

Tschugaeff observes that sodium hydroxide is without effect upon the nickel salt and that even boiling glacial acetic acid causes but little decomposition. It is to be observed that when the nickel salt is treated with a boiling solution of even dilute caustic soda complete decomposition will be effected. A 25% acetic acid solution will also slowly decompose the nickel salt, which will again reprecipitate when ammonium hydroxide is added.

From the properties which have been exhibited by dimethylglyoxime and isonitrosoacetone, it appears that treatment with sulfuric acid, if it is not too concentrated, will afford the most satisfactory conditions under which the monoxime will dissociate and the less soluble dioxime precipitate as a result of this dissociation.

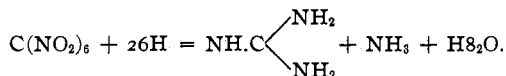
SYRACUSE UNIVERSITY.

LIMITS OF THE ATTACHMENT OF AMINO GROUPS TO A SINGLE CARBON ATOM; ATTEMPTS TO PREPARE TETRAMINO METHANE.

BY JITENDRA NATH RAKSHIT.

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All attempts to prepare compounds containing more than two amino groups attached to a single carbon atom have resulted in combinations of nitrogen with the carbon in some other form, such as the cyanogen or imido group. Ammonia and chloroform¹ at red heat give hydrocyanic acid. Aniline and chloroform² give formamidine, Ph.NH.CH : NPh. Chloropicrin³ or carbon tetrabromide⁴ and ammonia give guanidine. Carbon tetrachloride also yields triphenyl guanidine with aniline. Guanidine contains the largest number of nitrogen atoms which it has hitherto been found possible to combine with a single carbon atom. It was thought possible that the reduction of tetranitro methane might give tetramino methane, but on carrying out the experiment guanidine and ammonia were obtained.



Experimental.

Tetranitro methane was prepared according to Chattaway's⁵ method. Two hundred grams of zinc were kept immersed in a dilute solution of nickel sulfate over night. The nickel coated zinc was washed and transferred to an Erlenmeyer flask and 5 cc. of tetranitro methane and 20 cc.

¹ Andre, *Compt. rend.*, **102**, 553.

² Hofmann, *Proc. Roy. Soc.*, **9**, 229.

³ Hofmann, *J. Chem. Soc.*, **19**, 251.

⁴ Bolas and Groves, *Ibid.*, **24**, 782.

⁵ *J. Chem. Soc.*, **97**, 2099 (1910).

water were added. From a buret, 10% hydrochloric acid was added in 4 cc. portions with constant shaking, the temperature being maintained at 20-25°. When all oily drops had disappeared, further 20 cc. of dilute acid was added and the mixture was left over night in a cool place. The solution was then decanted and the zinc was precipitated as carbonate with soda. The filtrate from the zinc carbonate was evaporated on the water bath after acidulating with dilute hydrochloric acid. The residue obtained was powdered on a mortar and extracted with absolute alcohol. The alcoholic extract was evaporated on the water bath and the residue was again extracted with a mixture of equal volumes of absolute alcohol and ether, and the extract evaporated. The substance thus obtained was free from ammonium and sodium chlorides. It was a white crystalline deliquescent substance. The fact that guanidine hydrochloride, like most other amine hydrochlorides, is soluble in alcohol or in a mixture of alcohol and ether, and the insolubility of sodium and ammonium chlorides, rendered its separation simple.

0.3161 g. gave 0.4690 g. AgCl; calc. for $\text{NHC}(\text{NH}_2)_2\text{HCl}$: Cl = 36.84; found: 36.69.

0.1050 g. chloroplatinate gave 0.0392 g. Pt; calc. for $[\text{NHC}(\text{NH}_2)_2\text{HCl}]_2\text{PtCl}_4$: Pt = 37.00; found: 37.38.

The residue from the first extract was dissolved in a small quantity of water and distilled with caustic soda. The distillate was found to be ammonia pure and simple.

This reduction was also carried through with tin and hydrochloric acid, with subsequent removal of the tin as sulfide. In this case the product obtained was a mixture of ammonium chloride and guanidine hydrochloride.

CUSTOMS AND EXCISE LABORATORY,
CUSTOM HOUSE, CALCUTTA, INDIA.

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THE ADDITION COMPOUNDS OF DIMETHYLPYRONE WITH ORGANIC ACIDS.¹

By JAMES KENDALL.

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The addition products of dimethylpyrone with acids are of special interest in view of their connection with the oxonium theory of Collie and Tickle.² The hypothesis that oxygen may function as a quadrivalent atom was first brought into prominence by a study of these compounds, the action being regarded as proceeding according to the equation:

¹ Presented at the Cincinnati meeting of the American Chemical Society, April 9, 1914.

² *J. Chem. Soc.*, 75, 710 (1899).