

and catching any escaping hydrochloric acid gas in a connected wash-bottle. The contents of the two vessels are then titrated with standard alkali solution. The objection to this method is that the end of the titration reaction is very indefinite and indeterminate, due to a secondary reaction. (See "Grundlinien der anorganischen Chemie," Ostwald, pp. 433-436.)

## THE REDUCTION, IN AN ALKALINE SOLUTION, OF 2,4,5-TRIMETHYLBENZALAZINE AND THE PREPARATION OF SOME DERIVATIVES OF THE REDUCTION PRODUCTS.

BY EVERHART PERCY HARDING.

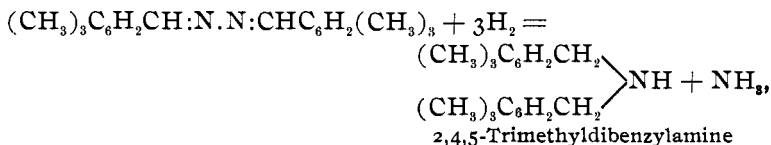
Received September 9, 1901.

THE experimental part of this paper was carried out in the chemical laboratory at the University of Heidelberg under the supervision of Prof. Curtius, and a short abstract of it has already been published in the July, 1900, number of the *Journal für praktische Chemie*.

The formation of azines by the condensation of aromatic aldehydes with hydrazine and their reduction in an acid or alkaline solution is a comparatively new line of work and the investigation along this line has largely been done by Prof. Curtius and his students at the University of Heidelberg.

### *2,4,5-Trimethylbenzalazine,*

$(\text{CH}_3)_3\text{C}_6\text{H}_2\text{CH:N:N:CHC}_6\text{H}_2(\text{CH}_3)_3$ , yields different reduction products, the kind depending upon the quality of the reducing agent used and the degree of the reduction. Curtius and Franzen,<sup>1</sup> by reducing in an acid solution, using zinc dust and acetic acid, obtained 2,4,5-trimethyldibenzylamine, a solid substance melting at  $78^\circ$  and insoluble in water. The reaction may be represented by the equation

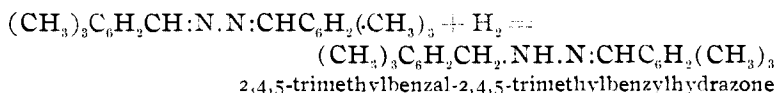


part of the nitrogen being reduced to ammonia.

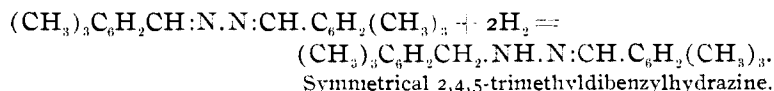
By reducing 2,4,5-trimethylbenzalazine in an alkaline solution, using sodium amalgam as a reducing agent, two reduction prod-

<sup>1</sup> *Ber. d. chem. Ges.*, 4, 1901.

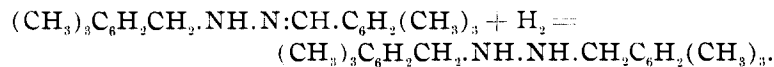
ucts were obtained, the kind depending upon the degree of reduction — one a 2,4,5-trimethylbenzal-2,4,5-trimethylbenzylhydrazone,  $(\text{CH}_3)_3\text{C}_6\text{H}_2\text{CH}_2\text{NH}\cdot\text{N}:\text{CHC}_6\text{H}_2(\text{CH}_3)_3$ , produced by a partial reduction, the other a symmetrical 2,4,5-trimethyldibenzylhydrazine,  $(\text{CH}_3)_3\text{C}_6\text{H}_2\text{CH}_2\cdot\text{NH}\cdot\text{NH}\cdot\text{CH}_2\text{C}_6\text{H}_2(\text{CH}_3)_3$ , produced by a complete reduction. The reactions may be represented by the following equations:



and



The symmetrical hydrazine may be obtained also from the hydrazone by a further reduction.



Each of these reduction products is a solid substance and comparatively unstable.

