

## Polycyclic Biphenylenes. Part 6.<sup>1</sup> Direct Routes to Benzo[*b*]biphenylene and Related Systems *via* Cycloaddition Reactions

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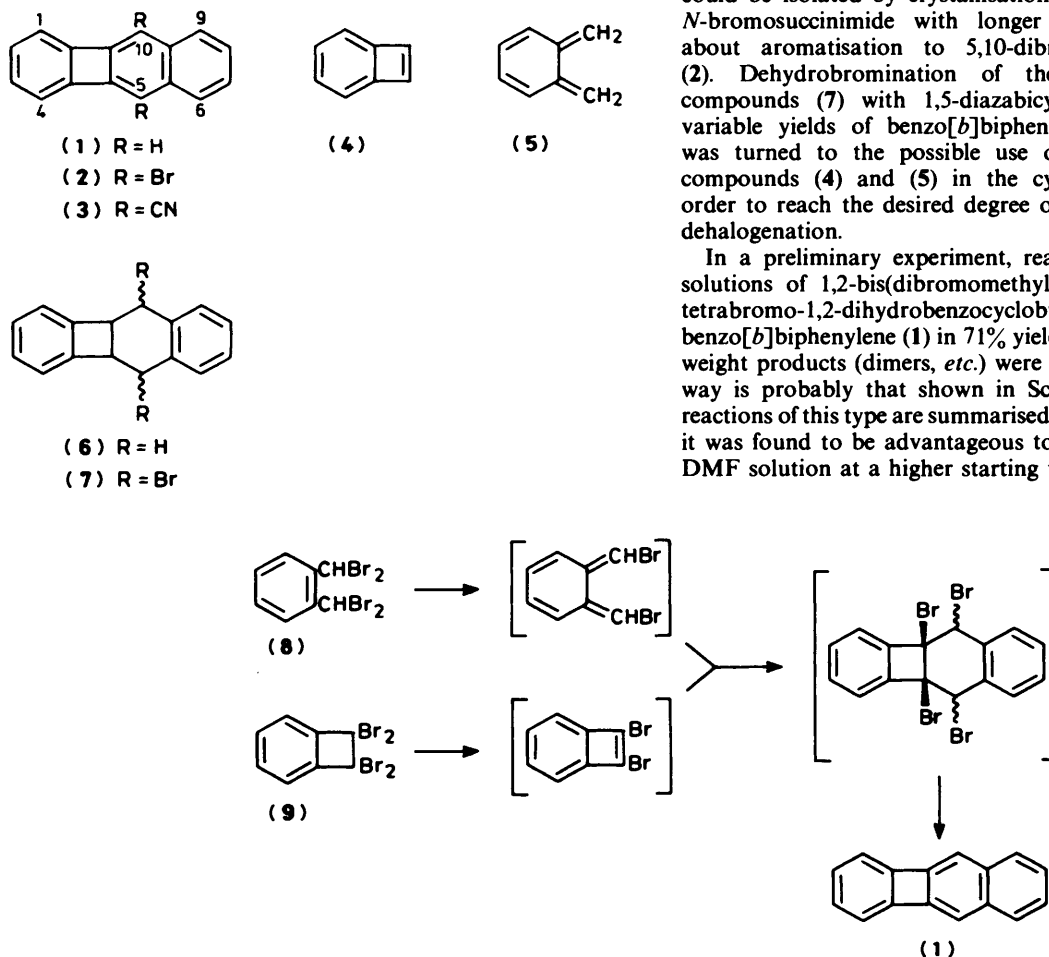
The simultaneous generation of 1,2-dibromobenzocyclobutene and 5,6-bis(bromomethylene)cyclohexa-1,3-diene gives benzo[*b*]biphenylene directly. Annelated derivatives of this ring system, including naphtho[2,3-*b*]-, biphenyleno[2,3-*a*]-, and biphenyleno[2,3-*b*]-biphenylenes may be obtained by variations of this procedure. Some cycloaddition reactions of 1,2-dibromobenzocyclobutene with cyclopenta-2,4-dienones and with thiophene 1,1-dioxides, giving rise to simple biphenylenes, are also described.

