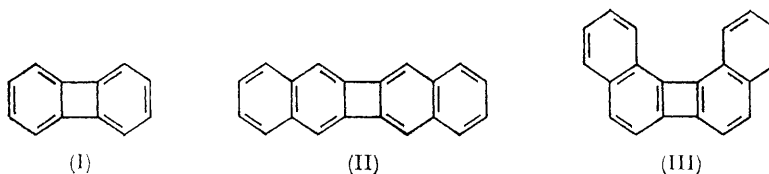


989. *The Synthesis of Dibenzo[*a,g*]biphenylene.*

By J. W. BARTON.

The synthesis of dibenzo[*a,g*]biphenylene (IV) from naphthalene derivatives is described and its stability relative to the other known dibenzo-biphenylenes is discussed. A by-product, obtained together with (IV), is shown to be dinaphtho[1,2-*b*:1',2'-*d'*]furan (VI).

RECENT work on biphenylene has shown that structure (I) is the main contributor to the resonance hybrid.^{1,2} No great difference in stability between the two monobenzobiphenylenes has been reported,^{3,4} but whereas the linear dibenzo[*b,h*]biphenylene (II) is very stable,⁵ dibenzo[*a,i*]biphenylene (III), in which the benzenoid annellation is angular, is much deeper in colour and behaves as a highly unsaturated compound.³ Ali and Coulson⁶ discussed the effects of annellation and calculated that the resonance energy of (II) exceeds that of (III) by about 4.3 kcal./mole. They conclude that the degree of bond fixation increases in the order (II) < (I) < (III) and that bond 6a-6b in (III) is longer than bond



12b-12c by some 0.005 Å. It is thus of interest to compare the stability of (III) with that of dibenzo[*a,g*]biphenylene (IV), the synthesis of which is now described. The annellation is the same in both (III) and (IV), but the latter is more symmetrical in that bonds 6a-6b and 12a-12b must be of equal length and bond order.

Cook, Hewett, and Kennaway⁷ investigated the reduction of 1,2'-azonaphthalene with sodium dithionite and obtained a diamine, thought to be 1',2-diamino-1,2'-binaphthyl (V; R = NH₂). As this compound appeared to be a promising starting material for a Lothrop-type synthesis⁸ of (IV), the work was repeated and the diamine shown to be (V; R = NH₂) by conversion into the known 7*H*-dibenzo[*a,g*]carbazole,⁹ prior to the publication of other studies^{10,11} of the reduction and benzidine rearrangement of 1,2'-azonaphthalene. Ward and Pearson¹⁰ also attempted to convert the diamine (V; R = NH₂) into 1,2'-dinaphthyl-2,1'-iodonium iodide and thence to dibenzo[*a,g*]biphenylene (IV) without success, but they obtained a compound, which they thought was (IV), by the reaction of 1-bromo-2-iodonaphthalene with magnesium.¹²

At this point an alternative route to 1,2'-azonaphthalene was sought, as the existing method, that of coupling diazotised 2-naphthylamine with 1-naphthylamine to give 4-amino-1,2'-azonaphthalene followed by deamination,¹³ was not suitable for large-scale working. The reaction of arylmagnesium halides with the zinc chloride double salts of aryl diazonium

¹ Baker, McOmie, Preston, and Rogers, *J.*, 1960, 414.

² Mak and Trotter, *Proc. Chem. Soc.*, 1961, 163; *J.*, 1962, 1.

³ Cava and Stucker, *J. Amer. Chem. Soc.*, 1955, **77**, 6022.

⁴ Jensen and Coleman, *Tetrahedron Letters*, 1959, No. 20, 7; Baker, Barton, McOmie, and Searle, *J.*, 1962, 2633.

⁵ Curtis and Viswanath, *Chem. and Ind.*, 1954, 1174; *J.*, 1959, 1670.

⁶ Ali and Coulson, *Tetrahedron*, 1960, **10**, 41.

