992. *2-Methoxy-2,4-diphenylchroman and 5,6-Dihydro-6-methoxy-4,6-diphenyl-4*H*- and 6,6-diphenyl-6*H*-naphtho(2′,1′:2,3)pyran.*

By R. Livingstone, D. Miller, and (Miss) S. Morris.

2-Methoxy-2,4-diphenylchroman and 5,6-dihydro-6-methoxy-4,6-diphenyl-4*H*-naphtho(2′,1′:2,3)pyran have been prepared from the corresponding chromens. 6,6-Diphenylnaphtho(2′,1′:2,3)pyran has been prepared by two methods and shown to be different from the compound obtained by Wizinger and Wenning.

In this paper we describe the preparation and some reactions of inter-related diphenylchromen and naphthopyran derivatives. 2,4-Diphenyl-4*H*-chromen[1] (I) and 4,6-diphenyl-4*H*-naphtho(2′,1′:2,3)pyran (VII) in refluxing 4% methanolic hydrogen chloride were converted almost quantitatively into 2-methoxy-2,4-diphenylchroman (IIa) and 5,6-dihydro-6-methoxy-4,6-diphenyl-4*H*-naphtho(2′,1′:2,3)pyran (VIIIa) respectively. The former product with ferric chloride in boiling acetic anhydride gave the ferrichloride[1] (IV)

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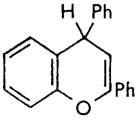
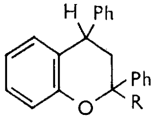
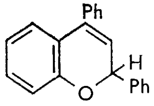
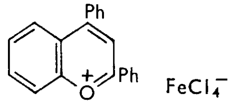
[1] Löwenbein, *Ber.*, 1924, **57**, 1517.

identical with that obtained from 2,4-diphenyl-4*H*-chromen (I), 2,4-diphenyl-2*H*-chromen (III), and 2,4-diphenylchroman-2-ol[1] (IIb). This chromanol with methanolic hydrogen chloride gave its methyl ether (IIa) which in boiling glacial acetic acid gave an excellent yield of the chromen (I). The ethyl ether was similarly obtained from the chromen (I) in ethanolic hydrogen chloride.

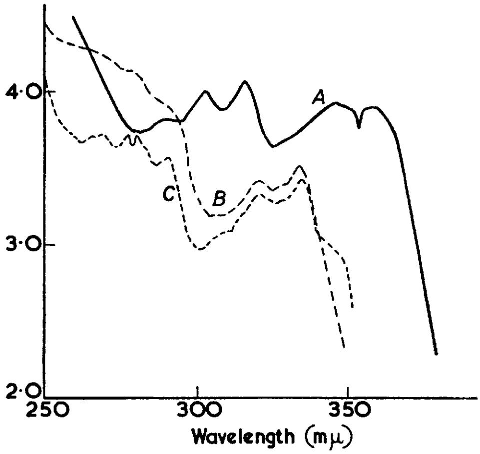

(I)


(II) a: R = OMe
b: R = OH


(III)


(IV)

Reaction of 5,6-benzocoumarin[2] (V) with phenylmagnesium bromide gave a mixture of 6,6-diphenylnaphtho(2′,1′:2,3)pyran[3] (VI) and 5,6-dihydro-4,6-diphenyl-4*H*-naphtho-(2′,1′:2,3)pyran-6-ol (VIIIb) which were separated. The alcohol (VIIIb) was dehydrated by boiling acetic acid to give 4,6-diphenyl-4*H*-naphtho(2′,1′:2,3)pyran (VII), which on hydrogenation afforded the dihydro-derivative (VIIId). The last compound was also obtained by reduction of 4,6-diphenyl-6*H*-naphtho(2′,1′:2,3)pyran (X), which was prepared by dehydration of the product from 2,3-dihydro-5,6-benzoflavone[4] (IX) and phenylmagnesium bromide. Wizinger and Wenning[5] assigned the structure (VI) to a compound, m. p. 194—195°, which they obtained by condensing 2-hydroxy-1-naphthaldehyde[6] with diphenylethylene[7] in acetic acid saturated with hydrogen chloride; our compound (VI) had m. p. 161°. Our compound was reduced by hydrogen and platinum to 5,6-dihydro-6,6-diphenyl-4*H*-naphtho(2′,1′:2,3)pyran (VIIIc), but Wizinger and Wenning's compound was unaffected under similar conditions and no evidence was obtained for the presence of a double bond in it. The structure of our compound is supported by the ultraviolet absorption spectra shown in the annexed Figure and by oxidation of our compound (VI), m. p. 161°, by potassium permanganate in acetone[8] to an acid (XIa); the ester of this acid was reduced to the alcohol (XIb) which was hydrolysed by dilute sulphuric acid to afford, in low yield, diphenylacetaldehyde[9] (isolated as its phenylhydrazone).



