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SYNTHESIS AND ^{19}F NMR SPECTRA OF FLUOROANTHRACENES, FLUOROACENAPHTHYLENES, AND FLUOROFLUORANTHENES, AND A PRACTICAL SYNTHESIS OF 7-SUBSTITUTED FLUORANTHENES[1]

M. J. S. DEWAR and J. MICHL[2]

Contribution from the Department of Chemistry, The University of Texas, Austin, Texas 78712, U.S.A.

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Abstract—The synthesis of the three fluoroanthracenes, of the three unknown fluoroacenaphthylenes, and of the four unknown fluorofluoranthenes is reported. The route used for the preparation of 7-fluorofluoranthene represents a practical approach to the hitherto poorly accessible 7-substituted fluoroanthenes. The ^{19}F NMR spectra of these compounds are reported.

INTRODUCTION

ALTHOUGH a great deal of work has been carried out on the effects of substituents on the chemical and physical properties of molecules, relatively little attention has been paid to the use of fluorine in this connection, in spite of the fact that the fluoro group offers a number of major advantages. Apart from being about the simplest of substituents, it is also very small and so relatively immune to complicating steric interactions; ^{19}F is also a very convenient nucleus for NMR studies, and quantum mechanical calculations can be carried out more easily for fluorine than for typical polyatomic substituents.

One particularly interesting and simple class of fluorides consists of those derived from aromatic hydrocarbons by replacement of an H atom by F; these are particularly well adapted to theoretical studies and to the interpretation of substituent effects, NMR chemical shifts, etc. However to get the maximum benefit from studies of this kind it is highly desirable to have, for each hydrocarbon, all the possible isomeric monofluoro derivatives; complete sets of this type are at present available only in a few simple cases. Furthermore, it is also very desirable to have such sets of derivatives of non-alternant hydrocarbons; for the special symmetry relationships between the MO's of alternant hydrocarbons tend to limit the scope of studies based solely on compounds of this type. As yet only two such non-alternant fluorides have been reported, viz. 1-fluoroacenaphthylene[3] and 3-fluorofluoranthene.[4a]

We became interested in this problem because part of an extensive theoretical project in these laboratoris has been concerned with the interpretation of ^{19}F chemical shifts in aryl fluorides. Here we report syntheses of the three fluoroanthracenes, of the three unknown fluoroacenaphthylenes, and of the four unknown fluorofluoranthenes and their ^{19}F NMR spectra.

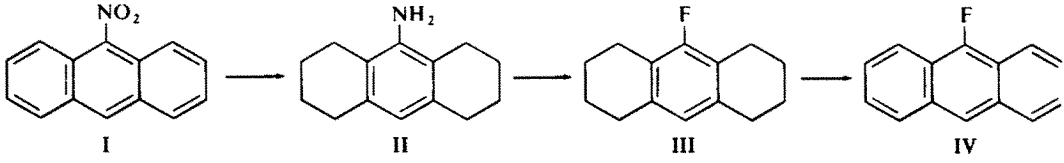
FLUOROANTHRACENES

1- and 2-fluoroanthracenes were prepared from the commercial amines by the Fletcher–Namkung[4a] modification of the Balz–Schiemann reaction as described.[4b]

A tedious gas chromatographic separation was necessary to remove traces of slightly less volatile anthracene from crude 1-fluoroanthracene. No difficulty was encountered in the case of the 2-fluoro isomer.

9-Fluoroanthracene has been prepared by Garvey, *et al.* by direct fluorination of anthracene with *p*-tolyl iodide difluoride.[5] Other investigators[6] have, however, failed to repeat this reaction and in our hands it also failed. Badger and Stephens[6a] failed to obtain 9-fluoranthracene by the Schiemann method, and although success has recently been reported by Rigaudy and Barcelo,[6b] their synthesis seems somewhat inconvenient.

