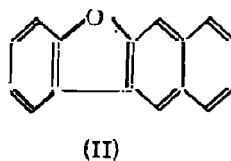
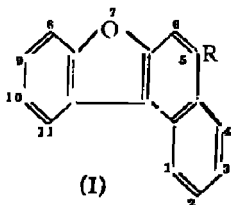


EXPERIMENTS ON THE SYNTHESIS OF FURANO COMPOUNDS.
PART VII. 1:2-BENZODIPHENYLENE OXIDE

BY J. N. CHATTERJEA

Two unequivocal syntheses of 1:2-benzodiphenylene oxide (γ -brazan) are recorded, proving the earlier descriptions of the compound in the literature as incorrect.

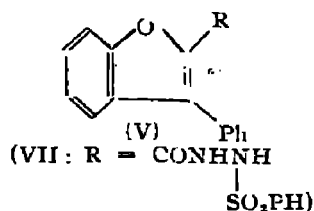
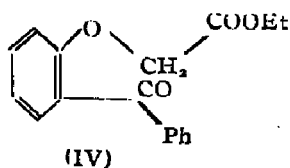
Derivatives of 1:2-benzodiphenylene oxide (γ -brazan*) (I), such as α -anhydro-trimethylbrazilone and allied products, have been synthesised by Johnson and Robertson (*J. Chem. Soc.*, 1950, 2381; also cf. Chatterjea, this *Journal*, 1953, 30, 103). There is discrepancy in the literature with regard to the parent compound (I). Graebe and Arx claimed to have prepared this compound by heating a mixture of β -naphthol and phenol with litharge and reported the m.p. 296° (*Annalen*, 1881, 209, 145). Sabatier and Mailhe (*Compt. rend.*, 1912, 155, 202) obtained a product, m.p. 200°, by heating a mixture of β -naphthol and phenol over thorium oxide and formulated it as either γ -(I) or β -brazan (II). But as the latter (m.p. 208°) did not produce the colour reactions described by Sabatier and Mailhe (*loc. cit.*) for the above product (Kostanceki and Lloyd, *Ber.*, 1903, 36, 2193), it appeared likely that they had really obtained (I). It was therefore desirable to resolve this obvious discrepancy.



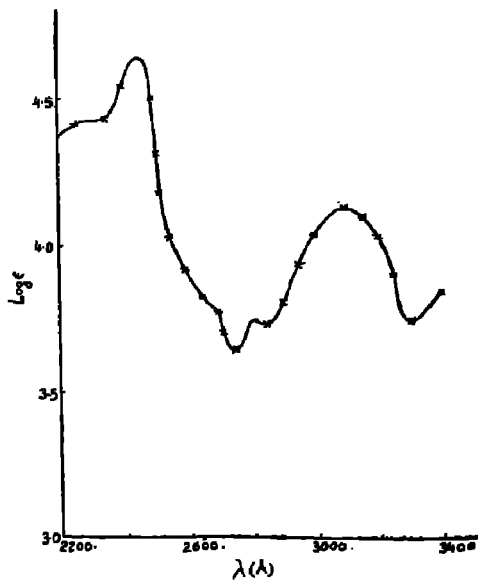
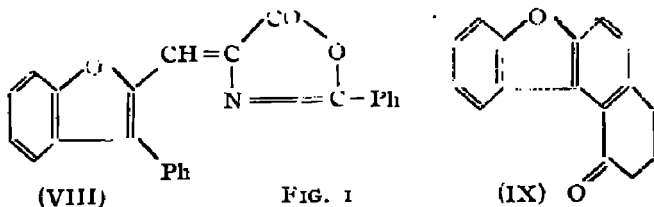
[I : R = H;
III : R = OH;
VI : R = COOH]

By an adaptation of the method of Johnson and Robertson (*loc. cit.*), the 5-hydroxy- γ -brazan (III) has been prepared from 2-hydroxybenzophenone. The latter was converted into ethyl 2-benzoylphenoxyacetate (IV) and then cyclised with sodium ethoxide in alcohol to ethyl 3-phenylcoumarone-2-carboxylate (V: R = CO₂Et). The corresponding acid (V: R = CO₂H) on homologation by the Arndt-Eistert procedure afforded 3-phenylcoumarone-2-acetic acid (V: R = CH₂COOEt), isolated by way of the amide. On cyclisation with phosphoric anhydride in benzene, a quantitative yield of the α -naphthol (III) was obtained. The phenol on reduction with hydriodic acid furnished a poor yield of γ -brazan which was obtained as a low-melting solid (m.p. 31-32°), characterised by a well-crystalline picrate.

