and nine-tenths grams of 2-amino-4-methyl-5-bromothiazole was suspended in 100 cc. of water. Two grams of thiourea was added and the mixture shaken until all solids had dissolved. The solution was made very alkaline by adding solid sodium hydroxide. In a few seconds, the characteristic glistening crystals of bis-(2-amino-4-methyl-5-thiazolyl) sulfide were thrown out. The yield was 0.3 g. With some bis-(2-amino-4-methyl-5-thiazolyl) sulfide previously prepared there was no melting point depression.

FRICK CHEMICAL LABORATORY
PRINCETON UNIVERSITY
PRINCETON, N. J.
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The Hydroxymethylation of Kojic Acid

BY L. L. WOODS

The reaction of formaldehyde with kojic acid introduces one hydroxymethyl group in either the 3 or the 6 position of the pyrone ring. An earlier report[1] indicates that both of these positions are reactive so that a definite structure cannot be assigned to the derivative herein described. However, the compound is probably 2,6-bis-(hydroxymethyl)-5-hydroxy-4-pyrone since base catalyzed reactions[2] presumably require a mechanism which depends upon the nucleophilic character of the phenolic ion, thus causing the primary substitution to take place at a position ortho to the phenolic hydroxyl, in this instance position 6.

Treatment of the above product with thionyl chloride, followed by recrystallization from boiling water, gives a substance containing only one chlorine atom. The 2-chloromethyl group is assumed to remain intact since Yabuta[3] has shown that 2-chloromethyl-5-hydroxy-4-pyrone resists hydrolysis by hot water.

Attempts to introduce two hydroxymethyl groups into kojic acid under forcing conditions always gave mixtures whose composition approached that of 2,3,6-tri-(hydroxymethyl)-5-hydroxy-4-pyrone, but the analysis of the benzoate indicated that it was contaminated with condensation products with similar physical properties.

Experimental[4]

Two grams of paraformaldehyde was added to a boiling mixture of 10 g. of kojic acid in 100 ml. of absolute ethanol, the solution was cooled slightly and 1 g. of potassium bicarbonate or anhydrous sodium carbonate was added with stirring. After standing for two hours, the solid was filtered and dried in a vacuum desiccator over sulfuric acid. Recrystallization of the crude product (9.8 g.) from absolute ethanol gave very pale yellow needles which melted at 155–156°, following an apparent change in structure above 132°, and which gave a red-purple coloration with ferric chloride solution.

Anal. Calcd. for $C_7H_8O_5$: C, 48.83; H, 4.65. Found: C, 49.20, 49.02; H, 4.37, 4.42.

Two grams of the above compound was refluxed with 7 ml. of thionyl chloride. The product, weighing 0.5 g. after recrystallization from 25 ml. of boiling water, separated either as needles or stout prisms which changed to needles between 120 and 140° and melted at 165°.

Anal. Calcd. for $C_7H_7O_4Cl$: C, 44.38; H, 3.16. Found: C, 44.71, 44.60, 44.68; H, 3.24, 3.08, 3.18.

Benzoylation of 2 g. of the compound by the usual Schotten–Baumann method produced a white solid which was recrystallized three times from absolute ethanol; yield 2.2 g., m. p. 134.5–135.5°.

Anal. Calcd. for $C_{28}H_{20}O_8$: C, 69.42; H, 4.13. Found: C, 69.04; H, 4.08.

In an attempt to introduce two hydroxymethyl groups into the pyrone nucleus, a mixture of 10 g. of kojic acid, 3.8 g. of paraformaldehyde, 1 g. of potassium bicarbonate and 50 ml. of absolute ethanol was heated for seventeen hours at 75°. Two ml. of concentrated hydrochloric acid was then added, the mixture was refluxed for thirty minutes, treated with Norite and filtered. After standing in the refrigerator for two days, the solution deposited 5.4 g. of a brown solid which was not appreciably soluble in alcohol or other organic solvents. Recrystallization from water, followed by digestion with absolute ethanol, gave a yellow powder which decomposed above 233° and gave a red coloration with ferric chloride.

Anal. Calcd. for $C_8H_{10}O_6$: C, 47.52; H, 4.95. Found: C, 47.99; H, 4.70.

Benzoylation of 1.8 g. of the above powder with 12 ml. of benzoyl chloride at 100–110° for one hour, followed by the action of 10% sodium hydroxide, gave a solid which was recrystallized once from benzene and four times from ethanol. The product, a yellow powder melting at 99–101°, failed to give the proper analysis, an indication that the substance from which the benzoate was prepared probably contained significant amounts of condensation products similar to 2,3,6-tri-(hydroxymethyl)-5-hydroxy-4-pyrone.