⁷ Cook, Hewett, and Kennaway, *Amer. J. Cancer*, 1940, **40**, 2.

⁸ Lothrop, *J. Amer. Chem. Soc.*, 1941, **63**, 1187.

⁹ Japp and Maitland, *J.*, 1903, 267.

¹⁰ Ward and Pearson, *J.*, 1959, 3378.

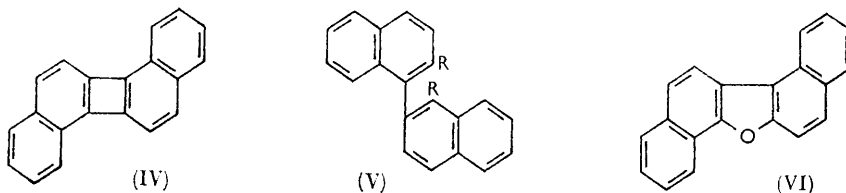
¹¹ Banthorpe and Hughes, *J.*, 1962, 2402.

¹² Ward and Pearson, *J.*, 1959, 1676.

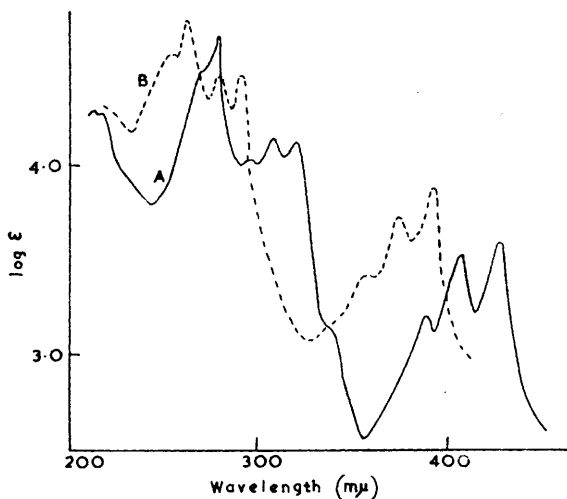
¹³ Nietzki and Göttig, *Ber.*, 1887, **20**, 612; Badger and Lewis, *J.*, 1953, 2154.

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chlorides has been employed recently for the preparation of azobenzene derivatives,¹⁴ although Hodgson and Marsden reported that the method gave low yields.¹⁵ In this case the reaction of 1-naphthylmagnesium bromide with the zinc chloride double salt of 2-naphthylidiazonium chloride gave good yields of 1,2'-azonaphthalene.



Reduction and rearrangement of 1,2'-azonaphthalene, using a method similar to that of Ward and Pearson,¹⁰ gave high yields of 1',2'-diamino-1,2'-binaphthyl (V; R = NH₂), accompanied by small amounts of 7H-dibenzo[a,g]carbazole. Tetrazotisation of the diamine (V; R = NH₂), best in sulphuric acid, and treatment with potassium iodide gave low yields of 1',2'-di-iodo-1,2'-binaphthyl (V; R = I), together with large amounts of light



Ultraviolet spectra of (A) dibenzo[a,g]biphenylene and (B) benzo[a]biphenylene, in ethanol.

brown, amorphous material. The latter, which was assumed to be 1,2'-binaphthyl-2,1'-iodonium iodide by Ward and Pearson,¹⁰ was somewhat soluble in organic solvents and was presumably polymeric as it gave no di-iodo compound (V; R = I) on thermal decomposition. A similar product was obtained by Cava and Stucker from 1,1'-diamino-2,2'-binaphthyl.³

