

**981.** *Dimerisation of 2,2-Diphenyl- and 2,2-Dimethyl-chromen. Part II.*<sup>1</sup> *Reaction between 3-(2-Hydroxyphenyl)-1,3-diphenylpropan-1-one and 3-(2-Hydroxyphenyl)-1,1-diphenylprop-2-en-1-ol*

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Barnes and his co-workers suggested a structure for the dimer obtained from 3-(2-hydroxyphenyl)-1,1-dimethylprop-2-en-1-ol. It has been shown that 3-(2-hydroxyphenyl)-1,3-diphenylpropan-1-one (I) reacts with 3-(2-hydroxyphenyl)-1,1-diphenylprop-2-en-1-ol (II) to give the compound (VIII) previously believed to be a dimer of 2,2-diphenylchromen (III). 2,2-Diphenylchromen and 6,6-diphenylnaphtho(2',1':2,3)pyran have been prepared by an unambiguous method.

BARNES, OCCOLOWITZ, and STRONG<sup>2</sup> indicated that the products of the reaction between coumarin and phenylmagnesium bromide are 3-(2-hydroxyphenyl)-1,3-diphenylpropan-1-one (I) and 3-(2-hydroxyphenyl)-1,1-diphenylprop-2-en-1-ol (II), and that the compound Löwenbein<sup>3</sup> believed to be 2,2-diphenylchromen (III) was in fact compound (II). We have found that Löwenbein did obtain 2,2-diphenylchromen, for the use of steam-distillation to remove biphenyl from the reaction mixture also resulted in some dehydration and cyclisation of (II). Following the removal of the 3-(2-hydroxyphenyl)-1,3-diphenylpropan-1-one, further dehydration and cyclisation occurred during recrystallisation. Barnes *et al.* removed the biphenyl from the crude diol fraction by grinding with light petroleum. 2,2-Diphenylchromen was isolated following the pyrolysis of the acetate of 2,2-diphenylchroman-4-ol (IVb) obtained by the reduction of 2,2-diphenylchroman-4-one (IVa), and was identical with the compound prepared by Löwenbein.<sup>3</sup>

2,2-Diphenylchroman-4-one was prepared by a modification of the method of Wawzonek,<sup>4</sup> the chromanone being separated from the 3,3-diphenyl-1-(2-hydroxyphenyl)prop-2-en-1-one (V) by chromatography. No ketone (IVa) was isolated after an attempted Fries rearrangement of phenyl  $\beta\beta$ -diphenylacrylate (VI).<sup>5</sup>

Since some of the 3-(2-hydroxyphenyl)-1,3-diphenylpropan-1-one (I) remained in the ether extract, the separation of the products of the Grignard reaction was not quite as complete as suggested by Löwenbein.<sup>3</sup> Consequently, traces of this compound could still be found in some samples of 2,2-diphenylchromen even after many recrystallisations. When present, it was this impurity which reacted with any diol (II) in the sample of 2,2-diphenylchromen when boiled with acetic acid<sup>3</sup> or methanolic hydrogen chloride;<sup>2</sup> as a result the so-called dimer was formed. Pure 2,2-diphenylchromen, prepared from

<sup>1</sup> Part I, R. Livingstone, D. Miller, and S. Morris, *J.*, 1960, 602.

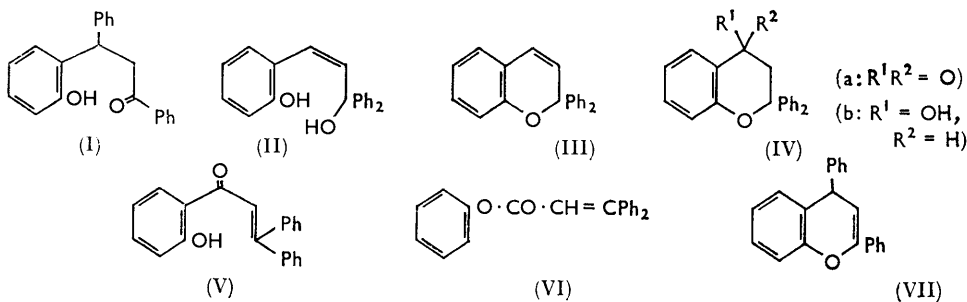
<sup>2</sup> C. S. Barnes, J. L. Occolowitz, and M. I. Strong, *Tetrahedron*, 1963, **19**, 839.

