*TRANSACTIONS, ILL. STATE ACAD. SCI.*
*Vol. 67, No.1 (1974)*

# CYCLIC CARBONATES. III. THE SYNTHESIS, PHYSICAL AND CHEMICAL PROPERTIES OF VINYLENE CARBONATES

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## ABSTRACT

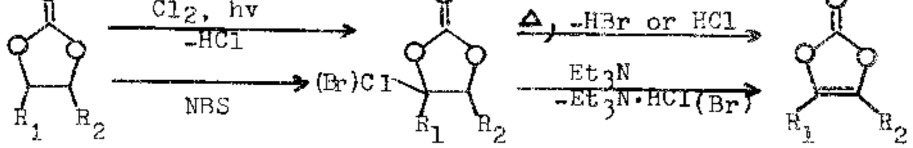
The synthesis and physical properties of four new vinylene carbonates (1,3-dioxol-2-ones) is described. They are dimethyl-, diphenyl-, methylphenyl- and methyl-(3-trifluoromethylphenyl)vinylene carbonate. General methods for the synthesis of vinylene carbonates are discussed along with their known reactions. A table enumerating the mode of synthesis, yield and physical properties of all known vinylene carbonates is presented.

In connection with our attempts to synthesize cyclopropanediols we required a series of substituted vinylene carbonates (IUPAC designation is 1,3-dioxol-2-ones). The synthesis and properties of several simpler members of this series have been reported previously. The parent compound, vinylene carbonate, was synthesized by Newman and Addor (1955) by triethylamine promoted dehydrochlorination of chloroethylene carbonate or by zinc dehalogenation of 1,2-dichloroethylene carbonate. Scharf, Droste and Liebig (1966) utilized the latter method to synthesize dichlorovinylene carbonate from tetrachloroethylene carbonate. Passing chloroehtylene carbonate over drierite at 250-60° (Johnson and Patton, 1960) and over salts and oxides of Groups I, II, VIIB metals at 300° (Holfermann and Springman, 1962) yields vinylene carbonate in fair to good yields also. Morris and Hubbard (1962) and Moss (1962) synthesized phenyl and methyl vinylene carbonates respectively by thermal dehydrohalogenation of the appropriately substituted chloroethylene carbonates. And phenylene carbonate (not formally a vinylene carbonate) can be synthesized by carbonylation of catechol using phosgene under basic conditions (see Org. Syntheses Coll. Vol. 4, 788, 1963). We have confirmed these syntheses and have extended the general methods to the synthesis of four new vinylene carbonates.

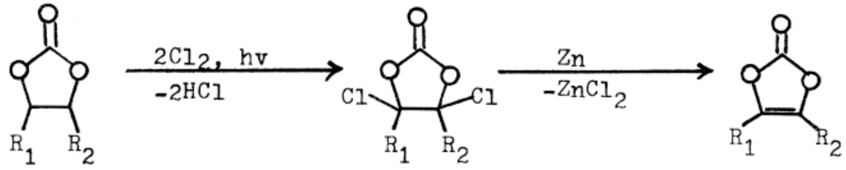
Successful synthesis of vinylene carbonates generally falls under three general methods:

a) halogenation--dehydrohalogenation.
b) halogenation-zinc dehalogenation and
c) carbonylation of enediols.

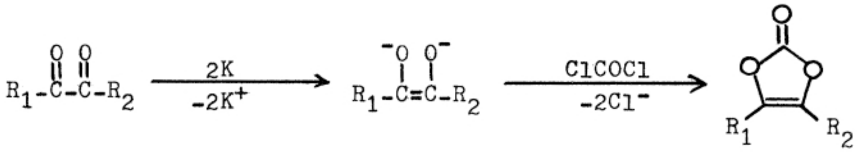
a)



b)



c)



1 $R_1=R_2=H$

2 $R_1=CH_3$, $R_2=H$

3 $R_1=R_2=CH_3$

4 $R_1=C_6H_5$, $R_2=H$

5 $R_1=R_2=C_6H_5$

6 $R_1=CH_3$, $R_2=C_6H_5$

7 $R_1=CH_3$, $R_2=C_6H_4$ $(3-CF_3)$

8 $R_1=R_2=Cl$

Using these methods, we wish to report the synthesis and physical properties of four new vinylene carbonates, dimethylvinylene carbonate (3), diphenylvinylene carbonate (5), methylphenylvinylene carbonate (6) and methyl-(3-trifluoromethyl)phenylvinylene carbonate (7). This data along with the corresponding data for the previously synthesized vinylene carbonates is enumerated in table 1.

