

## CONCERNING THE USE OF NITRO COMPOUNDS AS OXIDIZING AGENTS

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The use of nitro compounds as oxidizing agents upon aromatic side chains presents a type of double decomposition in which each of the reacting substances yields products of value. Thus if it were possible to oxidize the side chain of an aromatic alcohol, such as benzyl alcohol, the possible products would be benzaldehyde or benzoic acid on the one hand and azoxybenzene, azobenzene, hydrazobenzene or aniline on the other. If nuclear substitution products of nitrobenzene were used, such as the three nitrotoluenes—nitroanisoles, nitrophenetoles, dinitrobenzenes, etc, corresponding derivatives would be anticipated. The products formed and the amounts of each would depend upon temperature, pressure, acidity or alkalinity of the reacting medium.

### Experimental

Lyons and Smith<sup>2</sup> state that azobenzene is the chief product formed by autoclave reduction of nitrobenzene with sodium benzylate. These experiments have been repeated, using instead of the autoclave a three-necked flask equipped with a mercury seal stirrer, reflux condenser and dropping funnel. This apparatus permitted thorough and continuous stirring of the reacting materials. The use of xylene as a solvent was found helpful. The nitrogenous product was found to consist of a mixture of azoxybenzene and azobenzene, the greater per cent in most instances being azoxybenzene. In these experiments the sodium hydroxide and the benzyl alcohol were mixed in a three-necked flask and heated gently to facilitate the formation of sodium benzylate. After cooling the nitrobenzene was added dropwise, followed by the xylene. The amount of xylene required to bring about suitable consistency for stirring was 40 cc. The temperature was then slowly raised to 138-140° C. by means of a paraffin bath. The results of these experiments are as follows:

Table I

NaOH Gms.	Azoxy-azo- benzene Gms.	Azoxy-azo- benzene Yield %	Benzoic Acid Gms.	Benzoic Acid Yield %
3	7.19	64.69	7.26	64.37
5	8.52	69.73	8.61	76.87
6	9.58	78.36	9.18	81.96
7	9.18	75.12	9.98	89.51
8	9.05	73.85	9.32	83.19
9	9.16	74.94	9.83	87.77
10	9.01	73.78	9.90	88.39
11	9.27	75.86	9.86	87.99

<sup>1</sup> This paper is an abstract of a thesis for a Ph.D. degree at Indiana University.

<sup>2</sup> Lyons and Smith, J.A.C.S. 48:3156 (1926).

In determining the respective percentage yields of azoxybenzene and of azobenzene the method suggested by Snowden,<sup>2</sup> using the melting points of mixtures of known composition, was found to be satisfactory. The original article of Snowden did not contain the melting point of various mixtures of azoxybenzene and azobenzene, but this information was secured from a study of the same made by Fry and Cameron.<sup>3</sup> The melting points of mixtures of azoxybenzene and azobenzene obtained in four different experiments were determined and the respective percentages ascertained from the data of Fry and Cameron.

Table II

Azoxybenzene and Azobenzene Gms.	M. P. °C.	Azoxybenzene %	Azo-benzene %	Azoxybenzene Gms.	Azo-benzene Gms.	NaOH Gms.	Benzoic Acid Yield %
9.13	34.9	99.19	0.81	9.06	0.07	8	93.39
9.00	34.0	97.75	2.25	8.80	0.20	9	96.51
8.98	33.9	97.59	2.41	8.76	0.22	10	88.66
9.27	34.5	98.55	1.45	9.14	0.13	11	89.73

Tests of the steam distillates for benzaldehyde with Schiff's reagent were positive and those for aniline by the isonitrile reaction were negative in each experiment.

In a study of the action of sodium methylate upon nitrobenzene Fry and Cameron (loc. cit., p. 864) state that the increase of molar concentrations of pyridine, which is decidedly basic, promotes the acidic dissociation of sodium hydroxide, thereby increasing the extent of the reduction of nitrobenzene by sodium methylate. Furthermore, that pyridine, because of its marked property for forming salts and a great variety of unstable molecular compounds, lends support to the idea that it may function as a carrier of positive hydrogen ions and negative ONa ions, thereby facilitating the reaction:  $\text{CH}_3\text{OH} + \text{HONa} \rightarrow \text{HCOONa} + 2\text{H}_2$ . From analogy it would seem that pyridine might also have a favorable influence upon the extent of the reduction in the reaction under investigation. Accordingly, a study of the effects of concentrations of one-half mole and one mole of pyridine upon the reaction of nitrobenzene and benzyl alcohol was made.

