[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE GEORGE WASHINGTON UNIVERSITY]

THE CONDENSATION OF BROMAL WITH THE NITRANILINES[1]

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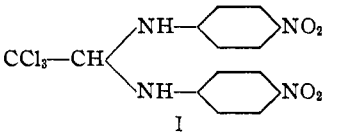
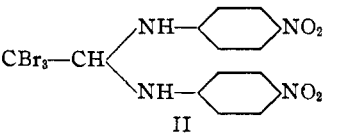
Eibner[2] condensed chloral with *p*-nitraniline to form a Schiff base, N,N′-β,β,β-trichloroethylidene-bis-*p*-nitraniline, of formula (I).



I



II

Wheeler and Weller[3] repeated his experiments and confirmed his results. In addition they condensed ortho and meta nitranilines with chloral to form the corresponding ortho and meta isomers.

It was thought to be of interest to investigate the condensation of bromal, tribromoacetaldehyde, with the three nitranilines. It was found that this condensation takes place as with chloral and there is formed, for example, N,N′,β,β,β-tribromoethylidene-bis-*p*-nitraniline from one mole of bromal and two moles of *p*-nitraniline. The formula (II) is given to the compound on the evidence of the analysis and the analogous behavior of this compound to the chloral condensation product. The ortho and meta isomers have also been prepared.

Treatment of the condensation products with hot, dilute or concentrated hydrochloric acid results in the decomposition of the molecule with the formation of bromal, which can be detected in the vapors, and the corresponding nitraniline, which can be recovered by neutralization of the acid solution with ammonium hydroxide.

Treatment of the ortho and para isomers with cold or hot alcoholic potash results in the formation of an intense red coloration. Wheeler and Jordan[4] report similar behavior for the chloral condensation products and that they prepared hydroxy and alkoxy derivatives by the replacement of one of the chlorine atoms by the hydroxy group by the use of alcoholic potash or alkoxy groups by the use of sodium alkoxides. We were unable to isolate such products. Apparently the treatment with alcoholic potash results in a complete decomposition of the molecule of the condensation product since we were able to isolate considerable amounts of the corresponding nitraniline from the reaction mixture.

[1] A portion of the material in this paper is taken from a thesis submitted to the Faculty of Columbian College, The George Washington University, by R. P. Jacobsen in partial fulfilment of the requirements for the degree of Master of Arts, October, 1931.

[2] Eibner, *Ann.*, **302**, 366 (1898).

[3] Wheeler and Weller, THIS JOURNAL, **24**, 1063 (1902).

[4] Wheeler and Jordan, *ibid.*, **31**, 937 (1909).

Treatment with an excess of bromine in glacial acetic acid results in a decomposition of the condensation product and we obtained various di- and tribromonitranilines which were identified by analysis and mixed melting points.

Experimental

Bromal was prepared by the bromination of paraldehyde in the presence of ethyl acetate according to the method of Pinner.[5]

N,N′,β,β,β-Tribromoethylidene-bis-*p*-nitraniline.—Twenty grams of powdered *p*-nitraniline was suspended in 100 cc. of benzene or ether. Twenty grams of freshly distilled bromal was dissolved in 25 cc. of the solvent and added slowly to the *p*-nitraniline. The mixture becomes warm and almost immediately a light yellow precipitate of the condensation product settles out. The mixture is allowed to stand overnight and then filtered. The light yellow sandy precipitate is washed many times with hot 70% alcohol to remove the unreacted *p*-nitraniline and then recrystallized from anhydrous acetone. It is insoluble in most organic solvents and only slightly soluble in acetone.

The condensation of ortho and meta nitranilines was carried out in the same manner except that the volume of the solvent is reduced since these condensation products are more soluble.

TABLE I

ANALYTICAL AND OTHER DATA FOR THE COMPOUNDS

Substance, N,N′,β,β,β,-tribromo-ethylidene-bis-	M. p., °C.	Needles from acetone	Yield, %	Analysis for Br, % Calcd. for $C_{14}H_{11}Br_3N_4O_4$		Found
o-Nitraniline	106–107	Light yellow	30	44.49	44.20	44.46
m-Nitraniline	117–118	Dark orange	34	44.49	44.71	44.24
p-Nitraniline	127–128	Dark orange	48	44.49	44.64	44.71

Summary

1. Bromal has been condensed with *o*-, *m*- and *p*-nitranilines to form three new Schiff bases.

2. These Schiff bases are decomposed completely by treatment with acids, alcoholic potash and bromine.

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[5] Pinner, *Ann.*, **179**, 68 (1875).