Anal. Calcd. for $C_{36}H_{26}O_{10}$: C, 69.90; H, 4.20. Found: C, 68.71; H, 4.00.

DEPARTMENT OF CHEMISTRY
TEXAS STATE UNIVERSITY FOR NEGROES
HOUSTON, TEXAS
RECEIVED DECEMBER 5, 1949

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[1] Woods, THIS JOURNAL, **68**, 2744 (1946).

[2] Price, "Reactions at Carbon–Carbon Double Bond," Interscience Publishers, New York, N. Y., 1946, p. 46.

[3] Yabuta, *J. Chem. Soc.*, **125**, 575 (1924).

[4] The kojic acid was obtained from the Corn Products Sales Company. Analyses were by Dr. Carl Tiedcke. The Fisher–Johns apparatus was used for all melting points

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Calcium Hydride as a Basic Catalyst in the Perkin Reaction

BY SAVERIO ZUFFANTI AND JOHN J. SARDELLA

Gibb[1,2] and others[3–6] have investigated the use of calcium hydride in the condensations of aldehydes, ketones and esters.

This note reports data on the use of calcium hydride in the Perkin reaction. Benzaldehyde has been treated with acetic, propionic, and *n*-butyric anhydrides.

Experimental

Materials.—The calcium hydride was the commercial gray grade of about 95% purity. The benzaldehyde was purified by keeping it in contact with calcium hydride for several days and then collecting the fraction distilling at 178–180°. The acetic, propionic and *n*-butyric anhydrides were purified by allowing each to stand over metallic sodium for a few days, distilling, then allowing to stand over calcium hydride for a few days, and distilling again before use.

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[1] Gibb and Mann, M. I. T., B.S. Thesis, 1946.

[2] Gibb and Horne, M. I. T., B.S. Thesis, 1946.

[3] Taboury and Godchot, *Compt. rend.*, **169**, 62–64 (1919).

[4] Porlezza and Gatti, *Gazz. chim. ital.*, **54**, 491 (1924); **55**, 224 (1925).

[5] Perkin and Pratt, *J. Chem. Soc.*, **95**, 159 (1909).

[6] Packendorff, *Ber.*, **64B**, 948–949 (1931).

Procedure.—Benzaldehyde (0.4 mole), the anhydride (0.6 mole), and the calcium hydride (0.6 mole) were refluxed for seven hours and then water was added to decompose the unreacted hydride. The mixture was then worked up in the usual manner.

The yields of cinnamic acids obtained with acetic, propionic, and *n*-butyric anhydrides were, respectively, 8.3, 9.1 and 7.4%. Increasing the molar ratio of the aldehyde (0.7 mole) increases the yield to 16.4% in the reaction with propionic anhydride. Varying the anhydride concentration did not affect the yield, but increasing the calcium hydride ratio produced increased amounts of the unsaturated acids.

DEPARTMENT OF CHEMISTRY
NORTHEASTERN UNIVERSITY
BOSTON 15, MASSACHUSETTS

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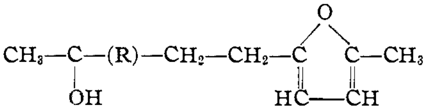
NEW COMPOUNDS

2-Substituted-4-(5-methyl-2-furyl)-2-butanols[1]

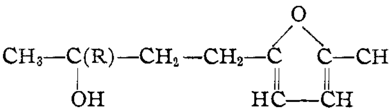
A series of compounds of the formula



has been prepared (Table I). The preparation of 4-(5-methyl-2-furyl)-2-butanol, a typical example, was carried out in the following manner. To a solution of *p*-tolylmagnesium bromide prepared from 6.1 g. of magnesium and 42.8 g. of *p*-bromotoluene was added dropwise during twenty-five minutes 22.8 g. (0.15 mole) of 4-(5-methyl-2-furyl)-2-butanone[2] dissolved in 75 ml. of ether, maintaining the temperature below 20°. After stirring for one hour at room temperature, a qualitative test for the Grignard reagent[3] was made to assure that an excess had been present. Decomposition was effected with crushed ice and 200 ml. of a saturated ammonium chloride solution and ether removed on a water-bath. The resulting product was steam distilled to remove toluene and 4,4′-bitolyl, the organic layer separated and the aqueous layer extracted with ether. The solvent was distilled from the dried combined ether solutions and the residue distilled at reduced pressure. The yield of light yellow oil, b. p. 144.5-146° (1 mm.), d^{25}_4 1.0451, was 28.4 g. (77.6%). The molecular refraction was calculated to be 72.52 (M^{25}_{D}) and the value found was 72.84.

