

153. *Polycyclic Aromatic Hydrocarbons. Part XXIX. Derivatives of  
1 : 2 : 5 : 6-Dibenzfluorene.*

By J. W. COOK and ROBERT W. G. PRESTON.

A series of derivatives of 1 : 2 : 5 : 6-dibenzfluorene (I) has been prepared directly from this hydrocarbon and from 1 : 2 : 5 : 6-dibenzfluorenone, in an endeavour to find compounds more inhibitory to tumour growth than the parent hydrocarbon. Two new synthetical routes to derivatives of 1 : 2 : 5 : 6-dibenzfluorene have been devised. One of these, starting from 2-benzoylnaphthalene, leads to compounds of types (X) and (XI). This method involves ring-closure of the acid (IV) to the *keto-acid* (V). A second *keto-acid* formed in this cyclisation is believed to have the structure (VI) and has been converted into pentacyclic compounds probably derived from 3 : 4-(1' : 2'-naphtha)fluorene. The second method consists in *cyclo*-dehydrogenation of 4-(2'-naphthoyl)-1-methoxynaphthalene (XV) to 3-hydroxy-1 : 2 : 5 : 6-dibenzfluorenone (XVI) by fusion with aluminium chloride.

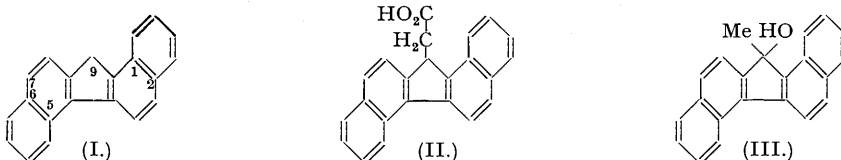
1 : 2 : 6 : 7-Dibenzfluorene has also been prepared, and some possible synthetical routes to the unknown

2 : 3-(2' : 1'-naphtha)fluorene (XVIII) have been explored. 9 : 10-Dihydrophenanthrene was found to undergo chloromethylation at position 3, although in Friedel-Crafts reactions the substituent enters at position 2.

1 : 2 : 5 : 6-DIBENZFLUORENE (I) has feeble cancer-producing activity (Bachmann, Cook, Dansi, de Worms, Haslewood, Hewett, and Robinson, *Proc. Roy. Soc.*, 1937, B, 123, 343) and has also a very pronounced effect in inhibiting the growth of tumours (Haddow and Robinson, *ibid.*, 1939, B, 127, 277). As part of a search for compounds having still more marked growth-inhibitory activity a series of derivatives of 1 : 2 : 5 : 6-dibenzfluorene has been prepared. By the synthetic method of Swain and Todd (J., 1941, 674) it was possible to obtain the hydrocarbon in sufficient quantity to prepare some of its derivatives by direct substitution. Biological tests carried out by Dr. Haddow on many of these will be reported elsewhere.

A monosulphonic acid and a mononitro-compound were readily obtained from 1 : 2 : 5 : 6-dibenzfluorene. The nitro-compound was reduced to amino-1 : 2 : 5 : 6-dibenzfluorene and was oxidised by selenious acid to a nitro-1 : 2 : 5 : 6-dibenzfluorenone which was also obtained by direct nitration of 1 : 2 : 5 : 6-dibenzfluorene. This nitro-ketone was reduced by stannous chloride to amino-1 : 2 : 5 : 6-dibenzfluorenone. By analogy with substitution reactions of fluorene and fluorenone, it is probable that in all these derivatives the substituent is at position 7, which is the only free position *para* to the bond joining the two naphthalene nuclei, and is also an  $\alpha$ -position of a naphthalene system. This orientation has not been proved, however, for, although 7-substituted derivatives of 1 : 2 : 5 : 6-dibenzfluorene have been prepared by an independent synthesis described below, it has not been possible to correlate them with the compounds obtained by direct substitution. All attempts to effect replacement of the amino-group in amino-1 : 2 : 5 : 6-dibenzfluorene by a hydroxyl group were unsuccessful.

A series of 9-substituted derivatives of 1 : 2 : 5 : 6-dibenzfluorene has also been prepared. Reduction of 1 : 2 : 5 : 6-dibenzfluorenone by zinc in acetic acid (compare Wanscheidt, *Ber.*, 1926, 59, 2096) gave 1 : 2 : 5 : 6-dibenz-9-fluorenol, from which 9-bromo-1 : 2 : 5 : 6-dibenzfluorene was obtained by means of hydrogen bromide. This bromo-compound could not be satisfactorily condensed with ethyl malonate. The desired 1 : 2 : 5 : 6-dibenzfluorenyl-9-acetic acid (II) was obtained by reduction of the crude hydroxy-ester resulting from interaction of 1 : 2 : 5 : 6-dibenzfluorenone with ethyl bromoacetate in presence of zinc. By treatment of 1 : 2 : 5 : 6-dibenzfluorenone with methylmagnesium iodide the tertiary carbinol (III) was readily formed. This carbinol



was reduced by hydriodic acid in boiling acetic acid to 9-methyl-1 : 2 : 5 : 6-dibenzfluorene, which was not obtained by dehydration of the carbinol followed by hydrogenation, a procedure used successfully in analogous cases (Fieser and Joshel, *J. Amer. Chem. Soc.*, 1940, 62, 957; Badger, J., 1941, 535). Condensation of 1 : 2 : 5 : 6-dibenzfluorenone with ethylmagnesium bromide gave capricious results, and 9-ethyl-1 : 2 : 5 : 6-dibenzfluorene has not been obtained.

An acetyl-1 : 2 : 5 : 6-dibenzfluorene of unknown orientation resulted from treatment of the hydrocarbon with acetyl chloride and aluminium chloride. The corresponding carboxylic acid could not be obtained by oxidation with sodium hypochlorite.

For the production of a hydroxy-1 : 2 : 5 : 6-dibenzfluorene of known structure, a new ring-synthesis of the 1 : 2 : 5 : 6-dibenzfluorene ring system was devised.\* The starting point was the  $\gamma$ -phenyl- $\gamma$ -2-naphthylitaconic acid (IV) which Hewett (J., 1942, 585) obtained by hydrolysis of the condensation product of 2-benzoylnaphthalene and ethyl succinate. Theoretically, monocyclisation of acids of this type might give either a 5- or a 6-membered ring, depending upon which carboxyl group is involved. Actually, the 5-membered ring appears to be formed exclusively (Stobbe and Vieweg, *Ber.*, 1902, 35, 1727; Haworth and Sheldrick, J., 1935, 636) and this was found to be the case with  $\gamma$ -phenyl- $\gamma$ -2-naphthylitaconic acid (IV), the anhydride of which was converted by aluminium chloride in nitrobenzene into a mixture of two orange keto-acids, 1-keto-3-phenyl-6 : 7-benzindene-2-acetic acid (V) and 1-keto-3-(2'-naphthyl)indene-2-acetic acid (VI).

These two acids were converted by ethereal diazomethane into their normal methyl esters, m. p. 136° and 98°, respectively. Esterification by the Fischer-Speier method gave two isomeric methyl esters, m. p. 84° and 102°, respectively. Like the parent acids, these four esters are deeply coloured. The two *pseudo*-esters are regarded as methoxy-lactones (VII and VIII). Similar *pseudo*-esters of derivatives of 2-benzoylbenzoic acid have been described (Newman *et al.*, *J. Amer. Chem. Soc.*, 1941, 63, 1537; 1944, 66, 731). The structure of a hydroxy-lactone corresponding with (VII) is suggested by Hewett for a product which he obtained by dehydration of  $\gamma$ -phenyl- $\gamma$ -2-naphthylitaconic acid (IV) with concentrated sulphuric acid. In view of the lack of colour in Hewett's lactone, we regard his alternative structure (IX) as more probable.

