111. *The Synthesis of 8-Methylbenzo*[k]*fluoranthene and of Dibenzo*[bk]*fluoranthene.*

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8-Methylbenzo[*k*]fluoranthene has been prepared from 8,9,10,11-tetrahydro-8-oxobenzo[*k*]fluoranthene, and dibenzo[*bk*]fluoranthene from succinic anhydride and 8,9,10,11-tetrahydrobenzo[*k*]fluoranthene. Several condensed fluoranthenocarbazoles have also been synthesised.

Recently 8,9,10,11-tetrahydro-8-oxobenzo[*k*]fluoranthene (I) was prepared from succinic anhydride and fluoranthene.[1] It has now been used in syntheses of polycyclic derivatives required for testing as potential carcinogenic substances.

Methylmagnesium iodide with ketone (I) gave an alcohol which was not isolated but was directly treated with selenium powder, to give a mixture of 8-methylbenzo[*k*]fluoranthene (II) and a considerable quantity of benzo[*k*]fluoranthene (III) resulting from loss of the methyl group.

8,9,10,11-Tetrahydrobenzo[*k*]fluoranthene being an 8,9-disubstituted fluoranthene, its reaction with succinic anhydride gave, as was to be expected, a single keto-acid which accordingly must have structure (IV). This acid, obtained in excellent yield, furnished, on

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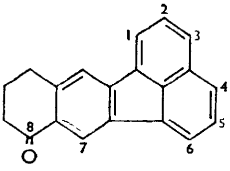
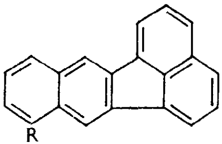
[1] Buu-Hoï, Lavit, and Lamy, *J.*, 1959, 1845.

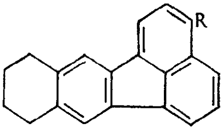
Wolff–Kishner reduction, the butyric acid (V) whose chloride on cyclisation led to the octahydro-4-oxodibenzo[*b*,*k*]fluoranthene (VI). Wolff–Kishner reduction then afforded the octahydrodibenzo[*bk*]fluoranthene (VII), which in turn underwent dehydrogenation to dibenzo[*bk*]fluoranthene (VIII), m. p. 236°. This hydrocarbon was identical with a product described in the literature as melting at 230—231° and obtained by cyclisation of 9-*o*-chlorobenzylidene-2,3-benzofluorene (IX) with potassium hydroxide in quinoline.[2] In view of the greater reactivity of naphthalene than of benzene rings, this cyclisation product was later tentatively considered as dibenzo[*be*]fluoranthene (X) rather than the isomeric dibenzo[*bk*]fluoranthene.[3] That the latter structure is correct is further proof of the difficulty in synthesising 3,4-benzophenanthrenes.



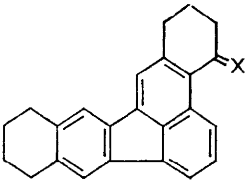
(I)



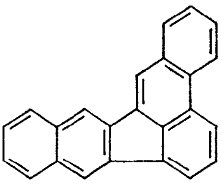
(II) R = Me
(III) R = H



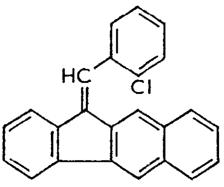
(IV) R = $CO\cdot[CH_2]_2\cdot CO_2H$
(V) R = $\cdot[CH_2]_3\cdot CO_2H$



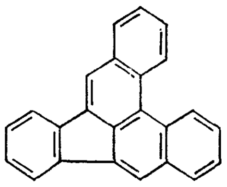
(VI) X = O
(VII) X = H_2



(VIII)

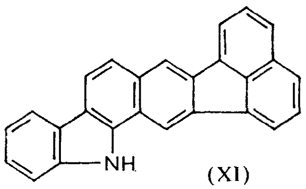


(IX)

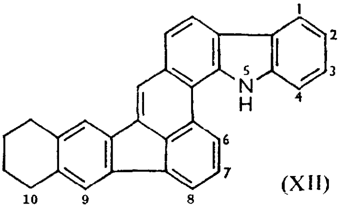


(X)

In view of the known carcinogenic activity of polycyclic carbazoles, several carbazoles bearing the fluoranthene group have been prepared. Fischer indolisation of the phenylhydrazone of ketone (I) afforded a dihydrocarbazole, which was readily dehydrogenated by means of chloranil to fluorantheno[8,9-*a*]carbazole (XI). The same reaction sequence, applied to ketone (VI), furnished the tetrahydro-compound (XII), which however resisted further dehydrogenation by chloranil. On the other hand, 9-benzylidene-8,9,10,11-tetrahydro-8-oxobenzo[*k*]fluoranthene, prepared by condensation of benzaldehyde with ketone (I), failed to undergo cyclodehydrogenation to the corresponding fluorene by means of phosphoric oxide in the usual experimental conditions.[4]