We therefore decided to try the route indicated in I–IV below. The catalytic hydrogenation of anthracene, and of 1- and 2-aminoanthracene, has been investigated by von Braun and Bayer,[7] and by Fries and Schilling;[8] in each case the 1,2,3,4,5,6,7,8-octahydro derivative was easily obtained. Using a rhodium catalyst in methanol containing a trace of acetic acid (to slow down reduction of the central ring, and reduce hydrogenolysis of the amino group),[9] we were able to convert commercial 9-nitroanthracene (I) directly to 9-amino-1,2,3,4,5,6,7,8-octahydroanthracene (II) in good yield. The structure of II, which darkened in air unless quite pure, was established by its proton NMR spectrum in acetone-d_6 which showed one aromatic proton (τ = 3·8) shifted upfield by the *p*-amino group, a broad band at τ = 6·2 (NH_2), and two multiplets (8 protons each) in the benzylic (τ = 7·5) and aliphatic (τ = 8·3) regions. On addition of trifluoracetic acid, the benzylic peaks separated into groups of four protons each at τ = 7·3 and 7·6, while the single aromatic proton shifted downfield as expected (τ = 3·3). The mass spectrum was also consistent with the assigned structure.



I II III IV

Thermal decomposition of the corresponding diazonium fluoroborate took place very readily and care had to be taken not to allow the precipitate to warm up to room temperature when still wet. This behaviour is reminiscent of the case of duridine.[10] The resulting 9-fluorooctahydroanthracene (III) was easily purified, even when an impure sample of the amine was used in the Schiemann reaction. Its structure was confirmed by its proton NMR spectrum in chloroform-d, which showed one aromatic proton (τ = 3·4) as a somewhat broadened singlet, and eight benzylic protons (τ = 7·35) and eight aliphatic protons (τ = 8·3) as poorly resolved multiplets. The ^{19}F NMR spectrum consisted of a slightly broadened singlet at 675 $\pm$ 1 Hz (reference and experimental conditions as in Table 1). The mass spectrum was also consistent with this structure.

Several attempts to dehydrogenate the octahydroderivative by the Ziegler bromination-dehydrobromination technique gave only very poor yields of a substance with anthracene-like absorption in the UV. This was surprising, given that octahydroanthracene has been converted to anthracene in 69% yield by the same procedure.[11] Dehydrogenation of 9-fluorooctahydroanthracene with sulfur gave

complex mixtures, apparently because the fluorine was partially removed, and similar results were obtained with Pd-C. However, dehydrogenation of III to IV could be effected with dichlorodicyanobenzoquinone (DDQ) in 36% yield.

Our product melted at 103–104° and satisifed the usual criteria for purity. Its UV and mass spectra, as well as elemental analysis, agreed with the structure proposed. All our attempts to bring the m.p. closer to the value 110° reported by Garvey *et al.*[5] by further purification failed.

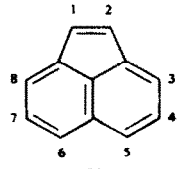
FLUOROACENAPHTHYLENES

Only a few monosubstituted derivatives of acenaphthylene (V) are known and most of these have the substituent in position 1. 1-Fluoroacenaphthylene has been prepared recently.[3] For the preparation of acenaphthylenes with substituents in other positions, the best procedure seems to be dehydrogenation[12,13] of the corresponding acenaphthenes with DDQ. It is curious that derivatives of acenaphthylene have been so little studied, given their accessibility and their potential theoretical interest, e.g. for kinetic studies.

The three fluoroacenaphthenes have been previously prepared[14] from the amines[15–17] by the classical version of the Balz–Schiemann reaction. We have used the Fletcher–Mamkung modification as described in detail.[4b] This gave a higher yield of 3-fluoroacenaphthene (83%, reported[14] 77%), and a much higher yield of 4-fluoroacenaphthene (50%, reported[14] 16·8%) than the classical procedure, but a lower yield of 5-fluoroacenaphthene (25·5%, lit.[14] 37·8%). In the last case fluorophosphate was also tried in place of fluoroborate but the yield was even poorer.

