$n^{25}D$ 1.4202, hence contained 22.4 g. (0.193 mole, 66%) of diisopropylcarbinol and 0.6 g. (0.005 mole, 2%) of diisopropyl ketone. The *n*-propyldiisopropylcarbinol (29%) was identified by b.p. and refractive index $n^{25}D$ 1.4400.

DEPARTMENT OF CHEMISTRY
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
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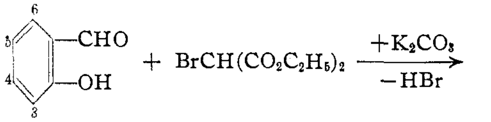
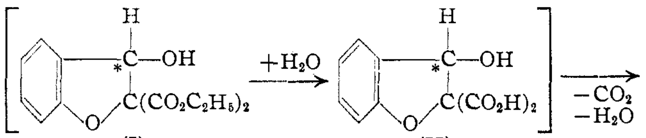
Coumarones from *o*-Hydroxyaldehydes and Bromomalonic Ester

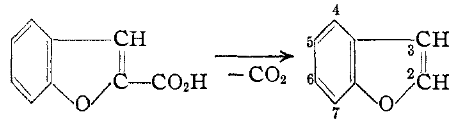
BY SANAE TANAKA

This paper describes the results obtained in substituting ethyl bromomalonate for ethyl bromoacetate in the coumarone synthesis from *o*-hydroxyaldehydes.[1,4] The reaction is given in the scheme





(I) (II)



(III) (IV)

Salicylaldehyde and ethyl bromomalonate refluxed in methyl ethyl ketone[2] in the presence of potassium carbonate condense to give DL-3-hydroxycoumaran-2,2-dicarboxylic acid ester (I). This product was converted without isolation to DL-3-hydroxycoumarandicarboxylic acid (II), which in turn was converted to coumarilic acid (III) on decarboxylation and dehydration. The salicylaldehyde has been replaced with its 4-methoxy, 5-methoxy and 4,5-dimethoxy derivatives. The yields of crude coumarilic acid and its derivatives range from 72–90%. The coumarilic acids have been decarboxylated in quinoline with copper powder[3] and gave coumarone (IV) and the corresponding derivatives, isolated in some cases as their picrates, in 80–93% yields. With *o*-hydroxyacetophenone a 38% yield of 3-methylcoumarilic acid was obtained. It has been shown previously[4] that isolation of the intermediate products I and II decreases over-all yields.

Experimental

Coumarilic Acid (III).—Salicylaldehyde (2.5 g.), ethyl bromomalonate[5] (5 g.), anhydrous potassium carbonate (2.5 g.) and methyl ethyl ketone (10 ml.) were mixed together and the whole was refluxed for 5 hours on a steam-bath. After distilling off the main part of the solvent, the residue was mixed with water and acidified with dilute sulfuric acid and then extracted with ether. The ethereal extract, after removal of the solvent, was dissolved in alcoholic potash (alcohol 20 ml., potassium hydroxide 2 g.) and then refluxed on a steam-bath for 1 hour. After concentrating to a small volume the residue was dissolved in water and acidified with dilute sulfuric acid. The colorless crystals thus formed were collected, washed with water and dried. Recrystallization from benzene gave colorless long plates; yield 2.5 g. (76%); m.p. 192–193°.[6]

Anal. Calcd. for $C_9H_6O_3$: C, 66.66; H, 3.70. Found: C, 66.45; H, 3.67.

Coumarone (IV).—Coumarilic acid (0.5 g.) and copper powder (0.1 g.) were refluxed in quinoline (10 ml.) for 30 minutes. After cooling ether was added, the mixture filtered from copper, then washed several times with 2 *N* hydrochloric acid, then with water to remove quinoline. This ethereal extract, when freed from the solvent, gave coumarone as an oil which possesses a guaiacol-like odor. It was warmed with picric acid. The coumarone picrate thus obtained was recrystallized from dilute alcohol; yield 0.75 g. (80%) yellow columns; m.p. 102–103°.[7] No melting point depression was observed when mixed with an authentic specimen.