Benzo[*b*]biphenylene (1) and certain of its derivatives have been prepared by multistep annelation reactions starting from biphenylene,<sup>2,3</sup> by crossed aryne reactions,<sup>4</sup> and by functional group transformations of the dibromo compound (2), which is one of the products of the reaction of 1,2-bis(dibromomethyl)benzene with potassium *t*-butoxide.<sup>5</sup> The dicyanide (3) has also been obtained by the condensation of benzocyclobutene-1,2-dione with 1,2-bis(cyanomethyl)benzene.<sup>6</sup>

In an attempt to find a more direct general synthesis of benzo[*b*]biphenylenes we first examined routes based on cyclo-

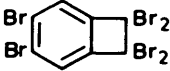
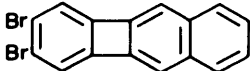
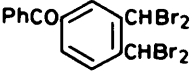
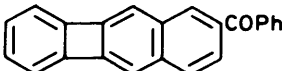
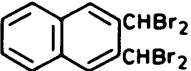
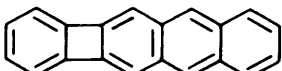
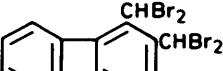
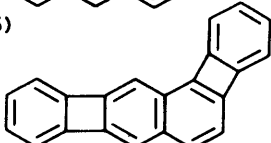
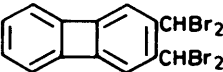
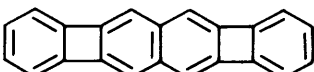
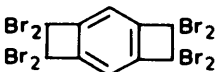
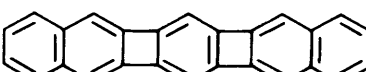
additions between benzocyclobutenes and 1,2-quinodimethanes, following the report by Nenitzescu and his co-workers that simultaneous generation of the parent species (4) and (5) gives their cycloadduct, 4b,5,10,10a-tetrahydrobenzo[*b*]biphenylene (6).<sup>7</sup> We confirmed this finding and effected some improvement in the yields of compound (6) by modification of the reaction conditions, but attempts to dehydrogenate (6) directly to the biphenylene (1) were unsuccessful, thus a two-step method was employed. Dibromination of (6) with *N*-bromosuccinimide gave a mixture of products from which one previously reported stereoisomer<sup>7</sup> of compound (7) could be isolated by crystallisation. The use of an excess of *N*-bromosuccinimide with longer reaction times brought about aromatisation to 5,10-dibromobenzo[*b*]biphenylene (2). Dehydrobromination of the mixture of dibromo compounds (7) with 1,5-diazabicyclo[4.3.0]non-5-ene gave variable yields of benzo[*b*]biphenylene (1), thus attention was turned to the possible use of halogen derivatives of compounds (4) and (5) in the cycloaddition reactions, in order to reach the desired degree of unsaturation during the dehalogenation.

In a preliminary experiment, reaction of equimolar THF solutions of 1,2-bis(dibromomethyl)benzene (8) and 1,1,2,2-tetrabromo-1,2-dihydrobenzocyclobutene (9) with zinc gave benzo[*b*]biphenylene (1) in 71% yield. No other low molecular weight products (dimers, *etc.*) were found. The reaction pathway is probably that shown in Scheme 1. Results of other reactions of this type are summarised in Table 1. In certain cases it was found to be advantageous to conduct the reactions in DMF solution at a higher starting temperature (95–100 °C).



Scheme 1.

Table 1.

