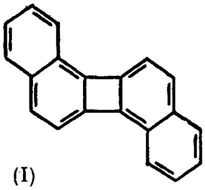
332. *The Synthesis of* 2 : 3-6 : 7-*Dibenzodiphenylene, and a Note on the Reaction of* 1-*Bromo*-2-*iodonaphthalene with Magnesium.*

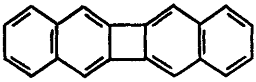
By E. R. Ward and B. D. Pearson.

2 : 3-6 : 7-Dibenzodiphenylene has been synthesised by the pyrolysis of 5 : 6 : 7 : 8 : 5′ : 6′ : 7′ : 8′-octahydro-2 : 2′-dinaphthyl-3 : 3′-iodonium iodide and is accompanied by two other products which appear to be hydrogenated derivatives of the dibenzodiphenylene. The pyrolysis of the corresponding 3 : 3′-tetrazonium sulphate has also been studied.

Four dibenzodiphenylenes are possible; the 1 : 2-5 : 6- (I), 1 : 2-6 : 7-, 1 : 2-7 : 8- and 2 : 3-6 : 7-isomers (II). Brief details of the synthesis of the last were given by Curtis and Viswanath[1] in 1954 and the synthesis of the third was described fully by Cava and Stucker[2] in 1955. As a first step in a study of the preparation and properties of dibenzodiphenylenes, we investigated the synthesis of the 2 : 3-6 : 7-isomer (II), since the third does not appear to be very stable. Our independent synthesis followed the second route described fully by Curtis and Viswanath,[3] and our results obtained closely parallel theirs, although at some stages our yields were higher. Thus, contrary to our previous experience[4] we were able, by using a new procedure, satisfactorily to nitrate 6-acetamido-1 : 2 : 3 : 4-tetrahydronaphthalene in reasonably large amounts and our yields were appreciably greater than those of Schroeter.[5] Like Curtis and Viswanath,[3] in the final pyrolysis of 5 : 6 : 7 : 8 : 5′ : 6′ : 7′ : 8′-octahydro-2 : 2′-dinaphthyl-3 : 3′-iodonium iodide with cuprous oxide, we obtained varying results for which we could not account but which seemed to depend on the activity of the oxide used (cf. Cava and Stucker[2]). Our pyrolyses were carried out in nitrogen under reduced pressure, and in one experiment we obtained the



(I)



(II)

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[1] Curtis and Viswanath, *Chem. and Ind.*, 1954, 1174, 1397.

[2] Cava and Stucker, *J. Amer. Chem. Soc.*, 1955, **77**, 6022.

[3] Curtis and Viswanath, preceding paper.

[4] Ward and Coulson, *J.*, 1954, 4545.

[5] Schroeter, *Annalen*, 1922, **426**, 1.

dibenzodiphenylene (II) in 4·5% yield, together with another yellow substance (*A*), m. p. 224—226°. However, in another experiment we obtained very thin pale yellow plates (*B*), m. p. 300—302°, together with more of (*A*). Like the dibenzodiphenylene (II), (*B*) but not (*A*) displayed, in dilute benzene, a strong blue fluorescence which disappeared on concentration. The ultraviolet spectra suggest that both (*A*) and (*B*) contain the 2 : 3-6 : 7-dibenzodiphenylene skeleton; (*A*) may be an octahydro-compound and (*B*) a tetrahydrodibenzodiphenylene. Further attempts to prepare the dibenzodiphenylene (II) by reaction of magnesium with 2-bromo-3-iodonaphthalene (see below) or by the pyrolysis of 5 : 6 : 7 : 8 : 5′ : 6′ : 7′ : 8′-octahydro-2 : 2′-dinaphthyl-3 : 3′-tetrazonium sulphate with cuprous oxide at red heat, under a reduced pressure of nitrogen, failed. In the latter experiment two apparently pure crystalline products were obtained: one possibly 2 : 3-6 : 7-dibenzocarbazole (ultraviolet spectra; analysis), the other an octahydrodibenzocarbazole, though not identical with the octahydrodibenzocarbazole reported by Curtis and Viswanath.[3]

FIG. 1.