The fluoroacenaphthenes were dehydrogenated by boiling with an excess (10%) of DDQ in benzene, yielding corresponding acenaphthylenes of ca 90% purity in ca 75% yield. The course of the reaction and the purity of the product could easily be followed by UV spectroscopy, mass spectrometry, and GLC. While reaction of the 3- and 5-fluoro isomers took about 4–5 hr, reaction of the 4-isomer proceeded much more slowly and required about 30 hr. This order would be predicted by the currently accepted picture of the reaction which involves formation of a benzylic-type carbonium ion by hydride abstraction in the rate-determining step.[13] A fluorine substituent in a *para* or *ortho* position should facilitate this process by its mesomeric effect.[18,19]

To prepare pure 3-, 4-, or 5-fluoroacenaphthylene, an excess of DDQ and much longer reaction times had to be used. This reduced the yield substantially. No trace of the starting materials could be detected in such products by GLC although 0·5% could have been easily detected.

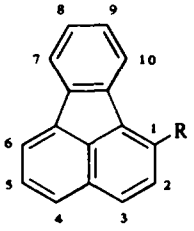


V

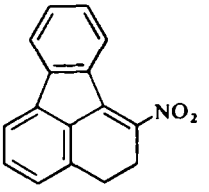
FLUOROFLUORANTHENES

3-Fluorofluoranthene has been prepared[4] by the Balz–Schiemann reaction from commercially available 3-aminofluoranthene; the other isomers are much less readily available.

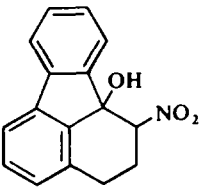
Fluoranthene-1-carboxylic acid (VIa) has been prepared[20,21] by Michael addition of maleic anhydride to fluorene, followed by cyclization, etc; however a better route to 1-substituted fluoranthenes (VI) seemed to be provided by nitration of 1,2,3,10b-tetrahydrofluoranthene which has been reported[22] to give a mixture of 1-nitro-2,3-dihydrofluoranthene (VII) and 1-nitro-10*b*-hydroxy-1,2,3,10*b*-tetrahydrofluoranthene (VIII); VIII can be dehydrated[22] to VII, which in turn has been dehydrogenated[22] to 1-nitrofluoranthene (VIb) with chloranil. This synthesis has recently been repeated,[23] but in neither case were adequate experimental details given.



VI a: R = COOH
b: R = NO_2
c: R = NH_2
d: R = F



VII



VIII

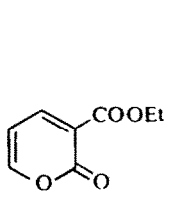
In our hands the nitration proceeded less satisfactorily than reported, the product apparently being contaminated with other isomers which were hard to remove; however we improved the conversion of VII to VIb by using DDQ instead of chloranil. Reduction of VIb with hydrazine hydrate in presence of Pd-C gave the amine VIc which was converted in good yield to 1-fluorofluoranthene (VId).

2-Aminofluoranthene has been prepared by Kloetzel *et al.*;[24] we modified their synthesis by using hydrazine hydrate/Pd-C to reduce the corresponding nitro compound in the final step. The amine was converted as before to 2-fluorofluoranthene.

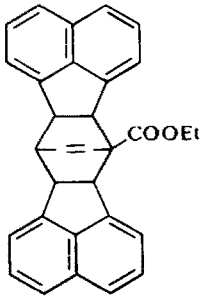
To date, 7-substituted fluoranthenes have been the hardest to make and only a few such compounds are known. The syntheses so far reported are moreover unsatisfactory. Thus Diels–Alder addition of 1-substituted butadienes to acenaphthylene, followed by dehydrogenation, gives poor overall yields;[25–27] this approach is moreover ill-adapted to the synthesis of 7-amino or 7-fluoro derivatives. A second route[28] involves a Schmidt reaction with 3-oxo-1,2,3,10*b*-tetrahydrofluoranthene, followed by a Sandmeyer reaction and ring closure etc; the overall yield in this 7-step synthesis was low. And thirdly, there is the approach used by Tucker[29,30] i.e. cyclization of the diazonium salt from a suitably substituted 1-(*o*-aminophenyl)naphthalene or 1-phenyl-8-aminonaphthalene by an intramolecular Gomberg reaction; here the necessary starting materials are unfortunately somewhat inaccessible.

