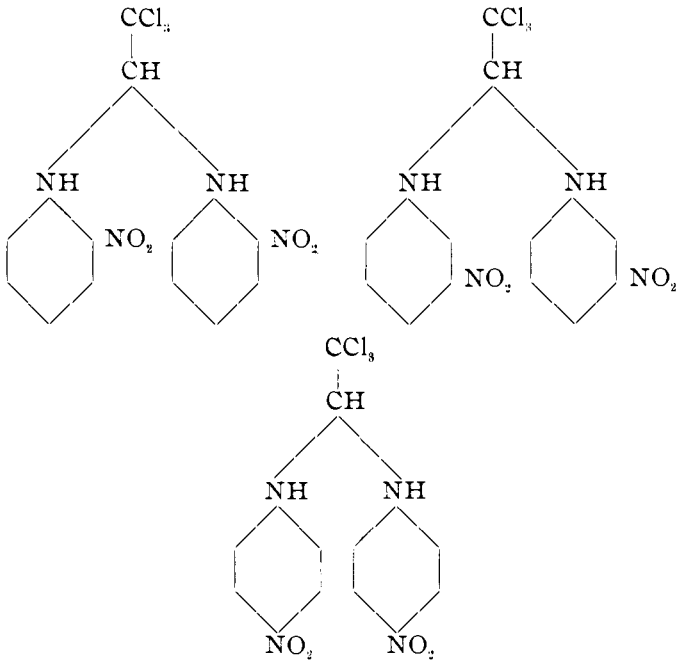


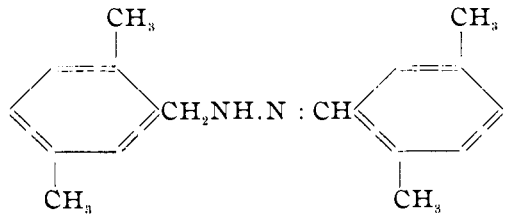
CHAPEL HILL, N. C.,
July 24, 1902.

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

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

amount of a 4 per cent. sodium amalgam sufficient to reduce the aldazine to its corresponding hydrazone. This was heated in a flask connected with a reflux condenser for from three to four hours upon a water-bath. The solution, nearly colorless, was then filtered and the filtrate left in a freezing-mixture of salt, ice and water until the hydrazone crystallized out. The hydrazone was then filtered off, washed with water and recrystallized from alcohol. It melted at 74°-78° (uncorr). The reaction takes place according to the following equation:

$$(CH_3)_2C_6H_3CH : N.N : CH.C_6H_3(CH_3)_2 + H_2 =$$
$$(CH_3)_2C_6H_3CH_2.NH.N : CH.C_6H_3(CH_3)_2.$$

The analysis gave: C, 81.03; H, 8.21. Calculated: C, 81.2; H, 8.04.

2,5-Dimethylbenzyl-2,5-dimethylbenzal hydrazone is soluble in ether, chloroform, benzene, carbon bisulphide, toluene, ethyl alcohol, methyl and amyl alcohols. It is insoluble in water. The hydrazone is very unstable and begins to decompose at once when exposed to the air.

Acetyl 2,5-dimethylbenzyl-2,5-dimethylbenzal Hydrazone,

$$(CH_3)_2C_6H_3CH_2N(C_2H_3O)N : CHC_6H_3(CH_2)_2.$$

To a concentrated alcoholic solution of the hydrazone was added a slight excess of acetic anhydride and the solution evaporated slowly to dryness upon a water-bath. The residue was recrystallized from alcohol. It gave long, white, satin-like needles which melted at 137°.

The analysis gave 9.11 per cent. N. Calculated, 9.09 per cent.

The acetyl derivative is soluble in benzene, toluene, ether, chloroform, carbon disulphide, acetic acid and in hot ethyl, methyl, and amyl alcohols. It is insoluble in water.

Benzoyl 2,5-dimethylbenzyl-2,5-dimethylbenzal Hydrazone,

$$(CH_3)_2C_6H_3CH_2N(C_6H_5CO)N : CHC_6H_3(CH_3)_2.$$

A slight excess of benzoyl chloride was added to a concentrated alcoholic solution of the hydrazone and the solution evaporated to dryness upon a water-bath. The residue was recrystallized from alcohol. Long satin-like crystals formed which melted at 134°-134.5°.

The analysis gave 7.60 per cent. N. Calculated, 7.57 per cent.

The benzoyl derivative is soluble in benzene, toluene, ether,

chloroform, carbon disulphide, acetic acid and in hot ethyl, methyl, and amyl alcohols. It is insoluble in water.

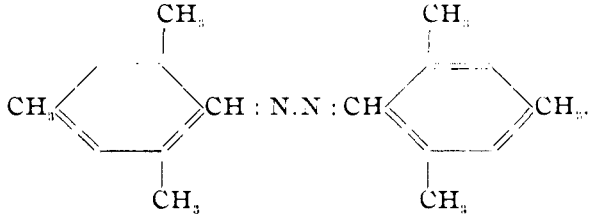
Nitroso and picric acid derivatives are at present being prepared.

PREPARATION OF 2,4,6-TRIMETHYLBENZALDAZINE; OF 2,4,6-TRIMETHYLBENZYL-2,4,6-TRIMETHYLBENZAL HYDRAZONE AND SOME OF ITS DERIVATIVES.

By Everhart Percy Harding.

Received August 11, 1902.

2,4,6-Trimethylbenzaldazine,



2,4,6-Trimethylbenzaldazine was prepared by adding to a weak alcoholic solution of 2,4,6-trimethylbenzaldehyde, which was prepared according to Gattermann,[1] a solution of hydrazine sulphate containing the calculated amount of sulphate to produce the corresponding aldazine. The mixed solutions were warmed to 60°, violently shaken for thirty minutes and allowed to stand for two hours. The yellow substance that separated formed spherulitic masses which recrystallized from acetic acid in beautiful light yellow prisms which melted at 167°.

$$(CH_3)_3C_6H_2CHO + H_2N'NH_2 + OHCC_6H_2(CH_3)_3 = (CH_3)_3C_6H_2.CH : N.N : CH.C_6H_2(CH_3)_3.$$

These gave 9.59 per cent. N. Calculated, 9.56 per cent.

2,4,6-Trimethylbenzaldazine is very soluble in chloroform. It is soluble in cold ether, benzene, toluene, acetone and in hot acetic acid, ethyl, methyl and amyl alcohols. It is insoluble in water. Like all known aldazines it is a very stable compound.

2,4,6-Trimethylbenzyl-2,4,6-trimethylbenzal Hydrazone,

$$(CH_3)_3C_6H_2CH_2NHN : CHC_6H_2(CH_3)_3.$$

More than the calculated amount of a 4 per cent. sodium amalgam

[1] W. Graf: Inaug. Diss., Heidelberg, 1899.