123. *Dimerisation of 2,2-Diphenyl- and 2,2-Dimethyl-chromen. Part I.*

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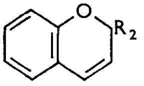
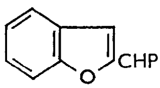
2,2-Diphenylchromen on treatment with methanolic hydrogen chloride gave a dimer, probably similar in structure to lapachenole dimer.[1] A dimer of 2,2-dimethylchromen was obtained by an indirect method.

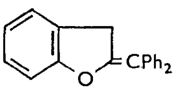
Löwenbein [2] reported that boiling 2,2-diphenylchromen (Ia) with acetic acid or methanolic hydrogen chloride gave a quantitative yield of a compound, $C_{21}H_{16}O$, whose molecular weight indicated that isomerisation had taken place to give either 2-diphenylmethylbenzofuran (II) or compound (III). We were unable to obtain this compound on boiling 2,2-diphenylchromen (Ia) with acetic acid, but succeeded by using methanolic hydrogen chloride. Ebullioscopic and cryoscopic determinations of molecular weight indicated that the compound was dimeric (IVa) and probably similar in structure to compounds obtained by the acid dimerisation of related dimethylpyrans.[1,3]



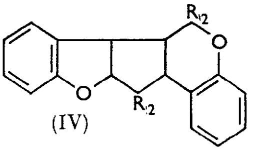
(I)



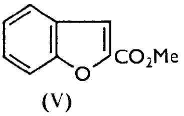
(II)



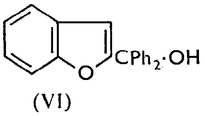
(III)



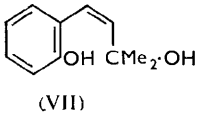
(IV)



(V)



(VI)



(VII)

(a) ; R = Ph
(b) ; R = Me

Reaction of methyl benzofuran-2-carboxylate (V) with phenylmagnesium iodide gave the alcohol (VI) which on reduction afforded a product (II), different from the compound obtained by Löwenbein. Attempts to prepare the diphenylmethylene compound (III) by dehydration of the 2,3-dihydro-derivative of the alcohol (VI) gave only the diphenylmethyl compound (II).

Treatment of the styrylcarbinol (VII) [4] with methanolic hydrogen chloride or with acetic acid containing a few drops of sulphuric acid gave a compound which, from its properties and by analogy, is considered to be a dimer of 2,2-dimethylchromen (Ib), probably (IVb) (cf. Shriner and Sharp [5]).

No evidence was obtained for the presence of an ethylenic linkage in this dimer; thus its ultraviolet absorption spectra closely resembled that of 2,2-dimethylchroman.[6] The same relation existed between the ultraviolet absorption spectra of 2,2-diphenylchromen dimer, 2,2-diphenylchromen, and 2,2-diphenylchroman (Figure).

Polymeric material (*M* 650—800) was obtained by treatment of 2,2-dimethylchromen (Ib) with acetic acid containing a few drops of concentrated sulphuric acid, or with boiling anhydrous formic acid.

Experimental

The Action of Methanolic Hydrogen Chloride on 2,2-Diphenylchromen.—2,2-Diphenylchromen (1 g.) was refluxed for ¾ hr. with methanolic hydrogen chloride (30 c.c.; 3%). The *dimer* had m. p. 240° after crystallisation from ethyl acetate [Found: C, 88·0; H, 5·6%; *M*, 530. $(C_{21}H_{16}O)_2$ requires C, 88·7; H, 5·6%; *M*, 580].

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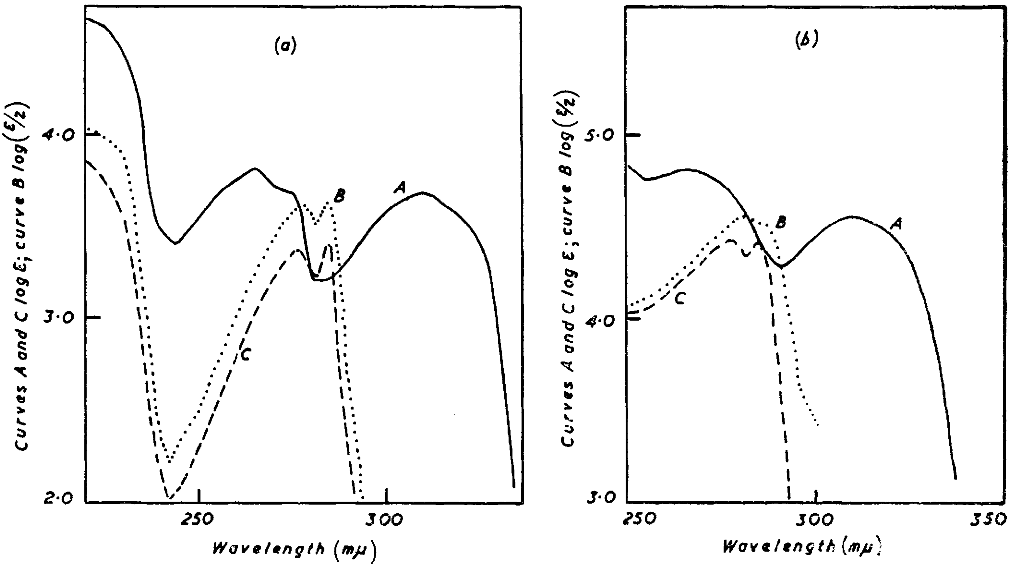
[1] Livingstone and Whiting, *J.*, 1955, 3631
[2] Löwenbein, *Ber.*, 1924, **57**, 1517.
[3] Livingstone, Miller, and Watson, *J.*, 1958, 2422.
[4] Smith and Ruoff, *J. Amer. Chem. Soc.*, 1940, **62**, 145.
[5] Shriner and Sharp, *J. Org. Chem.*, 1939, **4**, 575.
[6] Smith, Ungnade, and Prichard, *J. Org. Chem.*, 1939, **4**, 358.

