NOTES

Condensation Products from Acetaldehyde

By A. H. Andersen, R. M. Kitchen and C. H. Neufeld

Nord, *et al.*,[1] condensed acetaldehyde with magnesium aluminum alkoxide catalysts and isolated from the reaction product the monoacetate of 1,3-butanediol. No mention is made in their papers of the ethyl ester of β-hydroxybutyric acid which we have found to be present in the reaction mixture in approximately equimolecular proportion to the monoacetate of 1,3-butanediol. Similar proportions of the diol and the hydroxy acid have also been found in an oily by-product obtained in the commercial preparation of ethyl acetate from acetaldehyde.[2]

Experimental.—The procedure adopted for separating the constituents of the high-boiling oils was as follows:

(1) Acid hydrolysis with excess water and butanol: the mixture was heated in a flask provided with a packed distillation column. The overhead temperature was kept at the boiling point of the butyl acetate–butanol–water ternary azeotrope by adjusting the reflux ratio. The ester-containing top layer of the distillate was drawn off while the water layer was decanted back to the flask. This was continued until the temperature could no longer be kept below 90° by refluxing. The excess butanol was then removed in the same manner at a temperature of 92°.

(2) Neutralization and saponification: the saponification equivalent of the aqueous residue was determined, and just sufficient sodium hydroxide was added in 10% solution to neutralize the free acid and saponify the remaining esters. The mixture was boiled for an hour and cooled.

(3) Filtration to remove any resinous by-products.

(4) Vacuum distillation of filtrate: the excess water and the butanediol are removed leaving a fused residue of crude sodium β-hydroxybutyrate.

The glycol was purified by fractionation, b. p. 207°, $n^{20}D$ 1.441.

The sodium β-hydroxybutyrate was purified by recrystallization from butanol, m. p. 157–158°. It was identified by comparison with an authentic sample prepared through crotonic acid,[3] m. p. 157–158°; mixed m. p. 157–158°.

The butyl ester of β-hydroxybutyric acid was prepared from the sodium salt, hydrochloric acid and butanol, b. p. 103–104° (14 mm.).

The separation has also been carried out using potassium hydroxide. The potassium β-hydroxybutyrate melts at 148–149°. Care must be exercised since all the derivatives of β-hydroxybutyric acid so far examined by us are heat labile, dehydrating rather readily to the crotonates.

From our observations we conclude that termolecular condensation of acetaldehyde occurs under the influence of the coördination catalyst of Nord[1] and also to a much smaller extent under the influence of aluminum alkoxides. We believe that this reaction results from an initial aldolization followed by a condensation between the aldol and aldehyde molecules. This condensation can occur in either of two ways

$$CH_3CHO + CH_3CHOHCH_2CHO \longrightarrow CH_3CHOHCH_2CH_2OCOCH_3 \quad (1)$$

Monoacetate of 1,3-butanediol

$$CH_3CHO + CH_3CHOHCH_2CHO \longrightarrow CH_3CH_2OCOCH_2CHOHCH_3 \quad (2)$$

Ethyl ester of β-hydroxybutyric acid

Tischtschenko[4] mentions the formation of the ethyl ester of β-hydroxybutyric acid from acetaldehyde, and our observations confirm this and indicate that the ethyl ester is formed in similar quantities to the glycol ester.

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[1] (a) Kulpinski and Nord, *J. Org. Chem.*, **8**, 256–270 (1943); (b) Villani and Nord, This Journal, **68**, 1674 (1946); (c) F. F. Nord, U. S. Patent 2,403,876.

[2] Benson and Cadenhead, *J. Soc. Chem. Ind.*, **53**, 40–3T (1934).

[3] Billman, *Ber.*, **43**, 579 (1910).

[4] Tischtschenko, *Chem. Centr.*, **77**, II, 1309 (1906).

