509. *Biphenylenes. Part VI.*[1] *Synthesis of 2,3-Benzobiphenylene from Biphenylene.*

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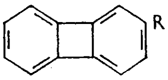
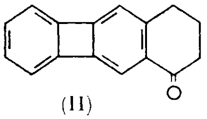
2,3-Benzobiphenylene (III; R = H) has been made from biphenylene by an unambiguous synthesis. The dehydrobromination of αα$\alpha'\alpha'$-tetrabromo-*o*-xylene has been shown to yield 3,4-dibromo-1,2-benzobiphenylene (V; R = Br) in addition to the previously reported compounds (III; R = Br) and (IV). The structure assigned to the dibromo-compound has been confirmed by synthesis from 3-bromo-1,2-benzobiphenylene (V; R = H).

Previous studies have shown [2,3] that biphenylene undergoes electrophilic substitution in position 2, and that its bond structure is best represented as in formula (I; R = H).[4] A synthesis of 2,3-benzobiphenylene from biphenylene has been based on these facts.

Reaction of biphenylene with β-carbomethoxypropionyl chloride under Friedel–Crafts conditions, followed by hydrolysis, gave 2-β-carboxypropionylbiphenylene (I; R = $CO{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$) which could be oxidised to the known biphenylene-2-carboxylic acid.[2] Reduction of the keto-acid gave 2-3'-carboxypropylbiphenylene (I; R = $CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$), and this was then cyclised by polyphosphoric acid to the ketone (II). Reduction to the tetrahydro-hydrocarbon and subsequent dehydrogenation by selenium gave 2,3-benzobiphenylene (III; R = H). A less satisfactory route from the ketone involved reduction by sodium borohydride followed by dehydration of the resulting alcohol and finally dehydrogenation with chloranil.


(I)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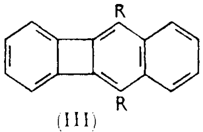
(III)

Although 2-3'-carboxypropylbiphenylene could possibly cyclise in two ways, previous work [4] indicated that it should give the ketone (II). This expectation was confirmed by the close similarity of the ultraviolet spectrum (cf. Table) of the ketone (II) with that of 2-acetylbiphenylene. Likewise the infrared spectra of the ketone (II) and of its reduction product showed the presence of one or more " isolated " aromatic C–H groups, whereas if cyclisation had occurred on to position 1 the infrared spectra of the two compounds would have shown a pair of adjacent aromatic C–H groups. Final confirmation of the structure of 2,3-benzobiphenylene, m. p. 242—243°, comes from the fact that it is different from the known 1,2-benzobiphenylene, m. p. 72—72·8°.[5]

During the course of our work, Jensen and Coleman [6] described, without experimental details, the reaction of αα$\alpha'\alpha'$-tetrabromo-*o*-xylene with potassium t-butoxide to give a mixture of 1,4-dibromo-2,3-benzobiphenylene (III; R = Br) and 1,2,5,6-tetrabromo-3,4:7,8-dibenzotricyclo[4,2,0,$0^{2,5}$]octadiene (IV). They showed that the dibromo-compound (III; R = Br) could be converted by successive treatment with n-butyl-lithium and methanol into 2,3-benzobiphenylene (III; R = H) whose structure was established by treatment with Raney nickel, whereby 2-phenylnaphthalene was obtained in 95·2% yield.

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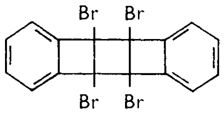
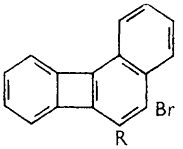
[1] Part V, Baker, Barton, McOmie, Penneck, and Watts, *J.*, 1961, 3986.
[2] Baker, Boarland, and McOmie, *J.*, 1954, 1476.
[3] Baker, Barton, and McOmie, *J.*, 1958, 2666.
[4] Baker, McOmie, Preston, and Rogers, *J.*, 1960, 414.
[5] Cava and Stucker, *J. Amer. Chem. Soc.*, 1955, **77**, 6022.
[6] Jensen and Coleman, *Tetrahedron Letters*, 1959, No. 20, 7.

