1662 © *1984 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, **57**, *1662—1666 (1984)* [Vol. 57, No. 6

Cyclic Carbonates Obtained by Reactions of Alkali Metal Carbonates with Epihalohydrins

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(Received July 11, 1983)

A study has been carried out on the reaction of alkali metal carbonates with epihalohydrins in the presence of cation complexing agents *e.g.* crown ethers. 3-Glycidyloxypropylene carbonate was found to be formed as the main product of the reaction of epichlorohydrin with potassium carbonate promoted by 18-crown-6. The effect of various epihalohydrins and alkali metal carbonates on the reaction course was examined. It was found that the reaction of potassium hydrogencarbonate with epichlorohydrin gives 4-hydroxymethyl-1,3-dioxolan-2-one. When the reaction of epihalohydrins with potassium carbonates was carried out in the atmosphere of carbon dioxide the products contained linear carbonate linkage apart from cyclic one. From these results, a plausible mechanism was proposed for the reaction of alkali metal carbonates with epihalohydrins in the presence of crown ethers.

The polycondensation reaction of alkali metal carbonates with α,ω-dihalo compounds in the presence of crown ethers, leading to polycarbonates,[1] prompted to develop studies on the application of alkali metal carbonates for the synthesis of high polymers.

Recently we have shown the possibility of using alkali metal carbonates as substrates for the synthesis of dialkyl carbonates, which when having been subjected to transesterification yielded high-molecular-weight polycarbonates.[2]

From the literature data[3] it results that alkali metal carbonates promoted by crown ethers initiate an anionic polymerization of oxiranes. The presence of carbon dioxide in the polymerization system with propylene oxide was found to stop the polymerization. In this system cyclic propylene carbonate was formed,[3] but in rather low yield.[4]

Recently, we have shown that cyclic carbonates could be obtained in nearly quantitative yield in the reaction of carbon dioxide with oxiranes in the presence of alkali metal halides, *e.g.* potassium iodide and anion-activating agents. Potassium carbonate, however, appeared also to be an efficient catalyst for the above reaction in the case of (halomethyl) oxiranes.[4] On the other hand, the reaction of potassium carbonate with α,ω-dibromo derivatives was reported to produce cyclic carbonates.[5]

In the course of investigations on the polymerization of epihalohydrins by the potassium carbonate–crown ether system, instead of a polymeric product, we found the formation of products containing a 1,3-dioxolan-2-one ring. Thus, in this paper we decided to study the synthesis of cyclic carbonates by the reaction of alkali metal carbonates with epihalohydrins in the presence of cation complexing agents.

Cyclic carbonates were found recently[6] as rather useful monomers for a number of new polymer syntheses.

Results and Discussion

It was found that the reaction of potassium carbonate (**1a**) with epihalohydrin (1-chloro-2,3-epoxypropane (**2a**)) carried out in the presence of 18-crown-6 or benzyltriethylammonium chloride (TEBA) yielded 3-glycidyloxypropylene carbonate [4-(oxiranylmethoxymethyl)-1,3-dioxolan-2-one (**3a**)]. The IR spectrum of the post-reaction mixture did not exhibit any absorption bands characteristic for a linear carbonate linkage.

The reactions of sodium and lithium carbonates in the presence of 15-crown-5 were found also to give **3a** but in lower yield than when **1a** was used (Table 1).

Considering the structure of cyclic carbonate **3a** the following scheme of the reaction of **1a** with **2a** can be proposed.

