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BIPHENYLENES—XXIX[1]

SYNTHESIS OF CYCLOBUTA[*b*]BIPHENYLENE-1-CARBOXYLIC ACID AND OF CYCLOPENTENO[*b*]BIPHENYLENE-1,2,3-TRIONE

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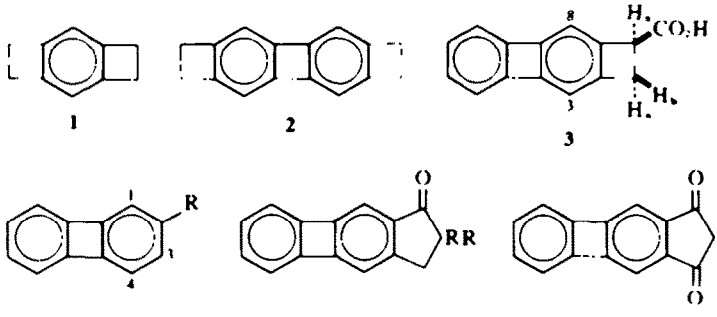
Abstract—Cyclobuta[*b*]biphenylene-1-carboxylic acid **3** has been made by photochemical ring-contraction of 2-diazocyclopenteno[*b*]biphenylene-1-one **10**. Evidence for increased strain in the acid **3** compared with 2,3-dimethylbiphenylene is discussed. Cyclopenteno[*b*]biphenylene-1,2,3-trione **12**, an analogue of anhydrous ninhydrin, was obtained by selenium dioxide oxidation of cyclopenteno[*b*]biphenylene-1-one. The preferred conformation of *Z*-2-*β*-cyanovinylbiphenylene **19** is such that the cyano group is close to the hydrogen atom at position 1 of the biphenylene ring.

The effect of ring strain on the properties of benzene rings fused to two 4-membered rings has aroused much interest and several compounds of this type have been synthesised recently, e.g. 1,2:4,5- - dicyclobutabenzene 1,[2] 1,2:3,4 - dicyclobutabenzene,[3] and 2,3:6,7 - dicyclobutabiphenylene 2.[4] We now describe the synthesis of cyclobuta[*b*]biphenylene - 1 - carboxylic acid **3**. We have also made cyclopenteno[*b*]biphenylene - 1,2,3 - trione **12** as a possible precursor of cyclobuta[*b*]biphenylene - 1,2 - dione.

2-Formylbiphenylene **4** was condensed with malonic acid to give the acrylic acid **5** which was reduced with di-imine to the propionic acid **6**. Cyclisation of the latter, via its acid chloride, then gave the indanone **8**. An alternative synthesis of this indanone, by heating 2 - (*β* - chloropropionyl)biphenylene **7** in molten sodium aluminium chloride (see Ref. 5), gave only a trace of the desired ketone. Nitrosation of the indanone **8** readily gave the oximino compound **9**, which was almost insoluble in all common organic solvents. Its sodium salt was also insoluble and, possibly for this reason, it gave only a poor yield (9%) of the diazo compound **10** when it was treated with chloramine. However, the required diazoketone **10** was conveniently prepared by first converting the indanone **8** into the hydroxymethylene derivative **11** and then treating this with *p*-toluenesulphonyl azide (method of Rosenberger *et al.*[6]). Irradiation of the diazo-ketone with UV light gave cyclobuta[*b*]biphenylene - 1 - carboxylic acid **3** in low yield (11% crude product). The structure of the acid follows from its method of preparation and was confirmed by a study of its IR and NMR spectra (see Experimental).

