651. *Synthesis of Fluoranthenes. Part VII.** 1 : 2-5 : 6-*Dibenzopyracylene.*

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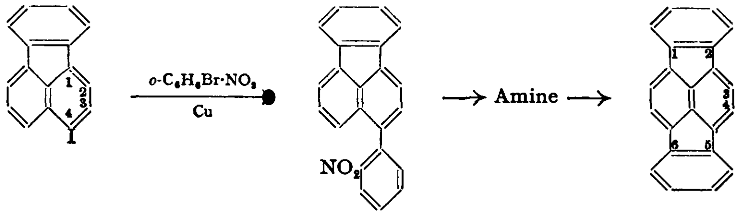
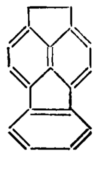
1 : 2-5 : 6-Dibenzopyracylene (III) has been unambiguously synthesised by a crossed Ullmann reaction from 4-iodofluoranthene and *o*-bromonitrobenzene, followed by the usual method of cyclisation. Attempts to obtain (III) by cyclisation of 4-phenylfluoranthene, and from 2-9′-fluorenylethyl *o*-nitrophenyl ketone (VI), prepared by a Mannich reaction, failed.

Very little work has been done on the ultra-violet absorption spectra of fluoranthene derivatives (Seshan, *Proc. Indian Acad. Sci.*, 1936, **43**, 148; Orchin and Reggel, *J. Amer. Chem. Soc.*, 1947, **69**, 505; 1951, **73**, 436; Kloetzel and Chubb, *ibid.*, 1950, **72**, 150; Deno, *ibid.*, p. 4057). 1 : 2-5 : 6-Dibenzopyracylene † (III) has now been examined (Clar, Stubbs, and Tucker, *Nature*, 1950, **166**, 1075) with particular reference to Clar's anellation theory (Clar, *J. Chem. Physics*, 1949, **17**, 741; *Chem. Ber.*, 1949, **82**, 495; " Aromatische Kohlenwasserstoffe," Berlin, Springer, 1941, p. 20) : it has been shown that *p*-absorption in 1 : 2-5 : 6-dibenzopyracylene and in fluoranthene is located in the naphthalene ring system present in these hydrocarbons. The spectra of (III) and of 4-phenylfluoranthene are now compared (see figure). The examination of other fluoranthene derivatives is proceeding.

Synthesis of 1 : 2-5 : 6-dibenzopyracylene was readily accomplished by the established method of synthesis of fluoranthene and its derivatives (Forrest and Tucker, *J.*, 1948, 1137; Tucker and Whalley, *J.*, 1949, 632, 3215; Hawkins and Tucker, *J.*, 1950, 3286) : 4-iodofluoranthene (I) by a crossed Ullmann reaction with *o*-bromonitrobenzene, by means of copper, gave 4-*o*-nitrophenylfluoranthene (II), catalytically reduced to the corresponding amine, which on diazotisation and treatment of the diazonium solution with copper bronze gave 1 : 2-5 : 6-dibenzopyracylene (III), bright orange needles, m. p. 261—262°. The iodine atom in (I) is definitely in the 4-position since (I) was prepared from 4-nitrofluoranthene (von Braun and Manz, *Annalen*, 1931, **488**, 111) by the usual reduction–diazotisation–Sandmeyer route. All attempts to iodinate fluoranthene directly failed to give pure 4-iodofluoranthene. 4-Iodofluoranthene was chosen in preference to the corresponding bromo-compound on account of the low reactivity of the latter; *e.g.*, 4-bromofluoranthene needs to be heated to 300° with copper to give 4 : 4′-difluoranthyl (*idem, Ber.*, 1937, **70**, 1607).



(I) (II) (III)



(IV)

The ease of cyclisation in the last stage of the synthesis of (III) is in striking contrast to the unsuccessful attempts of others to prepare ace-acenaphthene derivatives (see Fieser and Peters, *J. Amer. Chem. Soc.*, 1932, **54**, 4347; Mayer and Kaufmann, *Ber.*, 1920, **53**, 289; Fleischer and Wolff, *ibid.*, p. 925). On the other hand, Kloetzel and Chubb (*loc. cit.*) have prepared 4 : 5-dimethylenefluoranthene (5 : 6-dihydro-1 : 2-benzopyracylene) (IV) from 1 : 2 : 3 : 4- tetrahydro-4-ketofluoranthene. The structure of (IV) was supported by the similarity of its ultra-violet absorption spectrum to that of fluoranthene.

