the former. Hot naphtha and ligroin readily dissolved it. With hydrochloric acid this new derivative combined to form a hydrochloride and with sulphuric acid to form a sulphate. The hydrochloride was prepared by covering the condensation product with water and adding concentrated hydrochloric acid by drops. The solid slowly went into solution but, after a few minutes' standing, separated again as long, feathery needles. These were quite soluble in water and still more readily in the presence of a slight amount of hydrochloric acid. The sulphate was prepared in a similar manner from sulphuric acid but it was much less soluble and therefore separated more readily and completely.

With ferric chloride the hydrochloride gave a thick, reddish brown precipitate which dried to a brownish powder. This was soluble in alcohol and possessed a sharp astringent taste quite unlike the almost tasteless free valeryl base. This ferric derivative is analogous to ferripyrine—the ferric chloride compound of antipyrine. With Mayer's reagent both the hydrochloride and sulphate gave a white, curdy precipitate. When valeryl-di-antipyrine is warmed with concentrated sulphuric acid and sugar it gives a distinct odor like that of valerianic acid.

A determination of the nitrogen contained in valeryl-di-antipyrine gave 13 per cent. nitrogen. Calculated for $C_{27}H_{32}O_2N_4$, the nitrogen would be 12.3.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE NEBRASKA WESLEYAN UNIVERSITY.]

ON THE REDUCTION OF SOME AROMATIC NITRO-COMPOUNDS.

BY F. J. ALWAY AND M. D. WELSH.

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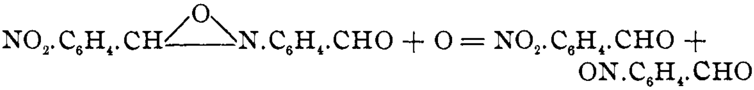
IN THE following paper we give the results thus far obtained from a study of the reduction of *p*-nitrobenzaldehyde and *m*-nitrobenzaldehyde in neutral solution. As this work is for a few months necessarily interrupted and as we will be unable to continue it together we consider it best to publish the results already at hand. The investigation was undertaken in the hope that we might be able to isolate from the reduction products of the nitrobenzaldehydes the corresponding N-formylphenyl ethers of the nitrobenzaldoximes,[1] of the formula,

$$NO_2.C_6H_4.CH\overset{O}{\overline{\qquad}}N.C_6H_4.CHO.$$

As these ethers, when oxidized, give almost the theoretical yield of the corresponding nitrosobenzaldeyhdes,[2] according to the equation,



$$NO_2.C_6H_4.CH\overset{O}{\overline{\qquad}}N.C_6H_4.CHO + O = NO_2.C_6H_4.CHO + ON.C_6H_4.CHO,$$

an economical method of preparing them would make the corresponding nitrosoaldehydes readily accessible compounds. The yield of these ethers obtained by the electrolytic reduction of the nitrobenzaldehydes, dissolved in concentrated sulphuric acid, is unsatisfactory, varying from 20 to 40 per cent. We failed to obtain these ethers by reduction in neutral solution. Various hydroxylaminobenzaldehyde derivatives were formed, all of which on oxidation yielded the corresponding nitroso-compounds.

In a previous article[3] one of us has described some of the phenomena observed when a solution of *p*-nitrobenzaldehyde in boiling water is treated with zinc dust.

By the action of zinc dust upon aromatic nitro-compounds in neutral aqueous or alcoholic solution, with or without addition of ammonium salts, Bamberger[4] has obtained a large number of hydroxylamino-compounds analogous to β-phenyl hydroxylamine, $C_6H_5NH.OH$. These are characterized by the ease with which they decompose, yielding a great variety of compounds. Wislicenus[5] has obtained the same compounds by the action of amalgamated aluminum upon the nitro-compounds in ethereal or alcoholic solution. Zinc amalgam with aluminum sulphate solution acts similarly.[6] By the oxidation of the hydroxylamine derivatives the corresponding nitroso-compounds were obtained. The latter are readily volatile with steam and, with the exception of the blue-green 3,4-dimethyl-nitrosobenzene[7] and the yellow

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[1] *Ber. d. chem. Ges.*, **29**, 3037 (1896).

