REDUCTION OF METANITROBENZALDEHYDE WITH SODIUM ARSENITE.—

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ABSTRACT.

In a study of sodium arsenite as a reducing agent in organic chemistry it was decided to examine its action on metanitrobenzaldehyde containing, as it does, two groups capable of reduction. This compound has been reduced by many investigators who have obtained varying products with various reducing agents; but in no case has azoxybenzyl alcohol been produced directly. Rarely, indeed, have both groups been attacked.

m-Nitrobenzaldehyde treated with sodium arsenite in excess at 105-6°C. for several hours gave m-azoxybenzyl alcohol and m-azoxybenzoic acid. This action is unique and affords a simple and direct method for preparing m-azoxybenzyl alcohol previously made indirectly and in small yield from m-nitrobenzaldehyde. This alcohol will be further used in connection with a study of the isomerism of azoxy compounds.

An examination of sodium arsenite as a reducing agent in the preparation of azoxybenzene from nitrobenzene[1] suggested a study of its action on metanitrobenzaldehyde, a compound in which two groups, a nitro and an aldehyde, both capable of reduction, would be at the same time subject to its action.

The reduction of this compound has been studied by numerous investigators who have obtained varying products, according to the reducing agent used. Treated with zinc dust[2] and water, alone or in the presence of various neutral solvents and reagents, it has been found to give a condensation product $(C_7H_5ON)x$ which on oxidation gives m-nitrosobenzaldehyde. With zinc dust[3] alcohol and acetic acid m-hydroxylaminobenzaldehyde and N–[3-formyl 1–phenyl]–3-nitro-isobenzaldoxime were the products. Electrolytic reduction[4] in strong sulphuric acid gave the same benzaldoxime as above. Long continued it gave a brown compound which oxidized to m-nitrosobenzaldehyde[5] and m-azoxybenzyl alcohol. Stannous chloride[6] in hydrochloric acid gave m-aminobenzaldehyde. In alkaline solutions quite different products were to be expected. Ferrous sulphate[7] and sodium hydroxide gave m-azoxybenzaldehyde. The reduction of the bi-

sulphite compound of m-nitrobenzaldehyde with ferrous sulphate[8] and calcium carbonate and heating of the reduction product with hydrochloric acid or sulphuric acid until sulphur dioxide was driven off gave m-amino-benzaldehyde. Potassium hydroxide[9] in alcohol or water gave m-nitrobenzyl alcohol and m-nitrobenzoic acid. Strong sodium hydroxide (40°Bé) gave m-nitrobenzoic acid and m-azobenzoic acid[10]. Electrolytic reduction[11] in aqueous alcoholic potassium hydroxide gave 3-m-oxymethyl-azobenzol-carboxylic acid-3 and small amounts of m-azobenzyl alcohol and m-azobenzoic acid. Aluminum ethylate[12] gave m-nitrobenzoic acid ester. Only one of the reducing agents, ferrous sulphate, gave directly an azoxy compound.

In view of the well known simultaneous oxidation and reduction of two molecules of benzaldehyde in the presence of strong alkalies, one might expect that a reducing agent active in strong alkaline solution, might be found which would give both azoxy alcohol and azoxy acid when acting on a nitro-aldehyde. None of the reducing agents so far used, however, has given both these products; and indeed none has given m-azoxybenzyl alcohol which was first made from m-nitrobenzyl alcohol by reduction with 10% aqueous sodium hydroide,[13] m-nitrobenzyl alcohol in turn being made from m-nitrobenzaldehyde[9]. The action of sodium arsenite on m-nitrobenzaldehyde is unique in that it gives both m-azoxybenzyl alcohol and m-azoxybenzoic acid.

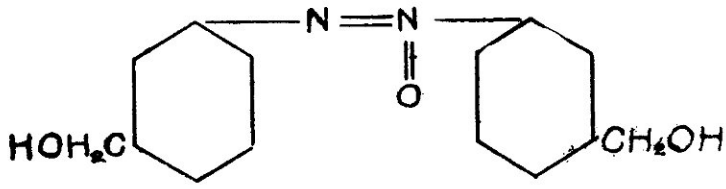
Experimental Part.

30.6 grams of m-nitrobenzaldehyde and a sufficient quantity of sodium arsenite to reduce both the nitro and aldehyde groups and to give twenty five percent excess were added with water, in a total volume of 250 c.c., to a three hole Pyrex flask with thermometer, mechanical stirrer and reflux condenser attached. The mixture was heated in an oil bath, at a temperature sufficient to keep the reaction mixture in the flask at 105°—6° C., for eight hours with vigorous stirring. 200c.c. of water was then added to the mixture and the heating interrupted. After

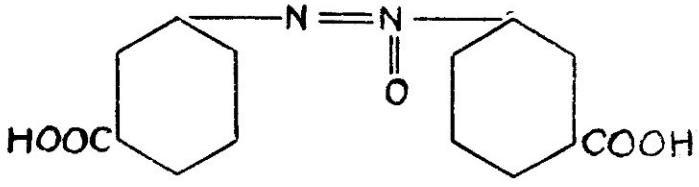
thorough mixing and slight cooling a yellow flocculent precipitate appeared. The contents of the flask were poured out and enough water added to make the volume about one liter or sufficient to prevent sodium arsenate from crystallizing out. After cooling, the organic matter was filtered off, washed thoroughly with water, and dried on a porous plate. Crystallization from alcohol and water and finally from benzene gave a product, crystalline and golden yellow in color melting at 86° C., the melting point of m-azoxybenzyl alcohol, Fig. I. A. An analysis for nitrogen gave 11.04%. The calculated value is 10.86%. The compound is therefore m-azoxybenzyl alcohol. Yield 25%.

Fig 1

A



B



The water solution from which the m-azoxybenzyl alcohol had been separated was red in color. Extraction with various solvents, ether, chloroform, carbon tetrachloride, petroleum ether, gave only slight extracts. The solution was acidified. The red color disappeared and a heavy brownish-white gelatinous precipitate was formed. It was filtered with difficulty and the dried precipitate was found to be very insoluble in all

ordinary organic solvents. It dissolved easily in sodium and ammonium hydroxide in agreement with our expectation that it was m-azoxybenzoic acid, Fig. I.B. The precipitate was several times dissolved in ammonium hydroxide and reprecipitated with hydrochloric acid but the brown color persisted. The original investigators describe it as a yellow powder without a sharp melting point but decomposing above 250°C. After these reprecipitations it was washed with water to remove the inorganic salts present, but because of its gelatinous nature this was imperfectly done. It was then extracted in a Soxlet extractor with 90% alcohol for several days. The color remained and very little of the original matter dissolved but the inorganic salts were completely removed. The product was brownish-yellow and amorphous, and decomposed at an uncertain temperature above 300°C. Analysis:

Mol. weight (Camphor method)	Calc. for $C_{14}H_{10}O_5N_2$	Found
	286	285

Calc. for $C_{14}H_{10}O_5N_2$, N = 9.72% Found. N = 9.79%.
Despite the slightly brownish color the compound is evidently m-azoxybenzoic acid.

The products, therefore, obtained by reducing m-nitrobenzaldehyde with excess of sodium arsenite at 105°—106°C are m-azoxybenzyl alcohol and m-azoxy-benzoic acid, both the nitro and aldehyde groups being reduced.

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