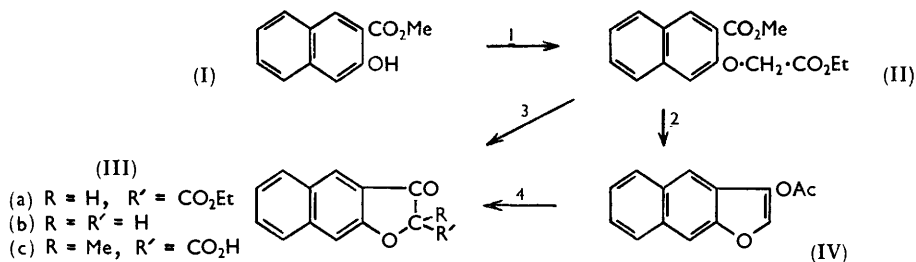


931. *Naphtho(2' : 3'-2 : 3)furan-4-one.*

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Naphtho(2' : 3'-2 : 3)furan-4-one has been prepared by two methods from 2-hydroxy-3-naphthoic acid and a study made of its properties.

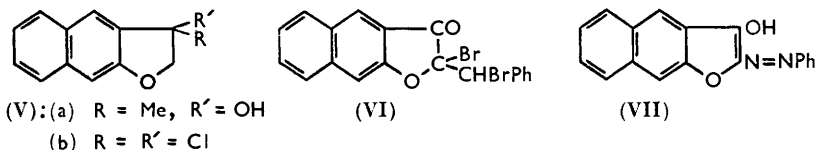
2 : 3-NAPHTHOFURANONES cannot be obtained by cyclisation of 2-naphthyl derivatives unsubstituted in the 1- and the 3-position;^{1,2} they can, however, be prepared from suitable 2 : 3-disubstituted compounds. Methyl 3-hydroxy-2-naphthoate (I) was condensed with



Reagents: 1, Br·CH₂·CO₂Et-K₂CO₃. 2, NaOH; Ac₂O-NaOAc. 3, Na-C₆H₆; NaOH. 4, 2N-NaOH.

ethyl bromoacetate to give, after ring closure and hydrolysis, the furanone (IIIb) in a high overall yield. The conditions required for the hydrolysis of the ester (IIIa) were found to be critical. If the time of reaction was increased from $\frac{1}{2}$ hr. to 3 hr., the product obtained was a high-melting orange solid, which was separated into a yellow solid insoluble in benzene, and a dark red solid soluble in benzene, neither of which could be obtained pure. The ester (IIIa) formed a sodio-derivative which condensed with methyl iodide. Hydrolysis of the product proceeded without decarboxylation and gave the acid (IIIc): ethyl 2-methyl-3-oxocoumaran-2-carboxylate was decarboxylated on hydrolysis, to afford 2-methylcoumaranone.³

Hydrolysis of the diester (II), followed by cyclisation with hot acetic anhydride and anhydrous sodium acetate, gave the acetate (IV). Hydrolysis with the calculated amount of 2N-sodium hydroxide solution afforded the furanone. The overall yield however was less than in the first method, mainly owing to the low yield of the acetate (IV).



Naphtho(2' : 3'-2 : 3)furan-4-one (IIIb) with methylmagnesium iodide gave the alcohol (Va) which was readily dehydrated by formic acid to 4-methylnaphtho(2' : 3'-2 : 3)furan. Treatment of the furanone (IIIb) with phosphorus pentachloride gave the dichloro-derivative (Vb) which readily lost hydrogen chloride to form 4-chloronaphtho(2' : 3'-2 : 3)-furan. The existence of the methylene group was confirmed by the preparation of the benzylidene derivative, which was converted into the dibromide⁴ (VI).

Treatment of the furanone with boiling potassium hydroxide solution for several hours afforded the same yellow and red products as were obtained from ethyl 4-oxonaphtho(2' : 3'-2 : 3)furan-5-carboxylate (IIIa).

¹ Ingham, Stephen, and Timpe, *J.*, 1931, 895.

