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POLYCYCLIC FLUOROAROMATIC COMPOUNDS—IV[1]

SOME REACTIONS OF OCTAFLUOROACENAPHTHYLENE

J. BURDON, D. HARRISON and R. STEPHENS
Chemistry Department, The University, Birmingham

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Abstract—Perfluoroacenaphthylene has been oxidized with potassium permanganate, to give hexafluoro-1,8-naphthalic anhydride and trifluorohemimellitic acid, with nitric acid, to give trifluorohemimellitic acid, and with oleum to give hexafluoroacenaphthene-1,2-quinone. It has been treated with a range of nucleophilic reagents and oxidation of the products has shown substitution to occur solely in the six-membered rings. In the particular reaction where sodium methoxide was used, multiple substitution products were obtained in addition to the primary one and in all cases attack was confined to the six-membered rings. Proton NMR spectroscopy has been used to establish the precise orientation of the mono-, di-, tri-, and tetramethoxy-polyfluoroacenaphthylenes so obtained.

BY ANALOGY with acenaphthylene,[2] octafluoroacenaphthylene might be expected to show the greatest double bond character between C_1 and C_2. This is probably reflected in its ready addition of bromine to give a 1,2-dibromide,[3] catalytic hydrogenation to a 1,2-dihydro-system and its easy oxidation.

Potassium permanganate in acetone has been used to oxidize fluoro-olefins[4] and fluoro-aromatic compounds.[5] Olefinic double bonds are cleaved to give carboxylic acids and under more vigorous conditions aromatic rings are completely broken down.[5] One molecular proportion of potassium permanganate rapidly oxidized octafluoroacenaphthylene (I) in an exothermic reaction to give hexafluoro-1,8-naphthalic anhydride (II), but a threefold excess also gave trifluorohemimellitic acid. The former was characterized as the crystalline monomethyl ester and the latter as its tris-(S-benzylthiuronium) salt and trimethyl ester. Attempted decarboxylations to give 2,3,4,5,6,7-hexafluoronaphthalene and 1,2,3-trifluorobenzene, under a variety of conditions failed; this probably results from processes of the type discussed for related systems.[6]

The oxidation of 2,3-disubstituted hexafluorobutenes to perfluorobiacetyl with chromium trioxide in sulphuric acid has been reported,[7] and a mechanism for the process described involving an intermediate chromate ester. A related, but hitherto unknown, process is believed to occur in the ready reaction of octafluoroacenaphthylene with oleum containing 20% sulphur trioxide to give hexafluoroacenaphthylene-1,2-quinone (III) as the sole product. The quinone was characterized by IR, UV and ^{19}F NMR spectroscopy, and by the ready formation of a quinoxaline derivative with

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[1] Part III; D. Harrison, M. Stacey, R. Stephens and J. C. Tatlow, *Tetrahedron* **19**, 1893 (1963).

[2] C. A. Coulson and V. A. Crawford, *J. Chem. Soc.* 1990 (1948).

[3] D. Harrison, R. Stephens and J. C. Tatlow, unpublished work.

[4] J. Burdon and J. C. Tatlow, *J. Appl. Chem.* **8**, 293 (1958).

[5] B. Gething, C. R. Patrick and J. C. Tatlow, *J. Chem. Soc.* 186 (1962); B. Gething, C. R. Patrick, B. J. K. Smith and J. C. Tatlow, *Ibid.* 190 (1962).

[6] (the late) E. V. Aroskar, M. T. Chaudhry, R. Stephens and J. C. Tatlow, *J. Chem. Soc.* 2975 (1964).

[7] L. O. Moore and J. W. Clark, 2nd *International Symposium on Fluorine Chemistry* p. 285 (1962).

o-phenylenediamine. The same 1,2-quinone was produced from decafluoroacenaphthene under more vigorous conditions, but presumably by a different mechanism involving the well known hydrolysis of *gem*-difluoro groups.[8] The 1,2-quinone was readily oxidized by potassium permanganate to hexafluoro-1,8-naphthalic anhydride.

Octafluoroacenaphthylene was oxidized by fuming nitric acid under vigorous conditions to trifluorohemimellitic acid, also produced in the same way from hexafluoro-1,8-naphthalic anhydride.

The susceptibility of aromatic polyfluoro compounds to attack by nucleophilic reagents is now well established[9] and, extending the earlier analogy with acenaphthylene, perfluoroacenaphthylene would be expected to undergo substitution at carbon centres in the more electron deficient six membered rings. This was clearly established using the oxidation procedure described above. Thus, all the products of nucleophilic substitution studied in this work gave polyfluoroacenaphthene-1,2-quinones and/or polyfluoro-1,8-naphthalic anhydrides with retention of the substituent(s).