Biphenylene itself is a strained molecule[7] and its cyclobuta derivative **3** is even more strained. The extra strain is evidenced by a bathochromic shift in the electronic spectrum of the acid **3** [λ_{max} (EtOH) 247 (log ϵ 4.59), 255 (4.74), 353 (3.89) and 373 (4.00) nm] compared with that of 2,3-dimethylbiphenylene [λ_{max}(EtOH) 244 (4.56), 253 (4.80), 346 (3.72) and 366 (3.83) nm]. Similar bathochromic shifts have been observed for benzocyclobutene[8] compared with *o*-xylene, 1,2:4,5-dicyclobutabenzene 1[2] compared with durene, and 2,3:6,7-dicy-



4: R = CHO
5: R = CH = CHCO₂H
6: R = CH₂CH₂CO₂H
7: R = CO·CH₂CH₂Cl

8: RR = H₂
9: RR = NOH
10: RR = N₂
11: RR = CHOH

12: RR = O
13: R = R = OH

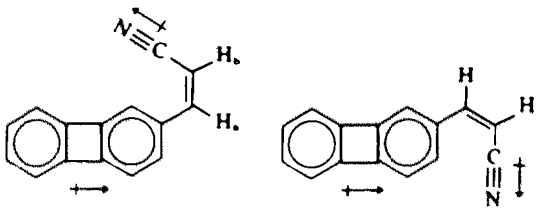
14: R = CH = CHCN
15: R = CH₂CH₂CONH₂
16: R = CH₂CH₂CN
17: R = CH₂OH
18: R = CH₂OCH₃

clobutabiphenylene **2**[4] compared with its 2,3:6,7-dicyclopenteno- and dicyclohexeno-analogues. In the NMR spectrum of the acid **3** the aromatic protons give a symmetrical AA'BB' multiplet centered at τ (d_6-DMSO) 3.38 for H-4,5,6,7 and a singlet at τ 3.51 for H-3 and H-8. These chemical shift values are almost the same as those of 2,3-dimethylbiphenylene which shows an AA'BB' multiplet at τ (d_6-DMSO) 3.35 and a singlet at 3.48. The effect of strain on the NMR spectra of benzocyclobutenes and related compounds has been discussed by Cooper and Manatt.[9] The effect on the chemical shift of the protons adjacent to the 4-membered ring in benzocyclobutene, τ ($CDCl_3$) 3.09 compared with those in *o*-xylene (3.00) is small. Our results show an even smaller effect. Similar results were found by Hillard and Vollhardt[4] for dicyclobutabiphenylene **2** compared with the dicyclohexeno-analogue, which have τ values ($CDCl_3$) of 3.72 and 3.67 respectively. This apparently orderly correlation was upset by their finding that the dicyclopentenobiphenylene analogue did not have a τ value intermediate between those of its lower and higher homologues, instead the τ value was 3.50. The authors discussed this discrepency and pointed out that there is unlikely to be a simple, direct correlation between ring-strain and chemical shift. In a footnote they drew attention to the fact that in the highly strained molecule, 1,2 - cyclopropa - 4,5 - cyclobutabenzene, the aromatic protons resonate at "normal" frequencies (τ 3.15).

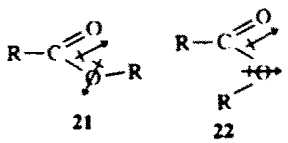
Synthesis of cyclopenteno[b]biphenylene - 1,2,3 - trione

We have studied two other possible routes to the cyclobuta[*b*]biphenylene system. The first of these was based on the work of Brown and Solly.[10] In 1965 they found that pyrolysis of indane - 1,2,3 - trione at 500° at 0.3 mm gave benzocyclobutenedione (11%) and biphenylene (17%). Under slightly different conditions we have obtained a 25% yield of the dione and this reaction has successfully been applied to the synthesis of naphtho[*b*]cyclobutene - 1,2 - dione.[11] The required cyclopenteno[*b*]biphenylene - 1,2,3 - trione **12** was obtained as its yellow hydrate **13** (61% yield) by the oxidation of the ketone **8** with selenium dioxide. When the hydrate was heated in boiling ethyl acetate it gave the reddish-orange trione **12**. This compound did not revert to the hydrate when it was exposed to the atmosphere in contrast to indane - 1,2,3 - trione and its derivatives which fairly rapidly absorb moisture to give the corresponding monohydrates. Brown and Solly[10] showed that the course of the pyrolytic fragmentation of indanetrione closely paralleled the mass spectral fragmentation of its molecular ion. The mass spectrum of the trione **12** showed successive loss of three molecules of carbon monoxide, the relative intensities of the ions (M$^+$ 234, 10%; 206, 23%; 178, 43%; 150, 100%) being closely similar to those of indane - 1,2,3 - trione (M$^+$ 160, 3%; 132, 14%; 104, 40%; 76, 100%). However, attempts to sublime the trione **12** into the pyrolysis apparatus were unsuccessful because of its lack of volatility below 140° at 0.001 mm Hg and its decomposition at higher temperatures.

