

908. *Biphenylenes. Part XIII.*<sup>1</sup> *Diacylation of Biphenylene*

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Biphenylene reacts with acetyl and propionyl chloride in the Friedel-Crafts reaction to give mixtures of the corresponding 2,6- and 2,7-diacyl derivatives, in which the former predominates. The pairs of isomers cannot be interconverted in the presence of aluminium chloride and hence they are most probably formed directly by competing reactions.

DIACETYLATION of biphenylene by the Friedel-Crafts reaction has previously been shown to yield 2,6-diacetylbiphenylene (I; R = Me), no other isomer being found despite a careful search.<sup>2,3</sup> During studies on the propionylation of biphenylene we have found that two isomeric compounds are formed, the major product (75%), m. p. 241—242°, being 2,6-dipropionylbiphenylene (I; R = Et) and the minor product (4%), m. p. 127—128°, the 2,7-isomer (II; R = Et). The orientation of these compounds is discussed below. The diacetylation of biphenylene was reinvestigated and this time both 2,6- (45%, m. p. 253—254.5°) and 2,7- (6%, m. p. 174°) diacetylbiphenylene were obtained. This pair of isomers is very much harder to separate than the dipropionyl pair and in retrospect it is not surprising that earlier attempts to detect isomers of 2,6-diacetylbiphenylene failed.



The ultraviolet spectrum of the higher-melting dipropionylbiphenylene is almost the same as that of 2,6-diacetylbiphenylene (I; R = Me), the constitution of which has been established previously.<sup>3</sup>

The nuclear magnetic resonance (n.m.r.) spectrum of the former compound is entirely consistent with the structure as 2,6-dipropionylbiphenylene, the two propionyl groups giving a single set of absorption bands characteristic of an ethyl group, *viz.*, a triplet ( $\tau = 8.71$ ) and a quartet ( $\tau = 6.95$ ) with  $J = 7.3$  c./sec. The aromatic protons showed as a singlet ( $\tau = 2.65$ ) and two doublets ( $\tau = 2.23$  and  $3.11$ ;  $J = 7.5$  c./sec.). No *meta* or *para* coupling was detected. The simplicity of the spectrum indicates an identical arrangement of protons on the two benzene rings. The singlet is clearly due to the isolated protons at the 1- and the 5-position, and the low-field doublet must be due to the protons at positions 3 and 7, *i.e.*, adjacent to the propionyl groups. It is noteworthy that the deshielding effect of the acyl groups is greater at the 3- and 7- than at the 1- and 5-positions; in biphenylene itself there is only a small chemical shift between the  $\alpha$ - and the  $\beta$ -position.<sup>4,5</sup> There is evidence<sup>6</sup> that the chemical shift of an aromatic proton increases (moves to higher field) with an increase in  $\pi$ -electron density at the carbon atom to which it is attached.\* That the 3-proton absorbs to low field of the 1-proton (by *ca.* 0.4 p.p.m.) is consistent with calculations of the L.C.A.O. model,<sup>7</sup> which, for a 2-biphenylenylmethyl ion predicts the charge at the 3-position to be four times that at the 1-position.

The structure of 2,6-dipropionylbiphenylene was confirmed by treating it with Raney nickel containing adsorbed hydrogen, when it gave 3,4'-dipropionylbiphenyl, m. p. 58—59°, as shown by its analysis and its ultraviolet absorption spectrum which is almost the

\* This is not the only factor determining the position of absorption of an aromatic proton, but when comparing the two protons *ortho* to the acyl group the other effects will be small or approximately the same for each proton.

<sup>1</sup> Part XII, J. W. Barton, D. E. Henn, K. A. McLauchlan, and J. F. W. McOmie, *J.*, 1964, 1622.

<sup>2</sup> W. Baker, M. P. V. Boarland, and J. F. W. McOmie, *J.*, 1954, 1476.

<sup>3</sup> W. Baker, J. W. Barton, and J. F. W. McOmie, *J.*, 1953, 2666.

<sup>4</sup> G. Fraenkel, Y. Asahi, M. J. Mitchell, and M. P. Cava, *Tetrahedron*, 1964, **20**, 1179.

<sup>5</sup> A. R. Katritzky and R. E. Reavill, *Rec. Trav. chim.*, 1964, **83**, 1230.

<sup>6</sup> V. R. Sandel and H. H. Freedman, *J. Amer. Chem. Soc.*, 1963, **85**, 2328.

<sup>7</sup> H. C. Longuet-Higgins, *Proc. Chem. Soc.*, 1957, 157.

same as that of 3,4'-diacetyl biphenyl and quite different from those of 3,3'- or 4,4'-diacetyl biphenyl.<sup>3</sup> The new dipropionyl biphenyl differs from the known 2,2'-compound, b. p. 122–123°/0.001 mm.,<sup>8</sup> and the 4,4'-isomer,<sup>9</sup> m. p. 168°; 2,7-dipropionyl biphenylene (I; R = Et) would be expected to yield 3,3'- and 4,4'-dipropionyl biphenyl, or a mixture of these two.