² Stoermer and Bartsch, *Ber.*, 1900, **33**, 3176.

³ Friedlander, *Ber.*, 1899, **32**, 1867.

⁴ Auwers and Muller, *Ber.*, 1908, **41**, 4233.

Some evidence was found for the existence of the enolic modification of the furanone (IIIb), for boiling the compound with acetic anhydride gave 4-acetoxynaphtho(2' : 3'-2 : 3)-furan (IV). Also a red dye, probably 4-hydroxy-5-phenyldiazonaphtho(2' : 3'-2 : 3)furan (VII) was formed on treatment of the furanone (IIIb) with benzenediazonium chloride, a reaction typical of enolic and phenolic compounds.

The furanone (IIIb) was stable, no appreciable decomposition was observed on storage, and its reactions usually took place without the formation of resin.

EXPERIMENTAL

Ethyl 3-Methoxycarbonyl-2-naphthylloxyacetate (II).—Ethyl bromoacetate (12 c.c.) and anhydrous potassium carbonate (40 g.) were added to a solution of methyl 2-hydroxy-3-naphthoate (20 g.) in dry acetone (200 c.c.). The mixture was refluxed for 6 hr., then filtered, and evaporated. The residue was dissolved in ether (200 c.c.), washed with dilute sodium hydroxide solution, and dried. Evaporation afforded the *diester* (23 g.) which from light petroleum (b. p. 60—80°) gave needles, m. p. 60—61° (Found: C, 66.6; H, 5.8. $C_{16}H_{16}O_5$ requires C, 66.7; H, 5.6%).

Ethyl 4-Oxonaphtho(2' : 3'-2 : 3)furan-5-carboxylate.—The foregoing ester (15 g.), benzene (70 c.c.), sodium dust (2 g.), and ethanol (0.2 c.c.) were refluxed for 3 hr., poured on ice and hydrochloric acid, and extracted with ether. The residue yielded to ether *ethyl 4-oxonaphtho(2' : 3'-2 : 3)furan-5-carboxylate* (12 g.), which from ethanol gave yellowish needles, m. p. 123° (Found: C, 70.2; H, 4.5. $C_{15}H_{12}O_4$ requires C, 70.3; H, 4.7%).

3-Carboxy-2-naphthylloxyacetic Acid.—The ester (II) (33 g.) was refluxed with 5% sodium hydroxide solution (600 c.c.) for 1 hr., poured over ice and dilute hydrochloric acid, and filtered. The product was treated with sodium hydrogen carbonate solution, filtered, and acidified. The precipitate was separated and crystallised from acetic acid, to afford the *diacid* (25 g.) as needles, m. p. 223—224° (Found: C, 62.9; H, 4.2. $C_{13}H_{10}O_5$ requires C, 63.4; H, 4.1%).

4-Acetoxynaphtho(2' : 3'-2 : 3)furan.—3-Carboxy-2-naphthylloxyacetic acid (4 g.) was refluxed with acetic anhydride (100 c.c.) and anhydrous sodium acetate (8 g.) for 3 hr. and set aside overnight. The mixture was poured into water and set aside until the oil solidified. The product was filtered off and dissolved in ether. The ethereal solution was washed with sodium hydrogen carbonate solution and with water, dried, and evaporated to afford a solid (0.4 g.). Crystallisation from methanol (carbon) gave *4-acetoxynaphtho(2' : 3'-2 : 3)furan* as needles, m. p. 78° (Found: C, 74.3; H, 4.4. $C_{14}H_{10}O_3$ requires C, 74.2; H, 4.4%).

Naphtho(2' : 3'-2 : 3)furan-4-one.—(i) (a) Ethyl 4-oxonaphtho(2' : 3'-2 : 3)furan-5-carboxylate (1 g.) and 17% hydrochloric acid (20 c.c.) were refluxed for 2 hr. The mixture was steam-distilled and the solid in the distillate crystallised from ethanol, to afford naphtho(2' : 3'-2 : 3)-furan-4-one (0.1 g.) as yellow plates, m. p. 148°.

