

Notes

Carboxylation of Styrene Oxide Catalyzed by Quaternary Onium Salts under Solvent-free Conditions

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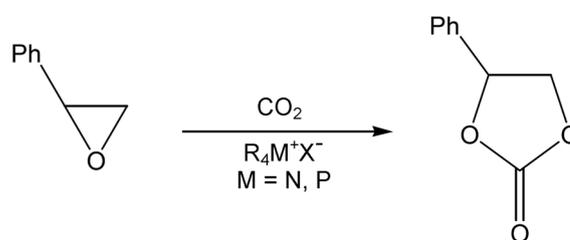
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Green chemistry has attracted much attention in organic chemistry.¹ Major goal in this area is to maximize the efficient use of raw materials and simultaneously to minimize waste. In this context, conversion of conventional organic processes into the highly atom-efficient protocol with good selectivity is the most desirable. The carboxylation of epoxides shows an interesting application in the utilization of carbon dioxide to produce cyclic carbonates.² These compounds are useful as monomers, polar aprotic solvents, and intermediates for the synthesis of pharmaceuticals and fine chemicals.³

Recently, we have studied the coupling of CO₂ with styrene oxide as a model reaction as the carboxylation of epoxides and have noticed the processes using quaternary onium salts such as tetraalkylammonium and phosphonium halides are of full-atom-economy-type⁴ to convert styrene oxide into styrene carbonate: efficient, clean and by-product-free under solvent-free reaction conditions. We found the detailed information on the use of onium salts for this reaction under solvent-free conditions is surprisingly limited except a few examples.^{5,6} The patent by McMullen *et al.* described the coupling reaction of ethylene oxide with CO₂ to produce ethylene carbonate in up to 99% yield when catalyzed by several ammonium salts such as tetraethylammonium chloride and a few other ammonium halides.^{5b} However, the detailed studies of the reaction profile and the catalytic efficiency of quaternary salts in the coupling of CO₂ with epoxides are still lacking so far.

Historically, quaternary ammonium halides have been often used as complexed with transition metal catalysts⁷ or as the reaction ionic medium⁸ to promote the reactions of the coupling of CO₂ with epoxides rather than used alone. Recent mechanistic studies suggest on the role of these catalytic systems that an epoxide is coordinated to the halogenated metal anion, generated from the interaction of the metal halide with the halide ion, and the resulting coordinated epoxide ring is opened by the halide ion to form an haloalkoxy species. Nucleophilic attack of the haloalkoxy species on CO₂ leads to a linear halocarbonate that is



Scheme 1

transformed into a cyclic carbonate by the intramolecular substitution of the halide.^{6i,7c,7d}

Herein, we report on the detailed reaction profile of carboxylation of styrene oxide catalyzed by various onium salts, particularly such as quaternary ammonium and phosphonium halides under various temperatures and CO₂ pressures as shown in Scheme 1.

Quaternary ammonium salts-catalyzed reaction. Table 1 shows the results of the experiments performed to optimize the conditions for the carboxylation of styrene oxide in the

Table 1. Effect of tetraalkylammonium halides on the carboxylation of styrene under 560 psi of CO₂ pressure

entry	catalyst	temp (°C)	time (h)	yield (%) ^a
1	(CH ₃) ₄ N(Br)	120	2	trace
2	(CH ₃ CH ₂) ₄ N(Br)	120	2	trace
3	[CH ₃ (CH ₂) ₇] ₄ N(Br)	80	4	32
4	[CH ₃ (CH ₂) ₇] ₄ N(Br)	120	2	42
5	[CH ₃ (CH ₂) ₇] ₄ N(Br)	120	4	48
6	C ₆ H ₅ CH ₂ N(Br)(C ₂ H ₅) ₃	80	4	30
7	C ₆ H ₅ CH ₂ N(Br)(C ₂ H ₅) ₃	120	2	39
8	C ₆ H ₅ CH ₂ N(Br)(C ₂ H ₅) ₃	120	4	55
9	(CH ₃ CH ₂ CH ₂ CH ₂) ₄ N(Cl)	120	2	60
10	(CH ₃ CH ₂ CH ₂ CH ₂) ₄ N(I)	120	2	56
11	(CH ₃ CH ₂ CH ₂ CH ₂) ₄ N(Br)	80	4	34
12	(CH ₃ CH ₂ CH ₂ CH ₂) ₄ N(Br)	120	2	81
13	(CH ₃ CH ₂ CH ₂ CH ₂) ₄ N(Br)	120	4	96

^aIsolated yields.