[2] *Am. Chem. J.*, **28**, 38.

[3] *Loc. cit.*

[4] *Ber. d. chem. Ges.*, **27**, 1548 (1894)'

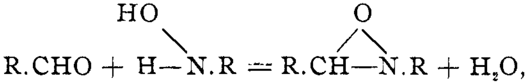
[5] *Ibid.*, **29**, 494 (1896).

[6] *Ibid.*, **29**, 863 (1896).

[7] *Ann. Chem.* (Liebig), **316**, 2857 (1901).

p-nitrosobenzaldehyde,[1] are colorless in the solid state. When fused or in solution they are green. Bamberger[2] has recently shown that 1-nitroso-2,6-xylene and nitrosomesitylene, whose cold solutions are much less intensely colored than the hot solutions, consist largely of double molecules in the former and of single molecules in the latter. Evidently the green color of the nitroso-compounds depends upon the presence of single molecules.[3] We find that *p*-nitrosobenzaldehyde, unlike the isomeric meta-compound, resembles nitrosomesitylene. Further, it is volatile with steam only when in the monomolecular condition.

The readiness with which aromatic hydroxylamines condense with aldehydes, according to the equation,



$$R.CHO + H-\overset{HO}{N}.R = R.\overset{O}{CH-N}.R + H_2O,$$

has rendered the isolation of the hydroxylaminobenzaldehydes difficult. The above reaction takes place so readily that to obtain the condensation product it is merely necessary to mix the alcoholic solutions of the compounds and allow the mixture to stand at the temperature of the room over night.

Bamberger and Friedmann[4] obtained, by the action of zinc dust upon *m*-nitrobenzaldehyde, a substance of the formula $(C_7H_5ON)_x$, which is very insoluble in all ordinary organic solvents and which, when oxidized by ferric chloride, yields, *m*-nitrosobenzaldehyde. Gattermann,[5] by the electrolytic reduction of *p*-nitrobenzaldehyde and of *m*-nitrobenzaldehyde, dissolved in concentrated sulphuric acid, obtained the two isomeric N-formylphenyl ethers of the nitrobenzaldoximes. These compounds are insoluble in ordinary solvents but may be recrystallized from pyridine. Each, on oxidation, yields together with the nitrosobenzaldehyde a small amount of what has since been found to be the corresponding azoxybenzaldehyde.[6]

Kirpal,[7] using zinc dust as a reducing agent, tried to obtain the N-*p*-formylphenyl ether of *p*-nitrobenzaldoxime. In this he was

[1] *Ber. d. chem. Ges.*, **29**, 3037 (1896).

[2] *Ibid.*, **34**, 3877 (1901).

[3] *Ztschr. phys. Chem.*, **26**, 50.

[4] *Ber. d. chem. Ges.*, **28**, 250 (1895).

[5] *Ibid.*, **29**, 3037 (1896).

[6] *Am. Chem. J.*, **28**, 34.

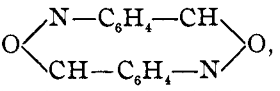
[7] *Ber. d. chem. Ges.*, **30**, 1597 (1897).

not successful but obtained a yellow solution which on oxidation yielded *p*-nitrosobenzaldehyde.

Later, Kalle & Co.[1] patented a process for the preparation of aromatic hydroxylamine compounds by the treatment of nitrocompounds with zinc dust and an aqueous solution of an ammonium salt in the cold. It was stated that *p*-hydroxylaminobenzaldehyde, like various other hydroxylamine derivatives, was obtained by this method in quantitative yield. No details of the method and no description of the aldehyde were given. By this method phenylhydroxylamine may be obtained in almost quantitative yield but we were unable to obtain a satisfactory yield of the hydroxylaminobenzaldehyde.