6-Methoxycoumarilic Acid.—4-Methoxysalicylaldehyde[4b] substituted for salicylaldehyde gives 6-methoxycoumarilic acid in 90% yield, m.p. 206°,[8] recrystallized from ethyl acetate.

Anal. Calcd. for $C_{10}H_8O_4$: C, 62.48; H, 4.19. Found: C, 62.31; H, 3.98.

6-Methoxycoumarone.—6-Methoxycoumarilic acid was decarboxylated by the technique described above. The product was isolated in its picrate, m.p. 64°.[9]

Anal. Calcd. for $C_9H_8O_2 \cdot C_6H_3O_7N_3$: N, 11.14. Found: N, 10.93.

5-Methoxycoumarilic Acid.—5-Methoxysalicylaldehyde[10] likewise gives 5-methoxycoumarilic acid in 72% yield, m.p. 212–213°, recrystallized from acetone.

Anal. Calcd. for $C_{10}H_8O_4$: C, 62.48; H, 4.19. Found: C, 62.61; H, 4.29.

5-Methoxycoumarone.—5-Methoxycoumarilic acid upon decarboxylation gave 5-methoxycoumarone in 93% yield, m.p. 32–33°, b.p. 120–125° (30 mm.).

Anal. Calcd. for $C_9H_8O_2$: C, 72.97; H, 5.45. Found: C, 73.25; H, 5.49.

5,6-Dimethoxycoumarilic Acid.—4,5-Dimethoxysalicylaldehyde[11] similarly gave 5,6-dimethoxycoumarilic acid, in 80% yield, m.p. 245° (dec.), recrystallized from alcohol.

Anal. Calcd. for $C_{11}H_{10}O_5$: C, 59.46; H, 4.50. Found: C, 59.48; H, 4.65.

5,6-Dimethoxycoumarone.—5,6-Dimethoxycoumarilic acid through decarboxylation gave 5,6-dimethoxycoumarone in 90% yield, m.p. 53–54°.

Anal. Calcd. for $C_{10}H_{10}O_3$: C, 67.41; H, 5.62. Found: C, 67.31; H, 5.66.

3-Methylcoumarilic Acid.—*o*-Hydroxyacetophenone, when condensed with ethyl bromomalonate, afforded 3-methylcoumarilic acid in 38% yield, the melting point of which (188.5–189.5° from diluted alcohol) coincides with those given by Hantzsch[12] or Peter.[13]

Anal. Calcd. for $C_{10}H_8O_3$: C, 68.18; H, 4.54. Found: C, 68.36; H, 4.68.

Further attempts to attain 3-methylcoumarone were abandoned owing to the scarcity of the material.

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CHEMICAL LABORATORY
TOKYO-BUNRIKA UNIVERSITY
BUNKYO-KU, TOKYO, JAPAN RECEIVED SEPTEMBER 18, 1950

(1) Kostanecki, *Ber.*, **42**, 901 (1909); **43**, 2155 (1910).

(2) Acetone can be used instead but somewhat poorer yields of coumarilic acid result.

(3) Shepard, THIS JOURNAL, **52**, 2083 (1930).

(4) (a) Kawai, Nakamura and Sugiyama, *Ber.*, **72**, 1146 (1939); (b) Kawai, Nakamura and Yoshida, *ibid.*, **73**, 581 (1940).

(5) "Organic Syntheses," Vol. VII, p. 34 (1927).

(6) Perkin [*J. Chem. Soc.*, **24**, 45 (1871)] gave m. p. 192–193°.

(7) Kraemer [*Ber.*, **23**, 3276 (1890)] described m.p. 102–103°.

(8) Robertson [*J. Chem. Soc.*, 787 (1940)] described m.p. 206°.

(9) Anderson [THIS JOURNAL, **60**, 1419 (1938)] described m.p. 64–65°.

(10) Rubenstein, *J. Chem. Soc.*, **127**, 1999 (1925).

(11) Robertson, *ibid.*, 2434 (1930).

(12) Hantzsch, *Ber.*, **19**, 1292 (1886); m.p. 188–189°.

(13) Peter, *ibid.*, **41**, 832 (1908); m.p. 188°.