Attempts were made to prepare a 3 - halogeno - 2 - β - cyanoethylbiphenylene which, on treatment with sodamide in liquid ammonia, might have given the cyanide corresponding to the acid **3**, cf. the synthesis of 1 - cyanobenzocyclobutene.[12] Treatment of 2-methylbiphenylene with iodine monochloride in acetic acid gave an inseparable mixture of 3-, 6- and 7 - chloro - 2 - methylbiphenylene. Condensation of 2-formylbiphenylene with cyano-acetic acid gave a mixture of *E*- and *Z* - 2 - β - cyanovinylbiphenylene **14**, but the side-chain could not be reduced using di-imine. 2 - β - Cyanoethylbiphenylene **16** was obtained, however, by dehydration of the amide **15** made from the propionic acid **6**. Bromination of the cyano compound **16** using thallium triacetate and bromine[13] gave an intractable mixture of mono- and di-bromo products. The crude mono-bromo products were treated with sodamide in liquid ammonia but none of the desired cyanide (3; CN in place of CO_2H) could be isolated. Finally attempts were made to emulate the exclusive *ortho*-iodination of benzyl alcohol and benzyl methyl ether by thallation followed by treatment with potassium iodide.[14] However, under these conditions, the corresponding biphenylene compounds **17** and **18** were oxidised to 2-formylbiphenylene.



19 **20**



21 **22**

Conformation of Z - 2 - β - cyanovinylbiphenylene

In the NMR spectrum of *E* - 2 - β - cyanovinylbiphenylene (see Experimental) the aromatic protons at positions 1, 3, 4, 5, 6, 7, 8 all lie in the region of τ 3.10–3.41 whereas in the *Z*-isomer the protons at positions 1 and 3 are downfield (τ 2.64 and 3.00 respectively) of the protons at 5, 6, 7, 8 (τ 3.11–3.25). This deshielding of protons H-1 and H-3 in the *Z*-isomer can be accounted for by considering the conformations shown in the coplanar structures **19** and **20**. These structures afford maximum π-orbital overlap and would therefore be expected to be the preferred conformers. It follows that, since both H-1 and H-3 lie in the deshielding zone of the cyano group in **19** and **20** respectively, the signals for these peaks will appear downfield from the remaining aromatic protons. The *greater* deshielding of H-1 relative to that of H-3 in the *Z*-isomer indicates that the majority of the molecules adopt conformations close to that shown in structure **19**. This result might be due to the fact that there is better cancellation of the dipole moment of the cyano group and that induced in the biphenylene ring in conformation **19** than in conformation **20**, cf. in esters the conformation **21** is preferred to that of **22**.

An alternative explanation for the downfield shifts of H-1 and H-3 in the *Z*-isomer, namely that these are caused by the electron-withdrawing effect of the cyano group transmitted *via* the C–C bonds, is inadmissible since an electron-withdrawing group at position 2 of biphenylene has a much greater effect at position 3 than at position 1, e.g. in 2,6-diacetylbiphenylene the τ values (in $F_3C{\cdot}CO_2H$) for H-3 and H-1 are 2.13 and 2.50 respectively.[15]

EXPERIMENTAL

IR and UV spectra were measured in Nujol mulls and in 95% ethanol respectively. NMR spectra were measured in $CDCl_3$ at 100 MHz unless otherwise stated. Petroleum refers to light petroleum (b.p. 60–80°). Silica gel M.F.C. (Hopkin & Williams Ltd.) was used for wet column chromatography and deactivated silica gel prepared in batches from silica gel M.F.C. (500 g) and water (75 ml) for dry column chromatography.[16] Columns were made in glass or in nylon tubing. The apparatus for attempted pyrolysis consisted of a horizontal silica tube (30 × 1.3 cm, i.d.) heated by an external electric furnace.

