## **189.** 2 : 3-*Benzorubicene, Rubicene, and their Derivatives.*

By E. Clar and W. Willicks.

2 : 3-Benzorubicene (II) and its tetrahydro-derivative (III) have been obtained from the diol (I) in a sodium chloride–aluminium chloride melt; 2 : 3-6 : 7-dibenzofluoranthene (V) and its tetrahydro-derivative (VI) were obtained as by-products. A new synthesis of rubicene (X) is reported. *iso*Rubicene (XVI) has been resynthesised and its absorption spectrum compared with that of rubicene.

Clar and Stewart[1] reported that 5-phenyltetracene is cyclised to 2 : 3-6 : 7-dibenzofluoranthene (V) in an aluminium chloride melt. The same treatment converted the diol (I) into a deep blue hydrocarbon which differs from the di-*o*-phenylenetetracene (IV) of Dufraisse and Girard:[2] although the absorption spectra (Fig. 1) are very similar, the melting point of the new hydrocarbon is 215° the lower; we concluded therefore that our compound has structure (II) and this is supported by the fact that its tetrahydro-derivative (III) contains the aromatic skeleton of rubicene (X) as shown by comparison of the absorption spectra (Fig. 1).

Other by-products resulted by loss of one phenyl group from compound (I) and cyclisation of the other, to give 2 : 3-6 : 7-dibenzofluoranthene (V) and its tetrahydro-derivative[1] whose structure (VI) is proved by comparison of its absorption spectrum with that of 2 : 3-benzofluoranthene[3] (XI) (Fig. 3). Benzorubicene (II) adds maleic anhydride, to give a yellow adduct whose disodium salt has structure (VII), a conclusion reached by comparison of its spectrum with that of 4-phenylfluoranthene[4] (VIII) (Fig. 2).

Analogous results were obtained with the diol (IX). Fusion of this diol with sodium chloride–aluminium chloride melt gave rubicene (X) and, by loss of one benzene ring,

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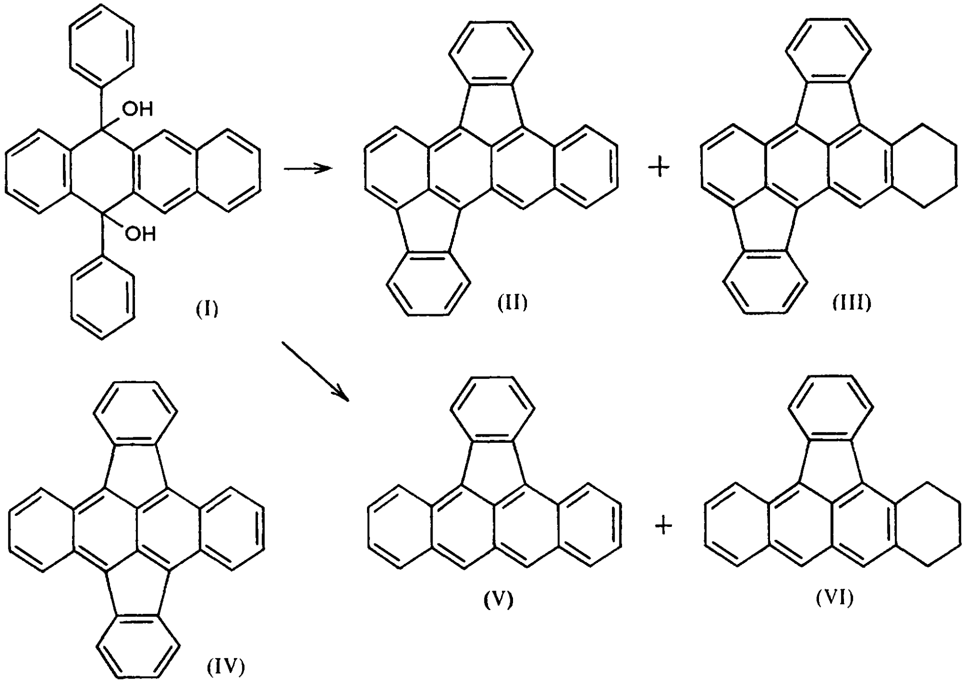
[1] Clar and Stewart, *J.*, 1952, 4783.

[2] Dufraisse and Girard, *Bull. Soc. chim. France*, 1934, **1**, 1359.

[3] Stubbs and Tucker, *J.*, 1951, 2939; Campbell and Marks, *J.*, 1951, 2941.