(XI)



(XII)

EXPERIMENTAL

8-Methylbenzo[k]*fluoranthene* (II).—To a Grignard reagent prepared from methyl iodide (2·1 g.) and magnesium shavings (0·36 g.) in anhydrous ether (20 c.c.), 8,9,10,11-tetrahydro-8-oxobenzo[*k*]fluoranthene (2 g., dissolved in 150 c.c. of anhydrous benzene) was added, and the

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[2] I.G. Farbenindustrie A.-G. B.P. 459,108/1936; French P. 807,704/1936.

[3] Clar, " Aromatische Kohlenwasserstoffe," Springer-Verlag, Berlin, 1952, p. 404.

[4] Cf. Buu-Hoï and Cagniant, *Rev. sci.*, 1942, **80**, 319, 384, 436; 1943, **81**, 30; Buu-Hoï and Saint-Ruf, *J.*, 1957, 3806; Saint-Ruf, Buu-Hoï, and Jacquignon, *J.*, 1958, 48.

yellow suspension obtained was refluxed on a water-bath for 90 min. After cooling, 10% aqueous sulphuric acid (100 c.c.) was added, the product extracted in benzene, washed with water, and dried (Na_2SO_4), and the solvent distilled off. The residue was heated with selenium powder (1·5 g.) for 3 hr. at 350°, the product taken up in benzene, the benzene distilled off, and the residue treated with acetic acid (150 c.c.), leaving undissolved a viscous brown impurity. The acetic acid solution was concentrated to 50 c.c., and the solid precipitate obtained on cooling was crystallised several times from benzene–ethanol, giving 8-*methylbenzo*[k]*fluoranthene* as colourless needles (0·1 g.), m. p. 207° (Found: C, 94·6; H, 5·2. $C_{21}H_{14}$ requires C, 94·7; H, 5·3%), along with the unsubstituted hydrocarbon (0·5 g.), m. p. 217°. The mixture of the two hydrocarbons melted at *ca.* 180°.

Fluorantheno[8,9-a]*carbazole* (XI).—A mixture of ketone (I) (1 g.) and phenylhydrazine (1 g.) was heated at 140° for 5 min., and the crude crystalline phenylhydrazone obtained on cooling was treated during 1 hr. with acetic acid saturated with hydrogen chloride (15 c.c.). After cooling, water was added, and the precipitate of the 3,4-*dihydrocarbazole derivative* was collected, washed with water, dried, and recrystallised from toluene, giving yellowish needles (1 g.), m. p. 246° (Found: C, 90·9; H, 5·1. $C_{26}H_{17}N$ requires C, 90·9; H, 5·0%). A solution of this compound (0·8 g.) in anhydrous xylene (50 c.c.) was refluxed for 3 hr. with chloranil (0·63 g.); *fluorantheno*[8,9-a]*carbazole*, precipitated on cooling, was collected and treated with hot aqueous sodium hydroxide, and the undissolved portion was filtered off, washed with water, dried, and recrystallised from xylene, giving cream-coloured needles (0·5 g.), m. p. 338° (Found: C, 91·4; H, 4·4. $C_{26}H_{15}N$ requires C, 91·5; H, 4·4%).

9-*Benzylidene*-8,9,10,11-*tetrahydro*-8-*oxobenzo*[k]*fluoranthene*.—A solution of ketone (I) (4 g.) and benzaldehyde (1·9 g.) in ethanol (67 c.c.) and dioxan (75 c.c.) was shaken with potassium hydroxide (6 g., in 7 c.c. of water), and the mixture was refluxed for 10 min.; after cooling and dilution with water, the precipitate formed was collected, washed with water, and recrystallised twice from ethanol–toluene. The *benzylidene derivative* formed yellowish prisms (2 g.), m. p. 187—188°, whose solutions in sulphuric acid were red (Found: C, 90·3; H, 5·1. $C_{27}H_{18}O$ requires C, 90·5; H, 5·1%).

γ-(8,9,10,11-*Tetrahydrobenzo*[k]*fluoranthen*-3-*yl*)-γ-*oxobutyric Acid* (IV).—To a solution of 8,9,10,11-tetrahydrobenzo[*k*]fluoranthene (8·2 g.) and succinic anhydride (3·2 g.) in anhydrous nitrobenzene (100 c.c.), finely powdered aluminium chloride (9·6 g.) was added in small portions with stirring at room temperature; the brown-red mixture was left for 4 days, then decomposed with dilute hydrochloric acid, the nitrobenzene was removed by steam-distillation, and the solid residue recrystallised twice from chlorobenzene. The *keto-acid* formed greenish-yellow needles, (8·8 g.), m. p. 252°, whose solutions in sulphuric acid were brown-red (Found: C, 80·6; H, 5·7. $C_{24}H_{20}O_3$ requires C, 80·9; H, 5·7%).

