oxalic acid. Its constitution, which has hitherto been surmised, has now been definitely proved to be $3^1,3^2,3^3$-trimethylaurin.

2. "New Fuchsin," which is a mixture of several substances, contains, as has been surmised, $3^1,3^2,3^3$-trimethyl-*p*-rosaniline, or ros-*o*-toluidine. This dye has been isolated and, by converting it to *o*-cresaurin, its constitution has been established.

3. The blue dye, N^1,N^2,N^3-triphenyl-$3^1,3^2,3^3$-trimethyl-*p*-rosaniline, or triphenyl-ros-*o*-toluidine, has been prepared from *o*-cresaurin and from ros-*o*-toluidine, and its constitution has thus been proved. Other blue dyes have been prepared by condensing α-naphthylamine, β-naphthylamine, or *p*-aminobiphenyl with the trimethyl ether of *o*-cresaurin.

ANN ARBOR, MICHIGAN

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

A SIMPLIFIED METHOD FOR THE PREPARATION OF DIMETHYLGLYOXIME

BY WALDO L. SEMON AND V. RICHARD DAMERELL

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A great many processes for the manufacture of dimethylglyoxime have been evolved during the last half century.[1] Recent work on the preparation of oximes[2] brought facts to our attention which led us to undertake a study of the reactions to determine the optimum conditions both as to chemical yield and simplicity of manipulations.

The method now used for the manufacture of dimethylglyoxime consists in preparing first biacetyl monoxime from methylethyl ketone and an alkyl nitrite, and allowing an alkaline solution of this to react with hydroxylamine. In every case the yield of dimethylglyoxime is approximately 60%, whether based upon the methylethyl ketone or the hydroxylamine used.[3] This very significant fact can be explained by assuming a yield of approximately 60% of biacetyl monoxime in the first reaction and an almost quantitative yield of dimethylglyoxime in the second reaction. This explanation we have verified and note that by the usual method of procedure, much of the hydroxylamine used is in effect wasted.

We have attempted first to determine the most favorable conditions for the formation of biacetyl monoxime, and second to simplify its preparation, purification and utilization.

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[1] For bibliography see (a) Adams and Kamm, THIS JOURNAL, **40**, 1282 (1918); (b) *Univ. Illinois Bull.*, **16**, No. 43, 57 (1919).

[2] Semon and Damerell, THIS JOURNAL, **46**, 1290 (1924).

[3] (a) Gandarin, *J. prakt. Chem.*, [2] **77**, 414 (1908), 59 to 64% on methylethyl ketone, 70% on hydroxylamine hydrochloride. (b) Biltz, *Z. anal. Chem.*, **48**, 164 (1909), 56 to 62% on methylethyl ketone, 54 to 60% on hydroxylamine hydrochloride. (c) Adams and Kamm, Ref. 1 a, 50 to 55% on methylethyl ketone, 49 to 53% on hydroxylamine sulfate.

Among the numerous references to the preparation of biacetyl monoxime[4] there are three which bear directly upon this problem. Diels and others describe the large scale preparation of biacetyl monoxime in a yield of 62% by the reaction of methylethyl ketone and amyl nitrite, using hydrochloric acid as a condensing agent. Claisen, however, used as a condensing agent an alkaline solution of sodium hydroxide. When four molecular equivalents of water were added with the sodium hydroxide, the yield of biacetyl monoxime reached a maximum of 88%. Although we have repeatedly tried, we have never been able even to approach a duplication of this yield. Biltz used an excess of hydrogen chloride for a condensing agent but moderated the vigor of the reaction by using ether as