2-*Formylbiphenylene* **4**. Stannic chloride (8 ml) was added all at once to a stirred solution of biphenylene (0.6 g) and dichloromethyl methyl ether (2 ml) in ethylene dichloride (60 ml). The mixture was stirred for 24 h at room temp. then it was added to ice-cold 3 M HCl (100 ml) with vigorous stirring. After the mixture had been stirred for 0.5 h, to ensure complete hydrolysis, it was extracted with methylene dichloride. The product was purified by passing a solution of it in benzene through a short (*ca.* 5 cm) column of alumina. Evaporation of the eluate gave 2-formylbiphenylene (0.6 g, 84%), m.p. 78–79° (lit.[17] m.p. 78–79°).

β - (2 - *Biphenylenyl)propionic acid* **6**. 2-Formylbiphenylene was condensed with malonic acid to give *β* - (2 - biphenylenyl)acrylic acid **5**[17] (70%) which was reduced as follows. Sodium periodate (37.5 g) in water (350 ml) was added dropwise during 1 h to a stirred mixture of the acrylic acid (7.78 g), acetic acid (18.5 ml), saturated aqueous solution of cupric sulphate (18.5 ml), and 99% hydrazine hydrate (70 ml) in THF (210 ml). The temp. of the mixture was kept between 20 and 30° during the reaction by cooling in ice. When addition of the periodate was complete, 10 M HCl (90 ml) was added gradually. Extraction with ether gave the crude product (9.3 g) which was placed in a Soxhlet thimble and extracted with toluene (80 ml) for 3 h. On cooling the toluene, the propionic acid (7.03 g, 89%) separated. It was recrystallised once from toluene and then sublimed at 140° and 0.01 mm Hg giving *β* - (2 - *biphenylenyl)propionic acid* as pale yellow needles, m.p. 156–157°. (Found: C, 80.7; H, 5.4. $C_{15}H_{12}O_2$ requires: C, 80.3; H, 5.4%). UV λ_{max} 244 (log ϵ 4.73), 252 (4.96), 342 (3.80), 347sh (3.79) and 364 (3.98) nm.

2 - (*β* - *Chloropropionyl)biphenylene* **7**. Powdered $AlCl_3$ (320 mg, 2.4 mmole) was added to a stirred mixture of biphenylene (304 mg, 2 mmole) and *β*-chloropropionyl chloride (266 mg, 2.1 mmole) in carbon disulphide (6 ml). After 24 h, TLC (toluene) showed that biphenylene was still present). More of the acid chloride (1.05 mmole) and aluminium chloride (1.2 mmole) were added, and stirring was continued until no biphenylene remained (4 h). 3 M HCl was added and the product (434 mg) was collected in methylene dichloride. It was chromatographed on five silica gel plates (20 × 20 cm, 1 mm thick) and elution with toluene gave two bands. That with the higher R_f value gave 2 - (*β* - *chloropropionyl)biphenylene* (304 mg, 63%) as yellow plates, m.p. 132–134° (from ethanol). (Found: C, 74.1; H, 4.75; Cl, 14.9. $C_{15}H_{11}ClO$ requires: C, 74.2; H, 4.6; Cl, 14.6%). IR 1664 cm^{-1} (C=O). λ_{max} 232sh (log ϵ 4.12), 241sh (4.20), 265 (4.58), 348 (3.59) and 365 (3.56) nm, NMR τ 2.55 (H-3, dd), 2.83 (H-1, dd), 3.23 (4 ArH, m), 3.31 (H-4, dd), 6.12 ($ClCH_2$, t) and 6.70 ($CO{\cdot}CH_2$, t). $J_{1,3}$ 1.25, $J_{1,4}$ 0.75, $J_{3,4}$ 7.25 and $J_{CH_2{\cdot}CH_2}$ 6.0 Hz. The band of lower R_f value gave 2,6 - bis(*β* - chloropropionyl)biphenylene (25 mg), (M^+, 332, 334, 336).