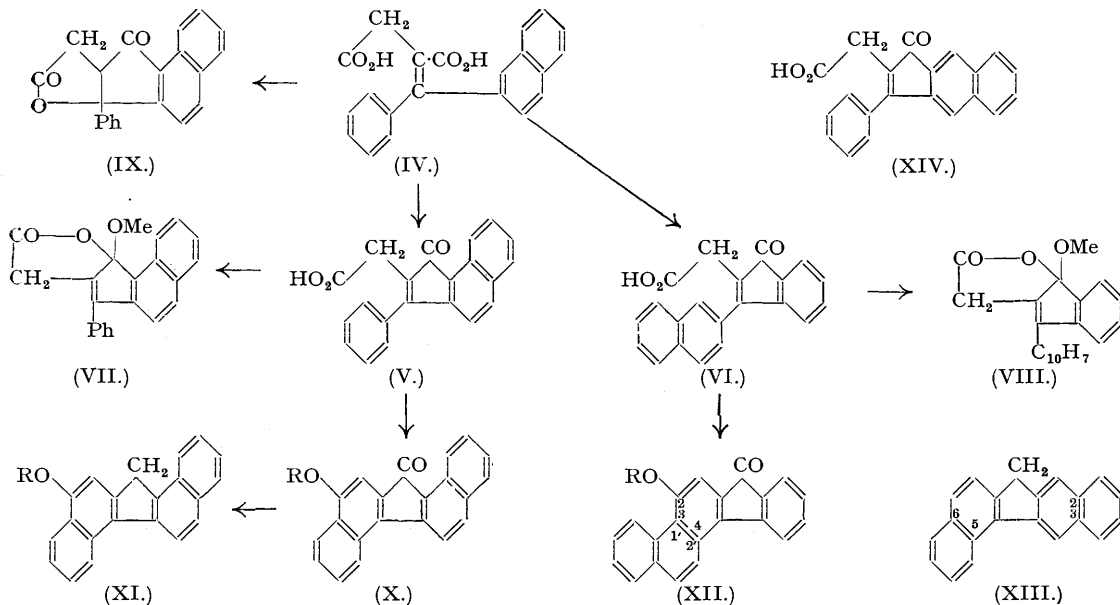
When 1-keto-3-phenyl-6 : 7-benzindene-2-acetic acid (V) was treated with boiling acetic anhydride it underwent cyclisation to the dark red 7-acetoxy-1 : 2 : 5 : 6-dibenzfluorenone (X; R = COMe), hydrolysed by alcoholic potash to the purplish-black 7-hydroxy-1 : 2 : 5 : 6-dibenzfluorenone (X; R = H). This phenol gave 1 : 2 : 5 : 6-

\* (Added in proof.) Our attention has been called to the prior use by Borsche (*Annalen*, 1936, 526, 1) of the same type of method for the synthesis of 2-hydroxy-3 : 4-benzfluorenone from  $\gamma\gamma$ -diphenylitaconic acid.

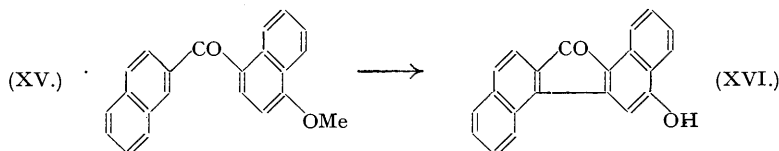
dibenzfluorene when distilled with zinc dust, and was reduced by zinc and acetic acid, followed by hydriodic acid, to 7-hydroxy-1:2:5:6-dibenzfluorene (XI; R = H). An attempt to convert this into 7-amino-1:2:5:6-dibenzfluorene, for comparison with the amino-compound prepared from nitrated 1:2:5:6-dibenzfluorene, was unsuccessful.

1-Keto-3-(2'-naphthyl)indene-2-acetic acid (VI) was converted by boiling acetic anhydride into an *acetoxy-ketone* to which we attribute tentatively the structure (XII; R = COMe). This is based on the probability that ring-closure would take place in the  $\alpha$ - rather than the  $\beta$ -position of the naphthalene system. The acetoxy-ketone was hydrolysed to the phenol (XII; R = H), from which was obtained, by distillation with zinc dust, a small amount of a compound, m. p. 189° [presumably 3:4-(1':2'-naphtha)fluorene]. On auto-oxidation in potassium methoxide solution, this passed into an orange-brown substance, m. p. 155° [presumably 3:4-(1':2'-naphtha)fluorenone].

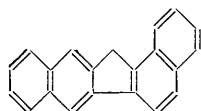
The keto-acid (VI) obtained by mono-ring closure of  $\gamma$ -phenyl- $\gamma$ -2-naphthylitaconic acid (IV) might have the alternative structure (XIV). This would lead, by the reactions outlined in the preceding paragraph, to 2:3:5:6-dibenzfluorene (XIII) and the corresponding fluorenone. Schmidlin and Huber (*Ber.*, 1910, **43**, 2824) obtained, as a by-product in the preparation of di-2-naphthylcarbinol, a hydrocarbon, m. p. 186°, which they oxidised by chromic acid to an orange-red ketone, m. p. 160—162°. If these compounds are fluorene derivatives, as Schmidlin and Huber postulated, they must have the 2:3:5:6-dibenz-structure (XIII) (compare Martin, J., 1941, 679). Their melting points are in reasonable agreement with those of the two compounds mentioned at the end of the preceding paragraph. However, Lothrop and Goodwin (*J. Amer. Chem. Soc.*, 1943, **65**, 363) have recently synthesised 2:3:5:6-dibenzfluorenone and found it to have m. p. 185°; they suggested that the compounds of Schmidlin and Huber were 2:2'-dinaphthyl and its quinone, a view to which we subscribe in spite of its inconsistency with the analytical figures quoted by Schmidlin and Huber for their oxidation product. These are the considerations which lead us to adopt structure (VI) in preference to the alternative structure (XIV) for one of the two keto-acids obtained by cyclisation of the acid (IV). This is admittedly inconclusive, for the amounts of the compounds obtained by zinc dust distillation of the phenol (XII; R = H), followed by auto-oxidation, were insufficient for analysis.



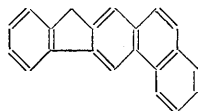
Another synthetic approach to derivatives of 1:2:5:6-dibenzfluorene was suggested by the finding of Fierz-David and Jaccard (*Helv. Chim. Acta*, 1928, **11**, 1042) that the Scholl ring-closure of 1-methoxy-4-benzoylnaphthalene gives 3-hydroxy-1:2-benzfluorenone and not the isomeric *mesobenzanthrone* derivative. We have improved the conditions for obtaining this hydroxybenzfluorenone, and have confirmed its structure by converting it by zinc dust distillation into 1:2-benzfluorene, identical with an authentic specimen. Extension of this reaction to 1-methoxy-4-(2'-naphthoyl)naphthalene (XV) gave 3-hydroxy-1:2:5:6-dibenzfluorenone (XVI), which was converted into 3-acetoxy-1:2:5:6-dibenzfluorenone, 3-hydroxy-1:2:5:6-dibenzfluorene, and thence, by zinc dust distillation, into 1:2:5:6-dibenzfluorene.



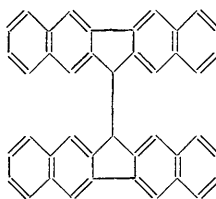
Promising results obtained by Dr. Haddow in tests for growth-inhibitory action carried out with certain polycyclic nitrogenous compounds suggested examination of their carbocyclic analogues, 1 : 2 : 6 : 7-dibenzfluorene (XVII) and 2 : 3-(2' : 1'-naphtha)fluorene (XVIII). 1 : 2 : 6 : 7-Dibenzfluorenone, prepared by the method of Martin (*loc. cit.*), could not be reduced to the fluorenol with zinc and acetic acid, which gives good results with other fluorenones, or by magnesium and methyl alcohol. 1 : 2 : 6 : 7-Dibenzfluorenol was readily obtained, however, by Ponderoff reduction of the ketone, and was converted by hydrogen bromide into 9-bromo-1 : 2 : 6 : 7-dibenzfluorenol. The yield of 1 : 2 : 6 : 7-dibenzfluorene obtained by reduction of 1 : 2 : 6 : 7-dibenzfluorenone by hydrazine hydrate in a sealed tube was much influenced by the amount of hydrazine hydrate used. Under suitable conditions good yields were obtained, but with excess of hydrazine hydrate a considerable proportion of the ketone was converted into by-products, apparently chiefly the azine. In the similar reduction of 2 : 3 : 6 : 7-dibenzfluorenone (cf. Martin, *loc. cit.*) there were obtained, in addition to 2 : 3 : 6 : 7-dibenzfluorene, 2 : 3 : 6 : 7 : 2' : 3' : 6' : 7'-tetraabenz-9 : 9'-difluorenyl (XIX) and the corresponding azine (XX).



