1226. 6,6-*Diphenyl*-6H-*naphtho*(2′,3′:2,3)*pyran and* 4,6-*Diphenyl*-4H-*naphtho*(2′,3′:2,3)*pyran*

By J. Cottam and R. Livingstone

Decomposition of the Grignard complex from 6,7-benzocoumarin [1] (I) and phenylmagnesium bromide gave a gum, which on trituration with ether yielded 3-(3-hydroxy-2-naphthyl)-1,3-diphenylpropan-1-one (II) as a solid, difficult to purify owing to the ease of cyclisation and dehydration to 4,6-diphenyl-4*H*-naphtho(2′,3′:2,3)pyran (III). Complete conversion into (III) occurred when compound (II) was boiled with acetic acid.[2] Compound (II) was shown to be a ketone by the carbonyl absorption (1655 cm.$^{-1}$) in the infrared region. 3-(3-Hydroxy-2-naphthyl)-1,1-diphenylprop-2-en-1-ol (IV) was isolated from the ether-soluble fraction, and when boiled with acetic acid, dehydrated, and cyclised gave 6,6-diphenyl-6*H*-naphtho-(2′,3′:2,3)pyran (V).[2]

The naphthopyran (V) was prepared from 2-acetyl-3-naphthol,[3] which condensed with

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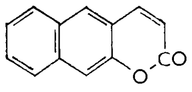
[1] T. Boehm and E. Profft, *Arch. Pharm.*, 1931, **269**, 25.

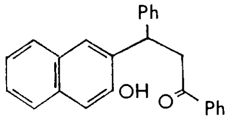
[2] J. Cottam and R. Livingstone, *J.*, 1954, 5228.

[3] Wilson Baker and G. N. Carruthers, *J.*, 1937, 479; I. M. Hunsberger, *J. Amer. Chem. Soc.*, 1950, **72**, 5633.

benzophenone in anhydrous benzene in the presence of sodium t-butoxide[4] to give 5,6-dihydro-6,6-diphenyl-4*H*-naphtho(2′,3′:2,3)pyran-4-one (VIa). Reduction of the ketone (VIa) with sodium borohydride in methanol gave the alcohol (VIb) which dehydrated on being heated with potassium hydrogen sulphate to give the naphthopyran (V).



(I)



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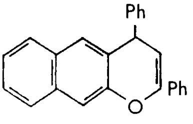

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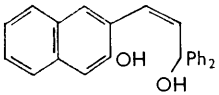

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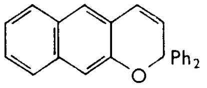

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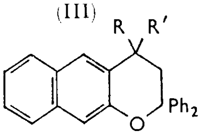
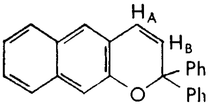


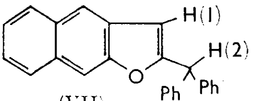
(VI)

(a : RR′ = O; b : R = H,R′ = OH)

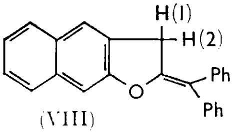
The nuclear magnetic spectrum of the naphthopyran (V) in deuterochloroform consisted of unresolved aromatic bands in the region τ 2·0—2·9, corresponding to sixteen protons, and two doublets, centred at τ 3·2 and 3·65, from an AB system with intensity equivalent to two protons. This spectrum is certainly compatible with structure (V); $J_{AB} = 10$ c./sec., which is of the correct order for *cis*-olefinic coupling. H_A is assigned to the doublet at τ 3·2 p.p.m. since this is decidedly broadened, presumably by an inter-ring coupling of <1 c./sec. Two other structures which could result from the dehydration of either the diol (IV) or the alcohol (VIb) by way of a mesomeric cation are (VII) and (VIII). Structure (VII) would be expected to give an AB system also but J_{AB} would be unlikely to be >2 c./sec. Both protons would also have opportunity for long-range coupling. H(1) and H(2) in (VIII) would be expected to be equivalent and give a single peak.