Ultraviolet absorption spectra of compounds: (*A*) (VI), (*C*) (VIIIc), *and* (*B*), *m. p.* 194—195°.

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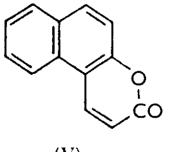
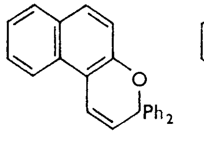
[2] Kauffmann, *Ber.*, 1883, **16**, 685.
[3] Livingstone, Miller, and Watson, *J.*, 1958, 2422.
[4] Jambor, Plattner, and Zäch, *Helv. Chim. Acta*, 1926, **9**, 463.
[5] Wizinger and Wenning, *Helv. Chim. Acta*, 1940, **23**, 247.
[6] Kauffmann, *Ber.*, 1882, **15**, 805.
[7] Allen, *Org. Synth.*, Coll. Vol. I (1st edn.), p. 221.
[8] Livingstone and Whiting, *J.*, 1955, 3631.
[9] Stroermer, *Ber.*, 1906, **39**, 2293.

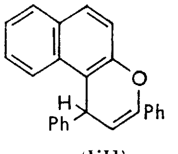
The possibility that the reaction between 2-hydroxy-1-naphthaldehyde and diphenylethylene had given 5-diphenylmethylnaphtho(2′,1′:2,3)furan (XIIc) was eliminated by an unambiguous synthesis of this compound. Reaction of methyl 5,6-benzocoumarilate [10] (XIIa) with phenylmagnesium bromide gave 5-(α-hydroxydiphenylmethyl)-naphtho(2′,1′:2,3)furan (XIIb) which on reduction afforded 5-diphenylmethylnaphtho-(2′,1′:2,3)furan (XIIc). Analyses of Wizinger and Wenning's compound indicated a formula $C_{39}H_{50}O$ and when we obtained it by treating the compound (VII) with diphenylethylene in acetic acid containing hydrogen chloride it became clear that in Wizinger and Wenning's preparation the pyran (VI) first formed had reacted with a second molecule of diphenylethylene to give the compound [8] (XIII).



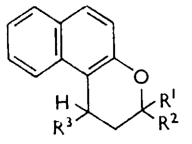
(V)



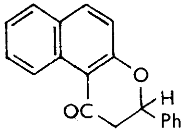
(VI)



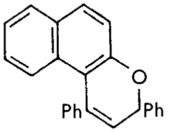
(VII)



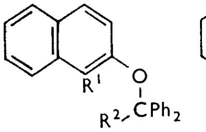
(VIII) a: $R^1 = R^3 = Ph$, $R^2 = OMe$
b: $R^1 = R^3 = Ph$, $R^2 = OH$
c: $R^1 = R^2 = Ph$, $R^3 = H$
d: $R^1 = R^3 = Ph$, $R^2 = H$



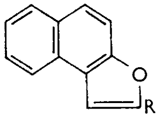
(IX)



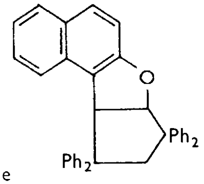
(X)



(XI) a: $R^1 = R^2 = CO_2H$
b: $R^1 = R^2 = CH_2{\cdot}OH$

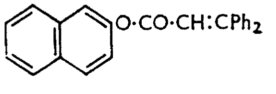


(XII)
a: $R = CO_2Me$
b: $R = CPh_2{\cdot}OH$
c: $R = CHPh_2$

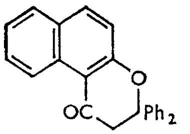


(XIII)

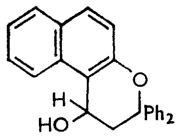
6,6-Diphenyl-6*H*-naphtho(2′,1′:2,3)pyran (VI) was also obtained by an unambiguous synthesis, an extension of a method for the preparation of substituted chromanones.[11] Esterification of β-naphthol with ββ-diphenylacryloyl chloride,[12] Fries rearrangement of the product (XIV) in the absence of solvent, and acidic isomerisation and ring closure by acid gave the dihydrobenzochromenone (XV). Reduction by lithium aluminium hydride readily gave the alcohol (XVI) and removal of water by glacial acetic acid gave the naphthopyran (VI).