[4] von Braun and Manz, *Ber.*, 1937, **70**, 1603; Stubbs and Tucker, *J.*, 1950, 3288.

9-phenylanthracene and 2 : 3-benzofluoranthene[3] (XI; see Fig. 3). Besides these, a hydrocarbon of unknown structure was isolated which was also obtained by fusing rubicene with sodium chloride–aluminium chloride. *iso*Rubicene (XVI) was not isolated in this reaction.



Rubicene (X) was easily prepared from 1 : 5-dichloro-9 : 10-diphenylanthracene (XII) by means of potassium hydroxide in boiling quinoline. However, *iso*rubicene was not obtained by the same treatment of 1 : 4-dichloro-9 : 10-diphenylanthracene (XVII): short treatment gave 5-chloro-4-phenyl-2 : 3-benzofluoranthene (XVIII); further similar treatment of this compound did not yield *iso*rubicene but removed chlorine and afforded an alkali-soluble product.

Treating 1-chloro-9 : 10-diphenylanthracene (XV) with potassium hydroxide in boiling quinoline gave 4-phenyl-2 : 3-benzofluoranthene (XIV), in good yield, whose absorption spectrum is very close to that of 2 : 3-benzofluoranthene (XI) (see Fig. 3). Compound (XIV) gave rubicene and its further reaction products (see above) in a sodium chloride–aluminium chloride melt, but no *iso*rubicene.

We have repeated Fedorov's synthesis[5] of *iso*rubicene (XVI) and obtained a very small yield of a hydrocarbon with the properties reported by him. However, the absorption spectrum of our *iso*rubicene is very different from that reported by Setkina and Fedorov[6] (see Fig. 4), being similar to that of rubicene (X) (Fig. 4). However, the relationship is not as close as in the case of 2 : 3-benzorubicene (II) and di-*o*-phenylenetetracene (VI) (Fig. 1).

## EXPERIMENTAL

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

The tetracene was supplied by Messrs. Shore Transit Co. Ltd., 80, Wolmer Gardens, Edgware, Middlesex. The tetracenequinone was prepared by oxidation with chromic acid in acetic acid.

[5] Fedorov, *Bull. Acad. Sci. U.R.S.S., Classe sci. Chim.*, 1947, 397; *Chem. Abs.*, 1948, 1585.

[6] Setkina and Fedorov, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1949, 545; *Chem. Abs.*, 1950, **44**, 1333.

FIG. 1.

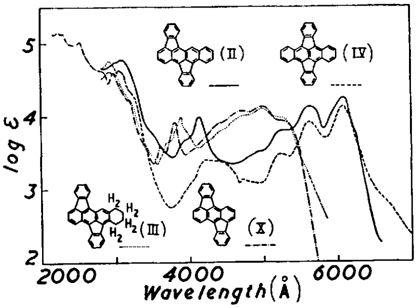


FIG. 2.

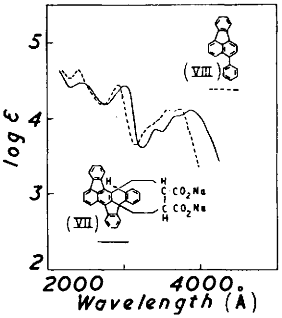


FIG. 3.

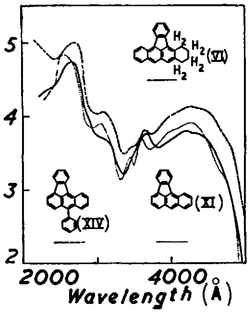
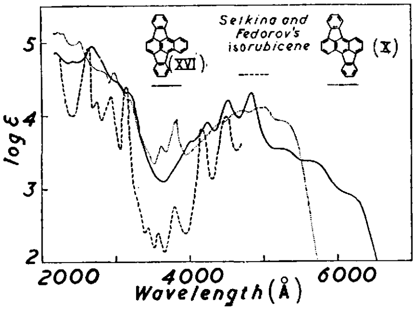


FIG. 4.



*Absorption max.* (Å) *and* log ε (*in parentheses*).