The azines are aliphatic compounds, derivatives of the hypothetical azimethylene — $\text{CH}\cdot\text{N}\cdot\text{N}\cdot\text{CH}$ —, and by a partial reduction one would expect a symmetrical reduction product—either a hydrazymethylene derivative,  $=\text{CH}\cdot\text{NH}\cdot\text{NH}\cdot\text{CH}=\text{}$ , in which the valence of nitrogen has changed from III to V or an azomethane derivative corresponding to the aromatic azo compounds and having the general formula  $\text{R}-\text{CH}_2\cdot\text{N}:\text{N}\cdot\text{CH}_2-\text{R}$ . But this is not the case as is evidenced by the decomposition products which show an unsymmetrical reduction, the compounds having the general formula  $\text{R}-\text{CH}_2\cdot\text{NH}\cdot\text{N}:\text{CH}-\text{R}$ . By hydrolyzing the hydrazones with dilute hydrochloric acid they form an aldehyde and a substituted hydrazine, which reaction is best explained by the hydrazone or unsymmetrical formula

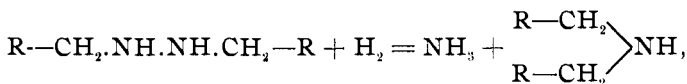


The formation of but one acetyl or benzoyl derivative favors the presence of but one imide group or one methylene group as exist in the unsymmetrical hydrazone while the two imide groups in the assumed hydrazimethylene derivative or the two methylene

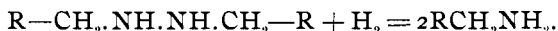
groups in the assumed azimethane derivatives would make a diacetyl or dibenzoyl derivative probable.

The symmetrical hydrazines produced by a complete reduction of the azines in an alkaline solution are also aliphatic compounds, derivatives of hydrazomethane,  $R-CH_2NH.NH.CH_2-R$ , which correspond to the aromatic hydrazo compounds  $R-NH.NH-R$ . The latter are easily reduced to primary amines while the former are stable in an alkaline solution. No attempt has been made to reduce the symmetrical hydrazine in an acid solution but the probability is that in the preparation of

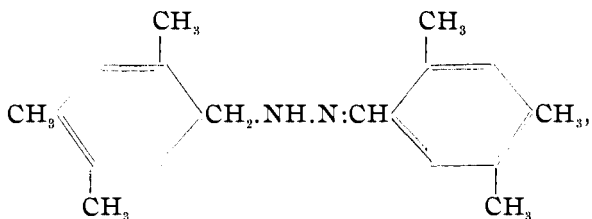
the secondary amines  $\begin{matrix} R-CH_2 \\ R-CH_2 \end{matrix} \rangle NH$ , by the reduction of the azines in an acid solution, the symmetrical hydrazine forms as an intermediate product and then reduces further to one molecule of ammonia and one molecule of a secondary amine instead of to two molecules of a primary amine as do the aromatic hydrazo compounds, the final reaction taking place according to the equation



instead of the equation



To make 2,4,5-trimethylbenzal-2,4,5-trimethylbenzylhydrazone,



10 grams of 2,4,5-trimethylbenzalazine were placed in a round bottomed flask, of 1 liter capacity, which was provided with a reflux condenser. This was dissolved in 700 cc. of 95 per cent. alcohol by boiling vigorously on a water-bath. To the solution which was kept at the boiling-point of the alcohol there was added, intermittently, aliquot parts of 300 grams of sodium amalgam, more than a sufficient amount to reduce the azine to the hydrazone. After an interval of four hours the amalgam had

become spent and the solution nearly colorless, maintaining a slight turbidity. The mercury and impurities were filtered off and the filtrate placed in a refrigerator. In twelve hours' time 4 grams of a flaky, white, crystalline substance had separated out, which was filtered off and well washed with water. From a dilute alcoholic solution, needle-like crystals formed, while from a concentrated alcoholic solution the crystals grouped themselves in the form of tufts which melted at  $134^{\circ}$ .