(XIV)



(XV)



(XVI)

EXPERIMENTAL

6,6-Diphenylnaphtho(2′,1′:2,3)*pyran* (VI) *and* 5,6-*Dihydro*-4,6-*diphenyl*-4H-*naphtho*(2′,1′:2,3)-*pyran*-6-*ol* (VIIIb).—5,6-Benzocoumarin (30 g.) in dry benzene (550 c.c.) was added in 1½ hr. to a stirred Grignard solution from bromobenzene (42 c.c.), magnesium (10 g.), and ether (150 c.c.). The solution was refluxed for 1 hr. and set aside overnight. After decomposition with 22%

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[10] Dey, Rao, and Sankaranarayanan, *J. Indian Chem. Soc.*, 1932, **9**, 71.

[11] Cavill, Dean, McGookin, Marshall, and Robertson, *J.*, 1954, 4573.

[12] Kharasch, Kane, and Brown, *J. Amer. Chem. Soc.*, 1942, **64**, 333.

ammonium chloride solution the mixture was steam-distilled and the product filtered off from the non-volatile portion. Extraction with ether, evaporation of the extract, and crystallisation of the residue from light petroleum (b. p. 80—100°) gave the *alcohol* (VIIIb) (6·3 g.) which recrystallised from light petroleum (b. p. 100—120°) as needles, m. p. 153—154° (Found: C, 85·8; H, 5·8. $C_{25}H_{20}O_2$ requires C, 85·2; H, 5·7%). The residue (34·9 g.) insoluble in ether recrystallised from acetic acid to give 6,6-*diphenylnaphtho*(2′,1′:2,3)*pyran* (VI) as needles, m. p. 160—161° (Found: C, 90·0; H, 5·7. $C_{25}H_{18}O$ requires C, 90·0; H, 5·4%).

4,6-*Diphenyl*-4H-*naphtho*(2′,1′:2,3)*pyran* (VII).—The alcohol (VIIb) (0·15 g.), when boiled with acetic acid (3 c.c.) for 1 min., gave a white precipitate which on recrystallisation from ethyl acetate afforded the *naphthopyran* (VII) (0·1 g.) as needles, m. p. 205° (Found: C, 89·5; H, 5·5. $C_{25}H_{18}O$ requires C, 90·0; H, 5·4%).

2-*Methoxy*-2,4-*diphenylchroman*.—(*a*) 2,4-Diphenyl-4*H*-chroman (5·0 g.) was boiled with a 4% solution of dry hydrogen chloride in methanol (150 c.c.) for 1 hr. On evaporation and cooling, a white solid separated. Recrystallisation from methanol gave 2-*methoxy*-2,4-*diphenylchroman* (4·6 g.) as plates, m. p. 106° (Found: C, 83·5; H, 6·6; OMe, 9·8. $C_{22}H_{20}O_2$ requires C, 83·5; H, 6·3; OMe, 9·8%).

(*b*) 2,4-Diphenylchroman-2-ol (1 g.) was refluxed with a 2% solution of hydrogen chloride in methanol (30 c.c.) for 2 hr. A white solid which separated on cooling was recrystallised from methanol to give 2-methoxy-2,4-diphenylchroman (0·81 g.), m. p. and mixed m. p. 106°.

2-*Ethoxy*-2,4-*diphenylchroman*.—(*a*) This *ether* was obtained by methods (*a*) and (*b*) above. Both gave prisms, m. p. 122° (Found: C, 83·7; H, 6·5. $C_{23}H_{22}O_2$ requires C, 83·7; H, 6·6%).

5,6-*Dihydro*-6-*methoxy*-4,6-*diphenyl*-4H-*naphtho*(2′,1′:2,3)*pyran*.—4,6-Diphenylnaphtho-(2′,1′:2,3)pyran (0·33 g.) and a 4% solution of hydrogen chloride in methanol (100 c.c.), when refluxed for $6\frac{1}{2}$ hr., gave this *ether* (isolated with ether, recrystallised from methanol), m. p. 174—175° (Found: C, 84·8; H, 6·3; OMe, 8·4. $C_{26}H_{22}O_2$ requires C, 85·2; H, 6·0; OMe, 8·5%).

