

Two Syntheses of Dibenzo[*b,h*]biphenylene

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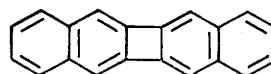
A one-step preparation of dibenzo[*b,h*]biphenylene *via* naphthalene is described, as well as a multi-step synthesis *via* biphenylene. Both routes yield about 2% of the hydrocarbon from commercially available materials.

SINCE the first multi-step synthesis of dibenzo[*b,h*]biphenylene (1) by Curtis and Viswanath,^{1a} several new syntheses have been reported.¹ However, these employ the relatively inaccessible 2,3-dihalogenonaphthalenes as precursors and proceed in low yields (1–2%). We describe here two new synthetic routes from readily available materials. While our work was in progress, Barton and Jones² reported a three-step synthesis from 2,3-diaminonaphthalene in which the final step gives a high yield.

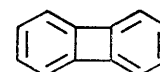
Biphenylene (2) has been prepared by decomposition

¹ (a) R. F. Curtis and G. Viswanath, *J. Chem. Soc.*, 1959, 1670; (b) E. R. Ward and B. D. Pearson, *ibid.*, p. 1676; B. D. Pearson, *Chem. and Ind.*, 1960, 899; E. R. Ward and J. E. Marriott, *J. Chem. Soc.*, 1963, 4999.

of benzenediazonium-2-carboxylate in 1,2-dichloroethane;³ we have investigated an analogous route from



(1)



(2)

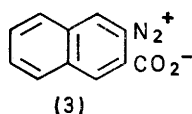
the commercially available 3-amino-2-naphthoic acid. The reported procedure for the preparation of benzenediazonium-2-carboxylate,⁴ applied to the preparation of the naphthalene analogue (3) gave a red solid, pre-

² J. W. Barton and S. A. Jones, *J. Chem. Soc.*, 1967, 1276.

³ L. Friedman and A. M. Seitz, personal communication.

⁴ L. Friedman and F. M. Logullo, *J. Amer. Chem. Soc.*, 1963, 85, 1549; *J. Org. Chem.*, 1969, 34, 3089.

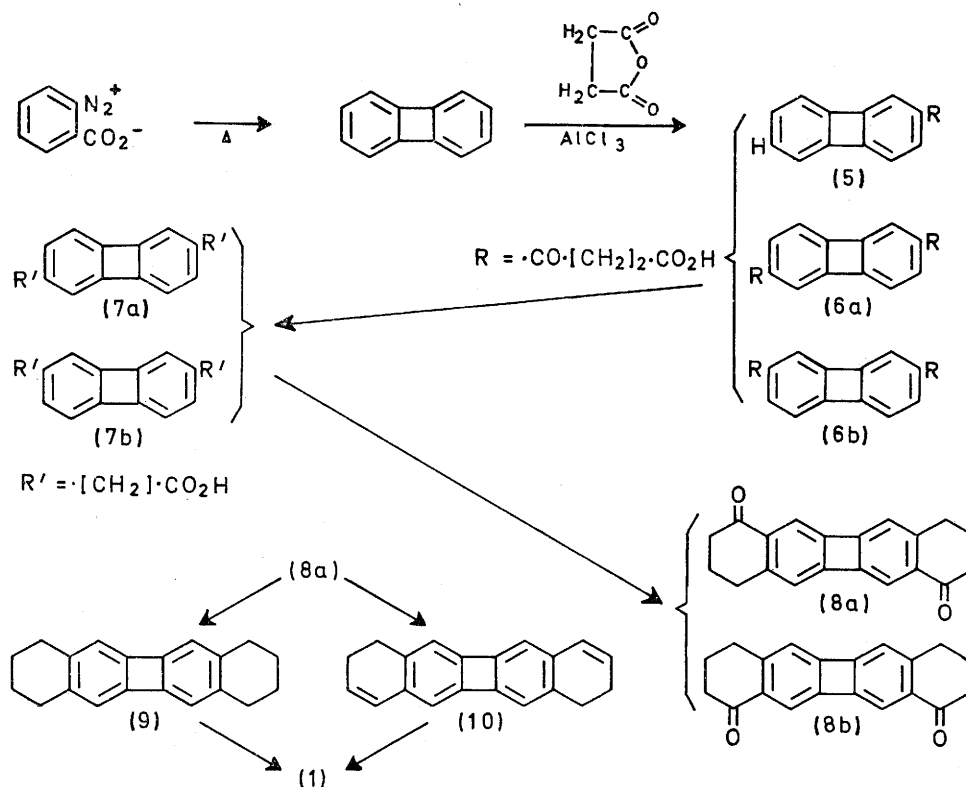
sumably a coupling product. However compound (3) could be obtained by slow addition of 3-amino-2-