(V)

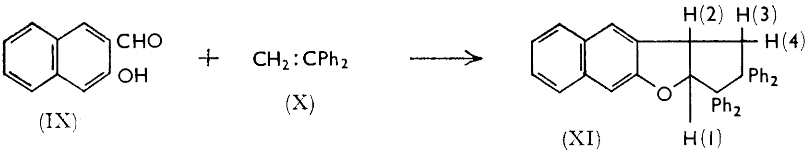


(VII)



(VIII)

3-Hydroxy-2-naphthaldehyde[1] (IX) reacted with an equimolecular proportion of 1,1-diphenylethylene (X) in acetic acid saturated with dry hydrogen chloride[5] to give two compounds. The compound with the lower m. p., which separated during 24 hr. contained chlorine and analysed for $C_{25}H_{19}ClO$. The higher-melting compound (XI) separated during 10 days and was the only product obtained when one mole of aldehyde reacted with two moles of 1,1-diphenylethylene.[5] Compound (XI) was also formed when 6,6-diphenyl-6*H*-naphtho(2′,3′:2,3)pyran reacted with 1,1-diphenylethylene in acetic acid saturated



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[4] S. Wawzonek, R. C. Nagler, and L. J. Carlson, *J. Amer. Chem. Soc.*, 1954, **76**, 1080.

[5] D. Abson, K. D. Bartle, J. Bryant, R. Livingstone, and R. B. Watson, *J.*, 1965, 2978.

with dry hydrogen chloride. Compound (XI) was shown to be 2,3,3a,10b-tetrahydro-2,2,3,3-tetraphenyl-1*H*-naphtho[2,3-b]cyclopenta[d]furan by comparing its nuclear magnetic spectrum with those of the derivatives derived from the reaction between *o*-hydroxyaldehydes and 1,1-diphenylethylenes.[5] The spectrum of compound (XI) in approximately 5% solution in deuterochloroform consisted of intense bands, mainly unresolved, in the region τ 2·1—3·15; a sharp doublet, intensity equivalent to one proton centred at τ 3·73, with separation 9·5 c./sec., assigned to H(1); an unresolved multiplet, intensity one proton, τ 5·85—6·55, assigned to H(2), a multiplet, intensity two protons, τ 6·90—7·85, assigned to H(3) and H(4).

Experimental.—Melting points were taken on a Kofler hot-stage apparatus. The proton magnetic resonance spectra were recorded at room temperature at 60 Mc./sec. in a Varian A-60 spectrometer. Chemical shifts were referred to internal tetramethylsilane.

3-(3-*Hydroxy*-2-*naphthyl*)-1,1-*diphenylprop*-2-*en*-1-*ol and* 4,6-*Diphenyl*-4H-*naphtho*(2′,3′:2,3)-*pyran*. 6,7-Benzocoumarin (3·0 g.) was added in *ca.* 0·5 hr., to a stirred Grignard solution from bromobenzene (7·5 g.), magnesium (1·4 g.), and ether (25 ml.), and boiled gently for 0·25 hr. The complex was decomposed with 22% ammonium chloride solution and the ether layer dried (Na_2SO_4). Removal of the solvent yielded a gum, which on trituration with ether (10 ml.) left a pale yellow solid. Recrystallisation from ethyl acetate gave 3-(3-hydroxy-2-naphthyl)-1,3-diphenylpropan-1-one (1·7 g., 31·5%), m. p. 207—208°. Boiling with acetic acid (25 ml.) for 0·5 hr., and pouring into water gave a solid which on recrystallisation from light petroleum (b. p. 100—120°) gave 4,6-*diphenyl*-4H-*naphtho*(2′,3′:2,3)*pyran* (1·29 g., 80%), m. p. 186—187° (Found: C, 88·9; H, 5·5. $C_{25}H_{18}O$ requires C, 89·8; H, 5·4%).

Removal of the ether and recrystallisation from light petroleum (b. p. 100—120°) gave 3-(3-*hydroxy*-2-*naphthyl*)-1,1-*diphenylprop*-2-*en*-1-*ol* (3·1 g., 57·4%), m. p. 130—131° (Found: C, 84·75; H, 6·0. $C_{25}H_{20}O_2$ requires C, 85·2; H, 5·7%).