Diene precursor	Dienophile precursor	Method	Yield (%)	Product
(8)	(9)	A B	71 45	(1)
(8)	 (10)	A B	3 13	 (11)
 (12)	(9)	A	95	 (13)
 (14)	(9)	A B	0 15	 (15)
 (16)	(9)	A	28	 (17)
 (18)	(9)	A B	0 30	 (19)
(8)	 (20)	B	0	 (21)

This was necessary when the starting materials were sparingly soluble or when dehalogenation appeared to be slow, however, polymer formation took place to a greater extent when this was done. Several factors obviously determine the success of reactions of this type, the main ones being that the reactive intermediates must form at comparable rates and have similar lifetimes. The use of sodium iodide as the dehalogenating agent was also examined, but the reaction between the tetrabromides (8) and (9) gave only traces of benzo[*b*]biphenylene. In reactions where compounds (8) or (9) bore a nitro group, which precluded the use of zinc as a dehalogenating agent, no nitrobenzo[*b*]biphenylenes could be obtained using sodium iodide. Reactions of compound (9) with 1,2- and 2,3-bis-(dibromomethyl)biphenylenes (16) and (18) led to two isomers (17) and (19) of the theoretically interesting biphenyleno-biphenylene system. An alternative synthesis of the linear isomer (19) *via* its 2,3,8,9-tetrakis(trimethylsilyl) derivative has been reported recently.<sup>8</sup> The angular isomer (17) is more deeply coloured than the linear isomer (19), reflecting the higher  $\pi$ -bond order in the 4-membered rings of compound (17). Unfortunately, the remaining [1,2-*a*] and [2,1-*a*] isomers, in which the bond order effect should be more pronounced, are not accessible by either of these methods. An attempted double cycloaddition reaction between compound (8) and the benzo-

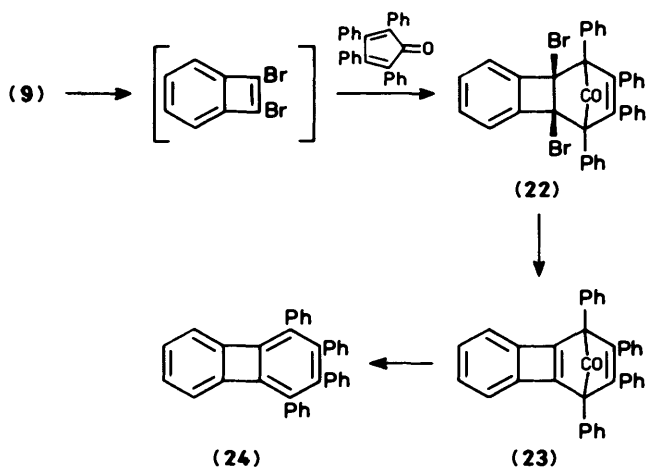
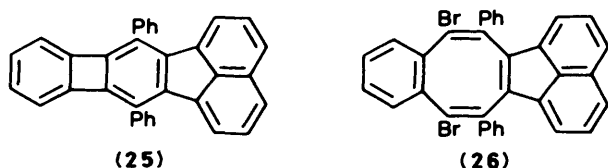
dicyclobutene derivative (20) failed to give the linear sesqui-biphenylene (21).

In a recent paper<sup>9</sup> we showed that reactions of benzocyclobutene (4) with cyclopenta-2,4-dienones, thiophene 1,1-dioxides, and 2*H*-pyran-2-ones give benzocyclo-octenes by way of dihydrobiphenylene derivatives which undergo valence isomerisation. Taking account of the reactions described above, we thought it of interest to investigate reactions of 1,2-dibromobenzocyclobutene with these cyclic dienes, the expected products being either biphenylenes or dibromobenzocyclo-octenes. Debromination of 1,1,2,2-tetrabromo-1,2-dihydrobenzocyclobutene (9) with zinc in the presence of 2,3,4,5-tetraphenylcyclopenta-2,4-dienone gave 1,2,3,4-tetraphenylbiphenylene (24) in 55% yield. The cycloadduct (22) could not be isolated and it is presumed that this must undergo debromination to the norbornadienone (23) prior to extrusion of carbon monoxide (Scheme 2). Similar results were obtained with 2-methyl-3,4,5-triphenyl- and 3,4-dimethyl-2,5-diphenyl-cyclopenta-2,4-dienones. The reaction with 7,9-diphenyl-8*H*-cyclopenta[*a*]acenaphthen-8-one, however, gave only small amounts of the biphenylene (25), the major product being the dibromobenzocyclo-octene (26). In this case it appears that extrusion of carbon monoxide from the cycloadduct, known to be a favourable process with accecyclone adducts,<sup>10</sup> is faster than the

