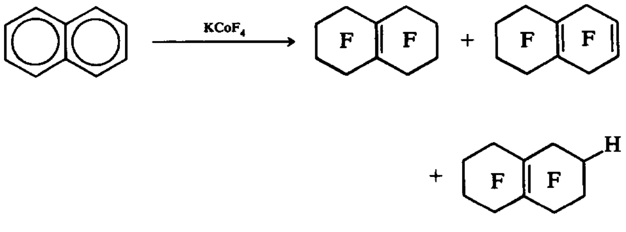
Abstract—Anthracene, phenanthrene, decafluorophenanthrene, pyrene, biphenyl and decafluorobiphenyl have been fluorinated over potassium tetrafluorocobaltate(III) and some of them over caesium tetrafluorocobaltate(III). All the product mixtures except those from pyrene and decafluorobiphenyl consisted mainly of perfluoro-olefins and -aromatics; the pyrene product was largely a perfluoroperhydropyrene, and that from decafluorobiphenyl was very largely perfluorobicyclohexyl. Only in the case of biphenyl was any hydrogen-containing product isolated. The mechanistic interpretation of these observations is attempted. Defluorination of the relevant crude fluorination mixtures provided a good route to perfluoro-pyrene and -phenanthrene. In the case of the fluorination product from anthracene the defluorination largely stopped at an intermediate, partially aromatic, stage.

In a recent rationalisation[2] of known high valency transition metal fluoride (HVMF) fluorinations, it was the central postulate that they are akin to oxidations by transition metal ions. The removal of an electron from the organic substrate by the transition metal ion, to give a radical cation, is considered an essential first step in both reactions. Fluorination then proceeds by reaction of this intermediate either with fluoride ion or with species acting as sources of fluorine radicals.

Because of the low ionisation potentials of polycyclic aromatics, it is a consequence of this theory that their fluorinations ought to be rapid under relatively mild conditions. Fluorinations of naphthalene and tetralin with the mild reagent potassium tetrafluorocobaltate(III) ($KCoF_4$)[3] were carried out some years ago,[1] and the main products formed contained no, or at most one, hydrogen; interestingly, the bulk of these products retained a double bond between the carbons common to both rings (Scheme 1).

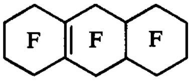
This latter observation suggested that simila fluorinations of other polycyclics might lead t olefinic products and hence to improved synthese of the related aromatic fluorocarbons, since defluorinations are known[4] to be much easier fo fluorocyclo-alkenes than for -alkanes. Accordingly we have studied the fluorinations of anthracene phenanthrene, pyrene and biphenyl over $KCoF_4$.

Anthracene was fluorinated in the usual way ove $KCoF_4$ at 350° using two different reactors. In thi case, although not in the later ones, yields from th smaller reactor were much poorer than those fron the larger one, albeit the products contained th same major components in each case. The reason for the poorer yields from one reactor are not clea The product mixture contained both solid an liquid fractions. The liquid fraction was separate into three major components (85% of the mixture) which proved to be: perfluoro 1,2,3,4,4a,5,6,7,8,9,9a,10 - dodecahydroanthracen (**1**), perfluoro - 1,2,3,4,5,6,7,8,9,10 - decahydroanth



SCHEME 1. In these and all subsequent formulae, an 'F' in a ring denotes 'all unmarked bonds to fluorine'.

racene (**2**), and perfluoro - 1,2,3,4,5,6,7,8 - octahydroanthracene (**3**), all identified by ^{19}F NMR and IR spectroscopy, supported by elemental analysis. The solid fraction was almost pure **3**. The percentages of these products in the crude fluorination product have been estimated by GLC and are shown in Table 1.



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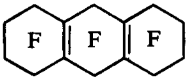

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Anthracene was also fluorinated at 400° over caesium tetrafluorocobaltate(III),[6] a reagent known to give high yields of perfluoroaromatics in other cases,[6,7] and the product obtained are also listed in Table 1. As can be seen, the differences are not great.

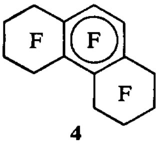
Table 1. Fluorination products from anthracene

Reagent	Temp.	Product weight % in crude fluorination mixture		
		1	2	3
$KCoF_4$				
(reactor C)[a]	350	22	19	43
(reactor B)[a]	350	33	24	38
$CsCoF_4$	460	29	20	34

[a] Reactors are described in the experimental part.