2,4-*Diphenyl*-4H-*chromen*.—2-Methoxy- or 2-ethoxy-2,4-diphenylchroman (1 g.), when refluxed with acetic acid (10 c.c.) for 2 hr. and then cooled, gave 2,4-diphenyl-4*H*-chromen as needles, m. p. and mixed m. p. 109—110°.

6 *Methoxy*-4,6-*diphenyl*-2,3-*benzopyrylium Ferrichloride*.—A solution of hydrated ferric chloride (1·5 g.) in glacial acetic acid (3 c.c.) was added dropwise to one of 2-methoxy-2,4-diphenylchroman (0·5 g.) in acetic anhydride (3 c.c.). The mixture was refluxed for $\frac{1}{2}$ hr. On cooling, the ferrichloride (0·5 g.) separated and recrystallised from glacial acetic acid as yellow-brown plates, m. p. 167—168° alone or mixed with the ferrichloride obtained from 2,4-diphenyl-4*H*-chromen.

4,6-*Diphenyl*-6H-*naphtho*(2′,1′:2,3)*pyran*.—2,3-Dihydro-5,6-benzoflavone [4] (4 g.) in dry benzene (15 c.c.) was added slowly to a stirred Grignard solution from bromobenzene (2 c.c.), magnesium (0·6 g.), and ether (7 c.c.). The solution was refluxed for 1 hr. and set aside overnight. Decomposition with 22% aqueous ammonium chloride and isolation with ether gave a gum which crystallised from acetic acid. Recrystallisation from ethyl acetate or ethanol afforded the *naphthopyran* (1·2 g.), m. p. 171—172° (Found: C, 89·5; H, 5·5. $C_{25}H_{18}O$ requires C, 90·0; H, 5·4%).

5,6-*Dihydro*-4,6-*diphenyl*-4H-*naphtho*(2′,1′:2,3)*pyran* (VIIId).—(*a*) 4,6-Diphenyl-4*H*-naphtho-(2′,1′:2,3)pyran (0·19 g.), platinic oxide (0·07 g.), and acetic acid (50 c.c.) were shaken in hydrogen until absorption (1 mol.) was complete. Filtration, isolation with ether, and recrystallisation from ethyl acetate gave the *dihydro-derivative* as needles, m. p. 192—193° (Found: C, 88·6; H, 6·0. $C_{25}H_{20}O$ requires C, 89·3; H, 6·0%).

(*b*) The 6*H*-analogue similary afforded the same product, m. p. and mixed m. p. 192—193°.

Reaction between 6,6-*Diphenylnaphtho*(2′,1′:2,3)*pyran and* 1,1-*Diphenylethylene*.—An acetic acid solution (60 c.c.) of the naphthopyran (0·84 g.) and 1,1-diphenylethylene (1·31 g.) was saturated with dry hydrogen chloride, refluxed for $\frac{1}{3}$ hr., and set aside. After 2 hr. a solid (0·84 g.) separated. Recrystallised from ethanol this had m. p. 194° alone or mixed with the compound obtained from 2-hydroxy-1-naphthaldehyde and 1,1-diphenylethylene [7] (Found: C, 90·5; H, 5·8. $C_{39}H_{30}O$ requires C, 91·05; H, 5·8%). It is considered to be 7*a*,9,10,10*a*-*tetrahydro*-8,8,10,10-*tetraphenyl*-8H-*naphtho*[2,1-b]*cyclopenta*[d]*furan* (XIII).

Oxidation of 6,6-*Diphenylnaphtho*(2′,1′:2,3)*pyran*.—This naphthopyran (1 g.), powdered potassium permanganate (5 g.), and acetone (20 c.c.) were refluxed for 7 hr., then cooled, and the mixture was filtered. The residue was suspended in water (50 c.c.), acidified with dilute sulphuric acid, and treated with sulphur dioxide until the manganese dioxide had dissolved.

Isolation with ether gave the dicarboxylic acid (IXa) (0·6 g.), which was treated with ethereal diazomethane. After 2 hr. the ester was isolated with ether and treated with a suspension of lithium aluminium hydride (0·1 g.) in ether (10 c.c.). The mixture was refluxed for 1 hr. and after addition of dilute sulphuric acid the product was isolatd by ether as a gum (0·34 g.). The product and 30% sulphuric acid (20 c.c.) were refluxed for ½ hr. Isolation with ether gave a brown gum (0·3 g.) which was dissolved in ethanol and treated with an excess of Brady's reagent. The crude dinitrophenylhydrazone was purified by chromatography on alumina from benzene. Crystallisation from ethanol afforded diphenylacetaldehyde 2,4-dinitrophenylhydrazone as orange red needles (0·01 g., 5%), m. p. and mixed m. p. 146—148°.