Table III

Reaction mixture: benzyl alcohol, 10 gms.; nitrobenzene, 12 gms.; sodium hydroxide, 9 gms.; xylene, 50 cc.; temperature, 138-140°C.; time, 4 hours.

Pyridine	Azoxybenzene and Azobenzene Gms.	Yield %	Benzoic Acid Gms.	Benzoic Acid Yield %
½ Mole	7.75	63.42	7.60	67.85
1 Mole	4.80	39.28	5.69	50.80
None	9.27	75.86	9.71	86.70

<sup>2</sup> Snowden, J. Phy. Chem. 15:797 (1911).

<sup>3</sup> Fry and Cameron, J.A.C.S. 49:869 (1927).

Under the conditions employed it is to be noted that the presence of pyridine results in a decrease of both azoxybenzene and benzoic acid.

### The Three Isomeric Nitrotoluenes and Benzyl Alcohol

In continuing the study of the oxidation of benzyl alcohol with nitro compounds the three nitrotoluenes were used. The use of *o*-nitrotoluene as an oxidizing agent upon benzyl alcohol has been studied by Lyons and Smith (*loc. cit.*, p. 3167), who report that the autoclave reduction yielded *o*-azotoluene and benzoic acid. The experimental work of this part concerns a study of the other two isomeric nitrotoluenes as well as a repetition of the experiments of Lyons and Smith using the open apparatus equipped with a stirrer.

#### *p*-Nitrotoluene and Benzyl Alcohol

The first experiment involved placing in the three-necked flask 10 grams of benzyl alcohol, 9 grams of sodium hydroxide, and 25 grams of *p*-nitrotoluene dissolved in 50 cc. of benzene. No reaction was noted at room temperature, so the flask and contents were heated by means of a water bath until the boiling point of the mixture was reached. The reaction mixture was kept at 83-85° C. during the first three hours and at 95° C. for the last three. The weight of the residue from the steam distillation was 12.34 grams. The benzoic acid amounted to 11.29 grams, which corresponds to a 100 per cent yield. The residue from the steam distillation was orange yellow in color and consisted principally of *p*-azoxytoluene. The melting point of the crude product was 70-75° C. The melting point of pure *p*-azoxytoluene as recorded in the literature is 70° C.

The experiment was repeated under the same conditions, except the amount of sodium hydroxide was reduced to 6 grams. A greater yield of *p*-azoxytoluene was obtained, 14.05 grams, corresponding to a 68.78 per cent yield. The yield of benzoic acid was 100 per cent.

#### *o*-Nitrotoluene and Benzyl Alcohol

The reaction mixture consisted of 5 grams of benzyl alcohol, 4.5 grams of sodium hydroxide, 12.5 grams of *o*-nitrotoluene mixed with 30 cc. of benzene. The contents of the flask were heated to the boiling point of the mixture, 85-90° C., for seven hours. During the heating period the mixture turned light yellow in color, which changed to a reddish purple on steam distillation. The *o*-azotoluene which was formed was separated from the alkaline sodium benzoate solution by means of a freezing mixture. The weight of the *o*-azotoluene was 4.02 grams corresponding to a 42.0 per cent yield. A portion of the *o*-azotoluene was crystallized from alcohol in the form of red needles, *M. P.* 55° C. The weight of the benzoic acid was 3.78 grams, or a 72.83 per cent yield.

#### *m*-Nitrotoluene and Benzyl Alcohol

In this experiment 4.5 grams of sodium hydroxide were used, 3 grams of which were added at the beginning and 1.5 grams after one-half of the reaction time had elapsed. The reaction was conducted at

the boiling point of the mixture. The residue from the steam distillation was light yellow in color, melted at 32-36° C. and weighed 5.80 grams. The melting point of pure m-azoxytoluene is 37-39° C. Traces of either m-hydrazotoluene or m-azotoluene in this product may be responsible for the lower melting point. The weight of the benzoic acid was 3.55 grams, which represents a yield of 68.4 per cent. The yield of the m-azoxytoluene was 62.56 per cent.

### The Three Isomeric Nitroanisoles and Benzyl Alcohol

The sodium benzylate and the nitro compound were allowed to react at room temperature for three hours, after which they were heated to 100° C. for an additional two hours. The reduction compounds were all of a yellow color and turned deep red, which is characteristic of the azo compound, when subjected to further reduction by means of iron and hydrochloric acid. The melting points of the compounds were determined and compared with those recorded in the literature.

Table IV

Reaction mixture: 5 gms. of nitro compound; 50 cc. xylene; 3 hours at room temperature and 2 hours at 100°C.