With sodium methoxide in methanol the nature of the product was dependant on the proportions of the reactants, and could be varied from essentially mono- to essentially tetramethoxypolyfluoroacenaphthylene. With this reaction and with all the other substitutions studied the yellow colour of the parent fluorocarbon was retained and this greatly facilitated separation of the crude reaction products by adsorption chromatography on alumina. Thus, using essentially one mole of sodium methoxide in methanol heptafluoro-3-methoxyacenaphthylene (IV) was obtained together with small amounts of octafluoroacenaphthylene (I) and hexafluoro-3,8-dimethoxyacenaphthylene (V). With 2 moles of sodium methoxide in methanol the principal product was hexafluoro-3,8-dimethoxyacenaphthylene (V) together with heptafluoro-3-methoxy-(IV) and pentafluoro-3,5,8-trimethoxy-(VI)-acenaphthylene. With 3 moles of sodium methoxide in methanol the principal product was pentafluoro-3,5,8-trimethoxy-acenaphthylene (VI) together with hexafluoro-3,8-dimethoxy-(V) and tetrafluoro-3,5,6,8-tetramethoxy-(VII) acenaphthylene. With 4 moles of this reagent the principal product was tetrafluoro-3,5,6,8-tetramethoxyacenaphthylene (VII) together with pentafluoro-3,5,8-trimethoxyacenphthylene (VI) and a trace of a tar. Reaction of the tetramethoxytetrafluoroacenaphthylene (VII) with 10 moles of sodium methoxide gave only unchanged starting material and a tar.

Heptafluoro-3-methoxyacenaphthylene (IV) and oleum gave pentafluoro-3-methoxyacenaphthylene 1,2-quinone (VIII) which was characterized as its quinoxaline with *o*-phenylenediamine. With potassium permanganate in acetone pentafluoro-2-methoxy-1,8-naphthalic anhydride (XI) was formed. The dimethoxy (V) gave a quinone (IX) and anhydride (XII). Pentafluoro-3,5,8-trimethoxy-acenaphthylene gave a trimethoxy-1,2-quinone (X), characterized as its quinoxaline, and trifluoro-2,4,7-trimethoxy-1,8-naphthalic anhydride (XIII). With tetrafluoro-3,5,6,8-tetramethoxy-acenaphthylene (VII) the yield of the suspected 1,2-quinone was too small to provide the pure compound, but oxidation with potassium permanganate gave difluoro-2,4,5,7-tetramethoxy-1,8-naphthalic anhydride (XIV).

Assuming that from their mode of preparation the methoxy compounds must be sequentially related, their precise structures were established by proton NMR measurements (tabulated in experimental section). Thus, previous work has shown that in

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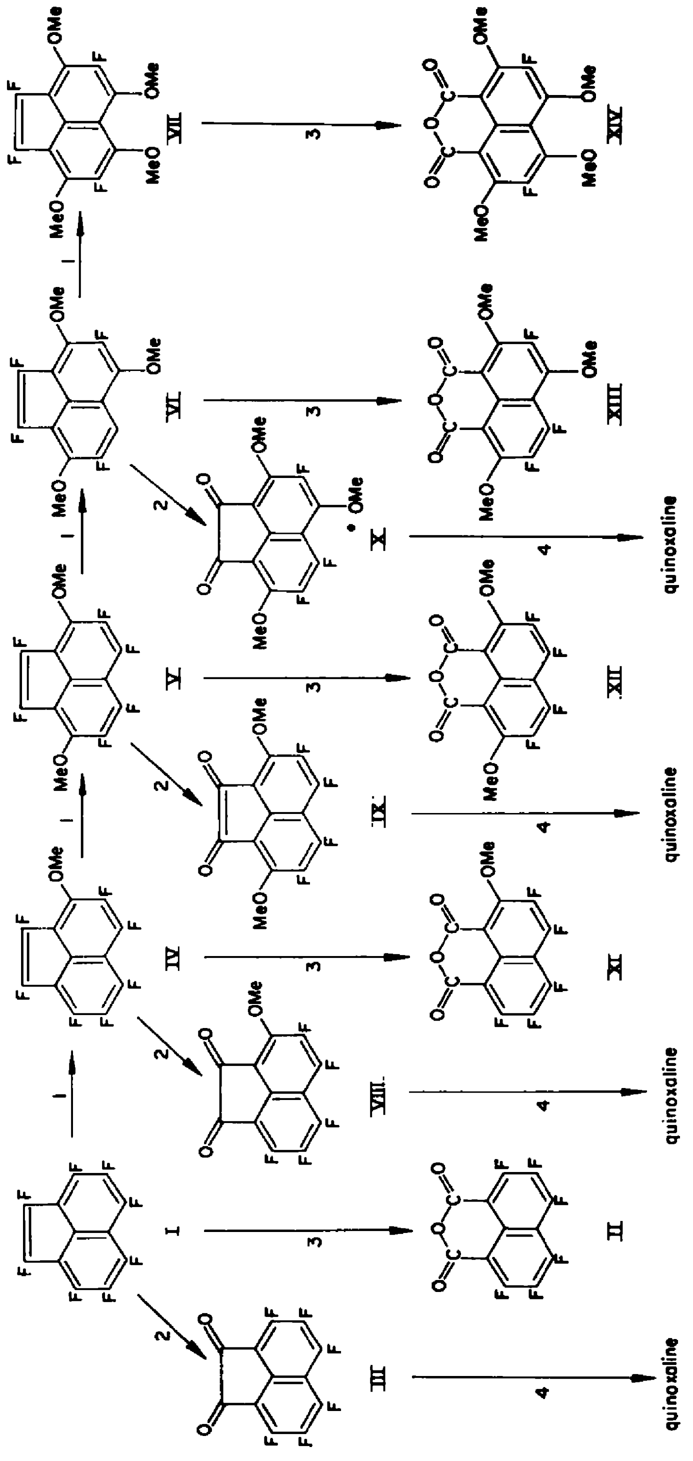
[8] M. Hudlicky, *Chemistry of Organic Fluorine Compounds* p. 203. Pergamon Press, London (1961).