**Table 2.** Biphenylenes from the cycloaddition reactions of 1,2-dibromo-1,2-dihydrobenzocyclobutene with thiophene-1,1-dioxides

Thiophene 1,1-dioxide	Reference	Biphenylene	Yield %	M.p. (°C)	Reference	Lit. m.p. (°C)
2,5-Dimethyl	11	1,4-Dimethyl	9	25	12	28
3,4-Dimethyl	13	2,3-Dimethyl	24	109—111	14	111—112
2,3,4,5-Tetramethyl	15	1,2,3,4-Tetramethyl	0.5	<i>a</i>	16	(Not reported)
2,3,4,5-Tetraphenyl	17	1,2,3,4-Tetraphenyl	35	260—262	(This paper)	
2,3,4,5-Tetrachloro	18	1,2,3,4-Tetrachloro	10	173	19	176

\* Identified on the basis of its n.m.r. and mass spectra.

**Scheme 2.**

debromination step. Reactions of 1,2-dibromobenzocyclobutene with thiophene 1,1-dioxides gave erratic results, only low yields of biphenylene derivatives being obtained (Table 2). The reaction temperatures required precluded the use of zinc as a dehalogenating agent and the best results were obtained using 1,1,2,2-tetrabromo-1,2-dihydrobenzocyclobutene (9) with sodium iodide in refluxing propan-2-ol. The reactivity of 1,2-dibromobenzocyclobutene towards thiophene 1,1-dioxides was noticeably lower than that of benzocyclobutene itself,<sup>9</sup> probably reflecting the increased energy differences between the frontier orbitals of the two components in the reactions rather than the steric effects due to the bromine atoms. No cycloadducts or derived products could be obtained from reactions of 1,2-dibromobenzocyclobutene with 2*H*-pyran-2-one or its 4,6-dimethyl derivative.

### Experimental

Organic extracts were dried over anhydrous (Na<sub>2</sub>SO<sub>4</sub>). <sup>1</sup>H N.m.r. spectra were obtained on a Jeol JNM-FX-200 spectrometer. Samples were run as solutions in CDCl<sub>3</sub> at ambient temperature and chemical shifts are recorded in p.p.m. downfield from internal tetramethylsilane. I.r. spectra were run as Nujol mulls unless otherwise stated. Mass spectra were obtained on an AEI MS902 instrument operated at 70 eV and a source temperature of 200 °C.

The following starting materials were obtained by literature routes: *trans*-1,2-dibromo-1,2-dihydrobenzocyclobutene,<sup>20</sup> 1,1,2,2-tetrabromo-1,2-dihydrobenzocyclobutene,<sup>21</sup> 1,2-dibromo-4,5-dimethylbenzene,<sup>22</sup> 2,3-bis(dibromomethyl)naphthalene,<sup>23</sup> 1,2-dimethylbiphenylene,<sup>24</sup> 2,3-bis(dibromomethyl)biphenylene,<sup>9</sup> 1,2,4,5-tetrahydrobenzo[*a,d*]dicyclobutene,<sup>25</sup> 2-methyl-3,4,5-triphenyl-<sup>26</sup> and 3,4-dimethyl-2,5-diphenylcyclopenta-2,4-dienone,<sup>27</sup> and 7,9-diphenyl-8*H*-cyclopenta-acenaphthylen-8-one.<sup>28</sup> References to methods used for preparing thiophene 1,1-dioxides are cited in Table 2.