(b) 30% Sodium hydroxide solution (150 c.c.) was added to a solution of ethyl 4-oxonaphtho(2' : 3'-2 : 3)furan-5-carboxylate (10 g.) in ethanol (50 c.c.), refluxed for $\frac{1}{2}$ hr., and poured over ice and dilute hydrochloric acid. Isolation with ether and crystallisation from ethanol or glacial acetic acid afforded *naphtho(2' : 3'-2 : 3)furan-4-one* (7 g.) as yellow plates, m. p. 148° (Found: C, 77.8; H, 4.4. $C_{12}H_8O_2$ requires C, 78.2; H, 4.3%).

(ii) 4-Acetoxynaphtho(2' : 3'-2 : 3)furan (0.2 g.) in ethanol (10 c.c.) at 0° was added to 10% sodium hydroxide solution (0.5 c.c.) at 0° and immediately acidified with 3*N*-hydrochloric acid (1 c.c.). The mixture was poured over ice and water, and the product crystallised from ethanol to give naphtho(2' : 3'-2 : 3)furan-4-one (0.07 g.) as yellow plates, m. p. and mixed m. p. 148°.

The furanone gave no colour with neutral ferric chloride solution and did not decolorise bromine water. With Fehling's solution, blue-violet flakes separated. A deep blue-violet colour was obtained on dissolving the furanone in concentrated sulphuric acid; it became dark brown on warming. Potassium permanganate solution was decolorised slowly in the cold, instantly on warming.

The 2 : 4-dinitrophenylhydrazone formed red needles (from nitrobenzene), m. p. 262°.

4-Acetoxynaphtho(2' : 3'-2 : 3)furan.—Naphtho(2' : 3'-2 : 3)furan-4-one (0.2 g.) was refluxed with acetic anhydride (5 c.c.) for 2 hr. The solution was poured into water and set aside overnight. The light brown solid was separated and crystallised from methanol, to give 4-acetoxynaphtho(2' : 3'-2 : 3)furan (0.2 g.), m. p. and mixed m. p. 78°.

4-Hydroxy-5-phenyldiazonaphtho(2' : 3'-2 : 3)furan.—Aniline hydrochloride in dilute hydrochloric acid was added to a solution of sodium nitrite. The cold mixture was added to a suspension of naphtho(2' : 3'-2 : 3)furan-4-one in dilute sodium hydroxide solution, and a bright red solid was immediately formed.

Action of Alkali on Ethyl 4-Oxonaphtho(2' : 3'-2 : 3)furan-5-carboxylate.—25% Potassium hydroxide solution (20 c.c.) was added to a solution of ethyl 4-oxonaphtho(2' : 3'-2 : 3)furan-5-carboxylate (1 g.) in ethanol (20 c.c.). The solution, with air passing through it, was refluxed for 4 hr., then filtered and poured over ice and dilute hydrochloric acid, to give a reddish-brown solid (0.7 g.). Extraction with benzene gave a yellow solid (0.1 g.), m. p. 220—230°, insoluble in benzene, and a red solid (0.1 g.), m. p. >250°, soluble in benzene.

5-Methyl-4-oxonaphtho(2' : 3'-2 : 3)furan-5-carboxylic Acid.—Ethyl 4-oxonaphtho(2' : 3'-2 : 3)furan-5-carboxylate (1 g.), dissolved in absolute alcohol (5 c.c.), was added to a solution from sodium (0.1 g.) in absolute alcohol (2 c.c.). Methyl iodide (0.4 c.c.) was added and the mixture refluxed for 3 hr. The ethanol was then evaporated, water added, and the product isolated with ether. On evaporation, ethyl 5-methyl-4-oxonaphtho(2' : 3'-2 : 3)furan-5-carboxylate was obtained as a light brown gum (0.4 g.); this was dissolved in ethanol (7 c.c.), and refluxed with 20% sodium hydroxide solution (7 c.c.) for 1 hr. The mixture was poured over ice and dilute hydrochloric acid, and filtered. The product was treated with sodium hydrogen carbonate solution, and the whole filtered, and the filtrate was acidified. The precipitate recrystallised from dilute ethanol (carbon), to afford 5-methyl-4-oxonaphtho(2' : 3'-2 : 3)furan-5-carboxylic acid as white spangles (0.07 g.), m. p. 206—207° (Found: C, 68.8; H, 4.3. $C_{14}H_{10}O_4$ requires C, 69.3; H, 4.1%).