<sup>3</sup> A. Löwenbein, *Ber.*, 1924, **57**, 1517.

<sup>4</sup> S. Wawzonek, R. C. Nagler, and L. J. Carlson, *J. Amer. Chem. Soc.*, 1954, **76**, 1080.

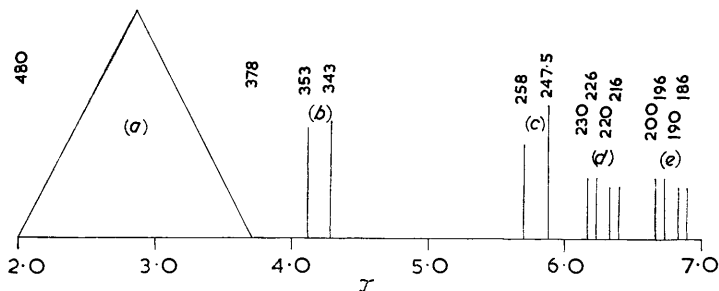
<sup>5</sup> S. Patai and R. Ikan, *J. Org. Chem.*, 1956, **21**, 1379.

2,2-diphenylchroman-4-one or from the diol (II), did not react when treated as above. The dehydration and cyclisation of the diol <sup>2</sup> to 2,2-diphenylchromen was more effectively carried out by boiling with acetic acid.



The compound of m. p. 242—243° (lit., 239°) was obtained when equimolecular proportions of 3-(2-hydroxyphenyl)-1,1-diphenylprop-2-en-1-ol (II) and either 3-(2-hydroxyphenyl)-1,3-diphenylpropan-1-one (I) or 2,4-diphenyl-4*H*-chromen (VI) were boiled with acetic acid. The same compound was prepared in good yield when a solution of equimolecular proportion of 2,2-diphenylchromen (III) and 2,4-diphenyl-4*H*-chromen (VII) in acetic acid was saturated with dry hydrogen chloride. No adduct was obtained when a mixture of the two chromens (III) and (VII) was boiled in acetic acid.

The proton magnetic resonance spectrum of the adduct in approximately 5% solution in deuteriochloroform, shown diagrammatically in the Figure, has the following bands, which were intensity-integrated to yield the numbers of contributing protons: (a) a broad unresolved band of intensity corresponding to about 30 protons,  $\tau$  2.0—3.7, from the aromatic protons; (b) a sharp doublet,  $J = 10$  c./sec., centred at  $\tau$  4.20; the total intensity



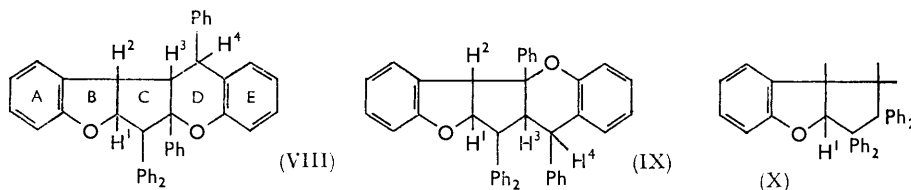
P.m.r. spectra of 5% adduct in deuteriochloroform (peak positions in c./sec. downfield from tetramethylsilane)