**3,4-Bis(dibromomethyl)benzophenone (12).**—3,4-Dimethylbenzophenone (1.05 g), *N*-bromosuccinimide (1.78 g), and dibenzoyl peroxide (0.05 g) were heated under reflux in dry carbon tetrachloride (25 ml). Further portions of *N*-bromosuccinimide (1.78 g) were added after 5 and 17 h. After 24 h, the hot reaction mixture was filtered and the residual succinimide washed with carbon tetrachloride. Evaporation of the combined solutions at reduced pressure gave an oil which was taken up in chloroform (50 ml), then shaken with saturated aqueous sodium thiosulphate and then with water. The dried solution was concentrated and diluted with hexane, to give a pale yellow solid which on recrystallisation gave the title compound (1.65 g, 73%) as prisms, m.p. 123—125 °C (from chloroform–hexane) (Found: C, 35.25; H, 1.8; Br, 60.4. C<sub>15</sub>H<sub>10</sub>Br<sub>4</sub>O requires C, 35.25; H, 1.9; Br, 60.8%);  $\nu_{\max}$  1 663, 1 600, 1 286, 996, 730, and 710 cm<sup>-1</sup>;  $\delta_{\text{H}}$  7.12 (1 H, s, 4-CH), 7.21 (1 H, s, 3-CH), 2.18—2.44 (7 H, m, ArH), and 8.09 (1 H, s, 1-H).

**1,2-Bis(dibromomethyl)biphenylene (16).**—1,2-Dimethylbiphenylene (1.0 g) and *N*-bromosuccinimide (4.0 g) in dry carbon tetrachloride (100 ml) were refluxed over a 60 W tungsten bulb for 1.5 h. Work-up as in the previous experiment gave 1,2-bis(dibromomethyl)biphenylene (1.49 g, 55%) as yellow needles, m.p. 187—189 °C (from chloroform–hexane) (Found: C, 34.0; H, 1.6; Br, 64.4. C<sub>14</sub>H<sub>8</sub>Br<sub>4</sub> requires C, 33.9; H, 1.6; Br, 64.5%);  $\nu_{\max}$  1 145 and 760 cm<sup>-1</sup>;  $\delta_{\text{H}}$  6.45—7.26 (m).

**1,1,2,2,4,5-Hexabromo-1,2-dihydrobenzocyclobutene (10).**—Bromination of 1,2-dibromo-4,5-dimethylbenzene with *N*-bromosuccinimide as in the preparation of compound (12), with a reaction time of 24 h, gave 1,2-dibromo-4,5-bis(dibromomethyl)benzene (82%), m.p. 137—138 °C, which was cyclised with sodium iodide in refluxing ethanol by the method of Cava and Napier.<sup>29</sup> The product, *trans*-1,2,4,5-tetrabromo-1,2-dihydrobenzocyclobutene (yield 70%) formed colourless prisms, m.p. 127.5—128.5 °C (from ethanol) (Found: C, 22.8; H, 0.98. C<sub>8</sub>H<sub>4</sub>Br<sub>4</sub> requires C, 22.9; H, 0.95%). A solution of this tetrabromo compound (7.5 g) and bromine (12 g) in dry carbon tetrachloride (100 ml) was refluxed over a 150 W tungsten bulb for 3 days. Evaporation of the solvent at reduced pressure and recrystallisation of the product from light petroleum (80—100 °C) gave the title compound (10) (9.8 g, 95%), m.p. 192—194 °C (Found: C, 16.6; H, 0.29; Br, 83.4. C<sub>8</sub>H<sub>2</sub>Br<sub>6</sub> requires C, 16.6; H, 0.35; Br, 83.1%);  $\nu_{\max}$  1 395, 942, 910, and 670 cm<sup>-1</sup>;  $\delta_{\text{H}}$  7.55 (s);  $m/z$  (%) 576 ( $M^+$  - 2, 25), 498, 496 (100), and 417 (88).

