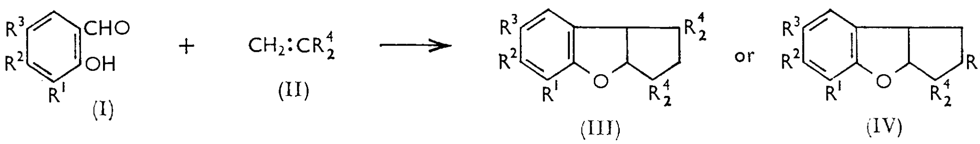
534. *The Reaction between* o-*Hydroxy-aldehydes and Diphenylethylenes*

By D. Abson, K. D. Bartle, J. Bryant, R. Livingstone, and R. B. Watson

o-Hydroxybenzaldehyde and some of its derivatives react with two molecules of certain diphenylenes in acetic acid saturated with dry hydrogen chloride to give benzocyclopentafuran derivatives and not chromens as indicated in related reactions described by Wizinger,[1] who used perchloric acid in acetic anhydride–acetic acid.

Wizinger and Wenning [2] prepared a number of compounds containing the pyran ring system in order to investigate the effect of structure on certain intramolecular ionisations in acid solution. Thus, certain diaryl derivatives of naphtho[2′,1′-*b*]pyran and chromen were prepared by treating the respective *o*-hydroxy-aldehyde with a diphenylethylene in acid solution,[1] a reaction now listed as a general method for preparing chromens.[3] The reaction between 2-hydroxy-1-naphthaldehyde and 1,1-diphenylethylene was investigated previously and reported to give probably 7a,9,10,10a-tetrahydro-8,8,10,10-tetraphenyl-8*H*-naphtho[2,1-*b*]cyclopenta[*d*]-furan and not 6,6-diphenylnaphtho[2′,1′-*b*]pyran,[4] but the product of the reaction could also be 7a,9,10,10a-tetrahydro-9,9,10,10-tetraphenyl-8*H*-naphtho[2,1-*b*]cyclopenta[*d*]furan. It has been shown conclusively that one molecule of a hydroxy-aldehyde (I) reacts with two molecules of a diphenylethylene (II) to give either compound (III) or (IV) analogous to the one obtained from 2-hydroxy-1-naphthaldehyde and 1,1-diphenylethylene,[4] and not a chromen from one molecule of each reactant as reported by Wizinger and Wenning.



(a) $R^1 = R^2 = R^3 = H$
(b) $R^2 = R^3 = H$, $R^1 = NO_2$
(c) $R^1 = R^3 = H$, $R^2 = NO_2$
(d) $R^1 = R^2 = H$, $R^3 = NO_2$
(e) $R^2 = R^3 = H$, $R^1 = OMe$
(f) $R^1 = R^3 = H$, $R^2 = OMe$
(g) $R^1 = R^2 = H$, $R^3 = OMe$

(a) $R^4 = Ph$
(b) $R^4 = o\text{-}C_6H_4{\cdot}OMe$
(c) $R^4 = m\text{-}C_6H_4{\cdot}OMe$
(d) $R^4 = p\text{-}C_6H_4{\cdot}OMe$

(a) $R^1 = R^2 = R^3 = H$, $R^4 = Ph$
(b) $R^1 = R^2 = R^3 = H$, $R^4 = o\text{-}C_6H_4{\cdot}OMe$
(c) $R^1 = R^2 = R^3 = H$, $R^4 = m\text{-}C_6H_4{\cdot}OMe$
(d) $R^1 = R^2 = R^3 = H$, $R^4 = p\text{-}C_6H_4{\cdot}OMe$
(e) $R^2 = R^3 = H$, $R^1 = NO_2$, $R^4 = Ph$
(f) $R^1 = R^3 = H$, $R^2 = NO_2$, $R^4 = Ph$
(g) $R^1 = R^2 = H$, $R^3 = NO_2$, $R^4 = Ph$
(h) $R^2 = R^3 = H$, $R^1 = OMe$, $R^4 = Ph$
(i) $R^1 = R^3 = H$, $R^2 = OMe$, $R^4 = Ph$
(j) $R^1 = R^2 = H$, $R^3 = OMe$, $R^4 = Ph$