FIG. 1. 2 : 3-*Benzorubicene* (II) *in* $C_6H_6$: 6100 (4·26), 5650 (4·14), 5300 (3·80), 4960 (3·52), 4140 (3·99), 3100 (4·80).
5 : 6-11 : 12-*Di*-o-*phenylenetetracene* (IV) *in* $C_6H_6$: 6090 (4·14), 5620 (3·92), 5220 (3·48), 4200 (3·40), 3050 (4·64), 2900 (4·63).
*Rubicene* (X) *in* $C_6H_6$: 5300 (3·82), 4940 (4·00), 4650 (3·95), 3790 (3·77), 3600 (3·45), 2970 (4·85); *in* EtOH, 2510 (5·00), 2300 (5·10).
1′ : 2′ : 3′ : 4′-*Tetrahydro*-2 : 3-*benzorubicene* (III) *in* $C_6H_6$: 5230 (3·98), 4980 (4·09), 4680 (4·00), 3870 (3·98), 3700 (3·64), 2910 (4·76).

FIG. 2. *Disodium salt of the maleic anhydride adduct* (VII) *in* EtOH: 3850 (4·18), 3670 (4·04), 3420 (3·76), 3030 (4·42), 2460 (4·45).
4-*Phenylfluoranthene* (VIII) *in* EtOH: 3700 (4·20), 3580 (4·18), 3145 (3·81), 2940 (4·45), 2405 (4·62).

FIG. 3. 1′ : 2′ : 3′ : 4′-*Tetrahydro*-2 : 3-6 : 7-*dibenzofluoranthene* (VI) *in* EtOH: 4250 (3·81), 3700 (3·78), 2660 (4·74).
4-*Phenyl*-2 : 3-*benzofluoranthene* (XIV) *in* EtOH: 4300 (4·13), 3660 (3·80), 3100 (4·06), 2700 (5·00).
2 : 3-*Benzofluoranthene* (XI) *in* EtOH: 4280 (3·92), 3630 (3·70), 3460 (3·46), 3080 (3·90), 2560 (4·85).

FIG. 4. iso*Rubicene* (XVI) *in* $C_6H_6$: 6250 (2·87), 5630 (3·37), 5300 (3·54), 4850 (4·31), 4530 (4·20), 4250 (3·90), 4020 (3·66), 3170 (4·34); *in* EtOH: 2680 (4·97).
*Setkina and Fedorov's* iso*rubicene*:[6] 4480 (4·00), 4150 (3·93), 3800 (2·81), 3600 (2·60), 3450 (2·66), 3150 (4·20), 2950 (4·10), 2760 (4·01), 2650 (4·63).
*Rubicene* (X) *in* $C_6H_6$: 5300 (3·92), 4940 (4·00), 4650 (3·95), 3790 (3·77), 3600 (3·45), 2970 (4·85); *in* EtOH: 2510 (5·00), 2300 (5·10).

*Condensation of Diol* (I).—5 : 12-Dihydro-5 : 12-diphenyltetracene-5 : 12-diol (I) was obtained from tetracenequinone and phenyl-lithium in good yield.[7] It (5 g.) was added with stirring within 5 min. to a melt of sodium chloride (10 g.) and aluminium chloride (50 g.) at 120°. The melt was decomposed with dilute hydrochloric acid, and the precipitate filtered off, washed with hot water, and treated with aqueous ammonia. The dried black condensation product

