# **742.** *Synthesis of Fluoranthenes. Part XI.* Iodination of Tetrahydrofluoranthenes, leading to the Syntheses of* 3-*Methyl*-1 : 2-5 : 6-*dibenzopyracylene.*

By John M. Beaton and S. Horwood Tucker.

1 : 2 : 3 : 4-Tetrahydrofluoranthene and its 2- and 3-methyl-derivatives (IV) have been directly iodinated to 5-iodo-derivatives (V). Dehydrogenation of these gave 4-iodo-, 5-iodo-2-methyl-, and 5-iodo-3-methyl-fluoranthene (VI), respectively. The last two, by the crossed Ullmann reaction, have been converted into 3-methyl-1 : 2-5 : 6-dibenzopyracylene (III).

Pyracene (I) has been synthesised by Anderson, jun., and Wade (*J. Amer. Chem. Soc.*, 1952, **74**, 2274) after many fruitless attempts (Mayer and Kaufmann, *Ber.*, 1920, **53**, 289; Fleischer and Wolff, *ibid.*, p. 925; Fieser and Peters, *J. Amer. Chem. Soc.*, 1932, **54**, 4347). Although pyracylene (II) has not been synthesised, four benzo-derivatives have been prepared: a monobenzo- (by Kloetzel and Chubb, *J. Amer. Chem. Soc.*, 1950, **72**, 150); a dibenzo- (by Stubbs and Tucker, *J.*, 1951, 2936); a tribenzo- (isorubicene) (by Fedorov, *Bull. Acad. sci., U.R.S.S., Classe sci. chim.*, 1947, 397; cf. Clar, *Ber.*, 1931, **64**, 2194, and Tucker and Whalley, *Chem. Reviews*, 1952, 529, footnote 2); and a tetrabenzo-pyracylene [by Badoche, *Ann. Chim.*, 1933, **20**, 200, and Dufraisse (Dufraisse and Girard, *Bull. Soc. chim.*, 1934, **1**, 1359; Dufraisse, *ibid.*, 1936, **3**, 1857; Dufraisse and Horclois, *ibid.*, p. 1894)].

Brown's molecular-orbital calculations (*J.*, 1951, 2391) for 1 : 2-5 : 6-dibenzopyracylene (Stubbs and Tucker, *loc. cit.*) give values which agree with those derived from its ultra-violet spectrum (Clar, Stubbs, and Tucker, *Nature*, 1950, **166**, 1075). To test Brown's predictions with regard to the position entered in electrophilic, nucleophilic, and radical substitution, reference compounds are being synthesised. At first, to test the generality of the method applied to the synthesis of the parent hydrocarbon, 1 : 2-5 : 6-dibenzopyracylene, we have similarly synthesised 3-methyl-1 : 2-5 : 6-dibenzopyracylene by two routes, and have widened the applicability of the method by starting with tetrahydrofluoranthenes instead of from fluoranthenes.

Although the direct action of electrophilic reagents on fluoranthene leads invariably, except under Friedel–Crafts conditions, to 4-monosubstituted derivatives, the yields are usually poor, since the mono- are separable with difficulty from poly-substituted derivatives (von Braun and Manz, *Annalen*, 1931, **488**, 111; cf. Garascia, Fries, and Ching, *J. Org. Chem.*, 1952, **17**, 227, who claim a "57% *crude*" yield of 4-nitrofluoranthene). Direct iodination by all the usual methods (including those described by Derbyshire and Waters,

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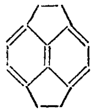
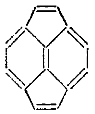
* Part X, *J.*, 1952, 3187.

*J.*, 1950, 3694; Barker and Waters, *J.*, 1952, 150; Henne and Zimmer, *J. Amer. Chem. Soc.*, 1951, **73**, 1362; Haszeldine and Sharpe, *J.*, 1952, 993) gave, at best, negligible quantities of 4-iodofluoranthene. It was, however, readily obtained as shown in the scheme. We find that fluoranthene can be conveniently hydrogenated to 1 : 2 : 3 : 4-tetrahydrofluoranthene by using Raney nickel at room temperature and under atmospheric pressure. Iodination of the tetrahydrofluoranthene was carried out with iodine and silver trifluoroacetate (Henne and Zimmer, *loc. cit.*). It is difficult to predict the position of substitution of 1 : 2 : 3 : 4-tetrahydrofluoranthene by this reagent; but it is found experimentally that electrophilic reagents invariably attack first the 5-position (von Braun and Manz, *Annalen*, 1932, **496**, 170). That this is also true of iodination by the above reagent, is now proved since dehydrogenation of the iodo-1 : 2 : 3 : 4-tetrahydrofluoranthene gives 4-iodofluoranthene, formerly prepared (Stubbs and Tucker, *loc. cit.*) from 4-nitrofluoranthene. The present work proves unmistakably that 1 : 2 : 3 : 4-tetrahydro-2- and -3-methylfluoranthene also iodinate similarly, to give 1 : 2 : 3 : 4-tetrahydro-5-iodo-2- and -3-methylfluoranthene, respectively.