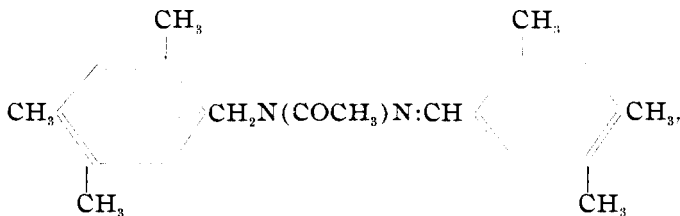
An analysis gave :

	Theoretical. Per cent.	Found. Per cent.
Carbon .....	81.63	81.85
Hydrogen.....	8.57	8.84
Nitrogen .....	9.36	9.53

The molecular weight, determined by the depression of the freezing-point method, was found to be 311 and 309.7 as against 294 the theoretical molecular weight. The hydrazone is very soluble in ether and ligroin, less soluble in alcohol and acetic acid, and insoluble in water. On exposure to the air it soon decomposes, assuming a yellow color and emitting an odor of pseudocumylaldehyde. It is unstable in an exhausted desiccator and is readily decomposed by the action of steam or hydrochloric acid.

The replaceable imide hydrogen atom makes substitution products possible. The acetylbenzoyl and nitroso groups form the corresponding stable and characteristic compounds.

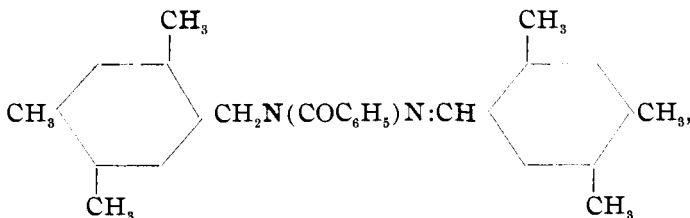
2,4,5-Trimethylbenzalacetyl-2,4,5-trimethylbenzylhydrazone,



was formed by treating a concentrated and hot alcoholic solution of the hydrazone with an excess of acetic anhydride and the excess evaporated off on a water-bath. Recrystallized from alcohol the long fine needles melted at  $184^{\circ}$ . An analysis gave :

	Theoretical. Per cent.	Found. Per cent.
Carbon .....	78.57	78.50
Hydrogen.....	8.33	8.36
Nitrogen .....	8.34	8.54
Oxygen .....	4.76	4.60

It is soluble in the organic solvents and insoluble in water.  
The benzoyl derivative,



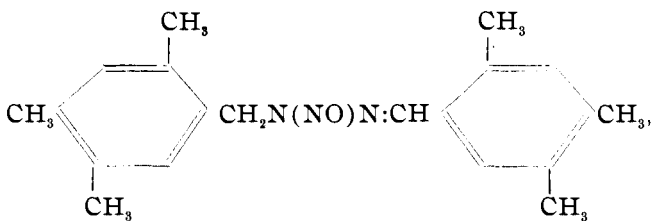
2,4,5-Trimethylbenzalbenzoyl-2,4,5-trimethylbenzylhydrazone.

was easily prepared by the Schotten-Baumann reaction. An analysis gave:

	Theoretical. Per cent.	Found. Per cent.
Carbon .....	81.41	81.48
Hydrogen.....	7.54	8.11
Nitrogen .....	7.03	6.89
Oxygen .....	4.02	3.52

It crystallizes from alcohol in fine needle-like crystals which melt at 187°. It is soluble in the organic solvents and insoluble in water.

The nitroso derivative,



2,4,5-Trimethylbenzalnitroso-2,4,5-trimethylbenzylhydrazone.

was prepared by adding to an ice-cold mixture of alcohol and hydrazone, concentrated hydrochloric acid, drop by drop, until the hydrazone dissolves. An ice-cold concentrated solution of sodium nitrite was then gradually added. A yellow crystalline substance separated at once, which increased upon the addition of water to the solution. The precipitate was filtered off and

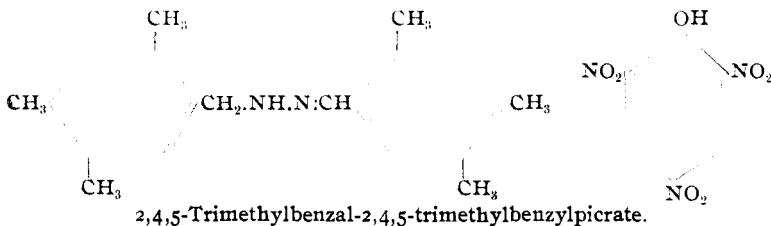
well washed with water to remove excess of sodium nitrite. Recrystallized from alcohol, the yellow needles melted at  $118^{\circ}$ .