The work of Jensen and Coleman has been confirmed and the identity of the two specimens of 2,3-benzobiphenylene has been established. It may be noted that the isomeric 1,2-benzobiphenylene [5] with Raney nickel gives a mixture of 1- (21%) and 2-phenylnaphthalene (50%). In our repetition of the work of Jensen and Coleman, in addition to (III; R = Br) and (IV) there was also obtained an orange compound, m. p. 147—148°, $C_{16}H_8Br_2$, which proved to be 3,4-dibromo-1,2-benzobiphenylene (V; R = Br). Its ultraviolet absorption spectrum was closely similar to that of 3-bromo-1,2-benzobiphenylene (V; R = H), and its infrared spectrum showed strong bands at 741 and 752 cm.$^{-1}$, corresponding to 1,2-disubstituted benzene rings. 3,4-Dibromo-1,2-benzobiphenylene (V; R = Br) was also synthesised from 3-bromo-1,2-benzobiphenylene [7] by reaction with bromine to give the pentabromo-compound (VI), followed by treatment with potassium t-butoxide.



(IV)



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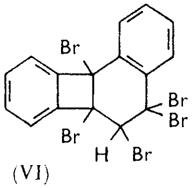

(VI)

Cava and Muth [8] recently discussed the mechanism of the dehydrobromination of $\alpha\alpha'\alpha'$-tetrabromo-*o*-xylene to give compounds (III; R = Br) and (IV). They concluded that 1,1,2-tribromobenzocyclobutene could not be an intermediate in the formation of these two compounds since a synthetic sample of 1,1,2-tribromobenzocyclobutene reacted with potassium t-butoxide to give 3,4-dibromo-1,2-benzobiphenylene, m. p. 149—150°. We agree with this conclusion but nevertheless the formation of 3,4-dibromo-1,2-benzobiphenylene which we have observed strongly suggests that the dehydrobromination proceeds by two routes simultaneously, one route leading to compounds (III; R = Br) and (IV), and the other to 1,1,2-tribromobenzocyclobutene which then gives compound (V; R = Br).

Ultraviolet absorption maxima in 95% ethanol.

Biphenylene deriv.	λ (mμ)	$\log_{10} \varepsilon$	λ (mμ)	$\log_{10} \varepsilon$	λ (mμ)	$\log_{10} \varepsilon$
2-Acetyl [2]	236	4·61	348	3·63	363	3·80
2-β-Carboxypropionyl	263	4·64	349	3·62	365	3·77
Ketone (II)	233	4·40	310	3·25	345	3·70
	270	4·75	327	3·45	363	3·89
2-3′-Carboxypropyl	252	4·86	334	3·39	346	3·62
					362	3·82
3′,4′,5′,6′-Tetrahydro-2,3-benzo	246	4·58	300	2·92	368	3·95
	255	4·87	348	3·78		
3′,4′-Dihydro-2,3-benzo	254	4·83	274	4·60	349	3·92
	266	4·63	333 infl.	3·63	367	4·12
					381	3·98
2,3-Benzo	255	4·87	285	4·40	348	3·71
	264	4·89	296	4·55	367	3·83
			331	3·68	386	3·78
1,2-Benzo [5]	254	4·58	279	4·47	359	3·41
	262	4·77	291	4·48	375	3·71
					393	3·87
3-Bromo-1,2-benzo	243	4·65	285	4·44	347	3·08
	255	4·61	295	4·45	380	3·75
	264	4·73	330	2·84	399	3·89
3,4-Dibromo-1,2-benzo	229	4·38	292	4·38	384	3·56
	266	4·67	304	4·39	402	3·66

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[7] Cava and Stucker, *J. Amer. Chem. Soc.*, 1957, **79**, 1706.
[8] Cava and Muth, *Tetrahedron Letters*, 1961, 140.

EXPERIMENTAL

2-β-*Carboxypropionylbiphenylene* (I; R = $CO{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$).—Biphenylene (4·0 g.) in tetrachloroethane (20 ml.) was added gradually at 0° to a stirred solution of β-carbomethoxypropionyl chloride (4·4 g.) in tetrachloroethane (30 ml.) containing aluminium chloride (8·8 g.). After being stirred for 4 hr., the mixture was kept overnight, ice (*ca.* 250 g.) and 4N-hydrochloric acid (300 ml.) were then added, and the mixture was steam-distilled. The solid residue was collected and extracted continuously with ethanol. Dilution of the extract with water gave 2-β-carbomethoxypropionylbiphenylene, yellow needles, m. p. 130—132° (from methanol). Hydrolysis with 10% sodium hydroxide (200 ml.) for 2 hr. yielded 2-β-*carboxypropionylbiphenylene* (5·5 g., 75%) which separated from ethanol as yellow needles, m. p. 215° (decomp.) (Found: C, 75·7; H, 4·7. $C_{16}H_{12}O_3$ requires C, 76·2; H, 4·8%), $\nu_{max.}$ 740vs, 815vs, and 881w cm.$^{-1}$ (1,2-di- and 1,2,4-tri-substituted benzene rings).