The facile cyclisations of diphenyl- and of dichlorodiphenyl-tetracenes to give 5 : 6-11 : 12-diphenylenetetracene (Badoche, *Ann. Chim.*, 1933, **20**, 200; Dufraisse and Girard, *Bull. Soc. chim.*, 1934, **1**, 1359; Dufraisse, *ibid.*, 1936, **3**, 1857; Dufraisse and Horclois, *ibid.*, p. 1894) bear a resemblance to that now reported by us since all involve formation of a *peri*-phenylene grouping. We found that formation of the second five-membered ring in the final stage of

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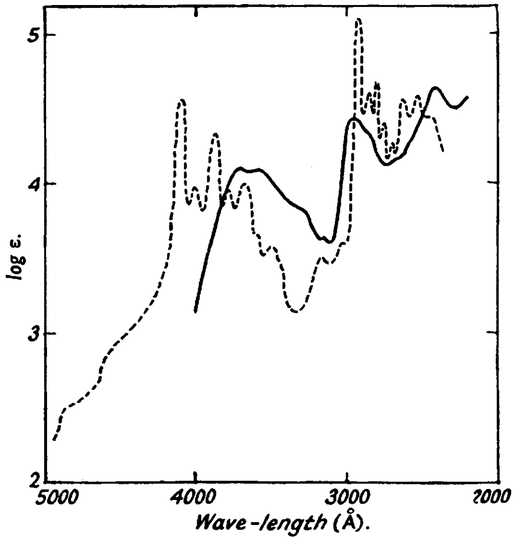
* Part VI, *J.*, 1950, 3288.

† For the name " pyracylene " see *J.*, 1951, 2391.

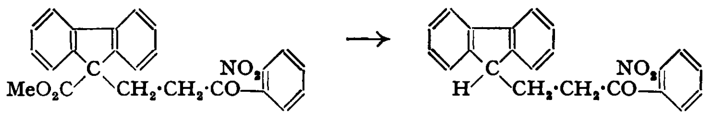
synthesis of (III) was as easy as that of the five-membered ring of fluoranthene, the method of cyclisation being the same in the two cases.

An attempt to synthesise (III) by utilization of the Mannich reaction (Stubbs and Tucker, *J.*, 1950, 3288) failed; although methyl fluorene-9-carboxylate readily condensed with 2-diethylaminoethyl *o*-nitrophenyl ketone, in the usual manner, to give 2-(9-carbomethoxy-9-fluorenyl)ethyl *o*-nitrophenyl ketone (V), smoothly hydrolysed with loss of carbon dioxide to 2-9′-fluorenylethyl *o*-nitrophenyl ketone (VI). This ketone, however, could not be reduced to the alcohol by the aluminium *iso*propoxide method although excellent results were obtained with the un-nitrated 2-9′-fluorenylethyl phenyl ketone (Stubbs and Tucker, *loc. cit.*), and with phenyl 2-9′-fluorenyl-2-phenylethyl ketone (Tucker and Whalley, *J.*, 1949, 50). Attempts to cyclise both (V) and (VI) by hydrogen bromide failed (cf. France, Tucker, and Forrest, *J.*, 1945, 7).



Absorption spectra of 1 : 2-5 : 6-*dibenzopyracylene* (– – – –) *and of* 4-*phenylfluoranthene* (——) *in ethanol. Band maxima* (*in* Å), 1 : 2-5 : 6-*dibenzopyracylene* : p-*bands* 4100, 4020, 3870, 3795, 3670, 3490; *β-bands* 2925, 2865, 2810, 2760, 2705; *β′-bands* 2625, 2530. 4-*Phenylfluoranthene* : p-*bands* 3700, 3580, 3145; *β-band* 2940; *β′-band* 2405.

(V)



(VI)

Heating of 4-phenylfluoranthene at 110—140° with a mixture of anhydrous aluminium chloride and sodium chloride failed to give 1 : 2-5 : 6-dibenzopyracylene.

EXPERIMENTAL.

4-*Iodofluoranthene* (I).—4-Nitrofluoranthene (8 g.), suspended in glacial acetic acid (150 ml.) with 10% palladium–charcoal catalyst (0·8 g.) added, was reduced by hydrogen (theoretical volume absorbed in 3—4 hours) to give a green fluorescent solution. After filtration, the catalyst was extracted several times with boiling glacial acetic acid, the combined filtrates were diluted with water (150 ml.), concentrated sulphuric acid (10 ml.) was added, and the solution diazotised at −5° to 0° by addition of sodium nitrite (2·5 g.) in water. After destruction of excess of nitrite with urea (1 g.), the solution was poured into a solution of potassium iodide (30 g.) in water (150 ml.) and kept at room temperature overnight. After filtration, thorough washing, and drying, the residue was extracted by light petroleum (b. p. 60—80°). After the usual treatment (thiosulphate–charcoal) and finally crystallisation from ethanol, cream-coloured micro-leaflets of 4-*iodofluoranthene*, m. p. 109—110° (2·95 g., 28%) (Found : C, 58·6; H, 2·9; I, 38·55. $C_{16}H_9I$ requires C, 58·6; H, 2·8; I, 38·7%), were obtained.

