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CONVENIENT SYNTHESES OF CYCLIC CARBONATES BY NEW REACTION OF OXIRANES WITH β-BUTYROLACTONE

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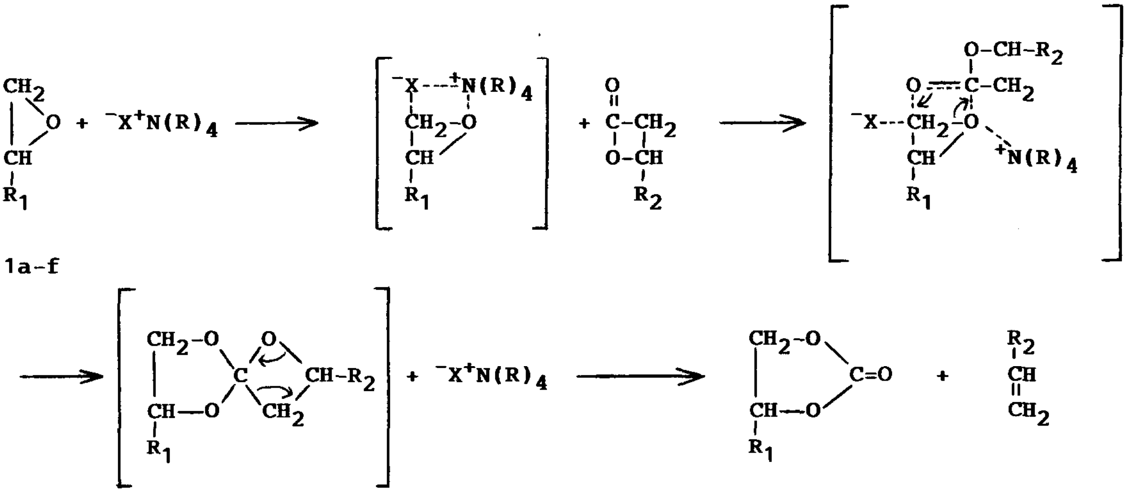
Summary: Cyclic carbonates were synthesized by reactions of the corresponding oxiranes with β-butyrolactone using quaternary salts such as tetrabutylammonium bromide or 18-crown-6 = KBr as a catalyst.

Addition reactions of oxiranes with phenols, alcohols, carboxylic acids and *prim*- or *sec*-amine compounds have been well known as a useful method in organic syntheses. Cycloaddition reaction of oxiranes with carbon dioxide using some catalyst to prepare the cyclic carbonates$^{1-3)}$ was previously carried out only under high pressure except in a recent report by Fujinami *et al*$^{4)}$. The reaction of oxiranes with cyclic esters using acidic catalyst to give spiro ortho esters$^{5,6)}$ have also been reported. However, addition reaction of oxirane with ester has not been reported so far except one study$^{7)}$. Recently, we reported successful addition reaction of poly(glycidyl methacrylate) with various active esters$^{8)}$, syntheses of self-sensitized photosensitive polymers containing a pendant *p*-nitrophenoxy group as a photosensitizer and the pendant photosensitive cinnamic ester moiety by addition reaction of pendant epoxide groups in the polymer with *p*-nitrophenyl cinnamate$^{9)}$, and insertion reaction of epoxy compounds into aryl ester linkage in the polymer$^{10)}$ using some quaternary salts as a catalyst. Therefore, it seemed likely that cyclic ester such as β-butyrolactone (BL) might also react to oxiranes under similar reaction conditions. As a result, interestingly, seven-member cyclic ester was not obtained from the reaction of oxirane with BL but five-member cyclic carbonate was synthesized.

This communication reports on the successful and convenient syntheses of some cyclic carbonates by addition reactions of the corresponding oxiranes with BL using quarternary ammonium salts such as tetrabutylammonium bromide (TBAB) or 18-crown-6 = KBr as a catalyst.

BL [4.3 g (50 mmol)] dissolved in toluene (10 ml) was added into the toluene solution (20 ml) of phenyl glycidyl ether **(1a)** [7.5 g (50 mmol)] and TBAB [1.7 g (5 mmol)] at 100°C for 6 h under N_2 stream, and then it was reacted for 9 h. Benzene (100 ml) was added to the solution, and then washed with a small amount of water for several times, and dried overnight using anhydrous magnesium sulfate. The dried solution was poured into hexane (500 ml), and then the precipitate was filtered and dried at 50°C *in vacuo*. Yield of crude product was 87.4 %. It was recrystallized twice from the mixed solvent of benzene and hexane (4 vol./5 vol.) to give white prism crystal of 4-phenoxymethyldioxolone-2 **(2a)**. M.p. 98-99°C (Lit. 90-92°C)[3]. On the other hand, the produced propylene was introduced into carbontetrachloride solution (70 ml) of bromine (100 mmol), and then it was recovered as 1,2-dibromopropane in 28 % yield (Other results of the reactions of oxiranes with BL are summarized in Table I). This suggests that the reaction of oxirane with cyclic ester BL proceeded through another reaction mechanism in the reaction with linear active esters[8] as follows. It seems that the produced four-member spiro ortho esters are unstable, and then they are converted instantly into the stable cyclic carbonate under these reaction conditions.