5,6-*Dihydro*-6,6-*diphenylnaphtho*(2′,3′:2,3)*pyran*-4-*one*. Benzophenone (15 g.) and 2-acetyl-3-naphthol (1·5 g.) in benzene (70 ml.) was added to sodium t-butoxide [from sodium (1·3 g.) and t-butyl alcohol (10 ml.)], refluxed with stirring for 20 hr., then poured into a stirred mixture of hydrobromic acid (60 ml.) and acetic acid (40 ml.). The benzene layer was steam-distilled to remove starting materials and left a gum, which was boiled with methanol saturated with dry hydrogen chloride for 0·5 hr. to cyclise any chalcone that may have been formed.[4] Following the removal of the solvent the product 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*(2′,3′:2,3)*pyran*-4-*one* (0·78 g., 27·5%), m. p. 136° (Found: C, 85·25; H, 5·1. $C_{25}H_{18}O_2$ requires C, 85·7; H, 5·2%).

6,6-*Diphenylnaphtho*(2′,3′:2,3)*pyran*. (*a*) 3-(3-Hydroxy-2-naphthyl)-1,1-diphenylprop-2-en-1-ol (0·50 g.) was boiled with acetic acid (10 ml.) for 0·5 hr. The product obtained after the removal of the solvent was chromatographed on alumina from benzene solution. Removal of the solvent yielded a white solid, which was recrystallised from light petroleum (b. p. 80—100°) to give 6,6-*diphenylnaphtho*(2′,3′:2,3)*pyran* (0·40 g., 84%), m. p. 165° (Found: C, 89·5; H, 5·5. $C_{25}H_{18}O$ requires C, 89·8; H, 5·4%).

(*b*) 5,6-Dihydro-6,6-diphenylnaphtho(2′,3′:2,3)-pyran-4-one (0·072 g.) was added to a solution of sodium borohydride (0·1 g.) in methanol and set aside for 10 hr. Addition of water yielded a gummy solid, which on recrystallisation from light petroleum (b. p. 60—80°) gave 5,6-*dihydro*-6,6-*diphenylnaphtho*(2′,3′:2,3)*pyran*-4-*ol* (0·051 g., 71%), m. p. 156—157° (Found: C, 84·5; H, 5·5. $C_{25}H_{20}O_2$ requires C, 85·2; H, 5·7%), which was heated to 220° with finely powdered freshly fused potassium hydrogen sulphate (0·034 g.). The residue was chromatographed on alumina from benzene solution to give a white solid on removal of the solvent. Recrystallisation from light petroleum (b. p. 80—100°) gave 6,6-diphenylnaphtho(2′,3′:2,3)pyran (0·037 g., 77%, overall 53·6%), m. p. and mixed m. p. 165°.

Reaction between 3-*Hydroxy*-2-*naphthaldehyde and* 1,1-*Diphenylethylene*. (*a*) A solution of 3-hydroxy-2-naphthaldehyde (0·30 g., 0·0017 mole) and 1,1-diphenylethylene (0·31 g., 0·0017 mole) in acetic acid (8 ml.) was saturated with dry hydrogen chloride and set aside. Filtration after 24 hr. yielded a solid, which on recrystallisation from light petroleum (b. p. 100—120°) gave a white solid (0·21 g.), m. p. 137° (Found: C, 80·5; H, 5·2; Cl, 9·8. $C_{25}H_{19}ClO$ requires C, 81·0; H, 5·3; Cl, 9·6%). Filtration after a further 10 days and recrystallisation of the solid from ethyl acetate gave 2,3,3a,10b-*tetrahydro*-2,2,3,3-*tetraphenyl*-1H-*naphtho*[2,3-b]*cyclopenta*[d]-*furan* (0·1 g.), m. p. 207° (Found: C, 90·6; H, 5·9. $C_{38}H_{30}O$ requires C, 91·0; H, 5·9%).

(*b*) A solution of 3-hydroxy-2-naphthaldehyde (0·30 g., 0·0017 mole) and 1,1-diphenylethylene (0·615 g., 0·0034 mole) in acetic acid (8 ml.) was saturated with dry hydrogen chloride and set aside for 10 days. Removal of the solid by filtration followed by recrystallisation from ethyl acetate gave the naphthocyclopentafuran (0·74 g., 83·5%), m. p. and mixed m. p. 205—207°.

(*c*) A solution of 6,6-diphenylnaphtho(2′,3′:2,3)-pyran (0·15 g.) and 1,1-diphenylethylene (0·106 g.) in acetic acid (25 ml.) was saturated with hydrogen chloride and set aside for 10 days. Removal of the solid by filtration followed by recrystallisation from ethyl acetate gave the naphthocyclopentafuran (0·19 g., 82·5%), m. p. and mixed m. p. 206—207°.

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