* Benzo[b]naphtho [1,2-d] furan (I) is termed γ -brazan and 3:4-benzodiphenylene oxide (benzo-[b] naphtho [2,1-d] furan) is termed α -brazan (Patterson and Capell, "The Ring Index", Reinhold, Ring System No: 2483 and 2482 respectively).



A better route to γ -brazan was from 2-formyl-3-phenylcoumarone (V: R = CHO) which was obtained in poor yield by the Gattermann synthesis from 3-phenylcoumarone (V: R = H), prepared conveniently by the action of sodium acetate and acetic anhydride on the acid (IV: H in place of Et). The aldehyde was, however, obtained in quantity from the corresponding acid by the Stevens-McFadyen method involving the decomposition of the sulphonylhydrazone (VII) with sodium carbonate in ethyleneglycol (*J. Chem. Soc.*, 1936, 584). The azlactone (VIII), derived from the aldehyde, afforded the pyruvic acid (V: R = CH₂CO.COOH), isolated by the sulphur dioxide method. It underwent cyclisation in quantitative yield to the acid (VI) with hydrobromic acid in acetic acid. On decarboxylation with the aid of lime, this acid afforded γ -brazan, identical with the product, mentioned above.



It is clear from the above work that the products of Graebe and of Sabatier must have different constitutions and this was further confirmed by an independent synthesis of γ -brazan from the cyclic ketone (IX), described earlier (Mosettig and Robinson, *J. Amer. Chem. Soc.*, 1939, **61**, 1148; Chatterjea, *loc. cit.*). γ -Brazan was obtained from this ketone either by reduction with lithium aluminium hydride to the corresponding carbinol, followed by treatment with palladised charcoal or by the Wolff-Kishner reduction to the tetrahydro- γ -brazan, followed by dehydrogenation with selenium. The absorption spectrum of (I) is shown in Fig. 1.

EXPERIMENTAL*

3-Phenylcoumarone-2-carboxylic Acid.—A mixture of 2-hydroxybenzophenone (5 g.), ethyl bromoacetate (5 c.c.) and dry potassium carbonate (12 g.) in dry acetone (40 c.c.) was refluxed for 8 hours. Isolated as usual, the resulting phenoxyacetic ester was obtained as a light brown oil (negative ferric reaction) which was heated in vacuum at 180° to remove all volatile impurities. The crude ester was cyclised by adding a solution of the compound in dry alcohol (15 c.c.) to a solution of alcoholic sodium ethoxide (Na, 0.5 g. in alcohol, 35 c.c.) and refluxing the mixture for 1 hour. The mixture was then poured into cooled water when ethyl 3-phenylcoumarone-2-carboxylate separated as an oil, which easily solidified, yield 3 g. The ester crystallised from alcohol in prisms, m.p. 64° and developed a pinkish red coloration with H_2SO_4 . (Found: C, 76.0; H, 5.5. $C_{17}H_{14}O_3$ requires C, 76.6; H, 5.3 per cent). The alkaline filtrate, after removal of alcohol, on acidification furnished 3-phenylcoumarone-2-carboxylic acid (0.3 g.). This acid was prepared from the above ester (3 g.) by hydrolysing with alcoholic sodium hydroxide (40 c.c., 10%) for $\frac{1}{2}$ hour on a boiling water-bath. On acidification, the acid was obtained which crystallised from acetic acid in yellowish needles (2.1 g.), m.p. 234° (Fuson *et al.*, *J. Org. Chem.*, 1941, **6**, 845, report m.p. $232-33^\circ$ for the same compound obtained by a different method). The compound dissolved in sulphuric acid with a yellow colour which became pinkish on warming.

3-Phenylcoumarone.—The crude ethyl 2-benzoylphenoxyacetate, obtained in the above preparation, on hydrolysis afforded the corresponding acid as an oil which was isolated with ether. This phenoxy-acid (5 g.) was dissolved in acetic anhydride (40 c.c.), anhydrous sodium acetate (8 g.) was added and the mixture heated on an oil-bath at 165° for $\frac{1}{2}$ hour. After the brisk reaction was over, the mixture was added to water (50 c.c.), extracted with ether and the ethereal layer washed several times with sodium bicarbonate solution. On removal of the ether, 3-phenylcoumarone (2.9 g.) was obtained as an oil which solidified, m.p. 42° (Stormer and Kippe, *Ber.*, 1903; **36**, 4005, record m.p. 42°). The compound developed an orange-yellow coloration with H_2SO_4 . (Found: C, 86.4; H, 5.4. Calc. for $C_{14}H_{10}O$: C, 86.6; H, 5.2 per cent).

