

Anal. Calcd. for $C_{18}H_{14}O_4Cl$: C, 58.98; H, 3.40. Found: C, 59.50; H, 3.70.

Acetylation.—The preparation of 2-acetoxymethyl-5-acetoxy-6-benzoyl-4-pyrone was accomplished by allowing 6-benzoylkojic acid to react with acetyl chloride in benzene. The benzene mixture was treated with water and the compound recrystallized from ethanol. White prisms were obtained which sublimed above 150° and melted at 182° .

Anal. Calcd. for $C_{18}H_{14}O_7$: C, 62.57; H, 4.09. Found: C, 62.66; H, 4.16.

Meerwein-Ponndorf-Verley Reduction.—Five grams of 6-benzoylkojic acid was refluxed with 7 g. of aluminum isopropoxide in absolute isopropyl alcohol for 8 hours, and all but 35 ml. of the isopropyl alcohol and acetone was distilled off. The residual material was acidified and 50 ml. of water added. Extraction with benzene gave 3.8 g. of a white solid which when boiled with 100 ml. of distilled water gave 1.3 g. of (2-hydroxymethyl-5-hydroxy-4-pyrone-6)-hydroxyphenylmethane as long white needles; m.p. $114-115^\circ$. This compound gave a very deep red coloration with iron salts.

Anal. Calcd. for $C_{13}H_{12}O_5$: C, 62.90; H, 4.83. Found: C, 63.16; H, 4.59.

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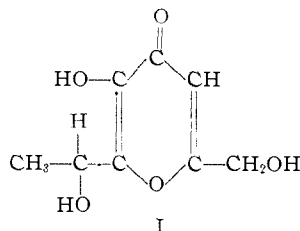
The Hydroxyethylation of Kojic Acid¹

By L. L. WOODS

The reactions described are an attempt to determine the general applicability of the method of hydroxy alkylation of kojic acid reported previously² in which paraformaldehyde condensed with kojic acid in the presence of potassium bicarbonate.

It has been found that acetaldehyde participates in the hydroxy alkylation of the pyrone if certain slight modifications are made in the method mentioned. No reaction was obtained with chloral, but benzaldehyde reacted with the kojic acid under the same conditions which effected condensation in the case of acetaldehyde. However, all efforts to isolate a pure substance from the resulting tacky mixture were unsuccessful. When the reflux time was increased to four hours it was found that two molecules of kojic acid had combined with each molecule of benzaldehyde to produce, in good yield, bis-(2-hydroxymethyl-5-hydroxy-4-pyrone-6)-phenylmethane whose melting point is in agreement with the product obtained by Barham and Reed³ using a different procedure.

The probable structure of the compound formed by hydroxy ethylation is given in (I) and the reason for assigning such a structure to the substance has been fully discussed elsewhere.²



(1) The author wishes to acknowledge the financial assistance given for this study by the Research Corporation with a grant-in-aid, and the Corn Products Company for the kojic acid used in these experiments.

(2) L. L. Woods, *THIS JOURNAL*, **72**, 4322 (1950).

(3) H. N. Barham and G. N. Reed, *ibid.*, **60**, 1541 (1938).

Unfortunately the compounds so far produced by hydroxy alkylation have melting points very close to that for kojic acid. This similarity extends to the chloro derivatives obtained with thionyl chloride.

Experimental⁴

1-(2-Hydroxymethyl-5-hydroxy-4-pyrone-6)-1-hydroxyethane.—A mixture of 14.2 g. of kojic acid, 100 ml. of absolute ethanol and 1 g. of potassium bicarbonate was heated to gentle reflux and then 10 ml. of acetaldehyde was added in 2-3 ml. portions. Refluxing was continued for one-half hour after the addition of the last of the acetaldehyde.

The mixture was then cooled somewhat, a small amount of Norite added, and filtered.

The filtrate was placed in the freezer overnight. Upon filtering the cooled material 9.9 g. of yellow crystals was obtained. The analytical sample was recrystallized twice from ethanol; the substance softened at 149° , melted at 155° and gave a red coloration with ferric chloride.

Anal. Calcd. for $C_8H_{10}O_5$: C, 51.61; H, 5.37. Found: C, 51.42; H, 5.08.

The reaction of the above compound with thionyl chloride in ligroin produced a dark colored mass which when recrystallized from alcohol and then sublimed produced white needles, m.p. 166.5° .

Anal. Calcd. for $C_8H_8O_3Cl_2$: C, 43.04; H, 3.57. Found: C, 43.45; H, 3.80.

The acetyl derivative was prepared by allowing the compound to react 24 hours with acetyl chloride at room temperature in a small flask protected from moisture with a calcium chloride tube. The reaction mixture was treated with a large amount of water and then extracted with benzene. After the removal of the benzene the compound was dried in a vacuum desiccator over sulfuric acid; rosettes of white crystals were formed which sublimed above 108° , m.p. 136.5° .

Anal. Calcd. for $C_{13}H_{16}O_8$: C, 53.84; H, 5.12. Found: C, 53.49; H, 4.98.

Bis-(2-hydroxymethyl-5-hydroxy-4-pyrone-6)-phenylmethane.—A reaction mixture consisting of 14.2 g. of kojic acid, 10.8 g. of benzaldehyde, 1 g. of potassium bicarbonate and 50 ml. of absolute ethanol was refluxed for 4 hours. A viscous material was obtained from which 10.8 g. of solid was obtained by suction filtration after the mass had remained in the refrigerator for two days.

Recrystallization of the compound several times from ethanol produced flesh colored aggregates which decomposed above 245° .

Anal. Calcd. for $C_{10}H_{16}O_8$: C, 61.29; H, 4.30. Found: C, 61.25; H, 4.54.

(4) All analyses were by Dr. Carl Tiedcke. All melting points were determined on a Fisher-Johns melting point assembly.

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NEW COMPOUNDS

2,5-Disubstituted Oxazoles and Thiazoles

Certain 2-aza-1,4-diketones have been prepared and cyclized to give 2,5-disubstituted oxazoles or thiazoles.

4-Acetylbiphenyl and 2-acetylnaphthalene were brominated and the derived α -bromoketones were converted to the hexamethylenetetraminium salts¹ whose acid hydrolysis gave the corresponding α -aminoketones.² These were treated with benzoyl chloride, 2-furoyl chloride or myristoyl chloride to give the 2-aza-1,4-diketones. Oxazoles were

(1) C. T. Bahner, M. D. Pickens, D. Pickens and W. K. Easley, *THIS JOURNAL*, **72**, 2266 (1950).

(2) C. Mannich and F. L. Hahn, *Ber.*, **44**, 1542 (1911).