naphthoic acid in tetrahydrofuran to a solution of isopentyl nitrite in tetrahydrofuran containing catalytic

residue of fairly pure dibenzo[*b,h*]biphenylene. Although the scale of the reaction is limited by the necessity of employing large volumes of solvent, the naphthalene route is convenient for the preparation of 0.1 g batches of hydrocarbon (1).

The second synthesis is outlined in Scheme 1. Biphenylene was prepared according to the benzyne route of Friedman⁴ in about 25% yield from anthranilic acid. Succinylation under Friedel-Crafts conditions⁶ in



SCHEME 1

amounts of trichloroacetic acid. The diazonium salt (3) is more stable than the benzene analogue,⁵ especially in an inert atmosphere, and may be stored in the refrigerator under nitrogen for several months without apparent decomposition. Solid (3) detonates at *ca.* 99 °C when heated in a capillary tube. Since the decomposition of the diazonium carboxylate (3) is slow at the b.p. of 1,2-dichloroethane (83°), solvents with higher b.p.s were tried (see Table). The best yield (1.4–2.7%) of hydrocarbon (1) was obtained by use of 1,2,3-trichloropropane (b.p. 157°).

The product was isolated by preliminary treatment to remove acidic by-products, followed by trituration of the remaining material with ethanol, which selectively extracted the remaining polar by-products and left a

tetrachloroethane gave three products, (5), (6a), and (6b). The 2-acid (5) and the 2,6-diacid (6a) were

Solvent ^a	Temp./°C	Yield (%) ^b
1,2-Dichloroethane	82	0.07 ^c
Tetrachloroethane	120	0.45 ^d
	144–145	0.9
Pentachloroethane	156–158	0
1,2,3-Trichloropropane	156–157	1.49
Dimethylene glycol diethyl ether	160	0.2 ^e
Diethylene glycol diethyl ether	180–184	0
	145	0
Perfluorokerosene (high-boiling; Peninsular Chemresearch, Inc.)	145	0.1 ^f
1,4-Dichlorobutane	154	0.1 ^f
Decalin	135 ^{f,g}	
<i>o</i> -Dichlorobenzene	100	0.06

^a The decompositions were conducted with 20 ml. of solvent for 780 mg. of diazonium salt. ^b Determined by u.v. spectroscopy. ^c Slow decomp. ^d 2-Chloronaphthalene (isolated). ^e Rapid decomp. ^f Yellow gas evolved. ^g Small amount of 2-naphthoic acid isolated.

⁵ This diazonium salt is potentially explosive and appropriate precautions are advised (see ref. 4); L. F. Fieser and M. J. Haddadim (*Canad. J. Chem.*, 1965, **43**, 1599) have prepared naphthalene in solution in the presence of dienophiles and report no difficulties.

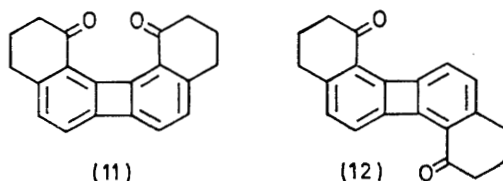
⁶ E. Berliner, *Org. Reactions*, 1952, **5**, 229.

isolated and characterized. The presence of the 2,7-diacid (6b) as a contaminant of (6a) was inferred by the

subsequent formation and isolation of small amounts of the *cis*-diketone (8b). Similar preferential formation of the 2,6-isomer accompanied by smaller amounts of the 2,7-isomer was observed by Blatchly, Boulton, and McOmie⁷ in related Friedel-Crafts reactions of (2). The succinylation reaction was erratic and gave variable amounts of the mono- and di-acids. The yield of diacid was 28% from a reaction at room temperature, but more typical yields were only about half of that.