The products from the fluorination of phenanthrene with $KCoF_4$ at 300–400° contained only two major components (GLC), which were separated by fractional distillation. One component was clearly perfluoro - 1,2,3,4,5,6,7,8 - octahydrophenanthrene, **4**, but identification of the other component presented more difficulty. It was shown (mass spectroscopy) to be an isomer of $C_{14}F_{22}$, and by infra-red spectroscopy to have no olefinic fluorine (no strong absorption between 1650 and 1800 cm^{-1}). ^{19}F NMR showed two tertiary fluorines per molecule (by integration), but could not distinguish with absolute certainty between the two remaining candidate structures **5a** and **5b**.

However, four distinct, equally intense tertiary fluorine signals were present, and this is strong evidence for **5a**, since equal amounts of the two isomers of this (*cis* and *trans* at the saturated ring junction) would be expected to be present and to show four such signals, whereas the two isomers of structure **5b**, being more symmetrical, cannot alone account for them. If both **5a** and **5b** were present, the four equal signals would require the unlikely combination of 50% of *one* isomer of **5a**, together with 25% of each isomer of **5b**.



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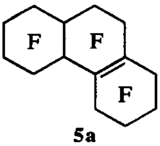
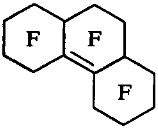
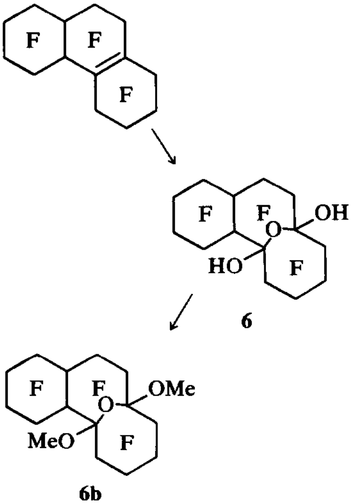


5a



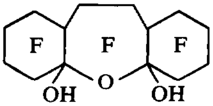
5b

A partially-successful attempt was made to confirm structure **5a** by oxidation with potassium permanganate in acetone. This gave as major product (70% yield) a compound which analysed as $C_{14}H_2F_{22}O_3$, and whose spectral properties suggested structure **6**.[8,9] This compound was methylated with diazomethane to yield, as expected, the dimethyl derivative, **6b** (Scheme 2).



SCHEME 2

Furthermore, standard work-up of an oxidation product later treated with alkali gave, in addition to **6**, the dianilinium salts of perfluoro-succinic, -glutaric and -adipic acids and the S-benzylisothiuronium salt of 5H-octafluoropentanoic acid, all identified by NMR spectroscopy.[10] These acids may all be explained as alkaline degradation products arising from haloform-type reactions on the bicyclic ketone formed from **5a** but not from the alternative ketone which would come from **5b**, giving hydrate **7**.



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Accordingly, the products from the fluorination of phenanthrene are as in Table 2; those of fluorinations of phenanthrene with $CsCoF_4$ at 360 and 390° are also included. Since decafluorophenanthrene is also available in this Department,[11] it was fluorinated on a small (1 g) scale and shown to produce the same product mixture as phenanthrene itself.

Table 2. Fluorination products from phenanthrenes

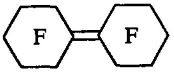
Reagent	Substrate	Wt. % in crude product	
		4	**5a**
$KCoF_4$	phenanthrene	20	65
$KCoF_4$	decafluorophenanthrene	20	65
$CsCoF_4$	phenanthrene	trace	95

Pyrene was fluorinated at 360–410°, and the (mainly solid) fluorination mixture was shown by GLC to contain a single major component (*ca* 70%) which was a perfluoroperhydropyrene: interestingly, this compound was highly crystalline and melted sharply, contrasting with earlier work[11] using cobalt trifluoride as reagent wherein the waxy perfluoroperhydropyrene fraction melted over a substantial range. We take this to mean that a single isomer prediminates in the $KCoF_4$ mixture, but lack of solubility prevented the acquisition of good NMR spectra of this material so that we cannot assign a stereochemistry to it.

At this point it was clear that fluorocarbon material can be made using $KCoF_4$ and that it is unsaturated in some cases. Very little hydrogen is left; this is taken as evidence that in each case most molecules must pass through the perfluoroaromatic in their fluorination pathways—see later for a discussion of this.