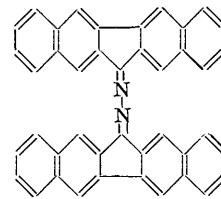
(XVII.)



(XVIII.)



(XIX.)

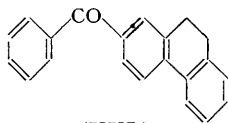


(XX.)

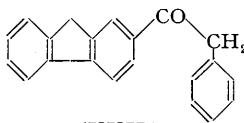
2 : 3-(1' : 2'-Naphtha)fluorene has been synthesised by a method which involves condensation of 3-chloromethylphenanthrene with ethyl cyclohexanone-2-carboxylate (J., 1935, 1319). As 9 : 10-dihydrophenanthrene normally undergoes substitution at position 2 (Burger and Mosettig, *J. Amer. Chem. Soc.*, 1935, 57, 2731; 1936, 58, 1857) it was anticipated that 2-chloromethyl-9 : 10-dihydrophenanthrene could be obtained by chloromethylation of dihydrophenanthrene, and used for a similar synthesis of 2 : 3-(2' : 1'-naphtha)fluorene (XVIII). The liquid product of chloromethylation consisted essentially, however, of 3-chloromethyl-9 : 10-dihydrophenanthrene as it was hydrolysed, through its acetate, to a carbinol, m. p. 89—92°, whereas 2-hydroxy-methyl-9 : 10-dihydrophenanthrene has m. p. 77—78° (*idem*, *J. Amer. Chem. Soc.*, 1937, 59, 1305). Moreover, reduction, followed by dehydrogenation, of the chloromethyl compound gave 3-methylphenanthrene.

Recourse was had, therefore, to a Friedel-Crafts reaction between benzoyl chloride and 9 : 10-dihydrophenanthrene. This gave a liquid mixture, of which the principal constituent was 2-benzoyl-9 : 10-dihydrophenanthrene (XXI), a pure sample of which was prepared by condensation of 9 : 10-dihydro-2-phenanthrolyl chloride with benzene. Reduction of the crude ketone with sodium amyloxide gave an oil which probably consisted mainly of the carbinol corresponding with (XXI), but cyclisation of this carbinol to a fluorene derivative with metaphosphoric acid or succinic anhydride could not be accomplished (compare Martin, *loc. cit.*).

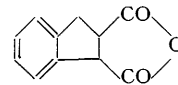
We have explored other possible routes to 2 : 3-(2' : 1'-naphtha)fluorene (XVIII). 2-Phenylacetylfluorene (XXII) was submitted to the conditions of an Elbs pyrolytic synthesis of anthracene hydrocarbons but gave no useful result. The corresponding 2-β-phenylethylfluorene might undergo *cyclo*-dehydrogenation by aluminium chloride (compare Ruzicka and Hösli, *Helv. Chim. Acta*, 1934, 17, 470), but in view of the uncertain structures of the products obtained by Clemmensen reduction of 2-phenylacetylfluorene (XXII) this project was dropped.



(XXI.)



(XXII.)



(XXIII.)

In a final attempt to synthesise the desired hydrocarbon, ethyl indene-2 : 3-dicarboxylate was prepared by the method of Bougault (*Compt. rend.*, 1914, 159, 745) and converted into the anhydride (XXIII) of *cis*-indane-1 : 2-dicarboxylic acid. This work had to be interrupted before it was possible to study the interaction of this anhydride with β-naphthylmagnesium bromide.

#### EXPERIMENTAL.

7(?)*-Nitro*-1 : 2 : 5 : 6-dibenzfluorene.—A mixture of nitric acid (*d* 1.5; 0.63 c.c.) and acetic acid was added dropwise to a stirred suspension of 1 : 2 : 5 : 6-dibenzfluorene (4 g.) in acetic acid (50 c.c.). After an hour, the brownish solid in suspension was collected and washed with acetic acid and then methyl alcohol. The *nitro*-compound (3.5 g.) crystallised from xylene in orange needles, m. p. 184—185° (Found: C, 81.0; H, 4.1; N, 4.7.  $C_{21}H_{13}O_2N$  requires C, 81.0; H, 4.2; N, 4.5%).

7(?)*-Amino*-1 : 2 : 5 : 6-dibenzfluorene was obtained when a solution of stannous chloride (10 g.) in concentrated hydrochloric acid (40 c.c.) was added slowly to a boiling suspension of the *nitro*-compound (3 g.) in acetic acid (120 c.c.), boiling being continued for an hour after the addition. The resulting solid was collected, extracted with boiling sodium hydroxide solution, and crystallised from benzene (yield, 2 g.). A sample, sublimed in a high vacuum at 180° and crystallised from benzene, formed yellowish needles, m. p. 245—249°, after sintering at 241° (Found: C, 89.7; H, 5.4; N, 5.2.  $C_{21}H_{15}N$  requires C, 89.7; H, 5.3; N, 5.0%). The *diacetyl*amino-compound crystallised when a solution of this amine

(0.1 g.) in acetic anhydride (3 c.c.) was boiled for 3 minutes, and the solution cooled. It formed brownish prisms (from ethyl acetate), m. p. 245—250° (decomp.) (Found: C, 82.1; H, 5.6.  $C_{22}H_{18}O_4N$  requires C, 82.2; H, 5.2%).

Unsuccessful attempts were made to convert the amino-1 : 2 : 5 : 6-dibenzfluorene into the corresponding hydroxy-compound through the diazo-compound, and also by heating it in a sealed tube at 190° with 10% sulphuric acid (compare Newman and Cathcart, *J. Org. Chem.*, 1940, 5, 621). Methods used for diazotisation included (a) addition of sodium nitrite solution to a suspension of amine in hydrochloric acid, (b) addition of solid sodium nitrite to a solution of the amine in concentrated sulphuric acid, and (c) treatment in pyridine solution with nitrosylsulphuric acid (compare de Milt and van Zandt, *J. Amer. Chem. Soc.*, 1936, 58, 2044).

1 : 2 : 5 : 6-Dibenzfluorene-7(?) -sulphuric acid.—A solution of concentrated sulphuric acid (1.8 c.c.) in acetic anhydride (18 c.c.) was slowly added to a stirred ice-cold suspension of 1 : 2 : 5 : 6-dibenzfluorene (3 g.) in acetic anhydride (150 c.c.). The mixture was kept overnight in the refrigerator, and the suspended solid collected and washed with dry ether. The sulphuric acid, crystallised from acetic acid and then ethyl acetate, formed colourless needles, m. p. 112—120° (decomp.) (Found: C, 72.7; H, 4.1.  $C_{21}H_{14}O_3S$  requires C, 72.8; H, 4.05%). The sparingly soluble sodium salt darkens on exposure to light.

7(?) -Nitro-1 : 2 : 5 : 6-dibenzfluorenone.—(a) Nitric acid (*d* 1.5; 0.6 c.c.) was added dropwise to a stirred suspension of 1 : 2 : 5 : 6-dibenzfluorenone (0.5 g.) in acetic acid (8 c.c.). After 10 minutes the solid was collected, dried, and recrystallised from xylene, in which it was very sparingly soluble. This nitro-ketone formed fine red needles, m. p. 324—326° (Found: N, 4.3.  $C_{21}H_{11}O_3N$  requires N, 4.3%).

(b) Nitro-1 : 2 : 5 : 6-dibenzfluorene (0.16 g.), prepared by nitrating the hydrocarbon, was heated at 230° for 6 hours in a sealed tube with selenium dioxide (0.3 g.) in water (0.3 c.c.). The product, after several recrystallisations from xylene, formed red needles (0.05 g.), m. p. 308—312°, not depressed by admixture with a specimen prepared as described under (a).