The trouble with syntheses based on acenaphthylene (V) is that V polymerizes quite easily; polymerization therefore competes with Diels–Alder reactions between V and dienes. It seemed to us that this problem might be circumvented by using a very electron-deficient diene, on the grounds that Diels–Alder reactions normally proceed most readily when one component is electron-rich and the other electron deficient,[31] and that the reactive double bond in V is electron-rich. We therefore tried reacting V with the very reactive[32] and electron-deficient diene, ethyl α-pyrone-3-carboxylate[33] (IX); indeed, above 140°, V and IX reacted rapidly with loss

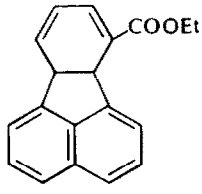
of carbon dioxide. The main product of the reaction seemed, however, to be the *bis* adduct (X), rather than the expected dihydrofluoranthene (XI); apparently XI is an even better enophile than IX and so competes with IX for V. The structure of X was indicated by its mass, IR, and UV spectra. After a number of trials we found that ethyl fluoranthene-7-carboxylate (XIIa) could be obtained by carrying out the reaction at higher temperatures in presence of a Pd catalyst. Apparently X was formed first, but was converted to XIIa by loss of hydrogen and V. The structure of XIIa was proved by elemental analysis, by its mass, UV, IR, and PMR spectra, and by the conversions described below.



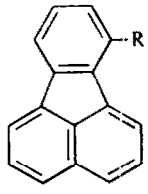
IX



X



XI



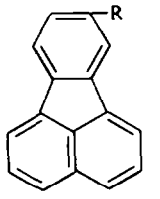
XII a: R = COOEt
b: R = COOH
c: R = COCl
d: R = CON_3
e: R = NHAc
f: R = NH_2
g: R = NO_2
h: R = F

Alkaline hydrolysis of XIIa to XIIb followed by decarboxylation with copper in quinoline gave fluoranthene, while treatment of the corresponding acid chloride (XIIc) with sodium azide gave the azide, XIId, which was not isolated in pure form but showed strong IR absorption at 2130 cm^{-1}. On boiling in acetic anhydride, XIId was converted to the acetylamino derivative (XIIe) which on hydrolysis gave 7-aminofluoranthene (XIIf). The structure of XIIf was indicated by the identity of its m.p. and UV spectrum with that of an authentic sample,[23] obtained by reduction of 7-nitrofluoranthene (XIIg) which can be separated[34] in very low yield from the mixture of mononitrofluoranthenes obtained by nitration of fluoranthene. The NMR spectrum of XIIf was also consistent with the assigned structure.

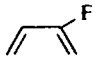
This series of reactions certainly provides by far the best route as yet available to 7-substituted fluoranthenes. The amine XIIf was converted as before to 7-fluorofluoranthene (XIIh).

8-Substituted fluoranthenes are major products from electrophilic substitution reactions of fluoranthene; it is, however, very difficult to separate them in pure form from the resulting mixture of isomers.[34,35] Here again the Diels–Alder route[35] gives low yields, as in e.g. the synthesis of 8-methylfluoranthene (XIIIa) by reaction of V with isoprene followed by dehydrogenation.[25] However we decided to follow this approach, since fluoroprene (XIV) was available to us and since its enophilic reactivity seems to be quite high.[36] Indeed V reacted with XIV smoothly, albeit in low yield, to give the adduct XV. The UV specctrum of XV was very similar to that of acenaphthene, while the IR spectrum (neat) showed in addition to strong bands in the CF region (1140 and 1375 cm^{-1}) a strong C=C absorption at rather high frequency

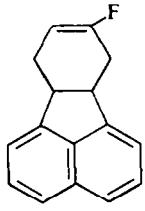
(1700 cm^{-1}) as would be expected for a vinyl fluoride. The PMR spectrum in carbon tetrachloride showed multiplets at $\tau = 2{\cdot}75$ (aromatic protons), $\tau = 6{\cdot}35$ benzylic protons), $\tau = 7{\cdot}6$ allylic protons), and a signal at $\tau = 4{\cdot}9$ corresponding to a single olefinic proton split by fluorine ($J_{HF} = 13$ Hz) into a pair of triplets ($J_{HH} = 5$ Hz). The integrated absorptions were in the ratio 6:2:4:1. This result is again consistent with the assigned structure.



