## THE 2,2-DIMETHYLCHROMEN DIMER 2,2-DIPHENYLCHROMEN AND RELATED COMPOUNDS

## C. S. BARNES\* and MARGARET I. STRONG\* C.S.I.R.O. Division of Organic Chemistry, Melbourne

## J. L. OCCOLOWITZ Defence Standards Laboratories, Maribyrnong, Victoria

(Received 23 December 1962)

Abstract—From consideration of physical data and the mode of formation, structure VII is suggested for the 2,2-dimethylchromen dimer. Reaction of coumarin with phenylmagnesium bromide gave 1,1-diphenyl-3(2-hydroxyphenyl)-prop-2-en-1-ol and 1,3-diphenyl-3(2-hydroxyphenyl)-propan-1-one. On acid treatment these cyclized to 2,2-diphenylchromen and 2,4-diphenyl-4H-chromen respectively. These findings contradict the conclusions of others.

THE 2,2-dimethylchromen system occurs in several kinds of natural product, where it most probably arises by introduction of an isoprene unit ortho to a phenolic hydroxyl group, followed by cyclization.<sup>1</sup> It might be expected that this system could be readily synthesized by reaction of a coumarin (I) with methylmagnesium iodide to give the unsaturated diol (II), followed by a cyclizing condensation.<sup>2</sup> In fact 2,2dimethylchromen (III) itself may be prepared<sup>3-5</sup> in this way by pyrolysis of the intermediate unsaturated diol (II), but the product is difficult to purify, the yield is low, and the method has obvious limitations with involatile or heat sensitive compounds. In contrast the analogous saturated diols obtained from dihydrocoumarins may be readily cyclized by treatment in homogeneous solution with acid reagents to give the 2,2-dimethylchromans<sup>6-8</sup> in good yield. This is a method for obtaining<sup>9</sup> reference compounds in the determination of structures of naturally occurring 2,2-dimethylchromens, which are readily hydrogenated to the chromans for comparison. When however the unsaturated diol (II) is treated with acid under conditions which lead to cyclization of the analogous saturated compound, the product is not the liquid 2,2-dimethylchromen, but there is formed in good yield<sup>10</sup> a high melting crystalline dimer of this substance. A dimer derived<sup>11</sup> in a similar way from lapachenole (IV), a naturally occurring 2,2-dimethylchromen, has been assigned<sup>12</sup> structure

- \* Present Address-C.S.R. Research Laboratories, Roseville, N.S.W.
- <sup>1</sup> W. D. Ollis and I. O. Sutherland, Recent developments in the Chemistry of Natural Phenolic Compounds (Edited by W. D. Ollis) Chap. 4. Pergamon Press (1961).
- \* For discussion of the synthesis and properties of the 2,2-dimethylchromen system see W. B. Whalley, Heterocyclic Compounds (Edited by R. C. Elderfield) Vol. 7; p. 89. J. Wiley (1961).
- \* J. Houben, Ber. Dtsch. Chem. Ges. 37, 489 (1904).
- <sup>4</sup> R. L. Shriner and A. G. Sharp, J. Org. Chem. 4, 575 (1939).
  <sup>5</sup> L. I. Smith and P. M. Ruoff, J. Amer. Chem. Soc. 62, 145 (1940).
  <sup>6</sup> L. Claisen, Ber. Dtsch. Chem. Ges. 54, 200 (1921).
- <sup>7</sup> W. John, P. Gunther and M. Schmeil, *Ber. Disch. Chem. Ges.* **71**, 2637 (1938). <sup>8</sup> L. I. Smith, H. E. Ungnade and W. W. Prichard, *J. Org. Chem.* **4**, 358 (1939).
- <sup>a</sup> R. Huls, Bull. Classc. Sci. Acad. roy Belg. 39, 1064 (1953).
- <sup>10</sup> R. Livingstone, D. Miller and S. Morris, J. Chem. Soc. 602 (1960).
- <sup>11</sup> R. Livingstone and M. C. Whiting, J. Chem. Soc. 3631 (1955).
- <sup>12</sup> R. B. Woodward, as quoted in ref. 11.