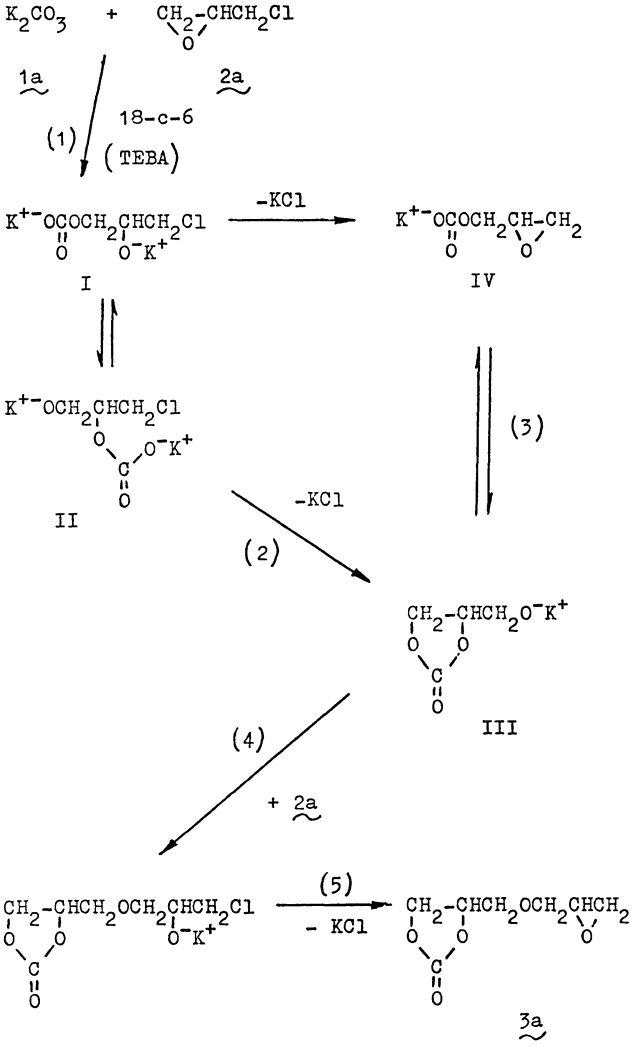


Table 1. The yield of **3a** in reaction of **2a** with alkali metal carbonates[a)]

Alkali metal carbonate	Anion activating agent	Reaction conditions			Yield of **3a**
		Molar ratio Carbonate/**2a**	Temp °C	Time h	%
K_2CO_3	18-c-6	1 : 4	85	24	53
		1 : 6	85	24	60
		1 : 10	90	24	65
	TEBA	1 : 6	80	20	43
Na_2CO_3	15-c-5	1 : 10	90	22	42
Li_2CO_3		1 : 10	85	24	10
$CaCO_3$	18-c-6	1 : 10	90	24	—

a) See Exptl part.

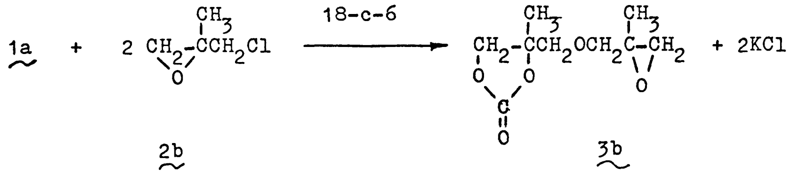
The carbonate ion, as an active nucleophilic agent when **1a** is complexed by a crown ether, can attack the C_α atom of the oxirane ring according to Eq. 1. The resulting **I** should undergo an intramolecular ester-exchange reaction leading to **II**, which can be followed by a cyclization reaction (Eq. 2) yielding **III**. The intermediate **III** can be also formed according to Eq. 3 involving an intramolecular nucleophilic attack of the carbonate ion on the oxirane ring in **IV**. The alcoholate ion in **III** can undergo reaction with **2a**, being in excess with respect to **1a** in the reaction system, and **3a** is formed as the final product (Eqs. 4 and 5).

When 1-chloro-2-methyl-2,3-epoxypropane (**2b**) was used instead of **2a** to the reaction with **1a**, a cyclic carbonate **3b** of a structure analogous to **3a** was formed (Eq. 6). This indicates that the reactions of substituted epihalohydrins with **1a** give also derivatives with oxirane and 1,3-dioxolan-2-one rings as the main reaction products.