The proton magnetic resonance spectra of the compounds obtained from salicylaldehyde and the diphenylethylenes (IIa) and (IIb), from the hydroxy-aldehydes (If) and (Ig) and diphenylethylene, and from 2-hydroxy-1-naphthaldehyde and diphenylethylene showed that, of the two structures (III) and (IV), the latter was the more likely. The naphthalene derivative (V) gave a much clearer spectrum than the other compounds, but the appearance of their spectra indicated similar structures, which seemed hardly compatible with structure (III) but could be explained by structure (IV). The spectrum of compound (V) consisted of intense bands, mainly unresolved, in the region $\tau = 1{\cdot}8$—$3{\cdot}2$ p.p.m.; a doublet, intensity equivalent to one proton centred at $\tau = 3{\cdot}9$ p.p.m., with separation 9 c./sec., assigned to H(1); a multiplet, intensity one proton, $\tau = 5{\cdot}65$—$6{\cdot}25$ p.p.m., assigned to H(2); a multiplet, intensity two protons, $\tau = 6{\cdot}7$—$7{\cdot}7$ p.p.m., assigned to H(3) and H(4).

---

[1] R. Wizinger, *Z. angew. Chem.*, 1939, **52**, 383.
[2] R. Wizinger and H. Wenning, *Helv. Chim. Acta*, 1940, **23**, 247.
[3] S. Wawzonek, " Heterocyclic Compounds," vol. II, ed. Elderfield, Wiley, New York, p. 296.
[4] R. Livingstone, D. Miller, and S. Morris, *J.*, 1960, 5148.

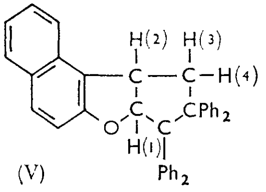
TABLE 1

Reactions between 2-hydroxy-6-aldehydes and 1,1-diphenylethylenes

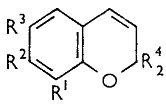
2-Hydroxy-1-aldehyde	1,1-Diphenylethylene	Product
o-HO·C_6H_4·CHO (Ia)	$Ph_2C{:}CH_2$ (IIa) [5]	$C_{35}H_{28}O$ (IVa)
o-HO·C_6H_4·CHO	(*o*-MeO·$C_6H_4)_2C{:}CH_2$ (IIb) [6]	$C_{39}H_{36}O_5$ (IVb)
o-HO·C_6H_4·CHO	(*m*-MeO·$C_6H_4)_2C{:}CH_2$ (IIc)	
o-HO·C_6H_4·CHO	(*p*-MeO·$C_6H_4)_2C{:}CH_2$ (IId) [7]	$C_{39}H_{36}O_5$ (IVd)
3-NO_2-2-HO·C_6H_3·CHO (Ib) [8]	$Ph_2C{:}CH_2$ (IIa)	$C_{35}H_{27}NO_3$ (IVe)
4-NO_2-2-HO·C_6H_3·CHO (Ic) [9]	$Ph_2C{:}CH_2$	$C_{35}H_{27}NO_3$ (IVf)
5-NO_2-2-HO·C_6H_3·CHO (Id) [8]	$Ph_2C{:}CH_2$	$C_{35}H_{27}NO_3$ (IVg)
3-MeO-2-HO·C_6H_3·CHO (Ie) [10]	$Ph_2C{:}CH_2$	$C_{36}H_{30}O_2$ (IVh)
4-MeO-2-HO·C_6H_3·CHO (If) [11]	$Ph_2C{:}CH_2$	$C_{36}H_{30}O_2$ (IVi)
5-MeO-2-HO·C_6H_3·CHO (Ig) [12]	$Ph_2C{:}CH_2$	$C_{36}H_{30}O_2$ (IVj)

Table 1 lists the 2-hydroxy-1-aldehydes and 1,1-diphenylethylenes that were allowed to react in acetic acid saturated with dry hydrogen chloride and gives the formulæ of the resulting products. The same products resulted irrespective of whether two or one mole of diphenylethylene were treated with one mole of hydroxy-aldehyde; only the yield changed correspondingly.