Preparation of 2-(α-*Hydroxydiphenylmethyl*)*benzofuran and* 2,3-*Dihydro*-2-(α-*hydroxydiphenylmethyl*)*benzofuran*.—The ester (0·02 mole) in dry ether (50 c.c.) was added slowly to a stirred Grignard solution from bromo- or iodo-benzene (0·06 mole), magnesium (0·06 g.-atom), and ether (50 c.c.). The solution was refluxed for 1 hr. and then set aside overnight. Decomposition with 22% ammonium chloride solution (100 c.c.), isolation with ether, and recrystallisation from a suitable solvent gave the hydroxydiphenylmethyl compound.

2-(α-*Hydroxydiphenylmethyl*)*benzofuran* (VI) (from methyl benzofuran-2-carboxylate) crystallised from light petroleum (b. p. 60—80°) as plates, m. p. 132—133° (33%) (Found: C, 83·9; H, 5·3. $C_{21}H_{16}O_2$ requires C, 84·0; H, 5·3%). 2,3-*Dihydro*-2-(α-*hydroxydiphenylmethyl*)*benzofuran* (from methyl 2,3-dihydrobenzofuran-2-carboxylate) crystallised from methanol as needles, m. p. 125—126° (40%) (Found: C, 83·4; H, 5·75. $C_{21}H_{18}O_2$ requires C, 83·4; H, 6·0%).

(*a*) *Ultraviolet absorption spectra of* (*A*) 2,2-*dimethylchromen*, (*B*) 2,2,-*dimethylchroman dimer, and* (*C*) 2,2-*dimethylchroman in hexane.*

(*b*) *Ultraviolet absorption spectra of* (*A*) 2,2,-*diphenylchromen*, (*B*) 2,2-*diphenylchromen dimer, and* (*C*) 2,2,-*diphenylchroman in chloroform.*



2-*Diphenylmethylbenzofuran*.—2-(α-Hydroxydiphenylmethyl)benzofuran (0·5 g.) was refluxed with acetic acid (10 c.c.) and zinc dust (5 g.) for 4 hr. Neutralisation with sodium hydrogen carbonate solution, followed by isolation with ether and crystallisation from light petroleum (b. p. 60—80°), gave 2-*diphenylmethylbenzofuran* as rosettes, m. p. 113—114° (50%) (Found: C, 88·6; H, 5·5. $C_{21}H_{16}O$ requires C, 88·6; H, 5·6%).

Dehydration of 2,3-*Dihydro*-2-(α-*hydroxydiphenylmethyl*)*benzofuran*.—(*a*) 2,3-Dihydro-2-(α-hydroxydiphenylmethyl)benzofuran (0·63 g.) was heated with phosphoric acid (25 c.c.; *d* 1·7) for $\frac{3}{4}$ hr. at 210°. The product was isolated with ether and crystallised from light petroleum (b. p. 60—80°), giving 2-diphenylmethylbenzofuran, m. p. and mixed m. p. 113—114°.

(*b*) The same benzofuran (0·07 g.) was refluxed with anhydrous formic acid (6 c.c.) for $\frac{1}{2}$ hr. Isolation and crystallisation gave 2-diphenylmethylbenzofuran, m. p. and mixed m. p. 113—114°.

2,2-*Dimethylchromen Dimer*.—(*a*) 3-*o*-Hydroxyphenyl-1,1-dimethylprop-2-en-1-ol (VII) (0·56 g.), methanol (5 c.c.), and methanol saturated with hydrogen chloride (6 c.c.) were set aside for 6 days at room temperature. The solid (0·28 g.) was crystallised from ethyl acetate, giving 2,2-dimethylchromen *dimer*, m. p. 189—190° [Found: C, 82·6; H, 7·5%; *M*, 330. $(C_{11}H_{12}O)_2$ requires C, 82·5; H, 7·5%; *M*, 320].

(*b*) The propenol (0·33 g.), acetic acid (5 c.c.), and concentrated sulphuric acid (3 drops) were set aside for 3 days at room temperature. Solid (0·13 g.) separated and gave 2,2-dimethylchromen dimer, m. p. and mixed m. p. 189—190°.

2,2-*Diphenylchroman.*—2,2-Diphenylchromen (0·86 g.), platinic oxide (0·06 g.), and ethanol (50 c.c.) were shaken in hydrogen until absorption (1 mole) was complete. Filtration, evaporation, and recrystallisation from methanol gave 2,2-*diphenylchroman* as plates, m. p. 79—80° (Found: C, 88·2; H, 6·45. $C_{21}H_{18}O$ requires C, 88·1; H, 6·3%).

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