7(?) -Amino-1 : 2 : 5 : 6-dibenzfluorenone.—A mixture of the nitro-ketone (0.3 g.), xylene (100 c.c.), and a solution of stannous chloride (6 g.) in concentrated hydrochloric acid (60 c.c.) was boiled under reflux for 20 hours. The resulting tin complex was extracted with boiling alkali, and the insoluble residue was recrystallised from xylene, forming black needles (0.12 g.), m. p. 265—270° (Found: C, 85.55; H, 4.8.  $C_{21}H_{13}ON$  requires C, 85.4; H, 4.4%).

1 : 2 : 5 : 6-Dibenz-9-fluorenone.—A solution of 1 : 2 : 5 : 6-dibenzfluorenone (2 g.) in acetic acid (200 c.c.) was boiled with zinc filings (2 g.) for 45 minutes. The carbinol was precipitated with water and crystallised from benzene, forming almost colourless needles (1.5 g.), m. p. 201—202° (Found: C, 89.2; H, 4.9.  $C_{21}H_{14}O$  requires C, 89.4; H, 5.0%).

9-Bromo-1 : 2 : 5 : 6-dibenzfluorene.—A hot solution of 1 : 2 : 5 : 6-dibenz-9-fluorenone (0.1 g.) in acetic acid (10 c.c.) was saturated with hydrogen bromide. The bromo-compound, which crystallised on cooling, formed yellow needles (from benzene), m. p. 197—199° (Found: Br, 23.4.  $C_{21}H_{13}Br$  requires Br, 23.2%). In the preparation of this bromo-compound from 1 : 2 : 5 : 6-dibenzfluorenone, isolation of the intermediate carbinol was unnecessary. It was sufficient to pass in hydrogen bromide after reduction of the ketone with zinc and acetic acid.

1 : 2 : 5 : 6-Dibenzfluorenyl-9-acetic acid (II).—Condensation of the bromo-compound with ethyl sodiomalonate in benzene-alcohol appeared to take place, but when the crude product was hydrolysed and the acid heated to 180° profound decomposition took place. The only crystalline product isolated appeared to be 1 : 2 : 5 : 6-dibenzfluorenone. The acetic acid (II) was obtained as follows. Pure zinc filings (2.5 g.) were added to a mechanically stirred solution of 1 : 2 : 5 : 6-dibenzfluorenone (1.5 g.) in dry benzene (150 c.c.) containing ethyl bromoacetate (4 c.c.) and pyridine (1 c.c.), and the mixture was boiled until reaction set in. Boiling was continued for 1½ hours, and the solution decanted into ice and dilute sulphuric acid. The benzene layer was separated, dried, and the solvent removed. As alkaline hydrolysis led to auto-oxidation to dibenzfluorenone, the crude hydroxy-ester was submitted to reductive hydrolysis by boiling for 2 hours with acetic acid (40 c.c.) and hydriodic acid (*d* 1.95; 5 c.c.). The 1 : 2 : 5 : 6-dibenzfluorenyl-9-acetic acid (II), precipitated by pouring into ice-cold sulphuric acid, crystallised from toluene in colourless needles (1.1 g.), m. p. 221—223° (Found: C, 85.6; H, 5.5.  $C_{23}H_{16}O_2$  requires C, 85.2; H, 4.9%). The sparingly soluble sodium salt crystallised from water in microscopic needles. The methyl ester, prepared by treatment of the acid with ethereal diazomethane, formed pale yellow needles (from alcohol), m. p. 127—128° (Found: C, 84.9; H, 5.3.  $C_{24}H_{18}O_2$  requires C, 85.2; H, 5.3%).

9-Methyl-1 : 2 : 5 : 6-dibenzfluorene.—A solution of 1 : 2 : 5 : 6-dibenzfluorenone (2 g.) in dry benzene (100 c.c.) was added to a stirred Grignard solution prepared from methyl iodide (4.5 g.) and magnesium (0.7 g.). After being kept overnight at room temperature, the ether was distilled, and the residual benzene solution was boiled for 2 hours. The cooled solution was treated with ice and ammonium chloride, and the benzene solution was washed, dried, and evaporated. The residual oil crystallised from benzene-ligroin in yellow rectangular prisms (1.7 g.), m. p. 131—132°, of 9-methyl-1 : 2 : 5 : 6-dibenz-9-fluorenone (III) (Found: C, 89.2; H, 5.5.  $C_{22}H_{16}O$  requires C, 89.2; H, 5.4%).

A solution of this carbinol (1.4 g.) in acetic acid (70 c.c.) and hydriodic acid (*d* 1.95; 7 g.) was boiled for 3 hours. The yellow precipitate formed by pouring into ice-cold sulphuric acid was collected, dried, and sublimed at 120° in a high vacuum. 9-Methyl-1 : 2 : 5 : 6-dibenzfluorene (1.2 g.) crystallised from alcohol in colourless plates, m. p. 144—145° (Found: C, 94.3; H, 5.6.  $C_{22}H_{16}$  requires C, 94.3; H, 5.7%). The bis-1 : 3 : 5-trinitrobenzene complex, prepared in alcoholic solution, formed orange needles (from benzene-cyclohexane), m. p. 139.5—140.5° (Found: N, 12.1.  $C_{22}H_{16}, 2C_6H_3O_6N_3$  requires N, 11.9%).

9-Ethyl-1 : 2 : 5 : 6-dibenz-9-fluorenone.—A solution of 1 : 2 : 5 : 6-dibenzfluorenone (0.7 g.) in dry benzene (50 c.c.) was added to ethereal ethylmagnesium bromide (from 0.25 g. of magnesium and 1.25 g. of ethyl bromide). The mixture was stirred at room temperature for ½ hour, the ether distilled off, and the benzene solution boiled for 14 hours. After decomposition with ice and ammonium chloride, the tertiary carbinol was isolated as colourless prisms (0.4 g.) (from methyl alcohol), m. p. 151° (Found: C, 88.7; H, 6.05.  $C_{23}H_{18}O$  requires C, 89.0; H, 5.8%). Repetition of this experiment gave an unsatisfactory yield.

Acetyl-1 : 2 : 5 : 6-dibenzfluorene.—A solution of anhydrous aluminium chloride (2 g.) in nitrobenzene (20 c.c.) was added to a solution of 1 : 2 : 5 : 6-dibenzfluorene (2 g.) in nitrobenzene (10 c.c.), and the ice-cooled mixture was treated with acetyl chloride (0.7 c.c.), stirred for 4 hours (1 hour at 0°; 3 hours at room temperature), and then kept without stirring for 16 hours. The product was decomposed with ice and hydrochloric acid, the nitrobenzene removed in steam, and the residue extracted with chloroform. The material obtained from the dried chloroform extract was crystallised twice from benzene and then from alcohol, forming straw-coloured needles (1.2 g.), m. p. 146—146.5° (Found: C, 89.4; H, 5.2.  $C_{23}H_{16}O$  requires C, 89.6; H, 5.2%). This acetyl-1 : 2 : 5 : 6-dibenzfluorene gave, with hydroxylamine hydrochloride in pyridine at 100°, an oxime, which crystallised from benzene in straw-coloured needles, m. p. 209—212° (Found: C, 84.9; H, 5.6.  $C_{23}H_{17}ON$  requires C, 85.45; H, 5.3%).

1-Keto-3-phenyl-6 : 7-benzindene-2-acetic Acid (V) and 1-Keto-3-(2'-naphthyl)indene-2-acetic Acid (VI).— $\gamma$ -Phenyl- $\gamma$ -2-naphthylitaconic acid (IV) (Hewett, *loc. cit.*) was esterified by 4 hours' boiling with methyl alcohol saturated in the cold with hydrogen chloride. The resulting methyl ester crystallised from methyl alcohol in colourless plates, m. p. 125—126° (Found: C, 76.4; H, 5.6; OMe, 17.4.  $C_{23}H_{20}O_4$  requires C, 76.7; H, 5.6; OMe, 17.2%). Another experiment, under the same conditions, gave the methyl ester, m. p. 94—95°, obtained by esterification of the acid with

diazomethane. This lower-melting ester was not changed by boiling its solution in methyl-alcoholic hydrogen chloride for 6 hours. The reason for the formation of the higher-melting ester in the earlier experiment is obscure.