The n.m.r. and i.r. spectra of the diacid (6a) were consistent with the assigned structure. The electronic absorption spectrum was similar to those of 2,6-diacetyl- and 2,6-dipropionylbiphenylene.⁷ The diacid apparently exhibits polymorphism; it gave a methyl ester with the expected properties, which on hydrolysis yielded a solid acid with a different m.p. and uniquely different i.r. fingerprint spectrum (KBr disc).⁸ The n.m.r. spectra of both samples in solution were identical.

The crude diketone-diacid mixture (6a and b) was reduced to a mixture of di-acids (7a and b) by the Huang-Minlon modification of the Wolff-Kishner method⁹ (yield 70%). Cyclization of the mixture (7a and b) was attempted with both anhydrous hydrofluoric acid and polyphosphoric acid.¹⁰ The latter was the more effective and yielded 70% of cyclized diketone (8a). The n.m.r. spectrum of the product has two broad singlets (each 2H) about 40 Hz apart in the aromatic region, as expected.¹¹ Structures (11) and (12) would show quartets in the aromatic region. Less symmetrical structures are similarly excluded.

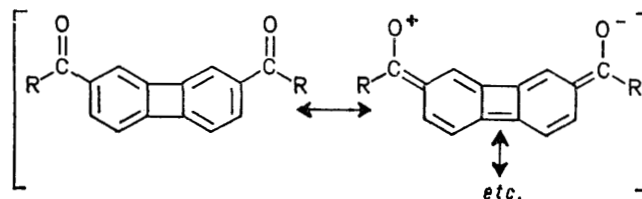


From the cyclization reaction a second, isomeric diketone (8b) could be isolated in a yield of 1–2%. The m.p., t.l.c., R_F value, and n.m.r., i.r., and u.v. spectra (see later) were similar to but distinguishable from those of (8a). The mass spectrum of (8b) had a parent ion at m/e 288 and a fragmentation pattern similar to that of (8a).

In the u.v. diketone (8b) absorbs at longer wavelengths than (8a) just as other 2,7-diacylbiphenylenes absorb at longer wavelengths than the corresponding 2,6-diacylbiphenylenes.⁷ This might be due to the contribution of the charge-separated quinonoid resonance structures that are possible only with the 2,7-isomer.

Ketone (8a) was converted into dibenzo[*b,h*]bi-

phenylene in two ways. In the first the ketone was reduced to octahydrodibenzo[*b,h*]biphenylene (9) (46%) by the Huang-Minlon method.⁹ The u.v. spectrum of



(9) was similar to that of 2,3,6,7-tetramethylbiphenylene.¹² Its n.m.r. spectrum consists of a singlet, τ (C_6D_6) 3.75 (4H), and A_2B_2 multiplets at τ 7.62 and 8.50 (8H each). An earlier report of an indirect synthesis of (9) seems to be incorrect.¹⁰ Hydrocarbon (9) was converted into dibenzo[*b,h*]biphenylene (1) in poor yield (5%) by heating with selenium.

Conversion of (6a) into (1) was better achieved by reduction of the diketone to a diol with lithium aluminum hydride which could then be dehydrated (80–90% for both steps) with 50% aqueous hydrochloric acid to give the hydrocarbon (10). This could be dehydrogenated by any of the reagents: selenium, 2,3,5,6-tetrachloro-1,4-benzoquinone, and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). The last was the most suitable and gave compound (1) in 80–90% yield.

The overall yield of compound (1) based on anthranilic acid is only 2.5%, which is not much better than the one-step naphthalene preparation. The multistep approach could prove useful for the preparation of substituted dibenzo[*b,h*]biphenylenes.

EXPERIMENTAL

M.p.s were taken with a Thomas-Hoover apparatus. Microanalyses were performed by the Galbraith Laboratories, Knoxville, Tennessee, or Scandinavian Microanalytical Laboratories, Denmark.