γ-(8,9,10,11-*Tetrahydrobenzo*[k]*fluoranthen*-3-*yl*)*butyric Acid* (V).—The foregoing acid (8 g.), 85% hydrazine hydrate (8 g.), and potassium hydroxide (8 g.) in diethylene glycol (75 c.c.) were refluxed for 6 hr. and, on cooling, acidified with dilute hydrochloric acid. The solid precipitate was collected, washed with water, dried, and recrystallised from toluene, to give cream-coloured needles of the *acid* (V) (6·5 g.) which melted first at 188°, became solid, and melted anew at 193°; its solutions in sulphuric acid were greenish-brown (Found: C, 84·0; H, 6·5. $C_{24}H_{22}O_2$ requires C, 84·2; H, 6·5%).

1,2,3,4,9,10,11,12-*Octahydro*-4-*oxodibenzo*[bk]*fluoranthene* (VI).—A suspension of the foregoing acid (5·8 g.) in anhydrous ether (100 c.c.) was refluxed for 4 hr. with thionyl chloride (2·9 g.) and 3 drops of pyridine. The acid gradually dissolved and a precipitate was formed; the solvent and thionyl chloride in excess were distilled off *in vacuo*, and the crude acid chloride obtained was treated in nitrobenzene (100 c.c.) with aluminium chloride (2·5 g.) portionwise at room temperature. The mixture was left overnight, then decomposed with dilute hydrochloric acid, the nitrobenzene steam-distilled, and the solid residue recrystallised from ethanol. The *ketone* formed yellow needles (3·5 g.), m. p. 169°, whose solutions in sulphuric acid were red (Found: C, 88·8; H, 6·3. $C_{24}H_{20}O$ requires C, 88·9; H, 6·2%).

1,2,3,4,9,10,11,12-*Octahydrodibenzo*[bk]*fluoranthene* (VII).—The ketone (VI) (1 g.), hydrazine hydrate (1 g.), and potassium hydroxide (1 g.) in diethylene glycol (20 c.c.) were refluxed for 2 hr.; after cooling and dilution with water, the precipitated *hydrocarbon* was collected, washed with water, and recrystallised from ethanol in pale yellow needles (0·85 g.), m. p. 113°, giving no colour in sulphuric acid (Found: C, 92·8; H, 7·1. $C_{24}H_{22}$ requires C, 92·9; H, 7·1%).

Dibenzo[bk]*fluoranthene* (VIII).—A mixture of the foregoing octahydro-compound (0·65 g.)

and selenium powder (1 g.) was heated for 4 hr. at 350°; after cooling, the product was taken up in toluene, and recrystallised several times from that solvent, to furnish pale yellow needles (0·35 g.), m. p. 236°, which gave no colour in sulphuric acid (Found: C, 95·5; H, 4·7. Calc. for $C_{24}H_{14}$: C, 95·3; H, 4·7%).

10,11,12,13-*Tetrahydrobenzo*[8,9]*fluorantheno*[3,2-a]*carbazole* (XII).—A mixture of ketone (VI) (2·2 g.) and phenylhydrazine (2 g.) was heated for 5 min. at 180°, and the crude phenylhydrazone heated for 30 min. with acetic acid saturated with hydrogen chloride (150 c.c.). After cooling and dilution with water, the precipitate was collected, washed with water, dried, and recrystallised from toluene, giving the *hexahydrocarbazole*, yellow needles (1·75 g.), which melted first at 307°, then resolidified, and melted anew at 315° (Found: C, 90·3; H, 5·9. $C_{30}H_{23}N$ requires C, 90·6; H, 5·8%). A solution of this compound (0·5 g.) and chloranil (0·31 g.) in anhydrous xylene (50 c.c.) was refluxed for 3 hr. The solid obtained on cooling was treated with hot aqueous sodium hydroxide, and the insoluble portion was washed with water, dried, and recrystallised from toluene (charcoal), giving *tetrahydro-compound* (XII), bright yellow leaflets (0·3 g.), m. p. 330° (Found: C, 91·0; H, 5·5. $C_{30}H_{21}N$ requires C, 91·1; H, 5·4%). The same compound was obtained when the hexahydrocarbazole (0·5 g.) was heated for 5 hr. with an excess of chloranil (1 g.) in xylene (50 c.c.).

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