* All m.p.'s are uncorrected.

3-Phenylcoumarone-2-acetic Acid.—(a). The acid (V: R = COOH) (3.0 g.) was converted into the acid chloride by boiling in thiophene-free benzene (10 c.c.) with purified thionyl chloride (6 c.c.). The colorless crystalline acid chloride, obtained on removal of benzene and volatile impurities in vacuum, was dissolved in benzene (10 c.c.) and added dropwise to a solution of diazomethane (from nitrosomethylurea, 12 g.) in ether (120 c.c.) at 0°. The next day the solution was filtered and the solvent removed in vacuum. The diazo-ketone (3.0 g.) crystallised from benzene-petroleum ether in yellow prisms, m.p. 112-14° (decomp.). (Found: N, 11.0. $C_{16}H_{16}O_2N_2$ requires N, 10.7 per cent). A solution of the diazo-ketone (2.9 g.) in purified dioxan (70 c.c.) was added during $\frac{1}{2}$ hour to a stirred solution of silver nitrate (40 c.c., 10%) in concentrated aqueous ammonium hydroxide (30 c.c.) at 70°. After heating on a water-bath for 3 hours, the mixture was left overnight, filtered and poured into a large volume of water. The crude 3-phenylcoumarone-2-acetamide was collected and hydrolysed with aqueous alcoholic potash (30 c.c., 10%) for 5 hours. After removal of the alcohol, the cooled residue was diluted with water, clarified with charcoal, filtered and acidified to afford the acid (V: R = CH_2COOH) (2.6 g.), crystallising from benzene-light petroleum in cream-coloured needles, m.p. 146°. (Found: C, 76.0; H, 5.0. $C_{16}H_{12}O_3$ requires C, 76.2; H, 4.7 per cent).

The compound dissolved in H_2SO_4 with an orange-yellow colour, turning green slowly with the appearance of a violet fluorescence. The acid also exhibited a violet fluorescence in acetic acid. The *p*-toluidide crystallised from acetic acid in colorless needles, m.p. 183°. (Found: C, 81.2; H, 5.8. $C_{23}H_{19}O_2N$ requires C, 80.9; H, 5.6 per cent).

(b). The pyruvic acid (V: R = $CH_2CO.COOH$) (0.3 g., *vide infra*) was dissolved in dilute NaOH solution (5 c.c., 5%), cooled to 5° and treated with perhydrol (0.6 c.c., 30%) during 5 minutes. After leaving for 2 hours, the mixture was acidified to yield the acid (V: R = CH_2COOH) (0.2 g.) as cream-coloured needles, m.p. 145-46° (from acetic acid).

Cyclisation of 3-Phenylcoumarone-2-acetic Acid.—The acid (1.2 g.) was dissolved in benzene (45 c. c.) and treated with constant stirring with P_2O_5 (7.2 g.) and refluxed for 4 hours. The mixture was then decomposed with ice and the benzene layer washed several times with sodium carbonate solution. On removal of benzene the phenol, 5-hydroxy- γ -brazan (III) was obtained (0.75 g.) which crystallised from acetic acid in cream-coloured prisms, m.p. 142°. (Found: C, 82.0; H, 4.4. $C_{16}H_{10}O_2$ requires C, 82.1; H, 4.3 per cent).

γ -Brazan.—The above α -naphthol (0.5 g.) was boiled with freshly distilled hydriodic acid (5 c. c.) for 8 hours. The mixture was extracted with ether, washed with sodium thiosulphate solution, dried (sodium sulphate) and distilled in vacuum at 180° (bath temp.). The mobile distillate furnished a crystalline picrate (0.08 g.) which crystallised from alcohol in orange needles, m.p. 124°. (Found: C, 59.5; H, 3.2; N, 9.4. $C_{16}H_{10}O.C_6H_5O_7N_3$ requires C, 59.1; H, 2.9; N, 9.4 per cent). γ -Brazan, liberated from the picrate by alkali, was obtained as a liquid which solidified on keeping, m.p. 31-32°. (Found: C, 88.3; H, 4.6. $C_{16}H_{14}O$ requires C, 88.1; H, 4.6 per cent). The compound showed with H_2SO_4 the following successive changes in colour: blue \rightarrow deep blue \rightarrow green \rightarrow pinkish \rightarrow yellowish green.