Naphthalene-2-diazonium-3-carboxylate.— 3-Amino-2-naphthoic acid (9.35 g, 0.05 mol) in tetrahydrofuran (THF) (1 l) was added during 9.5 h to a stirred solution of isopentyl nitrite (34 ml) and trifluoroacetic acid (69 mg; handled as a 1.5% solution in THF) in THF (1 l). The red mixture was then cooled below 10° and the precipitate was filtered off and washed with cold THF. The resulting brick-red powder was dried under a stream of nitrogen. The dry diazonium carboxylate (7.50 g, 76%) detonated at 99° (in a capillary); ν_{max} (Nujol) 2280 ($N=N$), 1648, and 1630 cm^{-1} , similar to that reported for benzenediazonium-2-carboxylate.¹³

The salt appeared to be stable at room temperature. During several days a red crust formed on the exposed surface of a sample stored in a stoppered bottle. However, when the bottle was flushed with dry nitrogen and stored

⁷ J. M. Blatchly, A. J. Boulton, and J. F. W. McOmie, *J. Chem. Soc.*, 1965, 4930.

⁸ C. N. R. Rao, 'Chemical Applications of Infrared Spectroscopy,' Academic Press, New York, 1963, p. 62. Alternatively, formation of a monoketol monoacid could accommodate our observations (see J. F. Grove and H. A. Willis, *J. Chem. Soc.*, 1951, 877).

⁹ Huang-Minlon, *J. Amer. Chem. Soc.*, 1946, **68**, 2487.

¹⁰ F. Uhlig and H. R. Snyder, *Org. Chem.*, 1960, **1**, 35.

¹¹ F. Uhlig and H. R. Snyder, *Adv. Org. Chem.*, 1960, **1**, 35.

¹² R. H. Martin, J. P. Van Trappen, N. Defay, and J. F. W. McOmie, *Tetrahedron*, 1964, **20**, 2373.

¹³ W. Baker, J. W. Barton, and J. F. W. McOmie, *J. Chem. Soc.*, 1958, 2666.

¹⁴ M. Stiles, R. G. Miller, and U. Burkhardt, *J. Amer. Chem. Soc.*, 1963, **85**, 1792.

in a refrigerator, the salt remained unchanged for several months. It was prepared about thirty times without incident; however, it is a potential explosive and should be treated as such. When 0.6 g of the salt in a thimble of a Soxhlet extractor came into contact with the vapour of 1,1,2,2-tetrachloroethane a violent explosion took place.

Dibenzo[b,h]biphenylene from Naphthalene-2-diazonium-3-carboxylate.—Most of the exploratory work (see Table 1 and Discussion section) was carried out on a small scale. In the procedure described here a large amount of the dibenzobiphenylene was precipitated and was isolated immediately rather than carried along as in the small-scale experiments.

A slurry of the diazonium salt (7.5 g) in 1,2,3-trichloropropane (60 ml) was added slowly (10 min) to boiling (156–157°) 1,2,3-trichloropropane (240 ml) with stirring. The solid decomposed immediately with vigorous evolution of gas. The resulting solution, when cooled to room temperature (overnight) deposited a solid, which was filtered off and washed with 1,2,3-trichloropropane (30 ml) and diethyl ether (100 ml) to leave 183 mg of material.

The 1,2,3-trichloropropane fraction of the filtrate was evaporated at 70° and 40 mmHg. The residue was boiled with a mixture of ethanol (95%; 500 ml) and 12% sodium hydroxide (200 ml) for 1 h. The warm solution was filtered and the residue was washed successively with ethanol and water. The dried residue (and filter paper) was leached with hot 1,2-dichloroethane (*ca.* 100 ml). The solution was filtered hot, diluted to *ca.* 250 ml with dichloroethane, and passed through a short alumina column (30 g); the eluate was concentrated to *ca.* 40 ml. The precipitated solid was filtered off and dried to yield dibenzobiphenylene (28 mg). The combined product yielded light yellow crystals (163 mg) [from 1,2-dichloroethane (200 ml)], identified by comparison of u.v. and i.r. spectral data. More dibenzobiphenylene was recovered from the mother liquor; overall yield 173 mg (2.7%).