Table 2. Melting points of tetraalkylammonium halides used in the carboxylation of styrene oxide

tetraalkylammonium halides	mp (°C)
(CH ₃) ₄ N(Br)	> 300
(CH ₃ CH ₂) ₄ N(Br)	285
[CH ₃ (CH ₂) ₇] ₄ N(Br)	95-98
(CH ₃ CH ₂ CH ₂ CH ₂) ₄ N(Cl)	83-86
(CH ₃ CH ₂ CH ₂ CH ₂) ₄ N(I)	141-143
(CH ₃ CH ₂ CH ₂ CH ₂) ₄ N(Br)	102-106
C ₆ H ₅ CH ₂ N(Br)(C ₂ H ₅) ₃	193-195

presence of catalytic amounts of several quaternary ammonium salts (2 mol %) under 580 psi of CO₂ and 120 °C. The coupling reactions depend greatly on the alkyl chain length of the substituents of the ammonium salts. The reaction catalyzed by tetrabutylammonium bromide gave the highest yield of styrene carbonate, while the reaction favored a longer alkyl chain length (entry 1, 2, 4, 7, 12). The activities of Bu₄NX (X = halogen) decreased as the following orders; X = Br > Cl > I (entry 9, 10, 12).⁹ The reaction temperature was found to be crucial to the progress of the carboxylation of styrene oxide using quaternary ammonium salts. The reaction of CO₂ with styrene oxide gave a higher yield of the carbonate at 120 °C for 2 h than at 80 °C for a longer time (entry 3, 6, 12). For tetrabutylammonium bromide-catalyzed reaction, the optimized yield was achieved with the reaction time of 4h (entry 11-13).

The trends observed from Table 1 suggest that the catalytic efficiency of the quaternary ammonium halides may correlate strongly with the melting points of the halides (Table 2). Compounds need to melt in the reaction condition so that the system becomes homogeneous to act as an effective catalyst. Ammonium bromides having higher mp's such as tetramethylammonium and tetraethylammonium bromide, which are solids at the reaction temperature (80-120 °C) are not expected to convert the reaction smoothly. Tetrabutylammonium bromide catalyst melts at the reaction temperature (120 °C) and the reaction was observed to be homogeneous at this temperature.

However, the reactions are found to be not much sensitive to the pressure of CO₂ (Table 3). The results from the reactions with tetrabutylammonium bromide at elevated CO₂ pressure (2,030 psi) (Table 3, entry 1-3, supercritical condition) showed almost the same patterns with those under 560 psi (Table 1, entry 11-13, gas phase).

Quaternary phosphonium salts-catalyzed reaction. Table 4 shows the effect of several quaternary phosphonium salts

Table 3. Effect of tetrabutylammonium bromide on the carboxylation of styrene under 2,030 psi of CO₂ pressure

entry	catalyst	temp (°C)	time (h)	yield (%) ^a
1	(CH ₃ CH ₂ CH ₂ CH ₂) ₄ N(Br)	80	4	34
2	(CH ₃ CH ₂ CH ₂ CH ₂) ₄ N(Br)	120	2	84
3	(CH ₃ CH ₂ CH ₂ CH ₂) ₄ N(Br)	120	4	95

^aIsolated yields.

