Preparation of Vinylene Carbonate

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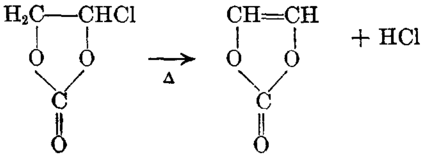
Vinylene carbonate (I), a novel monomer and dienophile, has been previously prepared by the dehydrochlorination of monochloroethylene carbonate (II) with triethylamine or from *sym*-dichloroethylene carbonate by the action of zinc dust.[2,3] We wish to report that chloroethylene carbonate can be thermally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