2,6- (and 2,7-)Bis-(3-carboxypropionyl)biphenylene (6a and b).—Small-scale Friedel–Crafts acylations with varied ratios of reactants and catalyst and of the temperature were run in an effort to find the conditions for maximum bisacylation. No obvious pattern emerged; a representative medium scale acylation is described.

A suspension of succinic anhydride (2.40 g, 0.24 mmol) and powdered aluminium chloride (5.85 g, 44 mmol) in tetrachloroethane (TCE) (75 ml) was maintained at about 0 °C while a solution of biphenylene (1.52 g, 10 mmol) in TCE (25 ml) was added dropwise during *ca.* 20 min. The mixture was allowed to warm to room temperature and stirred for 12 h. The mixture was acidified with 50% hydrochloric acid (60 ml) (ice) and the resulting two-phase suspension was steam-distilled. The residue was taken up in sodium carbonate solution, which, after filtration, was acidified to give a yellow solid (2.13 g), m.p. 200–210°. Extraction of refluxing 95% ethanol (150 ml) left the crude diacid (*ca.* 1 g), m.p. 270–274° (decomp.). The cooled extract deposited more diacid (0.36 g), m.p. 290–292° (decomp.). Concentration of the filtrate deposited a new yellow solid (0.6 g) subsequently identified as largely the monoacid.

The crude *diacid* showed ν_{\max} (Nujol or KBr disc) 910 and 824 cm^{-1} (also C=O and CO₂H bands); τ (sodium salt in D₂O) 2.70 (2H, d, AB, *J* 7.3 Hz), 3.14 (2H, s), 3.45 (2H, d, AB, *J* 7.3 Hz), and 7.02 and 7.60 (8H, m, A₂B₂) (Found:

C, 68.1; H, 4.1%; Equiv., 171. C₂₀H₁₆O₆ requires C, 68.2; H, 4.6%; Equiv., 176).

A sample of the diacid was converted (66%) into the yellow dimethyl ester, m.p. 215–215.5°, ν_{\max} 1670 (conj. C=O), 1734 (ester C=O), and 833 cm^{-1} (1,2,4-trisubstituted benzene), with methanol and catalytic amounts of sulphuric acid in refluxing 1,2-dichloroethane. The diester was hydrolysed to a diacid, m.p. 308–310° (decomp.), with i.r. fingerprint absorption (KBr) different from that of the precursor diacid (852, 802, and 794 cm^{-1}). The n.m.r. spectrum (solution) was identical with that of the previous diacid, and the u.v. spectrum (sodium salt in H₂O) showed λ_{\max} 228 (log ϵ 4.08), 261 (4.55), 286 (4.60), 290 (4.61), 349 (3.56), 361 (3.94), and 377.5 (4.07) nm. The new diacid gave a dimethyl ester identical with that obtained from the first diacid.

Both diacids could be converted in 60% yield into the same *diethyl ester*, m.p. 184–185°, ν_{\max} 740 and 805 cm^{-1} ; τ (CDCl₃) 8.75 (6H, t, *J* 7.0 Hz, O·CH₂·CH₃), 7.3 (4H, t, *J* 6 Hz, A₂B₂, CH₂·CH₂), 6.85 (4H, t, *J* 6 Hz, CH₂·CH₂), 5.86 (4H, q, *J* 7.0 Hz, O·CH₂·CH₃), 3.25 (2H, d, *J* 7.8 Hz, aromatic AB), 2.58 (2H, d, *J* 7.8 Hz, aromatic AB), and 2.74br (2H, s, aromatic); *m/e* (70 ev) 409 (18%), 408 (65.9), 363 (27), 307 (100), 308 (21.2), 279 (4.9), 206 (2.6), 178 (34), 177 (7.5), 151 (5.3), 150 (21.2), 131 (6.0), 103 (17.4), 89 (9.0), 75 (5.3), and 55 (7.5) (Found: C, 70.5; H, 5.7. C₂₄H₂₄O₆ requires C, 70.6; H, 5.9%).