However, in the case of the reaction of **1a** with 1-bromo-2,3-epoxypropane (**2c**) it appeared that this reaction leads to products with linear carbonate linkages besides those with 1,3-dioxolan-2-one ring as it is indicated by the appearance of an infrared absorption band at 1750 cm^{-1} (C=O in a linear carbonate linkage). This absorption band was twice less intense than that at 1803 cm^{-1}, characteristic for carbonyl of 1,3-dioxolan-2-one ring. Taking into account our previous results[7)] of studies on the reaction of **2c** with phenolates, one may consider that in the system studied a nucleophilic attack of a carbonate ion on the carbon atom bonded to a bromine atom is plausible and a linear carbonate linkage can be formed (Eq. 7).

In the course of our studies on the reaction of 4-bromomethyl-1,3-dioxolan-2-one with **1a** also a nucleophilic attack of the carbonate ion on the carbon atom bonded to bromine was shown to occur. As a result the product containing both cyclic and linear carbonate linkages was formed (Eq. 8).

When the reaction of **2a** with **1a**, promoted by a crown ether, was carried out in the presence of small amount of water, the post-reaction mixture was found to contain 4-hydroxymethyl-1,3-dioxolan-2-one (**4a**). The formation of **4a** probably results from the presence of potassium hydrogencarbonate (**1b**) in the above water-containing reaction mixture. **1b** should be formed by basic hydrolysis of carbonate groups (Eqs. 9 and 10).



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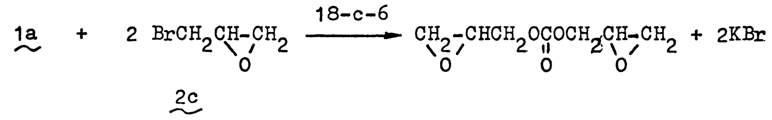

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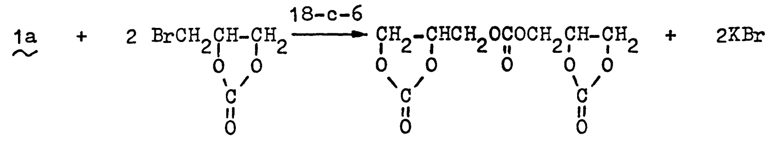

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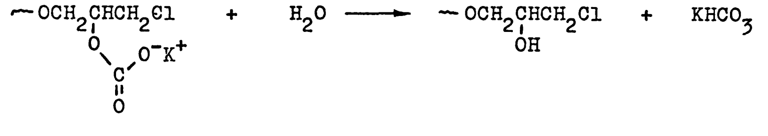

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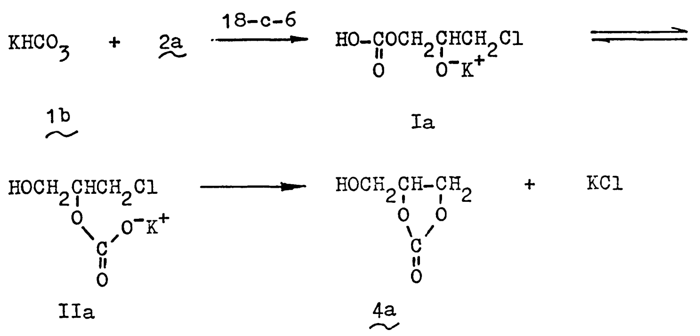

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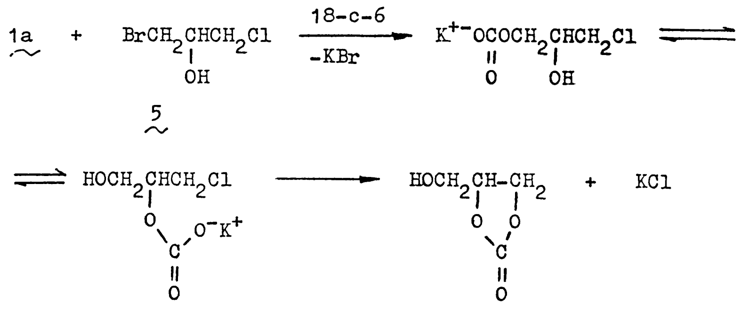