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The Addition of Dimethylamine to Benzoquinone

By Richard Baltzly and Emil Lorz

In the usual procedure for the preparation of *bis*-(dialkylamino)-quinones from benzoquinone two-thirds of the quinone is employed as an oxidizing agent so that, at best, only around 30% of the starting quinone can be isolated as the product.[1]

It has been found that re-oxidation of the intermediates can be accomplished by a stoichiometric amount of cupric salt or by a smaller quantity when the reaction mixture is stirred with oxygen. The latter procedure is preferable since the product crystallizes in virtually pure form from solution, uncontaminated by cuprous salts. The method was unsuccessful with methylamine, aniline and ammonia.

Procedure

A one-liter three-necked flask equipped with mercury-seal and stirrer was connected to a two-liter graduated cylinder having a levelling bulb and a stopcock for admission of oxygen. The system was flushed out with oxygen and a solution containing 20 g. (0.1 mole) of cupric acetate monohydrate and 27 g. (0.6 mole) of dimethylamine in 300 cc. of methanol was introduced. One-tenth mole (10.8 g.) of benzoquinone in 200 cc. of methanol was then added and the system was closed. The stirrer was started and the reaction was followed by the oxygen absorption which was initially about 120 cc. per minute. Considerable heat was evolved at the start of the reaction and the temperature was held near 25° by ice-water cooling. About five minutes after the beginning of the reaction, crimson platelets of *bis*-(dimethylamino)-benzoquinone became visible on the sides of the flask. After oxygen-absorption had ceased the flask was refrigerated overnight and the product was collected. This material melted at 171° (lit., 173°). A further crop of 2.5 g. was obtained by concentration of the filtrate (total yield, 93%).

bis-(Dimethylaminobenzoquinone is not itself oxidized

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[1] (a) Mylius, *Ber.*, **18**, 463 (1885); (b) Kehrmann, *Ber.*, **23**, 897 (1890); (c) Anslow and Raistrick, *J. Chem. Soc.*, 1449 (1939).

under the above conditions but benzoquinone (and perhaps the intermediate quinones) can be. If the concentration of cupric ion is significantly diminished such oxidations take place and the yield is less. In the presence of 0.01 mole of cupric acetate the oxygen-absorption was about the same but the bisaminoquinone was then obtained in 72–76% yield.

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Isolation of a Saponin from the Leaves of *Solidago canadensis* L.

BY R. C. BURRELL AND FORREST G. HOUSTON

In the course of the investigation of the chemical composition of several common weeds, leaves of *Solidago canadensis* L. were examined for the possible presence of a saponin. There are several reports of the recognition of both acid and neutral saponins in various other species of goldenrod,[1,2,3] but none of actual isolation.

Experimental

Method of Isolation.—Leaves of *Solidago canadensis* L. were gathered in late July, 1946, dried at room temperature, and ground to a fine powder. A 230-g. sample of this powder in a small cloth bag was exhaustively extracted, first with acetone, then with ether and finally twice with 95% ethyl alcohol. The combined alcoholic extracts were concentrated to a small volume (about 100 cc.) and 5 volumes of ether added with shaking. This produced a gummy, white precipitate. After decanting the ether, this precipitate was dissolved in the least possible amount of hot methanol. This solution, which had a light yellow color, was treated with acetone added from a large pipet while shaking the mixture vigorously. A flocculent white precipitate formed from which the liquid was decanted. The precipitate was once more dissolved in hot methanol and the acetone precipitation repeated. The final white flocculent precipitate was amorphous and very hygroscopic. It produced a stable creamy foam with water and stabilized an emulsion of kerosene in water. Fehling solution showed no reduction.

Preparation of the Sapogenin.—The moist saponin preparation was brought into solution in 50 cc. of 10% hydrochloric acid, 25 cc. of 95% ethyl alcohol added to reduce foaming and this solution refluxed for three hours. A grainy precipitate formed which consisted of microscopic, colorless needles. The supernatant liquid gave a positive Fehling reaction. The crystals were filtered off and brought into solution by refluxing with methanol. This solution was concentrated to about 50 cc. and on cooling some 500 mg. of colorless needles were isolated, representing a yield of 0.22% of the dried leaves.

