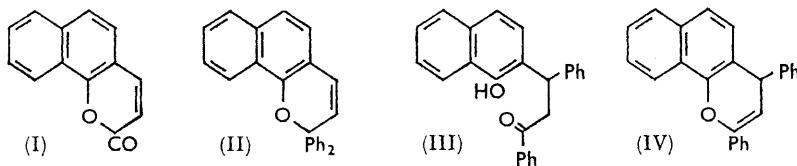


1000. 6,6-Diphenylnaphtho(1',2':2,3)pyran and 1,3-Diphenyl-3-(1-hydroxy-2-naphthyl)propan-1-one.

By J. COTTAM and R. LIVINGSTONE.

7,8-Benzocoumarin phenylmagnesium bromide gives a mixture containing 6,6-diphenylnaphtho(1',2':2,3)pyran and 1,3-diphenyl-3-(1-hydroxy-2-naphthyl)propan-1-one which was easily cyclised and dehydrated to 4,6-diphenylnaphtho(1',2':2,3)pyran.

DECOMPOSITION of the Grignard complex from 7,8-benzocoumarin¹ (I) and phenylmagnesium bromide gave a gum which consisted mainly of 6,6-diphenylnaphtho(1',2':2,3)pyran (II) and 1,3-diphenyl-3-(1-hydroxy-2-naphthyl)propan-1-one (III). The compound (III) was shown to be a ketone by the carbonyl absorption (1680 cm.⁻¹) in the infrared region. An analogous compound had been obtained previously from coumarin.² No such absorption band was given by any of the compounds obtained by the reaction between 5,6-benzocoumarin and phenylmagnesium bromide.³ A satisfactory isolation of compounds (II) and (III) was only afforded by chromatography: attempts to separate them by



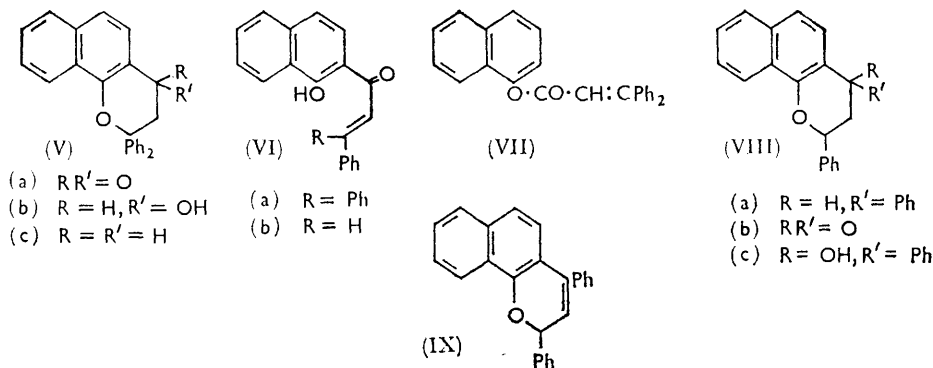
fractional crystallisation, either before or after removal of biphenyl by steam-distillation, were unsuccessful owing to the ease of ring closure and dehydration of the ketone to 4,6-diphenylnaphtho(1',2':2,3)pyran (IV).

¹ Koelsch and Masley, *J. Amer. Chem. Soc.*, 1953, **75**, 3596.

² Barnes, Occolowitz, and Strong, *Tetrahedron*, 1963, **19**, 839.

³ Livingstone, Miller, and Morris, *J.*, 1960, 5148.

The naphthopyran (II) was synthesised from 2-acetyl-1-naphthol,⁴ which condensed with benzophenone in anhydrous benzene in the presence of sodium butoxide⁵ to give, mainly, 5,6-dihydro-6,6-diphenylnaphtho(1',2':2,3)pyran-4-one (Va) together with some 3,3-diphenyl-1-(1-hydroxy-2-naphthyl)prop-2-en-1-one (VIa), which was converted into the ketone (Va) by boiling methanol and hydrobromic acid. Reduction of the ketone (Va) with lithium aluminium hydride in ether gave the alcohol (Vb), which was difficult to purify owing to the ease of dehydration to the naphthopyran (II), which was also obtained by



pyrolysis of the acetate. Hydrogenation of the naphthopyran (II) afforded the dihydro-compound (Vc). The ketone (Va) was not isolated after attempted Fries rearrangement of naphthyl β,β -diphenylacrylate (VII).^{6,7}

The structure of the ketone (III) was confirmed by ring closure and dehydration, followed by hydrogenation to give 5,6-dihydro-4,6-diphenylnaphtho(1,2':2,3)pyran (VIIIa), which was also obtained by the following method. 2-Acetyl-1-naphthol and benzaldehyde were condensed in the presence of sodium hydroxide to give the benzochalcone⁸ (VIb) which, on cyclisation in methanol saturated with dry hydrogen chloride,⁸ gave the ketone (VIIIb). Treatment of the ketone (VIIIb) with phenylmagnesium bromide gave the tertiary alcohol (VIIIc). Dehydration to 4,6-diphenylnaphtho(1',2':2,3)pyran (IX) followed by hydrogenation then yielded the dihydronaphthopyran (VIIIa).