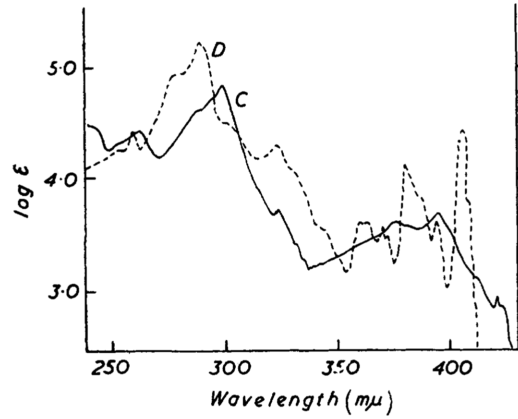

FIG. 2.

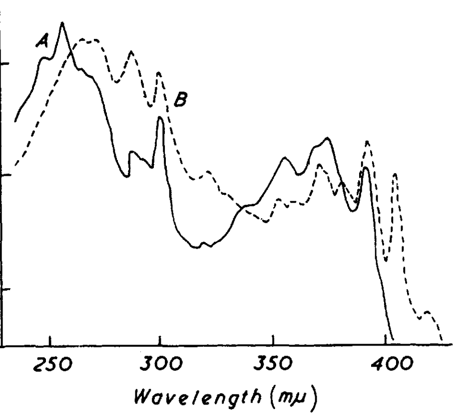

FIG. 1. *Ultraviolet spectra of* 2 : 3-6 : 7-*dibenzodiphenylene* (II) (D) *and substance* (C), *possibly* 1 : 2-5 : 6-*dibenzodiphenylene* [$\lambda_{max.}$ in mμ (log ε) 261 (4·37), 297 (4·82), 324 (3·66), 375 (3·62), 381 (3·59), 394 (3·71), 420 (2·93); $\lambda_{min.}$ 248 (4·23), 271 (4·16), 321 (3·63), 337 (3·17), 379 (2·57), 383 (3·55), 419 (2·80); λ_{sh} 241 (4·45), 288 (4·62), 293 (4·68), 340 (3·20), 411 (3·10), 423 (2·84)].

FIG. 2. *Ultraviolet spectra of substances* (A) *and* (B) *obtained by pyrolysis of* 5 : 6 : 7 : 8 : 5′ : 6′ : 7′ : 8′-*octahydro*-2 : 2′-*dinaphthyl*-3 : 3′-*iodonium iodide*: *Substance* (A) $\lambda_{max.}$ (mμ) 249, 258, 266, 288, 295, 300, 319, 339, 356, 375, 393; $\lambda_{min.}$ 253, 264, 286, 292, 297, 316, 324, 342, 363, 386.

Substance (B) $\lambda_{max.}$ 265, 272, 287, 300, 322, 353, 359, 371, 381, 393, 406, 419; $\lambda_{min.}$ 270, 281, 296, 316, 348, 356, 364, 378, 387, 401, 416.

Other spectra recorded, but not illustrated are:

(*a*) 3 : 3-Dinitro-5 : 6 : 7 : 8 : 5′ : 6′ : 7′ : 8′-octahydro-2 : 2′-dinaphthyl: $\lambda_{max.}$ 280 (4·15), $\lambda_{min.}$ 256 (4·12) λ_{sh} 352 (3·35), 378 (2·82).

(*b*) 3 : 3′-Diamino-5 : 6 : 7 : 8 : 5′ : 6′ : 7′ : 8′-octahydro-2 : 2′-dinaphthyl: $\lambda_{max.}$ 303 (3·81), $\lambda_{min.}$ 283 (3·69), λ_{sh} 348 (3·27).

(*c*) Products from pyrolysis of 5 : 6 : 7 : 8 : 5′ : 6′ : 7′ : 8′-octahydro-2 : 2′-dinaphthyl-3 : 3′-tetrazonium sulphate.

(i) A dibenzocarbazole (?): $\lambda_{max.}$ 245, 254, 267, 273, 279, 290, 300, 314, 319, 334, 360, 378; $\lambda_{min.}$ 261, 286, 296, 305, 316, 323, 354, 372.

(ii) An octahydrodibenzocarbazole (?): $\lambda_{max.}$ (mμ) 248, 256, 266, 301, 306, 312, 335, 337, 342, 349; $\lambda_{min.}$ (mμ) 251, 262, 271, 304, 309, 332, 336, 240, 346.