[9] J. C. Tatlow, *Endeavour* **22**, 89 (1963).


I
II
III
IV
V
VI
VII
VIII
IX
X
XI
XII
XIII
XIV
1
2
3
4
quinoxaline
F
MeO
OMe
O

compounds of the type $XC_6F_4OCH_3$ the methoxyl protons are coupled to the fluorines *ortho*- to the methoxyl-group.[10] The proton spectrum of the heptafluoro-monomethoxyacenaphthylene (IV) consisted of a doublet of doublets but the derived monomethoxy-1,2-quinone (VIII) and naphthalic anhydride (XI) each gave spectra consisting of a doublet only. Thus, in the heptafluoro-monomethoxyacenaphthylene the methoxy protons are coupled with the fluorine at C_2. The spectra of the dimethoxy compounds (V, IX and XII) showed analogous features: a doublet of doublets in the dimethoxy compound (V) itself and a doublet in the quinone (IX) and naphthalic anhydride (XII). This suggests 3,8-disubstitution and is supported by the ^{19}F NMR spectrum of the quinone which shows only two bands of equal intensity (demonstrating a symmetrical molecule). The tetramethoxy compound (VII) showed a doublet of doublets and a doublet of equal intensity, indicative of a symmetrical molecule and 3,5,6,8-tetrasubstitution; it is only with this pattern that the methoxyl groups can have the correct number of *ortho*-fluorine atoms to fit such spectral splittings. The trimethoxy compound (VI) must, therefore, be the 3,5,8-compound and its proton spectrum is consistent only with this structure; consisting of three doublets of doublets of equal intensity. Two of these are due to the C_3- and C_8-methoxy groups discussed above, and the third to the C_5-methoxy which must therefore be coupled both to the fluorine at C_4 and to the fluorine at C_6. That this last coupling vanishes in the spectrum of the tetramethoxy compound (VII) is further evidence for the allocation of this coupling and for the structure of the tetramethoxy compound. The C_3- and C_8-methoxy groups cannot be identified separately, only as a pair from the magnitude of the couplings to the fluorine atoms at C_1 and C_2, as can be seen in the Table. The trimethoxyquinone (X) also showed the expected spectral features: a doublet and a doublet of doublets in intensity ratio 2:1. The doublet is presumably due to the methoxy groups at C_3 and C_8 for which, unlike the parent trimethoxy compound, the chemical shifts and the couplings to the fluorines at C_4 and C_7 are equal. The doublet of doublets is due to unequal coupling by the protons of the methoxyl at C_5 to the fluorines at C_4 and C_6.

As can be seen from the Table, the magnitudes of similar couplings in the compounds are comparable.

Three other nucleophilic substitution reactions of octafluoroacenaphthylene were studied, *viz*., using ammonia, hydrazine and LAH. The first substitution was shown to occur at the same carbon atom in each case by conversion of the hydrazine to the amine—and to the hydro-compound.

Ammoniation of octafluoroacenaphthylene gave a heptafluoroacenaphthylene which was characterized as its N-acetyl derivative. Hydrazine in ethanol gave a heptafluoro-hydrazino-acenaphthylene which was converted to the same amine as the above ammoniation product by reduction of the acetone hydrazone. The same hydrazine and aqueous copper sulphate gave a heptafluoroacenaphthylene identical with that obtained from LAH and octafluoroacenaphthylene in ether. The latter reduction also gave ah exafluoroacenaphthylene which could be made the sole product by using an excess of LAH.

That substitution had occurred entirely in the six membered rings was established

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[10] J. Burdon, *Tetrahedron* **20**, 2163 (1964).

by oxidation of the heptafluoroacenaphthylene to a pentafluoro-1,8-naphthalic anhydride with nitric acid or potassium permanganate, and to a pentafluoroacenaphthene-1,2-quinone with oleum, the quinone giving a quinoxaline. The quinone was clearly different from that obtained from octafluoroacenaphthylene and oleum. The hexafluoroacenaphthylene was also substituted entirely in the six membered rings since it gave a tetrafluoroacenaphthene-1,2-quinone, characterized as its quinoxaline, which was clearly different from the above penta- and hexafluoroacenaphthene-1,2-quinones.

Whilst no orientation studies have yet been made on the above amine, hydrazine and hydro-derivatives, previous work on nucleophilic substitution of aromatic polyfluoro compounds[9] would suggest that the same position of substitution would be favoured as with attack by methoxide ion. Hence, by analogy, the above compounds should be heptafluoro-3-amino- and -3-hydrazino-acenaphthylene and 1,2,4,5,6,7,8-heptafluoroacenaphthylene.

It is of interest that molecular orbital calculations[11] on acenaphthylene itself suggest that the lowest electron density is at the 3-position, followed closely by the 5. Thus, if as before we suppose that replacement of hydrogen by fluorine does not change the relative polarization or polarizability of these positions, then the pattern of nucleophilic replacement in octafluoroacenaphthylene follows the electron densities. However, the same calculations[11] show that other indices of nucleophilic reactivity, which could be just as applicable as electron densities, indicate that replacement in acenaphthylene should be 5, then 3; although the reverse order is found in octafluoroacenaphthylene, these are, nevertheless, the only positions at which replacement occurs.