An olefin bearing four $-CF_2-$ groups as substituents (e.g. **1**, **2** or **5**) will be very resistant to further fluorination because it will probably have an ionisation potential as high as 12 eV, in contrast to probable values of about 9 eV or less for the perfluoropolycyclic aromatics, and thus be very difficult to oxidise (and hence to fluorinate). The aromatics isolated (**3** and **4**) will also be very difficult to fluorinate further because their ionisation potentials too are probably near 11 ev, since each has four electron-withdrawing $-CF_2-$ substituents. These difficultly oxidisable products might be the only ones formed or other unsaturated compounds may isomerise to them. In this context it is possible to argue that pyrene is saturated by $KCoF_4$ because there is in the fluorination pathway no possible structure with an isolated double bond bearing more than two $-CF_2-$ groupings; such double bonds will be more easily oxidised than those in **1**, **2** or **5a**, and they should come within reach of the oxidising, and hence fluorinating,[2] power of $KCoF_4$: (this may provide a further argument against **5b**).

The fluorinations of biphenyl and decafluorobiphenyl were undertaken next. The mos stable (in the sense of most difficult to fluorinate position for a double bond should be between th two rings, giving compound **8**, but even if this i accepted, and **8** is most stable end product, it ma not be formed if there is no straightforward route t it. In the event, none of this material was isolated although Cammagi and Gozzo[12] obtained it as major product from the fluorination of perfluorobicyclohexenyl over CoF_3 at 140°.



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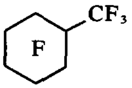
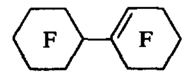
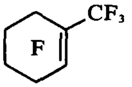
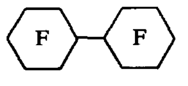
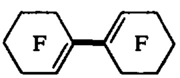
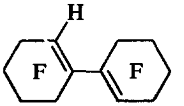
Biphenyl was fluorinated over $KCoF_4$ at variou temperatures between 260 and 410°. The product isolated and their percentages in the 300–310 fluorination product (GLC estimation) are shown i Table 3.

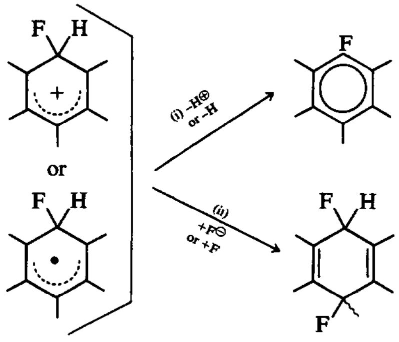
Table 3. Biphenyl fluorination products

Product	%	Product	%
	6·2	 **10**	20·
	1·6	 **11**	3·1
 **9**	26·1	 **12**	24·

On the other hand, the fluorination of decafluorobiphenyl, with $KCoF_4$ at 260°, gives perfluorobicyclohexyl[18] (**11**) as virtually the sole product (*c* 64% overall yield). Repeated attempts to obtai other products from this reaction were unsuccessful, and this result is not easily explained.

The significance of the biphenyl results is no clear; the bulk of the product is 1,3-dienes **9** and **1** (~50%) and a perfluoro-olefin, **10**, (~20%), a with the original structure intact. The presence o the dienes is puzzling, since previous work suggest that such products ought to oxidise relatively easil to radical-cations and so be fluorinated further. Th probable non-coplanar conformations of the olefinic bonds in these dienes provides a possibl explanation of their reluctance to react: this i supported by their low extinction coefficients [9, λ_{max} 279 nm, ϵ_{max} $2\cdot54\times10^3$; 12, λ_{max} 277 nm, ϵ_{max} $1\cdot56\times10^2$]. Thus, they may be effectively monoenes, with appropriate oxidation potentials, rather than having the lower oxidation potentials characteristic of full conjugation. The presence of product **10**, and the absence of **8** in the fluorination mixture suggests that 1,2-, rather than 1,4- addition to **9** must occur in our system, although Cammagi and Gozzo's result over CoF_3 suggests that both modes of addition occur in their system.

These fluorination results, overall, are not easily explained. It seems clear that the major fluorination pathways pass through the perfluoroaromatics, because the very small retention of hydrogen cannot be convincingly explained: also, phenanthrene and decafluorophenanthrene gave the same products upon fluorination. Why the hydrogen abstraction reaction is much faster than the addition (quenching) reaction [i.e. reaction (i) is much faster than (ii)] in these systems is, however, not clear.

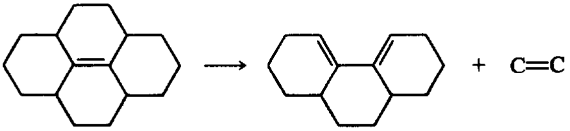


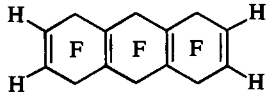
It may be that there is some sort of diffusion control, and that diffusion of fluoride ions or fluorine atoms through the inorganic lattice is in some way a controlling factor with these more easily oxidised systems, but it must be admitted that this is not yet understood.

