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Efficient Ring Opening Reaction of Epoxides with Oxygen Nucleophiles Catalyzed by Quaternary Onium Salt

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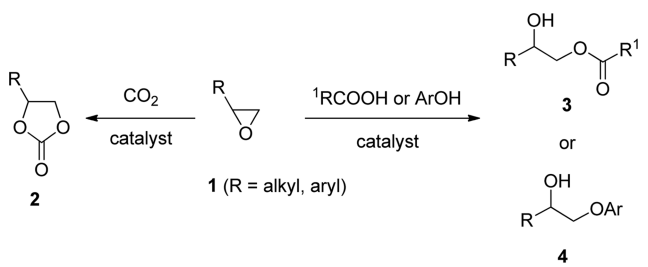
Ring opening reactions of epoxides with oxygen nucleophiles catalyzed by a variety of quaternary onium salt, such as ammonium or phosphonium salt were explored. The results showed that tetrabutylphosphonium bromide (TBPB) among salts serves as the most efficient catalyst for this process and that expoxide ring opening reactions with a variety of oxygen nucleophiles including carboxyic acid and phenol, promoted using this salt, lead to generate readily purifiable products in excellent yields.

Key Words : Ring opening reaction, Epoxide, Oxygen nucleophile, Quaternary onium salt

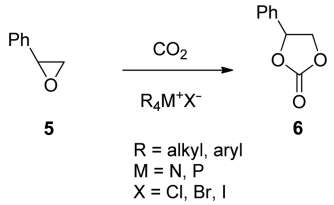
Introduction

Epoxides are highly versatile intermediates in organic synthesis owing to their relatively easy synthesis[1] and ability to undergo facile ring opening reactions with various nucleophiles.[2-5] The catalyzed ring opening reactions of epoxides **1** with carbon dioxide to produce cyclic carbonates **2** have attracted great interest in the area of carbon dioxide fixation[6-10] (Scheme 1). Ring opening reactions of epoxides **1** with oxygen nucleophiles, such as carboxylic acids and phenols, are also useful processes for the synthesis of β-hydroxy esters **3** and -ethers **4** (Scheme 1).[4b-c,5b,11,12]

Strong acids and bases have been frequently used to catalyze reactions of epoxides with both CO_2 and oxygen nucleophiles.[4b-c,13,14] More mild and efficient epoxide ring opening reactions with weak nucleophiles have been explored later.[4b-c,7a,7c,15-18] For instance, tetrabutylammonium bromide (TBAB) or its iodide analog (TBAI) either in MeCN or under solvent free conditions was used for ring opening reactions of epoxides to produce carbonates[7a] and β-hydroxyesters[5b] in an efficient and regioselective manner. In addition, Lau and his coworkers[13c] have found that bis(triphenylphosphine)immium salts act as catalysts for reactions of epoxides with CO_2. More recently, imidazolium based ionic liquid or ionic liquid/ammonium halide co-catalysts have been employed to catalyze reactions of this type.[19,20]



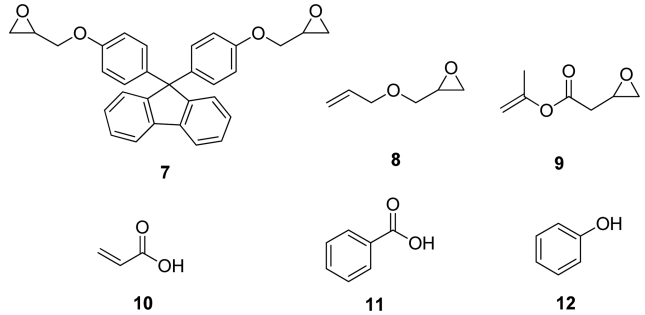
Scheme 1



Scheme 2

As part of recent effort to develop efficient methods for the ring opening reaction of epoxides with nucleophiles, we found that both ammonium and phosphonium halide salts participate as effective catalysts.[7b] For example, coupling reactions of styrene oxide **5** with CO_2 in the presence of ammonium or phosphonium halides under solvent free condition produced styrene carbonate **6** (Scheme 2). In addition, the efficiencies of these processes (32-99%) were dependent on both the substituents on nitrogen and phosphorus atom and the kinds of halide ions in the salts.[5b] Importantly, these reactions are byproduct-free and can be conducted under mild, metal- or base-free conditions.

In this study, we have investigated the ring opening reaction of epoxides **5**, **7-9** with carboxylic acids **10-11** and phenol **12** in order to explore the generality of the new conditions developed for these processes. The results of this study showed that a variety of quaternary onium halides



promote these processes and that tetrabutylphosphonium bromide (TBPB) is the most efficient catalyst.