V mainly on the basis of a proposed mechanism of formation and the observed absence of unsaturation. The 2,2-dimethylchromen dimer was therefore assigned<sup>10</sup> structure VI by analogy.

The mechanism proposed<sup>12</sup> for the formation of V seemed unlikely to us, and we have re-examined the reaction. In the sequel the structure VI for the 2,2-dimethylchromen dimer is shown to be incorrect, and there is advanced a new structure (VII) consistent with the physical properties and mode of formation of the dimer.



Reaction of coumarin with methylmagnesium iodide as described previously<sup>5</sup> gave 4-(2-hydroxyphenyl)-2-methyl-*cis*-but-3-en-2-ol (II). This substance, which decomposed on keeping, showed strong hydroxylic absorption in the infrared and had absorption maxima at 243 m $\mu$  and 283 m $\mu$  in the ultraviolet. The proton magnetic resonance (P.M.R.) spectrum showed besides absorption due to C-Me ( $\delta = 1.3$  p/m) and aromatic protons (400-440 c/s), two doublets (J = 12.5 c/s,  $\delta = 5.87$  and 6.33 p.p.m.) attributed to the vinylic protons. The mass spectrum of II showed no

molecular ion and was virtually identical with that of 2,2-dimethylchromen,<sup>13</sup> showing that cyclization had occurred during measurement. The base peak at m/e 145 corresponded to the 2-methylbenzopyrylium ion while a smaller peak at m/e 160 (13%) corresponded to 2,2-dimethylchromen itself. As would be expected the carbinol (II) gave a peak due to water (m/e 18, 17%) which was absent from the spectrum of 2,2-dimethylchromen.

In agreement with earlier work<sup>3-5</sup> pyrolysis of the carbinol (II) gave mainly 2.2-dimethylchromen (III) as shown by the physical properties of the product, which was difficult to obtain pure even by vapour phase chromatography. Treatment of the carbinol (II) with a trace of sulphuric acid in refluxing glacial acetic acid caused almost quantative conversion into the dimer,<sup>10</sup> which readily crystallized on the addition of water to the reaction medium. The same compound was obtained by the reaction of coumarin with methyllithium in ether followed by acid treatment of the total reaction product.

The dimer (m.p. 189–190°) had absorption maxima at 276 m $\mu$  and 283 m $\mu$ showing that no styryl system was present, the I.R. spectrum showed the absence of olefinic, hydroxy and carbonyl-groups, and the compound was recovered unchanged on attempted hydrogenation. That the structure VI was wrong was indicated by the mass spectrum which showed no ion due to the benzofuran fragment. On the basis of formula VI the very stable benzofuran ion would be expected<sup>13</sup> as a major product since it would be derived by a favoured fragmentation of two highly substituted carbon-carbon bonds. Final proof of the incorrectness of structure VI was given by the P.M.R. spectrum which showed absorption due to three methyl groups and not four as is required by structure VI.

A simpler and more reasonable mechanism than that previously proposed<sup>12</sup> for the formation of the dimer, would appear to be by way of the phenylisoprene (VIII) formed by dehydration of the allylic alcohol (II). This could dimerize to give the dipentene derivative IX or the diprene derivative X, which in turn could cyclize to VII or XI respectively. The dimerization step has historic analogies<sup>14,15</sup> in the formation of dipentene and diprene from isoprene itself, while somewhat similar Diels Alder additions have been observed with 1-phenylbutadiene,<sup>16</sup> 2-phenylbutadiene,<sup>17</sup> and 1,3-diphenylbut-2-enol.<sup>18,19</sup> In these last examples the dienophile was the terminal double bond of the butadiene system, but this could not be involved in the 2,2-dimethylchromen example as cyclization with the phenolic hydroxyl would result in a product containing only two methyl groups rather than the observed three, and with a benzofuran ring system which also has been shown to be absent. The final cyclization stage has many analogies in synthetic heterocyclic chemistry, including the osajin to iso-osajin<sup>20</sup> change. While this reaction is considered as a dimerization of a butadiene, it is possible that in fact the chromen is involved with one molecule

<sup>&</sup>lt;sup>18</sup> See forthcoming publication in the Austr. J. Chem. by C. S. Barnes and J. L. Occolowitz, for discussion of mass spectra of aromatic oxygen heterocycles.