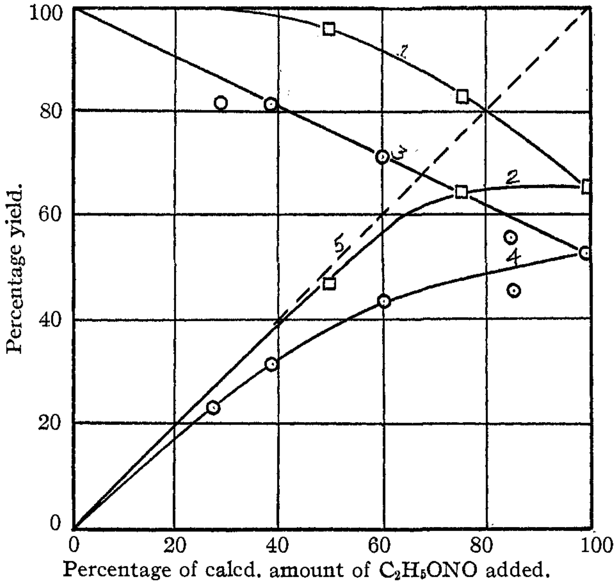

Fig. 1.—The effect of various amounts of ethyl nitrite upon the yield of biacetyl monoxime.

Curves 1 and 3 give the yields based on the ethyl nitrite used; 2 and 4, the yields based on the methylethyl ketone taken; 5, the calculated yield based on the methylethyl ketone.

Curves 1 and 2 represent specially purified methylethyl ketone containing 8% of phosphorus pentachloride; 3 and 4, a technical methylethyl ketone containing 3% of water and 2% of hydrogen chloride.

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[4] (a) Meyer and Züblin, *Ber.*, **11**, 322 (1878). (b) Ceresole *Ber.*, **15**, 1874 (1882). (c) Claisen and Manasse, *Ber.*, **22**, 526 (1889). (d) Thal, *Ber.*, **25**, 1720 (1892). (e) Kalischer, *Ber.*, **28**, 1518 (1895). (f) Diels and Yost. *Ber.*, **35**, 218, 3292 (1902). (g) Claisen, *Ber.*, **38**, 696 (1905). (h) Biltz, *Z. anal. Chem.*, **48**, 164 (1909). (i) Diels and Farkas, *Ber.*, **43**, 1957 (1910).

a diluent and keeping the reaction mixture ice-cold during the addition of amyl nitrite. A slight amount of work has been done using other alkyl nitrites in place of amyl nitrite, and one investigator has tried nitrous anhydride.[5]

The best nitroso-introducing reagent was first sought from among the alkyl nitrites and nitrosyl compounds. Separate samples of dried and specially purified methylethyl ketone containing 2% of hydrogen chloride were treated with equivalent quantities of amyl, *n*-butyl and ethyl nitrites at a temperature of 40° to 55°. When proper precautions were taken to prevent loss of the ketone and of the nitrite, identical yields were obtained in every case, namely 65%. Because of the cheapness and ease of its preparation, and because of the volatility and solubility in water of the ethyl alcohol formed, which made the usual ether extraction unnecessary, ethyl nitrite was used for subsequent experiments. Furthermore, ethyl nitrite is very soluble in methylethyl ketone, and perhaps reacts with it, since the solution becomes warm during its absorption. No biacetyl monoxime is formed, however, unless a condensing-agent is present. Another series of experiments, run with phosphorus pentachloride as a condensing agent, showed that the yield of biacetyl monoxime based upon the ethyl nitrite used was practically theoretical as long as the ratio methyl-