Table I. Vinylene Carbonates--Synthetic Methods and Physical Properties.

| Compound | Method | % Yield | b.p. | m.p. | $n_D$ | Reference |
|---|---|---|---|---|---|---|
| 1‡ | a | 72 | 73-4° (32 mm) | 22.0° | 1.4190 (25°) | Newman & Addor |
| 1 | a | 36 | 63-5° (18 mm) | - | 1.4190 (25°) | Johnson & Patton[a] |
| 1 | a | 87 | 52° (8 mm) | - | - | Holfermann & Springmann |
| 1 | b | 29 | - | - | - | Newman & Addor |
| 2 | a | 31 | 69° (17 mm) | -22.5°* | 1.4264 (20°) | Moss |
| 3 | a | 20-40 | - | 78-9° | - | * |
| 4 | a | 60 | 110° (0.5 mm) | 82-3° | - | Morris & Hubbard |
| 4 | b | 36 | - | - | - | ibid. |
| 5 | c | 30 | 155° (0.4 mm) | 75-6° | - | * |
| 6 | a | 39 | - | 79-80° | - | * |
| 6 | b | 4 | 107° (0.05 mm) | 80.5-1° | - | * |
| 7 | a | 43 | - | 75-6° | - | * |
| 8 | b | 78 | 78° (64 mm) | - | 1.4624 (25°) | * |
| 8 | b | - | 39-40° (10 mm) | - | 1.4602 | Scharf, et al. |

*this work

‡dipole moment u=4.57$_D$ (Dorriss, K. L., Britt, C.O., Boggs, J.E., J. chem. Phys. 44:1352 (1966).

In general vinylene carbonates undergo the classical chemical reactions of double bonds. Most interest to date has centered on the polymerization of vinylene carbonate and its utility in the cycloaddition reactions: [2+1] (carbene insertion), [2+2] (photocycloadditions), [2+3] (1,3-dipolar cycloadditions) and [2+4] (Diels-Alder Reactions). Vinylene carbonate is readily polymerized and then hydrolyzed to polyhydroxymethylene (Schaefgin and Field (1966). Copolymerization with a variety of other monomers had produced polymers with potential as semipermeable membranes. The synthetic interest in vinylene carbonates in cycloaddition reactions no doubt stems from the hydrolysis product, 1,2-diols. We (Breitbeil, et al., 1968) have synthesized a series of 1,2-cyclopropanediol cyclic carbonates by carbene insertion on vinylene carbonates ([2+1]-cycloaddition). The sensitized [2+2]-photocycloaddition of vinylene carbonate (Hartmann and Steinmetz, 1967; Hartmann, 1968) and dichlorovinylene carbonate (Scharf, 1968) to a variety of olefins to give 1,2-cyclobutanediol cyclic carbonates in good yields has been recently demonstrated. Vinylene carbonate can also dimerize under these conditions to give cyclobutane intermediates which hydrolyzed to 1,2,3,4-tetrahydroxycyclobutane (Hartmann and Steinmetz, 1967). The [2+3]-cycloaddition of vinylene carbonate to nitrile oxides (Desimoni, 1968) and subsequent hydrolysis has been shown to be a new route to 4-hydroxyisoxazoles. Perrini and Marxer (1963) found that treatment of vinylene carbonate with an amide and polyphosphoric acid at 165-170° gave the oxazole system. Vinylene carbonate also functions as a dieneophile in Diels-Alder reactions (2+4-cycloadditions), although somewhat reluctantly. Such dienes as cyclopentadiene and butadiene (Scharf, 1968), 2,3-dimethyl-1,3-butadiene, hexachlorocyclopentadiene, furan and cyclopentadiene (Newman and Addor, 1955), anthracene (Johnson and Patton, 1960b) and tetracyclone (Yates and Hyde, 1962) have been used. Vinylene carbonate hydrogenates with difficulty, but it and its derivatives add chlorine and bromine with ease (Newman and Addor, 1955). We have observed that vinylene carbonate adds hydrogen chloride to form monochloroethylene carbonate. We have also noted that the addition of chlorine to methylvinylene carbonate, under condiconditions that do not restrict free radical processes, yields 4-chloro-5-methylene-1,3-dioxolan-2-one. With zinc chloride vinylene carbonate readily adds chlorodimethyl ether (Rieche, et al., 1965). Vinylene carbonate hydrolyzes to yield glycolaldehyde and a detailed study of the mechanism involved has been carried out (Saadi and Lee, 1966).

