ported. An earlier publication[2] reported the preparation of 12-oxo-*cis*-9-octadecenoic acid by the rapid chromic acid oxidation of ricinoleic acid. The high melting by product reported by Ellis[3] from the chromic acid oxidation of ricinoleic acid was characterized as 9,12-dioxo-*trans*-10-octadecenoic acid.[1]

A method was developed for preparing 9,12-dioxo-*trans*-10-octadecenoic acid from ricinoleic acid in fair yield in a single step. The method consists of running the chromic acid oxidation under a controlled set of conditions so that both keto groups are introduced without decomposition. This development may be of economic importance for industrial preparations. Advantages of the single-step procedure are that considerably less handling of reactants and smaller quantities of raw materials are involved. Furthermore, problems of isolation and storage of the oxygen sensitive intermediate, 12-oxo-*cis*-9-octadecenoic acid, are completely eliminated.

EXPERIMENTAL

Hydrolysis of castor oil. Crude ricinoleic acid was prepared by refluxing 180 ml. of castor oil with a solution containing 350 ml. of ethanol, 53 ml. of water, and 71 g. of potassium hydroxide for a period of 5 min. After cooling, the reaction mixture was acidified with $4N$ hydrochloric acid. The oil layer was removed, washed three times with water, and dried over sodium sulfate. Yield was 146 g. of a pale yellow oil containing approximately 80% of ricinoleic acid.

9,12-Dioxo-trans-10-octadecenoic acid. To a vigorously stirred solution of 146 g. of crude ricinoleic acid in 1.6 l. of glacial acetic acid was added all at once an oxidizing solution composed of 107 g. of sodium dichromate dihydrate, 132 ml. of water, 57.5 ml. of concd. sulfuric acid, and 950 ml. of glacial acetic acid. The temperature of the mixture rose spontaneously to 54°. After about 2 min., the temperature began to drop. When the temperature had fallen to 45°, a fresh oxidizing solution composed of 120 g. of sodium dichromate dihydrate, 600 ml. of water, 60 ml. of concd. sulfuric acid, and 300 ml. of glacial acetic acid was poured in all at once. Vigorous agitation was continued, and the temperature of the reaction mixture was maintained at 40–45° by external heating for a period of 55 min. At the end of this time, the reaction was terminated by pouring in 4 l. of ice and water. This brought down the crude acid as a crystalline precipitate. The precipitated crude acid was collected by vacuum filtration and washed with water until free of chromous salts. The crude product was air dried and recrystallized from 300 ml. of ethanol (3A formulation). Yield was 32 g. (28.6%) of a white, crystalline product having an uncorrected melting point of 111–112°. (Lit.,[1] m.p. 112–113°). Upon comparison of this material with a sample of 9,12-dioxo-*trans*-10-octadecenoic acid prepared by the procedure of Nichols and Schipper,[1] it was found that the two products had identical melting points and infrared absorption. Mixed melting point of the two products was 111–112° (uncorrected).

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(2) J. Nichols, U. S. Patent **2,623,888** (1952).

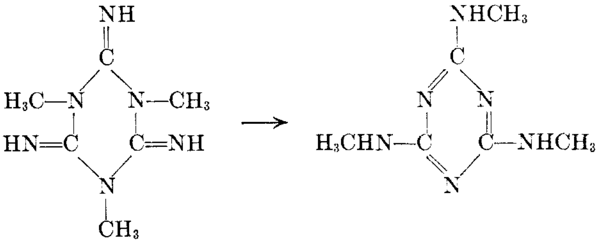
(3) G. W. Ellis, *J. Chem. Soc.*, 9 (1950).

Cyanamide Derivatives. LVI.[1] On the Isomers of Trimethylmelamine[2]

Rokuro Kitawaki and Kiichiro Sugino

Received August 11, 1959

We have indicated in a previous paper[3] that monomethylcyanamide was first obtained in a pure state as a liquid solidified at -40 -50°. In order to learn more about this compound, we have further investigated and reported[4] the reactions of monomethylcyanamide. The present report concerns the results of new observations on the transformation of trimethylisomelamine into its isomer by simple heating.