EXPERIMENTAL

*Hexafluoroacenaphthene-*1,2-*quinone* (III)

(a) *From octafluoroacenaphthylene* (I). This compound (1·2 g) was dissolved in oleum (20 ml; 20% SO_3) and a deep red colour was immediately produced. After ½ hr the red homogeneous solution was poured on to ice and the light solid dried and sublimed (100°/0·1 mm) to give a pale yellow solid (0·9 g) m.p. 187–188° which was recrystallized from benzene and the minimum volume of petrol (b.p. 60–80°) to give pale yellow plates of *hexafluoroacenaphthene-*1,2-*quinone* (0·26 g) m.p. 194–195°. (Found: C, 49·8; H, 0; F, 39·3. $C_{12}F_6O_2$ requires: C, 49·7; F, 39·3%) ν_{max} 1735 cm^{-1} (>C=O), λ_{max} 3265, 3040, 2455 and 2155 Å (ε, 3·4, 4·7, 12·1 and 53·0 × 10^3, respectively; in EtOH).

(b) *From decafluoroacenaphthene.* This compound (0·5 g) and oleum (20 ml; 20% SO_3) were kept at 100° for 90 min and then the red homogeneous solution poured onto ice. The light brown precipitate (0·32 g) was purified as before to give hexafluoroacenaphthene-1,2-quinone, m.p. 194° with a correct IR spectrum.

The quinone (0·11 g) in EtOH (10 ml) was refluxed with *o*-phenylenediamine (0·04 g) for 2 min and the pale brown precipitate (0·13 g) m.p. 223° afforded *hexafluoroacenaphthene-*1,2-*quinoxaline* (0·07 g) m.p. 223° from EtOH. (Found: C, 59·5; H, 1·3. $C_{18}H_4F_6N_2$ requires: C, 59·7; H, 1·1%.)

*Hexafluoro-*1,8-*naphthalic anhydride* (II)

(a) *From hexafluoroacenaphthene-*1,2-*quinone.* This compound (1·2 g) in acetone (1 l.) was added to $KMnO_4$ (0·66 g) in acetone (1 l.). Isolation of the acidic products by ether extraction afforded *hexafluoro-*1,8-*naphthalic anhydride* (0·2 g) with the correct IR spectrum (see following).

(b) *From octafluoroacenaphthylene.* In the same way, this compound (4·1 g) in acetone (200 ml) was allowed to react with $KMnO_4$ (2·0 g) in acetone (500 ml) to give a crude acidic product (2·0 g) which was sublimed (150°/0·5 mm) to give *hexafluoro-*1,8-*naphthalic anhydride* (1·2 g) m.p. 199–200°. (Found: C, 46·9; H, 0; F, 37·5. $C_{12}F_6O_3$ requires: C, 47·1; F, 37·3%.)

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[11] K. Fukui, T. Yonezawa and C. Nagata, *Bull. Chem. Soc., Japan* **34**, 37 (1961).

The anhydride (0·9 g), MeOH (25 ml) and conc H_2SO_4 (2 ml) was heated under reflux for 5 hr. After most of the MeOH (20 ml) had been removed by distillation, the residual liquid was poured into water and the solid (0·83 g) m.p. 155–160° recrystallized from aqueous MeOH to give *hexafluoro-monomethyl*-1,8-*naphthalate* (0·25 g) m.p. 188–192°. (Found: C, 46·0; H, 1·4, equiv. wt. 312. $C_{13}H_4F_6O_4$ requires: C, 46·1; H, 1·2%, equiv. wt. 338), ν_{max} 3,600 and 1755 cm^{-1} (—COOH).

Trifluorohemimellitic acid

(a) *From octafluoroacenaphthylene.* Potassium permanganate (6·0 g) in acetone (1 l.) was added to octafluoroacenaphthylene (4·0 g) in acetone (1 l.).

Isolation by ether extraction gave the crude acid product (3·0 g) which was largely dissolved by water; the residual solid (0·2 g) was hexafluoro-1,8-naphthalic anhydride with the correct IR spectrum. The brown aqueous solution was decolourized with charcoal and extracted with ether for 16 hr. The ethereal solution was evaporated to a brown solid (2·2 g) and this was sublimed and recrystallized from benzene to give *trifluorohemimellitic acid monohydrate* (1·0 g) m.p. 175–178°. (Found: C, 37·9; H, 1·7. $C_9H_3F_3O_6$, H_2O requires: C, 38·2; H, 1·8%.)

Trifluorohemimellitic acid (0·2 g) was converted to its *tris*-(S-*benzylthiouronium*) salt (0·1 g) m.p. 178·5–179·5° from aqueous EtOH. (Found: C, 51·8; H, 4·5. $C_{33}H_{33}F_3N_6O_6S_3$ requires: C, 52·0; H, 4·3%.) The acid (2·2 g) absolute MeOH (25 ml) and conc. H_2SO_4 (4·0 g) were heated under reflux for 12 hr to give *trifluoro trimethylhemimellitate* (0·8 g) m.p. 102·5° from aqueous MeOH. (Found: C, 47·3; H, 3·2. $C_{12}H_9F_3O_6$ requires: C, 47·1; H, 2·9%.) ν_{max} 1750 cm^{-1} (>C=O).

