

THE OXIDATION OF BENZYL ALCOHOL BY THE  
THREE ISOMERIC NITROCHLORBENZENES.

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This study of the oxidizing action of o,m,p-nitrochlorbenzenes in reaction with benzyl alcohol is a continuation of the work of Lyons with Smith,<sup>1</sup> Fletcher<sup>2</sup> and Pleasant,<sup>3</sup> concerning the reactions between various aromatic nitro compounds and alcohols, which has included determination of the optimum conditions for complete reaction and the qualitative and quantitative study of the course and extent of the reduction of the nitro compound and of the oxidation of the alcohol.

Karl Heumann<sup>4</sup> obtained 4-4' dichlorazoxybenzene (M.P. 155°C.) from p-nitrochlorbenzene by reaction with alcoholic potash, but was unable to reduce o-nitrochlorbenzene with this reagent.

Laubenheimer<sup>5</sup> successfully reduced m-nitrochlorbenzene with alcoholic potash to 3-3' dichlorazoxybenzene (M.P. 97° C.)

A. V. Bloom<sup>6</sup> has studied the rate of reaction between potassium ethoxide and both o- and p-nitrochlorbenzene. He reports the formation of p-nitrophenetole and 4-4' dichlorazoxybenzene from the para isomer, and o-nitrophenetole from the ortho isomer following a very slight and unsatisfactory reaction.

A study of the reaction, under somewhat different conditions and less complete quantitatively, between each of the three isomeric nitrochlorbenzenes and benzyl alcohol by Suter and Dains<sup>7</sup> has appeared since our experimental work was completed.

## EXPERIMENTAL.

**Apparatus:** The reactions were carried out in the apparatus devised by Smith and Fletcher. The essential parts consist of a 500 ml., three necked, round Pyrex flask with a metal stirring rod, equipped with a mercury seal, entering the center neck of the flask. At the end of the rod of the mechanical stirrer is a riveted, folding blade, shaped to the inner surface of the flask, which permits it to fold back in line with the rod and to pass through the flask neck. A reflux, water cooled, condenser is fitted into one of the side necks and a dropping funnel into the other.

<sup>1</sup> L. T. Smith with R. E. Lyons, *J. Am. Chem. Soc.*, *48*, 3156 (1926).

<sup>2</sup> W. A. Fletcher, Unpublished thesis (Ind. Univ.).

<sup>3</sup> R. E. Lyons and Meredith Pleasant. Paper presented at last meeting of Academy (Dec., 1928). To be published elsewhere.

<sup>4</sup> Heumann, *Ber.*, *5*, 911 (1872).

<sup>5</sup> Laubenheimer, *Ber.*, *8*, 1623 (1875).

<sup>6</sup> Bloom, *Chem. Centralblatt*, *92*, 1232 (1921).

<sup>7</sup> Suter and Dains, *J. Am. Chem. Soc.*, *50*, 2733 (1928).

"*Proc. Ind. Acad. Sci.*, vol. 38, 1928 (1929)."

I. **Para Nitrochlorbenzene and Benzyl Alcohol.** For the initial trials the following procedure was used. Theoretical portions of benzyl alcohol, p-nitrochlorbenzene, and sodium hydroxide, corresponding to the equation

$$2C_6H_4ClNO_2 + 2C_6H_5CH_2OH \rightarrow C_6H_4ClN = NC_6H_4 + 2C_6H_5COOH + 2H_2O$$

were used, the amount of caustic being determined by the theoretical amount of 78 per cent sodium hydroxide necessary to convert the alcohol to the corresponding sodium alcoholate. The alcohol and the sodium hydroxide were first allowed to react for a few minutes at room temperature, and then a solution of the nitro compound in xylene (b.p. 139° C.) was allowed to drip into the reaction mixture. Heating was started as soon as all of the nitro compound had been added, and the temperature gradually raised to 60° C.

After the reaction had continued at this temperature for four hours, the mass was transferred to a flask and steam distilled to remove the solvent, xylene. The insoluble product, appearing as small orange-yellow nodules, was filtered out, dried, and weighed. The filtrate was then acidified with dilute (1:1) hydrochloric acid, the benzoic acid separating out as a white, flaky precipitate, which was filtered out, dried, and weighed, proper correction in the final estimated yield being made for the solubility of benzoic acid in water.

The reduction product was further purified for identification by crystallization from alcohol, in which its solubility was very small at room temperature but rather high at the boiling point of alcohol. The purification of the product from each of these preliminary trials gave orange needles which had a melting point of 156°, 156°, and 159° C., respectively. Since the melting point of 4-4' dichlorazoxybenzene has been recorded in the literature as 155° C. and that of the corresponding azo compound as 185-186° C., it was assumed that the reduction had gone as far as the azoxy compound with the further formation of a small amount of azo product. Hence, the reaction apparently followed the equation



The first trials making it apparent that the reaction ran smoothly without any thermal decomposition, systematic trials were made to determine the optimum conditions, the factors indicated below being considered. Unless otherwise stated, theoretical proportions of the reacting materials were used according to the preceding equation.