Low-pressure pyrolysis of the di-iodo compound (V; R = I) with cuprous oxide at 250–350° gave very low yields of dibenzo[a,g]biphenylene (IV), accompanied by varying amounts of dinaphtho[1,2-*b*:1',2'-*d*]furan (VI). The hydrocarbon (IV) formed orange-red plates which decomposed at the melting point to become almost colourless. Solutions in hexane or methanol decomposed slowly at room temperature and more rapidly on heating or on exposure to ultraviolet light, with the formation of yellow amorphous material. Thus, the hydrocarbon appears to be similar in stability to the [a,*i*]-isomer (III). It was characterised as the stable, sparingly soluble complex with 2,4,7-trinitrofluorenone. The ultraviolet spectrum of dibenzo[a,g]biphenylene in ethanol (see Figure) showed a marked resemblance to that of benzo[a]biphenylene, except that there was the expected overall

¹⁴ Nomura, *Nippon Kagaku Zasshi*, 1958, **79**, 168 (*Chem. Abs.*, 1960, **54**, 4434).

¹⁵ Hodgson and Marsden, *J.*, 1945, 274.

shift of the curve to longer wavelengths. The ultraviolet spectrum of a decomposed sample showed a main peak at 210 μ .

Reduction of the hydrocarbon with Raney nickel in benzene-methanol resulted in the usual rapid rupture of the four-membered ring with the formation of 1,2'-binaphthyl. As it appeared likely that the light-induced decomposition of dibenzo[a,g]biphenylene involved 1,2'-binaphthyl radical, the decomposition was allowed to proceed in benzene saturated with sulphur dioxide. However, the most likely product of radical capture, dinaphtho[1,2-*b*:1',2'-*d*]thiophen-7,7-dioxide, was not found, only polymeric material was obtained.

Some of the pyrolyses of 1',2-di-iodo-1,2'-binaphthyl (V; R = I) to give (IV) gave the furan (VI), as mentioned above. The formation of furans in this type of reaction has been reported previously;⁵ the yield appears to depend on the particular batch of cuprous oxide used.

A compound, thought to be dinaphtho[1,2-*b*:1',2'-*d*]furan (VI) was first described by Orchin and Reggel¹⁶ and recently it has been obtained by a succinic anhydride synthesis on α -brazan.¹⁷ In the present work it was prepared by the following unambiguous methods. Decomposition of 1,2'-binaphthyl-2,1'-tetrazonium sulphate gave small yields of (VI), together with traces of 7*H*-dibenzo[a,g]carbazole. A more convenient preparation started from dinaphtho[2,1-*b*:2',3'-*d*]furan-8,13-quinone which is readily obtainable from the reaction of 2,3-dichloronaphtha-1,4-quinone with 2-naphthol in pyridine.¹⁸ This compound undergoes ring-opening in base to give 2-hydroxy-3-(2-hydroxy-1-naphthyl)naphtha-1,4-quinone which tautomerises and recycles on heating to give dinaphtho[1,2-*b*:1',2'-*d*]furan-12,13-quinone.¹⁹ Reduction of the latter with hydriodic acid gave (VI) in good yield.

EXPERIMENTAL

1,2'-Azonaphthalene.—2-Naphthylamine (14 g.), in water (140 ml.) and concentrated hydrochloric acid (58.5 ml.), was diazotised at 10° with sodium nitrite (7 g.) in water (50 ml.). The solution was treated with zinc chloride (20 g.) in 10% hydrochloric acid (10 ml.) giving the double salt, which was collected, washed with ether-ethanol and ether, and dried. The salt was suspended in ether (250 ml.) and a solution of 1-naphthylmagnesium bromide [from 1-bromonaphthalene (20 g.) and magnesium (2.6 g.) in ether (80 ml.)] added in portions with rapid stirring and slight cooling to moderate the reaction. After 30 min. dilute hydrochloric acid was added and the product extracted with benzene. Evaporation of the extract and chromatography of the residue on alumina in benzene-hexane (1 : 1) gave 1,2'-azonaphthalene (16.5 g., 60.5%), m. p. 143—144° (from ethanol).