(b) *From octafluoroacenaphthylene.* This compound (4·1 g) and HNO_3 (s.g. 1·5; 30 ml) were kept at 100° for 4 hr. Isolation by ether extraction gave *trifluorohemimellitic acid* (2·5 g) m.p. 176–178° (from acetone–$CHCl_3$) with the correct IR spectrum.

(c) *From hexafluoro*-1,8-*naphthalic anhydride.* This compound (0·77 g) and HNO_3 (sg. 1·5; 10 ml) were kept at 100° for 4 hr and ether extraction afforded *trifluorohemimellitic acid* (0·5 g) with the correct IR spectrum.

Heptafluoro-3-*methoxyacenaphthylene* (IV)

A solution of Na (0·33 g, 1·43 × 10^{-2} mole) in dry MeOH and octafluoroacenaphthylene (4·0 g, 1·35 × 10^{-2} mole) in dry MeOH (125 ml) were heated under reflux for 10 min, this solution was poured into water (600 ml) and the yellow precipitate dried. The latter was separated, in portions (1 g), by adsorption chromatography on a column of alumina (12″ × 1″) to give 3 yellow bands. The appropriate bands were combined and evaporated to give: *band* (i), a yellow solid (0·3 g) eluted with petrol (b.p. 60–80°) and recrystallized from EtOH to give octafluoroacenaphthylene with the correct IR spectrum; *band* (ii), a yellow solid (2·50 g) m.p. 102–107° eluted with petrol (b.p. 60–80°)–benzene (2:1) and recrystallized from EtOH to give yellow needles of IV (1·8 g) m.p. 111·5°. (Found: C, 50·9; H, 1·0. $C_{13}H_3F_7O$ requires: C, 50·6; H, 1·0%); *band* (iii), a yellow solid (0·95 g) m.p. 185–188° eluted with benzene–petrol (b.p. 60–80°) 2:1 and recrystallized from EtOH to give yellow needles of V with the correct IR spectrum.

Compound IV (1·0 g) slowly (1 hr) dissolved in oleum (10 ml; 20% SO_3) to give a dark red solution. After 12 hr at room temp this was poured onto ice and the brown solid (0·7 g) m.p. 174–177° sublimed (0·1 mm/140°) and then recrystallized from petrol (b.p. 60–80°)–benzene to give yellow needles of *pentafluoro*-3-*methoxyacenaphthene*-1,2-*quinone* (VIII; 0·5 g) m.p. 180·5–181°. (Found: C, 51·8; H, 1·2; $C_{13}H_3F_5O_3$ requires: C, 51·7; H, 1·0%), ν_{max} 1760 and 1740 cm^{-1} (>C=O).

An ethanolic solution of the quinone (0·10 g) and *o*-phenylene diamine (0·034 g) in EtOH (5 ml) readily gave white needles of *pentafluoro*-3-*methoxy-acenaphthene*-1,2-*quinoxaline* (0·056 g) m.p. 245° from EtOH. (Found: C, 61·2; H, 2·1. $C_{19}H_7F_5N_2O$ requires: C, 61·0; H, 1·9%.)

Heptafluoro-3-methoxyacenaphthylene (1·14 g) and $KMnO_4$ (0·58 g) in dry acetone (1 l.) gave a brown solid (0·38 g) which sublimed to a white solid m.p. 140–147° and this recrystallized from petrol (b.p. 60–80°)–benzene to give *pentafluoro*-2-*methoxy*-1,8-*naphthalic anhydride* (0·14 g) m.p. 148–149°. (Found: C, 48·8; H, 1·1. $C_{13}H_3F_5O_4$ requires: C, 49·1; H, 0·9%), ν_{max} 1785 and 1750 cm^{-1} (> C=O).

Hexafluoro-3,8-*dimethoxyacenaphthylene*

In the manner described earlier, octafluoroacenaphthylene (4·0 g, 1·35 × 10^{-2} mole) was heated under reflux with Na (0·61 g, 2·65 × 10^{-2} mole) in dry MeOH (420 ml) for 4 hr and the yellow product separated (1 g portions) by adsorption chromatography on alumina, to give: *band* (i), a yellow solid (0·35 g) eluted with petrol (b.p. 60–80°)–benzene (2:1) and recrystallized from EtOH to give yellow needles of 3-methoxy-heptafluoroacenaphthylene m.p. 111° with the correct IR spectrum; *band* (ii), a yellow solid (3·1 g) which was eluted with petrol (b.p. 60–80°)–benzene (1:2) and recrystallized from EtOH to give yellow needles of *hexafluoro*-3,8-*dimethoxyacenaphthylene* (2·0 g) m.p. 192·5–193·5°. (Found: C, 52·3; H, 1·7. $C_{14}H_6F_6O_2$ requires: C, 52·5; H, 1·9%); *band* (iii), a yellow solid (0·1 g) eluted with benzene and recrystallized from EtOH to give yellow needles of *pentafluoro*-3,5,8-*trimethoxyacenaphthylene* m.p. 214–215° with the correct IR spectrum.