1,1,2,2,4,4,5,5-Octabromo-1,2,4,5-tetrahydrobenzo[*a,d*]dicyclobutene (**20**).—1,2,4,5-Tetrahydrobenzo[*a,d*]dicyclobutene (0.8 g) was brominated as in the previous experiment using bromine (10 g, 20 equiv.). The pale brown precipitate of the octabromo compound which separated (1.7 g, 36%) was recrystallised from dimethyl sulphoxide to give tan needles, m.p. >360 °C (Found: C, 16.0; H, 0.29.  $C_{10}H_2Br_8$  requires C, 15.8; H, 0.26%).

4b,5,10,10a-Tetrahydrobenzo[*b*]biphenylene (**6**).—A solution of 1,2-bis(bromomethyl)benzene (5.3 g) and *trans*-1,2-dibromo-1,2-dihydrobenzocyclobutene (5.25 g) in *N,N*-dimethylformamide (150 ml) was added dropwise during 30 min to a rapidly-stirred suspension of zinc dust (40 g) in *N,N*-dimethylformamide (50 ml). After the reaction had been stirred overnight the solution was filtered, diluted with water, and steam distilled. The solid in the distillate was collected and crystallised from methanol to give the title compound (**6**) (2.25 g, 55%) as colourless needles, m.p. 123–124 °C (lit.,<sup>7</sup> m.p. 124–125 °C).

*Aromatisation of 4b,5,10,10a-tetrahydrobenzo[*b*]biphenylene.*—(a) A solution of the tetrahydro compound (**6**) (3.0 g), *N*-bromosuccinimide (5.4 g) and dibenzoyl peroxide (10 mg) in dry carbon tetrachloride (225 ml) was refluxed for 30 min, cooled to 50 °C, filtered, and evaporated under reduced pressure. The gummy residue was dissolved in dry benzene (250 ml), treated with 1,5-diazabicyclo[4.3.0]non-5-ene (6.0 ml), and the solution was refluxed for 16 h. The cooled solution was washed with dilute hydrochloric acid, dried, and concentrated, then charcoaled whilst hot and diluted with hexane to give benzo[*b*]biphenylene (**1**) (1.1 g, 37%), m.p. 243–245 °C (subl.) (lit.,<sup>5</sup> 242.6–243.2 °C) after recrystallisation from cyclohexane.

(b) The tetrahydro-compound (**6**) (0.47 g), *N*-bromosuccinimide (2.0 g) and dibenzoyl peroxide (10 mg) were heated under reflux for 60 h. The cooled solution was filtered from succinimide, then evaporated under reduced pressure to give an orange, oily solid. Chromatography on alumina in benzene solution gave, as the main fraction, 5,10-dibromobenzo[*b*]biphenylene (**2**) (0.65 g, 82%) as orange needles, m.p. 222–223 °C (from ethanol), identical with an authentic sample.<sup>5</sup>

*General Methods for the 'Crossed' Coupling of Reactive Intermediates (Table 1).*—The following procedures are typical: *Method A.* A solution of 1,2-bis(dibromomethyl)benzene (**8**) (2.0 g) and 1,1,2,2-tetrabromo-1,2-dihydrobenzocyclobutene (**9**) (2.0 g) in tetrahydrofuran (15 ml) was stirred at room temperature and activated zinc dust<sup>30</sup> (20 g) was added in one portion. The vigorous exothermic reaction which ensued was moderated by ice-bath cooling, if necessary. When the reaction had ceased, the solution was filtered and the zinc residues washed with tetrahydrofuran. The residue from reduced pressure evaporation of the combined solutions was dissolved in dichloromethane (100 ml), washed with 10% hydrochloric acid, dried, and evaporated. Crystallisation of the product from cyclohexane gave benzo[*b*]biphenylene (**1**) (0.6 g, 71%), m.p. 243–245 °C.