Cyclopenteno[b]*biphenylen* - 1 - *one* **8**. The propionic acid **6** (3.4 g) was added to a cooled mixture of thionyl chloride (2 ml), pyridine (1 drop), and ether (10 ml). After 30 min at room temp the mixture was boiled under reflux for 10 min. The solvent was removed under reduced pressure (temp. <40°). Ethylene dichloride (*ca.* 10 ml) was added, and the evaporation process repeated. The residual solid was dissolved in ethylene dichloride (16 ml) and powdered $AlCl_3$ (2.1 g) was added during 20 min with stirring. After 10 min more the mixture was heated at 60° for 30 min. The mixture was then diluted with more ethylene dichloride (16 ml) and added dropwise to ice-cold 3 M HCl. The organic layer gave a grown solid which was chromatographed on a column of silica gel (50 × 5 cm) using methylene dichloride–ethyl acetate (9:1) as eluent. The ketone (2.2 g, 70%), after sublimation at 140° and 0.02 mm Hg, formed lemon yellow needles, m.p. 182–183°. (Found: C, 87.45; H, 5.05. $C_{15}H_{10}O$ requires: C, 87.35; H, 4.9%), IR 1686 cm^{-1} (C=O), UV λ_{max} 216 (log ϵ 4.05), 234 (4.20), 247sh (4.32), 271 (4.58), 327sh (3.26), 347sh (3.62) and 366 (3.81) nm, NMR τ 3.04–3.30 (5H, m), 3.32 (H-4, s) and 7.25 (CH_2CH_2, m).

2 - *Oximinocyclopenteno*[b]*biphenylen* - 1 - *one* **9**. A gentle stream of hydrogen chloride was passed through a solution of the ketone **8** (824 mg) in methylene dichloride (15 ml) for 5 min, then freshly distilled isopentyl nitrite (0.55 ml) was added dropwise; the passage of hydrogen chloride being continued during the addition and for a further 15 min. The very sparingly soluble oxime (860 mg, 91%) separated during the reaction. An analytically pure sample was obtained by placing the solid in a Soxhlet thimble and extracting it for a few hours with acetonitrile and then for 12 h with acetone. The pure oxime gradually crystallised from the hot acetone extracts as orange needles, m.p. 270° (decomp). (Found: C, 76.6; H, 3.9; N, 6.1. $C_{15}H_9NO_2$ requires: C, 76.6; H, 3.9; N, 6.0%), UV λ_{max} 237 (log ϵ 4.13), 243 (4.09), 287 (4.16), 350 (3.27), 370 (3.55) and 410 (3.65) nm.

2 - *Hydroxymethylenecyclopenteno*[b]*biphenylen* - 1 - *one* **11**. The biphenylen - 1 - one **8** (600 mg) in benzene (16 ml) and ethyl formate (1.2 ml) was added to a stirred, ice-cold solution of NaOMe in MeOH (200 mg Na in 3 ml MeOH). After being stirred at room temp. for 17 h the mixture was acidified with 3 M HCl, and the product was collected in chloroform. The crude material (652 mg) was extracted with acetone (50 ml) in a Soxhlet apparatus for 1 h. The extract was discarded and the solid was further extracted with fresh acetone (50 ml) for 12 h. This extract was concentrated and gave the hydroxy methylene compound **11** as an orange powder (433 mg, 65%), m.p. 194–195° (decomp). (Found: M^+, 234.068. $C_{16}H_{10}O_2$ requires: 234.068).

2 - *Diazocyclopenteno*[b]*biphenylen* - 1 - *one* **10**. (a) The oxime **9** (100 mg) was suspended in 15 M ammonium hydroxide (5 ml) and a 5.1% solution of NaOCl (20 ml) was added dropwise at 0° during 1 h. Next day the mixture was extracted with CH_2Cl_2 and the crude product (30 mg) was chromatographed on a silica gel plate (20 × 20 cm, 0.3 mm layer) using CH_2Cl_2–EtOAc as eluent. The yellow band was removed from the plate and extracted with CH_2Cl_2; it gave the diazo compound **10** (9 mg, 9%), m.p. 176–177° (decomp.).

