of sulfur dioxide and the product was white and crystalline. To this excess of strong hydrochloric acid was added and the mixture exposed to the air, when in two days a fine, black, crystalline precipitate of the quinhydrone was formed, showing that the original product was the 1,2,4,5-tetrahydroxybenzene.

A stream of sulfur dioxide was passed into water containing potassium bromoanilate prepared as above. A red precipitate looking like bromoanilic acid was at first formed, but on longer action a colorless product was obtained, which, on exposure to the air, gave black crystals of a quinhydrone, while the aqueous liquid gave a strong test for a bromide.

Bromoanilic acid warmed with water and exposed to a stream of sulfur dioxide lost bromine, as was shown by a test for hydrobromic acid in the filtrate, but this reduction took place more slowly than in the case of the bromoanilate, and was not complete at the end of the reaction.

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THE PREPARATION OF DIMETHYLGLYOXIME WITHOUT THE USE OF HYDROXYLAMINE.

BY J. M. JOHLIN, JR.

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Schramm[1] has made the observation that isonitrosomethylacetone—the monoxime of diacetyl—dissociates, when treated with hydrochloric acid, into hydroxylamine, acetic acid and other unidentified products, yielding upon evaporation 81% of the theoretical amount of hydroxylamine hydrochloride. He also observed the formation of minute quantities of ethylmethylacetoximic acid—the dioxime of diacetyl—by the interaction of the liberated hydroxylamine with the still undissociated monoxime. He prepared larger amounts of the dioxime from the monoxime with hydroxylamine.

v. Pechmann[2] has since shown that, in part, the dissociation products of the isonitrosoketone are hydroxylamine and diacetyl. Diels and Jost[3] adapted this property as the basis of a method for the preparation of the diketone. Since dimethylglyoxime has been given added importance through its employment in the qualitative and quantitative determination of nickel, Gandarin[4] has more recently pointed out that it can be more economically prepared by adding hydroxylamine to the sodium salt of the monoxime without isolating the latter as the acid monoxime.

Operating according to the modified method of Diels and Stephan[5] for the preparation of diacetyl, 850 cc. of methylethylketone are mixed

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[1] *Ber.*, **16**, 180 (1883).

[2] *Ibid.*, **20**, 3213 (1887).

[3] *Ibid.*, **35**, 3290 (1902).

[4] *J. prakt. Chem.*, **77**, 414 (1908).

[5] *Ber.*, **40**, 4337 (1907).

with 30 cc. of concentrated hydrochloric acid and one liter of isoamylnitrite slowly added at 50°. The resulting mixture is shaken with caustic soda, the alkaline layer acidified with 25% sulfuric acid, and, upon the addition of concentrated sulfuric acid, distilled with steam for the recovery of the liberated diacetyl.

Recently, while operating according to this method of preparing the diketone, it was noted that if the reaction products are allowed to stand two hours before shaking with caustic soda, a mixture of minute quantities of ammonium chloride and dimethylglyoxime will separate from them. It was further observed that if, after shaking with caustic soda and acidifying with 25% sulfuric acid, the mixture is allowed to stand 24–36 hours large amounts of dimethylglyoxime will have crystallized out at the bottom of the flask, while the oily or solidified layer which rose to the surface of the liquid upon acidification will have almost disappeared. The mother liquor can be further treated for the recovery of diacetyl according to the prescribed method, while the crystalline dimethylglyoxime can be purified by boiling with animal charcoal and a large amount of water. Filtering by means of a steam funnel and cooling will result in a very pure product without considerable loss due to the recrystallization. 850 cc. of commercial methyl ethyl ketone will yield 50–60 g. of the pure glyoxime as a by-product.

Tschugaeff[1] has mentioned some of the properties of the nickel salt of dimethylglyoxime. It was nevertheless considered of interest to further investigate some of these properties, as well as to study the conditions under which the acid dioxime will form the monoxime without the additional use of hydroxylamine, and to study some of the properties of the dioxime itself.