It was concluded that the diacid existed in polymorphic forms possessing different i.r. spectra.

An alternate explanation is that one of the two forms is a monolactol (neither can be a dilactol since both forms exhibit two carbonyl bands). Both the diacid and the monolactol might reasonably be expected to give the same diketodiester.

2,6- (and 2,7-)Bis-(3-carboxypropyl)biphenylene (7a).—A solution of the diacid (6a) (7.69 g, 21.8 mmol), sodium hydroxide (7.08 g), and 85% aq. hydrazine (10 ml, *ca.* 265 mmol) in diethylene glycol (85 ml) was heated at 100–110 °C for 2 h. The bulk of the water and hydrazine was then distilled off (bath temp. up to 200°). After 2 h at this temperature the mixture was cooled and poured into water (400 ml). Acidification with 50% hydrochloric acid gave a solid product that was purified by repeated centrifugation with water until the supernatant liquid was free of acid. The product (6.62 g, 93%) yielded a yellow solid (3.96 g), m.p. 203–204.5° [from methanol (205 ml)]. Concentration of the mother liquor afforded a second crop (1 g).

The combined solids, dissolved in methanol, were passed through a column of silica gel (250 g, Will Corp.) (1.5 l of methanol used). The eluate yielded a yellow solid (4.8 g) which was employed without further purification. A sample of the *diacid* recrystallized from ethanol had m.p. 194–195.5°, ν_{\max} (KBr disc) 1695 (acid C=O) and 826 (1,2,4-trisubstituted benzene) cm^{-1} ; τ (sodium salt in D₂O) 3.55 (6H, m) and 7.9 and 8.2 (12H, m); λ_{\max} (MeOH) 365 (log ϵ 4.06), 350 (3.83), 345 (3.86), 253 (5.04), and 244 (4.78) nm (Found: C, 73.9; H, 6.3%; *M*, 317. C₂₀H₂₀O₄ requires C, 74.1; H, 6.2%; *M*, 324).

The mother liquor from the crystallizations was evaporated to leave a light yellow solid (1.4 g), which contained mainly compound (7a) (analysis).

3,4,9,10-Tetrahydrodibenzo[b,h]biphenylene-1(2H),7(8H)-dione (8a).—A mixture of the diacid (7a) (4.83 g) and polyphosphoric acid (192 g) was heated at 105–115 °C for 2 h

with occasional stirring, then poured cautiously into cold water (ca. 800 ml). The solid that precipitated was filtered off and washed by slurring with sodium hydrogen carbonate solution. The solution was centrifuged and the residue was washed with water; the product was filtered off and dried. Since the i.r. spectrum indicated the presence of some acid, the solid was dissolved in chloroform and the solution was extracted with sodium carbonate solution. The chloroform solution was washed with water, dried (MgSO_4), concentrated (to ca. 75 ml), and cooled overnight in the refrigerator. The precipitated solid was washed with cold chloroform and dried to give the yellow *diketone* (2.67 g), m.p. 315–320° (decomp.), ν_{max} (Nujol) 1658 (conj. C=O), 1601 (aromatic C=C), 915, 900, and 850 cm^{-1} , τ ($\text{CF}_3\cdot\text{CO}_2\text{H}$) 7.92, 7.27 (12H, m), 3.28 (2H, s), and 2.59 (2H, s); λ_{max} (CH_2Cl_2) 388.5 (log ϵ 4.27), 367 (4.08), 355 (3.69), 295 (4.71), 285 (4.67), 263 (4.35), and 245 (4.0) nm; m/e (70 ev) 288 (100%), 260 (8.5), 232 (25), 202 (6), 176 (80), 116 (50), 101 (5.5), 88 (85), and 28 (4.5) (Found: C, 83.0; H, 5.6%; M , 289. $\text{C}_{20}\text{H}_{18}\text{O}_2$ requires C, 83.3; H, 5.6%; M , 288).