U.V. absorption (Fig. 1) : $\lambda_{\max}^{\text{alcohol}}$, 2450 Å (log ϵ , 4.64), 2800 Å (log ϵ , 3.74), 3100 Å (log ϵ , 4.13).

The residual glassy material in the distilling flask in the above experiment solidified on trituration with acetone and was obtained as a greenish yellow mass, m.p. 246°. This was not investigated.

Attempt to prepare γ -Brazanquinone by oxidation of 5-Hydroxy- γ -brazan.*—The phenol (0.4 g.) was dissolved in acetic acid (10 c. c.) and to the boiling solution was added a solution of chromic acid (0.38 g.) in water (3 c. c.). After boiling for 5 minutes the mixture was poured into water. The deep orange-red resinous mass (0.1 g.) separating was a mixture of quinones (the colour was rapidly discharged on reduction with zinc dust in acetic acid). On attempting to isolate γ -brazanquinone as the azine, the above mixture was boiled with *o*-phenylenediamine (0.1 g.) in acetic acid (6 c. c.). An unidentified product, m.p. 245° (from acetic acid), was deposited as brownish prisms (20 mg.), developing a yellowish green coloration with H_2SO_4 . (Found : C, 78.5 ; H, 4.3 ; N, 0.0 per cent).

2-Formyl-3-phenylcoumarone.—(a). To a solution of 3-phenylcoumarone (2.8 g.) in ether (80 c. c.) fused zinc chloride (1.2 g.) and anhydrous hydrogen cyanide (4 c. c.) were added and the mixture saturated with hydrogen chloride at 0°. The next day the crystalline product separating was collected, washed with dry ether, treated with water (50 c. c.) and heated on a water-bath for $\frac{1}{2}$ hour. The oil (0.2 g.) separating was isolated with ether. The aldehyde did not crystallise. It dissolved in H_2SO_4 with a yellowish colour, turning green.

The semicarbazone crystallised from alcohol in cream-coloured needles, m.p. 246-48°. (Found : C, 68.7 ; H, 5.0. $\text{C}_{16}\text{H}_{15}\text{O}_2\text{N}_3$ requires C, 68.8 ; H, 4.7 per cent).

The 2:4-dinitrophenylhydrazone, prepared in alcohol with the aid of HCl, was obtained in two forms : (i) Dark red leaflets with a steel-blue reflex, m.p. 264° (from acetic acid. (Found : N, 14.1. $\text{C}_{21}\text{H}_{14}\text{O}_5\text{N}_4$ requires N, 13.9 per cent). (ii) Orange-yellow needles, m.p. 234° clearing at 260° (from acetic acid). (Found : N, 13.8. $\text{C}_{21}\text{H}_{14}\text{O}_5\text{N}_4$ requires N, 13.9 per cent).

(b). From 3-Phenylcoumarone-2-carboxylic Acid.—This acid was esterified with diazomethane yielding the methyl ester which crystallised from methyl alcohol in cream-colored prisms, m. p. 97°. (Found : C, 76.3 ; 5.0. $\text{C}_{16}\text{H}_{12}\text{O}_3$ requires C, 76.2 ; H, 4.7 per cent). A mixture of the ester (1 g.), hydrazine hydrate (2 c. c., 90%) and ethyl alcohol (3 c. c.) was boiled under reflux for 5½ hours and then poured into water. The hydrazide (V:R=CONHNH₂) (0.9 g) was obtained as a crystalline solid, crystallising from methanol in colorless long needles, m.p. 79-80°. (Found : N, 11.5. $\text{C}_{15}\text{H}_{12}\text{O}_2\text{N}_2$ requires N, 11.1 per cent). The picrate crystallised from alcohol in yellow prismatic needles, m.p. 195° (decomp.).

A solution of the hydrazide (1.5 g.) in dry purified pyridine (10 c. c.) was cooled to 0° and treated dropwise with benzenesulphonyl chloride (0.9 g.). The solution turned yellow and after sometime yellowish needles began to separate. The mixture was kept in a refrigerator for 6 hours and then poured into iced HCl. The gummy yellow mass

* Also named α -brazanquinone.

of the *sulphonhydrazide* (VII) (quantitative yield) solidified easily and was obtained in colorless prisms from methanol, m.p. 233-34° (decomp.). (Found: N, 6.8. $C_{21}H_{16}O_4N_2S$ requires N, 7.1 per cent).