All spectra were recorded by a Unicam S.P. 500 photoelectric spectrophotometer on ethanol solutions.

Heaney, Mann, and Millar[6] obtained diphenylene, in 3·5% yield, by reaction of magnesium (2·2 equiv.) with ethereal *o*-bromoiodobenzene. McOmie and his co-workers[7] have prepared substituted diphenylenes, in low yield, by a similar method. We were

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[6] Heaney, Mann, and Millar, *J.*, 1957, 3930.

[7] McOmie, personal communication.

unable to make ethereal 2-bromo-3-iodonaphthalene react, but found that ethereal 1-bromo-2-iodonaphthalene would react with *ca.* 1 equiv. of magnesium. After carboxylation, a solid product was isolated, and fractional crystallisation of this gave 2 : 2′-dinaphthyl, a small amount of thin orange plates (*C*); but mainly a heavy viscous oil which could not be purified. The ultraviolet spectrum of material (*C*) suggests that it may be 1 : 2-5 : 6-dibenzodiphenylene (I) as it strongly resembles the spectra of the 1 : 2-7 : 8- and 2 : 3-6 : 7-compounds. When this experiment was repeated on a double scale the yield of (*C*) was even smaller.

EXPERIMENTAL

1-*Bromo*-2-*iodonaphthalene*.—1-Bromo-2-naphthylamine (10 g.) was dissolved in warm sulphuric acid (*d* 1·84; 7 c.c.)–water (20 c.c.) and diazotised, at 0°, by rapid addition of sodium nitrite (5 g.) in water (15 c.c.). The diazonium solution was added to one of iodine (6 g.) and potassium iodide (18 g.) in water (120 c.c.) with stirring, and after 1 hr. the solids were collected. These were shaken with 10% w/v aqueous sodium thiosulphate (200 c.c.), collected again, washed with water, dried, and dissolved in benzene. The solution was filtered through alumina and allowed to crystallise; the product (6·0 g., 45%) had m. p. 94° (from benzene) (Meldola [8] gives m. p. 94°).

2-*Bromo*-3-*iodonaphthalene*.—3-Bromo-2-naphthylamine (10 g.) was dissolved in a solution of sodium nitrite (4 g.) in sulphuric acid (*d* 1·84; 40 c.c.), and the mixture stirred into acetic acid (80 c.c.) below 30°. After 1 hr. the diazonium solution was decomposed as above, and the product collected and washed as before, giving crude 2-*bromo*-3-*iodonaphthalene* (10 g., 75%); m. p. 120° from ethanol–ethyl acetate (2 : 1 v/v) (Found: C, 36·0; H, 1·9; Halogen, 61·8. $C_{10}H_6BrI$ requires C, 36·0; H, 1·8; Halogen, 62·2%).

2-*Iodo*-3-*nitronaphthalene*.—A solution of 3-nitro-2-naphthylamine (10 g.) in acetic acid (120 c.c.) was slowly added, with stirring, to one of sodium nitrite (4 g.) in sulphuric acid (*d* 1·84; 40 c.c.) below 30°. Crude 2-iodo-3-nitronaphthalene (14 g., 88%), was obtained, by the procedure given for the preparation above, m. p. 89° (from ethanol). (Cumming and Howie [9] give m. p. 89°.)

Nitration of 6-*Acetamido*-1 : 2 : 3 : 4-*tetrahydronaphthalene*.—The amide [4] (50 g.) in acetic anhydride (810 c.c.) was treated dropwise (*ca.* 80 min.), with stirring, with a mixture of acetic anhydride (16·7 c.c.) and nitric acid (*d* 1·42; 16·7 c.c.), the temperature being kept below 25°. Next morning, the mixture was poured, with stirring, into ice–water (5 l.) which yielded a sticky product. Most of the liquid was siphoned off and replaced by warm water, and further stirring then gave a granular product (cf. Ward and Coulson [4]). This was collected, washed with water, dried, and crystallised from hot ethanol (*ca.* 170 c.c.), yielding almost pure 6-acetamido-1 : 2 : 3 : 4-tetrahydro-7-naphthalene (yields 35—39%). Further amounts were obtained (total yield *ca.* 42%) by evaporation of the ethanolic mother-liquor to dryness and separation from accompanying 5-nitro-isomer by chromatography on alumina in benzene–ethyl acetate (2 : 1 v/v).