(I)



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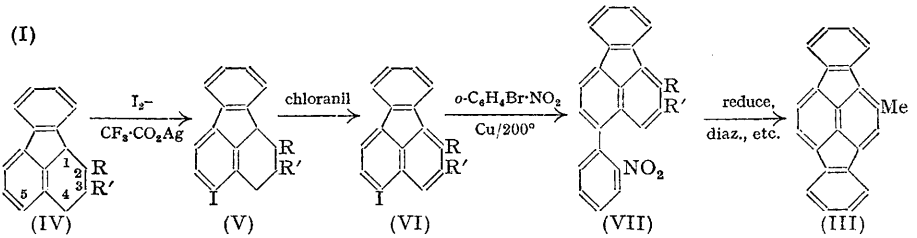


It is also important to note that the iodinating reagent iodine trifluoroacetate (trifluoroacetyl hypoiodite) has been shown to be an ionic and not a radical reagent, *i.e.*, the reaction is an electrophilic attack by " positive " iodine (Henne and Zimmer, *loc. cit.*; Haszeldine and Sharpe, *loc. cit.*). Thus the possibility that in the iodination process iodine displaces hydrogen attached to a saturated carbon atom (as in $>CH_2$ or in $-CH_3$) is excluded.

2- and 3-Methylfluoranthene on hydrogenation appear to give tetrahydro-derivatives; but the products have not yet been utilised in these syntheses since we have not yet proved which ring is hydrogenated. Fortunately, 1 : 2 : 3 : 4-tetrahydro-2- and -3-methylfluoranthene (IV; R = Me, R′ = H; and R = H, R′ = Me, respectively) are readily obtainable (Tucker, *J.*, 1949, 2182; 1952, 807). Synthesis was accordingly conducted with both, as described below for the 2-isomer: 1 : 2 : 3 : 4-tetrahydro-2-methylfluoranthene (IV; R = Me, R′ = H) was iodinated (Henne and Zimmer, *loc. cit.*) giving 1 : 2 : 3 : 4-tetrahydro-5-iodo-2-methylfluoranthene (V; R = Me, R′ = H), which, on dehydrogenation with chloranil in xylene (Clar and John, *Ber.*, 1930, **63**, 2967), gave 5-iodo-2-methylfluoranthene (VI; R = Me, R′ = H). This, as in the analogous example of 4-iodofluoranthene (VI; R = R′ = H) (Stubbs and Tucker, *loc. cit.*), was subjected to a crossed Ullmann reaction with *o*-bromonitrobenzene, and gave 2-methyl-5-*o*-nitrophenylfluoranthene (VII; R = Me, R′ = H); this, *via* the corresponding amine, followed by diazotisation, gave 3-methyl-1 : 2-5 : 6-dibenzopyracylene (III). By the same sequence 1 : 2 : 3 : 4-tetrahydro-3-methylfluoranthene (IV; R = H, R′ = Me) (Tucker, *J.*, 1952, 803) was also converted into 3-methyl-1 : 2-5 : 6-dibenzopyracylene (III), thus providing conclusive proof of structure.

A crossed Ullmann reaction between 1 : 2 : 3 : 4-tetrahydro-5-iodofluoranthene (V; R = R′ = H) and *o*-bromonitrobenzene gave a poor yield of 1 : 2 : 3 : 4-tetrahydro-5-*o*-nitrophenylfluoranthene, discouraging the preparation of this type of compound as intermediate.

The close similarity of the ultra-violet absorption curves of 1 : 2-5 : 6-dibenzopyracylene (Clar, Stubbs, and Tucker, *loc. cit.*) and of the synthesised 3-methyl derivative supports the constitution assigned to the latter.