Our knowledge of the hydroxylamino- and nitrosobenzaldehydes, may, accordingly, be summarized as follows: *m*-nitrobenzaldehyde and *p*-nitrobenzaldehyde, when subjected to electrolytic reduction in concentrated sulphuric acid solution, yield the corresponding N-formylphenyl ethers of the nitrobenzaldoximes, which, by oxidation with ferric chloride, give *m*-nitrosobenzaldehyde and *p*-nitrosobenzaldehyde. The same aldehydes when reduced by zinc dust form substances of unknown nature, which, by oxidation, yield nitrosobenzaldehydes identical with those mentioned above.

While we obtained various condensation products of the hydroxylaminobenzaldehydes neither of the above-mentioned insoluble ethers was detected among the reduction products. The insoluble compound obtained by Bamberger and Friedmann,[2] from *m*-nitrobenzaldehyde evidently has the formula,



and is not identical with the insoluble secondary product of electrolytic reduction as has been suggested.[3] *p*-Nitrobenzaldehyde forms a similar compound together with one or more insoluble condensation products of *p*-hydroxylaminobenzaldehyde.

EXPERIMENTAL.

Kirpal[4] boiled 200 cc. of water with 4 grams *p*-nitrobenzalde-

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[1] D. R. P. 899.781: *Chem. Centrbl.*, 1, 351 (1897).

[2] *Loc. cit.*

[3] *Ber. d. chem. Ges.*, **29**, 3037 (1896).

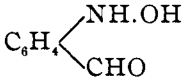
[4] *Loc. cit.*

hyde and 20 grams zinc dust for three minutes. A yellow solution was obtained, from which, by oxidation with ferric chloride solution, *p*-nitrosobenzaldehyde was obtained and from which, by the action of the air, *p*-azoxybenzaldehyde was formed. He was unable to isolate the hydroxylaminobenzaldehyde. Our repetition of Kirpal's work confirmed his results. The residue of zinc dust was colored slightly yellow. Attempts to extract this yellow substance with boiling water yielded *p*-azoxybenzaldehyde and a compound crystallizing in red needles and melting at 222° which has not been further investigated. By using benzene, instead of water, only *p*-azoxybenzaldehyde was obtained.

That these are decomposition products of the substance that colors the zinc dust yellow is evident from the fact that when covered with a great excess of ferric chloride solution and subjected to distillation with steam, *p*-nitrosobenzaldehyde was obtained. Neither of the two substances mentioned, when treated in the same manner, gave a nitroso-compound. That the nitroso-compound, in this case, does not result from the oxidation of the simple hydroxylaminobenzaldehyde may be seen from the following. The residue was treated with boiling alcohol and filtered. The filtrate was yellow in color. With ferric chloride it gave a very small quantity of *p*-nitrosobenzaldehyde. and when shaken with sodium hydroxide solution in contact with the air. *p*-azoxybenzaldehyde was formed. Using the same amount of alcohol in each case the extraction was repeated four times. Each of the solutions (except the last), so obtained, had the same color and gave the same oxidation products. The last was almost colorless and the zinc dust showed no trace of yellow. No *p*-nitrobenzaldehyde could be obtained from the oxidation products by recrystallizing them from glacial acetic acid.

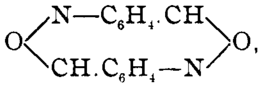
By using ammonium chloride the reduction product was obtained free from unchanged zinc. The latter, when present, seriously interferes with the investigation of the insoluble reduction product. A mixture of 10 grams *p*-nitrobenzaldehyde, 10 cc. alcohol, 30 cc. water and 10 cc. 2N ammonium chloride solution was warmed to 70°. Ten grams of zinc dust were added and the mixture violently agitated three to four minutes, keeping the temperature at 70°. The mixture became green, then yellow.