The lower-melting dipropionyl biphenylene gives an n.m.r. spectrum which is very similar to that of the 2,6-isomer, with minor differences in  $J$  and  $\tau$  values for the aromatic protons, a singlet ( $\tau = 2.67$ ) again appearing between two doublets ( $\tau = 2.30$  and  $3.14$ ;  $J = 7.8$  c./sec.). The only alternative arrangement which can give a similar pattern to that of the 2,6-isomer in each ring is that of 2,7-dipropionyl biphenylene.

The n.m.r. spectrum of the lower-melting diacetyl biphenylene shows that this compound must have the 2,6- or 2,7-orientation, but since the compound differs from the known compound, 2,6-diacetyl biphenylene (I; R = Me), it must be the 2,7-isomer (I; R = Me). Its ultraviolet absorption spectrum is closely similar to that of 2,7-dipropionyl biphenylene; it is also similar to, but distinct from, that of 2,6-diacetyl biphenylene. In the n.m.r. spectrum of 2,7-diacetyl biphenylene the methyl groups absorb at  $\tau = 7.30$  (singlet), the 1,8-protons at  $\tau = 2.59$ , the 3,6-protons at  $\tau = 2.17$  and the 4,5-protons at  $\tau = 3.00$  with  $J_{3,4} = 7.5$  c./sec. The n.m.r. spectrum of 2,6-diacetyl biphenylene shows bands at  $\tau = 7.28$  (singlet, methyl groups),  $\tau = 2.50$  (triplet, H-1 and H-5),  $\tau = 2.13$  and  $\tau = 3.00$  (double doublets, H-3, H-7 and H-4, H-8 respectively) with  $J_{1,3} = 1.4$  c./sec.,  $J_{1,4} = 0.8$  c./sec., and  $J_{3,4} = 7.8$  c./sec.

Unlike sulphonation, the Friedel-Crafts acylation of aromatic hydrocarbons is normally irreversible. However, the possibility that the 2,7-diacyl biphenylenes were being formed by isomerisation of the 2,6-compounds was investigated. Both 2,6- and 2,7-diacetyl biphenylene were treated with acetyl chloride and aluminium chloride in chloroform under the conditions used in the diacetylation of biphenylene but starting material only was recovered in each case. Hence, the two isomers must be formed by simultaneous, competing

Ultraviolet absorption maxima in 95% ethanol

Biphenylene deriv.	$\lambda$ (m $\mu$ )	$\log_{10} \epsilon$	$\lambda$ (m $\mu$ )	$\log_{10} \epsilon$	$\lambda$ (m $\mu$ )	$\log_{10} \epsilon$
2-Propionyl .....	261 <sup>a</sup>	4.58	348	3.60	362	3.76
2,6-Diacetyl <sup>b</sup> .....	219	4.08	284 <sup>c</sup>	4.60	344 <sup>c</sup>	3.64
	ca. 226	infl.	287	4.61	360	3.93
	261	4.51			377	4.10
2-Acetyl-6-propionyl .....	219	3.94	284	4.59	344 <sup>c</sup>	3.63
	ca. 227	infl.	287	4.59	359	3.92
	262	4.49			376	4.09
2,6-Dipropionyl .....	219	4.01	285 <sup>a</sup>	4.59	344 <sup>c</sup>	3.63
	ca. 227	infl.			359	3.92
	260	4.51			376	4.08
2,7-Diacetyl .....	220 <sup>c</sup>	4.18	267 <sup>c</sup>	4.74	325	3.37
	229	4.19	275	4.81	343 <sup>c</sup>	3.45
	237 <sup>c</sup>	4.13	308 <sup>c</sup>	3.31	ca. 369	infl.
					393	3.71
2,7-Dipropionyl .....	219 <sup>c</sup>	4.17	266 <sup>d</sup>	4.75	344 <sup>c</sup>	3.45
	228	4.18	274	4.82	367 <sup>d</sup>	3.64
	236 <sup>c</sup>	4.14	307 <sup>c</sup>	3.25	376	3.70
			326	3.32	388 <sup>c</sup>	3.69

<sup>a</sup> Very broad. <sup>b</sup> New measurement, cf. ref. 3. <sup>c</sup> Shoulder. <sup>d</sup> Inflexion.

acylations of the first-formed 2-acyl biphenylene, the rate of acylation being greater in the 6- than in the 7-position. The formation of small amounts of 2,7-diacyl biphenylenes does not invalidate previous conclusions<sup>3</sup> regarding the transmission of the electron-withdrawing effect of the 2-acyl group across the biphenylene ring system since position 7 is clearly much

<sup>8</sup> R. G. R. Bacon and W. S. Lindsay, *J.*, 1958, 1375.

