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

	Calculated for $NO_2.C_6H_4.CH_2Cl$.	Calculated for $(NO_2)_2C_6H_3.CH_2Cl$.	Found. I.	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 Friedlander[1] have recently obtained *o*-*p*-dinitrobenzyl chloride by an analogous method and have announced their intention of soon publishing the details of their work.

UNIVERSITY PLACE, NEB.,
June 16, 1902.

[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.

Received July 28, 1902.

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

$$CCl_3CHO + 2RNH_2 = CCl_3CH(NHR)_2 + H_2O.$$

O. Wallach[2] effected the condensation of chloral with aniline, the product being trichlorethylidenediphenylamine,

$$CCl_3CH(NHC_6H_5)_2.$$

In 1898 Eibner[3] 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,

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

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

[3] *Ibid.*, **302**, 366.

$CCl_3CH(NHNO_2C_6H_4)_2$.—Five grams of *o*-nitraniline were suspended in 75 cc. of benzene and 5 grams of chloral were added. Two and one-half grams of chloral are required by theory. The crystalline nitraniline was quickly converted into a flocculent precipitate which melted at 162°. The benzene solution was evaporated down to a gummy mass on the water-bath, the residue was taken up with boiling alcohol and, upon cooling, a beautiful yellow crystalline precipitate settled out. The two precipitates were recrystallized from hot alcohol until the melting-point was raised to 171°. A determination of chlorine gave 26.10 per cent. Calculated for $C_{14}H_{11}O_4N_4Cl_3$, 26.22 per cent.

Trichlorethylidenedi-*o*-nitrophenamine crystallizes from hot alcohol in yellow transparent rectangular plates and melts at 171°. It is insoluble in ether and ligroin but soluble in acetone, chloroform and benzene. It may be purified by dissolving in glacial acetic acid and precipitating with water. It is not decomposed by water and is insoluble in hot hydrochloric acid. The yield was about 45 per cent. of the theory.

Trichlorethylidenedi-m-nitrophenamine, $CCl_3CH(NHNO_2C_6H_4)_2$.—Five grams of *m*-nitraniline were suspended in 125 cc. benzene and 5 grams of chloral were added. The needle crystals of *m*-nitraniline were quickly converted into a flocculent precipitate, at first yellowish white but soon assuming a rich flesh color which was permanent. The crude substance decomposed at 208°. On digestion with acetone the impurities were dissolved out and the melting-point was raised to 212°. A determination of chlorine gave 26.18 per cent. Theory requires 26.22 per cent.

Trichlorethylidenedi-*m*-nitrophenamine crystallizes from alcohol in rectangular plates of a rich flesh color. It melts at 212°. It is readily soluble in alcohol and insoluble in ether, ligroin and benzene. It is decomposed by hot water and by hydrochloric acid, chloral and *m*-nitraniline being re-formed. The yield of the condensation product is about 30 per cent of the theory.

The reaction seems to run a different course if the materials are boiled for some time under a reflux condenser. Under these circumstances a body is obtained which, upon recrystalling once from alcohol, melts at 89°. A single analysis for chlorine showed the presence of 32.3 per cent. This substance will be examined further.

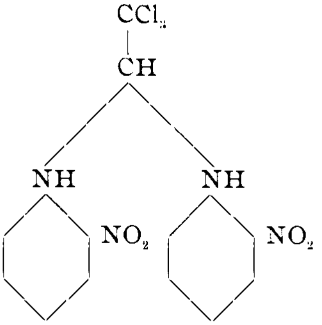
Trichlorethylidenedi-p-nitrophenamine, $CCl_3CH(NHNO_2C_6H_4)_2$.—Ten grams of *p*-nitraniline were suspended in 100 cc. benzene, and 15 grams of chloral were added slowly. A heavy yellow precipitate formed immediately. After heating for some time on the water-bath to complete the reaction, the precipitate was filtered off and dried. The melting-point of the crude substance was 210°. It is extremely insoluble and by removing the impurities with small amounts of cold acetone the melting-point was raised to 216°. A determination of the chlorine gave 26.35 per cent. Calculated, 26.22 per cent.

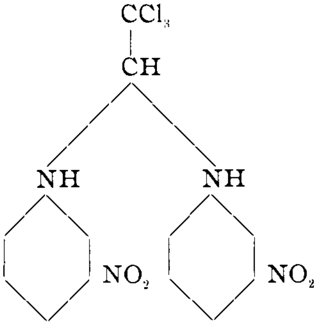
Trichlorethylidenedi-*p*-nitrophenamine is a yellow powder of very great insolubility. It is insoluble in water, alcohol, ether, ligroin and benzene. It is somewhat soluble in acetone and readily soluble in boiling nitrobenzene. The yield was 14.51 grams or nearly 54 per cent. of the theory. It is slowly decomposed by hot hydrochloric acid. Its conversion by acetic anhydride into *p*-nitroacetanilide and by benzoyl chloride into benzoyl *p*-nitroanilide, asdescribed by Eibner, was carried out.

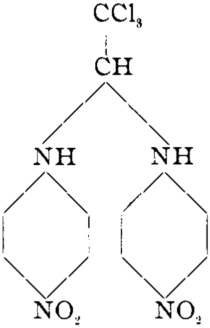
Reduction of the Nitroamines.—We have tried to reduce these nitroamines with various reducing agents but so far without success. If the nitro-group could be reduced, the resulting amine might again react with chloral, forming a complex ring body. Interesting results were obtained when the nitroamines were boiled with ammonium sulphide in alcoholic solution. In each case a volatile substance condensed on the walls of the reflux air condenser in white crystals. In the case of the para-compound, these crystals melted at 120° and were insoluble in water and alcohol, but dissolved readily in carbon disulphide. This group of bodies will be studied further in this laboratory.

In naming these compounds Eibner places the "di" after the "nitro" but it seems preferable to us to place it before the "*p*".

Constitution.—In the reaction between chloral and the nitranilines it might be possible for the oxygen to combine with hydrogen in the ring, leaving the amino groups untouched. But these substances do not possess any basic properties; hence they are to be represented as follows:







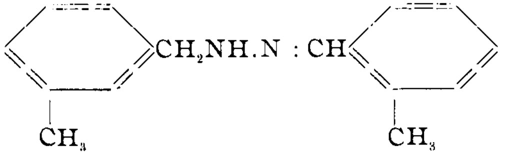
CHAPEL HILL, N. C.,
July 24, 1902.

PREPARATION OF 2,5-DIMETHYLBENZYL-2,5-DIMETHYLBENZAL HYDRAZONE AND ITS BENZOYL AND ACETYL DERIVATIVES.

BY EVERHART PERCY HARDING AND EDGAR W. RICE.

Received August 11, 1902.

2,5-Dimethylbenzyl-2,5-dimethylbenzal Hydrazone,



To an alcoholic solution of 2,5-dimethylbenzaldazine, prepared according to Curtius and Jay,[1] was added more than the calculated

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[1] *J. prakt. Chem.*, **89**, 43.