(b) The hydroxymethylene compound **11** (351 mg) was dissolved in hot dioxan (15 ml) and the solution cooled to 20°. *p*-Toluenesulphonyl azide (295 mg) then diethylamine (0.31 ml) were added to the stirred solution. After 45 min TLC showed starting material was still present. More *p*-toluenesulphonyl azide (100 mg) and diethylamine (0.1 ml) were added and the mixture was stirred for 17 h more. A third portion of azide (200 mg) was added and the mixture stirred for a further 2 h. The solvent was removed and the product was chromatographed on a dry, deactivated silica gel column (25 × 3 cm), eluting with $CHCl_3$–EtOAc (9:1). The eluate gave the diazo-ketone (275 mg, 79%) as orange needles (from toluene-hexane), decomp. *ca.* 175°. It could not be obtained analytically pure. IR 2068s (br) (C=N_2) cm^{-1}, NMR τ 3.05 (H-9, s), 3.07–3.31 (4H, m), 3.35 (H-4, s) and 6.13 (CH_2).

Cyclobuta[b]*biphenylene* - 1 - *carboxylic acid* **3**. A mixture of the diazo-ketone **10** (600 mg), $NaHCO_3$ (2 g), water (10 ml), and THF (90 ml) in a Pyrex vessel was irradiated under N_2 for 23 h at 25° using a 125 W Hanovia medium-pressure UV lamp. Most of the solvent was removed, then water (50 ml) was added, followed by 10 M NaOH (*ca.* 10 ml). The aqueous solution was decanted from the residue, washed with ether, then acidified with 10 M HCl. The precipitate (64 mg, 11%) was collected and sublimed at 130° and 0.001 mm Hg to give the acid **3** as a cream powder, m.p. 196–197° (Found: M^+ 222.069; C, 81.2; H, 4.5. $C_{15}H_{10}O_2$ requires: M 222.068; C, 81.1; H, 4.5%), IR 2710 m(br), 2610m(br), 1690s(v. br), 874s, 744vs and 734s cm^{-1}, UV λ_{max} 247 (log ϵ 4.59), 255 (4.74), 353 (3.89) and 373 (4.0) nm, NMR (d_6-DMSO) τ 3.38 (4H, m), 3.51 (H-3, H-8, s), 6.01 (H^a, m), 6.81 (H^b, m), 6.93 (H^c, m). J_{ab} 14.2, J_{ac} 6.1 and J_{bc} 2.4 Hz.

Benzocyclobutene - 1,2 - *dione*. Indan - 1,2,3 - trione (10 g) was sublimed at 155–175° and 0.1–0.3 mm Hg over a period of 16 h through an unpacked silica tube (40 cm × 1.3 cm i.d.) heated by an electric furnace at 620°. The pyrolysis products were removed from the tube and traps with the aid of CH_2Cl_2. Evaporation of

the solution gave a dark solid (3.7 g) which was chromatographed on a dry silica gel column (100 × 3 cm) and eluted with toluene. The yellow band gave the dione (2.16 g, 25%) as yellow needles, m.p. 131°.

Cyclopenteno[b]biphenylene - 1,2,3 - trione **12**. A mixture of the ketone **8** (824 mg), selenium dioxide (888 mg), water (0.2 ml), and peroxide-free dioxan (10 ml) was refluxed under nitrogen for 6 h. The mixture was filtered and evaporated to dryness giving a brownish-black solid (721 mg). A portion (82 mg) of this was purified by plate chromatography (20 × 20 cm × 1 mm) on silica gel with CH_2Cl_2–EtOAc (4:1) as eluent. The yellow band gave the trione hydrate **13** (70 mg, 61%) which was recrystallised from acetone–petroleum, m.p.—decomp. above 140°. On drying at room temperature *in vacuo* partial dehydration occurred and it was not possible to obtain a satisfactory analysis. IR 3415s(br), 1748vs, 1710vs, 940m and 752 cm^{-1}. UV λ_{max} 224 (log ϵ 4.06), 284 (4.62), 364 (3.69) and 382 (3.86) nm.

