Preparation of Vinylene Carbonate

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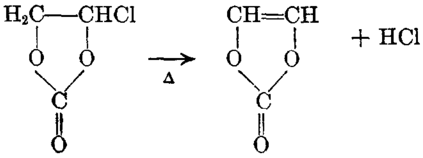
Vinylene carbonate (I), a novel monomer and dienophile, has been previously prepared by the dehydrochlorination of monochloroethylene carbonate (II) with triethylamine or from *sym*-dichloroethylene carbonate by the action of zinc dust.[2,3] We wish to report that chloroethylene carbonate can be thermally dehydrohalogenated to yield vinylene carbonate.



II I

This method has the advantage of being less time consuming and eliminates the use of ether and the amine.

The pyrolysis can be carried out at atmospheric or subatmospheric pressure, with or without a diluent of vaporized hydrocarbon or inert carrier gas. Materials which have been successfully used as column packings are granular anhydrous calcium sulfate (Drierite), granular anhydrous calcium chloride, and glass Raschig rings. Granular activated charcoal and granular activated alumina yielded only gaseous products under a variety of experimental conditions. The most suitable column packing found in our brief study was 8-mesh calcium sulfate (Drierite). The activity of this bed decreases rapidly with use as shown by yields of 44.5%, 21%, and 5% of vinylene carbonate on successive one mole runs under identical conditions. The activity of the bed may be restored to its original level by heating the system to about 500° and slowly passing air over the bed. Maximum conversions (35–40%) and maximum yields (40–45%) for one mole runs with a Drierite bed are obtained at 250° at reduced pressure (50–60 mm of Hg). Higher or lower temperatures lower both conversion and yield. A low yield and conversion to vinylene carbonate results when chloroethylene carbonate is pyrolyzed over glass Raschig rings at 400–425°. Attempts to obtain I by pyrolysis of *sym*-dichloroethylene carbonate have failed.

EXPERIMENTAL

Apparatus and Procedure. The pyrolysis was carried out by passing the compound or a mixture of the compound and a diluent through a 25 mm. o.d. Pyrex tube packed for a distance of 90 cm. and heated to the desired temperature by means of an electrically controlled furnace. The reactants were added dropwise to the reaction zone from a dropping funnel, and the pyrolyzate was collected in a receiver cooled in a Dry Ice bath. A water pump served as a source of reduced pressure.

Pyrolysis. A. Monochloroethylene carbonate over Drierite. The chloro carbonate (122.5 g.; 1 mole) in 100 ml. of dry toluene was added dropwise during a period of 90 min. to the reaction zone packed with 8-mesh Drierite and heated at 250–260°. The system was maintained at 50–60 mm. during the run. The pyrolyzate was neutralized by the addition of solid potassium acetate, was filtered, and distilled. There was obtained 5 g. of material, b.p. 29–30° (25 mm.) followed by 28 g. of vinylene carbonate, b.p. 63–65° (18 mm.), $n_{\rm D}^{25}$ 1.4190, and 13 g. of recovered monochloroethylene carbonate, b.p. 114–119° (18 mm.). The conversion to vinylene carbonate was 32%, and the yield was 36%.

The low boiling material [b.p. 29–30° (25 mm.)] was a mixture of compounds containing large quantities of chloroacetaldehyde. It reacted with ethanol saturated with hydrogen chloride to furnish chloroacetal, which was identified by comparison of its infrared spectra with that of an authentic sample.

The bed was regenerated for the following run by heating the system to 500° and slowly passing air over the bed for a period of about two hours.

B. Monochloroethylene carbonate over glass Raschig rings. The column described above was packed with Pyrex glass Raschig rings (6 × 6 mm.). The system was heated at 400–425° at 60–80 mm. while adding monochloroethylene carbonate (122.5 g.; 1 mole) in 100 ml. of dry toluene for thirty minutes. The pyrolyzate was distilled and furnished 5 g. of impure vinylene carbonate [b.p. 60–62° (18 mm.), $n_{\rm D}^{25}$ 1.4220] and 62 g. of recovered monochloroethylene carbonate.

The material collected at 60–62° (18 mm.) was shown to be composed largely of vinylene carbonate as it reacted with hexachlorocyclopentadiene to give a high yield of the adduct, m.p. 233–234° (dec.) [reported[3] m.p. 241–242.8° (corr.)].

Anal. Calcd. for $C_8H_2O_3Cl_6$: C, 26.77; H, 0.56; Cl, 59.28. Found: C, 26.97; H, 0.74; Cl, 59.37.

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[2] M. S. Newman and R. W. Addor, *J. Am. Chem. Soc.*, **75**, 1263 (1953).

[3] M. S. Newman and R. W. Addor, *J. Am. Chem. Soc.*, **77**, 3789 (1955).

A Simplified Procedure for Preparing 9,12-Dioxo-*trans*-10-octadecenoic Acid

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In a recent paper,[1] the preparation of 9,12-dioxo-*trans*-10-octadecenoic acid by the chromic acid oxidation of 12-oxo-*cis*-9-octadecenoic acid was re-

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[1] J. Nichols and E. Schipper, *J. Am. Chem. Soc.*, **80**, 5705 (1958).

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 4*N* 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]

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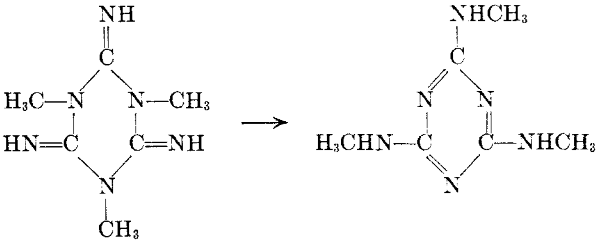
We have indicated in a previous paper[3] that monomethylcyanamide was first obtained in a pure state as a liquid solidified at −40 −50°. In order to learn more about this compound, we have further investigated and reported[4] the reactions of monomethylcyanamide. The present report concerns the results 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).