(1) **Temperature:** The reaction mixture seemed to withstand a fairly high temperature without decomposition. Hence, trials were made at the boiling point of the solvent used, 139° C., the reduction being approximately 100 per cent at that temperature, whereas at 60° C. the reduction was only 66.6 per cent complete. The oxidation of the alcohol to benzoic acid showed the same variation.

(2) **Amount of Caustic:** Trials using respectively 18/23 and 26/23 of the theoretical amount of sodium hydroxide showed no differ-

ence in results. A much higher amount of caustic tended to induce slight decomposition.

(3) Amount of Solvent: Though immediate decomposition resulted when no solvent was present, an increase over the original amount required to dissolve the nitro compound did not change the final results.

(4) Time of Reaction: The first trials being made at 4 hours, it was determined that an increase in this time-period was of no value, and that a decrease down as far as one and one-half hours produced the same results as the four hour period.

(5) Amount of Alcohol: An increase in the amount of alcohol used produced no further reduction of the nitro compound, whereas the alcohol itself was reduced partially to benzaldehyde and partially to benzoic acid.

(6) Method of Initial Mixing: When the nitro compound was introduced dissolved in the solvent into the mixture of alcohol and caustic, the reduction product was a mixture of azo and azoxy compounds. When the nitro compound was introduced in its solid form in the mixture of the alcohol, caustic, and solvent, the reaction seemed to be retarded sufficiently that the whole process ran smoothly to the azoxy stage, with a corresponding quantitative oxidation of the alcohol to benzoic acid.

An attempt was then made to identify the mixed products obtained in the first few runs, using a method suggested by Snowden<sup>1</sup>, whereby the melting points of various known mixtures of the two components were taken. However, this method fell short of our expectations, since the mixtures failed to give sharp melting points, the 50-50 mixture of azo and azoxy compounds varying, for example, over a range of 2.4° C. For an approximate determination, the following table, in which the average melting point is given, is satisfactory. Since the melting points of all reaction products were taken after the product had been crystallized from alcohol, we accordingly took the melting points of the crystals deposited from an alcoholic solution containing azo and azoxy compounds in the proportions named.

TABLE I. Melting Points of Mixtures of Azoxy and Azo Compounds

Azoxy Compound	Azo Compound	Melting Point	Azoxy Compound	Azo Compound	Melting Point
100%	0%	155.0°C.	50%	50%	163.9°C.
90%	10%	154.1°C.	40%	60%	169.5°C.
80%	20%	155.7°C.	30%	70%	173.0°C.
70%	30%	157.7°C.	20%	80%	176.7°C.
60%	40%	159.7°C.	10%	90%	181.2°C.
50%	50%	163.9°C.	0%	100%	185.5°C.

**II. Meta Nitrochlorbenzene and Benzyl Alcohol.** The same optimum conditions as determined for the para isomer were applied to the meta compound, with the result that it was reduced quantitatively to the pure 3.3' dichlorazoxybenzene (m. p. 97°C.), with the complete oxidation of

<sup>1</sup> J. Phys. Chem., 15, 841 (1911).

the alcohol to benzoic acid. Also, this reaction was found to run to completion at a much lower temperature than was the case in the para isomer, the autooxidation-reduction being 98.8 per cent, even at room temperature—25°C. Neither increase in temperature nor increase in the time-period induced any further reduction.

**III. Ortho Nitrochlorbenzene and Benzyl Alcohol.** When the conditions used successfully in the oxidation of benzyl alcohol by the para and meta nitrochlorbenzenes were applied to the ortho isomer, considerable thermal decomposition resulted immediately, the reaction being very violent. In an attempt to curb this decomposition, it was found that, by using a large excess of solvent and by introducing the caustic into a mixture of the other materials slowly, a product could be obtained from which a yellow orange substance could be extracted by means of petroleum ether. The best yield obtained by this method was 17.6 per cent of the theoretical.

The identification of this product was rather troublesome. Its crystals melted at 49° C. when obtained both from petroleum ether and from alcohol. Fractionation by crystallization was unsuccessful and no product corresponding to any of the reduction products to be expected could be obtained directly by reduction of the original nitro compound. Qualitative tests proved that the product contained either a nitroso, an azoxy, or an azo group. At the same time the melting point of the substance was materially raised by treating it with sulfuric acid—a method commonly used to convert an azoxy into the corresponding azo compound—indicating that we probably had, as before in the case of the para compound, a mixture of azo and azoxy compounds. A nitrogen determination by the Dumas method showed 9.91 per cent, as against 10.49 per cent required for the azoxy compound, a difference of 0.6 per cent. Since the compound in question volatilized very readily this difference was not considered surprising.

The yields of benzoic acid in these cases were all very low—15 per cent, or less. Some of the benzyl alcohol was oxidized to benzaldehyde, the distillates from the steam distillation of the reaction mixtures all showing the presence of benzaldehyde when tested with the Schiff reagent.