Certain of the chromens, which would have been formed had the reaction proceeded by the mechanism suggested by Wizinger and Wenning, have been prepared by an alternative and well-established method, namely the action of a Grignard reagent on a coumarin.[13a,b] However, in some instances with arylmagnesium halides, 1,4 addition also occurred, as in the reaction between coumarin and 4-methoxyphenylmagnesium bromide when, besides the required product, 1,3-di-(4-methoxyphenyl)-3-(2-hydroxyphenyl)propan-1-one (C=O, 1670 cm.$^{-1}$) [13a,b] was also isolated, and converted into 2,4-di-(4-methoxyphenyl)-4*H*-chromen when boiled with acetic acid. Some of these 2,2-diarylchromens, as happens with 6,6-diphenylnaphtho[2′,1′-*b*]pyran, also reacted with certain diphenylethylenes under similar acid conditions to give products identical with those obtained from the reaction between the corresponding 2-hydroxy-1-aldehyde and diphenylethylene (Table 2).



(V)



(VI)

(a) R¹ = R² = R³ = H, R⁴ = Ph
(b) R¹ = R² = R³ = H, R⁴ = *o*-C_6H_4·OMe
(c) R¹ = R² = R³ = H, R⁴ = *m*-C_6H_4.OMe
(d) R¹ = R² = R³ = H, R⁴ = *p*-C_6H_4·OMe
(e) R² = R³ = H, R¹ = OMe, R⁴ = Ph
(f) R¹ = R³ = H, R² = OMe, R⁴ = Ph
(g) R¹ = R² = H, R³ = OMe, R⁴ = Ph

2,2-Di-(4-methoxyphenyl)-2*H*-chromen failed to react with 1,1-diphenylethylene under identical and different conditions. As shown in Table 1 the 1,1-di-(3-methoxyphenyl)ethylene (IIc) and *o*-hydroxybenzaldehyde failed to yield compound (IVc). The deactivating effect of a *meta*-substituted methoxy-group was again indicated in the failure of the corresponding reaction between 1,1-di-(3-methoxyphenyl)ethylene (IIc) and 2,2-di-(3-methoxyphenyl)-2*H*-chromen (VIc).

---

[5] G. L. Stadnikov, *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 2037, 2115; C. F. H. Allen and S. Converse, *Org. Synth.*, Coll. Vol. I, 1st edn., p. 221; C. R. Noller and L. J. Lataillade, *Org. Synth.*, vol. 18, p. 87.

[6] E. Bergmann and A. Bondi, *Ber.*, 1931, **648**, 1455.

[7] A. G. Evans *et al.*, *J.*, 1956, 2757; R. Anschütz and A. Hilbert, *Ber.*, 1924, **57**, 1698.

[8] G. Mazzara, *Gazzetta*, 1877, 460.

[9] M. Calvin and J. R. Segesses, *J. Amer. Chem. Soc.*, 1942, **64**, 825.

[10] F. Tiemann and P. Koppe, *Ber.*, 1881, **14**, 2021.

[11] T. E. De Kiewiet and H. Stephen, *J.*, 1931, 84.

[12] F. Tiemann and W. H. M. Müller, *Ber.*, 1881, **14**, 1990.

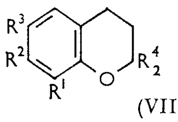
[13] (*a*) A. Löwenbein, *Ber.*, 1924, **57**, 1517; (*b*) C. S. Barnes, M. I. Strong, and J. L. Occolowitz, *Tetrahedron*, 1963, **19**, 839.

TABLE 2

Reactions between chromens and 1,1-diphenylethylenes

Chromen	1,1-Diphenylethylene	Product
2,2-Diphenyl-2*H*-chromen (VIa)	$Ph_2C{:}CH_2$	$C_{35}H_{28}O$ (IVa)
2,2-Di-(2-methoxyphenyl)-2*H*-chromen (VIb)	$(o\text{-}MeO{\cdot}C_6H_4)_2C{:}CH_2$	$C_{39}H_{36}O_5$ (IVb)
6-Methoxy-2,2-diphenyl-2*H*-chromen (VIg)	$Ph_2C{:}CH_2$	$C_{36}H_{30}O_2$ (IVj)
7-Methoxy-2,2-diphenyl-2*H*-chromen (VIf)	$Ph_2C{:}CH_2$	$C_{36}H_{30}O_2$ (IVi)
8-Methoxy-2,2-diphenyl-2*H*-chromen (VIe)	$Ph_2C{:}CH_2$	$C_{36}H_{30}O_2$ (IVb)