I II

It is a well known fact that the polymerization of monomethylcyanamide occurs very readily and produces trimethylisomelamine (I). In the course of our studies on this compound, it was found that trimethylisomelamine could be transformed into normal trimethylmelamine[5] (II) by heating it above its melting point for two to three hours. The properties of nor-trimethylmelamine are quite different from those of its isomer. Although it solidified as a resinous substance, it could be purified by distillation. It is easily soluble in water and alcohol but not its isomer. The difference in structure of the two isomers has been verified by the identification of their hydrolytic products and the absorption characteristics in ultraviolet and infrared spectrum. The hydrolysis of these compounds took place as follows:

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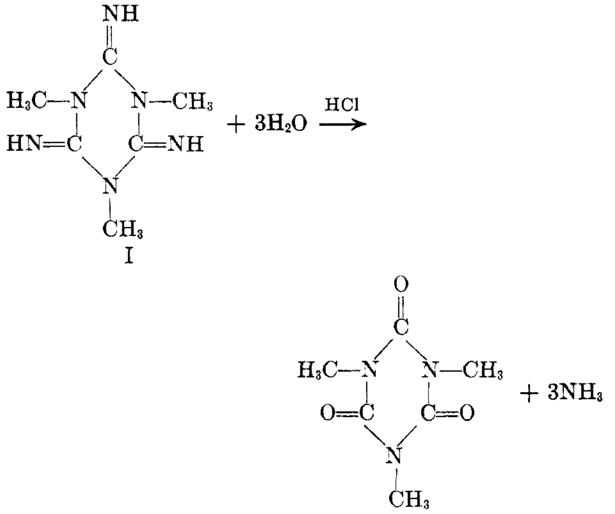
(1) Part LIV, *J. Org. Chem.*, **23**, 100 (1958), LV: *J. Electrochem. Soc.*, **105**, 598 (1958).

(2) This paper was prepared for delivery before the annual meeting of the Chemical Society of Japan held in April 1956.

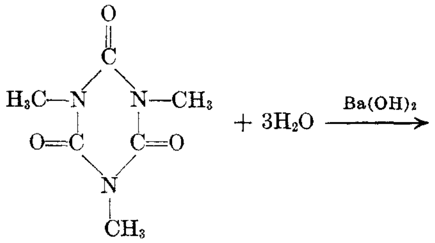
(3) R. Kitawaki, M. Yamashita, and K. Sugino, *J. Chem. Soc. Japan* (*Pure Chem. Sect.*), **78**, 567 (1957), (Part L of this series).

(4) R. Kitawaki, *J. Chem. Soc. Japan* (*Pure Chem. Sect.*), **78**, 1435, 1439 (1957), (Part LI and LII of this series).

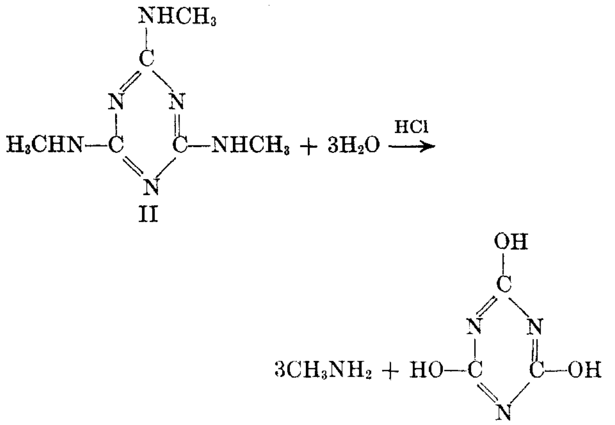
(5) A. W. Hofmann, *Ber.*, **18**, 2755 (1885).



I



$[CH_3NHCON(CH_3)CONHCH_3 + CO_2] \longrightarrow$
$CH_3NHCONHCH_3 + CH_3NH_2 + 2CO_2 \longrightarrow$
$3CH_3NH_2 + 3CO_2$



II

EXPERIMENTAL

Monomethylcyanamide. Because of the careful attention required for the preparation of pure monomethylcyanamide without formation of *sym*-dimethylguanidine and trimethylisomelamine, we shall repeat the description of the procedure we took.

A solution of perfectly dried cyanogen bromide, 26.5 g., in 200 cc. absolute ether cooled at −3-−7° was first placed in a four-necked flask fitted with stirrer, thermometer, gas inlet and outlet, and dry methylamine gas was bubbled in slowly with stirring. This resulted in the separation of methylamine hydrobromide. The bubbling was continued for 2 hr., keeping the reaction temperature at −3-−7° by cooling. At the end of the reaction the evolution of heat ceased; then the flow of methylamine gas was slowed and finally cut off entirely when the *p*H of the mixture reached about 7. The amount of methylamine used was about 100% of the theoretical. The resulting mixture was filtered with a glass filter and the ether removed below 5° without light to leave a liquid. This liquid was purified by dissolving it again in 30 cc. absolute ether, followed by filtration and evaporation of the solvent. The yield was 11.5 g.

Anal.[6] Calcd. for $C_2H_4N_2$: N, 49.97. Found: N, 49.27.

Monomethylcyanamide is a colorless liquid which melts at −40-−50° and may be preserved as crystals in a vessel containing Dry Ice.

Trimethylisomelamine. A solution containing 10 g. of methylcyanamide in 200 cc. of water was made alkaline by adding ammonia, heated on a water bath for 1 hr., and cooled to room temperature. The crystals were filtered and recrystallized from hot water, m.p. 178°.