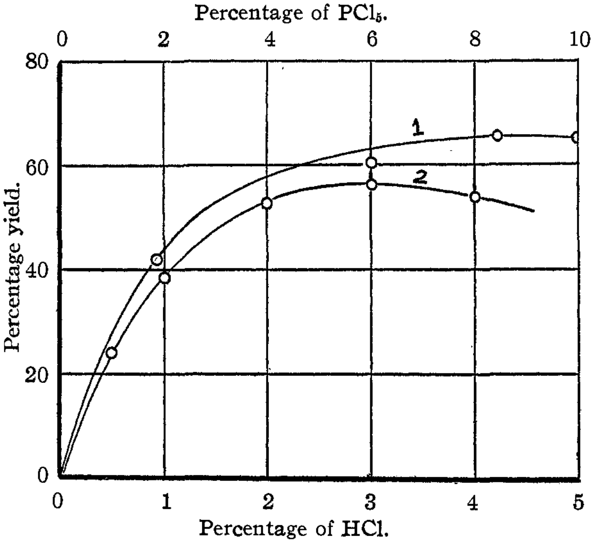

Fig. 2.—The effect of the quantity of condensing agent upon the yield of biacetyl monoxime. Curve 1, phosphorus pentachloride in specially purified anhydrous methylethyl ketone. Curve 2, hydrogen chloride in dried technical methylethyl ketone.

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[5] Behrend, *Ann.*, **283**, 244 (1894).

ethyl ketone/ethyl nitrite was greater than 2.0. With the ratio equal to 1.3 the yield became 84%, and when equal to 1.0 it dropped to 65%. When the yield is calculated on the basis of the methylethyl ketone, the yield of each of the last two approaches 65%. It is evident, therefore, that with the specially purified methylethyl ketone, the addition of more than 75% of the calculated amount of ethyl nitrite is useless. This is not necessarily true with respect to commercial methylethyl ketone as is shown by Fig. 1.

In an effort to decide upon the best condensing agent, various organic and inorganic acids, bases, salts, the halides of phosphorus and many amines were tried. A series of experiments showed the most satisfactory to be, in order, hydrogen chloride, phosphorus pentachloride and phosphorus oxychloride. Another series of experiments showed the yield of biacetyl monoxime to be strongly affected by the quantity of condensing agent present. The curves on Fig. 2 show that for phosphorus pentachloride the most efficient percentage is about 8% and for hydrogen chloride from 2.5 to 3%.

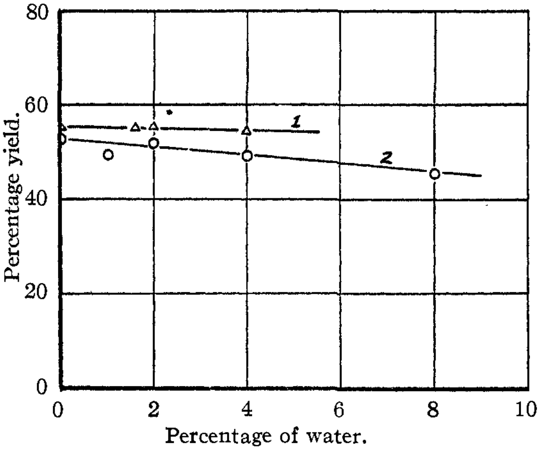

Fig. 3.—The effect of water upon the yield of biacetyl monoxime. Curve 1, technical methylethyl ketone containing 2.5% of hydrogen chloride. Curve 2, containing 2% of hydrogen chloride.

A small amount of water has very little effect upon the yield as is shown by the curves of Fig. 3. The effect is much less marked than that of the impurities present in the commercial methylethyl ketone. Apparently they cause a decrease in the yield of about 10% but in view of the difficulty and loss of material in the purification of commercial methylethyl ketone it is probably just as efficient to use the impure but dry product.

Biacetyl monoxime may also be prepared by means of nitrosyl chloride. In a typical experiment, nitrosyl chloride was passed into 20 g. of methylethyl ketone at —10° until an increase in weight of 50% was obtained. Hydrogen chloride and methylethyl ketone were largely removed by distillation under a vacuum and the residue allowed to solidify. Upon treating with monosulfonate,[6] 9.2 g. of dimethylglyoxime melting at 234° was secured; yield, 51%, based on nitrosyl chloride. For large scale preparation, nitrosyl chloride is unsatisfactory because (1) of the difficulty in preparing it, (2) the temperature must be kept very low during the reaction, (3) the nitrosyl chloride has a tendency to cause chlorination and (4) the hydrogen chloride formed in the reaction collects in the solution and tends to condense the methylethyl ketone with itself.