Should the quenching reaction (ii) predominate, then it would be expected[2] that species such as **13** would be formed. Removal of hydrogens from these by $KCoF_4$ would not be rapid, since major products[3] (unsaturated) from the fluorination of benzene with $KCoF_4$ contain 3 or 4 similarly situated hydrogens, and those[5] saturated from benzene/CoF_3 all contain hydrogen, in a 1,2,4,5-disposition.

Intermediacy of the perfluoroaromatics in the present work thus seems well established.

Considerable amounts of low-boiling materials were obtained from the fluorinations of all the fused-ring aromatics. It is interesting to speculate whether these arise from some sort of random degradation, or whether specific processes might be involved. One such possibility is a reverse Diels-Alder reaction, which could occur with any suitable olefin fragment, e.g:





13

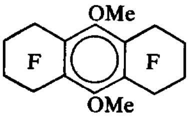
Defluorinations. An objective of this work was to improve the syntheses of perfluoropolycyclic aromatics. The crude fluorination mixtures from anthracene, phenanthrene and pyrene have been defluorinated using either ferric oxide[14] or metallic nickel,[15] and representative results are shown in Table 4.

Table 4

Fluorination mixture from:	Reagent	Temp range	% Yield of perfluoroaromatic, based on hydrocarbon
Anthracene	Fe_2O_3	310–420	Trace
	Ni	450–560	1
Phenanthrene	Fe_2O_3	320–400	23
Pyrene	Ni	420	20

Clearly, the yields of perfluoroanthracene are very unsatisfactory, as they were in the original preparation, although those of decafluorophenanthrene and -pyrene are improved. This work provides the best routes yet described to these compounds. Investigation of the products from the attempted defluorinations of the fluorination mixtures from anthracene showed them to be almost pure **3**, which is apparently very reluctant to defluorinate further. There is at present no satisfactory explanation of this apparent anomaly, though the intermediacy of perfluorotetralin[16] in the defluorination of perfluorodecalin to decafluoronaphthalene is perhaps significant.

For completeness we report the results of nucleophilic attack on the two benzenoid compounds **3** and **4**; treatment of these with methoxide ion in methanol in the cold readily gave the dimethoxy compounds **14** and **15**.



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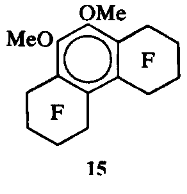

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EXPERIMENTAL

Fluorinations were carried out in several reactors of the usual type; the methods of fluorination have been described before.[5] All had stirred beds, A containing $KCoF_4$ (150 g); B, $KCoF_4$ (2 Kg), C, $KCoF_4$ (6 Kg) and D $CsCoF_4$ (250 g). GLC analyses and separations were carried out in the following units, with N_2 as carrier gas in each case: unit 1, Perkin Elmer F11 capillary column instrument packed with Ucon fluid LB550-X; unit 2, Pye Unicam 104 with a glass column 9·14 m × 8 mm, packed with Ucon fluid 50-HB-2000 on brickdust (1 : 9); unit 3 was as 2, with a stainless steel column 1·52 m × 4 mm packed with silicone gum rubber E301 on Chromosorb P (1 : 7); unit 4 was as 3, the packing being di-isodecylphthalate on Chromosorb P (1 : 2). The temperature employed is given in each case. Spectra were measured on the following instruments: IR: Perkin Elmer 257 grating spectrometer; NMR Perkin Elmer R10 spectrometer, operating at 60 MHz (^1H) and 56·4 MHz (^{19}F); Proton chemical shifts are quoted in δ (ppm downfield of TMS) and fluorine chemical shifts are in ϕ^* (ppm upfield of CCl_3F as internal standard); Mass spectra -A.E.I. MS9 double focussing instrument.

The fluorination of anthracene

(a) *With* $KCoF_4$. Anthracene (30·0 g) was introduced as a solid into reactor B in a stream of N_2 (10 dm^3/h) over 1 h, and the reactor swept out with N_2 (20 dm^3/h) for 4 h further. The products were condensed in a copper vessel cooled in solid CO_2, washed with water, and examined by GLC (unit 1, 110°). Recoveries of crude product varied with temp as shown.