XIII: a: R = CH_3
b: R = F



XIV



XV

Dehydrogenation of XV with sulfur proceeded readily at 170–200°; however fluorine was also lost, the product being fluoranthene. Dehydrogenation with DDQ on the other hand gave 8-fluorofluoranthene (XIIIb) in good yield.

The ^{19}F NMR spectra were measured with a Varian DP60 spectrometer operating at 56·4 MHz, using a solution of 47 ± 2 mg of the fluoro compound in 0·5 ml of dimethylformamide containing 24 mg of tetrachlorotetrafluorocyclobutane (TCTF) as internal standard. The chemical shifts relative to TCTF are listed in Table 1

TABLE 1. ^{19}F NMR SPECTRA OF AROMATIC MONOFLUORO COMPOUNDS

Nucleus	Position of F	Chemical shift[a] (Hz)	Splitting pattern[b]
Acenaphthene	3	535 ± 1	10 Hz (1H), 4 Hz (1H)
	4	−2·5 ± 0·5	10 Hz (2H)
	5	978 ± 1	[14 Hz (2H)][c]
Acenaphthylene	3	−130·5 ± 2	9·5 Hz (1H), 4 Hz (1H)
	4	22 ± 1	10 Hz (2H)
	5	555·5 ± 1	11 Hz (1H), 4 Hz (1H)
Anthracene	1	548·2 ± 2	9·5 Hz (1H), 5·5 Hz (1H)
	2	66 ± 3	unresolved complex pattern[d]
	9	1011 ± 1	singlet[e]
Fluoranthene	1	53 ± 1	10·5 Hz (1H), 4·5 Hz (1H)
	2	−50 ± 1	10·5 Hz (1H), 9 Hz (1H)
	3	563 ± 1	12 Hz (1H), 4·5 Hz (1H)
	7	505 ± 1	10 Hz (1H), 5 Hz (1H)
	8	75 ± 1	9·5 Hz (2H), 5 Hz (1H)

[a] Relative to TCTF at 56·4 MHz.
[b] Approximate coupling constant (Hz) (number of H atoms). Typical line half-width 1 Hz.
[c] Undoubtedly deceptively simple; not a first order case.
[d] Because of low solubility run in saturated solution.
[e] Half-width 4·5 Hz.

together with a tentative first order analysis of the F–H splitting pattern. More detailed studies of the NMR spectra of these and other fluoro compounds will be reported by one of us (J.M.) elsewhere.

EXPERIMENTAL

M.ps are uncorrected. Microanalyses were carried out by A. Bernhardt Microanalytisches Laboratorium, Max Planck Institut für Kohlenforschung, Mülheim, West Germany, and by Galbraith Laboratories, Knoxville, Tennessee, U.S.A.

2-*Fluoroanthracene.* Saturated $NaNO_2$ aq (2·68 g) was added dropwise over 10 min to a stirred mixture of 2-aminoanthracene (5·8 g), THF (60 ml), fluoboric acid (30 ml of 50%), and water (10 ml) at −10°. Stirring was continued for 2 hr, the temp rising to −2°. The ppt was collected, together with a further portion which separated from the filtrate on addition of water. After washing with water, MeOH, and ether, the combined material was dried in a vacuum dessicator, forming a yellow-brown powder (8 g), which was then decomposed by boiling in xylene. Chromatography on alumina, vacuum sublimation, crystallization from EtOH, and a second sublimation gave 2-fluoroanthracene (2·06 g, 35%) as lemon-yellow crystals, m.p. 213–214°, shown to be free from anthracene by GLC. (Found: C, 85·69; H, 4·68; F, 9·60. $C_{14}H_9F$ requires: C, 85·70; H, 4·62; F, 9·68%).

1-*Fluoroanthracene.* Prepared as above from 1-aminoanthracene, the crude product was an intractable mixture of 1-fluoroanthracene and anthracene which was eventually separated by preparative GLC on a 6-ft carbowax column at 227°. Vacuum sublimation gave 1-fluoroanthracene as colorless crystals, m.p. 108°. (Found: C, 85·47; H, 4·75; F, 9·93. $C_{14}H_9F$ requires: C, 85·70; H, 4·62; F, 9·68%).