*Method B.* A solution of 1,2-bis(dibromomethyl)benzene (**8**) (1.5 g) and hexabromo compound (**10**) (2.0 g) in *N,N*-dimethylformamide (15 ml) was stirred at 100 °C (bath), and activated zinc dust (15 g) was added in one portion (**CAUTION**: these reactions should only be performed on a small scale in a flask of adequate size, as a violent exothermic reaction usually ensues). When the reaction had ceased the solvent was removed under reduced pressure and the entire residue was extracted with dichloromethane (Soxhlet). Concentration of the extract gave 2,3-dibromobenzo[*b*]biphenylene (**11**) (0.165 g, 13%), m.p. 235–236 °C (subl.) (from chloroform) (Found:  $M^+$ , 359.8984.  $C_{16}H_8Br_2$  requires  $M$ , 359.8972;  $\delta_H$  6.75–7.51 (m). By similar procedures (Table 1) the following products were obtained.

7-Benzoylbenzo[*b*]biphenylene (**13**). Yellow plates from toluene, m.p. 224–226 °C (Found: C, 90.1; H, 4.7.  $C_{23}H_{14}O$  requires C, 90.1; H, 4.6%;  $\nu_{max}$  1 642, 1 275, 870, 745, and 700  $cm^{-1}$ ;  $\delta_H$  6.98 (6 H, m, 1–4-, 5-, 10-H) and 7.46–7.91 (8 H, m, 6-, 8-, 9-H and Ph);  $m/z$  (%) 306 ( $M^+$ , 100), 229 (56), 201 (36), and 200 (22).

Naphtho[2,3-*b*]biphenylene (**15**). Yellow crystals from toluene, m.p. >360 °C (subl. above 320 °C), identical with an authentic sample.<sup>3</sup>

Biphenylene[2,3-*a*]biphenylene (**17**). Deep yellow crystals from hexane, m.p. 187–189 °C (Found:  $M^+$ , 276.0941.  $C_{22}H_{12}$  requires  $M$ , 276.0939;  $\nu_{max}$  (KCl) 1 412, 1 160, 871, and 735  $cm^{-1}$ ;  $\delta_H$  6.46–7.06 (m);  $m/z$  (%) 276 ( $M^+$ , 100) and 138 (24).

Biphenylene[2,3-*b*]biphenylene (**19**) (cf.<sup>8</sup>). Pale yellow leaflets, m.p. >360 °C (Found:  $M^+$ , 276.0930.  $C_{22}H_{12}$  requires  $M$ , 276.0939;  $\nu_{max}$  (KCl) 1 412, 1 160, 871, and 735  $cm^{-1}$ ;  $\delta_H$  [ $^2H_5$ pyridine] 6.59 (4 H, s, 5-, 6-, 11-, 12-H) and 6.69 (8 H, m, 1–4-, 7–10-H);  $m/z$  (%) 276 ( $M^+$ , 100) and 138 (25).

*Reactions of 1,2-Dibromobenzocyclobutene with Cyclopenta-2,4-dienones.*—(a) With 2,3,4,5-tetraphenylcyclopenta-2,4-dienone. Activated zinc (10 g) was added in portions to a stirred solution of the ketone (2.0 g) and 1,1,2,2-tetrabromo-1,2-dihydrobenzocyclobutene (2.2 g) in tetrahydrofuran (15 ml) at room temperature, the exothermic reaction being controlled by water-bath cooling. When the reaction had ceased, the suspension was diluted with dichloromethane (100 ml), filtered from zinc residues, and the solution washed with 10% hydrochloric acid, and then with water. Evaporation of the dried solution yielded a gum which on crystallisation from light petroleum (100–120 °C) gave 1,2,3,4-tetraphenylbiphenylene (**24**) (1.1 g, 55%) as yellow crystals, m.p. 260–262 °C (Found: C, 94.6; H, 5.3.  $C_{36}H_{24}$  requires C, 94.7; H, 5.3%;  $\nu_{max}$  740, 700, and 690  $cm^{-1}$ ;  $\delta_H$  6.48–6.74 (4 H, m, 5–8-H) and 6.75–7.20 (20 H, m, 1–4-Ph);  $m/z$  (%) 456 ( $M^+$ , 100).