EXPERIMENTAL

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

6,6-Diphenylnaphtho(1',2':2,3)pyran (II) and 1,3-Diphenyl-3-(1-hydroxy-2-naphthyl)propan-1-one (III).—7,8-Benzocoumarin (12.5 g.) was added in *ca.* 2 hr. from the thimble of a Soxhlet extraction apparatus to a stirred Grignard solution from bromobenzene (31 g.), magnesium (4.5 g.), and ether (450 c.c.). Decomposition with 22% ammonium chloride solution and isolation with ether gave a gum (22 g.) which was chromatographed on alumina from benzene. Removal of the solvent and crystallisation from light petroleum (b. p. 40–60°) gave 6,6-diphenylnaphtho(1',2':2,3)pyran (3.42 g., 16.5%), m. p. 126–128° (Found: C, 89.9; H, 5.9. $C_{25}H_{18}O$ requires C, 89.8; H, 5.4%). Elution of the alumina with chloroform, followed by removal of the solvent and crystallisation from ethyl acetate–methanol, gave 1,3-diphenyl-3-(1-hydroxy-2-naphthyl)propan-1-one (6.4 g., 29.6%), m. p. 155°, characterised as the *acetate*, m. p. 139–140° (from methanol) (Found: C, 82.8; H, 5.6. $C_{27}H_{22}O_3$ requires C, 82.2; H, 5.6%).

4,6-Diphenylnaphtho(1',2':2,3)pyran (IV).—(a) The ketone (III) (1 g.) was boiled with acetic acid (8 c.c.) for 1 hr. Pouring the mixture into water then afforded a solid which recrystallised

⁴ Witt, *Ber.*, 1888, **21**, 323.

⁵ Wawzonck, Nagler, and Carlson, *J. Amer. Chem. Soc.*, 1954, **76**, 1080.

⁶ Cavill, Dean, McGookin, Marshall, and Robertson, *J.*, 1954, 4573.

⁷ Kharasch, Kane, and Brown, *J. Amer. Chem. Soc.*, 1942, **64**, 333.

⁸ Kostanecki, *Ber.*, 1898, **31**, 706.

from ethyl acetate to give 4,6-diphenylnaphtho(1',2':2,3)pyran (0.31 g., 33%), m. p. 150—151° (Found: C, 90.1; H, 5.3. $C_{25}H_{18}O$ requires C, 89.8; H, 5.4%).

(b) The gum (3.9 g.) obtained from the reaction between 7,8-benzocoumarin (2.5 g.) and phenylmagnesium bromide, on recrystallisation from acetic acid gave 4,6-diphenylnaphtho(1',2':2,3)pyran (1.2 g., 28.6%), m. p. and mixed m. p. 149—151°.

5,6-Dihydro-6,6-diphenylnaphtho(1',2':2,3)pyran-4-one (Va) and 3,3-Diphenyl-1-(1-hydroxy-2-naphthyl)prop-2-en-1-one (VIa).—Benzophenone (32 g.) and 2-acetyl-1-naphthol (2.65 g.) in benzene (300 c.c.) was added to sodium t-butoxide [from sodium (3 g.) and t-butyl alcohol (25 c.c.)], refluxed with stirring for 20 hr., then poured into a stirred mixture of hydrobromic acid (75 c.c.) and acetic acid (50 c.c.). The benzene layer was steam-distilled to remove starting materials and left an orange gum 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(1',2':2,3)pyran-4-one (2.86 g., 57%), m. p. 180—181° (Found: C, 85.6; H, 5.3. $C_{25}H_{18}O_2$ requires C, 85.7; H, 5.2%) [2,4-dinitrophenylhydrazone, m. p. 301—302° (from nitrobenzene)].

Elution of the alumina with methanol afforded an orange solid which on recrystallisation from methanol gave 3,3-diphenyl-1-(1-hydroxy-2-naphthyl)-prop-2-en-1-one (1.5 g.) as orange plates, m. p. 134° (Found: C, 85.4; H, 5.5. $C_{25}H_{18}O_2$ requires C, 85.7; H, 5.2%). The ketone (VIa) (1.0 g.) was boiled with methanol (20 c.c.) and 46% hydrobromic acid (2 c.c.) for 0.5 hr. and the solution concentrated to give the ketone (Va) (0.76 g., 76%), m. p. and mixed m. p. 180—181°.