<sup>14</sup> W. A. Tilden, J. Chem. Soc. 45, 410 (1884).

<sup>&</sup>lt;sup>15</sup> T. Wagner-Jauregg, *Liebig's Ann.* 488, 176 (1931).
<sup>16</sup> K. Alder, J. Haydn and W. Vogt, *Chem. Ber.* 86, 1302 (1953).

<sup>&</sup>lt;sup>17</sup> K. Alder and J. Haydn, Liebig's Ann. 570, 201 (1950).

<sup>&</sup>lt;sup>16</sup> W. Herz and E. Lewis, J. Org. Chem. 23, 1646 (1958).

<sup>&</sup>lt;sup>19</sup> T. L. Jacobs and M. H. Goodrow, J. Org. Chem. 23, 1653 (1958).

<sup>&</sup>lt;sup>20</sup> M. L. Wolfrom, B. S. Wildi, J. Amer. Chem. Soc. 73, 235 (1951).

of diene. It is noteworthy that 4-substituted coumarins do not give a dimer on acid treatment, 21-23 presumably due to steric inhibition.

From first principles VII and XI are capable of each existing as four racemates, depending on the stereochemistry of the ring fusions. The BC fusion must of necessity be *cis*, but may be either *syn* or *anti* to the CD fusion which may be either *cis* or *trans*. Although the primary product of the Diels-Alder condensation must be *cis*, suggesting a *cis*-CD fusion, the allylic proton adjacent to the isopropenyl group is capable of isomerization in the acid medium, thereby making the nature of the ring fusion uncertain.

Using conformational arguments coupled with P.M.R. observations, it is possible to decide with reasonable certainty on one of the eight possible racemates for the structure of the dimer. The P.M.R. spectrum at 60 m.c. of the 2,2-dimethylchromen dimer shows three uncoupled C-Me bands at  $\delta = 0.85$ , 1.45 and 1.65 p.p.m., with an additional proton unresolved under the methyl bands from 70-100 c/s A multiplet between 110-130 c/s contained three protons, while two more were in a multiplet spreading from 150-180 c/s. One proton was split into a quartet at  $\delta = 3.30$  p.p.m. The remaining eight protons were in the aromatic region. Of the eight possible racemates two have a single methyl group shielded sufficiently to account for the peak at  $\delta = 0.85$  p.p.m. These have a *cis-syn-trans* (VIIa) or a cis-syn-cis arrangement of rings BCD. The last of these is not favoured on steric grounds since the conformation which is required to produce a shielded methyl group has a boat ring C with several unfavourable steric interactions, and also brings one of the geminal methyl groups into contact with the aromatic ring A. Furthermore it has no methine proton in a shielded position to account for the proton at about 70-100 c/s Structure VIIa on the other hand has a shielded methyl (a) and a shielded proton (b) to account for the methyl  $\delta = 0.85$  p.p.m. and the proton 70-100 c/s

A methine proton (c) is almost in the plane of the aromatic ring A and so is deshielded to account for the absorption at  $\delta = 3.30$  p.p.m. This proton (c) has a dihedral angle of 60° with each of the protons of a methylene group and a methine group thereby accounting for its multiplicity. Spin decoupling shows that this proton (c), ( $\delta = 3.30$  p.p.m.) is coupled with the group,  $\delta = ca.$  1.9 p.p.m., and that a component of the group centered around 160 c/s is coupled to the partly obscured proton (b) at 70-100 c/s.

