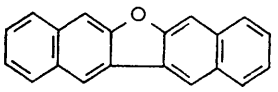
165. *The Synthesis of Dinaphtho(2′,3′-2,3)(2″,3″-4,5)furan.*

By J. N. Chatterjea, R. F. Curtis, and S. P. Dhoubhadel.

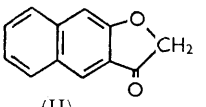
Dinaphtho(2′,3′-2,3)(2″,3″-4,5)furan (I) has been synthesised unambiguously and compared with a sample prepared during attempts to obtain 2,3-6,7-dibenzodiphenylene. The furan (I) is also shown to be a by-product of the aerial oxidation of 2-naphthol in the presence of calcium ions.

The isolation of a by-product assumed to be dinaphtho(2′,3′-2,3)(2″,3″-4,5)furan (I) in the preparation of 2,3-6,7-dibenzodiphenylene was described by Curtis and Viswanath.[1] The furan (I) has now been synthesised from 5,6-benzocoumaran-3-one (II) by the general procedure developed by Chatterjea [2] for β-brazans.

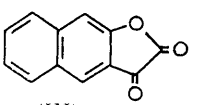
5,6-Benzocoumaran-3-one (II) [3] on treatment with nitrous acid in acetic acid gave 2-hydroxyimino-5,6-benzocoumaran-3-one; this was hydrolysed to 3-hydroxy-2-naphthylglyoxylic acid which was then cyclised with acetic anhydride (cf. Chatterjea [4]) to 5,6-benzocoumaran-2,3-dione (III). Condensation of the dione with phenacyl bromide in methanolic sodium methoxide produced methyl 2-benzoyl-5,6-benzocoumarone-3-carboxylate (IV). The acid (V) was converted into the acid chloride which was cyclised to dinaphtho(2′,3′-2,3)(2″,3″-4,5)furan-1,4-dione (VI). Reduction with hydriodic acid gave the furan (I).



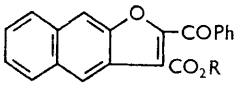
(I)



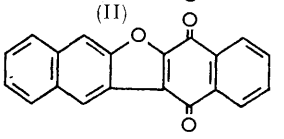
(II)



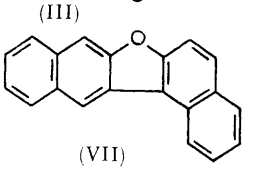
(III)



(IV) R = Me
(V) R = H



(VI)



(VII)

When this sample was compared with that originally prepared by Curtis and Viswanath [1] there were obvious differences, whereas the 2,4,7-trinitrofluorenone complexes prepared from the two samples were identical. Examination of the mass spectrum of the furan (I) prepared by the present method showed a highest significant molecular ion of mass number 268, corresponding to the molecular ion of $C_{20}H_{12}O$. Significant breakdown ions occurred at masses 239 (probably parent minus CHO) and 237 (probably parent minus CH_3O) together with small, doubly charged ions corresponding to the same masses and an isotope peak at mass 269. These results are consistent with a strong ring structure such as the furan (I).

Mass spectra of the original sample obtained at 15 and 20 ev confirmed the presence of parent molecular ions of masses 252, 268, and 284. The molecular ion at 252 is 2,3:6,7-dibenzodiphenylene [1] inseparable by crystallisation and that at 268 is the furan (I). The molecular ion at mass number 284, $C_{20}H_{12}O_2$, gives only one significant breakdown ion of mass number 256 (probably due to loss of CO). This suggests by analogy with the furan (I) a strong ring structure, but it has not yet been possible to isolate this compound. The aerial oxidation of 2-naphthol at 340° in the presence of calcium ions leads to the dinaphthofuran (VII) as the major product.[5-8] A minor product is a compound, $C_{20}H_{12}O$, m. p. 300°,

[1] Curtis and Viswanath, *J.*, 1959, 1670, 3650.
[2] Chatterjea, *J. Indian. Chem. Soc.*, 1954, **31**, 101.
[3] Haberland and Kleinert, *Ber.*, 1938, **71**, 470.
[4] Chatterjea, *J. Indian. Chem. Soc.*, 1954, **31**, 194.
[5] Niederhausen, *Ber.*, 1882, **15**, 1123.
[6] Clemo and Spence, *J.*, 1928, 2811.
[7] Clemo, Cockburn, and Spence, *J.*, 1931, 1265.
[8] Buu-Hoï, *J.*, 1952, 489.

which was investigated by Niederhausen [5] and Clemo.[6,7] Direct comparison with the dinaphthofuran (I) shows that these compounds are identical. The by-product is produced by oxidative coupling into the 3- rather than the 1-position of the second 2-naphthol molecule.