Hexafluoro-3,8-dimethoxyacenaphthylene (1·4 g) and oleum (10 ml, 20% SO_3), as before, afforded yellow needles of *tetrafluoro*-3,8-*dimethoxyacenaphthene*-1,2-*quinone* (0·5 g), m.p. 173–174° from petrol–benzene. (Found: C, 53·6; H, 1·9. $C_{14}H_6F_4O_4$ requires: C, 53·5; H, 1·9%), ν_{max} 1730 cm^{-1} (>C=O). The ^{19}F NMR spectrum of a 1 M solution in dimethyl sulphoxide consisted of two bands of equal intensity at ~7516 c/s and ~8638 c/s (upfield rel. to $CFCl_3$).

An ethanolic solution of the quinone (0·078 g) and *o*-phenylenediamine (0·028 g) in EtOH (10 ml) readily gave colourless needles of *tetrafluoro*-3,8-*dimethoxyacenaphthene*-1,2-*quinoxaline* (0·06 g) m.p. 271–272° from EtOH–acetone. (Found: C, 62·0; H, 2·7. $C_{20}H_{10}F_4N_2O_2$ requires: C, 62·2; H, 2·6%.)

Hexafluoro-3,8-dimethoxyacenaphthylene (0·65 g) and $KMnO_4$ (0·33 g) in acetone (1 l.) gave, after the standard procedure, *tetrafluoro*-2,7-*dimethoxy*-1,8-*naphthalic anhydride* (0·1 g) m.p. 195–204° from petrol (b.p. 60–80°) and toluene. (Found: C, 50·6; H, 1·4. $C_{14}H_6F_4O_5$ requires: C, 50·9; H, 1·8%), ν_{max} 1795 and 1755 cm^{-1} (>C=O).

Pentafluoro-3,5,8-*trimethoxyacenaphthylene*

Octafluoroacenaphthylene (4·15 g, 1·4 × 10^{-2} mole) and Na (0·92 g, 4·0 × 10^{-2} mole) were heated under reflux in dry MeOH (520 ml) for 4 hr and the usual isolation procedure using an alumina column 18″ × 1″ gave: *band* (i), a yellow solid (0·75 g) eluted with petrol–benzene (1:2) which was recrystallized from EtOH to give yellow needles of hexafluoro-3,8-dimethoxyacenaphthylene (0·5 g) m.p. 192–193° with the correct IR spectrum; *band* (ii), a yellow solid (2·6 g) eluted with benzene which was recrystallized from EtOH to give yellow needles of *pentafluoro*-3,5,8-*trimethoxyacenaphthylene* (1·8 g) m.p. 214–215°. (Found: C, 54·4; H, 2·7. $C_{15}H_9F_5O_3$ requires: C, 54·2; H, 2·7%); *band* (iii), a yellow solid (0·14 g) eluted with benzene which gave yellow needles of tetrafluoro-3,5,6,8-tetramethoxyacenaphthylene m.p. 170° from EtOH with the correct IR spectrum.

Pentafluoro-3,5,8-trimethoxyacenaphthylene (1·27 g) and oleum (20 ml; 20% SO_3) afforded orange needles of *trifluoro*-3,5,8-*trimethoxyacenaphthene*-1,2-*quinone* (0·2 g) m.p. 183–183·5° from petrol–benzene. (Found: C, 55·2; H, 2·9. $C_{15}H_9F_3O_5$ requires: C, 55·2; H, 2·8%), ν_{max} 1725 cm^{-1} (>C=O).

An ethanolic solution of the quinone (0·056 g) and *o*-phenylenediamine (0·023 g) in EtOH (15 ml) readily gave colourless needles of *trifluoro*-3,5,8-*trimethoxyacenaphthene*-1,2-*quinoxaline* (0·04 g) from EtOH–acetone, m.p. 223·5°. (Found: C, 63·2; H, 3·5. $C_{21}H_{13}F_3N_2O_3$ requires: C, 63·3; H, 3·3%.)

Pentafluoro-3,5,8-trimethoxyacenaphthylene (0·536 g) and $KMnO_4$ (0·267 g) in acetone (2 l.) gave a white solid (0·24 g) which was recrystallized from petrol (b.p. 60–80°) and toluene (1:1) to give *trifluoro*-2,4,7-*trimethoxy*-1,8-*naphthalic anhydride* (0·11 g) m.p. 202·5–204°. (Found: C, 52·9; H, 2·3. $C_{15}H_9F_3O_6$ requires: C, 52·7; H, 2·6%), ν_{max} 1795 and 1745 cm^{-1} (>C=O).

Tetrafluoro-3,5,6,8-*tetramethoxyacenaphthylene*

Octafluoroacenaphthylene (2·38 g, 0·8 × 10^{-2} mole) was heated under reflux with Na (1·05 g, 4·57 × 10^{-2} mole) in dry MeOH (620 ml) for 16 hr and the yellow product separated on a column of alumina (12″ × 1″) to give: *band* (i), a yellow solid (0·32 g) which gave yellow needles of pentafluoro-3,5,8-trimethoxyacenaphthylene from EtOH, m.p. 214–215° with the correct IR spectrum; *band* (ii), a yellow solid (2·15 g) which gave yellow needles of *tetrafluoro*-3,5,6,8-*tetramethoxyacenaphthylene* (1·5 g) m.p. 170°. (Found: C, 55·6; H, 3·3. $C_{16}H_{12}F_4O_4$ requires: C, 55·8; H, 3·5%); *band* (iii), a trace of tarry material.