Synthesis of 1 : 2-5 : 6-dibenzopyracylene from methyl fluorene-9-carboxylate and the Mannich base, *o*-chlorophenyl 2-diethylaminoethyl ketone (Mannich and Danneh1, *Arch. Pharm.*, 1938, **276**, 206) as attempted with the corresponding nitro-compound (Stubbs and Tucker, *loc. cit.*) failed, since the initial condensation could not be effected.

Reduction of 1 : 2 : 3 : 4-tetrahydro-4-keto-2(or 3)-methylfluoranthene to the corresponding hydrocarbon (IV) gave much better yields when carried out by King and Nord's method (*J. Org. Chem.*, 1949, **14**, 638) in which alkali is added after the formation of the hydrazone—than by the Huang-Minlon method (*J. Amer. Chem. Soc.*, 1946, **68**, 2487) (cf. Anderson, jun., and Wade, *loc. cit.*; Nelson, footnote 15).

## EXPERIMENTAL

4-*Iodofluoranthene*.—1 : 2 : 3 : 4-*Tetrahydrofluoranthene* (IV; R = R′ = H). Fluoranthene (1·01 g.) suspended in ethanol (10 ml.) was run into a suspension of hydrogen-saturated Raney nickel (*ca.* 2 g.) in ethanol (10 ml.) (Tucker, *J. Chem. Educ.*, 1950, **27**, 489). Absorption of hydrogen (237 ml.; theory, 224 ml.) ceased after 2·5 hours. The crystalline suspension did not change in appearance. The mixture was boiled and filtered, the nickel extracted with boiling ethanol, the combined solutions evaporated, and the residue crystallised from methanol giving long rectangular blades of 1 : 2 : 3 : 4-tetrahydrofluoranthene (0·81 g., 80%), m. p. 72—75° (lit. 75°) (Found : C, 93·3; H, 6·6. Calc. for $C_{16}H_{14}$: C, 93·2; H, 6·8%). Hydrogenation proceeded slightly faster in ethyl acetate which had been kept for ½ hour over Raney nickel, then distilled from it. Reducing the relative amount of nickel slowed the reaction: thus, fluoranthene (10·1 g.), ethyl acetate (20 ml.), Raney nickel (3 g.), and ethanol (10 ml.) required 17 hours, but gave tetrahydrofluoranthene (8·84 g., 85%). There was no absorption of hydrogen when 5- or 10%-palladium–charcoal (Cheronis and Levin, *J. Chem. Educ.*, 1944, **21**, 603) was used in acetic acid solution (cf. von Braun and Manz, *Ber.*, 1930, **63**, 2608).

1 : 2 : 3 : 4-*Tetrahydro-5-iodofluoranthene* (V; R = R′ = H).—A mixture of 1 : 2 : 3 : 4-tetrahydrofluoranthene (4·12 g.), iodine (5·08 g.), carbon tetrachloride (40 ml.), and glass beads was treated with silver trifluoroacetate (4·42 g.) in portions with shaking and warming. Complete discharge of the iodine colour required addition of more silver salt (0·5 g.). The filtered residue was extracted (3 times) with carbon tetrachloride and the combined filtrates extracted with water (to recover trifluoroacetic acid). The evaporated organic layer gave a yellow residue which was dissolved in acetone, and the solution treated with excess of ethanol, to give colourless crystals, m. p. 119—123° (4·97 g., 75%). Purification was difficult, but finally from light petroleum (b. p. 60—80°) leaflets of 1 : 2 : 3 : 4-*tetrahydro-5-iodofluoranthene*, m. p. 121—125° (slight decomp.) were obtained (Found : C, 57·8; H, 3·9; I, 38·0. $C_{16}H_{13}I$ requires C, 57·85; H, 3·95; I, 38·2%). Attempts to iodinate tetrahydrofluoranthene with iodine in the presence of the usual oxidising agents, especially persulphuric acid (Elbs and Jaroslawzew, *J. pr. Chem.*, 1913, **88**, 92) gave high yields of fluoranthene, and often recovered tetrahydrofluoranthene, but no isolable iodo-compounds.

4-*Iodofluoranthene* (VI; R = R′ = H). 1 : 2 : 3 : 4-Tetrahydro-5-iodofluoranthene (0·38 g.) and chloranil (0·55 g.) in xylene (3 ml.) were boiled for 2 hours and then cooled. The crystals which separated were washed with benzene, and the benzene–xylene filtrate extracted with a 5% solution of sodium hydroxide containing sodium metabisulphite. Evaporation of the organic portion gave an oil which crystallised from light petroleum (b. p. 60—80°) in cream tufts (0·18 g., 47%). This was purified by crystallisation from ethanol and then formed cream leaflets, m. p. and mixed m. p. with 4-iodofluoranthene (Stubbs and Tucker, *J.*, 1951, 2936) 109—110°.