Anal. Calcd. for $C_6H_{12}N_6$: N, 49.97. Found: N, 49.83.

Rearrangement of trimethylisomelamine to nor-trimethylmelamine. Five grams of completely dried trimethylisomelamine was placed in a test tube and heated gradually in an oil bath. It melted at 178° and formed a clear liquid. After keeping this liquid at 180° for 2 hr., it was allowed to cool, forming a resinous solid. A small heat evolution was seen in the heating curve 40 min. after the heating was started. An evolution of a small amount of ammonia was then witnessed and a weight loss of 0.102 g. (2.04%) was recorded. Four grams of the crude product was then purified by distillation. A fraction, b.p. 310–320°, was collected to give 2.5 g. of a product which was also a resinous solid at room temperature.

Anal. Calcd. for $C_6H_{12}N_6$: N, 49.97. Found: N, 49.87.

An oxalate was formed which was recrystallized from 70–80% alcohol, m.p. 223–224°.

Anal. Calcd. for $C_8H_{14}N_6O_4$: N, 32.55. Found: N, 33.13.

Hydrolysis of trimethylisomelamine. This was carried out in accordance with the direction provided by Hofmann.[7] A 7-cc. sample of concd. hydrochloric acid was gradually added to a mixture of 1.68 g. of trimethylisomelamine in 7 cc. of water, resulting in the formation of a clear solution. It was then heated at 140° for 5 hr. in a sealed tube and allowed to cool in order to separate trimethylisocyanuric acid crystals. The crystals (1.15 g., 67%) were collected and recrystallized from hot water, m.p. 175–176°.

Anal. Calcd. for $C_6H_9N_3O_3$: N, 24.55. Found: N, 24.20.

The filtrate was then diluted to 500 cc. and to it was added sodium hydroxide to form a 1*N* alkali solution; ammonia was distilled into 0.1*N* hydrochloric acid with steam. The hydrochloric acid solution was evaporated to dryness leaving 1.83 g. crude ammonium chloride. It was then purified by extraction with butanol to remove methylamine hydrochloride; yield, 1.38 g. (84%), m.p. above 300°. It gave a very clear reaction to Nessler's test.

Anal. Calcd. for NH_4Cl: N, 26.18. Found: N, 26.05.

Hydrolysis of trimethylisocyanuric acid. For the purpose of further identification, the hydrolysis of trimethylisocyanuric acid was carried out as follows:

A 1.71-g. sample of trimethylisocyanuric acid was dissolved in 100 cc. of water free from carbon dioxide and a clear solution of 9.4 g. barium hydroxide in 400 cc. of water was added to it. A precipitate of barium carbonate was immediately formed. The reaction mixture was subjected to distillation with steam and the distillate (350 cc.) was caught in 0.1*N* hydrochloric acid. This was evaporated to dryness leaving 0.70 g. methylamine hydrochloride, m.p. 225–226° after recrystallization from absolute butanol. The Nessler's test for ammonia proved completely negative. Identity was further confirmed by converting it to methylguanidine hydrochloride by treating it with cyanamide. The picrate derived from the hydrochloride melted at 199°.

The residue from steam distillation was filtered in order to separate barium carbonate. The yield was 4.45 g. The mother liquor, after removal of excess barium hydroxide,

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(6) 0.7% Bromide was involved as a contaminant.

(7) A. W. Hofmann, *Ber.*, **18**, 2781 (1885).

was concentrated at diminished pressure to obtain 0.40 g. of solid matter. This was treated with 5 cc. water and after removal of unchanged trimethylisocyanuric acid by filtration, the solution was again concentrated to dryness at diminished pressure leaving *sym*-dimethylurea, m.p. 80°. It formed a characteristic nitroso compound melted at 97–98°. It showed no depression of the melting point on admixture with the authentic sample.

Hydrolysis of trimethylmelamine. A 10-cc. sample of concd. hydrochloric acid was added to a solution of 2.20 g. of distilled trimethylmelamine in 10 cc. water, and the mixture was heated at 150–160° for 5 hr. in a sealed tube. The resulting solution was allowed to cool to room temperature resulting in the separation of cyanuric acid needle crystals. The crystals were filtered, dried, and weighed 1.32 g., 79%, m.p. above 350°.

Anal. Calcd. for $C_3H_3N_3O_3$: N, 32.55. Found: N, 32.23.

Identity was further confirmed by converting them to cyanuric chloride. It melted at 145° and gave no melting point depression with the authentic sample.

The filtrate was then diluted to 300 cc; made alkaline and subjected to steam distillation. The distillate was caught into 0.1*N* hydrochloric acid. The hydrochloric acid solution was evaporated to dryness leaving 2.46 g. methylamine hydrochloride, m.p. 225–226° after recrystallization from butanol. The Nessler's test for ammonia was completely negative. Identity was further confirmed by converting it to methylguanidine hydrochloride by treating it with cyanamide. The picrate derived from the hydrochloride melted at 199°.