5-(*α-Hydroxydiphenylmethyl)naphtho*(2′,1′:2,3)*furan* (XIIIb).—Methyl naphtho(2′,1′:2,3)-furan-5-carboxylate (6 g.) in dry ether (500 c.c.) was added slowly to a stirred Grignard solution from bromobenzene (9 c.c.), magnesium (4 g.), and ether (100 c.c.). The solution was refluxed for 1 hr. and set aside overnight. After decomposition with ammonium chloride solution the mixture was steam-distilled and the product extracted with ether from the non-volatile portion. Removal of the solvent and crystallisation from light petroleum (b. p. 40—60°) gave 5-(*α-hydroxydiphenylmethyl)naphtho*(2′,1′:2,3)*furan* (0·9 g.), m. p. 140° (Found: C, 85·0; H, 4·9. $C_{25}H_{18}O_2$ requires C, 85·7; H, 5·1%).

5-*Diphenylmethylnaphtho*(2′,1′:2,3)*furan*.—The foregoing alcohol (XIIIb) (0·5 g.) was refluxed in acetic acid (10 c.c.) with zinc dust (5 g.) for 5 hr. Neutralisation with sodium hydrogen carbonate solution, followed by isolation with ether and crystallisation from light petroleum (b. p. 60—80°), gave 5-*diphenylmethylnaphtho*(2′,1′:2,3)*furan* (0·16 g.), m. p. 177° (Found: C, 89·75; H, 5·5. $C_{25}H_{18}O$ requires C, 89·8; H, 5·4%).

2-*Naphthyl* ββ-*Diphenylacrylate*.—β-Naphthol (10 g.), ββ-diphenylacryloyl chloride [12] (14 g.), magnesium (1 g.), and benzene (30 c.c.) were refluxed for 2 hr., cooled, and filtered. A solid which separated on addition of ether to the filtrate was extracted (Soxhlet) with ether. Concentration of the ethereal solution and recrystallisation from ether or light petroleum (b. p. 100—120°) gave 2-*naphthyl* ββ-*diphenylacrylate* as needles (63%), m. p. 142° (Found: C, 85·3; H, 5·1. $C_{25}H_{18}O_2$ requires C, 85·7; H, 5·2%).

6,6-*Diphenylnaphtho*(2′,1′:2,3)*pyran*.—2-Naphthyl ββ-diphenylacrylate (1·84 g.) and anhydrous aluminium chloride (0·88 g.) were heated at 120—130° for 2 hr., then treated with dilute hydrochloric acid and ice. The product was isolated with ether as a gum and refluxed with ethanol (25 c.c.) and 3% hydrochloric acid (15 c.c.). Isolation with ether gave 5,6-*dihydro*-6,6-*diphenylnaphtho*(2′,1′:2,3)*pyran*-4-*one* (0·1 g.), m. p. 167—169° (Found: C, 85·2; H, 5·3. $C_{25}H_{18}O_2$ requires C, 85·7; H, 5·2%).

The ketone in ether (10 c.c.) was refluxed with a suspension of lithium aluminium hydride (0·13 g.) in ether (10 c.c.) for 1 hr. Addition of dilute sulphuric acid, isolation with ether, and recrystallisation from light petroleum gave 5,6-dihydro-6,6-diphenyl-4-*H*-naphtho(2′,1′:2,3)-4-ol, m. p. 138—140°, which was boiled with glacial acetic acid (4 c.c.) for ¼ hr. On cooling, 6,6-diphenylnaphtho(2′,1′:2,3)pyran (0·02 g.) separated as needles, m. p. and mixed m. p. 161°.

5,6-*Dihydro*-6,6-*diphenyl*-4H-*naphtho*(2′,1′:2,3)*pyran*.—6,6-Diphenylnaphtho(2′,1′:2,3)pyran (0·83 g.), platinic oxide (0·09 g.), and ethyl acetate (60 c.c.) were shaken in hydrogen until absorption (1 mol.) was complete. Filtration, evaporation, and recrystallisation from ethanol gave the *dihydro-derivative* as needles, m. p. 162° (Found: C, 89·4; H, 6·2. $C_{25}H_{20}O$ requires C, 89·3; H, 6·0%).

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