1 : 2 : 3 : 4-*Tetrahydro-5-o-nitrophenylfluoranthene*.—1 : 2 : 3 : 4-Tetrahydro-5-iodofluoranthene (1·33 g.), *o*-bromonitrobenzene (1·01 g.), and copper bronze (1 g.; added in portions) were heated at 200° for 6 hours. The melt was extracted with boiling benzene, and the filtered cold solution chromatographed ($Al_2O_3$). Unchanged *o*-bromonitrobenzene came through first, then a substance which crystallised from ethanol, and finally from ethyl acetate, in pale yellow leaflets (0·13 g., 10%) of 1 : 2 : 3 : 4-*tetrahydro-5-o-nitrophenylfluoranthene*, m. p. 152—154° (clear melt at 156°) (Found : C, 80·9; H, 5·0; N, 4·4. $C_{22}H_{17}O_2N$ requires C, 80·7; H, 5·2; N, 4·3%).

3-*Methyl*-1 : 2-5 : 6-*dibenzopyracylene* (III).—*First synthesis—from* β-9-*fluorenylbutyric acid* (Tucker, *locc. cit.*). The acid was converted into 1 : 2 : 3 : 4-tetrahydro-4-keto-2-methylfluoranthene by the method given for the corresponding cyclisation of β-9-fluorenyl*iso*butyric acid (*J.*, 1952, 803). The ketone was crystallised from benzene–light petroleum (b. p. 60—80°) :

the yield (62%) was as hitherto (*J.*, 1949, 2182). The ketone was reduced by King and Nord's method (*J. Org. Chem.*, 1949, **14**, 638; Tucker, *J.*, 1952, 803) in higher yield (75%) than that obtained (46%) when the Huang–Minlon process (*J. Amer. Chem. Soc.*, 1946, **68**, 2487) was used (*J.*, 1949, 2182).

1 : 2 : 3 : 4-*Tetrahydro*-5-*iodo*-2-*methylfluoranthene* (V; R = Me, R′ = H). Iodination was carried out as described above for 1 : 2 : 3 : 4-tetrahydrofluoranthene by using 2-methyl-1 : 2 : 3 : 4-tetrahydrofluoranthene (1·1 g.), iodine (1·27 g.), and silver trifluoroacetate (1·1 g.) in carbon tetrachloride (10 ml.). More (0·3 g.) silver salt was added. The product (1·28 g., 74%) crystallised from ethanol in cream, nacreous leaflets, m. p. 131—132°, of 1 : 2 : 3 : 4-*tetrahydro*-5-*iodo*-2-*methylfluoranthene* (Found: C, 58·7; H, 4·5; I, 36·5. $C_{17}H_{15}I$ requires 59·0; H, 4·4; I, 36·7%).

5-*Iodo*-2-*methylfluoranthene* (VI; R = Me, R′ = H). The above tetrahydro-compound (1·0 g.) was dehydrogenated by 45 minutes' refluxing with chloranil (1·45 g.) in xylene (5 ml.). 5-*Iodo*-2-*methylfluoranthene* crystallised from benzene (red solution) flooded with ethanol (1 : 2 v/v) in pale green needles, m. p. 129—130° (0·71 g., 72%) (Found: C, 59·5; H, 3·2. $C_{17}H_{11}I$ requires C, 59·7; H, 3·2%). Chromatography had no further effect.

2-*Methyl*-5-o-*nitrophenylfluoranthene* (VII; R = Me, R′ = H). 5-Iodo-2-methylfluoranthene (0·47 g.) and *o*-bromonitrobenzene (0·30 g.) were heated at 195—200°, and copper bronze (0·3 g.; washed with carbon tetrachloride) added gradually with stirring during 2 hours. After further heating (2 hours) with occasional stirring, the melt was cooled, extracted with acetone, and filtered, the acetone removed, and the brown residue dissolved in benzene–light petroleum (b. p. 60—80°) (1 : 1) and chromatographed ($Al_2O_3$). The first pale yellow band to be eluted gave pale yellow needles, m. p. 117—119° (unidentified), from benzene–ethanol. The second bright yellow band, after concentration of its eluate and addition of ethanol gave bright, lemon-yellow, rectangular prisms of 2-*methyl*-5-o-*nitrophenylfluoranthene* (0·20 g., 42%), m. p. 172—174° (Found: C, 81·8; H, 4·6; N, 3·9. $C_{23}H_{15}O_2N$ requires C, 81·9; H, 4·5; N, 4·15%).