is equivalent to one proton and the individual lines have about equal intensity; (c) a slightly less sharp doublet centred at  $\tau$  5.79 with the higher-field peak more intense than that shifted 10.5 c./sec. to lower field, and a total intensity of one proton; (d) a quadruplet of slightly broadened peaks, centred at  $J = 6.28$  p.p.m., with separation  $\sim 4$  c./sec.,  $\sim 6$  c./sec.,  $\sim 4$  c./sec.; the high-field pair is less intense than the lower-field pair, and the total intensity is one proton; (e) a quadruplet of sharper peaks with the same separations and approximately the same relative intensities as (d), centred at  $\tau$  6.78, intensity one proton. Because of poor solubility, signals (b) to (e) are rather weak compared with (a), but they still enable a decision to be made between structures (VIII) and (IX) for the adduct. If the adduct had structure (IX), one would expect to observe close coupling between H-1 and H-2 and between H-3 and H-4, with only very weak coupling (*i.e.*, not as much as 4 c./sec. or 10 c./sec.) between H-1 and H-3. If significant coupling occurred between H-1 and H-3, then the H-1 resonance would be a quadruplet. Analogy with H-1 in (X) <sup>6</sup> suggests that

<sup>6</sup> D. Abson, K. D. Bartle, J. Bryant, R. Livingstone, and R. B. Watson, *J.*, 1965, 2978.

H-1 in the adduct should be the proton with the smallest  $\tau$  value (apart from the aromatic protons). In fact, the lowest-field non-aromatic signal in the spectrum of the adduct is a doublet (*b*).

Structure (VIII) is assigned to the adduct because it would be expected to show a spectrum of the type observed: two doublets (from H-1 and H-4) and two quadruplets (from H-2 and H-3). The doublet at  $\tau$  4.20 arises from H-1 [cf.  $\tau$  3.9 in (X)] and the doublet at  $\tau$  5.79 from H-4. Since the couplings  $J_{12}$  and  $J_{34}$  are so similar, their values



cannot be used to decide which is the H-3 quadruplet. However, an assignment is possible by means of a comparison between the different intensities to be expected when H-4 (*c*) is regarded as coupled in an AB approximation in turn to signals (*d*) and (*e*). Even though the spectrum is more nearly ABCX the chemical shifts are sufficiently large for the AB approximation to be satisfactory for this purpose. Band (*e*) is slightly closer to (*c*) in pyridine than in deuteriochloroform solution, whereas bands (*c*) and (*d*) have the same frequency separation in the two solvents. Thus, if (*e*) arises from H-3, then H-3—H-4 coupling will require the relative intensities of the individual H-4 peaks to be in the ratio 1 : 1.43 in deuteriochloroform solution, or 1 : 1.49 in pyridine. If, however, signal (*d*) originates from H-3, then H-3—H-4 coupling should lead to a corresponding ratio 1 : 2.05 in both the solutions. While the limited solubility precluded direct intensity-integration of the individual peaks in the (*c*) doublet, these peaks have similar widths and are sufficiently well resolved to justify the approximation of peak heights. Their ratios were found to be  $1.35 \pm 0.13$  in deuteriochloroform, and  $1.39 \pm 0.10$  and  $1.41 \pm 0.06$  for more concentrated solutions possible in pyridine. Consequently, quadruplet (*d*) at  $\tau$  6.28 is attributed to H-2 and quadruplet (*e*) at  $\tau$  6.78 to H-3.

Summary of chemical shifts and coupling constants for adduct (VIII)

	$\tau$ (p.p.m.)		$\tau$ (p.p.m.)	$J$ (c./sec.)	$J$ (c./sec.)	
H-3	6.78	H-1	4.20	$J_{12}$	10	
H-2	6.28	$H_{\text{aromatic}}$	2.0—3.7	$J_{13}$	0	
H-4	5.79			$J_{14}$	0	
					$J_{23}$	4
					$J_{34}$	10.5

Both resonances (*c*) and (*d*) are broadened to an extent suggestive of an unresolved coupling of below 1 c./sec. Although this could be due to a longer-range coupling between H-2 and H-4, it is more likely to arise from coupling to protons of adjacent aromatic rings. Either interpretation supports the assignment of H-2 to (*d*) rather than (*e*).