Oxidation of the keto-acid by alkaline potassium permanganate gave biphenylene-2-carboxylic acid, m. p. alone or mixed with an authentic sample,[2] 223—224°.

2-3′-*Carboxypropylbiphenylene* (I; R = $CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$).—A mixture of the preceding keto-acid (1·35 g.), water (50 ml.), concentrated hydrochloric acid (20 ml.), acetic acid (5 ml.), toluene (40 ml.), and amalgamated zinc (10 g.) was boiled under reflux for 30 hr., hydrochloric acid (5 ml.) being added every 6 hr. The aqueous layer was extracted with ether (3 × 50 ml.), and the combined extracts and toluene layer were steam-distilled after the addition of 10% aqueous sodium hydroxide (150 ml.). The residual solution was acidified, giving 2-3′-*carboxypropylbiphenylene* (0·75 g., 58%), m. p. 115—117°. Recrystallisation from aqueous methanol gave pale yellow needles, m. p. 118·5—119·5° (Found: C, 80·3; H, 5·8. $C_{16}H_{14}O_2$ requires C, 80·7; H, 5·9%), $\nu_{max.}$ 733vs, 817s, and 863w cm.$^{-1}$ (1,2-di- and 1,2,4-tri-substituted benzene rings).

3′,4′,5′,6′-*Tetrahydro*-3′-*oxo*-2,3-*benzobiphenylene* (II).—The preceding acid (1·2 g.) and polyphosphoric acid (30 g.) were stirred at 80° for 1 hr., and the dark red molten mass was treated with water and then extracted with ether (3 × 250 ml.). The extracts, after being washed with aqueous sodium hydrogen carbonate, yielded a solid (1·0 g.) which was purified by passage of its benzene solution through a column of alumina. The product from the eluate crystallised from methanol, giving the *ketone* (II) as yellow plates (0·7 g., 63%), m. p. 134—135° (Found: C, 87·0; H, 5·7. $C_{16}H_{12}O$ requires C, 87·3; H, 5·5%), $\nu_{max.}$ 750s and 860w cm.$^{-1}$ (1,2-di- and 1,2,4,5-tetra-substituted benzene rings).

3′,4′,5′,6′-*Tetrahydro*-2,3-*benzobiphenylene*.—A mixture of the ketone (II) (0·21 g.), toluene (40 ml.), concentrated hydrochloric acid (10 ml.), acetic acid (10 ml.), water (1 ml.), and amalgamated zinc (10 g.) was boiled under reflux for 30 hr., hydrochloric acid (5 ml.) being added every 6 hr. The toluene layer and ethereal extracts of the aqueous layer yielded a solid which was purified by chromatography in benzene on alumina. The product (87 mg.) crystallised from aqueous methanol, giving 3′,4′,5′,6′-*tetrahydro*-2,3-*benzobiphenylene* as a yellow powder, m. p. 109·5—111° (Found: C, 93·0; H, 6·9. $C_{16}H_{14}$ requires C, 93·2; H, 6·8%), $\nu_{max.}$ 734s, 858m, and 870s cm.$^{-1}$ (1,2-di- and 1,2,4,5-tetrasubstituted benzene rings).

2,3-*Benzobiphenylene* (III; R = H).—(*a*) The tetrahydro-compound (0·2 g.) was heated with selenium (1·0 g.) at 270—340° for 24 hr. The product was extracted into benzene and treated with a benzene solution of 2,4,7-trinitrofluorenone. Addition of methanol gave the red trinitrofluorenone complex, m. p. 214—216°, which was dissolved in benzene and chromatographed on alumina. The liberated 2,3-benzobiphenylene (0·04 g., 20%) had m. p. 242—243° alone or admixed with a sample made by the method of Jensen and Coleman.[6] The infrared spectrum showed bands at 742s and 880s cm.$^{-1}$, corresponding to 1,2-di- and 1,2,4,5-tetra-substituted benzene rings.

(*b*) Sodium borohydride (3·0 g.) in methanol (50 ml.) was added slowly to a refluxing solution of the ketone (II) (1·0 g.) in methanol (35 ml.). After being boiled for 15 min. more, the solution was concentrated and poured on ice (200 g.) and concentrated hydrochloric acid (25 ml.). Extraction of the mixture with ether gave a yellow oil which was boiled with pyridine (10 ml.) and phosphoryl chloride (5 ml.) for ½ hr., then poured on ice (200 g.), and the solid was collected. 3′,4′-*Dihydro*-2,3-*benzobiphenylene* crystallised from light petroleum (b. p. 60—80°) as a yellow solid (0·33 g., 38%), m. p. 214—215° (Found: C, 93·8; H, 5·7. $C_{16}H_{12}$ requires C, 94·1; H, 5·9%).