5-o-*Aminophenyl*-2-*methylfluoranthene*. The nitro-compound (0·09 g.), suspended in ethanol (5 ml.), was reduced by hydrogen in the presence of Raney nickel (0·4 g.); absorption ceased after 45 minutes. The heated mixture was filtered, the nickel residue extracted with hot ethanol, and the united filtrates evaporated, giving pale green, matted needles; recrystallisation (methanol) gave 5-o-*aminophenyl*-2-*methylfluoranthene*, m. p. 147—148° (0·06 g., 70%) (Found: C, 89·7; H, 5·3; N, 4·8. $C_{23}H_{17}N$ requires C, 89·9; H, 5·6; N, 4·6%).

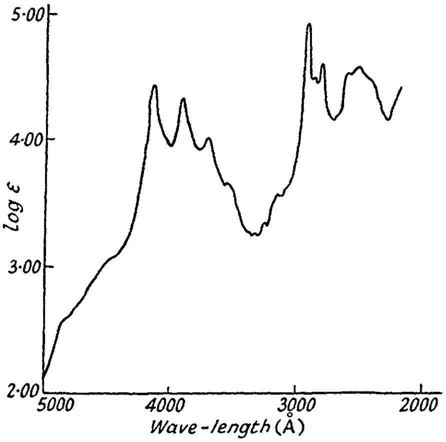
3-*Methyl*-1 : 2-5 : 6-*dibenzopyracylene* (III). 5-*o*-Aminophenyl-2-methylfluoranthene (0·02 g.) was dissolved in acetic acid and poured with stirring into excess of 10% (v/v) sulphuric acid. A solution of sodium nitrite (0·01 g.) in water (1 ml.) was added to the slightly warm solution, which immediately became orange in colour. After the solution had been shaken (15 minutes) urea was added, and after a further shaking (15 minutes), copper bronze was added. After 15 minutes at room temperature and 15 minutes on the boiling-water bath the pale green solution was filtered and gave a residue which was extracted with benzene, and the dry orange solution chromatographed ($Al_2O_3$). The orange eluate, after concentration, gave orange needles which on crystallisation (acetone) gave 3-*methyl*-1 : 2-5 : 6-*dibenzopyracylene*, m. p. 205—206° (Found: C, 95·0; H, 4·9. $C_{23}H_{14}$ requires C, 95·1; H, 4·9%). It dissolves in cold concentrated sulphuric acid to a yellow solution, deepening to yellow-brown when heated. The *picrate*, brick-red micro-needles from benzene, has m. p. 193° (softening at 187°) (Found: C, 66·9; H, 3·1; N, 8·2. $C_{23}H_{14},C_6H_3O_7N_3$ requires C, 67·0; H, 3·3; N, 8·1%). The 2 : 4 : 7-*trinitrofluorenone* complex, scarlet needles from acetic acid containing a small amount of acetic anhydride, has m. p. 263—264° (Found: C, 71·4; H, 3·3; N, 6·9. $C_{23}H_{14},C_{13}H_5O_7N_3$ requires C, 71·4; H, 3·2; N, 6·9%).

Renewed attempts to prepare the picrate of 1 : 2-5 : 6-dibenzopyracylene gave a mixture of bright yellow prisms, long scarlet needles, and stout orange-red polyhedra, from benzene. From dilute solutions it was possible to isolate the orange-red polyhedra, m. p. 200° (shrinkage at 180°), which were the *dipicrate* of 1 : 2-5 : 6-dibenzopyracylene (Found: C, 55·8; H, 2·6; N, 11·2. $C_{22}H_{12},2C_6H_3O_7N_3$ requires C, 55·6; H, 2·5; N, 11·4%). Recrystallisation of the polyhedra with slight excess of the hydrocarbon gave long scarlet needles mixed with yellow prisms. The 2 : 4 : 6-*trinitrofluorenone* complex of 1 : 2-5 : 6-dibenzopyracylene, brick-red microcrystals from acetic acid–acetic anhydride, has m. p. 262° (Found: C, 71·3; H, 3·1; N, 7·2. $C_{22}H_{12},C_{13}H_5O_7N_3$ requires C, 71·1; H, 2·9; N, 7·1%). A mixture with the corresponding complex from 3-methyl-1 : 2-5 : 6-dibenzopyracylene had m. p. 255°.