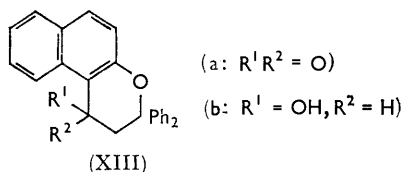
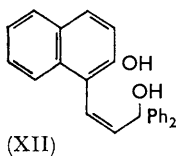
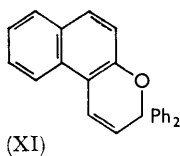
Scale models have been built in order to examine the stereochemical possibilities of structure (VIII) in the light of the coupling constants listed in the Table. The central ring, *c*, is likely to be nearly planar. Since H-1 and H-2 are attached to carbon atoms common to both rings *b* and *c*, their dihedral angle must be close to zero [this would be equally true for structure (IX)]. Therefore, according to the Karplus curve,<sup>7</sup> one would expect  $J_{12}$  to be relatively large, as is observed. The contiguity of the nearly planar ring *c* also implies that the hybrid ring *d* approximates more nearly to a "boat" than a "half-chair" conformation.

Rings *d* and *e* may be either on the same side of the ring *c* plane as rings *a* and *b*, or on the opposite side. If they are on the same side, H-2 and H-3 will have a dihedral angle near 0°, in disagreement with the observed  $J_{23}$  value. The H-3—H-4 dihedral angle will be either 90°, which would also be inconsistent with the observed  $J_{34}$ , or near 30°.

<sup>7</sup> M. Karplus, *J. Chem. Phys.*, 1959, **30**, 11.

If, however, D and E are on the opposite side of the c plane from A and B, then H-2 and H-3 have a dihedral angle in accord with  $J_{23}$ . The dihedral angle between H-3 and H-4 must then be close to either  $160^\circ$  or  $25^\circ$  according to the position of the phenyl group on the H-4 carbon; either arrangement would be in fair agreement with the large value observed for  $J_{34}$ .

After steam-distillation to remove any biphenyl, the mixture from the reaction between 5,6-benzocoumarin and phenylmagnesium bromide gave nearly pure 6,6-diphenyl-6*H*-naphtho(2',1':2,3)pyran (XI) after the non-steam-volatile fraction had been shaken with ether to remove the 4,5-dihydro-4,6-diphenylnaphtho(2',1':2,3)pyran-6-ol.<sup>8,9</sup> Removal of the biphenyl with the part soluble in ether left a solid which contained some 3-(2-hydroxy-1-naphthyl)-1,1-diphenylprop-2-en-1-ol (XII); this was indicated by the infrared hydroxyl absorption ( $3250\text{ cm.}^{-1}$ ). Owing to the ease of dehydration and cyclisation to the naphthopyran (XI) the diol (XII) could not be isolated. 6,6-Diphenyl-6*H*-naphtho(2',1':2,3)pyran (XI) was synthesised by the condensation of 1-acetyl-2-naphthol<sup>10</sup> with benzophenone in anhydrous benzene in the presence of sodium *t*-butoxide to give 5,6-dihydro-6,6-diphenylnaphtho(2',1':2,3)pyran-4-one (XIIIa). Reduction of the ketone (XIIIa) with lithium aluminium hydride in ether gave the alcohol (XIIIb). This was boiled with acetic acid to give the naphthopyran (XI) which could also be obtained by the pyrolysis of the acetate.



#### EXPERIMENTAL

Melting points were taken on a Kofler hot-stage apparatus. Acetates were prepared at room temperature with acetic anhydride and pyridine.

The proton magnetic resonance spectra were recorded at room temperature at 60 Mc./sec. on a Varian A-60 spectrometer. Chemical shifts were referred to internal tetramethylsilane.