Nitro Compound	Gms. Alcohol	Gms. NaOH	Gms. Azoxy Comp'd	% Azoxy Comp'd	M. P. Azoxy Comp'd	Gms. Benzoic Acid
o-Nitroanisole*	10	8	5.9	53.8	85-86°C.	4.5
m-Nitroanisole	10	8	3.2	76.0	51-52°C.	2.95
p-Nitroanisole	10	8	2.9	68.8	116.5-118°C.	3.30

\*13 gms. of the ortho compound was used in this experiment.

An experiment was made with o-nitroanisole in which the alkalinity was increased to 15 grams, other conditions remaining the same, whereby the yield of the o-azoxyanisole was increased to 4.5 grams corresponding to a 95.0 per cent yield.

### The Three Isomeric Nitrophenetoles and Benzyl Alcohol

The following table gives the results of these experiments:

Table V

Reaction mixture: 5 gms. of nitro compound; 50 cc. of xylene; 3 hours at room temperature and 2 hours at 100°C.

Nitro Compound	Gms. Alcohol	Gms. NaOH	Gms. Azoxy Comp'd	% Azoxy Comp'd	M. P. Azoxy Comp'd	Gms. Benzoic Acid
o-Nitrophenetole	5	5	3.5	76.4	101°C.	1.28
m-Nitrophenetole	5	5	3.1	67.6	46-47°C.	1.36
p-Nitrophenetole*	10	8	6.3	55.6	135°C.	4.00

\*13 grams of the para isomer was used in this experiment.

An experiment was made with *o*-nitrophenetole in which the alkalinity was increased to 15 grams, other conditions remaining the same, whereby the yield of the *o*-azoxyphenetole was increased to 4.5 grams corresponding to a 98.2 per cent yield.

#### **m-Dinitrobenzene and Benzyl Alcohol**

The possibilities of the formation of intermediate products are still more extended with the presence of two nitro groups on the benzene ring. Lyons and Smith (*loc. cit.*, p. 3166) report that *m*-dinitrobenzene and benzyl alcohol react producing ammonia and a charred mass when the experiment is carried out in the autoclave at a temperature of 138-140° C. Conditions have been found which permit the reaction to proceed under control without the decomposition of the organic material.

Ten grams of benzyl alcohol were placed in a three-necked flask. Eight grams of sodium hydroxide were added to the reaction mixture in portions of one gram each at intervals of one-half hour. A solution of 10.4 grams of *m*-dinitrobenzene in 50 cc. of xylene was added dropwise to the mixture at room temperature. The heat of reaction of the two substances was sufficient to keep the temperature at approximately 50° C. The experiment was run for five and one-half hours. After the initial heat of reaction had subsided the temperature was maintained at 30° C. At the end of the heating period the light brown mixture was steam distilled. The weight of the air-dried residue was 7.78 grams. A portion of the residue was dissolved in hot benzene, from which it separated as a pale yellow non-crystalline mass, M. P. 228-233° C. The melting was preceded by shriveling and accompanied by slight decomposition. A portion of the substance dissolved in hot glacial acetic acid was heated to boiling for fifteen minutes with a small portion of chromic acid. The mass which separated from the cooled mixture was washed several times with ether to free it from the acids and dissolved in hot toluene, from which it separated as a light yellow flocculent precipitate. The dried substance was a pale yellow powder melting at 239-241° C. (I). Solution of the substance in hydrochloric acid and treatment with sodium nitrite showed the compound free from amino groups.

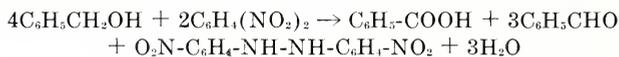
A quantitative determination of the nitrogen in the compound gave the following data: 0.1335 grams of the substance gave 25.2 cc. of nitrogen at 27.0° C. and 747.5 mm. = 20.63 per cent.

It was surmised that some of the nitrogen was present as unreduced nitro groups and that the compound under investigation was a dinitrohydrazo compound of the formula  $C_{12}H_{10}N_4O_4$  (N = 20.43 per cent) and a molecular structure 3-3'-O<sub>2</sub>N-C<sub>6</sub>H<sub>4</sub>-NH-NH-C<sub>6</sub>H<sub>4</sub>-NO<sub>2</sub>.

The compound was subjected to further reduction by boiling with a mixture of 50 cc. of ammonium hydroxide and 50 cc. of ammonium hydrosulphide for two hours. At the end of the heating period the mixture was filtered and water added to the filtrate to cause the precipitation of the reduction product. The substance, twice crystallized from alcohol, was found to melt sharply at 145°C. The crystals which grew from the alcohol were long yellow needles which were almost insoluble in water and ether and readily soluble in alcohol. The substance

3-3'-diaminohydrazobenzene, M. P. 151° C., described in the literature was found in exact agreement with the above preparation with the exception of the slightly higher melting point. The general department and the analytical data are such that the identity of the compound (I) is established as 3-3'-dinitrohydrazobenzene, a substance not heretofore described in the literature.