1a-f

2a-f

R_1: $-CH_2-O-C_6H_5$ (a), $-CH_2-O-CH_3$ (b), $-CH_2-O-C_4H_9$ (c), $-CH_2-O-CH_2-CH{=}CH_2$ (d), $-C_6H_5$ (e), $-CH_2-Cl$ (f), $-CH_2-OCO-C(CH_3){=}CH_2$ (g).

R_2: $-CH_3$, $-H$.

Interestingly enough, the reaction of **1a** with BL produced **2a** in high yield using either TBAB, tetrabutylammonium iodide (TBAI) or tetrahexylammonium bromide (THAB) as a catlalyst. Also the reaction of **1a** with BL occured to give the carbonate **2a** in 13-28% yields when tetrabutylammonium perchlorate (TBAP) or 18-crown-6 = KBr were used as a catalyst. However, the reaction did not proceed without the catalyst, or with tetramethylammonium bromide (TMAB), tetraethylammonium chloride (TEAC) or tetrabutylammonium hydrogensulfate (TBAH) as a catalyst, and the corresponding oxirane and BL were recovered. It suggests that the reaction of oxiranes with BL to produce the cyclic carbonates was strongly affected by kind of counter ion and length of alkyl chain of the quarternary ammonium salt used as a catalyst. The reactions of methyl glycidyl ether **(1b)**, butyl glycidyl ether **(1c)**, allyl glycidyl ether **(1d)**, styrene oxide **(1e)**, epichlorohydrin **(1f)** and glycidyl methacrylate **(1g)** with BL also yielded the corresponding cyclic carbonates5) **(2a-g)** using TBAB as a catalyst. It suggests that the yields of the cyclic carbonates from the reaction of BL with epoxy compounds having alkoxy or phenoxy groups such as **1a-d** were relatively higher than those from the reaction of BL with **1e-f** which have chloromethyl or phenyl groups. Furthermore, the cyclic carbonate was not obtained by the reaction of cyclohexene oxide with BL under the same reaction conditions applied to the reaction of **1a** with BL. The reaction of **1g** with BL proceeded to give the corresponding cyclic carbonate **(2g)**; however, the isolated yield of the carbonate was only a trace because the synthesized cyclic carbonate polymerized during the distillation. Furthermore, it was found that the reaction of **1a** with β-propiolactone (PL) yielded **2a** in 9.2 % and ethylene, which was confirmed by the ^{1}H NMR spectrum, in addition to the production of oligomer from the reaction of **1a** and PL using TBAB as a catalyst. The structure of all compounds were supported by spectroscopic data.

Table I The reaction conditions and resultsa)

No	Oxirane	Catalyst	Time (hr)	Yield (%)	B.p or m.p. (Lit.) (°C/ mmHg)
1	1a	None	15	0	-
2	1a	TBAB	15	87.4	98-99 (90-92)3)
3	1a	TBAI	10	58.7	-
4	1a	TBAH	10	0	-
5	1a	TBAP	10	13.1	-
6	1a	THAB	10	68.2	-
7	1a	TMAB	10	0	-
8	1a	TEAC	10	0	-
9	1a	18-crown-6/KBr	10	24.8	-
10	1b	TBAB	15	73.5 (96.1)b)	94-96/0.3 (105/0.2)11)
11	1c	TBAB	10	55.7	103-104/0.2 (124-125/0.5)3)
12	1d	TBAB	10	45.6	92-94/0.1 (100-102/0.4)3)
13	1e	TBAB	15	35.9	142-144/0.3 (134-135/0.4)3)
14	1f	TBAB	10	44.3	104-107/0.1 (108-109/0.4)3)
15	1g	TBAB	4	trace	72-73/0.112)

[a] The reaction was carried out with 50 mmol of epoxy compound and 50 mmol of BL using 10 mol-% of the catalyst at 100°C.

[b] 100 mmol of **1b** was used.

Further studies of the reactions of some oxiranes and cyclic esters using the quaternary salts or the crown ethers = inorganic salts as a catalyst are now in progress

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