Revised spectral data are presented for the furan (I).

Experimental

5,6-*Benzocoumaran*-3-*one* (II).—This ketone was prepared by the acid-catalysed decomposition of 2-diazoacetyl-3-methoxynaphthalene.[3] The oxime, prepared in pyridine, crystallised from ethanol as plates, m. p. 212—214° (decomp.) with previous darkening (Found: N, 7·1. $C_{12}H_9O_2N$ requires N, 7·0%).

5,6-*Benzocoumaran*-2,3-*dione* (III).—The ketone (II) (6·5 g.) was treated at room temperature in acetic acid (100 c.c.) with sodium nitrite (12 g.) in small quantities during 4 hr. The mixture was diluted with water (100 c.c.) and the solid collected after 8 hr. 2-*Hydroxyimino*-5,6-*benzocoumaran*-3-*one* (6·2 g.) crystallised from acetic acid as golden-yellow plates, m. p. 240° (decomp.) (Found: N, 6·5. $C_{12}H_7O_3N$ requires N, 6·6%).

The finely powdered oxime (6 g.) was triturated with concentrated hydrochloric acid (50 c.c.), the mixture filtered, and the solid dissolved in hot water (500 c.c.). The hot solution was filtered, concentrated, and then treated with concentrated hydrochloric acid (30 c.c.). 2-Hydroxy-3-naphthylglyoxylic acid was collected and boiled with acetic anhydride (15 c.c.) for a few minutes to give 5,6-*benzocoumaran*-2,3-*dione* (III) (4·1 g.), orange red needles, m. p. 228° (from acetic acid) (Found: C, 72·9; H, 3·2. $C_{12}H_6O_3$ requires C, 72·7; H, 3·0%). With *o*-phenylenediamine in acetic acid, the *quinoxaline* derivative was obtained as golden-yellow needles, m. p. 330° (decomp.) (Found: C, 75·1; H, 4·4; N, 9·9. $C_{18}H_{12}O_2N_2$ requires C, 75·0; H, 4·2; N, 9·7%).

2-*Benzoyl*-5,6-*benzocoumarone*-3-*carboxylic acid* (V).—To a solution of the foregoing benzocoumarandione (3·5 g.) in methanolic sodium methoxide (0·45 g. of sodium in 30 c.c. of methanol), phenacyl bromide (3·5 g.) was added and the mixture was heated under reflux for 3 hr. On cooling, the solution deposited *methyl* 2-*benzoyl*-5,6-*benzocoumarone*-3-*carboxylate* (IV) (2·2 g.), prismatic needles, m. p. 118—119° (from methanol) (Found: C, 76·6; H, 4·4. $C_{21}H_{14}O_4$ requires C, 76·35; H, 4·3%). The corresponding *acid* crystallised from acetic acid as yellow prisms, m. p. 245° (Found: C, 75·8; H, 3·8. $C_{20}H_{12}O_4$ requires C, 75·9; H, 3·8%).