A balanced equation accounting for all products of this reaction may be written as follows:



Since it was not possible to heat the reaction mixture above 100° C. on account of the decomposition, benzene instead of xylene was used as the solvent for the m-dinitrobenzene. Heating the reaction mixture to 70° C. after the initial heat of reaction had subsided was found to increase the yield of both the benzoic acid and the 3-3'-dinitrohydrazobenzene. The following table shows the effect of heating reaction mixtures of the same composition for different lengths of time at 70° C. In all of the experiments the sodium hydroxide was added in portions of one gram at intervals of one-half hour.

Table VI

Reaction mixture: benzyl alcohol, 10 gms.; m-dinitrobenzene, 8 gms.; sodium hydroxide, 8 gms.; benzene, 70 cc.; temperature 70°C. after initial heat of reaction had subsided.

Hours at 70°C.	3-3'-Dinitrohydrazobenzene Gms.	Yield %	Benzoic Acid Gms.	Benzoic Acid Yield %
1½	4.17	64.1	6.15	63.40
2	4.80	73.8	6.90	61.60
6	5.10	97.7	9.52	85.00
8	6.65	86.65	7.68	68.57

In the next group of experiments the amount of sodium hydroxide was increased to 19.5 grams and the time during which the reaction mixture was heated to 70° C. was made the variable factor.

Table VII

Reaction mixture: benzyl alcohol, 10 gms.; m-dinitrobenzene, 12.6 gms.; sodium hydroxide, 19.5 gms.; benzene, 70 cc.; temperature, 70°C. after the initial reaction had subsided.

Hours at 70°C.	3-3'-Dinitrohydrazobenzene Gms.	Yield %	Benzoic Acid Gms.	Benzoic Acid Yield %
6	8.65	84.22	10.63	94.91
7	7.15	69.62	10.29	91.87
8	6.94	67.57	10.57	94.37

## SUMMARY

1. The study of the reactions of sodium benzylate with aromatic nitro compounds as oxidizing agents has been extended to include *o*-, *m*-, *p*-nitrotoluene, *o*-, *m*-, *p*-nitroanisole, *o*-, *m*-, *p*-nitrophenetole and *m*-dinitrobenzene.

2. Optimum conditions have been found for obtaining the maximum percentage yields of benzoic acid and of the respective azoxy-, azo-, or nitrohydrazocompounds.

3. The preparation and properties of the new compound, 3-3'-dinitrohydrazobenzene, are reported.

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## DETERMINATION OF THE DEGREE OF HYDRATION OF MAGNESIA IN DOLOMITIC LIMES

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Hydrated limes made from dolomites quarried at Woodville and Gibsonburg, Ohio, are plastic, and hydrated limes made from dolomites quarried at all other places are not plastic. No reason for this unusual and valuable property of the Ohio dolomites has ever been discovered. All experiments and experiences indicate that this property depends in some way upon the magnesia.

At the plastic lime plants in Ohio the greatest care is taken to burn the lime at the lowest possible temperature. Too high a temperature is known to prevent the plastic property. No other single factor in manufacturing seems important inasmuch as all the other factors or conditions such as type and size of kiln, kind of fuel, type of hydrator, quantity of water used in hydration, and type of mill for final grinding are different in the different plants. On the other hand, no one has been able to burn any rock other than from this Ohio district into a plastic finishing hydrate in the ordinary commercial kilns. The scientific reason for this unusual quality of the Ohio finishing limes is interesting both in theory and in practice.

The low temperature of burning of these Ohio limes without doubt produces active magnesia. Campbell<sup>2</sup> showed that magnesia made by burning magnesium carbonate at 1000° C. hydrated to the extent of 18 per cent in one day, but if it was made at a temperature of 1100° the hydration dropped to 7 per cent, and if burned at 1200° the hydration was only 0.43 per cent. Johnston<sup>3</sup> found that magnesite decomposed at 756° and calcium carbonate rock at 898°. Artificially made magnesium carbonate decomposed at a lower temperature. A natural dolomite de-

<sup>1</sup> A portion of the thesis submitted by Mr. Fox for the Ph.D. degree at Indiana University in 1927. Delay in publication was due to the death of Mr. Fox.

<sup>2</sup> Jour. Ind. Eng. Chem., 1:665 (1909).

<sup>3</sup> J. Amer. Chem. Soc., 32:938 (1910).