9-*Amino*-1,2,3,4,5,6,7,8-*octahydroanthracene* (II). A mixture of 9-nitroanthracene (10·35 g), MeOH (200 ml), glacial AcOH (1 ml) and 5% rhodium/charcoal catalyst (2 g) was reacted with H_2 at 50 psi initial press in a Parr hydrogenator for 28 hr at room temp. Filtration (celite) and evaporation gave II (8·95 g, 96%) as a brown solid which was almost homogeneous to GLC and could be used for the next step if this was carried out immediately; otherwise it underwent oxidation. Pure II was obtained by repeated crystallization from light petroleum and then EtOH as colorless crystals, m.p. 84·5–85°, stable in air. (Found: C, 83·44; H, 9·54; N, 7·15. $C_{14}H_{19}N$ requires: C, 83·53; H, 9·51; N, 6·96%).

9-*Fluoro*-1,2,3,4,5,6,7,8-*octahydroanthracene* (III). Prepared as above from crude II (8·95 g), THF (30 ml), 50% fluoboric acid (50 ml), and $NaNO_2$ (3·3 g), and purified by chromatography from hexane on alumina, followed by vacuum sublimation, III formed colorless crystals (35% yield), m.p. 93–96°, raised by recrystallization and sublimation to 99·5–100°. (Found: C, 82·17; H, 8·52; F, 9·57. $C_{14}H_{17}F$ requires: C, 82·31; H, 8·39; F, 9·30%).

9-*Fluoroanthracene* (IV). A soln of III (m.p. 93–96°; 2·04 g) in dry benzene (25 ml) was added to one of DDQ (9·54 g) in dry benzene (150 ml) under N_2 and the mixture boiled under reflux for 19 hr in a N_2 atm. After cooling and filtering, the soln was evaporated, the residue taken up in a little benzene and passed through a short alumina column, again evaporated, and the residue sublimed at 120°/0·1 mm and crystallized from EtOH. Two further vacuum sublimations gave pure IV (0·7 g, 36%), m.p. 103–104°. (Found: C, 85·48; H, 4·71; F, 9·39. $C_{14}H_9F$ requires: C, 85·70; H, 4·62; F, 9·68%).

Fluoroacenaphthenes. 3-, 4-, and 5-Fluoroacenaphthene were prepared from the corresponding amines[15–17] by the Fletcher–Namkung[4b] modification of the Balz–Schiemann reaction in 83, 50 and 25·5% yield respectively. Their properties agreed with those reported[14] for materials made by the classical Balz–Schiemann reaction (yields 77, 16·8, 37·8%).

3-*Fluoroacenaphthylene.* A soln of 3-fluoroacenaphthene[14] (5·4 g) and DDQ (15 g) in benzene (600 ml) was boiled under reflux in a N_2 atm for 33½ hr. After repeated passage in light petroleum through a florex column and evaporation, vacuum sublimation of the residue gave 3-fluoroacenaphthylene (3·24 g, 61%), m.p. 51–52°, homogeneous to GLC. (Found: C, 84·43; H, 4·16; F, 11·14. $C_{12}H_7F$ requires: C, 84·69; H, 4·15; F, 11·16%).

4-*Fluoroacenaphthylene.* Dehydrogenation of 4-fluoroacenaphthene with DDQ, as above, gave in 45% yield a product, m.p. ca. 30°, which was shown by mass spectrometry to contain 10–15% of unchanged starting material. After treating this as before with excess DDQ for 4 days, followed by sublimation, a low temp crystallization from pentane, and a further sublimation, a low yield of pure 4-fluoroacenaphthylene was obtained, m.p. 35·5–35·8°. (Found: C, 84·88; H, 4·30; F, 11·43. $C_{12}H_7F$ requires: C, 84·69; H, 4·15; F, 11·16%).