The biacetyl monoxime produced when ethyl nitrite is used may be separated from the reaction mixture in several ways. It can be obtained by direct distillation since it boils at 186° under 760 mm. or at 83° under 8 mm. With the impure reaction mixture, direct distillation was not found to be advisable since the product secured was usually more or less dark colored and in about one-third of the experiments the residue in the flask exploded. Better results were secured by extracting the biacetyl monoxime with sodium hydroxide, setting it free with acetic acid and distilling in a vacuum. The pure product may also be obtained directly from the reaction mixture by distilling until a temperature of 90° has been reached in the liquid phase and then distilling in a current of superheated steam. Pure biacetyl monoxide crystallizes from the distillate when the latter is cooled to 0°. This product may be recrystallized from chloroform or petroleum ether, or since it has an appreciable vapor pressure and melts at 76°, it may be sublimed in a vacuum.

When dimethylglyoxime is to be the final product, it is not necessary to isolate the biacetyl monoxime, for when the aqueous distillate, containing the biacetyl monoxime, is allowed to stand for several hours with a slight excess of monosulfonate, pure, crystalline dimethylglyoxime is deposited.

Previous workers have always extracted the biacetyl monoxime from the reaction mixture with sodium hydroxide. We have found it just as satisfactory to evaporate off the alcohol, excess of ketone and ethyl nitrite and use the biacetyl monoxime exactly as obtained, thus preventing the formation of tar which always occurs in the alkaline extraction. A dark colored product of dimethylglyoxime is due to tarry matter in the biacetyl monoxime rather than to impurities in the hydroxylamine salt or monosulfonate. A whiter product is always secured by using the crude biacetyl monoxime and acid monosulfonate than with any partially or completely neutralized mixture. An alkaline solution of monosulfonate is entirely non-reactive.

Monosulfonate reagent may be prepared as described in previous articles[7]

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[6] Sodium hydroxylamine monosulfonate.

[7] Semon and others, THIS JOURNAL, **45**, 189 (1923); **46**, 1290 (1924).

or more rapidly as herein described by substituting analyzed sodium bisulfite for the sulfur dioxide. The yield is as good as by the previous method and although the solution is more dilute it may be used with excellent results for the preparation of either oximes or hydroxylammonium chloride. A 10–20% excess of monosulfonate is necessary to cause the complete formation of dimethylglyoxime from the biacetyl monoxime. Subsequent neutralization and evaporation of the mother liquor augments the yield very slightly.

Dimethylglyoxime may be formed from biacetyl monoxime and monosulfonate even in the presence of relatively large amounts of methylethyl ketone. Further, if methylethyl-ketoxime and biacetyl monoxime are mixed in acid solution, at equilibrium most of the methylethyl-ketoxime has been hydrolyzed. This was experimentally shown as follows: 8.7 g. of methylethyl-ketoxime, 10.1 g. of biacetyl monoxime, 100 cc. of water and 5 cc. of concd. sulfuric acid were mixed, warmed to 40° and allowed to stand overnight; yield of the precipitated dimethylglyoxime, 7.6 g., or 65%.

The preparation of dimethylglyoxime as finally worked out follows.

Preparation of Ethyl Nitrite.[8]—Two solutions were prepared: Solution A; 620 g. of actual sodium nitrite (650 g. of the technical 95% material), 210 g. of actual alcohol (285 cc. of 90% denatured alcohol), made up with water to 2.5 liters. Solution B, 440 g. of actual sulfuric acid (255 cc. of concd. sulfuric acid, d. 1.836), 210 g. of actual alcohol (285 cc. of 90% denatured alcohol), made up with water to 2.5 liters. Ethyl nitrite was then generated continuously in gaseous form by allowing Solution B to flow into Solution A.