Table 4. Effect of quaternary phosphonium salts on the carboxylation of styrene under 560 psi of CO₂ pressure

entry	catalyst	temp (°C)	time (h)	yield (%) ^a
	Ph ₃ PBr ₂	120	4	87
2	(CH ₃)PPh ₃ (Br)	120	4	99
3	(CH ₃)PPh ₃ (I)	120	4	85
4	(CH ₃ CH ₂)PPh ₃ (Br)	120	4	92
5	(PhCH ₂)PPh ₃ (Br)	120	4	89
6 ^b	(CH ₃ CH ₂ CH ₂ CH ₂ CH ₂) ₄ N(Br)	120	4	96
7 ^c	NaI/PPh ₃ /PhOH	120	4	97

^aIsolated yields. ^bSee Table 1, entry 13. ^cRef. 10.

Table 5. Effect of quaternary phosphonium salts on the carboxylation of styrene under 2,030 psi of CO₂ pressure

entry	catalyst	temp (°C)	time (h)	yield (%) ^a
1	(CH ₃)PPh ₃ (Br)	120	2	97
2	(CH ₃ CH ₂) ₄ PBr	120	2	97
3	(CH ₃ CH ₂)PPh ₃ (Br)	120	2	92
4	(CH ₃ CH ₂ CH ₂)PPh ₃ (Br)	120	2	80
5	[CH ₃ (CH ₂) ₇] ₄ PBr	120	2	70

^aIsolated yields.

(2 mol %) on the carboxylation of styrene oxide under 580 psi of CO₂ and 120 °C. While catalysts with a triphenyl phosphine structure and one small alkyl substituent generally a higher yield of styrene carbonate, the yields of the coupling reactions depend greatly on the alkyl substituent of the phosphonium salts (Table 4, entry 3-5). The activity of catalysts with a triphenyl phosphine structure and one alkyl substituent was nearly equivalent with NaI/PPh₃/PhOH system¹⁰ or the most active ammonium salt, (CH₃CH₂CH₂CH₂CH₂)₄N(Br).

The quaternary phosphonium salts gave even a higher yield when they were used at elevated pressure of CO₂ (Table 5). As revealed in Table 5, the reaction time at 2,030 psi of CO₂ pressure was shorter (2h) to reach almost the same conversion, which was obtained after 4 h at 560 psi.

In summary, the carboxylation of styrene oxide was catalyzed by some onium salts such as quaternary ammonium and phosphonium salts to produce styrene carbonate in an efficient and environmentally benign fashion. The coupling reactions depend greatly on the alkyl chain length of the substituents of the onium salts and the reactions using catalysts with an optimum chain length give a high yield of the cyclic carbonate. While the reactions with the quaternary ammonium halides are sensitive to the reaction temperature and not to the pressure, the reactions with the phosphonium halides are found to be less sensitive to the reaction temperature. Notably, both catalysts are highly effective for the conversion of styrene oxide to styrene carbonate even under gas phase without any solvent.

Experimental Section

A typical experimental procedure for the coupling of CO₂

with styrene oxide is as follows. Styrene oxide (266 mg, 2.2 mmol) was added to tetra *n*-butylammonium bromide (14 mg, 0.044 mmol) in a tubular stainless steel reactor of 24 mL capacity at room temperature. Then, CO₂ was introduced into the reactor and then the mixture was heated at 80 °C (or 120 °C) for 2h (or 4 h) with a magnetical stirring, at which time the pressure reached at 580 psi (or 2,030 psi). The reaction mixture was cooled and CO₂ was vented into dichloromethane. The residue was dissolved in dichloromethane, leaving the catalyst recovered as a white solid, and the organic solvent was evaporated under reduced pressure to give the crude carbonate as a colorless oil. Further purification was done by column chromatography on silica gel (eluant : ethyl acetate/*n*-hexane = 1/4) to give a colorless solid; mp 54-55 °C (lit. 50-51 °C).¹⁰ A similar experimental procedure was followed for the coupling of CO₂ with styrene oxide (2.2 mmol) using quaternary phosphonium salts (0.044 mmol).

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