The trione hydrate was heated in boiling ethylacetate for *ca.* 30 min then the solvent was removed and the residue was sublimed at 150° and 0.03 mm Hg to give the reddish orange trione **12**, m.p. 275° (decomp.). (Found: C, 76.6; H, 2.9. $C_{15}H_8O_3$ requires: C, 76.9; H, 2.6%). IR 1771s, 1731vs, 1696vs, 888w and 759m cm^{-1}.

E- and Z - 2 - β - Cyanovinylbiphenylene **14**. 2-Formylbiphenylene (1.8 g), cyano-acetic acid (1.19 g), and piperidine (0.18 ml) in pyridine (9 ml) were heated at 110–115° for 40 h. The mixture was cooled to 0° and acidified with 10 M HCl, added dropwise with stirring during 45 min. The precipitate (2.01 g) was collected and chromatographed on a column (100 × 5 cm) of dry, deactivated silica gel in a nylon tube, with benzene (1050 ml) as eluent. The bright yellow band (32 cm) was cut in half and each portion was extracted with ether. The fraction (295 mg) having the lower R_f value contained the *E*-isomer plus 2-formylbiphenylene. The fraction (1.03 g) with higher R_f value contained the *E*- and *Z*-isomers. A portion (125 mg) of this mixture was chromatographed on 5 silica gel plates (20 × 20 cm × 1 mm). The plates were eluted with benzene and the appropriate bands united thereby giving the *E*-isomer (59 mg) and *Z*-isomer (42 mg). The *E*-isomer formed bright yellow needles (from *n*-hexane), m.p. 142–143°. (Found: C, 88.65; H, 4.6; N, 7.0. $C_{15}H_9N$ requires: C, 88.6; H, 4.5; N, 6.9%). IR 3060w, 2220s, 1618s, 988s (trans HC=CH), 817s and 750vs cm^{-1}. UV λ_{max} 228 (log ϵ 4.18), 235 (4.16), 283 (4.47), 293 (4.47) and 386 (3.87) nm. NMR τ 2.83 (ArCH=, d), 4.33 (=CHCN, d), 3.10–3.41 (7 ArH, m), J 16.8 Hz. The *Z*-isomer formed yellow plates (from *n*-hexane), m.p. 78–79°. (Found: C, 89.1; H, 4.7; N, 7.0%). IR 3060w, 2217m, 1611w, 855s and 739vs (*cis* HC=CH) cm^{-1}. UV λ_{max} 230 (log ϵ 4.11), 235 (4.13), 282 (4.30), 291 (4.27) and 380 (3.68) nm. NMR (with decoupling) τ 2.64 (H-1, s, br), 3.00 (H-3, dd, br), 3.33 (H-4, dd), 3.18 (4H, m), 3.15 (Ha, dd) and 4.72 (Hb, d), $J_{1,3}$ 1.5, $J_{1,4}$ 1.0, $J_{3,4}$ 7.5, $J_{a,b}$ 12.3, $J_{a,3}$ 0.5 Hz.

2 - β - Cyanoethylbiphenylene **16**. 2-Carboxyethylbiphenylene (850 mg) was warmed with $SOCl_2$ (0.5 ml) and one drop of pyridine in ether (2.5 ml), then the volatile components were removed under reduced pressure and the residue treated with ammonium hydroxide to give *2 - β - carbamoylethylbiphenylene* **15** (808 mg, 95%) pale yellow plates (from benzene), m.p. 184–186°. (Found: C, 80.4; H, 5.6; N, 6.2. $C_{15}H_{13}NO$ requires: C, 80.7; H, 5.9; N, 6.3%). IR 3395m, br, 3202m, br, 1659s, br, 827m and 735s cm^{-1}. UV λ_{max} 243 (log ϵ 4.64), 252 (4.89), 343 (3.72), 347 (3.70) and 364 (3.90) nm. The above finely ground amide (743 mg) and SO_2Cl_2 (0.42 ml) in benzene (2.5 ml) was heated at 80° for 7 h. The crude product was chromatographed on a column (45 × 3 cm) of dry, deactivated silica gel: elution with benzene gave the cyano compound **16** (484 mg, 71%) as yellow plates (from *n*-hexane), m.p. 79–80°. (Found: C, 87.9; H, 5.5; N, 7.1. $C_{15}H_{11}N$ requires: C, 87.8; H, 5.4; N, 6.8%). IR (in CS_2) 2242vw, 818m and 737vs cm^{-1}. UV λ_{max} 243 (log ϵ 4.48), 252 (4.79), 342 (3.51), 347 (3.45) and 363 (3.69) nm.