1 : 2 : 3 : 4-*Tetrahydro*-6-*iodo*-7-*nitronaphthalene*.—This was prepared by diazotising [10,11] the above amine, and adding the diazonium solution to aqueous iodine–potassium iodide, underlaid with chloroform (cf. Kharasch, Kalfoyan, and Arterberry [12]), the product being obtained from the chloroform layer. Yields varied from 60 to 80% but the m. p. could not be raised to that given by Cumming and Howie,[9] *viz.*, 76°, despite repeated crystallisation. However, the compound behaved satisfactorily subsequently.

3 : 3′-*Dinitro*-5 : 6 : 7 : 8 : 5′ : 6′ : 7′ : 8′-*octahydro*-2 : 2′-*dinaphthyl*.—The halogeno-compound (1 g.) was heated to 132° in a constant-temperature heater,[13] and copper-bronze (0·6 g.) added portionwise, with good stirring, during 30 min., the temperature being kept below 140°; and the heating was continued for a further 30 min. The product was extracted with hot benzene (3 × 50 c.c.) and chromatographed on alumina; the first orange band gave the required dinaphthyl, m. p. 190—191° (0·42 g., 73%). This material was used in the next stage but it

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[8] Meldola, *J.*, 1885, 497.
[9] Cumming and Howie, *J.*, 1931, 3176.
[10] Hodgson and Walker, *J.*, 1933, 1620.
[11] Hodgson and Turner, *J.*, 1943, 86.
[12] Kharasch, Kalfoyan, and Arterberry, *J. Org. Chem.*, 1956, **21**, 925.
[13] Tucker, *J. Chem. Educ.*, 1953, **30**, 634.

could be purified by crystallisation from boiling ethanol–ethyl acetate (1 : 1 v/v), giving m. p. 197—198° (Cumming and Howie [9] give m. p. 201°).

3 : 3′-*Diamino*-5 : 6 : 7 : 8 : 5′ : 6′ : 7′ : 8′-*octahydro*-2 : 2′-*dinaphthyl*.—The nitro-product (3·5 g.) was dissolved in ethyl acetate (165 c.c.) and ethanol (15 c.c.) in the presence of B.D.H. stabilised Raney nickel (3 g.), and treated with hydrogen at *ca.* 75° and atmospheric pressure. After 8 hr. *ca.* 2 l. of hydrogen had been taken up and reduction appeared to be complete. After removal of catalyst the solution was concentrated to 60 c.c., yielding almost pure diamine (1·56 g.). More was obtained by evaporating the solution to dryness and extracting the residue with hydrochloric acid (*d* 1·2; 2 × 30 c.c.). The diamine (total yield 2·2 g., 76%) had m. p. 193—194°, from ethyl acetate–ethanol (1 : 1 v/v) (Found: C, 81·1; H, 8·1; N, 9·15. Calc. for $C_{20}H_{24}N_2$: C, 82·15; H, 8·3; N, 9·6%). Reduction at room temperature with hydrazine in the presence of Raney nickel or palladised charcoal was not successful.

Preparation and Pyrolysis of the 3 : 3′-*Iodonium Iodide*.—The diamine (0·15 g.) in hydrochloric acid (*d* 1·2; 1·5 c.c.)–water (2 c.c.) was treated at 0° with sodium nitrite (0·2 g.) in water (1 c.c.), and the diazonium solution decomposed by addition to iodine (0·3 g.) and potassium iodide (1 g.) in water (20 c.c.). After 1 hour's stirring, the solids were collected, dried, and extracted with benzene (200 c.c., Soxhlet). The residual iodonium iodide (0·24 g., 92%) was insoluble in boiling water or acetone, and decomposed at 240—245°. Diazotisation by Hodgson and Walker's method [10] and similar decomposition gave 83% yield. The benzene extract from either method was washed with aqueous sodium thiosulphate and water, dried, and chromatographed on alumina. After elution of a tarry band, further elution by benzene–ethyl acetate (1 : 2 v/v) gave green crystals (0·016 g.), m. p. 208° unchanged by further crystallisation from benzene.