Temp	Recovery (g)
350–360°	44·1
370–380	29·2
400–410	26·3

The products (part liquid, part solid) from the 370–380° run were filtered; the solid (6·7 g) was sublimed (110°, 20 mmHg) and recrystallised from CCl_4 to give *perfluoro - 1,2,3,4,5,6,7,8 - octahydroanthracene* (**3**) (3·4 g), m.p. 124–126·5°, (Found: C, 32·5; F, 67·1. $C_{14}F_{18}$ requires: C, 33·0; F, 67·0%), ^{19}F NMR showed peaks at 107·4, 112·5 and 134·7 ϕ^*, in the ratio 4 : 1 : 4 respectively. IR spectroscopy showed no peaks attributable to olefinic fluorine (1850–1650 cm^{-1}). A sample (1·2 g) of the filtrate was separated by preparative GLC (unit 2, 160°) to give (i) a mixture (approx 1 : 1) of the *cis*- and *trans*-isomers of *perfluoro - 1,2,3,4,4a,5,6,7,8,9,9a,10 - dodecahydroanthracene* (**1**) (0·31 g), *b.p.* 200–202° (*Found*: *C*, 28·6; *F*, 71·5. $C_{14}E_{22}$ requires: C, 28·7; F, 71·3%). ^{19}F NMR showed a complex mass of signals in the range 89–149ϕ^* (total relative intensity 10) and 2 broad singlets of approximately equal intensity at 185·4 and 188·2ϕ^* (total relative intensity 1) (ii) *perfluoro - 1,2,3,4,5,6,7,8,9,10 - decahydroanthracene* (**2**) (0·22 g) m.p. 67° (Found: C, 31·1; F, 69·0. $C_{14}F_{20}$ requires: C, 30·7; F, 69·3%), ^{19}F NMR peaks at 96·6, 112·7 and 137·3ϕ^*, in the ratio 1 : 2 : 2 respectively. (iii) Compound **3** (0·14 g) identified by IR. Proportions of **1**, **2** and **3** in the crude product are given in Table 1. Fluorinations in reactor C of 90 g anthracene gave approximately double the recoveries of product.

(b) *With* $CsCoF_4$. In each run anthracene (5·0 g) was sublimed into reactor D in a stream of N_2 (1·0 dm^3/h). The reactor was flushed with N_2 (5·0 dm^3/h) for 4 h, and the products collected in a solid CO_2 cooled vessel as usual Recoveries were as below.

Temp °C	Recovery (g)	Temp °C	Recovery (g)
280	1·4	360	2·9
290	1·1	400	3·1
360	1·7	460	4·2
360	0·8	465	5·6

Analytical GLC showed these mixtures to be very simila to those from the $KCoF_4$ fluorinations with some mino additional short-retained components, presumably degradation products.

The Fluorination of phenanthrene

(a) *With* $KCoF_4$. In each run, the molten hydrocarbo (25·0 g) was added to reactor B dropwise from a heate funnel; otherwise the details were as for the anthracen fluorination. The results of four such runs are shown.

Run No.	Reactor temp (°C)	Recovery (g)
1	300	37·2
2	350	50·6
3	370–80	39·9
4	390–400	33·4

The products were analysed by GLC, which showe several components. The combined products from th first 3 runs above were filtered, and the solid portio (6·0 g) crystallised (CCl_4) and sublimed to give unreacte phenanthrene (4·1 g). The viscous filtrate (96·7 g) wa fractionally distilled through a vacuum jacketed colum (30 × 1·5 cm) packed with Dixon gauzes, many sma fractions being taken, and assayed by analytical GLC Pure samples were thus obtained of (i) a mixture (appro 1 : 1) of the *cis*- and *trans*-isomers of 10,10a - *dodecahydrophenanthrene* (**5a**, 25·1 g) b.p. 195–196°. (Found: C 29·0; F, 71·5. $C_{14}F_{22}$ requires: C, 28·7; F, 71·3%), *m/* 585·969 ($C_{14}F_{22}^+$ requires 585·965). ^{19}F NMR showed complex mass of signals in the range 93–153ϕ^* (tot integral intensity 10) and 4 broad singlets of approximately equal intensity at 162·0, 179·4, 186·3 and 191·5ϕ (total integral intensity 1) (ii) *perfluoro* - 1,2,3,4,5,6,7,8 *octahydrophenanthrene* (**4**; 8·0 g) b.p. 225–226° (Found C, 33·2; F, 67·3. $C_{14}F_{18}$ requires:C, 33·0; F, 67·0%), ν_m 1635 and 1495 cm^{-1} (aromatic C=C), *m/e* 509·972 ($C_{14}F_{18}$ requires: 509·971). ^{19}F NMR showed 5 signals at 103·9 an 106·3 (fluorines on C_1 and C_4), 122·7 (aromatic fluorine and 135·5 and 136·8ϕ^* (fluorines on C_2 and C_3) in ratios c 2 : 2 : 1 : 2 : 2. The amounts of compound **4** and **5** in th product mixtures were estimated by GLC and given i Table 2.