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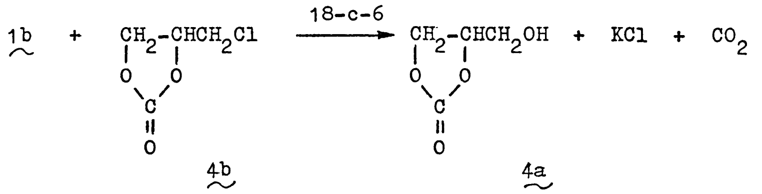

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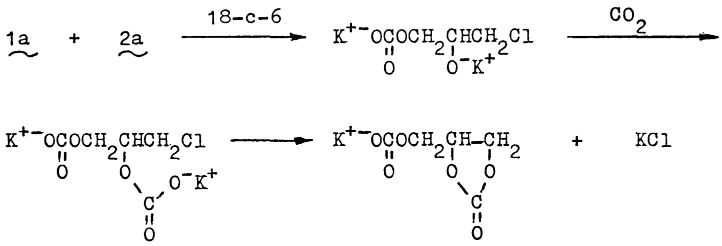

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In order to confirm the above suggestion, the reaction of **1b** with **2a** in the presence of a crown ether was studied and it appeared to produce **4a** as the main product. The course of this reaction may be represented by Eq. 11.

Also in this case a nucleophilic attack of the hydrogencarbonate ion on the C_α atom of the oxirane ring of **2a** takes place, analogously as in the reaction of **1a** with **2a**. The resulting **Ia** exists in an equilibrium with the corresponding product of the intramolecular ester exchange **IIa**, which undergoes cyclization to **4a**.

Another reaction between **1a** and 1-bromo-3-chloro-2-propanol with 18-crown-6 was carried out to confirm the proposed pathway of **4a** formation (Eq. 12). Also in this case the product formed appeared to be **4a** but not 5-hydroxy-1,3-dioxan-2-one.

4a was shown to be formed also by heating of **1b** with 4-chloromethyl-1,3-dioxolan-2-one (**4b**) in the presence of a crown ether. Carbon dioxide was found to evolve during this reaction (Eq. 13).

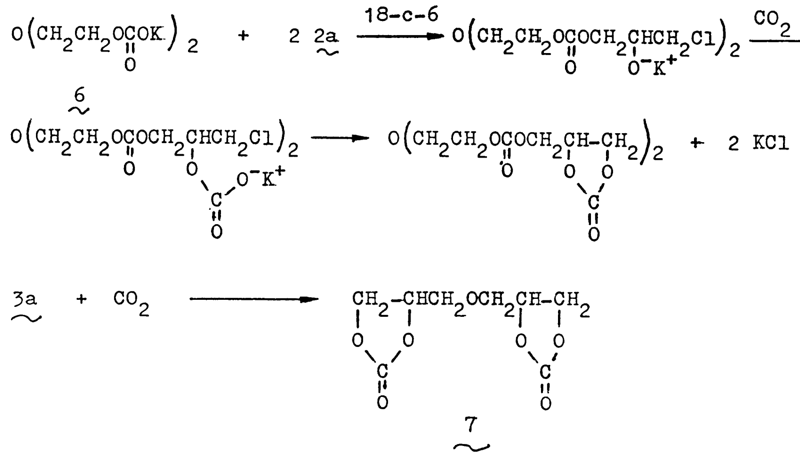
The above data obtained are consistent with the proposed mechanism of the **4a** formation involving **1b** in the system containing **2a**, **1a**, crown ether and slight amount of water (Eqs. 9 and 10).

The reaction of **1a** with **2a** in the presence of a crown ether carried out under carbon dioxide atmosphere was found to yield products containing linear carbonate linkages (IR absorption band 1740 cm^{-1}) apart from the cyclic ones (IR absorption band 1805 cm^{-1}). Thus, this reaction occurs most probably involving the carbon dioxide addition to the secondary alcoholate ion and relatively stable carbonate ion formation followed by the cyclization to the 1,3-dioxolan-2-one ring (Eq. 14).