*Second synthesis—from* β-9-*fluorenyl*iso*butyric acid* (Tucker, *J.*, 1952, 803). The acid was cyclised to 1 : 2 : 3 : 4-tetrahydro-4-keto-3-methylfluoranthene and this was reduced to 1 : 2 : 3 : 4-tetrahydro-3-methylfluoranthene, as recorded. Crystallisation of the last by addition of hot ethanol to a suspension in methanol until no oil separated on cooling gave practically colourless, rectangular plates, m. p. 47—49° (yield 77%).

All the 3-methyl derivatives described below were prepared by the methods used for the corresponding 2-methyl isomers (above).

1 : 2 : 3 : 4-*Tetrahydro*-5-*iodo*-3-*methylfluoranthene* (V; R = H, R′ = Me) was obtained in faintly green, short blades or needles (71%) (from ethanol), m. p. 110—111° (clear melt at 112°) (Found: C, 59·0; H, 4·6; I, 37·0. $C_{17}H_{15}I$ requires C, 59·0; H, 4·4; I, 36·7%). 5-*Iodo*-3-*methylfluoranthene* (VI; R = H, R′ = Me) crystallised from a concentrated solution in benzene to which a few drops of methanol were added, as salmon, diamond-shaped plates (78%), m. p. 113—114·5° (iodine-pink melt) (Found: C, 59·5; H, 3·35; I, 36·8. $C_{17}H_{11}I$ requires C, 59·7; H, 3·25; I, 37·1%). 3-*Methyl*-5-o-*nitrophenylfluoranthene* (VII; R = H, R′ = Me) was prepared at 200—210°. In the chromatographic separation, the first band gave pale yellow needles (ethanol), m. p. 100—102° (unidentified); the bright yellow second band, thick lath-prisms (55%), m. p. 138—140°, from ethyl acetate to which an equal volume of methanol was added (Found: C, 81·8; H, 4·4; N, 4·1. $C_{23}H_{15}O_2N$ requires C, 81·9; H, 4·5; N, 4·15%). 5-o-*Aminophenyl*-3-*methylfluoranthene* (VIII; R = H, R′ = Me) crystallised (ethanol) in green-yellow rhombohedral, thick plates (80%), m. p. 123—125°. When powdered, it exhibited in sunlight and in ultra-violet light a pale green fluorescence (Found: C, 90·1; H, 5·8; N, 4·7. $C_{23}H_{17}N$ requires C, 89·9; H, 5·6; N, 4·6%). On several occasions this compound separated in feathery crystals which on recrystallisation gave rhombs, as above, but softened at a lower temperature and were partly unmelted at 128°. The *acetyl* derivative, which formed pale green needles in burrs from petroleum (b. p. 80—100°) containing a trace of benzene, had m. p. 136° (softening at 133°) (Found: C, 85·9; H, 5·4. $C_{25}H_{19}ON$ requires C, 85·9; H, 5·5%).



3-*Methyl*-1 : 2-5 : 6-*dibenzopyracylene.*

3-Methyl-1 : 2-5 : 6-dibenzopyracylene (III), prepared from 5-*o*-aminophenyl-3-methylfluoranthene, had m. p. 205—206° alone or mixed with the material prepared from 5-*o*-aminophenyl-2-methylfluoranthene. The specimens prepared by the two routes were indistinguishable.

*Ultra-violet Absorption Spectrum of* 3-*Methyl*-1 : 2-5 : 6-*dibenzopyracylene*.—This was recorded on the Unicam spectrophotometer, ethanol being used as solvent: maxima occurred at (λ in Å) *p*-Bands: 4160 (log ε 4·46), 3930 (4·37), 3720 (4·06), 3560 (3·70). β-Bands: 2940 (4·99), 2880 (4·56), 2820 (4·68). β′-Bands: 2620 (4·60), 2540 (4·66).

We are grateful to Mr. A. J. N. Hope, B.Sc., for preparing the ultra-violet absorption curve; and to Mr. J. M. L. Cameron and Miss M. W. Christie for micro-analyses.

UNIVERSITY OF GLASGOW. [*Received, June* 13*th*, 1952.]