The anhydride of  $\gamma$ -phenyl- $\gamma$ -2-naphthylitaconic acid (40 g.) was prepared by boiling under reflux for 2 hours with acetyl chloride (80 g.). The solvent was removed, and the anhydride, dissolved in nitrobenzene (400 c.c.), was treated slowly at 0° with anhydrous aluminium chloride (40 g.). The mixture was kept at 0° for 24 hours, then decomposed with ice and hydrochloric acid, and the nitrobenzene removed in steam. The residue was extracted with ether and the ethereal extract shaken with a very large volume of sodium carbonate solution (about 0.25N). The ethereal solution, on evaporation, gave a red solid which, after crystallisation from benzene, had m. p. 240—255° (decomp.). This (2 g.) was not further investigated. The benzene liquors from which it crystallised gave, on standing, colourless crystals which, after several crystallisations from benzene, had m. p. 164.5—165.5°, and were identical with the lactone (IX?) obtained by Hewett (*loc. cit.*) by the action of concentrated sulphuric acid on  $\gamma$ -phenyl- $\gamma$ -2-naphthylitaconic acid (Found : C, 80.2; H, 4.5. Calc. : C, 80.25; H, 4.5%). Boiling methyl-alcoholic hydrogen chloride transformed this lactone into the red methyl ester, m. p. 136°, of the acid (V) described in the following paragraph.

Addition of sodium chloride to the sodium carbonate extract referred to in the preceding paragraph precipitated the mixed sodium salts (24 g.) of the acids (V) and (VI). Two recrystallisations from water, followed by precipitation of the acid and crystallisation from benzene, gave pure 1-*keto*-3-phenyl-6 : 7-benzindene-2-acetic acid (V) (8.5 g.) in orange needles, m. p. 176—177° (Found : C, 80.2; H, 4.3.  $C_{21}H_{14}O_3$  requires C, 80.25; H, 4.5%). The normal methyl ester, obtained by addition of excess of ethereal diazomethane to an ethereal solution of this acid, crystallised from methyl alcohol in red needles, m. p. 136° (Found : C, 80.4; H, 4.95; OMe, 9.25.  $C_{22}H_{16}O_3$  requires C, 80.5; H, 4.9; OMe, 9.45%). The pseudo-methyl ester (VII), obtained from the acid by 20 minutes' boiling with methyl-alcoholic hydrogen chloride (10 c.c.), crystallised from methyl alcohol in bright red prisms, m. p. 83.5—84.5° (Found : C, 80.1; H, 5.25; OMe, 9.2%).

The aqueous mother-liquors from which the sodium salt of the acid (V) had crystallised were acidified, and the precipitated acid was converted into its potassium salt which, after two recrystallisations from water gave 1-*keto*-3-(2'-naphthyl)indene-2-acetic acid (VI). This crystallised from benzene-cyclohexane in yellow prisms (6.5 g.), m. p. 150—153° (Found : C, 80.2; H, 4.3.  $C_{21}H_{14}O_3$  requires C, 80.25; H, 4.5%). The normal methyl ester of (VI), prepared by treatment with ethereal diazomethane, formed yellow needles, m. p. 98—99° (from methyl alcohol) (Found : C, 80.45; H, 5.0; OMe, 9.4%). The pseudo-methyl ester (VIII), prepared from the acid (VI) by boiling methyl-alcoholic hydrogen chloride, crystallised from cyclohexane in yellow needles, m. p. 101.5—102.5° (Found : C, 80.7; H, 5.0; OMe, 9.4%). This pseudo-ester depressed the m. p. of the normal ester to 93—94°. Both the normal and the pseudo-ester were hydrolysed by alcoholic potash to the acid from which they were obtained.

7-Acetoxy-1 : 2 : 5 : 6-dibenzfluorenone (X; R = COMe).—A solution of 1-*keto*-3-phenyl-6 : 7-benzindene-2-acetic acid (6 g.) in freshly distilled acetic anhydride (60 c.c.) was boiled for 15 minutes. The acetate (X; R = COMe) (6.2 g.) which crystallised on cooling was sufficiently pure for the next stage. For analysis, a specimen was crystallised twice from acetic acid and formed deep red needles, m. p. 245—246° (Found : C, 81.3; H, 4.3.  $C_{23}H_{14}O_3$  requires C, 81.7; H, 4.1%). Hydrolysis of this acetate (2.5 g.) to 7-hydroxy-1 : 2 : 5 : 6-dibenzfluorenone (X; R = H) was effected by boiling for one minute with a solution of potassium hydroxide (1.8 g.) in methyl alcohol (90 c.c.). The resulting dark green solution was poured into much ice-water, the solution acidified, and the precipitated phenol collected and recrystallised from alcohol. Its dark purple solution gave black needles (2 g.), which decomposed above 250° (Found : C, 85.1; H, 4.3.  $C_{21}H_{12}O_2$  requires C, 85.1; H, 4.05%). The methyl ether (X; R = Me), formed by the action of excess methyl sulphate on a solution of this phenol in alcoholic potassium hydroxide, crystallised from benzene in very dark red needles, m. p. 196—197° (Found : C, 85.1; H, 4.8; OMe, 9.5.  $C_{22}H_{14}O_2$  requires C, 85.2; H, 4.5; OMe, 10.0%).

For conversion into 1 : 2 : 5 : 6-dibenzfluorene, the hydroxy-ketone (X; R = H) (0.5 g.) was intimately mixed with zinc dust (20 g.) and heated to dull redness in an atmosphere of hydrogen until sublimation ceased. The sublimate, dissolved in benzene-ligroin, was purified by chromatographic adsorption on alumina. The first fractions of the benzene eluate gave almost colourless needles of 1 : 2 : 5 : 6-dibenzfluorene, m. p. 170—173°, alone or mixed with an authentic specimen.

7-Acetoxy-1 : 2 : 5 : 6-dibenz-9-fluorenone was obtained when a solution of 7-acetoxy-1 : 2 : 5 : 6-dibenzfluorenone (0.1 g.) in acetic acid (10 c.c.) was boiled with zinc filings (0.1 g.) until the red colour had faded (about an hour). The precipitate formed by decanting the cooled solution into ice-water crystallised from alcohol in colourless needles, m. p. 222° (decomp.) (Found : C, 80.5; H, 4.9.  $C_{23}H_{16}O_3$  requires C, 81.2; H, 4.7%). In another experiment, 7-acetoxy-1 : 2 : 5 : 6-dibenzfluorenone (2.5 g.) was reduced with zinc and acetic acid, and hydriodic acid (*d* 1.95; 8 c.c.) was added to the solution which had been decanted from the undissolved zinc. The mixture was then boiled for 2 hours, cooled, and poured into ice-cold sulphurous acid. The precipitate was collected, crystallised from benzene, then sublimed in a high vacuum at 170°, and finally recrystallised from benzene. The resulting colourless leaflets of 7-hydroxy-1 : 2 : 5 : 6-dibenzfluorenone (XI; R = H) (1.8 g.) sublimed above 200°, but had no sharp m. p. (Found : C, 89.5; H, 4.95.  $C_{21}H_{14}O$  requires C, 89.4; H, 5.0%). The acetate (XI; R = COMe), formed by the action of boiling acetic anhydride, crystallised from alcohol in colourless plates, m. p. 164—165° (Found : C, 85.0; H, 4.6.  $C_{22}H_{16}O_2$  requires C, 85.2; H, 4.9%), and the methyl ether (XI; R = Me) was obtained by alternate treatment of a boiling solution of the phenol (100 mg.) in absolute alcohol (50 c.c.) with alcoholic potash and methyl sulphate (2.7 g. in all). This methylation was carried out in an atmosphere of hydrogen to avoid auto-oxidation. The methyl ether (XI; R = Me), which was not formed by the action of diazomethane on the phenol, formed colourless prisms (from benzene), m. p. 217—218° (Found : C, 89.5; H, 5.5.  $C_{22}H_{16}O$  requires C, 89.2; H, 5.4%).

In an attempt to prepare 7-amino-1 : 2 : 5 : 6-dibenzfluorene, a mixture of 7-hydroxy-1 : 2 : 5 : 6-dibenzfluorenone (0.2 g.), sodium bisulphite (0.9 g.), dioxan (1.1 c.c.), concentrated ammonia (2.2 c.c.), and water (2.2 c.c.) was heated in a sealed tube at 190—200° for 10 hours. The only pure material subsequently isolated was unchanged hydroxy-compound.