<sup>9</sup> L. M. Long and H. R. Henze, *J. Amer. Chem. Soc.*, 1941, **63**, 1939.

less reactive than position 6 as shown by the disparity in yields\* of the products. If the effect of the 2-acyl group were not transmitted across the molecule then approximately equal amounts of 2,6- and 2,7-diacylbiphenylenes would be expected to be formed.

The preparation of 2-propionyl- and 2-acetyl-6-propionyl-biphenylene is recorded in the Experimental section. The diacyl compound was made both by acetylation of 2-propionyl-biphenylene and by propionylation of 2-acetyl-biphenylene; its orientation follows from the close similarity of its ultraviolet absorption spectrum to that of 2,6-dicetyl- and 2,6-di-propionyl-biphenylene.

#### EXPERIMENTAL

Infrared spectra were measured in Nujol mulls unless otherwise stated. The n.m.r. spectra were measured at 60 Mc./sec. in trifluoroacetic acid, with tetramethylsilane as internal standard.

*Reaction of Biphenylene with Propionyl Chloride.*—Aluminium chloride (6.5 g.), biphenylene (2.0 g.), and propionyl chloride (9.0 g.) in carbon disulphide (140 ml.) were made to react in the usual way.<sup>2,3</sup> The product was recrystallised from acetic acid thereby giving 2,6-dipropionyl-biphenylene (I; R = Et) (2.6 g., 75%) as pale yellow needles, m. p. 241—242° (Found: C, 81.6; H, 6.0. C<sub>18</sub>H<sub>16</sub>O<sub>2</sub> requires C, 81.8; H, 6.1%),  $\nu_{\text{C=O}}$  1670s cm.<sup>-1</sup>. The mother-liquor was diluted with water and the precipitate was sublimed under reduced pressure and then recrystallised from methanol, thereby giving 2,7-dipropionylbiphenylene (II; R = Et) (0.15 g., 4%) as bright yellow blades, m. p. 127—128° (Found: C, 81.7, 81.8; H, 5.7, 6.2%),  $\nu_{\text{C=O}}$  1672s cm.<sup>-1</sup>.

When the above experiment was repeated using a less active sample of aluminium chloride the product was 2-propionylbiphenylene (1.5 g., 52%) which crystallised from methanol as yellow plates, m. p. 95° (Found: C, 86.4; H, 5.8. C<sub>15</sub>H<sub>12</sub>O requires C, 86.5; H, 5.8%),  $\nu_{\text{C=O}}$  1675s cm.<sup>-1</sup>. A trace only of dipropionylbiphenylene was formed. The monopropionylbiphenylene gave the corresponding oxime which crystallised from 95% ethanol as yellow prisms, m. p. 160—161° (Found: C, 80.5; H, 6.1. C<sub>15</sub>H<sub>13</sub>NO requires C, 80.7; H, 5.9%).

2,6-Dipropionylbiphenylene was converted into the dioxime, m. p. 240—242°, and thence, by reaction with boron trifluoride in acetic acid, into 2,6-dipropionamidobiphenylene, m. p. 308—310° (from ethanol) (Found: C, 72.9; H, 6.0. C<sub>18</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub> requires C, 73.4; H, 6.2%). Attempts to convert this compound into the known 2,6-diacetamidobiphenylene were unsuccessful.

*Reduction of 2,6-Dipropionylbiphenylene to 3,4'-Dipropionylbiphenyl.*—2,6-Dipropionylbiphenylene (1.5 g.) was refluxed for 1.5 hr. in ethanol (125 ml.) with Raney nickel (made from 5 g. alloy). The hot solution was filtered and, on cooling, yield a few mg. of starting material. The mother liquor from this was evaporated and the residue was purified by vacuum sublimation and recrystallisation from light petroleum (b. p. 40—60°) then several times from aqueous ethanol gave 3,4'-dipropionylbiphenyl (0.05 g.) as needles, m. p. 58—59° (Found: C, 81.2; H, 6.7. C<sub>18</sub>H<sub>18</sub>O<sub>2</sub> requires C, 81.2, 6.8%),  $\lambda_{\text{max}}$  (EtOH) 216, 255, 280 m $\mu$  (log<sub>10</sub>  $\epsilon$  4.39, 4.29, 4.38, respectively).

The biphenyl gave a mono-2,4-dinitrophenylhydrazone as a dark red powder, m. p. 104—105° (Found: C, 64.5; H, 5.1. C<sub>24</sub>H<sub>22</sub>N<sub>4</sub>O<sub>5</sub> requires C, 64.6; H, 5.0%). This hydrazone is probably derived from the 4'-propionyl group since 4-acetyl-biphenyl gives a red 2,4-dinitrophenylhydrazone whereas 3-acetyl-biphenyl gives an orange derivative.<sup>2</sup> Under similar conditions, 4,4'-dipropionylbiphenyl, m. p. 168°, gave an orange bis-2,4-dinitrophenylhydrazone, m. p. 276° (Found: C, 57.6; H, 4.2. C<sub>30</sub>H<sub>26</sub>N<sub>8</sub>O<sub>8</sub> requires C, 57.5; H, 4.15%).