5-Fluoroacenaphthylene. A soln of 5-fluoroacenaphthene[14] (1·35 g) and DDQ (3·56 g) in benzene (35 ml) was boiled under reflux for 22 hr and the excess DDQ then destroyed with 1,3-cyclohexadiene. The mixture was diluted with hexane, filtered through florex, evaporated, and the residue sublimed under reduced press, giving 5-fluoroacenaphthylene (0·65 g, 49%) as yellow crystals, m.p. 73–74·5°. The middle fraction (m.p. 75–76°) was isolated separately for analysis. (Found: C, 84·63; H, 4·32; F, 11·11. Calc. for $C_{12}H_7F$: C, 84·69; H, 4·15; F, 11·16%).

1-Aminofluoranthene (VIc). (cf. Ref. 22) Fuming HNO_3 (*d* 1·49–1·50; 13·6 ml) was added dropwise over 15 min to a stirred soln of 1,2,3,10*b*-tetrahydrofluoranthene[37] (38·5 g) in glacial AcOH (375 ml) at 80°. After 30 min an exothermic reaction took place; the flask was removed from the bath until the temp reverted to 80°, then kept at 80° for 40 min, allowed to cool over 2½ hr, and the contents then poured on ice. The ppt was dissolved in glacial AcOH (200 ml), concentrated H_2SO_4 (6 drops) added, and the soln then boiled 6 hr under reflux. After removing half the solvent, the remaining soln was poured into water and the ppt isolated with ether and chromatographed from light petroleum on alumina, giving crude VII (15·5 g) as bright red needles. TLC on alumina showed this to still contain some unchanged starting material. The crude VII was dissolved in warm benzene (250 ml), DDQ (30 g) added, and the soln boiled 24 hr under reflux in a N_2 atm. After filtering the cooled soln through florex, chromatography on florisil from first benzene–light petroleum, and finally benzene–ether, gave crude VIb (13·7 g), m.p. 127–135° (lit.[23], 152·5–153·5°). The crude VIb was dissolved in 95% EtOH (600 ml), hydrazine hydrate (20 ml) and 10% Pd-C (2·5 g) added, and the mixture boiled 1 hr under reflux, then filtered through celite and evaporated. Crystallization from EtOH, and then benzene–light petroleum, gave VIc (11%), m.p. 132·5–133·5° (lit.[23] 133–134°). Additional (9%) less pure material was recovered from the mother liquors.

1-Fluorofluoranthene (VId). Prepared as before from VIc (1·6 g), THF (5 ml), 50% fluoboric acid (9 ml), water (15 ml) and $NaNO_2$ (0·8 g), VId (1·28 g, 79%) after crystallization from EtOH and vacuum sublimation had m.p. 78·5–79°. (Found: C, 87·06; H, 4·23; F, 8·66. $C_{16}H_9F$ requires: C, 87·26; H, 4·12; F, 8·63%).

2-Fluorofluoranthene. Prepared as before from 2-aminofluoranthene[24] (1·6 g), THF (5 ml), 50% fluoboric acid (9 ml), water (5 ml), and $NaNO_2$ (0·8 g), and purified by chromatography from benzene on alumina followed by vacuum sublimation, 2-fluorofluoranthene (0·88 g, 54%) had m.p. 86–87°. (Found: C, 87·42; H, 4·15; F, 8·74. $C_{16}H_9F$ requires: C, 87·26; H, 4·12; F, 8·63%).

Ethyl fluoranthene-7-carboxylate (XIIa). A mixture of acenaphthylene (4·0 g), ethyl α-pyrone-3-carboxylate[33] (1·2 g), and 10% Pd-C (0·2 g) was heated to 140–150° until gas evolution slackened, and the temp then raised slowly to 320–340° and held there for 2 hr. Extraction of the cold reaction mixture with boiling benzene, evaporation, extraction of the residue with several portions (total, 250 ml) of boiling EtOH, and evaporation, gave a dark solid which was chromatographed on silica gel first with hexane, which gave acenaphthene, and then with benzene, which gave XIIa, purified by vacuum sublimation and crystallization from hexane, m.p. 71–72°, yield 0·69 g (33%). (Found: C, 83·29; H, 5·10. $C_{19}H_{14}O_2$ requires: C, 83·19; H, 5·14%).