2,2-Di-(4-methoxyphenyl)-2*H*-chromen was not obtained on repeating the experiment of Wizinger and Wenning [1,2] by treating 1,1-di-(4-methoxyphenyl)ethylene with salicylaldehyde and perchloric acid in acetic anhydride and acetic acid. The only material isolated was an amorphous powder, m. p. 260—265°, which could not be purified. A similar product of high melting point was also obtained on treating 1,1-di-(4-methoxyphenyl)ethylene with salicylaldehyde in acetic acid saturated with dry hydrogen chloride, but in this case a small amount of a compound, m. p. 142° (Table 1), with the empirical formula $C_{39}H_{36}O_5$ was also isolated. Treating 1,1-diphenylethylene with salicylaldehyde under the conditions used by Wizinger and Wenning failed to give any chromen (VIa).[13a,b] The only compound isolated in small yield melted at 224° and was identical with that obtained when the above components reacted together in acetic acid saturated with dry hydrogen chloride. On reduction with hydrogen and platinum oxide the chromens afforded the corresponding chromans.



(VII)

(a) $R^1 = R^2 = H, R^3 = OMe, R^4 = Ph$
(b) $R^1 = R^3 = H, R^2 = OMe, R^4 = Ph$
(c) $R^2 = R^3 = H, R^1 = OMe, R^4 = Ph$
(d) $R^1 = R^2 = R^3 = H, R^4 = o\text{-}MeO{\cdot}C_6H_4$

EXPERIMENTAL

The 60 Mc./sec. proton magnetic resonance spectra were recorded on a Varian A60 spectrometer for ~10% solutions in deuterochloroform. Chemical shifts were measured on the τ-scale from the resonance of tetramethylsilane added as internal reference.

Preparation of 2,2-*Diaryl*-2H-*chromens*.—The coumarin (0·1 mole) in dry benzene (55 c.c.) was added to a stirred Grignard solution from aryl bromide (0·21 mole), magnesium (0·22 g.-atom), and ether (100 c.c.). The solution was refluxed for 1 hr., set aside overnight, and decomposed with 22% ammonium chloride solution; the benzene–ether layer was steam-distilled and the product filtered off from the non-volatile portion.

2,2-*Di*-(2-*methoxyphenyl*)-2H-*chromen* (VIb). The non-volatile residue (29·6 g.) was dried and triturated with ethanol, and the ethanolic extracts were decanted. Crystallisation of the white residue from light petroleum (b. p. 80—100°) gave 2,2-*di*-(2′-*methoxyphenyl*)*chromen* (5·5 g., 16%), m. p. 163° (Found: C, 80·4; H, 6·0. $C_{23}H_{20}O_3$ requires C, 80·2; H, 5·8%).

2,2-*Di*-(3′-*methyoxyphenyl*)-2H-*chromen* (VIc). The non-volatile residue was dried, dissolved in ether, and purified by chromatography on alumina to give a gum, which slowly crystallised from ethanol. Recrystallisation from methanol gave 2,2-*di*-(3-*methoxyphenyl*)-2H-*chromen* (1·7 g., 5%), m. p. 109—110° (Found: C, 79·6; H, 6·1; OMe, 16·1. $C_{23}H_{20}O_3$ requires C, 80·2; H, 5·8; OMe, 18·0%).

2,2-*Di*-(4-*methoxyphenyl*)-2H-*chromen* (VId). The residue was dried and extracted with ether leaving an insoluble residue which was crystallised from benzene to give 1,3-*di*-(4-*methoxyphenyl*)-3-(2-*hydroxyphenyl*)*propan*-1-*one* as needles, m. p. 139·5—141° (Found: C, 76·3; H, 6·3; OMe, 17·6. $C_{23}H_{22}O_4$ requires C, 76·2; H, 6·1; OMe, 17·1%). Evaporation of the ethereal extract yielded a viscous liquid from which the alcohol slowly separated and was removed by filtration. The filtrate was dissolved in benzene and purified by chromatography on alumina to give an oil (7·7 g., 22·4%) which solidified after 1 week at 0°. Crystallisation from methanol gave 2,2-*di*-(4-*methoxyphenyl*)-2H-*chromen* as platelets, m. p. 96—97° (Found: C, 80·1; H, 6·1. $C_{23}H_{20}O_3$ requires C, 80·2; H, 5·8%).