2-Acetoxy-3 : 4-(1' : 2'-naphtha)fluorenone (XII; R = COMe) was formed when a solution of the keto-acid (VI) (1.4 g.) in acetic anhydride (14 c.c.) was boiled for 30 minutes. The acetate which crystallised on cooling (1.45 g.) formed bright yellow needles (from toluene), m. p. 204—206° (Found : C, 81.7; H, 4.2.  $C_{23}H_{14}O_3$  requires C, 81.7; H, 4.1%). Hydrolysis of this acetate (1 g.) with potassium hydroxide (0.5 g.) in methyl alcohol (25 c.c.) (3 minutes' boiling) gave a deep blue solution from which dilute acid precipitated 2-hydroxy-3 : 4-(1' : 2'-naphtha)fluorenone (XII; R = H). This crystallised from alcohol in claret-coloured needles, m. p. above 250° (decomp.) (Found : C, 85.15; H, 4.2.  $C_{21}H_{12}O_2$  requires C, 85.1; H, 4.05%).

This hydroxy-ketone (0.5 g.) was distilled with zinc dust (30 g.) as described for the isomeride (X). The product crystallised from alcohol in greyish prisms, m. p. 189° [probably 3 : 4-(1' : 2'-naphtha)fluorene], but the amount was insufficient for analysis. The material from the mother-liquors was dissolved in acetone (5 c.c.) and boiled for 10 minutes with potassium methoxide (from 0.02 g. of potassium and 0.1 c.c. of methyl alcohol). After dilution with water the product was extracted with chloroform and the material obtained from the extract was crystallised from alcohol. It had m. p. 155°.

1-Hydroxy-3-phenyl-6 : 7-benzindene-2-acetic acid was obtained when the keto-acid (V) (0.5 g.) was reduced in toluene solution (50 c.c.) by boiling for 1½ hours with 6*N*-hydrochloric acid (50 c.c.) and amalgamated zinc (2 g.). The acidic product was crystallised from aqueous acetic acid and then benzene-hexane, forming colourless prisms, m. p. 165–168°. The same product was obtained in better yield when a solution of the keto-acid (V) in acetic acid was boiled with zinc dust for 10 minutes and then with hydriodic acid for 2 hours. The pure hydroxy-acid crystallised from aqueous alcohol in colourless needles, m. p. 170° (Found : C, 80.3; H, 5.3. C<sub>21</sub>H<sub>16</sub>O<sub>3</sub> requires C, 79.75; H, 5.1%). The methyl ester, obtained with ethereal diazomethane, formed colourless prisms (from cyclohexane), m. p. 105–106° (Found : C, 80.1; H, 5.8. C<sub>22</sub>H<sub>18</sub>O<sub>3</sub> requires C, 80.0; H, 5.45%). Failure to reduce the hydroxyl group is evidently due to steric hindrance.

3-(2'-Naphthyl)indene-2-acetic Acid.—A solution of the keto-acid (VI) (4 g.) in toluene (400 c.c.) was boiled for 4 hours with 6*N*-hydrochloric acid (400 c.c.) and amalgamated zinc (16 g.). Acidification of a sodium carbonate extract of the resulting toluene solution precipitated 3-(2'-naphthyl)indene-2-acetic acid, which crystallised from benzene in colourless needles (1.5 g.), m. p. 177–178° (Found : C, 83.7; H, 5.4. C<sub>21</sub>H<sub>16</sub>O<sub>2</sub> requires C, 84.0; H, 5.3%).

Action of Fused Potassium Hydroxide on 1 : 2 : 5 : 6-Dibenzfluorenone.—The finely ground ketone (1 g.) was added to fused potassium hydroxide (2 g.) at 290°, and the temperature slowly raised to 340°. The cooled mass was extracted with water, and the solution acidified. Purification of the resulting acid gave 1 : 2'-dinaphthyl-2-carboxylic acid, m. p. 204° (from benzene) not depressed by admixture with an authentic specimen (Swain and Todd, *loc. cit.*). There was no evidence of the formation of 1 : 2'-dinaphthyl-1'-carboxylic acid.

4-Benzoyl-1-methoxynaphthalene (compare Fierz-David and Jaccard, *loc. cit.*).—Anhydrous aluminium chloride (40.5 g.) was slowly added to a stirred ice-cold solution of 1-methoxynaphthalene (24 g.) and benzoyl chloride (21.5 g.) in carbon disulphide (100 c.c.). The mixture was stirred at 0° for 6 hours, during which a deep red complex crystallised, and then decomposed with ice and hydrochloric acid. The carbon disulphide was removed in steam, the residue made alkaline, and passage of steam continued for 2 hours. The product, dried in ethereal solution, was distilled in a vacuum, and the distillate was recrystallised from alcohol, forming long colourless needles (24 g.), m. p. 80–81°.

3-Hydroxy-1 : 2-benzfluorenone.—A stirred mixture of 1-methoxy-4-benzoylnaphthalene (5 g.), anhydrous aluminium chloride (12 g.), and sodium chloride (4 g.) was heated in an oil-bath at 140° for 30 minutes. The cooled mass was decomposed with ice and hydrochloric acid, extracted with ether, and the ethereal extract shaken with dilute sodium hydroxide solution. Acidification of the alkaline solution precipitated crude 3-hydroxy-1 : 2-benzfluorenone (4.3 g.), a solution of which in acetic anhydride was boiled for an hour. On cooling, 3-acetoxy-1 : 2-benzfluorenone (2.3 g.) crystallised. It formed dark yellow needles (from acetic acid), m. p. 184–185° (Found : C, 79.1; H, 4.5. C<sub>18</sub>H<sub>12</sub>O<sub>3</sub> requires C, 79.2; H, 4.2%). On hydrolysis this gave pure 3-hydroxy-1 : 2-benzfluorenone.

1 : 2-Benzfluorene.—A mixture of 3-hydroxy-1 : 2-benzfluorenone (2 g.) and zinc dust (20 g.) was heated in an atmosphere of hydrogen until distillation ceased. The distillate, in benzene solution, was purified by chromatographic adsorption on alumina, and gave 1 : 2-benzfluorene (chrysofluorene), m. p. 174–176°, not depressed by admixture with an authentic specimen, m. p. 182° (Cook *et al.*, J., 1934, 1727).

3-Acetoxy-1 : 2-benzfluorenone.—A solution of 3-acetoxy-1 : 2-benzfluorenone (2 g.) in acetic acid (200 c.c.) was boiled for 2 hours with zinc filings (6 g.). The colourless solution was decanted into ice water, and the precipitate was collected, dried, and crystallised several times from benzene-cyclohexane. 3-Acetoxy-1 : 2-benzfluorenone formed fine colourless needles, m. p. 157° (Found : C, 78.9; H, 4.9. C<sub>19</sub>H<sub>14</sub>O<sub>3</sub> requires C, 78.6; H, 4.8%). By further reduction with hydriodic acid in boiling acetic acid (2 hours) this was converted into 3-hydroxy-1 : 2-benzfluorenone, which, after sublimation at 175°/0.3 mm. and recrystallisation from benzene, formed colourless needles, m. p. 219° (Found : C, 87.8; H, 5.5. C<sub>17</sub>H<sub>12</sub>O requires C, 87.9; H, 5.2%). Its acetate had m. p. 155–156° (Found : C, 83.1; H, 5.1. C<sub>19</sub>H<sub>14</sub>O<sub>2</sub> requires C, 83.2; H, 5.1%).

1-Methoxy-4-(2'-naphthoyl)naphthalene (XV).—Anhydrous aluminium chloride (38 g.) was slowly added to a stirred ice-cold solution of 2-naphthoyl chloride (32 g.) and 1-methoxynaphthalene (26 g.) in carbon disulphide (200 c.c.). The mixture was stirred at 0° for 6 hours, and worked up as described above for the benzoyl compound. The ketone, b. p. 250–260°/0.5 mm., crystallised from alcohol in pale yellow prisms, m. p. 114° (43 g.) (Found : C, 84.5; H, 5.2. C<sub>22</sub>H<sub>16</sub>O<sub>2</sub> requires C, 84.6; H, 5.1%).