## EXPERIMENTAL

Melting points were obtained using a circulating silicone oil bath and are uncorrected. Elemental analyses were carried out by Micro-Tech Laboratories, Inc., Skokie, Illinois. Infrared spectra were obtained from Perkin-Elmer 21 and 337 Infrared Spectrometers. Ultraviolet spectra were obtained from a Beckmann Model DK-2A spectrometer. The NMR spectra were obtained from a Varian A-60 spectrometer.

Dimethylvinylene Carbonate (3). To 58.0 g. (0.50 mole) of 2,3-butanediol cyclic carbonate (7) in 250 ml. of carbon tetrachloride in a conventional photolysis apparatus was added a chilled solution of 17.5 g. (0.50 mole) of chlorine in carbon tetrachloride. The mixture was cooled to 0-5° and photolyzed for 20 min. using a 450 watt high pressure mercury lamp in a quartz water-cooled insert. If desired the course of the reaction could be followed by observing the disappearance of the yellow color due to chlorine or the disappearance of two phases. Chlorinated ethylene carbonates are soluble in carbon tetrachloride while ethylene carbonates are not. After degassing with nitrogen, the carbon tetrachloride was slowly distilled from the reaction mixture. Vacuum distillation gave three fractions, the first of which (b.p. 90-116° at 17 mm) was mostly 3 (15.5 g.) by NMR analysis; subsequent fractions were mostly starting material (b.p. 117-132° at 17 mm) and dichlorinated products. The total yield of 3 was 32% (NMR integration analysis). Crystalline 3 was separated by filtration from the distillate and recrystallized from carbon tetrachloride to give 9.7 g. of white solid, m.p. 78-79°. Carbonate 3 has an unusually high vapor pressure--several grams on a watch glass exposed to the air evaporated overnight. Attempted distillation of 3 caused fouling of glassware constrictures and vacuum tubing. The NMR spectrum ($CCl_4$, TMS std showed a singlet at 2.01δ; IR (dilute $CCl_4$) absorptions at 1850 (s), 1830 (s), 1745 (m), 1230 (s), 1210 (s) and 1010 $cm^{-1}$ (s); UV absorption (hexane) at 277.5 nm ($\epsilon_{max}$ 7.5).

Anal. Calcd. for $C_5H_6O_3$: C, 52.6; H, 5.3. Found: C, 52.45; H, 5.72.

Diphenylvinylene Carbonate (5). To 80 g. (0.38 mole) of benzil in 800 ml. of dry tetrahydrofuran was added 1393 g. of a 1.5% sodium amalgam. The reaction mixture turned bright orange. After refluxing 8 hrs., 45 g. (0.46 mole) of phosgene in cold tetrahydrofuran was added dropwise over a period of 30 min. After refluxing 24 hrs., most of the tetrahydrofuran was removed by distillation. About 800 ml. of slightly acidified water was carefully added and the mixture was extracted with ether, dried, solvent stripped and the residue distilled through a short path column. The desired product was collected at 155° (0.4 mm) and after recrystallization from heptane, 27 g. of white crystalline 5 was obtained, m.p. 75-6° (30% yield). The NMR spectrum ($CCl_4$, TMS std.) showed a singlet at 7.45δ; IR (dilute $CCl_4$) absorptions at 1825 (s), 1436 (m), 1235 (s), 1065 (s) and 755 $cm^{-1}$ (s); UV absorption (hexane) at 294 n ($\epsilon_{max}$ = 7.420), 218 nm ($\epsilon_{max}$ = 11,400), sh 236 nm ($\epsilon_{max}$ = 5,825).