The remaining two methyl groups have absorption ( $\delta = 1.45$  and 1.65 p.p.m.) moved downfield from the normal value of 2,2-dimethylchroman ( $\delta = 1.30$  p.p.m.), showing them to be under the influence of different degrees of deshielding. It is therefore possible to assign absorption at  $\delta = 1.65$  p.p.m. to (d) and at  $\delta = 1.45$  p.p.m. to (e) because the former is closer to the deshielding of the aromatic ring A, than is the latter to the aromatic ring E.

Support for structure VII without reference to the stereochemistry came from the mass spectrum which showed the molecular ion (320, 33%) which lost  $CH_3$  (305, 23%) and possibly  $C_3H_7$  (277, 23%). Apart from these the only peak of significance was the base peak at m/e 145. At lower mass regions the spectrum was very similar to 2,2-dimethylchromen with no peak more than 10% the abundance of the base peak.

<sup>&</sup>lt;sup>21</sup> W. Bridge, A. J. Crocker, T. Cubin and A. W. Robertson, J. Chem. Soc. 1530 (1937).

<sup>&</sup>lt;sup>22</sup> R. Livingstone, D. Miller and R. B. Watson, J. Chem. Soc. 2422 (1958).

<sup>&</sup>lt;sup>23</sup> I. M. Heilbron and D. W. Hill, J. Chem. Soc. 2005 (1927).

This stability points to the base peak being due to the fully aromatic benzopyrylium ion identical with that given by 2,2-dimethylchromen,<sup>13</sup> and arising very readily from VII by fission of the molecule at two favourable positions adjacent to branched carbon atoms. The ion at mass 118 which could represent benzofuran amounted to only 1% of the base peak.

The evidence above points exclusively to structure VIIa for the 2,2-dimethylchromen dimer, and presumably the lapachenole dimer<sup>11</sup> has an analogous structure. The 2,2-dimethylchromen dimer (VII) proved rather unreactive, and no satisfactory conditions could be found for opening any of the rings by acid hydrolysis or by ozonolysis. Reduction with lithium in n-propylamine gave a crystalline product of molecular weight 328, which has not been degraded to recognizable products.



The dimer of 2,2-diphenylchromen next attracted our attention, for although it is reputed<sup>10</sup> to be formed from 2,2-diphenylchromen in the same way as the 2,2-dimethylchromen dimer is formed from 2,2-dimethylchromen, a structure such as VII is precluded since phenyl groups can not be involved in the cyclization in the same manner as is postulated above for a methyl group of 2,2-dimethylchromen. In the past there has been some confusion concerning the products of the reaction of phenylmagnesium bromide with coumarin. Initially it was believed<sup>3</sup> that the main product was the diphenylcarbinol (XII), but it was acknowledged that the properties of the compound obtained did not unambiguously fit that structure. Later it was thought<sup>24</sup> that the product previously isolated was in fact the chromanol (XIII) isomeric with XII. In addition a second compound m.p. 93°, isolated in 35% yield by its solubility in ether, was claimed<sup>24</sup> to be the 2,2-diphenylchromen XIV. On treatment with hot acetic acid or methanolic hydrochloric acid the supposed 2,2-diphenylchromen was converted into a high melting compound believed to be<sup>24</sup> an isomeric benzofuran or coumarone derivative. Subsequently<sup>10</sup> this compound was claimed to be a dimer and to be formed in methanolic hydrochloric acid but not acetic acid solution. A structure analogous to the incorrectly formulated<sup>12</sup> 2,2-dimethylchromen dimer was assigned<sup>10</sup> to it. In the sequel it is shown that the main product of the Grignard reaction is neither XII nor XIII, but the ketone XV, and that the second product is not XIV, 24 A. Lowenbein, Ber. Dtsch. Chem. Ges. 57, 1517 (1924).