1',2-Diamino-1,2'-binaphthyl.—Zinc dust (5 g.) and ammonia (25 ml.; *d* 0.880) were added to 1,2'-azonaphthalene (5 g.) in boiling acetone (250 ml.). After 10 min., the addition was repeated and the solution refluxed until colourless, then filtered, the zinc residues being extracted with hot acetone. The combined filtrate and extracts were cooled to 0° and stirred whilst concentrated hydrochloric acid (25 ml.) was added dropwise. After 3 hr., the solution was diluted with water (1 l.) and filtered to remove 7*H*-dibenzo[a,g]carbazole (0.35 g., 7%), m. p. 230—234°. The solution was charcoaled then neutralised with ammonia which precipitated 1',2-diamino-1,2'-binaphthyl as a white powder (4.3 g., 85.5%), m. p. 144—147°. It was used without further purification.

7*H*-Dibenzo[a,g]carbazole.—1',2-Diamino-1,2'-binaphthyl (0.1 g.) and concentrated hydrochloric acid (10 ml.) were heated under reflux for 3 hr. On cooling, the solid was collected and crystallised from benzene-hexane, giving the carbazole as colourless needles (0.084 g.), m. p. 238—239° (lit.,⁹ 231°).

1',2-Di-iodo-1,2'-binaphthyl.—1',2-Diamino-1,2'-binaphthyl (7 g.) in water (50 ml.) and sulphuric acid (20 ml.) was tetrazotised at 0—5° with sodium nitrite (3.5 g.) in water (12 ml.). After 15 min. the solution was added to potassium iodide (29 g.) in ice-water (300 ml.), kept cold for 30 min., then allowed to come to room temperature. Next day the mixture was warmed on

¹⁶ Orchin and Reggel, *J. Amer. Chem. Soc.*, 1951, **73**, 1877.

¹⁷ Chatterjea, Mehrotra, and Roy, *Ber.*, 1963, **96**, 1156.

¹⁸ Buu-Hoi, *J.*, 1952, 489.

¹⁹ Clemo and Spence, *J.*, 1928, 2811.

a water-bath, treated with sodium pyrosulphite, cooled, and filtered. The product was continuously extracted with hot metanol for 24 hr., leaving a tan-coloured solid (5.8 g.) (see text). Evaporation of the methanol extract and chromatography of the residue, in benzene, on alumina gave a red solid. This was further purified by vacuum sublimation at 180°/0.25 mm., giving 1',2-di-iodo-1,2'-binaphthyl (1.4 g., 11%) as colourless prisms, m. p. 182—184° (from acetone-methanol) (Found: C, 47.35; H, 2.4. $C_{20}H_{12}I_2$ requires C, 47.5; H, 2.4%).

Dibenzo[a,g]biphenylene.—An intimate mixture of the above di-iodo compound (0.2 g.) with dry cuprous oxide (15 g.) was heated in a cold-finger sublimation apparatus under nitrogen at 15 mm. The bath temperature was raised from 250° to 350° during 15 min. and maintained at 350° for a further 15 min. The orange sublimate was washed off the cold finger with benzene into a benzene solution of 2,4,7-trinitrofluorenone. Addition of methanol precipitated the 2,4,7-trinitrofluorenone complex of *dibenzo[a,g]biphenylene* as deep green needles, m. p. 224—225° (from benzene-methanol) (Found: C, 69.7; H, 3.0; N, 7.6. $C_{33}H_{17}N_3O_7$ requires C, 69.9; H, 3.0; N, 7.4%). The total yield of complex from 8 runs was 0.072 g. (9%, based on starting material consumed). A benzene solution of the complex was passed through an alumina column, the eluate vacuum evaporated below 40°, and the residue rechromatographed in hexane on alumina, giving *dibenzo[a,g]biphenylene* as orange-red plates, m. p. 146—147.5° (decomp.), λ_{max} (EtOH) 213, 271.5, 278, 296, 307.5, 320, 339, 407, 428 m μ (log ϵ 4.29, 4.50, 4.65, 4.02, 4.14, 4.12, 3.19, 3.52, 3.59). Satisfactory analyses could not be obtained on samples which were apparently pure (ultraviolet spectrum) when freshly prepared. Concentration of the pyrolysate mother-liquors gave the 2,4,7-trinitrofluorenone complex of dinaphtho[1,2-b:1',2'-d]furan (0.025 g.) as light red needles, m. p. 229—231° (lit.,¹⁶ 230—231°). Chromatographic cleavage of the complex gave the furan as very pale yellow needles, m. p. 154.5—156° (from hexane) (lit.,¹⁶ 155—156.5°) (Found: C, 89.6; H, 4.5. Calc. for $C_{20}H_{12}O$: C, 89.6; H, 4.5%). λ_{max} (EtOH) 214, 226, 240sh, 246, 260, 268, 292, 305, 325, 339, 350 m μ (log ϵ 4.78, 4.65, 4.62, 4.67, 4.71, 4.72, 4.42, 4.45, 4.50, 4.64, 4.43). Further evaporation of the mother-liquors and chromatography of the residue on alumina in benzene solution gave starting material (0.9 g.).