The dihydro-compound (0·1 g.) and chloranil (0·5 g.) in xylene (15 ml.) were boiled under reflux for 15 hr. The dark red solution was concentrated and pentane (b. p. 25—40°) was added. The precipitated quinhydrone was removed by filtration, the solution was evaporated, and the 2,3-benzobiphenylene isolated as before as the trinitrofluorenone complex, m. p. 213—215°. Regeneration from the complex gave 2,3-benzobiphenylene (15 mg., 15%), m. p. and mixed m. p. 242—243°.

Action of Potassium t-Butoxide on αα*α'*α*'-Tetrabromo-*o*-xylene.*—Tetrabromo-*o*-xylene (20 g.) was added with stirring to a solution of potassium t-butoxide (made from 14 g. of potassium and 270 ml. of t-butyl alcohol) at 70° under nitrogen. After 10 min. the mixture was poured on ice, and the excess of base neutralised by addition of glacial acetic acid. The product (10 g.) was fractionally crystallised from ethanol, giving (*a*) 1,4-dibromo-2,3-benzobiphenylene (III; R = Br) (4·85 g., 57%), golden-yellow needles, m. p. 222—223° (Found: C, 53·2; H, 2·32. Calc. for $C_{16}H_8Br_2$: C, 53·3; H, 2·32%), (*b*) yellow needles and white plates, which were then crystallised from light petroleum (b. p. 60—80°; charcoal), giving the tetrabromo-compound (IV) (4·0 g., 32·5%) as white plates, m. p. 214° decomp. (Found: C, 36·7; H, 1·7. Calc. for $C_{16}H_8Br_4$: C, 36·9; H, 1·5%). The light petroleum mother-liquors, after chromatography on alumina and elution with light petroleum (b. p. 80—100°) containing 10% of benzene, gave a small quantity of the tetrabromo-compound (IV) and by further elution with light petroleum–benzene (1 : 1) there was obtained an orange solid which, after recrystallisation from aqueous ethanol and chromatographic purification as before, gave 3,4-dibromo-1,2-benzobiphenylene (0·35 g., 4%) as orange needles, m. p. 147—148° (sublimes near m. p.) (Found: C, 52·9; H, 2·28. Calc. for $C_{16}H_8Br_2$: C, 53·3; H, 2·22%).

Conversion of the Tetrabromo-compound (IV) *into* 1,4-*Dibromo*-2,3-*benzobiphenylene* (III; R = Br).—The tetrabromo-compound (IV) (0·5 g.) in *o*-dichlorobenzene (50 ml.) was boiled for 4 hr., then cooled; ether was added and the solution washed successively with water, aqueous sodium hydrogen carbonate, and aqueous sodium metabisulphite. Removal of both organic solvents under reduced pressure yielded a residue, which was dissolved in light petroleum (b. p. 80—100°) and was filtered through a column of alumina. The filtrate yielded orange-brown needles of 1,4-dibromo-2,3-benzobiphenylene (0·16 g.), m. p. and mixed m. p. 222—223° after one recrystallisation from ethanol.

Conversion of 3-*Bromo- into* 3,4-*Dibromo*-1,2-*benzobiphenylene.*—Bromine (3·2 g.) in carbon tetrachloride (15 ml.) was added to a stirred solution of 3-bromo-1,2-benzobiphenylene[7] (2·0 g.) in the same solvent (30 ml.). The mixture was stirred for 2 hr. and the solid was then collected, washed with pure solvent, and recrystallised from benzene. The *pentabromo-compound* (VI) formed prisms, m. p. 177—178° (decomp.) (Found: C, 31·6; H, 1·4. $C_{16}H_9Br_5$ requires C, 31·9; H, 1·5%). This compound (1·0 g.) was added to a stirred solution of potassium t-butoxide (from 2·0 g. of potassium and 100 ml. of t-butyl alcohol) at 50° and boiled for 4 hr., then cooled and poured into ice–water (400 ml.). The solid crystallised from ethanol, giving 3,4-dibromo-1,2-benzobiphenylene as orange needles, m. p. and mixed m. p. 147—148°. The ultraviolet and infrared spectra of the dibromo-compound prepared by this method were identical with those of the dibromo-compound made from αα*α'*α*'*-tetrabromo-*o*-xylene.

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