The mother liquor showed four spots on t.l.c. After evaporation the residue was sublimed between 98 and 133 °C at 0.1–1 mmHg. Recrystallization of the sublimate (78 mg) from methanol gave a yellow solid, m.p. 132–133° (lit.¹⁴ 135°), ν_{max} 1661 (conj. C=O), 1607, 906m, 854w, and 752vs cm^{-1} identified as 8,9-dihydrobenzo[*b*]biphenylene-6(7H)-one. The residue after sublimation yielded more of compound (8a) (400 mg); overall yield 3.07 g (70%).

The crude diacid (7) was also cyclized in hydrofluoric acid, to yield the diketone (8a) (41%).

3,4,7,8-Tetrahydrodibenzo[*b,h*]biphenylene-1(2H),10(9H)-dione (8b).—Cyclization with polyphosphoric acid of the residue (1.4 g) obtained in the preparation of (7a) gave a yellow-brown solid (1.15 g) containing at least four components. This was extracted by refluxing methanol (50 ml) for 0.5 h and the extract was concentrated to ca. 15 ml, and cooled to yield crystals (40 mg) which gave the pale yellow *diketone*, m.p. 305–310° (from methanol-chloroform), ν_{max} (Nujol) 1662 (conj. C=O), 1655sh, 895, and 845 cm^{-1} ; τ (CDCl_3) 2.65 (2H, s), 3.33 (2H, s), 7.40 (8H, m), and 7.88 (4H, m); λ_{max} (MeOH) 236 (log ϵ 4.23), 246 (4.21), 265sh (4.44), 273 (4.79), 283 (4.94), 326 (3.23), 344 (3.55), 353 (3.48), 405 (3.82), and 425sh (3.70); λ_{max} (CH_2Cl_2) 235 (4.36), 246 (4.29), 265sh (4.50), 274 (4.83), 284 (5.00), 309sh (3.70), 325 (3.65), 343 (3.57), 351 (3.60), and 400br (3.78); m/e (70 ev) 288 (100%), 260 (4.6), 246 (4.8), 232 (24.3), 202 (5.1), 176 (6.4), 116 (3.8), 102 (2.8), 101 (4.9), and 88 (8.2) [high resolution m/e 288.1138 (calc. 288.1150)] (Found: C, 81.3; H, 5.4%; M , 286. $\text{C}_{20}\text{H}_{16}\text{O}_2$ requires C, 83.5; H, 5.6%; M , 288).

1,2,3,4,7,8,9,10-Octahydrodibenzo[*b,h*]biphenylene (9).—A solution of the diketone (8a) (361 mg, 1.25 mmol), sodium hydroxide (370 mg), and 85% hydrazine (0.8 mg, ca. 2.1 mmol) in diethylene glycol (8 ml) was heated under reflux for 2.5 h. The bath temperature was then gradually raised to 190° (to remove excess of hydrazine) and maintained there for 2 h. The mixture was poured into water (15 ml) and the precipitate was filtered off. The filtrate was passed through a column of silica gel (Will Corp., 100–200 mesh). The first 75 ml of the eluate was concentrated and two crops of straw-coloured crystals were collected (147 mg, 54%). Further elution led to highly coloured mixtures which were discarded. Sublimation between 150 and 170 °C at 0.1 mmHg yielded the straw-

coloured *hydrocarbon* (9), m.p. 238–239°, ν_{max} (KBr disc) 860 and 915 cm^{-1} ; τ (C_6D_6) 8.5 (8H, m, A_2B_2), 7.6 (8H, m, A_2B_2), and 3.7 (4H, s); λ_{max} (methylcyclohexane) 249 (log ϵ 4.66), 259 (5.05), 358 (4.17), and 378.5 (4.23) (Found: C, 92.1; H, 7.9%; M , 263. $\text{C}_{20}\text{H}_{20}$ requires C, 92.2; H, 7.7%; M , 260).

Dibenzo[*b,h*]biphenylene (1).—A mixture of compound (9) (104 mg) with powdered selenium (1 g) was heated at 260 °C for ca. 21 h. The product was leached with benzene (ca. 30 ml). Evaporation of the solvent yielded a pink solid (98 mg), which chromatographed in cyclohexane (20 ml) on a column of alumina (40 g, 5/8 × 8 in). The following fractions were obtained: starting compound (9) (25 mg), an unidentified compound (13 mg), almost pure compound (1) (5 mg) (identified by u.v.), and an unidentified carbonyl-containing compound (5.3 mg).