4-o-*Nitrophenylfluoranthene* (II).—4-Iodofluoranthene (1 g.) and *o*-bromonitrobenzene (0·65 g.) were heated to 210—220°, and copper bronze (0·5 g.; washed with carbon tetrachloride) was added in portions during 2 hours, with frequent stirring. Heating was continued for a further 2 hours, the cooled mass extracted with acetone, and the residue obtained on evaporation of the acetone was dissolved in light petroleum (b. p. 60—80°) and chromatographed (alumina). Benzene–light petroleum (1 : 1, v/v) gave a yellow eluate with a green fluorescence from which a yellow solid, crystallising from ethanol, was obtained (0·85 g., 83%). Recrystallisation, with loss of material, by dissolution in ethyl acetate and then addition of an equal volume of methanol gave lemon-yellow needles, m. p. 157—160° (softening at 155°), of 4-o-*nitrophenylfluoranthene* (Found : C, 81·3; H, 4·1. $C_{22}H_{13}O_2N$ requires C, 81·7; H, 4·05%). The use of three times the above amount of *o*-bromonitrobenzene facilitated mixing and gave similar results but removal of excess was troublesome, as also was removal of *oo'*-dinitrodiphenyl formed.

4-o-*Aminophenylfluoranthene*.—Reduction of the nitro-compound (II) was accomplished by hydrogen with either (*a*) 10% palladium–charcoal and glacial acetic acid or (*b*) Raney nickel and ethanol. Since the isolated amine, a pale brown oil, could not be crystallised, it was dissolved in ether, and dry hydrogen chloride passed in to precipitate the *hydrochloride*, reprecipitated by addition of ether to the ethanol solution, to give pale green needles, m. p. 210—250° (Found : C, 79·3; H, 4·8. $C_{22}H_{16}NCl$ requires C, 80·1; H, 4·9%). A *picrate* of the amine was prepared in ethanol, and gave golden-brown cubes, m. p. 217—219° (softening at 200°), from chloroform (Found : C, 64·4; H, 3·6; N, 10·6. $C_{22}H_{15}N,C_6H_3O_7N_3$ requires C, 64·4; H, 3·5; N, 10·7%).

1 : 2-5 : 6-*Dibenzopyracylene* (III).—4-*o*-Nitrophenylfluoranthene (0·46 g.) was reduced (hydrogen, Raney nickel, and ethanol), and the uncrystallised amine obtained was dissolved in acetic acid and poured with stirring into excess of 10% (v/v) sulphuric acid solution. A solution of sodium nitrite (0·12 g.) in water (3 ml.) was added all at once to the slightly warm solution; after diazotisation was complete, urea was added to destroy excess of nitrous acid, copper bronze (washed with carbon tetrachloride) added, and the mixture kept with occasional stirring. During *ca.* 1 hour an orange solid gradually separated : reaction was completed by heating the mixture on the steam-bath for ½ hour. The filtered, washed, and dried precipitate was extracted with benzene, and the red-green fluorescing solution chromatographed (alumina). The concentrated orange eluate gave orange needles of 1 : 2-5 : 6-*dibenzopyracylene*, m. p. 261—262° (0·15 g., 38% overall yield from 4-*o*-nitrophenylfluoranthene) (Found : C, 95·6; H, 4·4. $C_{22}H_{12}$ requires C, 95·6; H, 4·4%). Picric acid and 2 : 4 : 7-trinitrofluorenone gave unstable complexes.