Such a reaction mechanism could be supported by the course of the reaction of potassium alkyl carbonate **6** with **2a** under the carbon dioxide atmosphere (Eq. 15).

The reactions run according to Eqs. 14 and 15 were accompanied by the addition of carbon dioxide to **2a** yielding **4b**. The mechanism of this addition is discussed elsewhere.[4]

3a, which is the main product of the **1a** with **2a** reaction, was subjected to the reaction with carbon



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dioxide using the potassium iodide–crown ether catalyst. The product appeared to be bis(2,3-dihydroxypropyl) ether dicarbonate (**7**) (Eq. 16). **7** was obtained also in the reaction of diglycidyl ether with carbon dioxide under analogous reaction conditions.

It seems noteworthy to mention that **3a** appeared to be very well soluble in water in contrast to **7** and **4a**.

Preliminary studies on the reactions of bis(cyclic carbonate) monomers, such as **7**, showed them to be useful for the synthesis of high-molecular-weight polymers like poly(hydroxy ether)s and poly(hydroxy urethane)s.[6]

Experimental

IR spectra were recorded on a Perkin-Elmer 521 spectrometer. The ^{1}H-NMR spectra were recorded with a 100 MHz JEOL NMR spectrometer using TMS as a standard. Elemental analyses of the products were carried out with a Perkin-Elmer model 240 microanalyzer.

The content of epoxy groups in products was determined by titration with a HCl solution in dioxane.

*Reaction of Potassium Carbonate (**1a**) with 1-Chloro-2,3-epoxy propane (**2a**).* A mixture of 13.8 g (0.1 mol) of **1a**, 0.2 g (0.76 mmol) of 18-crown-6 and 55.2 g (0.6 mol) of **2a** was heated at 85 °C within 24 h. After cooling the post-reaction mixture to room temperature KCl precipitate containing unreacted **1a** was filtered off. The filtrate was distilled to give **3a**. Bp 160—166 °C/0.4 mmHg (1 mmHg≈133.322 pa). Yield 10.6 g (60%). $d^{20}=1.2793$ g/cm^3; $n^{20}=1.4605$. Found: C, 48.02; H, 5.73%. Calcd for $C_7H_{10}O_5$: C, 48.27; H, 5.80%. IR: 1805 (C=O of 1,3-dioxolan-2-one ring), 1120 (H_2C-O-CH_2), 910 cm^{-1} (HC—CH_2 \O/). Epoxide content—0.57. Molecular weight of **3a** found from epoxide content was 176 (Calcd 174.1).

*Reaction of Potassium Carbonate (**1a**) with 1-Chloro-2-methyl-2,3-epoxypropane (**2b**).* A mixture of 13.8 g (0.1 mol) of **1a**, 0.2 g (0.76 mmol) of 18-crown-6 and 63.6 g (0.6 mol) of **2b** was heated at 90 °C within 24 h. The resultant mixture was cooled and potassium salt precipitate was filtered off. 3-(β-Methylglycidyloxy)-2-methylpropylene carbonate (**3b**) was distilled at 170—174 °C/0.8 mmHg. Yield 10.5 g (52%). Found: C, 52.85; H, 6.78%. Calcd for $C_9H_{14}O_5$: C, 53.45; H, 6.99%. IR: 1800 (C=O of 1,3-dioxolan-2-one ring), 1120 (H_2C-O-CH_2), 955 cm^{-1} (C—CH_2 \O/). ^{1}H-NMR: $\delta=1.42$ (3H, CH_3C—C \O/), 1.56 (3H, CH_3C-C-O$\overset{\text{O}}{\text{C}}$-O), 4.28 and 4.68 (2H, CH_2-C-O$\overset{\text{O}}{\text{C}}$-O).

*Reaction of Potassium Carbonate (**1a**) with 1-Bromo-2,3-epoxypropane (**2c**).* A mixture of 7.9 g (0.05 mol) of **1a**, 0.1 g (0.38 mmol) of 18-crown-6 and 34.2 g (0.25 mol) of **2c** was heated at 70 °C within 15 h. After filtration of precipitate the filtrate contained products with linear carbonate linkages beside cyclic carbonate ones. IR: 1803 (C=O of 1,3-dioxolan-2-one ring) and 1750 cm^{-1} (C=O of linear carbonate linkages). Yield 2.8 g (32%) of **3a**.