Ultraviolet and infrared spectrums. The ultraviolet absorption spectrum of trimethylisomelamine indicated no maxima from 250 mμ to 280 mμ. On the other hand, that of trimethylmelamine showed a weak maxima at about 235 mμ which might have been due to the conjugated double bond.

The infrared absorption spectrum of trimethylmelamine[8] indicated a very distinct absorption at 12.25 μ, pointing to the presence of triazine ring.[9] Trimethylisomelamine[10] had no absorption at the same region.

The infrared absorption spectrum of cyanuric acids[11] derived from melamine and trimethylamine was also measured. They showed the same spectrum indicating the same identity and had an absorption at 12.80 μ.

Acknowledgment. This investigation was promoted by a grant for fundamental scientific research from the Ministry of Education of Japan and also a grant from Nippon (Japan) Carbide Industries Inc., for which the authors wish to express their deep appreciation. Our gratitude goes to Dr. Motoji Yamashita[12] of our laboratory for his valuable help. We also wish to thank Mr. Hiroshi Kobayashi of the laboratory of Inorganic Chemistry of the Institute and Mr. Yoshiki Matsui of Research Laboratory of Shionogi Pharmaceutical Co. for the ultraviolet and infrared work, respectively.

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(8) Film from ether.

(9) Same result was obtained by W. M. Padgett and W. F. Hamner, *J. Am. Chem. Soc.*, **80,** 803 (1958), for trimethylmelamine.

(10) In Nujol.

(11) Pressed into a potassium bromide disk.

(12) Present address, Nippon (Japan) Carbide Industries Inc., Uozu City, Toyama-Pref. Japan.

Cyanamide Derivatives. LVII.[1] New Route for Preparation of Biguanide[2]

KOZO SHIRAI AND KIICHIRO SUGINO

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O-alkylisuorea is a substance quantitatively obtainable from crystalline cyanamide on a commercial basis.

We have discovered that biguanide can be obtained in a pure state and good yield by treating *O*-alkylisourea with guanidine in ethanol.

The reactions are indicated schematically as follows:

$$NH_2C(NH)OR + NH_2C(NH)NH_2 \longrightarrow NH_2C(NH)NHC(NH)NH_2 + ROH$$

$$NH_2C(NH)NHC(NH)NH_2 + NH_2C(NH)NH_2{\cdot}HCl \longrightarrow NH_2C(NH)NHC(NH)NH_2{\cdot}HCl + NH_2C(NH)NH_2$$

Melamine was a main by-product resulting from the reaction of *O*-alkylisourea with biguanide as well as other reactions of the former.[3] A small amount of dicyandiamide was also formed.

Although we have been able to obtain the biguanide salt by treating dicyandiamide with the ammonium salt in the fused state,[4] we do not consider it a convenient method to prepare biguanide because of the low yield and complexity of purification. Therefore, this method offers a practical route for the preparation of biguanide.

EXPERIMENTAL

A 500-cc. sample of an ethanolic solution[5] of 88.1 g. of *O*-ethylisourea, 59.1 g. of guanidine, and 191 g. of guanidine hydrochloride was placed in a four necked flask fitted with a condenser, stirrer, thermometer, and a sodium hydroxide tube. The solution was heated at 60°–65° with stirring and a precipitate formed after 2 hr. Heating was continued for 3 hr. and then allowed to cool overnight. The separated crystals were filtered and washed with ethanol, dried, and weighed 64.2 g. They were dissolved in 200 cc. of cold water and the insoluble residues were filtered. Evaporation of the filtrate at diminished pressure gave 57.0 g. of pure biguanide monohydrochloride, m.p. 224°–225°. The melting points of free base, mononitrate, and monopicrate derived from the monohydrochloride were 130°,[6] 202°,[7] and 232°,[7] respectively. The yield was 54% based on

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(1) Part LVI, *J. Org. Chem.*, **25,** 1043 (1960).

(2) This paper was prepared for delivery before the annual meeting of the Chemical Society of Japan held on April 1957.

(3) K. Sugino and K. Shirai, unpublished results. U. S. patent application, Serial No. 782675, Dec. 24, 1958.

(4) For example, K. Sugino, *J. Chem. Soc. Japan*, **60,** 351 (1939), (Part VII of this series).

(5) This solution was prepared in the following manner: Free guanidine ethanolic solution was first prepared from a solution of guanidine hydrochloride in ethanol by removing the acid with metallic sodium. It was concentrated at diminished pressure to a concentration of 3–5*N*. A quantity of *O*-ethylisourea and guanidine hydrochloride crystals was added to a certain volume of the solution and diluted to a certain concentration by ethanol.