Fluoroanthene-7-carboxylic acid (XIIb). A soln of NaOH (2·3 g) in water (10 ml) was added to one of XIIa (8·3 g) in EtOH (100 ml) and the mixture boiled 3·5 hr under reflux and then diluted with water (300 ml) and acidified with HCl. The ppt of XIIb (7·1 g, 95%) was washed, dried, and sublimed at 230°/0·1 mm, m.p. 253–254·5°. A sample (100 mg) was heated with copper bronze (200 mg) in freshly distilled quinoline (6 g) for 1 hr under reflux, giving fluoranthene (50 mg), identical (mixture m.p., IR and UV spectra) with an authentic sample.

7-Aminofluoranthene (XIIf). XIIb (6·1 g) was warmed with $SOCl_2$ (50 ml) until evolution of HCl ceased, then boiled under reflux for 45 min and evaporated under reduced press. The residue of XIIc was dissolved in dry acetone (180 ml), cooled to −1°, and a saturated aqueous solution of sodium azide (1·7 g) added dropwise with stirring. After 30 min, water was added and the azide (XIId) isolated with ether and boiled 3 hr under reflux with Ac_2O (100 ml) and the solvent then hydrolyzed with water (100 ml). When cold, the residue was collected, washed, and dried at 120°, giving XIIe (4·35 g); the IR spectrum showed no residual azide (2130 cm^{-1}), but strong amide bands (3270, 1718, and 1540 cm^{-1}). Hydrolysis of crude XIIe (3·45 g) by boiling for 7 hr with a soln of NaOH (2·0 g) in ethylene glycol (150 ml) and water (20 ml) gave XIIf (2·1 g) m.p. 136–138°, raised by recrystallization to 137–138° (lit.[23] 136–137·5°).

7-Fluorofluoranthene (XIIh). The amine XIIf (0·5 g) was converted as before to XIIh which after vacuum sublimation formed yellow crystals (0·22 g, 43%), m.p. 93–95°, raised by recrystallization from EtOH, followed by a second vacuum sublimation, to 95°. (Found: C, 87·02; H, 4·24; F, 8·75. $C_{16}H_9F$ requires: C, 87·25; H, 4·12; F, 8·63%).

8-*Fluorofluoranthene* (XIIIb)

A. Diels–Alder reaction of V *with* XIV. A mixture of acenaphthylene (30 g), *p*-xylene (60 g), hydroquinone (0·2 g), and a soln containing fluoroprene (6·5 g), *p*-xylene (6·5 g), and t-butylpyrocatechol (0·13 g), was heated in a stirred autoclave for 3 days at 140°, followed by 7 days at 160°. The autoclave was extracted with chloroform, the extracts washed repeatedly with KOH aq and water, $CHCl_3$ was evaporated, and MeOH was added to the residue. The precipitated polymer was filtered off and the filtrate concentrated and treated with light petroleum when more polymer separated. The filtrate was chromatographed from light petroleum on Florisil, giving 4·5 g of an orange oil which from GLC analysis contained 40% of acenaphthylene and acenaphthene and 60% of XV. The latter was isolated by careful chromatography from light petroleum on alumina (Woelm, act. I), monitored by GLC, as an almost colorless oil (2·1 g) which solidified in the freezer and from GLC still contained ca 2% of acenaphthene and/or acenaphthylene. Evidence for the structure of XV was given earlier.

B. Dehydrogenation of XV. Crude XV (1·2 g), containing ca 20% of acenaphthene and acenaphthylene, was boiled under reflux in a N_2 atm for 2 days with DDQ (2·5 g) dissolved in the minimum amount of benzene. Light petroleum was added to the cooled reaction mixture and the soln passed through a column of Florex and evaporated. The residue was chromatographed on alumina (Woelm, act. I) first with light petroleum, then with 1:1 benzene–light petroleum, giving XIIIb which crystallized from EtOH in pale yellow needles (0·33 g, 28%), m.p. 96–96·5°. (Found: C, 87·42; H, 4·04; F, 8·76. $C_{16}H_9F$ requires: C, 87·25; H, 4·12; F, 8·63%).

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Added in proof: 2-fluorofluoranthene has recently been prepared (m.p. 88–89°) by E. H. Charlesworth and A. J. Dolenko, *Can. J. Chem.* **45**, 96 (1967).