An intimate mixture of the iodonium iodide (*ca.* 0·3 g.) and cuprous oxide (3 g.), in an atmosphere of nitrogen at 0·3 mm., was heated at 340° in a sand-bath for 30 min.; then the temperature allowed to fall to *ca.* 220° at which it was kept for 1 hr. The product was extracted with benzene (150 c.c.; Soxhlet) for 8 hr., and the solution concentrated to 20 c.c., very thin, pale yellow plates crystallising. The benzene mother-liquor was chromatographed on alumina, giving a yellow solid, which formed yellow needles from ethanol.

(*a*) When freshly prepared cuprous oxide was used, 0·288 g. of iodonium iodide afforded very thin yellow plates of (II), which sublimed at 344—346° without melting (5 mg., 4·5%). The ultraviolet spectrum of this was identical with that recorded by Curtis and Viswanath.[3] The yellow needles (*A*) (3 mg.) had m. p. 224—226°.

(*b*) With an old sample of cuprous oxide, 0·3 g. of iodonium iodide afforded very thin pale yellow plates (*B*), m. p. 300—302° (4 mg.; 2·6% calc. as a *tetrahydrodibenzodiphenylene*) (Found: C, 93·2; H, 6·0. $C_{20}H_{16}$ requires C, 93·8; H, 6·2%), and yellow needles, m. p. 224—226° (4 mg.).

Preparation and Pyrolysis of the 3 : 3′-*Tetrazonium Sulphate*.—The appropriate diamine (0·5 g.) was dissolved in a solution of sodium nitrite (0·4 g.) in sulphuric acid (*d* 1·84; 4 c.c.) and added with stirring to acetic acid (9 c.c.), below 30°. After 1 hour's stirring, ice-cold dry ether (100 c.c.) was added, and then after 1 hr. at room temperature the tetrazonium sulphate was collected, washed with acetic acid–ether (1 : 1 v/v), and then with ether alone, and dried under reduced pressure (*ca.* 0·8 g.). This was ground with cuprous oxide (7 g.), the mixture covered with more cuprous oxide (5 g.), and the whole pyrolysed at dull red heat, in nitrogen at 0·3 mm. After cooling *in vacuo*, the mixture was extracted by benzene (200 c.c.; Soxhlet); the extract on concentration to *ca.* 30 c.c. gave pale yellow crystals which, recrystallised from benzene, had m. p. 299—301° (subliming above 285°) (5 mg.) (Found: C, 89·9; H, 5·2. A *dibenzocarbazole*, $C_{20}H_{13}N$, requires C, 89·9; H, 4·9%). The mother-liquors were chromatographed on alumina giving, by elution with benzene, a solid (36 mg.), m. p. 157—158° (from ethanol) (Found: C, 86·9; H, 7·9. An *octahydrodibenzocarbazole*, $C_{20}H_{21}N$, requires C, 87·3; H, 7·6%). Further elution with ethyl acetate gave a yellow residue (3 mg.) not investigated further.

Interaction of 1-*Bromo*-2-*iodonaphthalene with Magnesium*.—1-Bromo-2-iodonaphthalene (11 g.) in ether (120 c.c.) was added during 30 min. to a stirred mixture of magnesium (1·75 g., 2·2 equiv.) and ether (50 c.c.), the reaction being initiated by addition of iodine and a trace of methylmagnesium iodide, and conducted under nitrogen. After 1 hour's refluxing, dry benzene (60 c.c.) was added at 0°, and refluxing continued for a further hour. Unchanged magnesium was removed, and carboxylation carried out by pouring on to a slurry of ether and solid carbon dioxide followed by acidification with 20% w/v hydrochloric acid (500 c.c.). Fractional crystallisation from benzene of solids from the ether layer gave 2 : 2′-dinaphthyl (0·5 g.), some orange *plates* (12 mg.), m. p. 271° (Found: C, 92·0; H, 6·0. $C_{20}H_{12}$ requires C, 95·2; H, 4·8%), and a heavy viscous liquid which could not be distilled at 3 mm. The red *trinitrofluorenone* derivative of the plates had m. p. 267° (Found: C, 70·8; H, 5·2. $C_{33}H_{17}O_7N_3$ requires C, 69·9; H, 3·0%).

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