*Reaction of Potassium Hydrogencarbonate (**1b**) with 1-Chloro-2,3-epoxypropane (**2a**).* A mixture of 10.0 g (0.1 mol) of **1b**, 0.2 g (0.76 mmol) of 18-crown-6 and 27.6 g (0.3 mol) of **1a** was heated at 80 °C under stirring within 36 h. After cooling and filtration of the potassium salt an organic layer was washed with water and **4a** was distilled at 152—160 °C/0.6—0.8 mmHg. Yield 4.83 g (41%). Found: C, 40.57; H, 5.21%. Calcd for $C_4H_6O_4$: C, 40.68; H, 5.03%. IR: 1800 (C=O of 1,3-dioxolan-2-one ring), 3500 cm^{-1} (OH).

*Reaction of Potassium Carbonate (**1a**) with 1-Bromo-3-chloro-2-propanol (**5**).* A mixture of 13.8 g (0.1 mol) of **1a**, 0.2 g (0.76 mmol) of 18-crown-6 and 51.9 g (0.3 mol) of **5** was heated at 80 °C within 24 h. After cooling and filtration of potassium salt precipitate, an organic layer was washed with water and **4a** was distilled at 150—160 °C/0.8 mmHg. Yield 8.8 g (75%). Found: C, 40.52; H, 5.23%. Calcd for $C_4H_6O_4$: C, 40.68; H, 5.13%.

*Reaction of **6** with 1-Chloro-2,3-epoxypropane (**2a**) in the Carbon Dioxide Atmosphere.* In a 50 cm^3 pressure autoclave 1.3 g (7.0 mmol) of the dipotassium salt of diethylene glycol, 10 cm^3 of dioxane, 0.3 g (1.14 mmol) of 18-crown-6 were added under nitrogen. Gaseous carbon dioxide was than introduced to the system under a pressure of 30 atm during 20 min. The carbon dioxide was released and 1.65 g (17.5 mmol) of **2a** was added to the autoclave containing resulting **6** and carbon dioxide introduction under pressure was repeated. The autoclave was then heated at 80 °C within 26 h. After cooling, carbon dioxide was released and the post-reaction mixture was extracted with benzene to remove **4b**. The residue contained a product with linear and cyclic carbonate linkages. IR: 1805 (C=O of 1,3-dioxolan-2-one ring), 1740 cm^{-1} (C=O of linear carbonate linkage).

*Reaction of 3-Glycidyloxypropylene Carbonate (**3a**) with Carbon Dioxide.* In a autoclave 17.4 g (0.1 mol) of **3a**, 0.2 g (1.2 mmol) of KI and 0.1 g (0.38 mmol) of 18-crown-6 were placed. Carbon dioxide was then introduced to the system under a pressure of 30 atm. The autoclave was heated at 120 °C within 12 h. The post-reaction mixture was washed with water. 20.2 g (93% yield) of **7** was obtained. Mp 62—64 °C. Found: C, 44.84; H, 4.74%. Calcd for $C_8H_{10}O_7$: C, 44.04; H, 4.63%.

Addition Reaction of Carbon Dioxide to Diglycidyl Ether (8) In a autoclave 13.0 g (0.1 mol) of **8**, 0.2 g (1.2 mmol) of KI and 0.1 g (0.38 mmol) of 18-crown-6 were placed.Carbon dioxide was then introduced to the system under a pressure of 30 atm and the autoclave was heated at 120 °C within 14 h. After cooling, carbon dioxide was released and the reaction product was washed with water. 21.1 g (97% yield) of **7** was obtained. Mp 62—63 °C. Found: C, 43.97; H, 4.71%. Calcd for $C_8H_{10}O_7$: C, 44.04; H, 4.63%.

The authors wish to thank the Polish Academy of Sciences for financial support within the programme MR-I-31.

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