3-Hydroxy-1 : 2 : 5 : 6-dibenzfluorenone (XVI).—A mixture of the foregoing ketone (10 g.), anhydrous aluminium chloride (10 g.), and sodium chloride (3 g.) was stirred for an hour while being heated in an oil-bath at 130–140°. The cooled melt was decomposed with ice and hydrochloric acid, and the insoluble material collected and extracted with a large volume of dilute sodium hydroxide solution. Acidification of the filtered solution precipitated crude 3-hydroxy-1 : 2 : 5 : 6-dibenzfluorenone. This was purified through its acetate, obtained by an hour's boiling with acetic anhydride. The acetate (5.6 g.), which crystallised from the solution on cooling, recrystallised from xylene in deep red needles, m. p. 262–265° (Found : C, 81.7; H, 4.0. C<sub>23</sub>H<sub>14</sub>O<sub>3</sub> requires C, 81.7; H, 4.1%). Hydrolysis of this acetate with boiling methyl-alcoholic potash solution was complete in 10 minutes. Dilution with water, filtration, and acidification of the filtrate precipitated 3-hydroxy-1 : 2 : 5 : 6-dibenzfluorenone (XVI), which crystallised from anisole in dark brown needles which melted slowly above 300° (Found : C, 85.2; H, 4.05. C<sub>21</sub>H<sub>12</sub>O<sub>2</sub> requires C, 85.1; H, 4.05%).

3-Hydroxy-1 : 2 : 5 : 6-dibenzfluorenone.—A solution of 3-acetoxy-1 : 2 : 5 : 6-dibenzfluorenone (2.5 g.) in acetic acid (600 c.c.) was boiled for 2 hours with zinc filings (10 g.) added in two portions. Decantation of the pale yellow solution into ice-water precipitated 3-acetoxy-1 : 2 : 5 : 6-dibenzfluorenone, which crystallised from toluene in almost colourless needles, m. p. 237–238° (Found : C, 81.4; H, 4.8. C<sub>22</sub>H<sub>16</sub>O<sub>3</sub> requires C, 81.2; H, 4.7%). A solution of this carbinol in acetic acid (250 c.c.) and hydriodic acid (*d* 1.95; 10 c.c.) was boiled for 2 hours and poured into ice-cold sulphurous acid. The yellow precipitate (2.1 g.) was collected, dried, and recrystallised from benzene. For analysis, a specimen was sublimed at 195°/0.3 mm. and the sublimate was recrystallised from benzene. 3-Hydroxy-1 : 2 : 5 : 6-dibenzfluorenone formed colourless needles, m. p. 205–206° (decomp.) (Found : C, 89.6; H, 5.0. C<sub>21</sub>H<sub>14</sub>O requires C, 89.4; H, 5.0%). Distillation of this phenol (0.5 g.) with zinc dust (20 g.) in a slow stream of hydrogen gave 1 : 2 : 5 : 6-dibenzfluorene (0.25 g.), m. p. 170°, alone or mixed with an authentic sample.

1 : 2 : 6 : 7-Dibenzfluorenone.—A solution of aluminium isopropoxide (4 g.) in isopropyl alcohol (30 c.c.) was added to a solution of 1 : 2 : 6 : 7-dibenzfluorenone (Martin, *loc. cit.*) (1 g.) in dry toluene (150 c.c.), and the mixture distilled slowly during 6 hours, the volume being kept constant by addition of isopropyl alcohol. More toluene was then added, and the cold solution treated with dilute sulphuric acid. Evaporation of the washed toluene solution gave 1 : 2 : 6 : 7-dibenzfluorenone, which crystallised from toluene in small colourless prisms (0.8 g.), m. p. 233–234° (Found : C, 89.2; H, 5.1. C<sub>21</sub>H<sub>14</sub>O requires C, 89.4; H, 5.0%). When hydrogen bromide was passed into a warm suspension of this carbinol (0.1 g.) in acetic acid (15 c.c.) it dissolved, and 9-bromo-1 : 2 : 6 : 7-dibenzfluorenone crystallised. It formed long, pale yellow needles (from cyclohexane) which decomposed at 186–187°, after darkening (Found : Br, 22.9. C<sub>21</sub>H<sub>13</sub>Br requires Br, 23.2%).

1 : 2 : 6 : 7-Dibenzfluorene (XVII).—1 : 2 : 6 : 7-Dibenzfluorenone (0.2 g.) was heated in a sealed tube for 6 hours with 50% hydrazine hydrate. The hydrocarbon was isolated from the products by vacuum sublimation followed by recrystallisation from benzene. 1 : 2 : 6 : 7-Dibenzfluorene formed colourless plates, m. p. 294–295° (Found : C, 94.5;

H, 5.6.  $C_{21}H_{14}$  requires C, 94.7; H, 5.3%. The yields, using 0.6, 1.5, and 2 c.c. of 50% hydrazine hydrate were 0.17, 0.08, and 0.06 g., respectively. The other products consisted of red material, probably partly the *azine*, which did not sublime (Found, after recrystallisation : C, 90.4; H, 4.4.  $C_{42}H_{24}N_2$  requires C, 90.65; H, 4.3%).

*Reduction of 2 : 3 : 6 : 7-Dibenzfluorenone* (compare Martin, *loc. cit.*).—A mixture of 2 : 3 : 6 : 7-dibenzfluorenone (3 g.) and 50% hydrazine hydrate (18 c.c.) was heated in a sealed tube at 210° for 8 hours. The product was sublimed at 210—220°/0.2 mm., and the sublimate, after recrystallisation from benzene, gave 2 : 3 : 6 : 7-dibenzfluorene (1.1 g.), m. p. 281—282°.

The residue from the sublimation was extracted with hot benzene. The filtered extract gave, on cooling, colourless needles (0.13 g.), probably consisting of 2 : 3 : 6 : 7 : 2' : 3' : 6' : 7'-*tetrabenz-9 : 9'-difluorenyl* (XIX). This had m. p. 310° (decomp.) (from xylene) (Found : C, 95.0; H, 5.3.  $C_{42}H_{26}$  requires C, 95.1; H, 4.9%). The residue insoluble in benzene crystallised from nitrobenzene in dark red needles, not molten at 310°, probably consisting of 2 : 3 : 6 : 7 : 2' : 3' : 6' : 7'-*tetrabenzbisfluorenylideneazine* (XX) (Found : C, 90.7; H, 4.1; N, 5.2.  $C_{42}H_{24}N_2$  requires C, 90.65; H, 4.3; N, 5.0%).

*Chloromethylation of 9 : 10-Dihydrophenanthrene*.—The dihydrophenanthrene was obtained from purified phenanthrene by hydrogenation over copper chromite at 150° and 115 atm. (compare Fieser and Johnson, *J. Amer. Chem. Soc.*, 1939, **61**, 169).\* Paraformaldehyde (3.6 g.) was added to an ice-cold solution of 9 : 10-dihydrophenanthrene (10 g.) in acetic acid (30 c.c.), and dry hydrogen chloride was passed into the suspension until the paraformaldehyde had dissolved. The most satisfactory results were obtained when this mixture was kept at room temperature for 10 days. The whole was then poured into water, extracted with benzene, and the benzene extract was washed, dried, and distilled. Unchanged dihydrophenanthrene (3.75 g.) distilled at 130—140°/0.5 mm. The fraction, b. p. 140—180°/0.5 mm. (5 g.), seemed to consist largely of chloromethyl compound. A solution of this fraction (0.65 g.) and anhydrous sodium acetate (0.65 g.) in acetic acid (5 c.c.) was boiled for an hour. The product was hydrolysed with methyl-alcoholic potash and gave 3-hydroxymethyl-9 : 10-dihydrophenanthrene (0.2 g.), which crystallised from ether-ligroin in colourless needles, m. p. 89—92°.

A solution of the crude chloromethyl compound (2 g.) in alcohol (25 c.c.) and water (5 c.c.) was boiled with zinc dust (3 g.) for 3 hours. The product, distilled from an air-bath at 130°/0.4 mm., was free from halogen and was heated with palladium-black (0.1 g.) at 280° for 13 hours. This product of dehydrogenation was distilled at 140°/0.3 mm., the distillate (1.2 g.) crystallising. It gave a picrate, m. p. 137°, from which was obtained a hydrocarbon, m. p. 61—62° (3-methylphenanthrene and its picrate have m. p. 62—63° and 137°, respectively).

