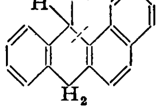
933. *Aromatic Hydrocarbons. Part LXIV.** 2 : 3-6 : 7-*Dibenzofluoranthene.*

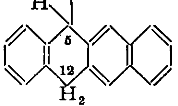
By E. Clar and D. G. Stewart.

2 : 3–6 : 7-Dibenzofluoranthene was synthesised and identified with a by-product obtained from the ring closure of 9-phenyl-1 : 2-benzanthracene to 1 : 2-3 : 4-dibenzopyrene.

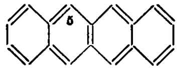
When 9-phenyl-1 : 2-benzanthracene was condensed to 1 : 2-3 : 4-dibenzopyrene by means of aluminium chloride a deep red hydrocarbon was obtained as a by-product (Clar and Stewart, *J.*, 1951, 687). This has now been identified as 2 : 3-6 : 7-dibenzofluoranthene (IV) and synthesised from 5 : 12-dihydro-5-ketonaphthacene. The ketone with phenylmagnesium bromide gave the 5-phenyl hydrocarbon (III) which was treated with aluminium chloride. Besides (IV), its tetrahydro-derivative (V) is formed as a by-product. This can be dehydrogenated to (IV) and has an absorption spectrum closely related to that of 2 : 3-benzofluoranthene (Tucker and Stubbs, *J.*, 1951, 2939; Campbell and Marks, *J.*, 1951, 2941).



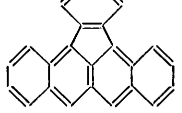
(I)



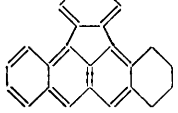
(II)



(III)



(IV)



(V)

The formation of (IV) from 9-phenyl-1 : 2-benzanthracene can be explained by the hydrogenation of the latter to (I) during the ring closure to 1 : 2-3 : 4-dibenzopyrene and

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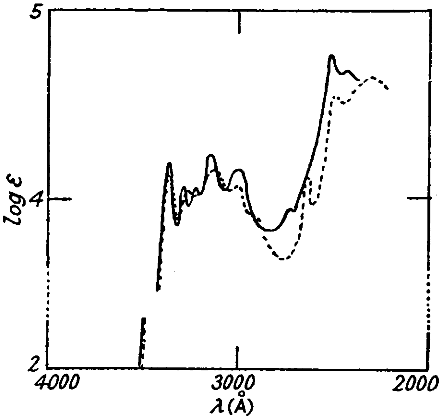
* Part LXIII, *J. Amer. Chem. Soc.*, 1952, in the press.

rearrangement to (II). This is related to the rearrangement of 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydrophenanthrene to 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydroanthracene.

2 : 3-6 : 7-Dibenzofluoranthene is readily photo-oxidized and with maleic anhydride rapidly forms (VI), whose absorption spectrum (Figure) is very similar to that of 9-phenyl-1 : 2-benzofluorene (Clar, *Ber.*, 1930, **63**, 513).



——— *Disodium salt of the maleic anhydride adduct of* (IV) *in water. Band maxima in* Å *with log* ε *in parentheses*: 3365 (4·18), 3295 (4·04), 3220 (4·04); 3140 (4·22), 3005 (4·14); 2740 (3·93); 2510 (4·76), 2420 (4·67).

- - - - 9-*Phenyl*-3 : 4-*benzofluorene in alcohol*. *Maxima*: 3360 (4·13), 3270 (4·05); 3130 (4·12), 3000 (4·02); 2640 (4·11); 2500 (4·50); 2320 (4·65).

2 : 3-6 : 7-Dibenzofluoranthene (IV), prepared as above, was identical with a hydrocarbon synthesized by Dr. Neil Campbell by a different method to be described later.

EXPERIMENTAL

M. p.s are uncorrected, in evacuated capillaries. Microanalyses are by Mr. J. M. L. Cameron and Miss M. W. Christie.

5-*Keto*-5 : 12-*dihydronaphthacene*.—This was prepared by the reduction of naphthacene-5 : 12-quinone, by a modification of Fieser's method (*J. Amer. Chem. Soc.*, 1931, **53**, 2336). A finely divided suspension of the quinone (8 g.), obtained by precipitation from concentrated sulphuric acid with water, was heated in 4% sodium hydroxide solution (500 c.c.) to 95° and sodium dithionite (12 g.) added, giving a deep green solution. After several minutes pale crystals separated, and the solution became deep orange-brown. Two further portions (4 g.) of sodium dithionite were added at 15-minute intervals and the mixture boiled for 1 hour. The light brown precipitate, after filtration from the hot solution and washing, was recrystallised from acetic acid, small amounts of naphthacene being removed by the addition of a little maleic anhydride. The dark yellow needles of the ketone (7 g.), m. p. 185—190° (Fieser, *loc. cit.*, gives m. p. 196°, but states that it varies with rate of heating), gave an orange-red solution in concentrated sulphuric acid.

