

New Addition Reaction of Active Ester or Cyclic Ester with Epoxy Compounds Catalyzed by Insoluble Polystyrene-bound Quaternary Phosphonium or Ammonium Salts

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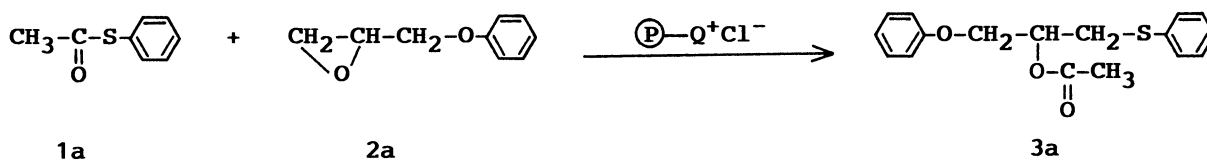
Regioselective addition reaction of active ester S-phenyl thioacetate with 2-phenoxy-methyloxirane was catalyzed by insoluble polystyrene-bound quaternary phosphonium or ammonium salts and gave 1-phenoxy-3-thiophenoxy-2-propyl acetate. Five-membered cyclic carbonates were also synthesized by the reaction of cyclic ester β -butyrolactone with some epoxy compounds using the same polymeric catalysts.

It is well known that crosslinked polystyrene gel containing quaternary ammonium salt has been widely used for anion exchange resin. Recently, polymers containing quaternary ammonium or phosphonium salts have come to be extensively used^{1,2)} as phase transfer catalysts as well as the low molecular weight quaternary ammonium or phosphonium salts. We have previously investigated^{3,4)} synthesis of functional polymers and chemical modification of polymers using such phase transfer catalysis. We also found⁵⁾ that an addition reaction of active ester with epoxy compound proceeded very smoothly in the presence of either low molecular weight quaternary ammonium or phosphonium salts, or crown ether complexes. Similar reactions of acyl halide⁶⁾, alkyl halide^{7,8)} and carbon dioxide⁹⁾ with epoxy compounds using the same catalyst system have also been reported.

This paper reports on the successful regioselective addition reaction of active ester S-phenyl thioacetate (**1a**) with 2-phenoxy-methyloxirane (**2a**) and synthesis of five-membered cyclic carbonates by the reaction of β -butyrolactone (**1b**) with some epoxy compounds catalyzed by insoluble polystyrene-bound quaternary ammonium or phosphonium salts ($\text{P-Q}^+\text{Cl}^-$).

The catalyst was synthesized by the reaction of chloromethylated polystyrene gel with *tert*-phosphines or -amines as reported previously.²⁾ A typical addition reaction was carried out as follows: **1a** [1.52 g (10 mmol)] and 1.50 g (10 mmol) of **2a** were dissolved in 5 ml of diglyme, and then 0.208 g (0.5 mmol as a phosphonium salt) of the 3% crosslinked polymeric catalyst having tributylbenzylphosphonium chloride was added into the solution. The mixture was stirred at 110 °C for 24 h, and then the catalyst was filtered off. The yield of 1-phenoxy-3-thiophenoxy-2-propyl acetate (**3a**) was 87%, which was monitored by gas chromatography (GLC). To the filtrate was added about 30 ml of diethyl ether, washed with water, dried over magnesium sulfate, and filtered. The solvent was evaporated *in vacuo*. The crude product thus obtained was purified by silica gel (Merck Co., Kiesegel 60) column

using benzene as an eluent, and then further purified by reduced distillation (190-195 °C/0.05 mmHg). IR spectrum; 1750 (ν C=O), and 1230 cm^{-1} (ν C-O). $^1\text{H-NMR}$ spectrum (CDCl_3); δ 2.00 (s, 3H, CH_3), 3.30 (d, 2H, $\text{CH}_2\text{-S}$), 4.17 (d, 2H, $\text{CH}_2\text{-O}$), 5.30 (m, 1H, methin), and 6.8-7.4 ppm (m, 10H, aromatic protons). Found: C, 67.56; H, 6.27%. Calcd for $\text{C}_{17}\text{H}_{18}\text{O}_3\text{S}$: C, 67.52; H, 6.00%.



