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Note

Formation, during liquefaction of cellulose, of 2,5-dimethyl-1,4-benzenediol *via* aldol addition and a reduction–oxidation pathway*

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Our interest in benzenediol formation was initiated by the isolation and identification of 2,5-dimethyl-1,4-benzenediol from the liquefaction product of cellulose*. During that work, 2,5-dimethyl-2,5-cyclohexadiene-1,4-dione (**1**), 2,3-butanedione (biacetyl), and 3-hydroxy-2-butanone (acetoin) were also detected as liquefaction products under aqueous, alkaline conditions. Several alkylbenzenediols have been isolated as alkaline-degradation products of D-xylose and D-glucose[1]; **1** was observed after treatment of sucrose[2] with alkali.

Quite early work had indicated that both **1** and 2,5-dimethyl-1,4-benzenediol (**2**) could be prepared[3] by warming biacetyl (10 g) in dilute caustic solution (200 mL). However, information on the yield was given only for the product from 2,3-pentanedione (10% of 2,5-diethyl-2,5-cyclohexadiene-1,4-dione). Our experience with biacetyl under similar conditions (see Experimental section) suggested that **2** was formed in <0.5% yield, and **1** was barely detectable. The failure to isolate **1** may be partially attributed to the rapid oxidation of quinones in alkaline solution[4]. Condensations of **1**, such as that affording quinhydrone, may further lower the apparent low yield. When acetoin was subjected to similar conditions, neither **1** nor **2** was detected during the initial 4 h. However, with additional time (4 h) beyond that initial period, the yield of **1** was 0.2% and of **2** was 3.5%.

In order to improve the yields of **1** and **2**, a higher temperature and pressure were utilized with a milder base, namely, for 1 h in 0.35M sodium carbonate at 300° and 10.3 MPa. Neither **1** nor **2** was detected in proportions >0.1% when these conditions were applied to biacetyl. However, exposure of acetoin to the same conditions was considerably more successful; yields of 18% of **2** and 0.1% of **1** were obtained.

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TABLE I

YIELDS OF PRODUCTS FROM REACTION OF 3-HYDROXY-2-BUTANONE IN 0.35M Na_2CO_3 AT 10.3 MPa

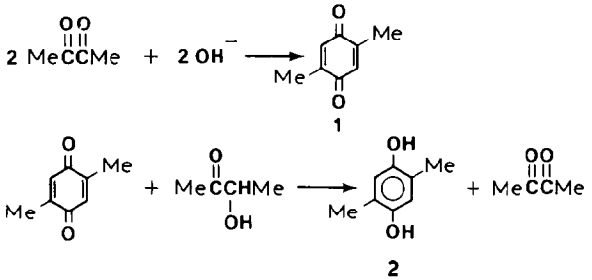
Temperature (degrees)	**1** (%)	**2** (%)[a]
50	0.01	0.01
100	0.01	0.01
150	0.03	1.4
200	0.04	8.7
250	0.07	11.7
300	0.10	18.6
350	0.10	9.1

[a]Crystalline **2** was isolated from reactions performed at and above 150°. The other values were determined by gas–liquid chromatography of the reaction mixtures.

The effects of temperature on the yields of **1** and **2** from acetoin are presented in Table I. The yield of **2** was significantly increased at temperatures above 150°, whereas that of **1** remained low throughout the temperature range. The diminution in the yield of **2** at temperatures above 300° was inexplicable, as no new major components were observed in the reaction mixture.

Von Euler and Hasselquist[5] had presented a mechanism for the formation of **1** from biacetyl that involved the formation of biacetyl from acetoin, both as enediols, together with the reduction of **1** to **2**. The biacetyl then underwent bimolecular combination to afford **1**. They suggested that acetoin and acetic acid were initially formed from biacetyl. Unfortunately, no experimental evidence was presented to support the formation of acetoin. However, there is evidence supporting the formation of enediolates from biacetyl in alkaline solution[6,7]. In alkaline solution, the u.v. spectrum of acetoin is quite similar to that of the enediolate of biacetyl[8].

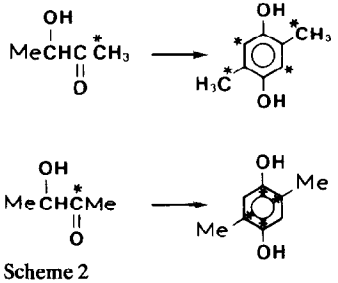
During our work, very small proportions of biacetyl were detected in the product mixtures, but acetic acid was not present. Of greater importance was the presence of a minute amount of biacetyl in the acetoin reagent. Several attempts were made to remove the biacetyl, but to no avail. Acetoin has been shown[9] to be slowly oxidized to biacetyl in air. The presence of biacetyl would allow initiation of the reaction sequences shown in Scheme 1. Further requirements for biacetyl are provided by internal generation.



Scheme 1

The prior mechanism[5] does remain attractive, in part because it suggests that **1** is an intermediate, with **2** as the final product; this could explain the very low amounts of **1** found in the autoclave experiments. The modified mechanism (see Scheme 1) depends upon aldol reaction for the formation of **1**, and would generate no acetic acid. Furthermore, the oxidative conversion of acetoin into biacetyl could be linked* to the reduction of **1** and **2**.

