

leaves the first term, corresponding to an order of 1.5, predominating over the remainder of the reaction.

This is the first of a series of papers on the characteristics of *n*-butane decomposition.

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## NOTES

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### The Preparation of Methyleneaminoacetonitrile

BY LAWRENCE H. AMUNDSEN AND RUTH VELITZKIN

After repeated experimentation the method of preparing methyleneaminoacetonitrile as described in "Organic Syntheses"<sup>1</sup> has been improved. The following modifications have been made: (1) time of reaction decreased; (2) higher temperatures; (3) internal cooling with solid carbon dioxide;<sup>2</sup> (4) acetic acid added in one portion before the addition of sodium cyanide.

#### Experimental

A mixture of 150 cc. (1.9 moles) of 35% formaldehyde, 54 g. (1 mole) of ammonium chloride and 38 cc. (0.66 mole) of glacial acetic acid was cooled to below 15° by the addition of crushed ice. When as much as 10% more formaldehyde was used, no significant difference in yield or purity of the product was observed but 50% more formaldehyde appeared to decrease the yield. It has been found possible to add small pieces of solid carbon dioxide instead of crushed ice. When one works with ten times the quantities stated here, the necessity for handling such a large volume of solution is thus avoided. There is probably no advantage in making this substitution if sufficiently large vessels are available. The mixture was stirred vigorously and a solution of 49.5 g. (0.98 mole) of 96-98% sodium cyanide in approximately 100 cc. of water was added from a dropping funnel over a period of fifteen to twenty minutes. The temperature was kept at 15-20° by the addition of crushed ice. When the temperature was permitted to go as low as 0°, no difference was noted in the results. Also momentary increases in temperature above 20° caused no significant change but when the temperature was maintained throughout at 35-40° an oily product was formed. After the addition was completed, the stirring was continued for fifteen minutes while the same temperature was maintained. Somewhat longer periods of stirring gave identical results, but if the solution was filtered at once, a small additional

(1) Adams and Langley, "Organic Syntheses," edited by Gilman, John Wiley and Sons, Inc., New York, N. Y., 1932, Coll. Vol. I, p. 347. This method in a more or less modified form has been described or mentioned several times in the literature. A complete bibliography is given in "Organic Syntheses." As far as the authors have been able to determine, no more recent information has appeared.

(2) The authors are indebted to Raymond I. Longley, Jr., for proposing temperature control by adding solid carbon dioxide directly to the mixture.

quantity of the compound was deposited from the filtrate. The precipitate was filtered off and washed well with water. It seemed to be best to filter off the product the same day for the product was less pure, as indicated by the melting point, when the reaction mixture was allowed to stand for several days. This may be due to the formation of the lower melting isomer.<sup>3</sup> When the product was not thoroughly washed, the melting point was low and suspended solid material seemed to be present in the melt. This may have been ammonium chloride. The yields with few exceptions have been from 45-55% of the theoretical and the melting points have been between 124 and 129° (uncorr.) with a 2 or 3° range. Although these yields are somewhat lower than those reported by Adams and Langley,<sup>1</sup> they are equal to those obtained in this Laboratory by following their directions. This method has given equally satisfactory results with batches ten times the size of the one described, *i. e.*, the same size batch used by Adams and Langley.<sup>1</sup> When solid carbon dioxide was used for cooling these larger batches, 3-4 kg. was sufficient to keep the temperature at 15-20°.

(3) Johnson and Rinehart, THIS JOURNAL, 46, 772 (1924).

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### Comment on "Absence of Combined Fatty Acid in Cereal Starches"

BY LEO LEHRMAN

No doubt all the workers in the field of starches will note with a great deal of interest the above entitled communication of Schoch.<sup>1</sup> The author reports the complete removal of the fatty acids in three cereal starches by extraction with water-miscible fat solvents, particularly methanol, the cellosolves and 80% dioxane. He gives two other results, *viz.*, (1) the de-fatted starch retains the usual properties of starch; (2) fatty acid can be reintroduced into the defatted starch by treatment with alcoholic oleic acid, and then concludes that "the fatty acid is distributed throughout the starch granule as an extraneous impurity."

It is with the interpretation of the experimental work that I think exception must be taken.

(1) Schoch, THIS JOURNAL, 60, 2824 (1938).