Anal. Calcd. for $C_{15}H_{10}O_3$: C, 75.6; H, 4.2. Found: C, 75.97; H, 4.21.

Methylphenylvinylene Carbonate (6). 3-Phenyl-2,3-propanedione was synthesized according to the procedure in Organic Synthesis (Vol. 23, 1 (1943)) was reduce with lithium aluminum hydride in the conventional way to obtain 1-phenyl-1,2-propanediol. Transesterification with diethyl carbonate (7) yielded a diastereomeric mixture of 1-methyl-2-phenylethylene carbonates in an overall yiel of 41%. A weighed amount of this mixture (64.6 g., 0.32 mole) and 800 ml. of carbon tetrachloride was placed in the photoreaction vessel and cooled to 0°C. To this was added 33.4 g. (0.33 mole) of chlorine dissolved in cold carbon tetrachloride. With ice cooling and stirring the reaction mixture was irradiated for 20 min. with a 450 watt Hanovia-679A high pressure mercury lamp in which time it turned from yellow to colorless. After passing $N_2$ through for about 1 hr., the reaction mixture was slowly heated to reflux. A copious amount of hydrogen chloride was noted. The volume was halved by distillation and cooled. The desired crystallized product was collected by filtration and the entire process repeated four times to give after recrystallization from carbon tetrachloride, 22.0 g. of 6 as a white crystalline solid, m.p. 79-80°C. (39% yield). The NMR spectrum ($CCl_4$, TMS std.) showed singlets at 2.38δ and 7.42δ integrating 3:1; IR (dilute $CCl_4$) absorptions at 1830 (s), 1240 (s), 1192 (s) and 758 (s); UV absorption (hexane) at 271 nm ($\epsilon_{max}$ = 10,700), sh at 264 nm ($\epsilon_{max}$ = 10,250).

Methyl-(3-trifluoromethylphenyl)vinylene Carbonate (7). 3-Trifluoromethylpropiophenone was synthesized from 3-trifluoromethylbenzonitrile and ethylmagnesium bromide in the conventional way, and then converted to the 1,2-dione via the isonitroso derivative. Lithium aluminum hydride reduction and then transesterification using diethylcarbonate gave 1-methyl-2-(3-trifluoromethyl)-phenylethylene carbonate as a diastereomeric pair in overall 25% yield. In 200 ml. of dry carbon tetrachloride was dissolved 11.5 g. (0.0468 mole) of 1-methyl-2-(3-trifluoromethyl)phenylethylene carbonate and 8.9 g. (0.050 mole) of N-bromosuccinimide. This mixture, under an atmosphere of nitrogen, was irradiated in a Rayonet Srinivasan-Griffin Photochemical Reactor with eight RPR-3500 Å lamps for one hour. Succinimide was filtered and the solvent was removed under reduced pressure. The oily residue was heated in a flask with glass wool at 130° at 10 mm-Hg for 30 min. The pressure was reduced to 0.5 mm-Hg and the bromoethylene carbonate that had not dehydrobrominated was distilled at 95-105° (1.7 g.) The glass wool in the distillation flask was extracted two times with hot cyclohexane. On cooling and filtering, 4.9 g. of white crystalline 7 was obtained (48% yield based on consumed 1-methyl-2-(3-trifluoromethyl)phenylethylene carbonate). The NMR spectrum ($CCl_4$, TMS std.) showed singlets at 2.45δ and 7.68δ integrating 3:4; IR (dilute $CCl_4$) absorptions at 1840 (s), 1240 (s), 1130 (s); UV absorption (hexane) at 263 nm ($\epsilon_{max} = 24,600$).

Anal. Calcd. for $C_{11}H_7F_3O_3$: C, 54.0%; H, 2.86%. Found: C, 53.27%; H, 2.93%.

## ACKNOWLEDGMENT

We gratefully acknowledge the support of this work by the Research Corporation. Thanks are due Mr. Mahendra Patel for the ultraviolet spectra.

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