The results of experiments performed at 300° with ^{13}C-labeled acetoin suggested that two molecules of biacetyl or enediolate combine to form **1** and **2**; the results are presented in Scheme 2. The ^{13}C-n.m.r. spectra of **2**, formed by [1-^{13}C]acetoin or [2-^{13}C]acetoin, indicated equal distribution of the ^{13}C label in four representative positions. This would imply that a symmetrical precursor, such as biacetyl or its enediolate, was required prior to an aldol reaction–cyclization.



Scheme 2

In order to investigate the possible intermediacy of **1** in Scheme 1, a sample of **1** was added to acetoin, and subjected to aqueous alkaline conditions at 300°; the yield of crystalline **2** was 50%. Assuming that a reaction based solely upon acetoin would yield 18% of **2**, then 70% of the supplementary **1** was converted into **2**. Such a conversion tends to support the concept of **1** as an intermediate in Scheme 1. Similarly, **1** was added to biacetyl and subjected to aqueous alkaline conditions at 300°. Only traces of **1** and **2** were isolated by sublimation of the tar-like, reaction mixture. Under the latter conditions, it appeared that condensation of biacetyl with **1**, or other pathways, was favored, rather than self-condensation to form **1**. Thus, the evidence gathered so far corroborates the formation of **2** from acetoin, with a mechanism similar to that suggested in Scheme 1.

EXPERIMENTAL

General. — Melting points were determined on a Thomas–Hoover capillary melting-point apparatus and are uncorrected. Nuclear magnetic resonance spectra (^1H and ^{13}C) were recorded with a Varian FT-80 spectrophotometer. Gas–liquid

*It is also possible that **1** could be formed as a byproduct, as samples of **2** kept for 4 months gave both **1** and **2** on resublimation. However, when thoroughly degassed water and acetoin (freeze–thaw under vacuum) were combined with base at 300°, no change in the yield of **1** or **2** was observed.

chromatographic analyses were obtained with a Hewlett–Packard 5880A instrument. Two capillary columns (2 mm × 30 m) were quite useful for biacetyl and acetoin product elution: SE-54 and Superox, both on fused silica. Column-temperature requirements for these columns were 50° isothermal for 10 min, programmed to 250° at 3°/min. The labeled compounds 3-hydroxy-2-[2-^{13}C]butanone and 3-hydroxy-2-[1-^{13}C]butanone were obtained from Merck Sharp and Dohme Canada, Ltd., Quebec.

Alkaline treatment of 2,3-butanedione and 3-hydroxy-2-butanone. — The liquefaction procedure was applied to acetoin and biacetyl. To a 180-mL capacity autoclave were added 11.5 g of an 85% solution of acetoin in water, sodium carbonate (0.219 g), and distilled water (5.75 g). The biacetyl reaction was performed with 9.8 g of this intermediate. The autoclave was sealed, and flushed with nitrogen for 5 min. The temperature of the autoclave was then raised to the desired level (heating time, 1 h to reach 300°) and kept thereat for 1 h. The mixture was cooled during 3 h, the gas vented, and the autoclave opened. The mixture was filtered to remove **2** (1.4 g) that was present during acetoin reactions. (No solid was precipitated from the biacetyl reaction mixture.) Solid **2** was washed with water and dichloromethane. The filtrate and washes were combined, and extracted with dichloromethane, and the extract was dried (anhydrous sodium sulfate), and evaporated *in vacuo*.

In a further series of experiments, 3.6 g of **1** was added to respective autoclaves containing acetoin and biacetyl as just described. From the acetoin reaction-mixture, 3.9 g of **2** was isolated by filtration. However, only a trace of **1** and **2** could be isolated by sublimation of the biacetyl reaction-mixture. Attempted isolation of **2** from the tar-like mixture by filtration was unsuccessful.

Alkaline treatment of biacetyl and acetoin was also performed under atmospheric conditions. Either 11.5 g of 85% acetoin or 9.8 g of biacetyl was added to 0.1M sodium hydroxide (100 mL). The solution was sparged with nitrogen, and kept thereunder during heating. Reflux was generally maintained for 1 h. The aqueous solution was acidified to pH 5, extracted with dichloromethane, and the extract evaporated *in vacuo*. The product mixture was examined by g.l.c.

2,5-Dimethyl-1,4-benzenediol. — This compound was isolated in 18% yield from the autoclave reaction of acetoin with base at 300°. It could be readily purified by sublimation; m.p. 223–224°; ^{13}C-n.m.r. data (decoupled, CD_3OD): δ 149.03 (aromatic C-1), 123.43 (aromatic C-2), 118.30 (aromatic C-3), and 15.87 (methyl), with Me_4Si as the internal reference. The g.l.c. retention-time was ~68 min with both capillary columns.

Anal. Calc. for $C_8H_{10}O_2$: C, 69.56; H, 7.25; O, 23.10. Found: C, 69.51; H, 7.33; O, 23.29.

2,5-Dimethyl-2,5-cyclohexadiene-1,4-dione. — This compound was prepared in quantitative yield by dissolving 2,5-dimethylhydroquinone (1.0 g) in ether, adding sodium sulfate (1.0 g) and silver oxide (2.0 g) and stirring overnight. The mixture was filtered, and the filtrate evaporated, to give yellow, needle-like crystals,

m.p. 124–126°; ^{13}C-n.m.r. data (decoupled, $CDCl_3$): δ 187.89 (cyclohexadienyl C-1), 145.82 (cyclohexadienyl C-2), 133.42 (cyclohexadienyl C-2), and 15.35 (methyl). The g.l.c. retention-time was ~29 min with both capillary columns.

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