5-*Phenylnaphthacene* (III).— Phenylmagnesium bromide (from bromobenzene, 15·7 g.) in ether (50 c.c.) was added dropwise to a fine suspension of the ketone (4 g.) in benzene (50 c.c.). After ½ hour's refluxing the clear red-brown solution was decomposed with dilute hydrochloric acid and the mixture steam-distilled, to remove solvents and diphenyl. Crystallisation of the resulting solid *hydrocarbon* from benzene gave brownish-yellow crystals (3·75 g.) which yielded orange-yellow prisms, m. p. 187—188°, from acetic acid (Found: C, 94·6; H, 5·3. $C_{24}H_{16}$ requires C, 94·7; H, 5·3%). This sublimed in a vacuum, and gave a green solution in concentrated sulphuric acid, which changed to violet on storage.

1′ : 2′ : 3′ : 4′-*Tetrahydro*-2 : 3-6 : 7-*dibenzofluoranthene* (V) *and* 2 : 3-6 : 7-*Dibenzofluoranthene* (IV).—The phenyl compound (III) (2 g.) was added to a sodium chloride (2 g.)–aluminium chloride (10 g.) melt at 110°. The initial dark green solution rapidly changed to red and when uniform (after approx. 2½ minutes) was poured into hydrochloric acid solution (1 : 1). After filtration and washing with hydrochloric acid, ammonia, and water, the dark red precipitate was heated at 170—180°/1 mm., an orange-yellow sublimate being obtained. The sublimate, which gave a green solution in concentrated sulphuric acid, was extracted with cold benzene and crystallised from xylene in orange-yellow plates which melted at 331—333° and gave a mixed m. p. of 332—333° with an authentic sample of naphthacene. The visual spectrum of the sublimate was identical with that of naphthacene. The residue after sublimation was dissolved in benzene and chromatographed (alumina), with benzene–light petroleum (b. p. 40—60°) as eluant. The first yellow band gave a yellow eluate with a green fluorescence, which yielded on concentration yellow needles (0·4 g.), m. p. 151—152°, of 1′ : 2′ : 3′ : 4′-*tetrahydro*-2 : 3-6 : 7-*dibenzofluoranthene* (V) (Found : C, 93·8; H, 5·9. $C_{24}H_{18}$ requires C, 94·1; H, 5·9%). The compound dissolved gave a yellow solution in concentrated sulphuric acid, changing to red. A second dark red band gave on elution a violet-red solution which was sensitive to light and on prolonged exposure was decolorised. This red eluate gave on concentration and crystallisation from benzene stout red needles (0·8 g.), m. p. 216·5—217°, of 2 : 3-6 : 7-*dibenzofluoranthene* (IV) (Found : C, 95·5; H, 4·7. $C_{24}H_{14}$ requires C, 95·3; H, 4·7%), identical with the red condensation product from 9-phenyl-1 : 2-benzanthracene (cf. Clar and Stewart, *loc. cit.*) and with a sample kindly supplied by Dr. Neil Campbell. It gave in concentrated sulphuric acid, a red-brown solution which on storage changed to violet.

Dehydrogenation of (V).—The tetrahydro-derivative (V) (0·1 g.) and 20% palladium–charcoal (0·1 g.) were heated at 180° for 5 minutes in air-free carbon dioxide. The product was then sublimed at 1 mm., giving dark red needles. Crystallisation from benzene gave needles, m. p. 213—216° and mixed m. p. 214—216° with the sample of 2 : 3-6 : 7-dibenzofluoranthene obtained as above. The visual spectrum was identical with that of the previous sample.

Maleic Anhydride Adduct.—2 : 3-6 : 7-Dibenzofluoranthene (IV) (0·1 g.) and excess of maleic anhydride were heated under reflux in benzene (1·5 c.c.) for 5 minutes; the deep red colour was thus discharged and, on cooling, colourless needles were obtained. Crystallisation from acetic anhydride gave the *adduct* as needles (Found : C, 84·0; H, 4·2. $C_{28}H_{16}0_3$ requires C, 84·0; H, 4·0%), decomp. from 256°, clear at 284° (red).

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[*Received, August* 21*st*, 1952.]