Mass No (m/e)	Ion intensities as % of base peak								
	II	III	VII	XIV	XII	XV	XVI	XVII	XVIII
51						10		7	6
77			6			25		10	30
91	13	8	10					15	26
94						9			
105						29			
107	5		10						
115	9	11	7					8	17
120	10								
131			9						
145	100*	100*	100*						
146	11	12	13						
147			12						
152				6		6		18	18
159			5	-		-			
160	13†	13†	6						
161	5		8						
165				8	6	7		14	100*
176				5					
177				5					
178				24	13	15	12		77
179				7		5			86
180									73
181						9		100*	10
182						-		22	
183						10			
185			15			10			
191			15	5					18
192				5				25	83
195								25	45
200			7					21	-1-5
205			,	5					
207				100*	100*	100*	100*	13	22
208				18	17	22	17	19	45
200			23	10	11		17		
283			20	15	13	19	21		
284				60+	46+	34	38+		
285				13	11	7	8		
286				10	••		Ũ	42†	86†
302						5†		1-1	001
305			23			51			
320			33+						
321			8						
			* hase neak		t parent ion				

TABLE 1.—MASS SPECTRAL DATA

but XII. The high melting compound could not be prepared by either literature method,<sup>10,24</sup> the only product formed under the conditions used being the 2,2-diphenyl-chromen XIV.

Reaction of coumarin with phenylmagnesium bromide under the conditions previously described<sup>24</sup> gave a compound having a melting point similar to that of the compound obtained in the same way and assigned either the chromanol<sup>24</sup> (XIII) or the diol<sup>3</sup> (XII) structure. That it is actually the ketone XV was shown by the presence of hydrogen bonded hydroxyl (3360 cm<sup>-1</sup>) and carbonyl (1670 cm<sup>-1</sup>)

absorption in the infrared using either paraffin mulls of chloroform solutions. The ultraviolet absorption in neutral solution showed bands (243, 275 m $\mu$ ) which underwent a bathochromic shift and increased in intensity on addition of alkali. The proton magnetic resonance spectrum was equivocal, but the mass spectrum showed a strong ion due to  $C_8H_8CO$  which could be formed by fission  $\alpha$  to the carbonyl group. The remainder of the mass spectrum was very similar to that of 2,4-diphenyl-4H-chromen, showing that cyclization had occurred. The ether soluble part of the reaction product had melting point 99°, in reasonable agreement with the product (93°) isolated in the same way and formulated<sup>24</sup> as the diphenylchromen XIV. It was shown to be the diol XII by elementary analysis, by its I.R. spectrum which showed strong hydroxyl absorption, and by its U.V. absorption which underwent a bathochromic shift on the addition of alkali and showed the presence of a styryl and a diphenylmethane system (bands at 240, 290 m $\mu$ ). Acid treatment of the ketone XV caused cyclization and dehydration to the known 2,4-diphenyl-4H-chromen (XVI) which had earlier been prepared<sup>24</sup> by the same and an alternative method. In the P.M.R. spectrum the two protons of the heterocyclic ring showed as a pair of doublets (J = 4 c/s)at  $\delta = 4.80$  and 5.52 p.p.m. The mass spectrum showed a parent ion (m/e 284, 38%) which gave a benzopyrylium ion<sup>13</sup> by loss of either one hydrogen atom (283, 21%) or a phenyl radical (207, 100%). Hydrogenation gave 2,4-diphenylchroman (XVII) having a simple mass spectrum with a parent ion (286, 42%) and a base peak due to fission of the chroman ring at the 1,2- and 3,4- bonds, with the retention of the charge on the oxygen containing fragment (XIX). A small peak (208, 19%) resulted from loss of benzene. The P.M.R. spectrum of XVII showed the two protons of the methylene group in a multiplet at 125-150 c/s, and the two single protons in multiplets at 250-275 c/s and 305-325 c/s. The aromatic protons were in a complex series of bands spreading from 405-450 c/s.