(b) With 2-methyl-3,4,5-triphenylcyclopentadienone. Reaction of the ketone (2.0 g), as described in the previous experiment, gave 1-methyl-2,3,4-triphenylbiphenylene (1.25 g, 51%) as pale yellow crystals, m.p. 140–142 °C [from light petroleum (80–100 °C)] (Found: C, 94.3; H, 5.5.  $C_{31}H_{22}$  requires C, 94.4; H, 5.6%;  $\nu_{max}$  1 160, 744, 740, and 710  $cm^{-1}$ ;  $\delta_H$  1.90 (3 H, s, 1-Me) and 6.50–7.18 (19 H, m, ArH);  $m/z$  (%) 394 ( $M^+$ , 100).

(c) With 3,4-dimethyl-2,5-diphenylcyclopenta-2,4-dienone. Reaction of the ketone (2.5 g), as described above, gave 2,3-dimethyl-1,4-diphenylbiphenylene (2.75 g, 86%) as pale yellow crystals, m.p. 149–151 °C (from light petroleum 80–100 °C) (Found: C, 94.0; H, 5.9.  $C_{26}H_{20}$  requires C, 94.0; H, 6.0%;  $\nu_{max}$  (KCl) 1 440, 1 010, 753, 722, and 700  $cm^{-1}$ ;  $\delta_H$  2.12 (6 H, s, 2-, 3-Me), 6.28–6.59 (4 H, m, 5–8-H), and 7.29–7.48 (10 H, m, 1-, 4-Ph);  $m/z$  (%) 332 ( $M^+$ , 100) and 315 (10).

(d) With 7,9-diphenyl-8H-cyclopenta[*a*]acenaphthen-8-one. Reaction of the ketone (2.0 g), as described above, gave a mixture of products which was separated by chromatography over silica in hexane-toluene (5:1) solution. Elution gave first 5,6-dibromobenzo[*a*]biphenylene (0.4 g), identical with an authentic sample,<sup>31</sup> formed by dimerisation and subsequent debromination of 1,2-dibromobenzocyclobutene. The second fraction gave 7,12-diphenylacenaphtho[1,2-*b*]biphenylene (**25**) (0.315 g, 13%) as orange-red crystals, m.p. 246–248 °C (Found: C, 95.5; H, 4.6.  $C_{34}H_{20}$  requires C, 95.3; H, 4.7%;  $\nu_{max}$  765, 759, and 702  $cm^{-1}$ ;  $\delta_H$  6.41–6.68 (4 H, m, 5–8-H) and 7.33–7.74 (16 H, m, 1–6-H and Ph);  $m/z$  (%) 428 ( $M^+$ , 100). Further elution gave 8,13-dibromo-7,14-diphenylbenzo[*a*]acenaphtho[1,2-*e*]cyclooctene (**26**) (0.9 g, 27%) as bright yellow crystals, m.p. 231–232 °C (slow decomposition above 210 °C) (Found: C, 69.1; H, 3.2; Br, 27.2.  $C_{34}H_{20}Br_2$  requires C, 69.4; H, 3.4; Br, 27.2%;  $\nu_{max}$  765, 759, and 702  $cm^{-1}$ ;  $\delta_H$  7.05–7.76 (m);  $m/z$  (%) 588 ( $M^+$ , 3), 510, 508 ( $M^+$  – Br, 14), and 428 ( $M^+$  – 2 Br, 100).

*Reactions of 1,2-Dibromobenzocyclobutene with Thiophene 1,1-Dioxides (Table 2).*—The following procedure is typical: A solution of 3,4-dimethylthiophene 1,1-dioxide (5.0 g), 1,1,2,2-tetrabromo-1,2-dihydrobenzocyclobutene (14.6 g) and sodium iodide (20 g) in propan-2-ol (200 ml) was refluxed for 48 h, then diluted with water and treated with sodium metabisulphite to remove iodine. Steam distillation, followed by crystallisation of the product from aqueous ethanol, gave 2,3-dimethylbiphenylene (1.49 g, 24%), m.p. 109–111 °C, identical with an authentic sample.<sup>9</sup>

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