Dinaphtho(2,′3′-2,3)(2″,3″-4,5)*furan*-1′,4′-*dione* (VI).—A suspension of the preceding acid (1·2 g.) in benzene (10 c.c.) was heated with purified thionyl chloride (1·2 c.c.) for 20 min. After removal of benzene and thionyl chloride under reduced pressure, a solution of the acid chloride in carbon disulphide (40 c.c.) was cooled and treated with anhydrous aluminium chloride (4 g.). The mixture was kept for 6 hr. at room temperature, most of the solvent removed by decantation, and the aluminium complex decomposed with ice. The orange-red mass was collected, dried, and dissolved in benzene, and the solution chromatographed on alumina. The yellow band was eluted with benzene and concentrated, *dinaphtho*(2′,3′-2,3)-(2″,3″-4,5)*furan*-1′,4′-*dione* (VI) being obtained as an orange-red mass (0·2 g.) which was purified by sublimation in a vacuum. The pure quinone was formed as fine orange-red needles, m. p. 298—299° (Found: C, 80·2; H, 3·6. $C_{20}H_{10}O_3$ requires C, 80·5; H, 3·4%). Reductive acetylation gave 1′,4′-*diacetoxydinaphtho*(2′,3′-2,3)(2″,3″-4,5)*furan*, needles, m. p. 272° (from acetic acid) (Found: C, 74·6; H, 4·0. $C_{24}H_{16}O_5$ requires C, 75·0; H, 4·2%).

Dinaphtho(2′,3′-2,3)(2″,3″-4,5)*furan* (I).—The quinone (0·05 g.) was boiled with freshly distilled hydriodic acid (15 c.c.) for 96 hr. The solid obtained on dilution was washed with hot sodium hydroxide solution, dried, and chromatographed in benzene on alumina. *Dinaphtho*-(2′,3′-2,3)(2″,3″-4,5)*furan* (I) crystallised from benzene as plates (0·025 g.), m. p. 308—310° (corr.); subliming at the m. p.) (Found: C, 89·6; H, 4·6; Mass number, 268. $C_{20}H_{12}O$ requires C, 89·5; H, 4·5%; *M*, 268).

The melting point of a mixture with a sample, m. p. 266°, prepared by Curtis and Viswanath [1] was m. p. 280—285°. A mass spectrum of the sample, m. p. 266°, showed mass number 268 together with compounds of mass number 252 and 284.

The furan shows in ethanol, $\lambda_{max.}$ (log ε) at 218 (4·41), 246 (4·67, shoulder), 254 (5·09), 272 (4·76), 279 (4·69), 290 (4·32), 300 (4·02), 318 (4·38), 335 (4·78), 359 (3·69), 379 (3·63) mμ; in

potassium bromide at 6·14(w), 6·67(w), 6·87(w), 7·45(w), 8·28(w), 8·66(w), 8·87(m), 10·52(m), 11·46(v.s.), 13·32(m), 13·50(v.s.) μ.

The 2,4,7-trinitrofluorenone complex crystallised from benzene in brownish red needles, m. p. 244—246° undepressed on admixture with the specimen obtained by Curtis and Viswanath.[1] Decomposition of the latter complex by sublimation (high vacuum at 160°) gave pure dinaphthofuran (I) the infrared spectrum of which was identical with a sample prepared by the synthetic method now described.

Dinaphtho(2′,3′-2,3)(2″,3″-4,5)*furan* (I) *from* 2-*Naphthol*.—2-Naphthol (100 g.) and calcium oxide (1 g.) were heated at 270° increasing to 320° during 8 hr. as described by Clemo *et al.*[6,7] The product was cooled and poured into excess of 20% sodium hydroxide, the mixture filtered, and the solid acidified and steam-distilled. The solid residue was collected and dried (29·5 g.), and from the alkaline filtrate 2-naphthol (60·5 g.) was recovered.

The crude product (1 g.) in benzene was passed through alumina (under ultraviolet illumination). The early fractions gave dinaphtho(2′,3′-2,3)(1″,2″-4,5)furan (VII) (460 mg.), pale yellow plates, m. p. 157° (from benzene) (Clemo and Spence [6] give m. p. 157°). Later fractions gave the furan (I), (31 mg.) as thin almost colourless plates (from benzene), m. p. (corr.) 310°; mixed m. p. with the synthetic specimen showed no depression and the infrared curves were identical.

Semimicroanalyses were by Mr. H. Mukherjee. Infrared spectra were determined by Mr. D. Jones, Swansea. Mass spectra were kindly determined by Imperial Chemical Industries Limited, Dyestuffs Division. One of us (S. P. D.) thanks the authorities of the Colombo Plan for a research scholarship.

Chemical Laboratory, Science College, Patna 5, India (J. N. C.; S. P. D.).
University College of Swansea, Singleton Park,
Swansea (R. F. C.).

[*Received, May 5th,* 1960.]