Although the reaction of **1a** with **2a** could be expected to produce two isomers due to α - and β - cleavage of the oxirane ring using $\text{P}^+\text{-Q}^+\text{Cl}^-$, only one isomer was obtained and identified as **3a** by the $^1\text{H-NMR}$ spectrum and GLC analysis. The same regioselective insertion has also been found¹⁰⁾ in the reaction of **1a** and other active esters with various epoxy compounds using low molecular weight catalysts.

Table 1. Reactions of **1a** with **2a** by polymeric catalysts^{a)}

No.	$\text{P}^+\text{-Q}^+\text{Cl}^-$	Degree of crosslinking / %	Temp °C	Time h	Yield of 3a %
1	$\text{-P}^+(\text{Et})_3\text{Cl}^-$	1	90	24	85
2	$\text{-P}^+(\text{Pr})_3\text{Cl}^-$	1	90	24	87
3	$\text{-P}^+(\text{Bu})_3\text{Cl}^-$	1	90	24	93
4	$\text{-P}^+(\text{Hex})_3\text{Cl}^-$	1	90	24	88
5	$\text{-P}^+(\text{Oct})_3\text{Cl}^-$	1	90	24	82
6	$\text{-P}^+(\text{Bu})_3\text{Cl}^-$	3	90	5	80
7	$\text{-P}^+(\text{Bu})_3\text{Cl}^-$	3	90	24	87
8	$\text{-P}^+(\text{Bu})_3\text{Cl}^-$	3	110	24	92
9	$\text{-N}^+(\text{Bu})_3\text{Cl}^-$	1	90	24	43
10	BTBPC ^{b)}	-	90	24	61

a) Carried out with 4 mmol of **1a** and **2a** in diglyme (2 ml) using 5 mol % of the catalyst. b) Benzyltributylphosphonium chloride.

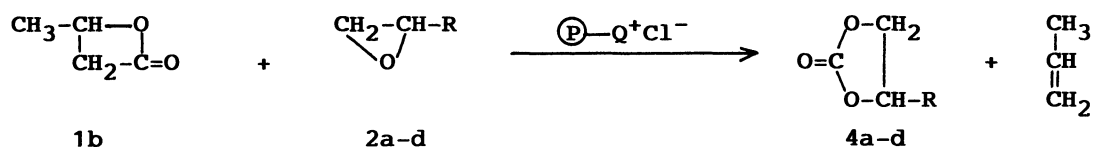
As summarized in Table 1, the reaction of **1a** with **2a** was catalyzed by various $\text{P}^+\text{-Q}^+\text{Cl}^-$ to produce **3a** in high yield. The polystyrene-bound benzyltributylphosphonium chloride [$\text{P}^+\text{-P}^+(\text{Bu})_3\text{Cl}^-$] showed the highest activity among the polymeric catalysts. It seems that the activity of polymeric catalyst having pendant quaternary phosphonium salt was strongly affected by the kind of alkyl chain on the phosphonium salt.

Interestingly, the activity of the polymer having pendant benzyltributylammonium chloride [$\text{P}^+\text{-N}^+(\text{Bu})_3\text{Cl}^-$] was less than that of $\text{P}^+\text{-P}^+(\text{Bu})_3\text{Cl}^-$ under the same conditions. It was also found that the catalytic activity was affected by the degree of crosslinking of the polymer, that is, the polymeric

catalysts with low degree of crosslinking have higher activity than the catalysts with high degree of crosslinking.

When the reaction of **1a** with **2a** was carried out using 5 mol% of benzyltributylphosphonium chloride (BTBPC) in DMSO at 90 °C for 24 h, the yield of **3a** was only 61%. This indicates that the crosslinked polymeric catalysts containing pendant quaternary phosphonium salt show higher activity than the corresponding low molecular weight catalyst for the regioselective addition reaction of active ester with epoxy compound under the same conditions. It seems that the polymeric catalyst, especially the polymer containing pendant quaternary phosphonium salt, have strong substrate-attracting efficiency for active ester and epoxy compound, and the reaction proceeds smoothly in the vicinity of the catalyst.