The whole was at once filtered under suction. The filtrate was light red in color and the residue yellow. The latter was extracted with 100 cc. boiling alcohol. The filtrate from this resembled the first except that the color was of a lighter shade. By the addition of water to these two filtrates we obtained a yellow crystalline substance, soluble in alcohol, ether, benzene and hot water. Aqueous alkalies imparted a deep red coloration to its aqueous and alcoholic solutions, from which the color slowly faded, *p*-azoxybenzaldehyde separating out. With ferric chloride solution it gave *p*-nitrosobenzaldehyde. It was unstable when exposed to the air in moist condition, various red and yellow compounds being formed. On account of the ease with which it underwent decomposition we failed to obtain it in pure condition from the limited amount of *p*-nitrobenzaldehyde that we had at our disposal. A nitrogen determination was made of a specimen obtained by recrystallizing the crude substance from absolute alcohol and drying the crystals at once. It melted at 98° to 101°. Calculated for $HO.NH.C_6H_4.CHO$, $N = 10.2$. Found, 10.1. It was evidently *p*-hydroxylaminobenzaldehyde,



$$C_6H_4\left\langle\begin{matrix}NH.OH\\CHO\end{matrix}\right.$$

The yellow residue of zinc oxide remaining after the treatment with alcohol was extracted six times with boiling alcohol, using 100 cc. each time. All the filtrates so obtained, acted alike. All were yellow in color, gave no precipitate with water, gave *p*-nitrosobenzaldehyde with ferric chloride and *p*-azoxybenzaldehyde with aqueous alkalies. No *p*-nitrobenzaldehyde was obtained by the oxidation. The residue was still yellow in color. It was extracted twice with boiling benzene and the cooled filtrates treated with ligroin. The first gave a yellow precipitate, the second was colored yellow but gave no precipitate and on complete evaporation left only a trace of yellow solid. The residue of zinc dust was colored brown. It was extracted twice with boiling alcohol without any sign of the extraction being complete. Both of these filtrates were similar to the other alcoholic filtrates in color and reactions. The yellow compound precipitated from benzene by ligroin melted at 205° to 206° and was very sparingly soluble in boiling alcohol, forming a yellow solution which gave the characteristic red coloration with aqueous alkalies, and yielded *p*-nitrosobenzaldehyde but no *p*-nitrobenzaldehyde when oxidized by ferric chloride. This compound, which was also obtained in small quantity by the action of amalgamated aluminum upon *p*-nitrobenzaldehyde in ethereal solution, has not been further investigated. The brown residue on oxidation yielded *p*-nitrosobenzaldehyde. It gave no *p*-nitrobenzaldehyde when covered with dilute sulphuric acid and treated with steam. The substance causing the brown color did not dissolve in boiling pyridine. It is evident from the above that there was, at most, no appreciable amount of the N-*p*-formylphenyl ether of *p*-nitrobenzaldoxime among the reduction products. The yellow and brown substances were condensation products of *p*-hydroxylaminobenzaldehyde. the former being probably



$$O\begin{array}{l}\diagup N{-}C_6H_4.CH\diagdown \\ \diagdown CH.C_6H_4{-}N\diagup\end{array}O,$$

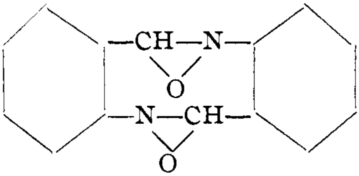
which, when warmed with aqueous alcohol, changes partly into the simple hydroxylaminobenzaldehyde, according to the equation

$$C_{14}H_{10}O_2N_2 + 2H_2O = 2C_7H_7O_2N.$$

If the mixture of *p*-nitrobenzaldehyde, alcohol, water and ammonium chloride solution be kept at 16° to 18° and the zinc dust added in small portions in the course of two hours, frequently shaking the mixture, the same compounds are obtained but the amount of the condensation products is less. If the mixture of all the compounds be made in the cold and left to itself the temperature rises until the liquid boils violently. The reaction product is brown in color and reacts in the same manner as the insoluble condensation product already described.