5,6-Dihydro-6,6-diphenylnaphtho(1',2':2,3)pyran-4-ol (Vb).—The ketone (Va) (1.3 g.) in benzene (50 c.c.) was added dropwise to lithium aluminium hydride (0.2 g.) in ether (100 c.c.) and boiled for 0.5 hr. Addition of dilute sulphuric acid, isolation with ether, and recrystallisation from light petroleum (b. p. 100—120°) or benzene-light petroleum (b. p. 60—80°) afforded 5,6-dihydro-6,6-diphenylnaphtho(1',2':2,3)pyran-4-ol (0.86 g., 66%), m. p. 94—101°, characterised as the acetate, m. p. 157° (from methanol) (Found: C, 82.1; H, 5.6. $C_{27}H_{22}O_3$ requires C, 82.2; H, 5.6%).

6,6-Diphenylnaphtho(1',2':2,3)pyran (II).—(a) The alcohol (Vb) (0.50 g.) was boiled with acetic acid (10 c.c.) for 0.5 hr. Pouring into water, isolation with ether, and recrystallisation from light petroleum (b. p. 40—60°) gave the naphthopyran (0.12 g., 25.3%), m. p. and mixed m. p. 126—128°.

(b) The acetate (0.12 g.) of the alcohol (Vb) was heated at 200° for 0.5 hr. Recrystallisation from light petroleum (b. p. 40—60°) gave the naphthopyran (0.03 g., 20.4%), m. p. and mixed m. p. 125—127°.

5,6-Dihydro-4,6-diphenylnaphtho(1',2':2,3)pyran-4-ol (VIIIc).—The ketone⁸ (VIIIb) (4 g.) in benzene (100 c.c.) was added during 0.5 hr. to a stirred Grignard solution from bromobenzene (2.23 g.), magnesium (0.35 g.), and ether (10 c.c.) and the solution was refluxed for 2 hr. After decomposition with 22% ammonium chloride solution the mixture was steam-distilled and the product filtered off from the non-volatile portion. Recrystallisation from cyclohexane afforded 5,6-dihydro-4,6-diphenylnaphtho(1',2':2,3)pyran-4-ol (2.4 g., 47%), m. p. 165—166° (Found: C, 85.2; H, 5.7. $C_{25}H_{20}O_2$ requires C, 84.7; H, 5.8%).

4,6-Diphenylnaphtho(1',2':2,3)pyran (IX).—The alcohol (VIIIc) (1.8 g.) was boiled with acetic acid (20 c.c.) for 2 hr., then poured into water. Isolation with ether gave a gum which was chromatographed on alumina from benzene. Removal of the solvent and recrystallisation from light petroleum (b. p. 100—120°) gave 4,6-diphenylnaphtho(1',2':2,3)pyran (0.41 g., 24%), m. p. 98° (Found: C, 90.0; H, 5.4. $C_{25}H_{18}O$ requires C, 89.8; H, 5.4%).

5,6-Dihydro-4,6-diphenylnaphtho(1',2':2,3)pyran (VIIIa).—(a) The naphthopyran (IV) (0.61 g.), platinum oxide (0.052 g.), and acetic acid (20 c.c.) were shaken in hydrogen until absorption (1 mol.) was complete. Filtration, followed by pouring into water, gave a solid. Recrystallisation from light petroleum (b. p. 40—60°) afforded 5,6-dihydro-4,6-diphenylnaphtho(1',2':2,3)pyran (0.12 g., 19.7%), m. p. 128—130° (Found: C, 88.5; H, 6.1. $C_{25}H_{20}O$ requires C, 89.3; H, 6.0%).

(b) The naphthopyran (IX) similarly afforded the same product, m. p. and mixed m. p. 127—129°.

5,6-Dihydro-6,6-diphenylnaphtho(1',2':2,3)pyran (Vc).—The naphthopyran (II) (0.4 g.), platinum oxide (0.04 g.), and ethyl acetate (70 c.c.) were shaken in hydrogen until absorption (1 mol.) was complete. Filtration, isolation with ether, and recrystallisation from light petroleum

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(b. p. 60—80°) afforded the *dihydro-derivative* (0.32 g., 80%), m. p. 117° (Found: C, 88.85; H, 6.0. $C_{25}H_{20}O$ requires C, 89.3; H, 6.0%).

1-Naphthyl $\beta\beta$ -Diphenylacrylate (VII).—1-Naphthol (20 g.), magnesium (2 g.), and benzene (60 c.c.) were added to $\beta\beta$ -diphenylacryloyl chloride [from 1,1-diphenylethylene (21.4 g.) and oxalyl chloride (50 c.c.)], and refluxed for 2 hr. Removal of the solvent, followed by distillation at 15—20 mm. and recrystallisation from light petroleum (b. p. 60—80°), gave 1-naphthyl $\beta\beta$ -diphenylacrylate (8.5 g., 21%), m. p. 95—96°, b. p. 155°/20 mm. (Found: C, 83.9; H, 5.4. $C_{24}H_{18}O_2$ requires C, 85.7; H, 5.2%).

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COLLEGE OF TECHNOLOGY, HUDDERSFIELD.

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