6-*Methoxy*-2,2-*diphenyl*-2H-*chromen* (VIg) (*from* 6-*methoxycoumarin* [13]). The residue was dried, dissolved in benzene, and purified by chromatography on alumina to give a gum, which on repeated crystallisation from light petroleum (b. p. 80—100°) gave *6-methoxy-2,2-diphenyl-2*H*-chromen* (2·8 g., 9%), m. p. 165—166° (Found: C, 83·2; H, 5·7. $C_{22}H_{18}O_2$ requires C, 84·1; H, 5·7%).

*7-Methoxy-2,2-diphenyl-2*H*-chromen* (VIf) (*from 7-methoxycoumarin* [14]). The non-volatile fraction was dried, dissolved in benzene, and purified by chromatography on alumina to give *7-methoxy-2,2-diphenyl-2*H*-chromen* (5·6 g., 19%), m. p. 81—82° (from methanol) (Found: C, 84·1; H, 5·6. $C_{22}H_{18}O_2$ requires C, 84·1; H, 5·7%).

*8-Methoxy-2,2-diphenyl-2*H*-chromen* (VIc) (*from 8-methoxycoumarin* [15]). The residue was dried and crystallised from ethanol to give *8-methoxy-2,2-diphenyl-2*H*-chromen* (7·2 g., 23%), m. p. 109° (Found: C, 83·8; H, 6·2. $C_{22}H_{18}O_2$ requires C, 84·1; H, 5·7%).

*2,4-Di-(4-methoxyphenyl)-4*H*-chromen.*—1,3-Di-(4-methoxyphenyl)-3-(2-hydroxyphenyl)-propan-1-one (0·3 g.) was boiled with acetic acid (6 c.c.) for 1 min. and cooled, yielding a white solid, which afforded 2,4-di-(4-methoxyphenyl)-4*H*-chromen (0·1 g.) as needles (from methanol), m. p. 119—120° (Found: C, 79·9; H, 6·1. $C_{23}H_{20}O_3$ requires C, 80·2; H, 5·8%).

1,1-Di-(3-methoxyphenyl)ethylene (IIc).—Ethyl acetate (5·1 g.) in ether (10 c.c.) was added slowly to a stirred Grignard solution from *m*-bromoanisole [16] (25 g.), magnesium (3·1 g.), and ether (60 c.c.). The solution was refluxed for 45 min., decomposed by the addition of ammonium chloride solution and extracted with ether. The ether was removed and the residue was heated at 230—235° for 45 min. and distilled to give *1,1-di-(3-methoxyphenyl)-ethylene* (5·2 g., 34%) b. p. 205—206°/15 mm., n_D^{20} 1·6014 (Found: C, 79·5; H, 6·8. $C_{16}H_{16}O_2$ requires C, 79·8; H, 6·7%).

Reaction between 1,1-Diphenylethylenes and o-Hydroxybenzaldehydes.—An acetic acid solution of the 1,1-diphenylethylene and the *o*-hydroxybenzaldehyde in molecular ratio 2 : 1 was saturated with dry hydrogen chloride and set aside for 2 days. A solid separated and was crystallised from a suitable solvent.

The ease of separation of a crystalline product was improved by using the minimum volume of acetic acid necessary to prevent reactant crystallising out before the solution was saturated with hydrogen chloride.

Reaction between o-Hydroxybenzaldehyde and 1,1-Di-(4-methoxyphenyl)ethylene.—*o*-Hydroxybenzaldehyde (0·4 g.) and 1,1-di-(4-methoxyphenyl)ethylene (1·65 g.) were dissolved in acetic acid (15 c.c.) saturated with dry hydrogen chloride and boiled for 2 hr. The mixture was set aside for 2 hr. and water was then added. The solid that separated was dried and extracted with methanol. The addition of water to the methanolic solution caused the separation of a crystalline solid, which was recrystallised from dilute methanol to give a white solid (0·1 g.) m. p. 142—143°, depressed on admixture with 2,2-di-(4-methoxyphenyl)chromen, and 1,1-di-(4-methoxyphenyl)ethylene (Found: C, 79·8; H, 6·1. $C_{39}H_{36}O_5$ requires C, 80·1; H, 6·2%).