TABLE I

2-SUBSTITUTED 4-(5-METHYL-2-FURYL)-2-BUTANOLS



R	Boiling point °C.	Boiling point Mm.	Yield, %	n^{25}_{D}	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
n-Butyl	101–106	1	75.6	1.4740	$C_{13}H_{22}O_2$	74.24	73.83	10.54	10.35
Phenyl	151–154	9	73.5	1.5386	$C_{15}H_{18}O_2$	78.23	78.08	7.88	8.05
Cyclohexyl[a]	131–161	1	18.9	1.5010	$C_{15}H_{24}O_2$	76.22	76.03	10.24	10.38
Benzyl	154–157	2	83.9	1.5347	$C_{16}H_{20}O_2$	78.65	78.34	8.25	8,36
p-Tolyl	144.5–146	<1	77.6	1.5355	$C_{16}H_{20}O_2$	78.65	78.31	8.25	8.08
1-Naphthyl	219–219.5	9	84.8	1.601[b]	$C_{19}H_{20}O_2$	81.40	81.10	7.19	6.95

[a] Yield, refractive index and analytical data are given for a redistilled product. [b] n^{28}_{D} (Fischer refractometer) for supercooled liquid.

UNIVERSITY OF KANSAS CITY
KANSAS CITY 4, MO.
W. M. HOEHN
WARREN J. MURBACH

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[1] The work reported in this paper is taken in part from the thesis submitted by Warren J. Murbach to the Graduate School of the University of Kansas City in partial requirements for the degree of Master of Arts.

[2] Alder and Schmidt, *Ber.*, **76B**, 183 (1943).

[3] Gilman and Schulze, THIS JOURNAL, **47**, 2002 (1925).

Aryl Isothiocyanates and Thioureas

o-**Biphenyl Isothiocyanate.**—Prepared in 24% yield by the procedure (A) of Dains, Brewster and Olander[1]; b. p. 122° (0.04 mm.), n^{25}_{D} 1.6572.

Anal. Calcd. for $C_{13}H_9NS$: C, 73.90; H, 4.29; N, 6.63. Found: C, 73.92; H, 4.15; N, 6.68.

N,N′-Bis-(*o*-biphenyl)-thiourea.—Obtained, in a few per cent. yield, as a by-product in the above preparation; m. p., after two recrystallizations from benzene–Skellysolve C, 142–143°.

Anal. Calcd. for $C_{25}H_{20}N_2S$: C, 78.91; H, 5.30; N, 7.36. Found: C, 79.17; H, 5.61; N, 7.42.

p-**Diethylaminophenyl Isothiocyanate.**—Prepared in 36% yield by procedure A; b. p. 148° (1.2 mm.); n^{25}_{D} 1.6690.

Anal. Calcd. for $C_{11}H_{14}N_2S$: S, 15.54. Found: S, 15.79.

N,N′-Bis-(*p*-diethylaminophenyl)-thiourea.—Obtained as a minor by-product in the above preparation; m. p., after three recrystallizations from alcohol, 165–166.5°.

Anal. Calcd. for $C_{21}H_{30}N_4S$: C, 68.06; H, 8.16; N, 15.12. Found: C, 68.07; H, 7.87; N, 15.05.

p,p′-**Methylenebis-(phenyl) Isothiocyanate.**—Prepared by procedure A in 48% yield; m. p., after two recrystallizations from glacial acetic acid, 143–144°.

Anal. Calcd. for $C_{15}H_{10}N_2S_2$: C, 63.80; H, 3.57; N, 9.92. Found: C, 63.96; H, 3.84; N, 10.07.

p-(*t*-**Amyl)-phenyl Isothiocyanate.**—Prepared in 49% yield by procedure A; b. p. 104° (0.2 mm.).

Anal. Calcd. for $C_{12}H_{15}NS$: C, 70.20; H, 7.36; N, 6.82. Found: C, 70.40; H, 7.30; N, 6.66.

m-**Acetylphenyl Isothiocyanate.**—Prepared in 76% yield by the procedure of Dyson[2]; b. p. 112° (0.2 mm.); n^{25}_{D} 1.6453.

Anal. Calcd. for C_9H_7NOS: C, 60.99; H, 3.98; N, 7.90. Found: C, 60.77; H, 4.20; N, 7.83.

N-(*m*-Acetylphenyl)-N′-phenylthiourea.—Prepared by mixing and allowing to spontaneously react *m*-acetylphenyl isothiocyanate and aniline, and by warming until homogeneous a mixture of *m*-acetylaniline and phenyl isothiocyanate. In each case the product melted, after recrystallization from benzene–Skellysolve C, at 108–110°,

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[1] Dains, Brewster and Olander, "Organic Syntheses," Coll. Vol. I, Second Ed., 1944, p. 447.

[2] Dyson, "Organic Syntheses," Coll. Vol. I, sec ond ed., John Wiley and Sons, Inc., New York, N. Y., 1944, p. 65.