

tion 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.,
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[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

has been described by different investigators, no definite information has been furnished as to the yield of *p*-nitrobenzyl chloride obtained at different temperatures. There is, also, little agreement as to the nature of the oily by-product.

Beilstein and Geitner¹ were the first to obtain *p*-nitrobenzyl chloride from benzyl chloride. Grimaux² repeated their work. Strakosch³ improved the method by keeping the temperature at -15° during the operation. The later investigators, Abelli,⁴ Nölting⁵ and Klumpf,⁶ followed the method of Strakosch. As attempts made in this laboratory to verify the statement of Strakosch, that very little except *p*-nitrobenzyl chloride is obtained at the above-mentioned temperature and that the oily by-product consists essentially of unchanged benzyl chloride, were unsuccessful, various nitration methods were tried in order to determine the conditions under which the maximum yield of *p*-nitrobenzyl chloride is obtained. It was found that the yield of *p*-nitrobenzyl chloride under the most favorable conditions, was 50 per cent. of the theoretical and that the oily by-product obtained by the different methods consists of nitrobenzyl chlorides, in some cases mixed with dinitrobenzyl chloride. If a mixture of slightly more than the theoretical amount of fuming nitric acid with concentrated sulphuric acid be added to cooled benzyl chloride a very low temperature is not required to ensure the maximum yield. If a considerable excess of fuming nitric acid be used, dinitrobenzyl chloride is formed. Ordinary concentrated nitric acid may be used instead of the fuming acid, the yield of *p*-nitrobenzyl chloride, however, being less.

EXPERIMENTAL.

The crude nitration product obtained in each of the cases described below, was added to a mixture of ice and water. The more or less pasty solid, so obtained, was transferred to a Büchner funnel and subjected to powerful filtration until oily drops ceased to pass through. The residue, when recrystallized

¹ *Ann. Chem.* (Liebig), **139**, 337 (1866).

² *Ibid.*, **145**, 46 (1868).

³ *Ber. d. chem. Ges.*, **6**, 1059 (1873).

⁴ *Ibid.*, **16**, 1232; *Gazz. chim. ital.*, **13**, 97 (1883).

⁵ *Ber. d. chem. Ges.*, **17**, 385 (1884).

⁶ *Ann. Chem.* (Liebig), **224**, 96 (1884).

from alcohol, gave pure *p*-nitrobenzyl chloride. By treating the mother-liquor with water a further yield was obtained. In estimating the yield of solid and liquid nitration products, the residue, without further treatment, was weighed, while the liquid was washed with water, separated and dried before weighing.

Three hundred grams of fuming nitric acid (sp. gr. 1.5) were placed in a flask surrounded by a mixture of ice and salt. Benzyl chloride was added drop by drop. As each drop came in contact with the acid a reddish brown coloration was produced. At first this coloration quickly disappeared but as the addition of benzyl chloride proceeded the color disappeared more and more slowly until, after 120 grams of benzyl chloride had been added, it remained. During the operation the temperature was kept at -15° to -13° . Yield of solid, 85 grams; of liquid, 85 grams. Time required, two hours and thirty minutes. The yield of the two products was the same when the temperature was kept at -25° , as well as when fuming nitric acid was added to benzyl chloride kept at -15° . At 20° to 30° the yield of the solid was only half so great and of liquid half as great again.

The following was found to be the most satisfactory method of obtaining *p*-nitrobenzyl chloride. A mixture of 90 grams fuming nitric acid and 180 grams concentrated sulphuric acid was added to 120 grams benzyl chloride, kept at -5° to -10° . After about half the acid mixture had been added, white crystals began to separate. At the end of the operation the contents of the flask were almost solid. Yield of solid, 85 grams; of liquid, 87 grams. Time required one hour and ten minutes. At temperatures above 0° the yield was less.

To determine the action of a considerable excess of fuming nitric acid, 40 grams of benzyl chloride were added to a mixture of fuming nitric acid (80 grams) and concentrated sulphuric acid (180 grams). The temperature was kept below 40° . After being allowed to stand two hours the mixture was poured into ice water. An oily liquid separated. This passed through the filter, leaving no residue. It was washed well with water, dried with calcium chloride, filtered and analyzed. It consisted essentially of one or more dinitrobenzyl chlorides.

The specific gravity and the nitrogen content were determined

in the case of each of the oily liquids obtained by the above methods.

	Calculated for NO ₂ .C ₆ H ₄ .CH ₂ Cl.	Calculated for (NO ₂) ₂ C ₆ H ₃ .CH ₂ Cl.	I.	Found. II.	III.
Nitrogen.....	8.2	12.9	8.7	8.6	12.1
Specific gravity at 27°	1.333	1.332	1.476

From the above it is evident that not only is the yield of *p*-nitrobenzyl chloride practically the same but that the by-products are also the same, whichever of the two methods of preparing *p*-nitrobenzyl chloride is employed. The further investigation of the dinitrobenzyl chloride was not proceeded with as Cohn and Friedlander¹ have recently obtained *o-p*-dinitrobenzyl chloride by an analogous method and have announced their intention of soon publishing the details of their work.

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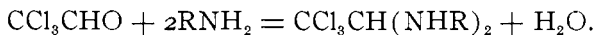
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA].

CONDENSATION OF CHLORAL WITH THE NITRANILINES.

BY ALVIN S. WHEELER AND H. R. WELLER.

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CHLORAL forms condensation products readily with aromatic amines according to the equation



O. Wallach² effected the condensation of chloral with aniline, the product being trichlorethylidenediphenylamine,



In 1898 Eibner³ and Baskerville, working independently, carried out the condensation of chloral with *p*-nitraniline. Baskerville's results are incorporated in the present paper. Our investigation shows that similar products are obtained with ortho- and meta-nitraniline. The melting-points of the condensation products form an ascending series as in the nitranilines. The chloral used was prepared by distilling chloral hydrate with concentrated sulphuric acid and the nitranilines were recrystallized until pure.

Trichlorethylidenedi-o-nitrophenamine,

¹ *Ber. d. chem. Ges.*, **35**, 1266 (1902).

² *Ann. Chem.* (Liebig), **173**, 278.

³ *Ibid.*, **302**, 366.