An analysis gave :

	Theoretical. Per cent.	Found. Per cent.
Carbon .....	74.31	74.13
Hydrogen.....	7.74	8.27
Nitrogen .....	13.00	13.28
Oxygen.....	4.95	3.32

The nitroso derivative is soluble in the organic solvents and insoluble in water. It decomposes with concentrated sulphuric acid assuming a red color which disappears upon the addition of water and emits at the same time an odor of aldehyde. By treating an alcoholic solution of the nitroso compound with dried hydrochloric acid gas and placing the partially evaporated alcoholic solution in a refrigerator, crystals separated which melted at  $155^{\circ}$ - $156^{\circ}$ . This compound appeared to be a hydrochloride of the nitrosohydrazone, for by treating it with sodium hydroxide it formed the hydrazone melting at  $134^{\circ}$  and by treating with sodium nitrite it formed again the nitroso compound melting at  $118^{\circ}$ . In preparing the nitroso compound, the temperature must be kept near the freezing-point or the derivative will decompose.

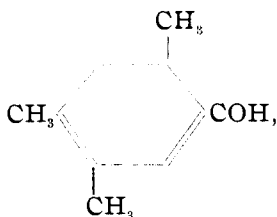
The hydrazone is a weak base. With dilute organic acids it forms addition products, the molecule remaining intact at the double bond. With picric acid it forms a hydrazone picrate.



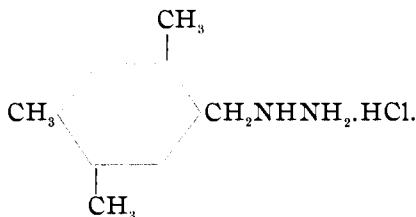
The picrate is formed by adding a concentrated alcoholic solution of picric acid to an alcoholic solution of freshly prepared hydrazone. Upon the addition of water a yellow flaky precipitate formed, which crystallized from ether in yellow needles which melted at  $169^{\circ}$ . An analysis gave :

	Theoretical. Per cent.	Found. Per cent.
Carbon .....	59.66	59.73
Hydrogen.....	5.54	5.16
Nitrogen .....	13.39	13.52
Oxygen.....	21.41	21.59





and 2,4,5-trimethylbenzaldehyde hydrochloride,

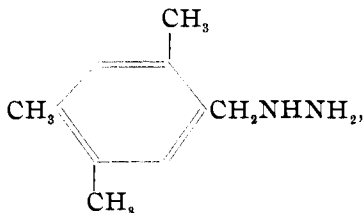


In preparing the hydrazine hydrochloride, 4 grams of the hydrazone were treated in a round-bottomed flask with 150 cc. of water and 10 cc. of dilute hydrochloric acid. Steam was then conducted through the solution; an oil-like substance distilled over which had the odor of pseudocumyl aldehyde and which formed a condensation product with hydrazine hydrate that melted at  $180^{\circ}$ , the melting-point of 2,4,5-trimethylbenzalazine. The hot residue in the flask was filtered and the filtrate distilled in a vacuum. The residue, recrystallized from alcohol, melted at  $240^{\circ}$ . An analysis gave:

	Theoretical. Per cent.	Found. Per cent.
Carbon .....	59.85	59.78
Hydrogen.....	8.51	8.47
Nitrogen.....	14.11	13.97
Chlorine .....	17.60	17.71

The hydrochloride is a very stable compound. It is soluble in water and insoluble in ether.

The free base 2,4,5-trimethylbenzylhydrazine,

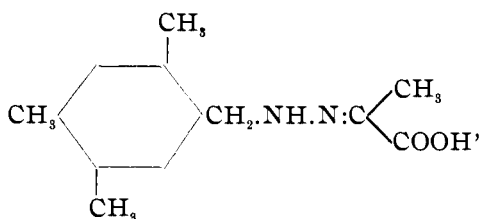




was prepared from the hydrochloride by the action of caustic potash. Four grams of the hydrochloride and an excess of caustic potash were placed into an Erlenmeyer flask. A few drops of water were added and subsequently 50 cc. of ether. The flask was provided with a soda-lime tube to protect the base from the moisture and carbon dioxide of the atmosphere. The flask was shaken at times so as to bring the hydrochloride in contact with the potash. After twenty-four hours the ether was separated from the water layer and dried with fused caustic potash. The ether was then evaporated and the residue distilled in a vacuum. At 25 mm. pressure the base distilled over at  $165^{\circ}$  as a colorless oil, which solidified upon cooling. It is very unstable, decomposing at once when exposed to the air. An analysis gave 16.89 per cent. nitrogen as against 17.08 theoretical per cent. Upon standing three days in a desiccator, an analysis gave but 5.8 per cent. nitrogen. It began to melt at  $78^{\circ}$ , and at  $85^{\circ}$  there began a rapid evolution of nitrogen.