By the action of amalgamated aluminum upon the ethereal solution of *p*-nitrobenzaldehyde, similar condensation products were obtained.

m-Nitrobenzaldehyde, when treated in the same manner, yielded a brownish yellow solution from which *m*-nitrosobenzaldehyde and *m*-azoxybenzaldehyde were obtained by methods analogous to those used in the case of the para-compounds. Mixed with the zinc oxide and unchanged zinc was the gray substance, insoluble in solvents, which Bamberger and Friedmann have found to have the formula $(C_7H_5ON)_x$. Analogous to the para-compound it gave a yellow solution when boiled with aqueous alcohol. The alcoholic solutions, so obtained, yielded small amounts of *m*-nitrosobenzaldehyde and *m*-azoxybenzaldehyde. The insoluble substance is probably the inner anhydride of *m*-hydroxylaminobenzaldehyde,



p-Nitrosobenzaldehyde.—When this compound is prepared by the oxidation of the N-*p*-formylphenyl ether of *p*-nitrobenzaldoxime the yield varies from 10 to 15 per cent. of the weight of *p*-nitrobenzaldehyde reduced. It is much more readily obtained as follows: The red colored solution, described above, containing *p*-hydroxylaminobenzaldehyde is at once treated with an excess of 10 per cent. ferric chloride solution and allowed to stand for a few hours. The yellow *p*-nitrosobenzaldehyde gradually separates out. Steam is passed through the mixture, the nitroso compound being carried over. The yield varies from 15 to 20 per cent. of the weight of the nitrobenzaldehyde used. The yield may be increased by oxidizing the insoluble condensation products.

The liquid that collects in the receiver, when this compound is separated from the ferric chloride by distillation with steam, is deep green in color. On cooling, the color gradually disappears, the yellow nitroso-compound separating out. If this is filtered out and dried at a low temperature it sometimes shows a distinctly green tint. The filtrate, if the mixture has been allowed to stand long enough, is colorless. By recrystallizing the nitrosobenzaldehyde, from glacial acetic acid, yellow needles are obtained. When these are dried and boiled with water they do not dissolve, the liquid remaining colorless. If a current of steam be passed through the boiling mixture of water and *p*-nitrosobenzaldehyde, the same result is not always observed. Sometimes no nitroso-compound is carried over with the steam, while at other times it passes over very slowly, collecting in the receiver as a green solution from which, on cooling, very little nitrosobenzaldehyde separates. In one experiment in which the distillate was colorless after steam had been passed through the mixture for some time, finely divided calcium chloride was added in small portions, a burner being kept under the distilling flask. When the temperature in the latter had thus been raised to 130° the *p*-nitrosobenzaldehyde floated unchanged on the surface of the liquid. The addition of the next portion of calcium chloride, which raised the temperature to 140°, caused the nitroso-compound to pass over very rapidly. Very impure specimens of the nitrosoaldehyde were purified by adding them to this calcium chloride solution which was kept at the boiling-point while steam was passed through. When the mixture of water and *p*-nitrosobenzaldehyde collecting in the receiver in the preparation of the latter is divided into two portions and the one immediately subjected to the action of a current of steam while the other is allowed to stand ten or twelve hours before undergoing similar treatment, a marked difference is to be noticed. In the case of the first the nitrosobenzaldehyde passes over rapidly but in the second very slowly. It dissolves in hot solvents, as acetic acid, alcohol and acetone with a deep green color. As these cool, the color slowly changes to yellow with or without separation of crystals. While the green color usually disappears within a few hours it sometimes remains for several days. As *p*-nitrosobenzaldehyde melts at 137° it would necessarily pass into the green or monomolecular condition when brought into contact with the calcium chloride solution boiling at 140°.

m-Nitrosobenzaldehyde, unlike the isomeric para-compound, is colorless in the solid state, distils readily with steam and dissolves in cold solvents with a deep green color.

UNIVERSITY PLACE, NEB.,
June 20, 1902.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE NEBRASKA WESLEYAN UNIVERSITY.]

ON THE NITRATION OF BENZYL CHLORIDE.

BY FREDERICK J. ALWAY.

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WHILE the three nitrobenzyl chlorides are well-known compounds and the action of fuming nitric acid upon benzyl chloride