4 : 5-Dihydro-4-hydroxy-4-methylnaphtho(2' : 3'-2 : 3)furan.—A solution of naphtho(2' : 3'-2 : 3)furan-4-one (1.8 g.) in dry ether (200 c.c.) was slowly added to a stirred solution of methylmagnesium iodide (2.6 g.) in dry ether (10 c.c.). The mixture was refluxed for 1 hr. and poured over ice and ammonium chloride solution. The product was isolated with ether as a yellow solid (1.9 g.). Crystallisation from light petroleum (b. p. 80—100°) gave 4 : 5-dihydro-4-hydroxy-4-methylnaphtho(2' : 3'-2 : 3)furan as pale yellow needles, m. p. 113—114° (Found: C, 78.2; H, 5.9. $C_{13}H_{12}O_2$ requires C, 78.0; H, 6.0%).

4-Methylnaphtho(2' : 3'-2 : 3)furan.—The preceding compound (0.16 g.) was refluxed for $\frac{1}{2}$ hr. with formic acid (5 c.c.; *d* 1.2). Removal of the acid afforded a white solid (0.14 g.); addition of a saturated solution of picric acid and crystallisation from methanol gave red needles, m. p. 121—122° (Found: C, 55.7; H, 3.4; N, 10.4. $C_{19}H_{13}O_6N_3$ requires C, 55.6; H, 3.1; N, 10.2%). This *picrate* in ether was decomposed by chromatography, giving 4-methylnaphtho(2' : 3'-2 : 3)furan as needles, m. p. 63° (Found: C, 85.2; H, 6.0. $C_{13}H_{10}O$ requires C, 85.6; H, 5.5%).

4-Chloronaphtho(2' : 3'-2 : 3)furan.—Naphtho(2' : 3'-2 : 3)furan-4-one (0.3 g.) was mixed with phosphorus pentachloride (3 g.) and set aside overnight in a vacuum-desiccator. The mixture was extracted with ether, and the ethereal solution treated with solid sodium carbonate. The whole was filtered and the filtrate evaporated. Isolation with ethanol (carbon) and crystallisation from methanol gave 4-chloronaphtho(2' : 3'-2 : 3)furan (0.07 g.) as pale yellow plates, m. p. 81—82° (Found: C, 70.5; H, 3.7. $C_{12}H_7OCl$ requires C, 70.9; H, 3.4%).

5-Benzylidenenaphtho(2' : 3'-2 : 3)furan-4-one.—10% Sodium hydroxide solution (0.6 c.c.) was added to a hot solution of naphtho(2' : 3'-2 : 3)furan-4-one (0.5 g.) and benzaldehyde (0.4 g.) in ethanol (10 c.c.). After 1 min. a solid separated and was isolated. Crystallisation from ethanol afforded the 5-benzylidene derivative (0.7 g.) as yellow needles, m. p. 189—190° (Found: C, 83.7; H, 4.6. $C_{19}H_{12}O_2$ requires C, 83.8; H, 4.4%).

5-Bromo-5- α -bromobenzylidene-naphtho(2' : 3'-2 : 3)furan-4-one (VI).—A solution of 5-benzylidene-naphtho(2' : 3'-2 : 3)furan-4-one (0.3 g.) in chloroform (10 c.c.) was treated with bromine (0.07 c.c.) in chloroform (1 c.c.) and set aside for 24 hr. The chloroform was removed and the product crystallised from ethanol, to give the dibromo-derivative (0.4 g.) as yellow needles, m. p. 166—167° (Found: C, 52.5; H, 2.8. $C_{19}H_{12}O_2Br_2$ requires C, 52.7; H, 2.8%).