*Reaction between 1,1-Diphenylethylenes and 2,2-Diphenyl-2*H*-chromens.*—An acetic acid solution of the 1,1-diphenylethylene and the 2,2-diphenylchromen in equal molecular proportions was saturated with dry hydrogen chloride and set aside for 1 day. The solid that separated was crystallised from a suitable solvent.

Preparation of 2,2-Diarylchromans.—The diarylchromen, platinic oxide, and ethyl acetate were shaken in hydrogen until absorption (1 mole) was complete. Filtration followed by removal of the solvent and crystallisation from a suitable solvent gave the diarylchroman. The following were obtained: *2,2-di-(2-methoxyphenyl)chroman* (VIId) [from 2,2-di-(2-methoxyphenyl)chromen], m. p. 151° [from light petroleum (b. p. 80—100°)] (Found: C, 79·6; H, 6·6; OMe, 18·6. $C_{23}H_{22}O_3$ requires C, 79·8; H, 6·4; OMe, 17·9%); *2,2-diphenyl-6-methoxychroman* (VIIa) (from 2,2-diphenyl-6-methoxychroman), m. p. 82—83° [from light petroleum (b. p. 80—100°)] (Found: C, 84·1; H, 6·6. $C_{22}H_{20}O_2$ requires C, 83·5; H, 6·3%); *2,2-diphenyl-7-methoxychroman* (VIIb) (from 2,2-diphenyl-7-methoxychromen) (65%), m. p. 103° (from methanol) (Found: C, 83·1; H, 6·5. $C_{22}H_{20}O_2$ requires C, 83·5; H, 6·3%). *2,2-Diphenyl-8-methoxychroman* (VIIc) (from 2,2-diphenyl-8-methoxychromen), m. p. 97—98° [from light petroleum (b. p. 60—80°)] (Found: C, 83·9; H, 6·6. $C_{22}H_{20}O_2$ requires C, 83·5; H, 6·3%).

Reaction between Salicylaldehyde and 1,1-Diphenylethylene.—Salicylaldehyde (1·2 g.) and

---

[14] W. Bridge, A. J. Crocker, T. Cubin, and A. Robertson, *J.*, 1937, 1530.

[15] B. B. Dey and A. Kutti, *Proc. Nat. Inst. Sci. India*, 1940, **6**, 641; N. Mauther, *J. prakt. Chem.*, 1939, **152**, 23.

[16] O. Diels and F. Bunzl, *Ber.*, 1905, **38**, 1496.