The base forms, with benzaldehyde benzal-2,4,5-trimethylbenzylhydrazine, a very unstable compound which melts at  $89^{\circ}$ - $90^{\circ}$ , and which dissolves in the organic solvents. It was formed by adding benzaldehyde to the free base and then rubbing the walls of the beaker with a glass rod. It was purified by crystallizing from alcohol.

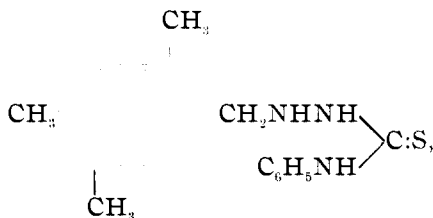
With pyrroacemic acid the base forms 2,4,5-trimethylbenzylhydrazonopyrroacemate,



a white crystallized substance which melted at  $92^{\circ}$ . It was prepared by adding an excess of pyrroacemic acid to the hydrochloride of the base. An oil immediately formed which settled to the bottom of the flask and then crystallized. An analysis gave 11.79 per cent. of nitrogen as against 11.97 theoretical per cent. It is soluble in water and the organic solvents.

The base, 2,4,5-trimethylbenzylhydrazine, forms addition

products. With phenyl mustard oil it forms 2,4,5-trimethylbenzylphenylthiosemicarbazide,

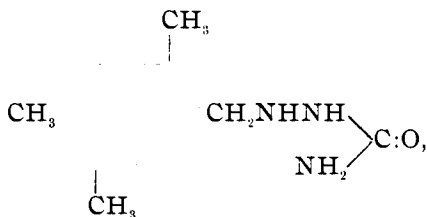


white hair-like crystals which melt at  $167^\circ$ – $168^\circ$ . It was prepared by adding to an alkaline solution of the base an excess of phenyl mustard oil, and then warming the solution. By warming at too high a temperature or with an excess of alkali the thiosemicarbazide decomposed and a black lustrous crystalline substance formed. An analysis gave :

	Theoretical.	Found.	
		I.	II.
Nitrogen .....	14.09	14.42	14.22

It is soluble in ethyl alcohol, methyl alcohol, ether, benzene, and acetic acid. It is difficultly soluble in ligroin and water.

With hydrocyanic acid, the base forms 2,4,5-trimethylbenzylsemicarbazide,

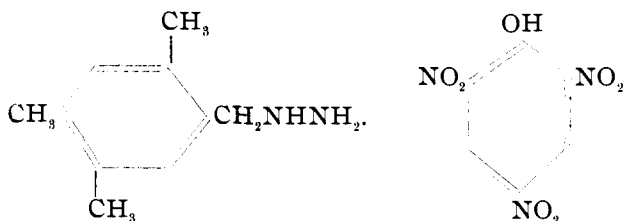


white needle-like crystals which melt at  $174^\circ$ – $175^\circ$ . It was prepared by adding to the hydrochloride a solution of potassium cyanate and crystallizing from alcohol. An analysis gave :

	Theoretical.	Found.
	Per cent.	Per cent.
Nitrogen .....	20.29	20.47

It is easily soluble in ethyl alcohol, methyl alcohol, acetic acid, and benzene. It is difficultly soluble in water and insoluble in ether and ligroin.

With picric acid 2,4,5-trimethylbenzylhydrazine forms 2,4,5-trimethylbenzylhydrazine picrate.

