in good yields, its effect on acids, esters,[6] anhydrides and nitriles is negligible; they have also reduced the carbonyl function in the presence of side-chain halogens and aromatic nitro groups.

Experimental[7]

Reduction of 2-Methyl-6,7-dimethoxy-3,4-dihydroisoquinolinium Iodide to 2-Methyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline.—To a solution of 10 g. (0.03 mole) of the methiodide in 200 ml. of absolute methanol was added 4 g. (0.105 mole) of solid sodium borohydride in small portions. The reaction was exothermic, hydrogen was evolved, and a clear, colorless solution was obtained at the end of the addition. It was evaporated to 25 ml., poured into 300 ml. of 2% sodium hydroxide, extracted with ether, and the combined ethereal extracts dried over anhydrous magnesium sulfate. The solution was then filtered and the ether removed by distillation to leave 5.5 g. (89% of the theoretical amount) of a light-yellow oil which quickly hardened to a white solid. This crude product melted at 55–57° and, on dissolving in a hot solution of picric acid in absolute ethanol and allowing to cool, formed a picrate (needles) of m.p. 157–158°.[8] Further recrystallization did not raise this melting point.

Reduction of 1-(3-Bromo-4-methoxybenzyl)-2-methyl-6-methoxy-7-benzyloxy-3,4-dihydroisoquinolinium Iodide (I) to 1-(3-Bromo-4-methoxybenzyl)-2-methyl-6-methoxy-7-benzyloxy-1,2,3,4-tetrahydroisoquinoline (II).—To a slurry of 0.5 g. (0.0133 mole) of sodium borohydride in 85 ml. of absolute methanol was added, as quickly as foaming would allow, 0.5 g. (0.00082 mole) of the methiodide. The clear, colorless solution was then concentrated to 15 ml. and poured into 300 ml. of 1% sodium hydroxide. It was extracted three times with ether, the ether was dried over anhydrous magnesium sulfate and filtered, and hydrogen chloride gas was passed into the filtrate. A light-yellow oil separated. The ether was removed on the steam-cone and 30 ml. of benzene was added to the residual oil. On evaporation white crystals separated slowly. The last of the benzene was removed in a stream of dry air to give 0.35 g. (82% of the theoretical amount) of the hydrochloride. An analytical sample prepared by recrystallization from 2-propanol consisted of white needles which melted first at 104–105°, resolidified at 127–130°, and remelted at 202–204°. The sample was dried *in vacuo* at 64°.

Anal. Calcd. for $C_{26}H_{29}O_3NBrCl$: C, 60.17; H, 5.63; N, 2.70. Found: C, 60.01; H, 5.74; N, 2.83.

The first procedure outlined above, which involves the solution of the methiodide in the solvent and subsequent addition of borohydride, is preferable, since it allows the use of a much smaller molar ratio of the reducing agent. In the second procedure a large excess of sodium borohydride must be used in order to get all of the methiodide in before the heat of reaction causes complete destruction of the hydride by the solvent.

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(6) M. L. Wolfrom and K. Anno, THIS JOURNAL, **74**, 5583 (1952), have reported that the esters and sodium salts of acids of sugars are reduced to alcohols.

(7) All melting points were obtained on a calibrated apparatus. Analysis by Galbraith Laboratories, Knoxville, Tenn.

(8) F. L. Pyman, *J. Chem. Soc.*, **95**, 1274 (1909), reports a melting point of 159–160° (cor.).

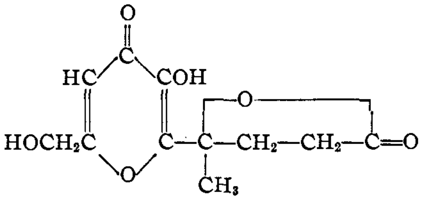
The Reaction of Kojic Acid with Ethyl Levulinate

BY L. L. WOODS[1]

RECEIVED DECEMBER 6, 1952

During the course of investigating the reactivity of kojic acid, many attempts have been made by the author to condense the pyrone with ketones, all unsuccessful except the one described in this report.

The compound produced as a result of the condensation of kojic acid with ethyl levulinate in mildly alkaline media is shown to be 3-(2-hydroxymethyl-5-hydroxy-4-pyrone-6)-3-valerolactone (I).



I

The derivatives of this compound were nearly all as expected; however, the reaction with 2,4-dinitrophenylhydrazine was unusual. Repeated experiments reveal that the compound reacts with two molecules of the hydrazine to form an addition compound of the pyridazinone.

Experimental[2]

Four grams of sodium bicarbonate, 28.4 g. of kojic acid, 28.8 g. of ethyl levulinate and 100 ml. of absolute ethanol were mixed together and refluxed vigorously for about 20 hours. The mixture was then acidified with hydrochloric acid, treated with a small amount of charcoal, and filtered while hot. The solution slowly deposited soft brown crystals as the alcohol was removed by surface evaporation, yield 39 g. Two recrystallizations from hot benzene, in which the compound is only fairly soluble, gave light tan crystals, m.p. 153.5°.

Anal. Calcd. for $C_{11}H_{12}O_6$: C, 55.00; H, 4.58. Found: C, 54.78; H, 4.16.

The acetylated derivative was made in the usual manner using acetic anhydride; the excess anhydride was decomposed with water and the ester extracted with benzene. The ester was recrystallized twice from benzene and once from a 1–4 mixture of benzene and ligroin. The compound produced rosettes of white prisms, m.p. 98–100°.

Anal. Calcd. for $C_{17}H_{20}O_{10}$: C, 53.12; H, 5.20. Found: C, 53.35; H, 5.18.

Treating compound (I) with an excess of thionyl chloride followed by recrystallization from hot water and then from absolute ethanol gave the expected 2-chloromethyl derivative of (I) which easily sublimed to give white needles, m.p. 167–169°. The compound gave a red color with dilute ferric chloride solutions.

Anal. Calcd. for $C_{11}H_{11}ClO_5$: C, 51.06; H, 4.25. Found: C, 51.30; H, 4.09.

The *p*-bromophenacyl derivative was prepared from (I) and *p*-bromophenacyl bromide in essentially the manner as before,[3] but in this instance 1.5 g. of the phenacyl halide was used for each gram of (I).

However, the bisphenacyl derivative was formed. The compound was of a very light texture resembling white wool after having been recrystallized three times from ethanol, m.p. 180°. It had no acidic character and gave negative results with dilute solutions of ferric chloride.

Anal. Calcd. for $C_{27}H_{24}Br_2O_9$: C, 49.69; H, 3.68. Found: C, 49.87, 49.83; H, 3.32, 3.26.

When equal weights of (I) and 2,4-dinitrophenylhydrazine were refluxed for 15 minutes in ethanol, an orange compound was obtained upon cooling and filtering. The substance was purified by washing with water followed by two recrystallizations from ethanol, an orange-yellow powder was obtained, m.p. 100–102°.

Anal. Calcd. for $C_{17}H_{16}N_4O_9 \cdot C_6H_6N_4O_4$: N, 18.12. Found: N, 18.05.

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(1) The author wishes to acknowledge, with thanks, the financial support of the Research Corporation in this project. The kojic acid used in these experiments was furnished by the Corn Products Company.

(2) Analyses were performed by Dr. Carl Tiedcke, Teaneck, N. J., and Clark Microchemical Laboratory, Urbana, Ill. All melting points were determined on a Fisher–Johns melting point assembly.

(3) L. L. Woods, THIS JOURNAL, **74**, 3959 (1952).