Properties of the Sapogenin.—The crystals, which melted at 310–315° with decomposition, were slightly soluble in ethanol methanol, acetone, ether and ethyl acetate, insoluble in water, but dissolved easily in cold concentrated sulfuric acid, giving a faintly yellow colored solution which became deep red on warming or on the addition of a few drops of acetic anhydride, suggesting the behavior of a triterpene. The Rast method indicated a molecular weight of approximately 500.

Anal. Calcd. for $C_{30}H_{50}O_5$ (490.4): C, 73.41; H, 10.28. Found: C, 72.97; H, 10.02.

Insolubility in hot alkali and a neutral reaction in alcoholic solution indicates the absence of a carboxyl group. The acetate was prepared as flat rectangular crystals which melt at 182–183°. A search of the literature failed to reveal a compound approximating $C_{30}H_{50}O_5$ which possesses the above properties.

CONTRIBUTION FROM THE
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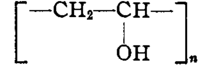
[1] L. Krober, *Heil-gewurz Pflanzen*, **12**, 131 (1930).

[2] F. P. Rey, *Rev. farm.* (*Buenos Aires*), **74**, 93 and 131 (1932).

[3] E. Wagner, *Seifensieder-Ztg.*, **68**, 35 (1941).

The Infrared Spectrum of Polyvinyl Alcohol

BY ELKAN R. BLOUT AND ROBERT KARPLUS

Despite two previously reported measurements on the infrared spectrum of polyvinyl alcohol[1,2] we should like to record some of our data, using carefully purified samples, because of their possible bearing on the details of the molecular structure of this material. The presence of chemical groups and arrangements other than those of the poly-1,3-glycol  $\left[-CH_2-\underset{OH}{\underset{|}{CH}}-\right]_n$ has been shown by chemical investigation. For example, terminal acetal,[3] keto or ketal[4] and 1,2-glycol groups[5] have been shown to be present in low percentage in the material known as polyvinyl alcohol.

The infrared spectra for the region 700–4000 cm.$^{-1}$ of carefully purified and dried films of polyvinyl alcohols of various degrees of polymerization are shown in Fig. 1. These spectra correspond in most salient features to those reported by Thompson and Torkington[2] except that there is no evidence of a band at 1650 cm.$^{-1}$. Other samples prepared so that water was not rigidly excluded at the time of measurement show a characteristic absorption band in this region. Another band typical of incompletely hydrolyzed polyvinyl alcohol is seen at 1710 cm.$^{-1}$ in Fig. 2, curve A. This figure also shows the effect of careful acid hydrolysis (removal of residual acetate groups) and drying on the spectrum in the region 1400–1800 cm.$^{-1}$.

It is difficult to correlate absorption bands definitely with molecular structure except through mathematical analysis. In the spectra shown in Fig. 1 the assignments of the bands above 1400 cm.$^{-1}$, *viz.*, 3350 cm.$^{-1}$ (O—H stretching), 2940 cm.$^{-1}$ (C—H stretching) and 1435 cm.$^{-1}$ (C—H bending) seem reasonable, based on analogy with the spectra of simple molecules and on the calculated characteristic frequency of various molecular groups.[6] In the region 1000 cm.$^{-1}$ to 1400 cm.$^{-1}$ five bands are observed at 1380, 1330, 1240 1135 and 1085 cm.$^{-1}$ which are probably associ-

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[1] Barnes, Liddel and Williams, *Ind. Eng. Chem., Anal. Ed.*, **15**, 659 (1943).

[2] Thompson and Torkington, *Trans. Far. Soc.*, **41**, 246 (1945).

[3] Marvel and Inskeep, THIS JOURNAL, **65**, 1710 (1943).

[4] Clarke and Blout, *J. Pol. Sci.*, **1**, 419 (1946).

[5] Flory and Leutner, "The Occurrence of Head-to-Head Arrangements of the Structural Units in Polyvinyl Alcohol and Acetate," paper presented at the New York meeting of the American Chemical Society, September 15, 1947.

[6] Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., New York, N. Y., 1945.