A solution of the *sulphonhydrazide* (0.4 g.) in ethyleneglycol (3 c.c.) at 160° was treated with anhydrous sodium carbonate (0.4 g., added in one lot). A vigorous evolution of gas took place and after 80 seconds the reaction was quenched by pouring the mixture into hot water which was then cooled and the oily aldehyde (0.15 g.) was extracted with ether.

3-Phenylcoumarone-2-pyruvic Acid.—The crude aldehyde (3.0 g.) was converted into the *azlactone* (VIII) by heating on a boiling water-bath with a mixture of hippuric acid (2.0 g.), fused sodium acetate (1 g.) and acetic anhydride (20 c.c.) for 20 minutes. Dilute alcohol (40 c.c., 50%) was then added to the mixture and the crystalline material collected after 2 hours, washed with boiling water and then with cold alcohol. The *azlactone* (3.4 g.) crystallised from benzene in orange-yellow needles, m.p. 240-42°. (Found: C, 79.4; H, 4.5. $C_{24}H_{18}O_3N$ requires C, 78.9; H, 4.1 per cent).

The *azlactone* (2.5 g.) was boiled under reflux with KOH (35 c.c., 10%) for 4½ hours. An oily product separated. The mixture was filtered, cooled, diluted with water (30 c.c.) and saturated with SO_2 at 25°. The *pyruvic acid* (V: R = $CH_2CO.COOH$) was isolated in the usual manner. It crystallised from acetic acid as a colorless powder (0.4 g.), m. p. 242-44° showing a violet ferric reaction. (Found: C, 72.2; H, 4.6. $C_7H_{12}O_4$ requires C, 72.8; H, 4.3 per cent). The compound developed a yellowish green coloration with H_2SO_4 .

Cyclisation of the Pyruvic Acid.—The foregoing ketonic acid (0.3 g.) was dissolved in acetic acid (3 c.c.) and boiled under reflux with HBr (2 c.c., 48%) for 3 hours. On cooling, *γ-brazan-5-carboxylic acid* (VI) separated, crystallising from acetic acid in colorless slender needles, m. p. 290°, yield 0.22 g. (Found: C, 77.4; H, 3.9. $C_{17}H_{16}O_5$ requires C, 77.9; H, 3.8 per cent).

* The *methyl ester*, obtained by the action of diazomethane, crystallised from methanol in colorless needles, m.p. 101°. (Found: C, 78.2; H, 4.8. $C_{16}H_{12}O_3$ requires C, 78.3; H, 4.4 per cent).

γ-Brazan.—(i). The decarboxylation of the above acid was carried out by mixing with 3 times its weight of lime and heating in a horizontal tube. The *γ-brazan* distilled as a colorless oil, yielding a crystalline picrate, m.p. 123-24°, undepressed on admixture with the specimen obtained before.

(ii) (a).—A solution of *1-keto-1:2:3:4-tetrahydro-γ-brazan* (IX, 0.1 g.) in ether (5 c.c.) was treated with the usual precautions with lithium aluminium hydride (50 mg.) and left for 1 hour. The mixture was carefully decomposed with dilute acid, the ethereal layer worked up to give the corresponding carbinol, *1-hydroxy-1:2:3:4-tetrahydro-γ-brazan*, as colorless prisms, m.p. 105-106°. (Found: C, 80.1; H, 6.0. $C_{16}H_{14}O_2$ requires C, 80.7; H, 5.9 per cent). This carbinol (60 mg.) was mixed with palladised charcoal (50 mg.) and heated at 300° for 3 hours. The resulting violet fluorescing oil was taken up in ether and obtained from low-boiling petroleum ether in colorless prisms, m.p. 31-32° (picrate, m.p. 123-24°), identical with the specimen of *γ-brazan* obtained above.

(ii) (b).—The ketone (IX, 1.0 g.) was heated in a sealed tube with hydrazine hydrate (1 c.c., 100%) and alcoholic sodium ethoxide (0.5 g. of sodium in absolute alcohol, 10 c.c.) at 180°-190° for 8 hours. The oily product was distilled in an oil pump affording the reduced product as a colorless oil (0.3 g.) which did not solidify on keeping. It was mixed with selenium (1.0 g.) and heated at 300° for 2 hours. The resulting oily product was dissolved in alcohol (10 c. c.), filtered and treated with picric acid. The picrate of γ -brazan separated; it was collected and crystallised from alcohol in orange needles, m.p. and mixed m.p. 123-24°, yield 0.12 g.

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