(b) *With* $CsCoF_4$. These were carried out as for th anthracene fluorination, with the variation that the molte hydrocarbon (5·0 g) was added dropwise from a heate inlet.

Run No.	Reactor temp °C	Recovery (g)
1	360	5·1
2	360	5·4
3	390	4·9

Each product mixture was analysed by GLC (Unit 3, 200°): the product mixture from run 2 (5·0 g) was vacuum distilled through a 6″ column to give the mixed perfluoro - 1,2,3,4,4a,5,6,7,8,9,10,10a - dodecahydrophenanthrenes, identified by IR spectroscopy.

The fluorination of perfluorophenanthrene with $KCoF_4$

Perfluorophenanthrene (1·0 g) was sublimed into reactor A in a stream of N_2 (2·0 dm^3/h), and the products were collected and worked up as usual. Two such runs were carried out, and the details are shown.

Run No.	Reactor temp (°C)	Recovery (g)
1	310	0·84
2	340	0·70

Examination of the product mixtures by analytical GLC (Unit 3, 200°) showed them to be almost identical with those obtained from phenanthrene and $KCoF_4$; this conclusion is supported by ^{19}F NMR of the crude product.

The fluorination of pyrene with $KCoF_4$

This fluorination was carried out exactly as for the phenanthrene case: the product mixture was dissolved in CCl_4, washed well with water, and the solvent largely removed by distillation up a 15 cm vacuum jacketed column packed with glass helices. The yields thus obtained were:

Run No.	Reactor temp (°C)	Recovery (g)
1	360–365	51·2
2	400	43·1
3	400	49·0
4	410	47·2

The combined products from runs 3 and 4 were fractionally distilled from P_2O_5 through a vacuum jacketed column (30 × 1·5 cm) packed with Dixon gauzes. One of the major fractions, b.p. 250–266 (10·7 g) yielded white crystals of a perfluoroperhydropyrene, m.p. 148–149° (from perfluoromethyl cyclohexane) (Found: C, 28·2; F, 72·3. $C_{16}F_{26}$ requires: C, 28·0; F, 72·0%), *m/e* 685·962. [$C_{16}F_{26}^+$ requires: 685·958]. This material was 70% of the crude product.

Oxidation and alkaline degradation of the mixed perfluoro - 1,2,3,4,4a,5,6,7,8,9,10,10a - *dodecahydrophenanthrenes*

Compound **5a** (10·0 g) was added dropwise to a stirred soln of $KMnO_4$ (4·0 g) in dry acetone (200 ml) during 30 min, and the mixture stirred for 19 h. Water (100 ml) was then added, the acetone removed *in vacuo*, excess of permanganate removed with SO_2 and the soln made 2M in KOH. After stirring for 45 h the mixture was extracted with ether (1 × 100, 2 × 50 ml) and the combined ether extracts washed first with 2M KOH solution (100 ml) and then with water (100 ml). The combined alkaline aqueous extracts were retained.

The ether extracts were dried ($MgSO_4$), filtered and the ether was removed by distillation up a 15 cm column. The oily residue (7·9 g) was distilled (20 mm Hg) through a 6·0 cm vacuum jacketed column packed with glass helices to give: (i) ether (0·6 g), (ii) a colourless viscous liquid (6·2 g) b.p. 138–139°/20 mm Hg, identified as the mixed (approx 1:1) *cis*- and *trans*-isomers of *docosafluoro - 1,10 - dihydroxy - 15 - oxatricyclo*(8,4,1,0^{2,7}) *pentadecane* (**6**) b.p. 268–269° (Found: C, 26·2; H, 0·6; F, 65·7. $C_{14}H_2F_{22}O_3$ requires: C, 26·4; H, 0·3; F, 65·7%), ν_{max} 3500 and 3080 cm^{-1} (OH). The ^1H NMR spectrum displayed a broad singlet at 7·03 and the ^{19}F spectrum showed a complex mass of signals in the range 103–144ϕ^* (total relative intensity 10) and 4 broad singlets at 168·2, 173·7, 181·7 and 184·3ϕ^* (total relative intensity 1).

Treatment of the oxidation product with diazomethane (with D. F. Thomas)

A soln of diazomethane (*ca* 1·2 g) in ether (25 ml) was added to a soln of **6** (2·0 g) in ether (20 ml). When the solution was colourless, removal of solvent gave an oil (1·7 g) which had no OH groupings present (IR). This oil was therefore the mixed isomers of *docosofluoro - 1,10 - dimethoxy - 15 - oxatricyclo*(8,4,1,0^{2,7})*pentadecane* b.p. 274–275° (Found: C, 28·9; H, 0·9; F, 62·6. $C_{16}H_6F_{22}O_3$ requires: C, 28·9; H, 0·9; F, 62·9%).