1,2,3,4,7,8,9,10-Octahydrodibenzo[*b,h*]biphenylene-1,7-diol.—A slurry of diketone (8a) (576 mg, 1.97 mmol) and lithium aluminium hydride (40 mg, 1.05 mmol) in tetrahydrofuran (30 ml) was heated under reflux for 2 h and then stirred at room temperature for 2 h. The excess of hydride was destroyed with water and the solution was diluted to ca. 250 ml with water; the light yellow alcohol that was precipitated was filtered off and dried (506 mg, 88%), m.p. 221–225°, ν_{max} (Nujol) 3340 (OH), 1070 (CO), and 871 cm^{-1} , was used directly in the next step.

1,2,7,8-Tetrahydrodibenzo[*b,h*]biphenylene (10).—(a) *By use of phosphoryl chloride and pyridine.* A mixture of the diol (500 mg), phosphoryl chloride (5 ml), and dry pyridine (10 ml) was heated under reflux for 1 h, then cooled to room temperature and poured slowly into ice-cold water. The resulting slurry yielded a little impure (10) (88 mg).

(b) *By use of 50% hydrochloric acid.* A slurry of diketone (8a) (576 mg, 2 mmol) and lithium aluminium hydride (40 mg, 1.05 mmol) in dried tetrahydrofuran (30 ml) was heated under reflux for 1 h then cooled to room temperature. The excess of hydride was decomposed with water and 50% hydrochloric acid was added dropwise until the solution was just acidic. A further portion (10 ml) of acid was added and the mixture was heated at 70–85 °C for 30 min, then diluted with water (50 ml) and cooled to room temperature; a yellow solid (94%) was filtered off and dried, and gave bright yellow shiny plates, m.p. 261–265° (from 1,2-dichloroethane), ν_{max} (KBr) 833s, 775w, 740w, and 690 cm^{-1} ; m/e 256 (100%), 252 (12), 239 (15), 226 (4), 128 (13), 126 (9), 120 (5), and 113 (5.8) [high resolution m/e 256.1249 (calc. 256.1252)].

Dibenzo[*b,h*]biphenylene (1).—(a) *With selenium.* Compound (10) (89 mg) and selenium powder (1 g) were heated together at 253–270 °C under a slow stream of nitrogen. After 24 h, more selenium (0.5 g) was added and heating was continued for 18 h. The contents were leached with benzene (2 × 50 ml) and chloroform (30 ml). Concentration of the combined extracts to ca. 30 ml, yielded a pink solid which was filtered off. The filtrate was transferred to a sublimator, the solvent was removed, and the residue was sublimed. The fractions collected over the range 130–230° at 0.05–0.07 mmHg were combined with the pink solid and the mixture was crystallized from chloroform to yield a slightly pink solid identified as compound (1) by comparison of i.r. and u.v. spectra.¹ T.l.c. indicated the presence of small amounts of an impurity.

(b) *With 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ).*

¹⁴ W. Baker, J. W. Barton, J. F. W. McOmie, and R. J. G. Searle, *J. Chem. Soc.*, 1962, 2633.

—A solution of 1,2,7,8-tetrahydrodibenzo[*b,h*]biphenylene (0.978 g, 3.88 mmol) in benzene (400 ml) was brought to reflux temperature and a solution of DDQ (2.08 g, 7.5 mmol) in benzene (50 ml) was added. A solid was precipitated and the red colour of the DDQ faded immediately. After 1 h more DDQ (194 mg, 0.77 mmol) was added and the refluxing was continued for 2 h more. The solvent was evaporated off and the residue was stirred with aqueous

10% sodium hydroxide (100 ml) for 1 h. The residue was washed with water and then dried to yield almost pure (i.r.) dibenzo[*b,h*]biphenylene (925 mg, 95%) (1). Recrystallization from xylene gave pure product (805 mg, 84%). Nitrobenzene and 1,2-dichloroethane were also effective solvents for recrystallization.

[0/160 Received, February 9th, 1970]