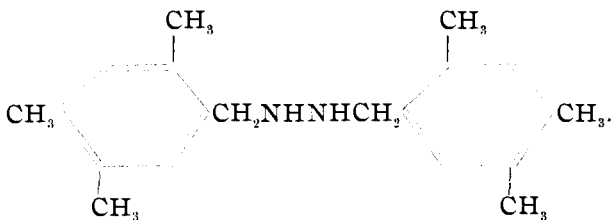


This addition product crystallizes in yellow needles which melt at  $163^{\circ}$ . In its preparation an ether solution of picric acid was gradually added to a water solution of the hydrochloride. The picrate formed at once as yellow crystals at the contact point of the two layers. By adding an ether solution of picric acid to a warm solution of the hydrochloride, the picrate formed as an oil, which settled to the bottom of the flask and subsequently crystallized. An analysis gave:

	Theoretical. Per cent.	Found. Per cent.
Nitrogen .....	17.81	17.64

It is difficultly soluble in warm water and insoluble in ligroin and benzene.

Preparation of symmetrical 2,4,5-trimethyldibenzylhydrazine,



As has previously been given, 2,4,5-trimethylbenzal-2,4,5-trimethylbenzylhydrazone was formed by a partial reduction of 2,4,5-trimethylbenzalazine. By a further reduction of the hydrazone or a stronger reduction of the azine solution the symmetrical 2,4,5-trimethyldibenzylhydrazone was formed. In the preparation of this compound 10 grams of 2,4,5-trimethylbenzalazine were dissolved in 500 cc. of 95 per cent. alcohol. To this warm solution in a round-bottomed flask provided with a reflux condenser was added, at times, aliquot parts of 300 grams of a 4 per cent. sodium amalgam. The solution was kept on a water-bath at the boiling-point of the alcohol for six hours dur-

ing which time the amalgam was added. The mercury and impurities were filtered off and the filtrate cooled in a refrigerator. Two grams of the hydrazone separated out. This was filtered off and the cold filtrate treated with cold concentrated hydrochloric acid. A voluminous precipitate formed which increased by the addition of water. This was rapidly filtered off, washed well with water and its dilute alcoholic solution treated with sodium hydroxide. A voluminous precipitate formed which, when re-crystallized from alcohol, melted at  $128^{\circ}$ . An analysis gave:

	Theoretical. Per cent.	Found. Per cent.
Nitrogen .....	9.46	9.47

The molecular weight by the depression of the freezing-point method gave:

	Theoretical.	Found.	
		I.	II.
Mol. wt. ....	296	305.7	321

The free base cannot be obtained directly from the filtrate from the hydrazone. By evaporating the filtrate, the dibenzylhydrazine is oxidized to the hydrazone and by the addition of water to the filtrate the hydrazine decomposes. It is very unstable. It soon becomes a yellowish white, emitting an odor of 2,4,5-trimethylbenzaldehyde.

The molecular weights and melting-points of the hydrazone and dibenzylhydrazine vary but little. It was by means of the hydrochloride of the dibenzylhydrazine that it was possible to distinguish between the two compounds. The hydrazone forms no hydrochloride but decomposes, yielding 2,4,5-trimethylbenzaldehyde and 2,4,5-trimethylbenzylhydrazine while the dibenzylhydrazine forms a stable and characteristic hydrochloride which melts at  $171^{\circ}$ . In an alcoholic solution it soon decomposed, and by boiling the solution almost immediately.

2,4,5-trimethyldibenzylhydrazine, as was previously given, is an aliphatic compound, a symmetrical derivative of hydrazinethane,  $\text{CH}_2\text{NH.NHCH}_2$ , corresponding to the hydrazo compounds of the aromatic series. The aromatic hydrazo compounds oxidize very readily, the colorless hydrazobenzene oxidizing in a very short time to the red azobenzene by means of atmospheric oxygen. The corresponding aliphatic hydrazine compounds also oxidize readily but do not form the corresponding azo compounds. They form either symmetrical tetrazones with the general formula

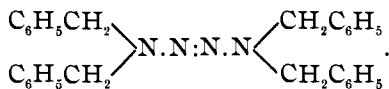
= N.N:N.N =,<sup>1</sup> or oxidize first to the corresponding hydrazone and then to the unsymmetrical tetrazone with the general



formula  $\begin{array}{c} | \\ -N-N: \end{array}$ , or to the azines with the general formula