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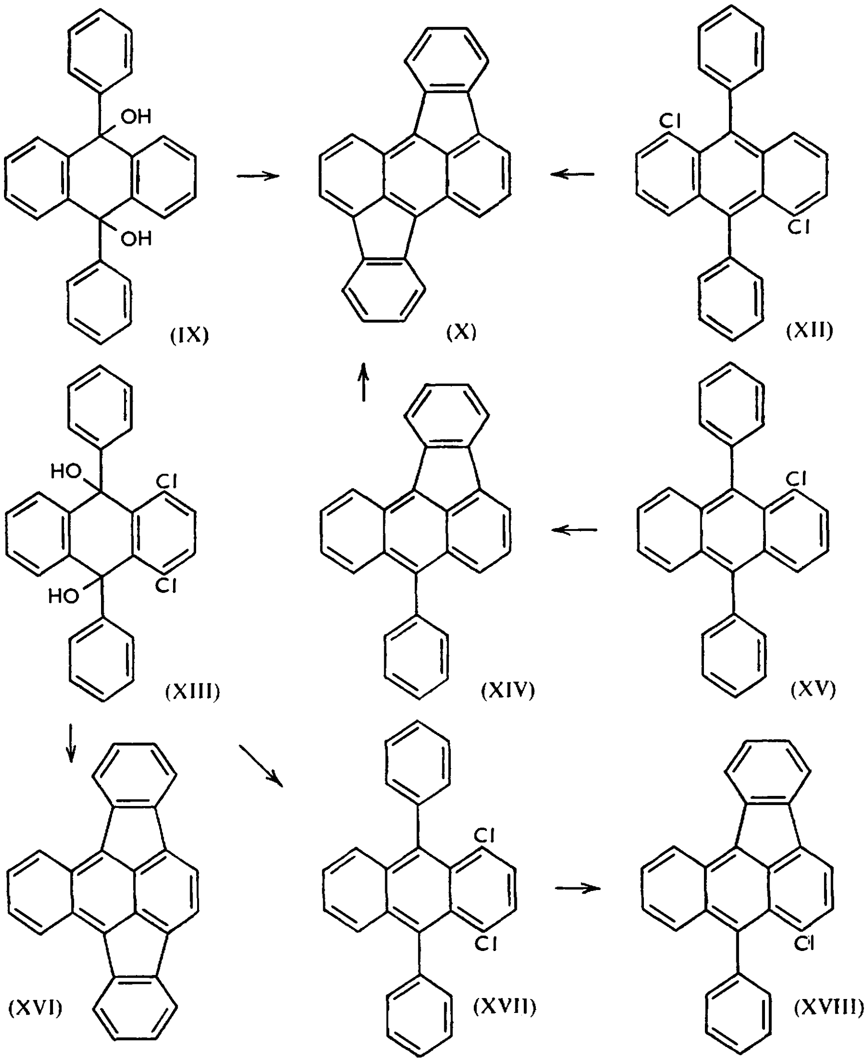
[7] Cf. Dufraisse and Horclois, *Bull. Soc. chim. France*, 1936, **3**, 1894, 1899; Allen and Gilman, *J. Amer. Chem. Soc.*, 1936, **58**, 937; 1940, **62**, 2408.



(4 g.) was chromatographed on alumina, elution being with light petroleum with increasing proportions of benzene. The hydrocarbons were eluted in the following order:

1′ : 2′ : 3′ : 4′-Tetrahydro-2 : 3-6 : 7-dibenzofluoranthene (VI) (9 : 1 light petroleum–benzene), yellow needles (120 mg.), m. p. and mixed m. p. 150°.

2 : 3-6 : 7-Dibenzofluoranthene (V) (4 : 1 light petroleum–benzene), red needles (25 mg.) which after recrystallisation from xylene had m. p. and mixed m. p. (ref. 1) 215°.

1′ : 2′ : 3′ : *4′-Tetrahydro-2 : 3-benzorubicene* (III) (1 : 1 light petroleum–benzene), reddish-brown needles (85 mg.), m. p. 182°, dissolving in concentrated sulphuric acid to give an orange solution changing to green (Found: C, 95·0; H, 5·1. $C_{30}H_{20}$ requires C, 94·7; H, 5·3%).

2 : *3-Benzorubicene* (II) (eluant: benzene): the main fraction was violet and yielded deep blue needles (450 mg.), m. p. 250°, dissolving to a deep green solution in concentrated sulphuric acid; the blue solution in benzene showed an intense red fluorescence (Found: C, 95·4; H, 4·4. $C_{30}H_{16}$ requires C, 95·7; H, 4·3%).

*Maleic Anhydride Adduct* (VII; Fig. 2) *of* 2 : *3-Benzorubicene.*—Benzorubicene (20 mg.) and maleic anhydride (20 mg.) were refluxed for 30 min. in xylene (20 ml.). The blue solution became yellow. The *adduct* crystallised on concentration. The crystals decomposed gradually above 300° into the hydrocarbon and maleic anhydride (Found: C, 85·2; H, 4·6. $C_{34}H_{18}O_3$ requires C, 86·0; H, 3·8%).

*Condensation of* 9 : 10-*Dihydro*-9 : 10-*diphenylanthracene*-9 : 10-*diol* [8] (IX).—This was carried out as in the previous case, chromatography giving:

9-Phenylanthracene (eluant : light petroleum), needles (75 mg.), m. p. 154° (absorption spectrum identical with that reported).

2 : 3-Benzofluoranthene (XI; Fig. 3) (eluant: light petroleum): The second fraction was yellow with a green fluorescence and yielded on concentration orange-yellow needles (15 mg.), m. p. 143—145°. They dissolved in concentrated sulphuric acid with a violet colour. The absorption spectrum was in accordance with that recorded.[1]

Rubicene (X) (4 : 1 light petroleum–benzene), red needles (50 mg.), m. p. and mixed m. p. 303°, giving a reddish-brown solution in hot concentrated sulphuric acid (Found: C, 95·5; H, 4·5. Calc. for $C_{26}H_{14}$: C, 95·7; H, 4·3%).