Attempted Synthesis by Mannich Reaction.—o-*Nitroacetophenone*. Direct nitration of acetophenone (Elson, Gibson, and Johnson, *J.*, 1930, 1128; Morgan and Moss, *J. Soc. Chem. Ind.*, 1923, 461T; Simpson, Atkinson, Schofield, and Stephenson, *J.*, 1945, 646) was unsuitable owing to difficulty of removal of the *m*-isomer. The following modification of the synthesis from *o*-nitrobenzoic acid (Walker and Hauser, *J. Amer. Chem. Soc.*, 1946, **68**, 1386; Schofield and Swain, *J.*, 1948, 384; Bowman, *J.*, 1950, 324) was adopted : Magnesium turnings (10·7 g., 1·1 atoms) were allowed to react vigorously with anhydrous ethanol (10 ml.) and carbon tetrachloride (1 ml.) for a few minutes, then anhydrous benzene (150 ml.) was added. The mixture was heated to the b. p., the source of heat removed, and the contents of the flask stirred vigorously while a mixture of ethyl malonate (70·4 g., 1·1 mols.), anhydrous ethanol (40 ml.), and anhydrous benzene (50 ml.) was added at such a rate that vigorous refluxing was maintained, with heating if necessary. The mixture was stirred under reflux till all the magnesium was in solution (*ca.* 30 minutes), the source of heat removed, and vigorous stirring maintained while *o*-nitrobenzoyl chloride (74·2 g., 1 mol.) in anhydrous benzene (100 ml.) was added as rapidly as the violence of the reaction would allow. After being boiled (30 minutes), the mixture was cooled slightly, and dilute sulphuric acid added cautiously with stirring. The mixture at first became very pasty, but further addition of acid gave two clear layers. The whole was then submitted to distillation till the temperature of the vapour reached 95°, a mixture of acetic acid (120 ml.), concentrated sulphuric acid (15 ml.), and water (80 ml.) was added, and the mixture boiled (4 hours). It was cooled (ice–salt), made strongly alkaline with solid potassium hydroxide, and shaken with ether, the whole was filtered, and the residue washed well with ether. The organic layer of the filtrate was separated, washed with water, dried, and distilled. The fraction of b. p. 158·5—159°/16 mm. (166·5°/21 mm.) was pure *o*-nitroacetophenone (58·2 g., 88%). [*o*-Nitrobenzoyl chloride was prepared as required by boiling the acid (67 g.) with thionyl chloride (100 ml.) till all was in solution. Excess of thionyl choride was removed under reduced pressure, last traces being removed by addition and distillation of benzene (50 ml., 3 times). The acid chloride was used without further purification, as distillation under reduced pressure led to explosive decomposition.]

2-(9-*Carbomethoxy*-9-*fluorenyl*)*ethyl* o-*nitrophenyl ketone* (V). 2-Diethylaminoethyl *o*-nitrophenyl ketone hydrochloride (3·6 g., 1·5 mols.) (Mannich and Dannehl, *Arch. Pharm.*, 1938, **276**, 206) was dissolved in dry methanol (7 ml.), and a solution of sodium (0·3 g., 1·5 atoms) in methanol (3 ml.) added; after a few minutes' stirring, sodium chloride was filtered off, washed with a little methanol, and the combined filtrates were mixed with methyl iodide (1·6 g., 1·3 mols.) and added to a warm solution of methyl fluorene-9-carboxylate (2·4 g., 1·3 mols.) and sodium (0·24 g., 1·3 mols.) in methanol (10 ml.). Crystals appeared immediately and, on cooling, practically pure 2-(9-*carbomethoxy*-9-*fluorenyl*)*ethyl* o-*nitrophenyl ketone* (V) (3 g., 71%) was deposited. Crystallisation from methyl cyanide gave needles, m. p. 168—169° (Found : C, 71·6; H, 4·95; N, 3·5. $C_{24}H_{19}O_5N$ requires C, 71·8; H, 4·8; N, 3·5%).

2-9'-*Fluorenylethyl* o-*nitrophenyl ketone* (VI). The ketone (V) (3 g.) was boiled (1 hour) with a mixture of acetic acid (90 ml.), concentrated sulphuric acid (6 ml.), and water (30 ml.), and poured into water (300 ml.); the resulting acid was filtered off and washed with water, but it was decarboxylated too readily for purification. It was boiled (15 minutes) in methyl cyanide (30 ml.), and the mixture diluted at the b. p. till crystallisation commenced; on cooling, 2-9'-*fluorenylethyl* o-*nitrophenyl ketone* (VI) (1·7 g., 66%) was obtained. Crystallisation from ethanol or methyl cyanide gave needles, m. p. 147—149° (Found : C, 77·2; H, 4·8; N, 4·1. $C_{22}H_{17}O_3N$ requires C, 77·0; H, 5·0; N, 4·1%).

The acid was also decarboxylated by heating it at 170—180° till evolution of carbon dioxide ceased (21%). Attempted hydrolysis of (V) by aqueous-alcoholic sodium hydroxide gave a tarry product.

The ketone (VI) could not be induced to give an oxime (cf. Von Auwers, Lechner, and Bundesmann, *Ber.*, 1925, **58**, 50, who prepared an oxime of *o*-nitroacetophenone).

Reduction of (VI) by hydrogen and Raney nickel in ethyl acetate gave theoretical absorption of hydrogen for reduction of the nitro-ketone to the carbinol-amine compound, but neither could this nor its picrate be isolated, and ring closure to (III) could not be effected.

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