*Reaction between Phenylmagnesium Bromide and Coumarin.*—Coumarin (50 g.) in benzene (200 ml.) was added in 1 hr. to a stirred Grignard solution from bromobenzene (83 ml.), magnesium (23 g.), and ether (160 ml.). The solution was refluxed for 1 hr. After decomposition with 22% ammonium chloride solution the benzene-ether extract was dried ( $\text{Na}_2\text{SO}_4$ ) and the solvent removed to yield a gum. Trituration with ether (100 ml.) gave crude 3-(2-hydroxyphenyl)-1,3-diphenylpropan-1-one (27.5 g., 26.6%) m. p.  $160\text{--}166^\circ$ . The ethereal solution gave a gum, which, on trituration with light petroleum (b. p.  $60\text{--}80^\circ$ ) (150 c.c.), gave crude 3-(2-hydroxyphenyl)-1,1-diphenylprop-2-en-1-ol (43 g., 44.2%). Recrystallisation from benzene-light petroleum (b. p.  $60\text{--}80^\circ$ ) and then from ethyl acetate-light petroleum (b. p.  $60\text{--}80^\circ$ ) gave 3-(2-hydroxyphenyl)-1,1-diphenylprop-2-en-1-ol (20.5 g., 21.1%) as white needles, m. p.  $99\text{--}100^\circ$  (lit.,<sup>2</sup>  $99^\circ$ ).

*2,2-Diphenylchromen.*—(a) 3-(2-Hydroxyphenyl)-1,1-diphenylprop-2-en-1-ol (2 g.) was boiled with acetic acid (25 ml.) for 1 hr. and poured into water. Isolation with ether gave a gum which on recrystallisation from light petroleum (b. p.  $60\text{--}80^\circ$ ) yielded 2,2-diphenylchromen (1.64 g., 87%) as needles, m. p.  $93\text{--}94^\circ$ .

(b) 2,2-Diphenylchroman-4-yl acetate (0.5 g.) was pyrolysed at  $220^\circ$  until evolution of acetic acid ceased. The product was purified by chromatography on alumina (type H) from benzene to give, on recrystallisation from light petroleum (b. p.  $60\text{--}80^\circ$ ), 2,2-diphenyl-2*H*-chromen (0.24 g., 62.2%), m. p. and mixed m. p.  $93\text{--}94^\circ$ .

*2,2-Diphenylchroman-4-one (IVa).*—*o*-Hydroxyacetophenone (4.9 g.) in benzene (100 ml.) was added to a solution of benzophenone (70 g.) and sodium *t*-butoxide [from sodium (6.4 g.)

<sup>8</sup> R. Livingstone, D. Miller, and S. Morris, *J.*, 1960, 5148.

<sup>9</sup> J. Cottam and R. Livingstone, *J.*, 1964, 5228.

<sup>10</sup> M. Imoto, *J. Chem. Soc. Japan*, 1937, 58, 932.

and t-butyl alcohol (32 ml.)] in benzene (250 ml.), refluxed with stirring for 20 hr., then poured into a stirred mixture of hydrobromic acid (125 ml.) and acetic acid (185 ml.). The benzene layer was steam-distilled to remove starting materials. Isolation with ether gave a yellow glass (6.8 g.) which was chromatographed on alumina (type H) from benzene solution. Removal of solvent and crystallisation from light petroleum (b. p. 80—100°) gave 2,2-diphenylchroman-4-one (4.1 g., 36%), m. p. 136—138° (lit.,<sup>4</sup> 137°).

Elution of the alumina with methanol afforded a yellow solid which on recrystallisation from light petroleum (b. p. 80—100°) gave 1-(2-hydroxyphenyl)-3,3-diphenylprop-2-en-1-one (2.1 g., 18.5%), m. p. 89° (Found: C, 84.0; H, 5.4.  $C_{21}H_{16}O_2$  requires C, 84.0; H, 5.3%) (2,4-dinitrophenylhydrazone, m. p. 239—240°). The ketone (V) (0.2 g.) was boiled with methanol (10 ml.) and 46% hydrobromic acid (1 ml.) for 2 hr. and the solution concentrated to give the ketone (IVa) (0.19 g., 95%), m. p. and mixed m. p. 136—137°.