The tetrafluoro-tetramethoxyacenaphthylene (0·75 g) and $KMnO_4$ (0·347 g) in acetone (900 ml) gave a brown solid (0·22 g) which was sublimed (120°/1 mm) and then recrystallized from benzene–petrol (b.p. 60–80°) to give pale brown needles of the suspected *difluoro*-2,4,5,7-*tetramethoxy*-1,8-*naphthalic anhydride* (0·05 g) m.p. 217–218°. (Found: C, 54·5; H, 3·0. $C_{16}H_{12}F_2O_7$ requires:

C, 54·2; H, 3·4%), ν_{max} 1785 and 1730 cm^{-1} (>C=O), the IR spectrum was different from that of the trifluorotrimethoxynaphthalic anhydride described above.

Nuclear magnetic resonance measurements

(a) ^{1}H *Spectra of polyfluoromethoxyacenaphthylenes and derived compounds.* These were measured on a Varian A60 instrument at 60 Mc/sec in acetone solution. Chemical shifts (δ) are in ppm downfield from tetramethyl silane as internal reference.

Compound	Position of methoxyl	δ	J* (c/s)	approx conc^{n} (*M*)
Heptafluoro-3-methoxyacenaphthylene (IV)	3	4·25	4·6 1·2	2·5
Pentafluoro-3-methoxyacenaphthene-1,2-quinone (VIII)	3	4·45	1·0	0·5
Pentafluoro-2-methoxy-1,8-naphthalic anhydride (XI)	2	4·23	2·5	0·5
Hexafluoro-3,8-dimethoxyacenaphthylene (V)	3 and 8	4·19	3·8 1·5	0·1
Tetrafluoro-3,8-dimethoxyacenaphthene-1,2-quinone (IX)	3 and 8	4·38	1·0	0·2
Tetrafluoro-2,7-dimethoxy-1,8-naphthalic anhydride (XII)	2 and 7	4·21	2·7	0·02
Pentafluoro-3,5,8-trimethoxyacenaphthylene (VI)	3 or 8	4·12	3·6 1·6	0·1
	8 or 3	4·11	3·9 1·3	
	5	4·00	2·6 0·5	
Trifluoro-3,5,8-trimethoxyacenaphthene-1,2-quinone (X)	3 or 8	4·33	1·2 1·0	0·1
	8 or 3	4·32	1·2 1·0	
	5	4·17	3·5 0·4	
Tetrafluoro-3,5,6,8-tetramethoxyacenaphthylene (VII)	3 and 8	4·12	3·4 1·4	0·02
	5 and 6	3·97	1·4	

* Each coupling constant refers to a doublet splitting.

^{19}*F spectrum.* The spectrum of tetrafluoro-3,8-dimethoxyacenaphthene-1,2-quinone (IX) was measured by Dr. R. W. King of Iowa State University on a Varian HR60 at 56·4 Mc/sec.

A heptafluoro-aminoacenaphthylene

Octafluoroacenaphthylene (3·4 g) and aqueous ammonia (2 ml, *d.* 0·88) were kept at 127° in a sealed tube for 16 hr. Isolation by ether extraction afforded yellow crystals of a *heptafluoro-amino-acenaphthylene* (0·6 g) m.p. 191·5° from benzene–petrol (b.p. 60–80°). (Found: C, 49·5; H, 1·0. $C_{12}H_2F_7N$ requires: C, 49·2; H, 0·7%), ν_{max} 3550 and 3450 cm^{-1} (NH_2.)

The heptafluoro-aminoacenaphthylene (0·12 g), acetic anhydride (0·2 ml) and conc H_2SO_4 (1 drop) were heated under reflux for 5 min to afford the yellow *N-acetyl derivative* (0·09 g) m.p. 239° from aqueous EtOH. (Found: C, 50·3; H, 1·5. $C_{14}H_4F_7NO$ requires: C, 50·1; H, 1·2%.)

A heptafluoro-hydrazino-acenaphthylene

Octafluoroacenaphthylene (3·02 g) and hydrazine hydrate (0·495 ml) in EtOH (200 ml) were heated under reflux for 2 hr, diluted with water (600 ml) and the precipitate dried, dissolved in benzene–petrol (b.p. 60–80°) (1:1) and passed down a column (12″ × 1″) of silica gel. No separate bands were discernible, but the first eluates, which gave a black residue (0·2 g) were discarded. The remaining material washed from the silica gel with benzene and was a brown solid (2·05 g) m.p. 180–185° which afforded a *heptafluoro-hydrazinoacenaphthylene* (1·74 g) m.p. 188–189° (dec). (Found: C, 46·9; H, 1·2. $C_{12}H_3F_7N_2$ requires: C, 46·8; H, 1·0%), ν_{max} 3300 cm^{-1} (—$NHNH_2$).

The heptafluoro-hydrazino-acenaphthylene (0·4 g), acetone (10 ml) and conc H_2SO_4 (0·5 ml) were heated under reflux for 10 min. Most of the acetone was removed by distillation, the product precipitated with water (50 ml) and extracted with ether and this afforded an orange coloured residue (0·4 g) which gave the *hydrazone* m.p. 156·5–157·5° from benzene–petrol. (Found: C, 51·6; H, 2·1. $C_{15}H_7F_7N_2$ requires: C, 51·7; H, 2·0%.)