Dinaphtho[1,2-b:1',2'-d]furan.—(a) 1',2-Diamino-1,2'-binaphthyl (7 g.) was tetrazotised as described above and the tetrazonium solution was warmed on a water-bath until the evolution of nitrogen ceased. The precipitated solid was stirred with 10% sodium hydroxide solution and benzene. The residue from the benzene extract was chromatographed in benzene-hexane on alumina, giving the dinaphthofuran (0.3 g., 4.5%), m. p. 154.5—156°, identical with that from the pyrolysis above. A benzene solution exhibited a strong blue-green fluorescence in ultraviolet light. A strongly adsorbed band (blue fluorescence in ultraviolet light) was extruded from the column. Extraction with chloroform yielded 7*H*-*dibenzo[a,g]carbazole* (0.1 g., 1.5%), m. p. 238—239° (from benzene-hexane).

(b) A suspension of powdered dinaphtho[1,2-b:1',2'-d]furan-12,13-quinone¹⁹ (0.25 g.) in hydriodic acid (6 ml.; *d* 1.7) was refluxed for 70 hr., then diluted with water. The furan (0.2 g., 89%) was collected and washed with sodium hydrogen sulphite solution, when it had m. p. 151—153°.

Reduction of Dibenzo[a,g]biphenylene.—The 2,4,7-trinitrofluorenone complex of the hydrocarbon (35 mg.) was dissolved in the minimum volume of benzene and passed through a short alumina column. Freshly prepared, methanol-wet Raney nickel (~5 g.) was added with swirling to the orange eluate. The colour of the solution was completely discharged after 5 min. The solution was filtered, evaporated, and the residue treated with an equivalent amount of 2,4,7-trinitrofluorenone in acetic acid-ethanol, giving the complex of 1,2'-binaphthyl (24 mg.), m. p. and mixed m. p. 144—145° (lit.,²⁰ 145—147°).

Dinaphtho[1,2-b:1',2'-d]thiophen-7,7-dioxide.—A suspension of dinaphtho[1,2-b:1',2'-d]thiophen²¹ (0.75 g.) in acetic acid (4 ml.) was treated with 30% hydrogen peroxide (3.1 ml.) and refluxed for 1 hr. On cooling, the solid was collected and recrystallised from benzene giving the *dioxide* as yellow needles (0.65 g., 78%), m. p. 244.5—245.5° (Found: C, 76.0; H, 3.8; S, 9.95. $C_{20}H_{12}O_2S$ requires C, 76.0; H, 3.8; S, 10.1%).

THE UNIVERSITY, BRISTOL.

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²⁰ Orchin, Reggel, and Woolfolk, *J. Amer. Chem. Soc.*, 1947, **69**, 1225.

²¹ Rabindran and Tilak, *Proc. Indian Acad. Sci.*, 1953, **38**, A, No. 4, 272.