Haloform cleavage products

The retained alkaline aqueous extracts were acidified (HCl) and continuously extracted into ether (150 ml) over 24 h. The ether extracts were dried ($MgSO_4$), filtered, and the ether was removed by distillation up a 15 cm column. The oily residue (1·3 g) was redissolved in dry ether (50 ml) and filtered before freshly distilled aniline was added dropwise until precipitation was complete. The solid material (1·15 g) was filtered off (the filtrate being retained) dried, and examined by ^{19}F NMR spectroscopy (in perdeutero dimethyl sulphoxide), which showed signals corresponding to the dianilinium salts of perfluorosuccinic (29%), -glutaric (37%) and -adipic (34%) acids.[10]

The ethereal filtrate and washings were washed with 4M HCl and the ether removed by distillation. The residue was dissolved in water (100 cm^3), the pH adjusted to *ca* 4, the solution filtered, and a saturated solution of S-benzylisothiuronium hydrochloride added. The precipitate which formed on cooling was filtered off and recrystallised to give a white solid (0·41 g) identified as the salt of $5\underline{H}$-octafluoropentanoic acid, m.p. 167–169° (lit[17] 172–173°) with correct IR and ^{19}F NMR[10] spectra.

The 1,10-dihydroxy compound was obtained in 70% yield, when the oxidation was terminated before the first addition of the alkali. Isolation was by ether extraction.

Fluorination of biphenyl with $KCoF_4$

These fluorinations were performed as were those of phenanthrene, using 30 g of starting material in each run. The results of 6 such runs were:

Run No.	Reactor temp (°C)	Recovery (g)
1	260	37·1
2	260	44·8
3	300–310	34·1
4	300–310	39·7
5	300–310	39·0
6	410–420	11·3

The product mixtures were examined by GLC (unit 4, 130°) which showed 6 major components, which were isolated by fractional distillation followed by preparative GLC (Units 2 and 4) to give in order of increasing retention time: (i) perfluoromethylcyclohexane, identified by IR and ^{19}F NMR; (ii) perfluoro - 1 - methylcyclohexene,[18] identified by IR and ^{19}F NMR; (iii) perfluoro-1,1′ - bicyclohexenyl, identified by IR and ^{19}F NMR spectroscopies, λ_{max} 279 nm (ϵ_{max} $2 \cdot 54 \times 10^3$) (*cf* lit[18] vlaues of λ_{max} 280 nm, ϵ_{max} $1 \cdot 16 \times 10^4$); (iv) *perfluoro - 1 - cyclohexylcyclohexene*, b.p. 163–164·5° (Found: C, 27·2; F, 72·3. $C_{12}F_{20}$ requires: C, 27·5; F, 72·5%) ν_{max} 1685 cm^{-1} (C=C), *m/e* 524 (M^+); (v) perfluorobicyclohexyl, identified by IR spectroscopy[12]; (vi) 2H - *heptadecafluoro* - 1,1′ - *bicyclohexenyl*, b.p. 170° (Found: C, 30·5; H, 0·4; F, 69·2. $C_{12}HF_{17}$ requires: C, 30·8; H, 0·2; F, 69·0%), ν_{max} 1705 cm^{-1} (C=C), λ_{max} 277 nm (ϵ_{max} $1 \cdot 56 \times 10^2$), *m/e* 468 (M^+) ^{1}H NMR spectroscopy showed a single signal centred at 6·50δ. ^{19}F spectroscopy gave peaks which are interpreted as shown.

Signal (ϕ*)	Intensity	Assignment
109·7	4	1
111·5	2	2
113·2	1	3
120·6	2	4
134·6 135·2	8	5

The fluorination of decafluorobiphenyl with $KCoF_4$

Decafluorobiphenyl (10·0 g) was sublimed into reactor B at 260° over 30 min in a stream of N_2 (5 dm^3/h) and the reactor flushed out with N_2 (15 dm^3/h) for a further 3 h before the products were worked up in the usual way to give an off-white solid (10·7 g); sublimation of a sample (5·0 g) (*in vacuo* yielded perfluorobicyclohexyl) (3·49 g), m.p. 75° (identified by IR spectroscopy).

