dilute neutral solution however suggest that hydrolysis of monomethylolurea is negligible and under such conditions it is unlikely that the nucleophilic nitrogen of urea would attack any but an electrophilic center of monomethylolurea, if such a center existed. This latter point awaits clarification by further studies of the reactions of methylolureas.

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The Condensation of Kojic Acid with Crotonic Acid and with β-Bromopropionic Acid[1]

BY L. L. WOODS

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Kojic acid reacts with crotonic acid in the presence of sodium bicarbonate to give a new acid, probably the 2-methyl-2-(2-hydroxymethyl-5-hydroxy-4-pyrone-6)-propionic acid, but possibly 1-(2-hydroxymethyl-5-hydroxy-4-pyrone-6)-butyric acid. The evidence for condensation at the 6-position of kojic acid lies in the fact that the 2- and 5-positions in the product are available for acetylation.

The reaction of kojic acid with β-bromopropionic acid gives 2-(2-hydroxymethyl-5-hydroxy-4-pyrone-6)-propionic acid, a product previously obtained by the cyanoethylation of kojic acid.[2]

Experimental[3]

Reaction of Crotonic Acid with Kojic Acid.—One hundred ml. of absolute ethanol, 8.6 g. of crotonic acid and 8.4 g. of sodium bicarbonate were thoroughly agitated and warmed, after which 14.2 g. of kojic acid was added. The mixture was then refluxed for 20 hours, acidified with concentrated hydrochloric acid and filtered while warm. Evaporation of the filtrate to about 50 ml., followed by chilling the solution, gave 14.4 g. of a solid. This solid was recrystallized twice from absolute ethanol and once from benzene (in which it is only slightly soluble), giving white prisms which melt at 154.5° and give a red coloration with ferric chloride solution.

Anal. Calcd. for $C_{10}H_{12}O_6$: C, 52.61; H, 5.26. Found: C, 52.40; H, 5.04.

The above product and acetic anhydride gave an ester which was crystallized from ethanol and benzene. The ester separates as pale-yellow rosettes melting at 133–135°.

Anal. Calcd. for $C_{14}H_{16}O_8$: C, 53.87; H, 5.12. Found: C, 53.44; H, 4.89.

The high melting point of the ester suggests that the product of the condensation of crotonic acid with kojic acid may be 1-(2-hydroxymethyl-5-hydroxy-4-pyrone-6)-butyric acid, rather than 2-methyl-2-(2-hydroxymethyl-5-hydroxy-4-pyrone-6)-propionic acid.

The *p*-bromophenacyl bromide derivative, prepared as was the corresponding derivative of 2-(2-hydroxymethyl-5-hydroxy-4-pyrone-6)-propionic acid[2] and recrystallized from absolute ethanol and benzene, separated as white crystals melting at 182.5°.

Anal. Calcd. for $C_{18}H_{17}O_7Br$: C, 50.82; H, 4.00. Found: C, 50.49; H, 3.88.

Reaction of β-Bromopropionic Acid with Kojic Acid.—A mixture of 14.2 g. of kojic acid, 15.3 g. of β-bromopropionic acid and 8.4 g. of sodium bicarbonate in 100 ml. of absolute ethanol was refluxed for five hours, acidified with 4 ml. of concentrated hydrochloric acid, and filtered while hot. Evaporation of the filtrate to dryness on the steam-bath gave 25 g. of a waxy product. Twelve grams of pale yellow crystals, melting at 146–147°, were obtained from the waxy solid by solution in 50 ml. of boiling absolute ethanol, addition of 70 ml. of hot ethyl acetate, treatment with Norite, filtration and cooling of the filtrate. Three more crystallizations from absolute ethanol gave white crystals melting at 152°. The product gives a deep red coloration with ferric chloride solution.

Anal. Calcd. for $C_9H_{10}O_6$: C, 50.46; H, 4.67. Found: C, 50.78; H, 4.82.

The product gives the same *p*-bromophenacyl bromide and acetic anhydride derivative as were obtained from 2-(2-hydroxymethyl-5-hydroxy-4-pyrone-6)-propionic acid,[2] thus proving the identity of the compound.

Treatment of the product with thionyl chloride in ligroin gave a dark solid which was crystallized from hot water, giving yellow-orange needles. Sublimation produced white needles, melting at 164.5° and giving a red coloration with ferric chloride solution.

Anal. Calcd. for $C_9H_9O_5Cl$: C, 46.45; H, 3.87. Found: C, 46.09; H, 3.64.

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[1] The author wishes to express his thanks to the Research Corporation for a grant-in-aid on this research. The kojic acid used in these experiments was furnished through the courtesy of the Corn Products Company.

[2] L. L. Woods, THIS JOURNAL, **74**, 3959 (1952).

[3] All analyses were performed by Dr. Carl Tiedcke. Melting points were determined on a Fisher-Johns melting point assembly.

Some Ketonic Derivatives of Triaminoguanidine

BY F. L. SCOTT, M. CASHMAN AND J. REILLY

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We have recently[1] reported the reactions between triaminoguanidine nitrate and some aldehydes. This present communication extends these observations to ketonic derivatives. The most reactive ketones prove to be the 2-acetylthiophene and 3-acetylthionaphthene. Alloxan, benzylideneacetone, benzoin, cyclohexanone, acetophenone and isatin reacted fairly readily. Reactions between the triaminoguanidine salt and benzophenone, *m*-aminoacetophenone, *m*-cyanoacetophenone, chalcone and dibenzalacetone were slow. The cyclohexanone derivative was isolated as its picrate.

Methyl isopropyl ketone, methyl nonyl ketone, methyl ethyl ketone, methyl heptyl ketone, benzylidenebenzyl phenyl ketone, methyl benzyl ketone all failed to react—triaminoguanidine being recovered unchanged in yields of from 95–100%. Both acetone and β-ionone did react, but the nitrates and picrates of the derivatives were sticky solids and have proved difficult to purify. Hydroquinone was the main reaction product of the vigorous interaction of triaminoguanidine and *p*-benzoquinone. With β-naphthoquinone reaction again was brisk, this time, however, with the formation of black tars.

Experimental[2,3]

The hydrazones were formed by refluxing triaminoguanidine (1 mole) with the ketone (3 moles) in aqueous ethanolic solutions. A few drops of nitric acid were used as catalyst.

1,1-Bis-(3,5-dimethyl-1-pyrazolyl)-4-methyl-2,3-diazahepta-1,3-diene-6-one.—To 1.6 g. of triaminoguanidine nitrate dissolved in 100 ml. of water was added 3 ml. of acetylacetone. The mixture was well agitated, adopted a slight yellow tint, and on standing globules of a greenish-yellow oil separated. These then slowly crystallized, were filtered off and recrystallized from ethanol; yield 64–70%. These

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[1] F. L. Scott, M. Cashman and J. Reilly, THIS JOURNAL, **74**, 5802 (1952).

[2] All m.ps. have been taken with short stem Anschütz thermometers.

[3] All analyses are by Drs. Weiler and Strauss, Oxford.