Acid treatment of the diol (XII) gave 2,2-diphenylchromen (XIV), the structure of which followed from the presence of two coupled protons (J = 10 c/s) at  $\delta = 6.13$ and 6.61 p.p.m., and the mass spectrum which resembled that of the isomeric 2,4diphenylchromen except that the (p-1) peak was less intense. In agreement with the absence of phenolic hydroxyl, the absorption in the ultraviolet remained unchanged on addition of alkali. Hydrogenation gave 2,2-diphenylchroman (XVIII) having a melting point similar to that recorded<sup>10</sup> earlier for an otherwise uncharacterized specimen. The mass spectrum of 2,2-diphenylchroman was more complex than that





of 2,4-diphenylchroman and showed a parent ion (286, 86%) which lost benzene (208, 45%) to form a relatively stable chromen ion. The base peak (165, 100%) was formed by fission of both the 1,2- and 2,3- bonds to give an ion presumably of the same structure as that of the same mass formed from diphenylmethane itself. Fragmentation of the chroman ring also occurred by fission of the 1,2- bond together with each of the C—C bonds to give the homologues (178, 77%), and (192, 83%). That rearrangement of a phenyl group had occurred seems possible from the peak m/e 195 due to  $C_{14}H_{11}O$  which could arise by migration of a phenyl radical from  $C_2$  to  $C_3$  followed by the favoured fissions of the activated 1,2- and 2,3- bonds. A similar rearrangement seems necessary to account for the (p-1) peak in 2,2-diphenylchromen. In our hands it was not possible to obtain a compound melting point 239°, by acid treatment of any of the compounds obtained above. In each case the appropriate diphenylchromen was the sole product.

## EXPERIMENTAL

General. Unless otherwise stated m.p's. were corrected and were measured in open capillaries. Proton magnetic resonance spectra were measured in  $CDCl_3$  solution using a Varian A-60 spectrometer, mass spectra were measured using an Atlas CH4 spectrometer with an inlet temperature of 250° and at 70 eV. Microanalyses were by the C.S.I.R.O. and University of Melbourne Microanalytical Laboratory, Melbourne. Thin layer chromatography with silica gel and appropriate mixtures of hexane-ethyl acetate for developing solvent was used to follow the course of reactions and to establish the homogeneity of the compounds described.

2,2-Dimethylchromen dimer. Coumarin (1 g) dissolved in ether (50 ml) was added over a period of 1 hr to a solution of methyllithium (from Li (3.8 g) and MeI (15.6 ml)) in ether (150 ml), and the solution refluxed with stirring for 1 hr. The product was isolated by pouring the reaction mixture on to ice and sulphuric acid and extraction with ether. It was then treated with refluxing acetic acid (50 ml) containing sulphuric acid (1 drop) for 30 min and the product isolated by addition of water. Crystallization from light petroleum (b.p. 40-60°) gave dimer VII, m.p. 189-190°,  $\lambda_{max}^{EtOH}$  276, 283 m $\mu$  ( $\varepsilon$  5500, 5500). M.p. undepressed on mixing with the same compound prepared from coumarin and methylmagnesium iodide.<sup>10</sup>

1,3-Diphenyl-3-(2-hydroxyphenyl)-propan-1-one (XV). Coumarin (30 g) in toluene (500 ml) was reacted with phenylmagnesium bromide (from Mg (28 g) and bromobenzene (120 ml) in ether (1 1.)), under reflux for 1 hr and worked up in the usual way. The crude product was washed with ether leaving 26 g solid m.p. 156-160°. Recrystallization from CHCl<sub>3</sub>-MeOH, gave 1,3-diphenyl-3-(2-hydroxyphenyl)-propan-1-one (XV) m.p. 168-169°,  $\lambda_{max}^{\rm HO}$  275 m $\mu$  ( $\epsilon$  3970), 243 m $\mu$  ( $\epsilon$  11850)  $\lambda_{max}^{\rm BOH/KOH}$  291 m $\mu$  ( $\epsilon$  4550) 240 m $\mu$  ( $\epsilon$  19700). Infrared (nujol) 3360 cm<sup>-1</sup> 1670 cm<sup>-1</sup>. (Found: C, 83·1; H, 5·9%. Calc. for C<sub>21</sub>H<sub>18</sub>O<sub>2</sub>: C, 83·4; H, 6·0%).