TABLE 3

Reactions between 1,1-diphenylethylenes and *o*-hydroxybenzaldehydes

Hydroxy-benzaldehyde	Diphenylethylene	Acetic acid (c.c.)	Time (days)	Product
o-HO·C_6H_4·CHO (0·6 g.)	$Ph_2C{:}CH_2$ (1·8 g.)	10	2	(IVa) (1·06 g., 44·2%) (from ethyl acetate), m. p. 222—223° (Found: C, 90·2; H, 6·2. $C_{35}H_{28}$ requires C, 90·5; H, 6·0%)
o-HO·C_6H_4·CHO (1·31 g.)	$(o\text{-MeO}\cdot C_6H_4)_2C{:}CH_2$ (5·13 g.)	50	2	(IVb) (5·47 g., 85%) (from acetic acid), m. p. 199° (Found: C, 79·6; H, 6·2. $C_{39}H_{36}O_5$ requires C, 80·1; H, 6·2%)
3-NO_2-2-HO·C_6H_3·CHO (0·8 g.)	$Ph_2C{:}CH_2$ (1·8 g.)	20	1	(IVe) (2·0 g., 77%) (from acetic acid), m. p. 151—152° (Found: C, 82·1; H, 5·4; N, 3·0. $C_{35}H_{27}NO_3$ requires C, 82·3; H, 5·3; N, 2·7%)
4-NO_2-2-HO·C_6H_3·CHO (1·2 g.)	$Ph_2C{:}CH_2$ (2·5 g.)	15	2	(IVf) (1·6 g., 43%) (from acetic acid), m. p. 235—236° (decomp.) (Found: C, 82·0; H, 5·7; N, 3·0. $C_{35}H_{27}NO_3$ requires C, 82·3; H, 5·3; N, 2·7%)
5-NO_2-2-HO·C_6H_3·CHO (0·8 g.)	$Ph_2C{:}CH_2$ (1·8 g.)	20	several	(IVg) (0·8 g., 31%) (from acetic acid), m. p. 241—242° (decomp.) (Found: C, 82·1; H, 5·2; N, 2·5. $C_{35}H_{27}NO_3$ requires C, 82·3; H, 5·3; N, 2·7%)
3-MeO-2-HO·C_6H_3·CHO (1·9 g.)	$Ph_2C{:}CH_2$ (4·6 g.)	30	1	(IVh) (4·5 g., 70%) [from light petroleum (b. p. 80—100°)], m. p. 162° (Found: C, 87·5; H, 6·1; OMe, 6·5. $C_{36}H_{30}O_2$ requires C, 87·4; H, 6·1; OMe, 6·3%)
4-MeO-2-HO·C_6H_3·CHO (1·1 g.)	$Ph_2C{:}CH_2$ (3·0 g.)	10	18	(IVi) (0·86 g., 25%) [from light petroleum (b. p. 80—100°)], m. p. 181—182° (Found: C, 87·4; H, 6·4. $C_{36}H_{30}O_2$ requires C, 87·4; H, 6·1%)
5-MeO-2-HO·C_6H_3·CHO (1·0 g.)	$Ph_2C{:}CH_2$ (2·9 g.)	10	15	(IVj) (1·56 g., 50%) (from ethyl acetate–ethanol), m. p. 151—153° (Found: C, 88·3; H, 5·9; OMe, 6·3. $C_{36}H_{30}O_2$ requires C, 87·4; H, 6·1; OMe, 6·3%)

TABLE 4

Reactions between 1,1′-diphenylethylenes and 2,2′-diphenyl-2*H*-chromens

2*H*-Chromen	Diphenylethylene	Acetic acid (c.c.)	Product
2,2-Diphenyl- (0·24 g.)	$Ph_2C{:}CH_2$ (0·2 g.)	8	(IVa) (from ethyl acetate), m. p. 223°
2,2-Di-(2-methoxyphenyl)- (0·26 g.)	$(o\text{-MeO}\cdot C_6H_4)_2C{:}CH_2$ (0·18 g.)	8	(IVb) (from acetic acid), m. p. 199—200°
6-Methoxy-2,2-diphenyl- (0·13 g.)	$Ph_2C{:}CH_2$ (0·22 g.)	4	(IVj) [from light petroleum (b. p. 80—100°) and then ethyl acetate], m. p. 151—153°
7-Methoxy-2,2-diphenyl- (0·11 g.)	$Ph_2C{:}CH_2$ (0·08 g.)	5	(IVi) [from light petroleum (b. p. 80—100°)], m. p. 181—182°
8-Methoxy-2,2-diphenyl- (0·11 g.)	$Ph_2C{:}CH_2$ (0·07 g.)	4	(IVh) [from light petroleum (b. p. 80—100°)], m. p. 162°

1,1-diphenylethylene (1·8 g.) were dissolved in acetic acid (2 c.c.), acetic anhydride (2 c.c.), and 60% perchloric acid (0·5 c.c.), set aside for 2 days, and poured into water. The solid that separated was crystallised from light petroleum (b. p. 60—80°)-ethyl acetate to give a solid with m. p. and mixed m. p. 222—224° (0·08 g., 2·6%).

A grant from Imperial Chemical Industries Limited is gratefully acknowledged. We are indebted to Drs. R. L. Elliot and D. W. Jones for permitting use of the Bradford Institute of Technology n.m.r. spectrometer, as well as to Dr. J. A. S. Smith for discussion.

COLLEGE OF TECHNOLOGY, HUDDERSFIELD.
COLLEGE OF TECHNOLOGY, DARTFORD.

[*Received, June* 17*th*, 1964.]