*Condensation of 9 : 10-Dihydrophenanthrene with Benzoyl Chloride*.—A solution of benzoyl chloride (4.85 g.) in nitrobenzene (10 c.c.) was added dropwise, during  $\frac{1}{2}$  hour, to an ice-cold solution of anhydrous aluminium chloride (14.6 g.) and 9 : 10-dihydrophenanthrene (10 g.) in nitrobenzene (100 c.c.). The mixture was kept at 0° for a further 2 hours, and then at room temperature for 20 hours. After decomposition with ice and hydrochloric acid, the nitrobenzene was removed in steam, and the residual ketone was extracted with ether. Distillation gave an oil (8.5 g.), b. p. 228—233°/0.5 mm., which did not crystallise. It gave a homogeneous 2 : 4-dinitrophenylhydrazone, which crystallised from ethyl acetate in deep salmon-coloured needles, m. p. 234—235° (Found : C, 69.9; H, 4.4.  $C_{27}H_{20}O_4N_4$  requires C, 69.8; H, 4.3%). The *oxime*, prepared by treatment of the distilled ketone with hydroxylamine hydrochloride in pyridine at 100°, formed colourless needles, m. p. 219° (from alcohol) (Found : C, 83.7; H, 6.1.  $C_{21}H_{17}ON$  requires C, 84.3; H, 5.7%).

For oxidation, a solution of this liquid ketone (1.3 g.) in acetic acid (10 c.c.) was boiled for a few minutes with a solution of chromic acid (1.2 g.) in water (2 c.c.). The resulting quinone (0.35 g.) crystallised from chlorobenzene in orange needles, m. p. 217°, raised to 219° by vacuum sublimation, with two further crystallisations. This m. p. is in agreement with that given by Bachmann (*J. Amer. Chem. Soc.*, 1935, **57**, 555) for 2-benzoylphenanthraquinone (m. p. 218°).

Confirmation that the original ketone was essentially 2-benzoyl-9 : 10-dihydrophenanthrene was obtained as follows. 9 : 10-Dihydro-2-phenanthroic acid (Burger and Mosettig, *ibid.*, p. 2731; 1936, **58**, 1857) (1.4 g.) was converted into its chloride by 2 hours' boiling with thionyl chloride (12 c.c.). The solid obtained by removal of the excess of thionyl chloride under reduced pressure was dissolved in benzene (30 c.c.), and the solution was added to a cold suspension of anhydrous aluminium chloride (0.9 g.) in benzene (9 c.c.). The mixture was boiled for 2 hours, and the product isolated in the usual way. The distilled ketone (0.9 g.) solidified when triturated with alcohol. After recrystallisation from alcohol, 2-benzoyl-9 : 10-dihydrophenanthrene (XXI) formed colourless needles, m. p. 72—73° (Found : C, 88.9; H, 5.6.  $C_{21}H_{14}O$  requires C, 88.7; H, 5.6%). Its 2 : 4-dinitrophenylhydrazone, m. p. 235°, was identical with that obtained from the oily ketone prepared from 9 : 10-dihydrophenanthrene and benzoyl chloride.

*2-Phenylacetylfluorene* (XXII).—Anhydrous aluminium chloride (42 g.) was added to an ice-cooled solution of fluorene (26 g.) and phenylacetyl chloride (25 g.) in carbon disulphide (100 c.c.). The mixture was stirred at 0° for 6 hours, decomposed with ice and hydrochloric acid, and the carbon disulphide and excess of fluorene removed in steam. Crystallisation of the residue from benzene gave 2-phenylacetylfluorene (28 g.), m. p. 153° (compare Păpcke, *Ber.*, 1888, **21**, 1331). An equally good result was obtained when the condensation was carried out in nitrobenzene solution at room temperature (20 hours).

When this ketone was heated at 350° for 3 hours about 60% was recovered. The mother-liquors, after vacuum distillation, gave a very small amount of colourless needles (from toluene), m. p. 265—270°. This was not investigated.

*Reduction of 2-Phenylacetylfluorene*.—(a) Clemmensen reduction, using the modification of Martin (*J. Amer. Chem. Soc.*, 1936, **58**, 1438) gave, in 45% yield, a compound which crystallised from toluene in colourless prisms, m. p. 273—274°. This probably consisted essentially of a pinacol (Found : C, 88.95; H, 5.9.  $C_{42}H_{34}O_2$  requires C, 88.4; H, 6.0%). (b) By using anisole instead of toluene as the inert solvent in the above reduction, and by increasing the duration of boiling to 72 hours, there was obtained, in 25% yield, a hydrocarbon which crystallised from alcohol in long colourless needles, m. p. 146° (Found : C, 93.3; H, 6.8; *M*, Rast, 234.  $C_{21}H_{18}$  requires C, 93.3; H, 6.7%; *M*, 270). (c) When a mixture of 2-phenylacetylfluorene (1 g.) and 50% hydrazine hydrate (5 c.c.) was heated in a sealed tube at 270° for 7 hours the *azine* was the chief product. This formed yellow needles (from anisole), m. p. 285—288°. Satisfactory analytical figures were not obtained, probably owing to retention of solvent (Found : C, 87.5; H, 5.8.  $C_{42}H_{32}N_2$  requires C, 89.4; H, 5.7%). A mixture of this *azine* (0.5 g.) and sodium ethoxide solution (from 0.5 g. of sodium and 7 c.c. of alcohol) was heated in a sealed tube at 200° for 8 hours. The product was extracted with ether, distilled in a vacuum, and the distillate recrystallised from methyl alcohol, forming yellow prisms, m. p. 113—114°. This hydrocarbon should be 2-( $\beta$ -phenylethyl)fluorene (Found : C, 93.5; H, 6.7; *M*, Rast, 236.  $C_{21}H_{18}$  requires C, 93.3; H, 6.7%; *M*, 270). (d) An impure specimen of the foregoing hydrocarbon, m. p. 113°, was obtained from the semicarbazone, m. p. 221—224°, of 2-phenylacetylfluorene, by 8 hours' heating at 190—200° with alcoholic sodium ethoxide.

*cis-Indane-1 : 2-dicarboxylic Anhydride* (XXIII).—Ethyl indene-2 : 3-dicarboxylate was prepared by the method of Bougault (*Compt. rend.*, 1914, **159**, 745). A solution of this ester (2 g.) in alcohol (50 c.c.) was shaken with hydrogen

\* This hydrogenation was carried out in an autoclave purchased from a grant from the Carnegie Trust for the Universities of Scotland.



and palladium-black (0.1 g.) until absorption ceased. The saturated ester was not obtained crystalline and was hydrolysed by boiling alcoholic potash to *cis*-indane-1:2-dicarboxylic acid, m. p. 228° (1.4 g.). In all, 20.5 g. of this acid were obtained from 30 g. of the unsaturated ester. A suspension of the saturated acid (6.7 g.) in acetyl chloride (30 c.c.) was boiled for 6 hours. The solvents were removed, and the residue distilled from an air-bath at 145°/0.2 mm. The distillate (3.5 g.) crystallised on standing, and recrystallised from benzene-cyclohexane in colourless plates of *cis*-indane-1:2-dicarboxylic anhydride, m. p. 97—98° (Found: C, 70.4; H, 4.1.  $C_{11}H_8O_3$  requires C, 70.2; H, 4.3%). This anhydride, which must be derived from the *cis*-acid, is hydrolysed to the acid, m. p. 228°, from which it was prepared. The latter therefore has the *cis*-configuration. The anhydride reacts with alcohol to give the *monoethyl* ester, m. p. 123—124° (Found: C, 67.1; H, 6.2.  $C_{13}H_{14}O_4$  requires C, 66.7; H, 6.0%).

We are much indebted to Imperial Chemical Industries Ltd. (Dyestuffs Division) for financial provision which has enabled one of us (R. W. G. P.) to carry out the experiments here recorded, and also for gifts of chemicals. All analyses were micro-analyses carried out by Mr. J. M. L. Cameron.

UNIVERSITY OF GLASGOW.

[Received, June 26th, 1944.]

---