Preparation of Biacetyl Monoxime.—In a flask fitted with a reflux condenser and arranged for external cooling were placed 620 g. (775 cc.) of methylethyl ketone which had been dried with anhydrous copper sulfate and freshly distilled. Forty cc. of concd. hydrochloric acid was added, the temperature raised to 40° and the ethyl nitrite from the previous solutions passed in, while the temperature was kept between 40° and 55°. The alcohol obtained in the reaction was then distilled until the temperature of the liquid reached 90°.

Steam Distillation of the Biacetyl Monoxime.—When the monoxime from the above procedure is rapidly distilled using superheated steam, practically all comes over with the first five liters of distillate. Upon cooling to 0° the solid crystallizes and may be filtered off. If dimethylglyoxime is the desired product this steam distillation may be omitted.

Preparation of Monosulfonate Reagent.—In an 11-liter (3-gallon) crock was placed 5 kg. of shaved ice, and 569 g. of actual sodium nitrite (594 g. of the technical 95% material) was thoroughly mixed with it. Into this mixture was stirred a suspension of sodium bisulfite containing 1100 g. of available sulfur dioxide (about 1775 g. of technical bisulfite) in 750 cc. of water. To this was added beneath the surface of the solution, during constant stirring, 150 cc. of glacial acetic acid followed by a solution prepared by adding 550 cc. of concd. hydrochloric acid to 400 g. of shaved ice. The entire solution was kept below 0°, further ice being added when there was a tendency for the temperature to rise. The solution upon standing became acid to Congo red paper and contained

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[8] Adapted from directions by Wallach and Otto, *Ann.*, **253**, 251 (1889).

6 or more moles of sodium hydroxylamine disulfonate which rapidly hydrolyzed to an acid solution of monosulfonate.

Preparation of Dimethylglyoxime.—The biacetyl monoxime and monosulfonate were filtered to remove any sediment, mixed in a 15-liter flask, the mixture was heated to 70° and allowed to remain warm and occasionally stirred for several hours. The dimethylglyoxime separated in crystals that were filtered from the solution after it had become cold. They were washed with cold water until free from sulfate; yield, 575 g.; 235–240°. Recrystallization was unnecessary since the product was pure white and free from tarry matter.

Summary

A study has been made of the conditions affecting the formation of dimethylglyoxime, and simplified and efficient methods have been devised for the preparation of biacetyl monoxime, sodium hydroxylamine monosulfonate and dimethylglyoxime.

SEATTLE, WASHINGTON

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

GERMANIUM. XII. TETRA-ALKYL AND TETRA-ARYL COMPOUNDS OF GERMANIUM. GERMANIUM TETRA-ETHOXYL[1]

BY D. L. TABERN, W. R. ORNDORFF AND L. M. DENNIS

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The investigations of the organic compounds of silicon, begun by Friedel and Crafts in 1863, and continued during recent years by Kipping, Bygdén, Polis, Martin, Ladenburg and others, have shown that this element exhibits in this regard close similarity to carbon, its adjacent analog in Group IV.

Mendeléeff predicted in 1871 that ekasilicon (germanium), which follows silicon in Group IV of his Periodic Table, would form volatile "metallo-organic" compounds, such as tetra-ethyl.[2] That substance was prepared[3] in 1886 by Winkler, the discoverer of germanium, and it recently has been further studied by Dennis and Hance.[4] Morgan and Drew have described[5] a few substances of the type germanium-acetylacetone dichloride. These three articles are all that have hitherto appeared on the organic compounds of germanium.

In the systematic study of this class of substances which has now been taken up in the Cornell Laboratory, germanium tetrachloride was selected

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[1] The investigation upon which this article is based was supported by a grant from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University.

[2] *Ann.*, 8th Spl., p. 202 (1871).

[3] Winkler, *J. prakt. Chem.*, **144** (N. F. 36), 177 (1887).

[4] Dennis and Hance, THIS JOURNAL, **47**, 370 (1925).

[5] Morgan and Drew, *J. Chem. Soc.*, **105**, 1261 (1924).