The hydrazone (0·25 g), Zn dust (0·2 g) and acetic acid (15 ml) were heated under reflux for 2 hr, diluted with water and steam distilled. The distillate was made alkaline (Na_2CO_3) and extracted with ether (3 × 50 ml). The dried ($MgSO_4$) ether solution was filtered and evaporated to give a heptafluoro-amino acenaphthylene the same as the ammoniation product of acenaphthylene (see earlier); it gave an N-acetyl derivative, m.p. 241° (from EtOH) alone and in admixture with the previously described heptafluoro-N-acetylacenaphthylene; their IR spectra were also identical.

The heptafluoro-hydrazino-acenaphthylene (0·5 g) was heated under reflux with $CuSO_4$ aq (30 ml) for 4 hr and the yellow sublimate which collected in the condenser was periodically (every 15 min) washed into a separate flask with ether. The dried ($MgSO_4$) ether solution was filtered and evaporated to give a yellow solid (0·35 g) which was recrystallized from EtOH to give yellow needles of a *heptafluoroacenaphthylene* (0·2 g) m.p. 122°. (Found: C, 52·0; H, 0·5. $C_{12}HF_7$ requires: C, 51·8; H, 0·4%), analytical g.p.c. of a solution in xylene revealed only one component in addition to xylene.

Lithium aluminium hydride reduction of octafluoroacenaphthylene

Octafluoroacenaphthylene (2 g) in dry ether (100 ml) was added to a stirred solution of LAH (0·26 g) in dry ether, (200 ml). After 1 hr, dil. H_2SO_4 was added to the green solution and the ether layer separated and combined with the ether extracts (2 × 100 ml) of the aqueous phase. The dried ($MgSO_4$) ether solution was filtered and evaporated to leave an orange coloured solid (1·75 g), m.p. 103–113° and 3 recrystallizations from EtOH gave yellow needles of a *heptafluoroacenaphthylene* (0·7 g) m.p. 119·5–120° alone, and in admixture with the above dehydrazination product; their IR spectra were also identical. Analytical g.p.c. of a solution of the crude product in xylene showed 4 peaks with retention times correct for xylene, octafluoroacenaphthylene, a heptafluoroacenaphthylene (major peak) and a hexafluoroacenaphthylene.

Octafluoroacenaphthylene (2 g) and LAH (1 g) in ether (300 ml) were stirred under reflux for 24 hr. The isolation resulted in an orange coloured solid (1·4 g) which afforded orange needles of a *hexafluoroacenaphthylene* (0·9 g) m.p. 124°. (Found: C, 55·3; H, 0·8. $C_{12}H_2F_6$ requires: C, 55·4; H, 0·8%.)

The heptafluoroacenaphthylene (2 g) and HNO_3 (sg. 1·5, 20 ml) were kept at room temp for 16 hr and gave a *pentafluoro-*1,8*-naphthalic anhydride* (0·2 g) m.p. 162° from benzene–petrol. (Found: C, 50·3; H, 0·1; F, 33·3. $C_{12}HF_5O_3$ requires: C, 50·0; H, 0·3; F, 33·0%), ν_{max} 1790 and 1760 cm^{-1} (>C═O).

The heptafluoroacenaphthylene (2 g) and $KMnO_4$ (1 g) in acetone (500 ml) gave the same *pentafluoro-*1,8*-naphthalic anhydride*, m.p. 158–159°, with the correct IR spectrum.

The heptafluoroacenaphthylene (0·2 g) and oleum (8 ml; 20% SO_3) gave pale yellow needles of a *pentafluoroacenaphthene*-1,2-*quinone* (0·06 g) m.p. 179° from benzene–petrol (b.p. 60–80°). (Found: C, 52·7; H, 0·4. $C_{12}HF_5O_2$ requires: C, 53·0; H, 0·4%), ν_{max} 1800 and 1750 cm^{-1} (>C=O).

The quinone (0·05 g) and *o*-phenylenediamine (0·03 g) in EtOH readily gave a *pentafluoroacenaphthene*-1,2-*quinoxaline* (0·02 g) m.p. 228° from EtOH-acetone. (Found: C, 62·5; H, 1·7. $C_{18}H_5F_5N_2$ requires: C, 62·8; H, 1·5%.)

The hexafluoroacenaphthylene (0·45 g) and oleum (10 ml) were kept at room temp for 16 hr and gave a pale yellow solid (0·25 g) m.p. 165–172° which was recrystallized from petrol (b.p. 60–80°)–benzene to give a yellow *tetrafluoroacenaphthene*-1,2-*quinone* (0·12 g) m.p. 184·5°. (Found: C, 56·5; H, 0·5. $C_{12}H_2F_4O_2$ requires: C, 56·7; H, 0·8%), ν_{max} 1740 cm^{-1} (>C=O).

The quinone (0·07 g) and *o*-phenylenediamine (0·04 g) in EtOH (10 ml) readily gave colourless needles of a *tetrafluoroacenaphthene*-1,2-*quinoxaline* (0·04 g) m.p. 242° from EtOH–acetone. (Found: C, 65·8; H, 1·6. $C_{18}H_6F_4N_2$ requires: C, 66·3; H, 1·8%.)

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