

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_D^{20} 1.441.

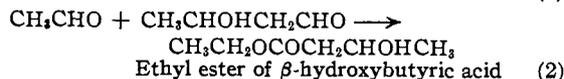
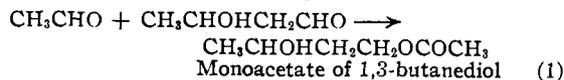
The sodium β -hydroxybutyrate was purified by recrystallization from butanol, m. p. 157–158°. It was identified by comparison with an authentic sample prepared through crotonic acid,³ m. p. 157–158°; mixed m. p. 157–158°.

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 coordination catalyst of Nord¹ 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



Tischtschenko⁴ 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.

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

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The Addition of Dimethylamine to Benzoquinone

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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

(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) Bilman, *Ber.*, **43**, 579 (1910).

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