2,2-Diphenylchroman-4-ol (IVb).—2,2-Diphenylchroman-4-one (0.84 g.) in ether (25 ml.) was added to lithium aluminium hydride (0.14 g.) in ether (10 ml.) and the mixture refluxed for 0.5 hr. After the addition of dilute sulphuric acid, the product was isolated with ether and dried ( $Na_2SO_4$ ). Removal of the solvent followed by recrystallisation from light petroleum (b. p. 100—120°), gave 2,2-diphenylchroman-4-ol (0.48 g., 57%), m. p. 111° (Found: C, 83.2; H, 6.1.  $C_{21}H_{16}O_2$  requires C, 83.4; H, 6.0%); acetate, m. p. 91—92° (from methanol).

5,6-Dihydro-6,6-diphenylnaphtho(2',1':2,3)pyran-4-one (XIIIa).—Benzophenone (54.6 g.) and 1-acetyl-2-naphthol (5.36 g.) in benzene (450 ml.) were added to sodium t-butoxide [from sodium (5 g.) and t-butyl alcohol (40 ml.)], refluxed with stirring for 20 hr., and then poured into a stirred mixture of hydrobromic acid (100 ml.) and acetic acid (150 ml.). The benzene layer was steam-distilled to remove starting materials; it left a brown crystalline solid which was chromatographed on alumina from benzene solution. Removal of the solvent and crystallisation from light petroleum (b. p. 100—120°) gave 5,6-dihydro-6,6-diphenylnaphtho(2',1':2,3)pyran-4-one (8.58 g., 85%), m. p. and mixed m. p. 169—171°. Elution of the alumina with chloroform and methanol gave no uncyclised derivative.

5,6-Dihydro-6,6-diphenylnaphtho(2',1':2,3)pyran-4-ol (XIIIb).—5,6-Dihydro-6,6-diphenylnaphtho(2',1':2,3)pyran-4-one (2.07 g.) was added to lithium aluminium hydride (0.39 g.) in ether (10 ml.) and boiled for 0.5 hr. Addition of dilute sulphuric acid, isolation with ether, and recrystallisation from light petroleum (b. p. 100—120°) gave 5,6-dihydro-6,6-diphenylnaphtho(2',1':2,3)pyran-4-ol (1.66 g., 79.7%), m. p. 156—158° (Found: C, 84.9; H, 5.6.  $C_{25}H_{20}O_2$  requires C, 85.2; H, 5.7%); acetate, m. p. 134—136° (from methanol).

6,6-Diphenylnaphtho(2',1':2,3)pyran (XI).—(a) The alcohol (X) (0.26 g.) was boiled with acetic acid (20 ml.) for 0.5 hr. Pouring into water, filtration, and recrystallisation from light petroleum (b. p. 80—100°) gave the naphthopyran (0.22 g., 86.7%), m. p. and mixed m. p. 161—162°.

(b) The acetate (0.37 g.) of the alcohol (X) was heated at 200° for 0.5 hr. Recrystallisation from light petroleum (b. p. 80—100°) gave the naphthopyran (0.25 g., 79.5%), m. p. and mixed m. p. 161—162°.

Adduct of 2,2-Diphenylchromen (III) and 2,4-Diphenyl-4H-chromen (VI).—(a) Diol (II) (0.5 g.) and ketone (I) (0.5 g.) were boiled in acetic acid (25 ml.) for 2 hr. Pouring into water, isolation with ether, and recrystallisation from ethyl acetate gave the adduct (0.2 g., 21%) m. p. and mixed m. p. 242—243°.

(b) Diol (II) (0.5 g.) and 2,4-diphenyl-4H-chromen (VI) (0.5 g.) treated as above gave adduct (0.57 g., 57%) m. p. and mixed m. p. 241—243°.

(c) 2,2-Diphenylchromen (0.16 g.) and 2,4-diphenyl-4H-chromen (0.16 g.) in acetic acid (12 ml.) saturated with dry hydrogen chloride gave some adduct after 0.5 hr. Isolation with ether after being set aside for 48 hr. gave adduct (0.28 g., 87.5%).

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