Later fractions became increasingly violet and the m. p.s rose from 300° to above 450° when the eluant was gradually replaced by benzene and finally by trichlorobenzene. The latter gave on concentration deep violet-black needles (60 mg.), decomp. >455° (red solution in hot concentrated sulphuric acid) (Found: C, 95·7; H, 4·0. Calc. for $C_{26}H_{14}$: C, 95·7; H, 4·3. Calc. for $C_{26}H_{12}$: C, 96·3; H, 3·7%). The same product was obtained when rubicene (1 g.) was added to a melt of aluminium chloride (10 g.) and sodium chloride (2 g.) at 130° and heated for 15 min.; after decomposition the condensation product (0·6 g.) gave reddish-black needles from trichlorobenzene.

*Rubicene* (X) *from* 1 : 5-*Dichloro*-9 : 10-*diphenylanthracene* [9] (XII).—The dichloro-compound (2 g.) was refluxed in quinoline (50 ml.) with potassium hydroxide (2 g.). After 10 min. the mixture became deep yellow and after 30 min. deep red. It was poured into dilute hydrochloric acid. The precipitate was washed with water and recrystallised from xylene. The bright yellow needles (1·4 g.) had m. p. and mixed m. p. 304°.

5-*Chloro*-4-*phenyl*-2 : 3-*benzofluoranthene* (XVIII).—1 : 4-Dichloro-9 : 10-diphenylanthracene [10] (XVII) (2 g.) was refluxed with quinoline (20 ml.) and potassium hydroxide (2 g.). After 10 min. the mixture became deep yellow and it was poured into dilute hydrochloric acid after 15 min. The *product* was filtered off, washed, dried, and repeatedly recrystallised from light petroleum (b. p. 60—80°). The yellow needles had m. p. 215° (Found: Cl, 9·9. $C_{26}H_{15}Cl$ requires Cl, 9·8%). When treatment with quinoline and potassium hydroxide was considerably prolonged an alkali-soluble product and no *iso*rubicene (XVI) was obtained.

4-*Phenyl*-2 : 3-*benzofluoranthene* (XIV).—1-Chloro-9 : 10-diphenylanthracene [10] (XV) (3 g.), potassium hydroxide (3 g.), and quinoline were refluxed for 30 min. The mixture was poured into dilute hydrochloric acid, and the washed precipitate recrystallised from alcohol. The yellow leaflets (2·2 g.) had m. p. 185—186° and gave a green solution in concentrated sulphuric acid (Found: C, 94·8; H, 5·1. $C_{26}H_{16}$ requires C, 95·1; H, 4·9%). When this *product* (XIV) was melted with sodium chloride and aluminium chloride at 120° for 10 min. the same products were obtained as were described for 9 : 10-dihydro-9 : 10-diphenylanthracene-9 : 10-diol (IX).

iso*Rubicene* (XVI).—1 : 4-Dichloro-9 : 10-dihydro-9 : 10-diphenylanthracene-9 : 10-diol [10] (XVII) (1 g.), dry oxalic acid (12 g.), sodium acetate (3 g.), copper powder (0·3 g.), and aluminium powder (0·3 g.) were heated at 30 mm. for 30 min. to 300° and then for one hour to 360°. The mixture was extracted with hot water and then with benzene (15 ml.). The dried benzene solution was chromatographed on alumina, with light petroleum as eluant which was gradually replaced by benzene. The first fraction gave dichlorodiphenylanthracene (XVII) (50 mg.), m. p. 178°; the next fraction was 5-chloro-4-phenyl-2 : 3-benzofluoranthene (XVIII) (200 mg.), m. p. 214°; and the third fraction (obtained by pure benzene) gave reddish-brown needles (10 mg.), m. p. 279°, of *iso*rubicene (Found: C, 95·7; H, 4·4. Calc. for $C_{26}H_{14}$: C, 95·7; H, 4·3%).

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[8] Haller and Guyot, *Compt. rend.*, 1904, **138**, 1251; *Bull. Soc. chim. France*, 1904, **31**, 795.

[9] Barnett, Cook, and Wiltshire, *J.*, 1927, 1724; Fedorov, *Bull. Acad. Sci. U.R.S.S.*, *Classe sci. Chim.*, 1947, 397.

[10] Dufraisse and Velluz, *Bull. Soc. chim. France*, 1942, **9**, 186; Fedorov, *Bull. Acad. Sci. U.R.S.S.*, *Classe sci. Chim.*, 1947, 397.