2-Hydroxymethylbiphenylene **17**. Sodium borohydride (570 mg) in ethanol (45 ml) was added to 2-formylbiphenylene (1.8 g) in tetrahydroguran (5 ml). After 30 min the mixture was evaporated to dryness and the residue boiled with water (40 ml) for 45 min. The alcohol (100% yield) formed white plates (from CCl_4), m.p. 113–114° (lit.[10] 103–105°). (Found: C, 85.5; H, 5.5. Calc. for $C_{13}H_{10}O$: C, 85.6; H, 5.5%). NMR τ 3.21–3.47 (7 ArH, m), 5.57 (CH_2) and 8.34 (OH).

2-Methoxymethylbiphenylene **18**. 2-Hydroxymethylbiphenylene (182 mg) was added to powdered potassium (97.5 mg) in benzene (5 ml) and the mixture stirred under N_2 for 15 h. Methyl iodide (1.6 ml) was added and refluxing was continued for 3 h more. The mixture was filtered and solvent was removed under reduced pressure. The residual oil (205 mg) was distilled at 50° and 0.01 mm Hg and gave the methyl ether **18** as a pale yellow oil. (Found: M^+ 196.089. $C_{14}H_{12}O$ requires: M 196.089). NMR τ 3.2–3.45 (7 ArH, m), 5.78 (CH_2) and 6.66 (CH_3).

2-Methylbiphenylene (Dr. D. V. Gardner). 2-Formylbiphenylene (406 mg), KOH (0.4 g) and 99% hydrazine hydrate (0.6 ml) in diethylene glycol (20 ml) were heated under reflux for 1 h. Water and excess hydrazine were then removed by distillation until the temp. of the boiling solution reached 180°. After 3 h at this temperature, the solution was cooled, diluted with water and the solid collected by filtration. It was chromatographed on silica gel in *n*-hexane then sublimed at 60° and 0.5 mm Hg to give 2-methyl biphenylene (288 mg, 77%), m.p. 48° (lit.[19] 45–46°).

2 - Formyl - 3 - methylbiphenylene. Stannic chloride (1.55 ml) was added to a stirred solution of 2-methylbiphenylene (1.49 g) and Cl_2CHOMe (1.15 ml) in CH_2Cl_2 (40 ml). The mixture was kept for 12 h then it was acidified with 3 M HCl. The organic layer was washed with water, dried, and evaporated. The crude product was chromatographed on a column of aluminium oxide. Elution with toluene gave a mixture of formyl compounds (1.11 g, 64%) shown by NMR to contain approximately 85% of 2 - formyl - 3 - methyl- and 15% 2 - formyl - 6(or 7) - methylbiphenylene. A sample, purified by chromatography and then by sublimation at 100° and 0.5 mm Hg, gave *2 - formyl - 3 - methylbiphenylene* as bright yellow crystals, m.p. 136–138°. (Found: C, 86.4; H, 5.4. $C_{14}H_{10}O$ requires: C, 86.6; H, 5.2%). NMR τ 0.06 (CHO), 2.94 (H-1, br, s), 3.2 (4 ArH, m), 3.44 (H-4, br, s) and 7.50 (CH_3).

2,3-Dimethylbiphenylene. 2 - Formyl - 3 - methylbiphenylene was reduced as described above for 2-methylbiphenylene. 2,3-Dimethylbiphenylene formed pale yellow crystals (from methanol) m.p. 110–112° (lit.[20] 111–112°). NMR (d_6-DMSO) τ 3.26–3.44 (H-5, 6, 7, 8, m), 3.48 (H-1, H-4) and 7.97 (2 × CH_3).

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