2,4-Diphenyl-4H-chromen (XVI). 1,3-diphenyl-3(2-hydroxyphenyl)-propan-1-one (XV; 2 g) dissolved in glacial acetic acid (50 ml) and boiled for 1 hr. After cooling, the precipitate was filtered,

washed with water and recrystallized from ethanol giving white needles m.p. 106° of 2,4-diphenyl-4Hchromen (XVI).  $\lambda_{max}^{\text{BtoB}}$  235 m $\mu$  ( $\epsilon$  26200), 276 m $\mu$  ( $\epsilon$  7300), doublet  $\delta$  = 4.80 p.p.m., J = 4 c.p.s., 1 proton; doublet  $\delta$  = 5.52 p.p.m., J = 4 c.p.s., 1 proton. (Found; C, 88.9; H, 5.8% Calc. for C<sub>21</sub>H<sub>16</sub>O: C, 88.7; H, 5.7%).

1,1-Diphenyl-3(2-hydroxyphenyl)-prop-2-en-1-ol (XII). The ether soluble from the preparation of XV above was ground with light petroleum (b.p. 60–80°) and filtered. The solid was crystallized from light petroleum-ethyl acetate to give 1,1-diphenyl-3(2-hydroxyphenyl)-prop-2-en-1-ol m.p. 98–99°,  $\lambda_{max}^{\rm htoH}$  290 m $\mu$  ( $\epsilon$  4080), 240 m $\mu$  ( $\epsilon$  10550)  $\lambda_{max}^{\rm BtoH/ROH}$  317 m $\mu$  ( $\epsilon$  6000) infrared max (CHCl<sub>3</sub>) 3400, 3600 cm<sup>-1</sup>. (Found: C, 83.6; H, 6.0%. Calc. for C<sub>21</sub>H<sub>13</sub>O<sub>2</sub>; C, 83.4; H, 6.0%).

2,2-Diphenylchromen (XIV). 1,1-diphenyl-3(2-hydroxyphenyl)-prop-2-en-1-ol (XII 1 g) was dissolved in methanolic HCl (100 ml, 3%) and refluxed for 1 hr.<sup>10</sup> The solvent was removed and the product chromatographed on alumina. Elution with light petroleum (b.p. 60-80°) –ethyl acetate (20 : 1) gave white crystals m.p. 85-87°. Recrystallization from light petroleum ether (b.p. 40-60°) gave needles of 2,2-diphenylchromen (XIV), m.p. 87-88°,  $\lambda_{\rm HOH}^{\rm Ret}$  307 m $\mu$  ( $\varepsilon$  2800), 265 m $\mu$  ( $\varepsilon$  6750), unchanged when made alkaline, doublet  $\delta = 6.13$  p.p.m., J = 10, 1 proton; doublet  $\delta = 6.61$  p.p.m., J = 10 c. p.s., 1 proton. (Found: C, 88.8; H, 5.7%. Calc. for C<sub>a1</sub>H<sub>16</sub>O: C, 88.7; H, 5.7%).

2,2-Diphenylchroman (XVIII). 2,2-diphenylchromen (XIV) was hydrogenated in ethyl acetate at 25° using platinic oxide catalyst.<sup>30</sup> Needles from methanol m.p. 79–80°.

2,4-*Diphenylchroman* (XVII). 2,4-diphenylchromen (XVI) was hydrogenated in ethyl acetate at 25° using platinic oxide catalyst. Needles from methanol m.p. 145–147°,  $\lambda_{max}^{BOH}$  276 m $\mu$  ( $\epsilon$  2400), 284 m $\mu$  ( $\epsilon$  2400). (Found: C, 88·1; H, 6·5%. Calc. for C<sub>81</sub>H<sub>18</sub>O; C, 88·1; H, 6·3%).

Acknowledgements—Dr. L. F. Johnson is thanked for 100 mc. proton magnetic resonance spectrum and spin decoupling measurements on the dimer (VII), and one of us (J. L. O.) thanks the Chief Scientist, Australian Defence Scientific Service, Department of Supply, for permission to publish this paper.