*2,7-Diacetyl-biphenylene* (II; R = Me).—Acetyl chloride (13 g.) in chloroform (120 ml., dried over phosphoric anhydride) was added with stirring to powdered aluminium chloride (22 g.). The mixture was warmed gently until the solid had dissolved. Biphenylene (2.0 g.) in dried chloroform (30 ml.) was added during 0.5 hr. with vigorous stirring. After being stirred for a further 2 hr. the mixture was poured on ice (500 g.) and concentrated hydrochloric acid (100 ml.). More chloroform (400 ml.) was added and the whole was stirred until all the ice had melted. The chloroform was separated and the aqueous layer and precipitate were extracted several times with chloroform. The combined chloroform extracts yielded a yellow-brown solid which

\* The yields of diacylbiphenylenes in this and previous papers are based on the initial amount of biphenylene used: they do not allow for the amount of monoacylated compound nor for unreacted biphenylene. In all but one of the diacylations which we have carried out in this and in previous work the yield of 2,6-diacylbiphenylene calculated in this way has been between 60 and 75%.

was dissolved in hot acetic acid, from which 2,6-diacetylbiphenylene was deposited on cooling. This was recrystallised from benzene-chloroform (1 : 1) and gave the pure 2,6-diacetyl compound (1.34 g., 43%), m. p. and mixed m. p. with authentic material,<sup>3</sup> 253—254.5°,  $\nu_{\text{C=O}}$  1668s  $\text{cm}^{-1}$ .

The mother-liquor from the acetic acid crystallisation was poured into water and the precipitate was separated into its components by chromatography on alumina. The column was first eluted with benzene-light petroleum (b. p. 60—80°) (1 : 1) until the band containing 2-acetylbiphenylene (0.34 g., 13%) was completely removed. Elution was continued with benzene-light petroleum (b. p. 60—80°) (3 : 1) until the bright yellow band containing diacetylbiphenylene was clear of an upper brown band of tarry material. The alumina was then extruded from the column and the portion containing the brown band was discarded. The remaining alumina was extracted with hot methanol (3  $\times$  100 ml.) and after removal of solvent the residue solid was recrystallised from benzene-light petroleum (b. p. 60—80°) (3 : 1), giving more 2,6-diacetylbiphenylene. The mother-liquors were again evaporated and the solids were recrystallised from methanol giving 2,7-diacetylbiphenylene, which was separated from traces of the 2,6-isomer by crystallisation from benzene-light petroleum to low recovery, followed by evaporation of the solvent and crystallisation of the residue from methanol. Final crystallisation from the mixed solvent gave 2,7-diacetylbiphenylene (0.13 g., 4%) as bright yellow plates, m. p. 174° (Found: C, 81.3; H, 5.1.  $\text{C}_{16}\text{H}_{12}\text{O}_2$  requires C, 81.3; H, 5.1%),  $\nu_{\text{C=O}}$  (in chloroform) 1678s;  $\nu_{\text{C=O}}$  (Nujol mull) 1668s and 1648s  $\text{cm}^{-1}$ . The splitting in the solid phase may be due to Fermi resonance with the first overtone of the band appearing at 824s  $\text{cm}^{-1}$ . After recrystallisation from methanol the biphenylene contained solvent of crystallisation (Found: C, 77.5; H, 5.7.  $\text{C}_{16}\text{H}_{12}\text{O}_2 \cdot 0.75\text{CH}_3\text{OH}$  requires C, 77.3; H, 5.8%). Similar results were obtained when carbon disulphide was used in place of chloroform as solvent for the reaction.

*2-Acetyl-6-propionylbiphenylene.*—(a) Powdered aluminium chloride (0.2 g.) was added in portions to a solution of 2-acetylbiphenylene (0.27 g.) and propionyl chloride (3.5 g.) in carbon disulphide. The product was isolated as usual and after recrystallisation from acetic acid it formed yellow needles (0.26 g., 75%), m. p. 206.5—208°.

(b) A similar reaction using 2-propionylbiphenylene and acetyl chloride gave the same product, 2-acetyl-6-propionylbiphenylene (61%), m. p. and mixed m. p. 206.5—208° (Found: C, 81.6; H, 5.6.  $\text{C}_{17}\text{H}_{14}\text{O}_2$  requires C, 81.6; H, 5.6%),  $\nu_{\text{C=O}}$  1670s  $\text{cm}^{-1}$ .

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