Furthermore, small amounts of 1-phenoxy-3-thiophenoxy-2-propanol (**3b**) were produced in the above reaction as by-product, and were isolated on a silica gel column and identified by GLC and ¹H-NMR. It seems that **3b** came from hydrolysis of **3a** by the moisture in the reaction system.



R: -CH₂-O-C₆H₅ (a), -CH₂-O-C₄H₉ (b), -C₆H₅ (c), -CH₂-Cl (d).

Table 2. Reactions of **1b** with various epoxy compounds (**2a-d**) by polymeric catalysts^{a)}

No.	$\text{P}^+\text{-Q}^+\text{Cl}^-$	Degree of crosslinking / %	Epoxy compound	Solvent	Yield of 4a-d / %
11	-P ⁺ (Bu) ₃ Cl ⁻	1	2a	toluene	60
12	-P ⁺ (Bu) ₃ Cl ⁻	1	2a	diglyme	43
13	-P ⁺ (Bu) ₃ Cl ⁻	1	2a	DMF	74
14	-P ⁺ (Bu) ₃ Cl ⁻	1	2a	anisole	61
15	-P ⁺ (Bu) ₃ Cl ⁻	3	2a	anisole	51
16	-P ⁺ (Bu) ₃ Cl ⁻	10	2a	anisole	22
17	-N ⁺ (Bu) ₃ Cl ⁻	1	2a	anisole	36
18	-P ⁺ (Bu) ₃ Cl ⁻	1	2b	anisole	53
19	-P ⁺ (Bu) ₃ Cl ⁻	1	2c	anisole	52
20	-P ⁺ (Bu) ₃ Cl ⁻	1	2d	anisole	26

a) Carried out with 6 mmol of **1b** and 5 mmol of epoxy compound in various solvents (5 ml) using 0.25 mmol of the catalyst at 100 °C for 24 h.

Similarly, the reaction of 0.52 g (6 mmol) of **1b** with 0.75 g (5 mmol) of **2a** was performed in 5 ml of DMF using 0.104 g (0.25 mmol) of the same catalyst at 100

$^{\circ}\text{C}$ for 24 h according to the reported methods.¹⁰⁾ 4-(Phenoxy)methyl-1,3-dioxolane-2-one (**4a**) was produced in 74% yield, which was determined by GLC. The reaction mixture was poured into hexane, filtered, and dried. The crude product was recrystallized twice from the mixed solvent of benzene and hexane, mp 98-99 $^{\circ}\text{C}$ (lit. 90-92 $^{\circ}\text{C}$).⁹⁾ IR spectrum; 1790 (ν C=O), and 1160 cm^{-1} (ν C-O). $^1\text{H-NMR}$ spectrum (CDCl_3); δ 4.15 (t, 2H, $\text{CH}_2\text{-O}$), 4.55 (t, 2H, $\text{CH}_2\text{-O}$), 5.00 (m, 1H, methin), and 6.7-7.7 (m, 5H, aromatic protons).

As summarized in Table 2, the reaction of **1b** with **2a** was also carried out in toluene, diglyme and anisole; however, the yields of **4a** were lower than in DMF. When the reaction of **1b** with **2a** was performed in the presence of polymeric catalysts with various degrees of crosslinking, it was found that the polymeric catalysts with low crosslinking had relatively higher activity. Furthermore, the catalysts containing pendant benzyltributylphosphonium chloride showed higher activity than the catalysts containing pendant benzyltributylammonium chloride for the synthesis of **4a** under the same condition. The reaction of **1b** with other epoxy compounds such as **2b**, **2c**, and **2d** also gave the corresponding five-membered cyclic carbonates^{9,12)} such as **4b**, **4c**, and **4d** in 53, 52, and 26% yield, respectively.

These results indicate that the reactions of active ester or cyclic ester with epoxy compounds are strongly affected by the length of alkyl group on the onium salts and the degree of crosslinking of the polymeric catalyst. Furthermore, the polymeric catalyst containing pendant phosphonium salt shows higher activity than either the corresponding low molecular weight catalyst or polymer containing ammonium salts.

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