Reaction of perfluoro - 1,2,3,4,5,6,7,8 - *octahydroanthracene* (3) *with sodium methoxide*

Sodium methoxide soln in MeOH (3·0 ml, 2·6M) was run into a stirred suspension of 3 (1·25 g) in dry MeOH (7·0 ml) an the mixture stirred for 2 h at 15° before water (20 ml) was added and the mixture extracted with ether (3 × 25 ml). The dried ($MgSO_4$) ether extracts were distilled to remove the ether and the solid residue (0·93 g) was sublimed *in vacuo* to give *dimethoxyhexadecafluoro* - 1,2,3,4,5,6,7,8 - *octahydro* - 9,10 - *dimethoxyanthracene* (11) (0·82 g) (63%), m.p. 144–147° (Found: C, 35·6; H, 1·0; F, 56·4. $C_{16}H_6F_{16}O_2$ requires: C, 36·0; H, 1·1; F, 56·9%), *m/e* 534 [$C_{16}H_6F_{16}O_2^+$]. ^{1}H NMR showed a sharp singlet at 4·18δ. ^{19}F NMR showed two signals of equal intensity at 106·5 (α F) and 135·2ϕ* (β F).

Reaction of perfluoro - 1,2,3,4,5,6,7,8 - *octahydrophenanthrene* (4) *with sodium methoxide*

The starting material (1·25 g) was methoxylated and worked up as in the previous experiment to yield *hexadecafluoro* - 1,2,3,4,5,6,7,8 - *octahydro* - 9,10 - *dimethoxyphenanthrene* (0·76 g) m.p. 107–108·5° (Found: C, 36·1; H, 1·2; F, 57·3. $C_{16}H_6F_{16}O_2$ requires: C, 36·0; H, 1·1; F, 56·9%), *m/e* 534 (M^+). ^{1}H NMR showed a sharp singlet at 4·13δ. ^{19}F NMR showed four signals of equal intensity at 103·9, 106·7, 135·1 and 137·5ϕ.*

Attempted preparation of decafluoroanthracene

(a) *Using iron* (III) *oxide.* In each experiment the crude fluorination product (5·0 g) was passed down a heated vertical glass column (30 × 2·6 cm), packed with iron (III) oxide, in a stream of N_2 (1·5 dm^3/h) and the products collected in a glass trap cooled by liquid air: the recoveries at various temps are given:

Run No.	Furnace temp (°C)	Recovery (g)
1	310	2·3
2	335	2·6
3	375	1·9
4	390	2·6
5	410	2·3
6	415–20	2·9

The product mixtures were examined by IR spectroscopy and analytical GLC (Unit I 110°), which showed them to be predominantly (3). Separation of the product from run 6 (2·0 g) by fractional vacuum sublimation gave (i) a mixture (0·4 g) (not examined further), (ii) impure (3) (0·86 g) and (iii) impure decafluoroanthracene (*ca* 0·1 g), identified by IR spectroscopy, m.p. 187–193, lit[11] 199°.

(b) *Using nickel turnings.* In each experiment the fluorination mixture (10·0 g) was passed in a stream of N_2 (2 dm^3/hr) through a Ni tube (120 × 6·0 cm) packed with Ni turnings, and the products collected at liquid air temp. These again proved to be predominantly 3. The product weights from 3 runs are shown:

Run No.	Furnace temp (°C)	Recovery (g)
1	450	5·7
2	450–70	6·4
3	560	2·2

The product mixture from run 2 was separated by fractional vacuum sublimation to give (i) a mixture (1·5 g) (not examined further), (ii) 3 (2·5 g) identified by IR spectroscopy, and (iii) decafluoroanthracene (0·2 g) m.p. 198–199°, identified by IR spectroscopy.[11]

Preparation of decafluorophenanthrene using Fe_2O_3

This was carried out using the crude fluorination product from phenanthrene (5 g) and $KCoF_4$ exactly as in the attempted defluorination of the anthracene products. Some results were:

Run No.	Temp (°C)	Recovery (g)
1	320–30	1·4
2	380	1·95
3	400	1·6

The combined products (3·50 g) were recrystallised from benzene to give decafluorophenanthrene (2·29 g) m.p. 55·0–56·6° (lit[11] 51–52°), identified by IR spectroscopy.

Preparation of decafluoropyrene using nickel turning

The crude pyrene fluorination product (2·0 g) was passed in a stream of N_2 (2 dm^3/h) at 420° through a nickel tube (46 × 3·0 cm) packed with Ni turnings, and the products were condensed at liquid air temp. These products (1·2 g) were recrystallised twice from benzene to give decafluoropyrene (0·39 g), m.p. 223–226° (lit[11] 225–226°), identified by IR spectroscopy.

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