Thirty-five grams of pure dimethylglyoxime were steam-distilled in the presence of 200 cc. of 25% sulfuric acid freshly prepared from concentrated. The otherwise insoluble dioxime dissolved in the hot mixture, which, due to the fact that diacetyl was set free, became colored a greenish yellow. The diketone thus liberated was carried over in the course of the distillation and the liquid in the flask as well as the space above it became colorless. The steam-distillation was continued until the volume of distillate amounted to 500 cc. This distillate was saturated with salt and the mixture again steam-distilled. It was noted that after all the diacetyl had apparently been distilled over there still remained on the surface of the liquid in the flask a colorless oil which solidified upon cooling, while the condenser had become clogged with a crystalline substance which proved to be the monoxime of diacetyl. The distillation was continued and additional amounts of the monoxime recovered.

The first part of the distillate was again steam-distilled, and the diketone

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[1] *Z. anorg. Chem.*, **46**, 145 (1905).

which was recovered dried over calcium chloride. Subjected to a distillation it was found to boil within the range of 60–90°. It is evident, then, that pure dimethylglyoxime upon its dissociation with sulfuric acid yields other products besides diacetyl. The yield amounted to 10% of the theoretical. Because of the small amount of the oil obtained, the nature of its complexity has not been investigated. Since the monoxime of diacetyl is readily soluble in water, no doubt the larger part of the original 35 g. of dioxime used remained behind in the form of the monoxime when the steam-distillation in the presence of sulfuric acid was carried on, while a lesser part was carried over as diacetyl or its monoxime during the distillation.

The monoxime which was recovered as mentioned was dried upon a porous plate and found to melt sharply at 76°. It possesses the sweet pungent taste of diacetyl itself and when exposed to the air in an open dish will volatilize completely at room temperature. Its dissociating properties were further studied.

A small portion of the monoxime was dissolved in water, a few drops of dilute hydrochloric acid added and to the mixture immediately added a few drops of ammoniacal nickel solution. An immediate heavy precipitation of the nickel salt of dimethylglyoxime resulted, indicating the readiness with which the monoxime will dissociate into hydroxylamine and diacetyl which products recombine in neutral or alkaline solution to form the less soluble dioxime.

A second portion similarly treated with dilute sulfuric acid was found to dissociate less readily. The dissociation was hastened by boiling, whereupon an immediate precipitation of the nickel salt was obtained when a few drops of an ammoniacal nickel solution were added to the mixture.

A third portion was allowed to stand with dilute acetic acid for two weeks. Tests made with ammoniacal nickel solution at repeated intervals showed that none of the monoxime had dissociated.

A fourth portion was dissolved in water, a few drops of ammoniacal nickel solution added and the mixture allowed to stand for two weeks. The mixture gradually assumed a slight yellow color but there were no indications of the formation of a precipitate, even upon boiling.

Further indications of the dissociating powers of these acids are exhibited by their action upon the nickel salt of dimethylglyoxime. When this salt is treated even with dilute hydrochloric acid the insoluble acid dioxime is at once liberated; upon standing for an hour the dioxime will also completely dissolve in the hydrochloric acid.

Similar treatment with dilute sulfuric acid will set free the acid dioxime from the nickel salt less readily, and, even when boiled, the action goes on at a much slower rate than when dilute hydrochloric acid is used.

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.

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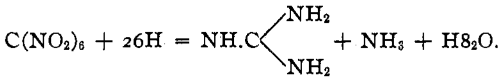
LIMITS OF THE ATTACHMENT OF AMINO GROUPS TO A SINGLE CARBON ATOM; ATTEMPTS TO PREPARE TETRAMINO METHANE.

BY JITENDRA NATH RAKSHIT.

Received January 3, 1914.

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 chloroform[1] at red heat give hydrocyanic acid. Aniline and chloroform[2] give formamidine, Ph.NH.CH : NPh. Chloropicrin[3] or carbon tetrabromide[4] 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.



$$C(NO_2)_6 + 26H = NH.C\begin{matrix}\diagup NH_2\\ \diagdown NH_2\end{matrix} + NH_3 + H8_2O.$$

Experimental.

Tetranitro methane was prepared according to Chattaway's[5] 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.

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[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).