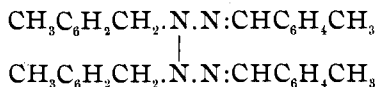
—CH:N.N:CH—.<sup>2</sup> Curtius and Franzen<sup>3</sup> succeeded in oxidizing dibenzylhydrazine,  $C_6H_5CH_2.NH.NH.CH_2C_6H_5$ , to dibenzyltetrazone and gave it the formula



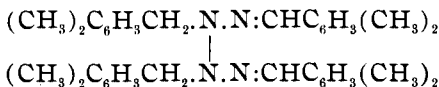
Curtius and Propfe attempted to obtain the symmetrical 4-methyldibenzyltetrazone,  $(CH_3C_6H_4CH_2)_2N.N:N.N(CH_2C_6H_4CH_3)_2$ , by oxidizing symmetrical 4-methyldibenzylhydrazine,



but succeeded in obtaining the unsymmetrical 4-methylbenzal-4-methylbenzyltetrazone,



Likewise Curtius and Haagar,<sup>4</sup> in attempting to oxidize 2,4-dimethyldibenzylhydrazine,  $(CH_3)_2C_6H_3CH_2NHNHCH_2C_6H_3(CH_3)_2$ , to the symmetrical tetrazone, obtained the unsymmetrical 2,4-dimethylbenzal-2,4-dimethylbenzyltetrazone,



Neither the symmetrical nor unsymmetrical tetrazone could be isolated by oxidizing symmetrical 2,4,5-trimethyldibenzylhydrazine with mercuric oxide. Either or both of these compounds may have formed as intermediate products but the only compound that could be isolated after the oxidation was 2,4,5-trimethylbenzalazine.

Schmidt and Schulz<sup>5</sup> succeeded in substituting two acetyl groups for the two imide hydrogen atoms in the aromatic hydrazobenzene, thus forming a diacetyl derivative,

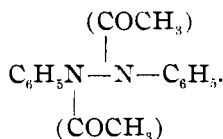
<sup>1</sup> *Ber. d. chem. Ges.*, **4**, 1901.

<sup>2</sup> *J. prakt. Chem.*, N. F., **62**, (1900).

<sup>3</sup> *Ber. d. chem. Ges.*, (1900).

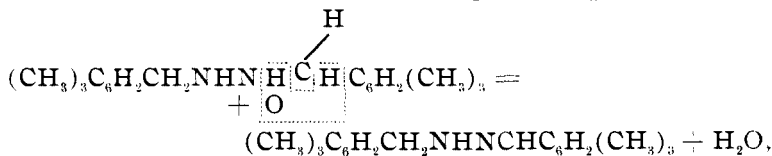
<sup>4</sup> *J. prakt. Chem.*, N. F., **62**, (1900).

<sup>5</sup> *Ann. Chem. (Liebig)*, **207**, 327.



The diacetyl, dibenzoyl, and dinitroso derivatives<sup>1</sup> of dibenzylhydrazine have been prepared. Also the dibenzoyl derivative<sup>1</sup> of 4-methyldibenzylhydrazine and the diacetyl derivative<sup>1</sup> of 2,4-dimethyldibenzylhydrazine.

None of the corresponding diderivatives of 2,4,5-trimethyldibenzylhydrazine have been prepared. In every trial a mono-derivative of 2,4,5-trimethylbenzal-2,4,5-trimethylbenzylhydrazone was formed. It is assumed that the symmetrical hydrazine was oxidized to the hydrazone according to the equation



and that then a hydrogen atom of the imide group was replaced by one of the substituting radicals.

## THE PRECIPITATION OF COLLOIDS BY ELECTROLYTES

BY W. R. WHITNEY AND J. E. OBER.

Received August 23, 1901.

### PART I.

#### REVIEW OF THE WORK OF PREVIOUS INVESTIGATORS.

THE purpose of this article is to call attention to the present condition of our knowledge concerning colloids by coordinating some of the facts and conceptions which have resulted from the work of various investigators in this field, and to append thereto a contribution to the subject, the result of recent experiments of our own together with a fairly complete index to the literature. It is hoped that the significance of this subject and its probable importance in connection with biological chemistry in its widest significance, as well as its claim to general chemical interest, may be brought more fully to the attention of chemists.

Any discussion of the subject which considers its history must begin with a reference to the work of Graham. He distinguished

<sup>1</sup> *J. prakt. Chem.*, N. F., 62 (1900).