Results and Discussion

In the first phase of the investigation, the epoxide ring opening reaction profile of 9,9-bis[4-(glycidyloxy)phenyl]-fluorene **7**, a precusor of photocurable epoxy resins often used for protective coatings of optical materials, which had been prepared by the previously reported procedure,[21] was explored. The results of earlier efforts[21] showed that 9,9'-bis[4-(2'-hydroxy-3'-acryloyloxypropoxy)phenyl]fluorene **13**,[21] the product of reaction of **7** with acrylic acid **10**, was not produced in a satisfactory yield, and its isolation and handling was difficult. We observed that ring opening reactions of epoxide **7** with **10** in the presence of 3 mol % of several quaternary ammonium and phosphonium halides took place in modest to high yields (Scheme 3 and Table 1). All of the ammonium and phosphonium salts, regardless of types of N- (and) or P-type substituents and counter halide anions, serve as efficient catalysts (Table 1). However, several features of the data are noteworthy. Firstly, increasing the length of the alkyl chain (*i.e.*, from methyl to *n*-butyl) in the ammonium salts used as catalysts leads to increase the yield of the process. In addition, the bromide anion in the salt, nBu$_4$NBr serves as a better catalyst than its iodide analog. Importantly, tetrabutylphosphonium bromide (TBPB) was observed to be a superior catalyst (90%) for the epoxide ring opening reaction between **7** and **10**. These observations are consistent with the findings from our earlier studies of the ring opening reaction between styrene oxide and CO_2.[7b]

Table 1. Quaternary ammonium and phosphonium halide salt promoted ring opening reactions of **7** with acrylic acid **10** (2.2 eq.) to form **13** in propylene glycol monomethyl ether-1,2-acetate (PGMEA) at 110 °C for 12 h

Entry	Catalyst	Yield (%)[a]
1	-	0
2	Me$_4$NCl	63
3	nBu$_4$NI	70
4	nBu$_4$NBr	74
5	BnNEt$_3$Br	73
6	BnPPh$_3$Br	86
7	MePPh$_3$Br	84
8	Et$_4$PBr	83
9	EtPPh$_3$Br	81
10	nBuPPh$_3$Br	83
11	nBu$_4$PBr	90

[a]Isolated yields based on reacted **7**

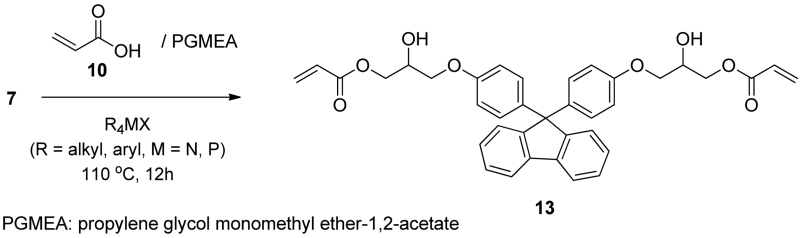
Table 2. Solvent Effects on the ring opening reaction of **7** with **10** in the presence of TBPB

Solvent	Yield (%)[a]
CH_2Cl_2[a]	No reaction
THF[a]	No reaction
DMF[b]	Polymer
PGMEA[b]	90
toluene[c]	> 95

[a]At reflux for 5 h. [b]110 °C for 12 h. [c]110 °C for 5 h.

To uncover optimal conditions for the reaction of **7** with **10** in the presence of TBPB (3 mol %) (Scheme 3) in several solvents were explored. The results in Table 2 show that while reactions do not occur in the anhydrous aprotic solvents such as CH_2Cl_2 and THF, and a polymeric product is obtained in DMF, efficient formation of **13** takes place when both PGMEA and toluene are employed as solvents. These observations suggest that the efficiency of the ring opening reactions of **7** does not correlate with the polarity of the solvent,[5b] but rather that it is dependent on the relationship between reaction temperature and melting point of the catalyst. Thus, under higher temperature conditions (*e.g.*, 110 °C) the catalyst TBPB (mp 100-103 °C)[5b] melts and becomes homogeneously dispersed in the reaction mixture and consequently more able to promote the conversion of **7** to **13**. These findings indicate that refluxing toluene (110 °C) is the ideal solvent system for this reaction and that a simple purification process, involving washing with aqueous sodium bicarbonate to remove acrylic acid (when necessary followed by silica gel column chromatography), can be employed.

The optimized reaction conditions were utilized in reactions of terminal epoxide **5** and **7**-**9** with various oxygen nucleophiles **10**-**12** to explore the scope of the new protocol (Figure 1 and Table 3). Accordingly, each reaction was carried out by heating the solution containing prescribed amounts of epoxides and oxygen nucleophiles in toluene at 110 °C for 5 h in the presence of TBPB (3 mol %). In the respective processes involving **11**-**12**, excess (1.5 eq of **11**) and less (0.8 eq of **12**) than stoichiometric amounts of the nucleophiles were used in order to simplify the purification process. Finally, di-*tert*-butyl *p*-cresol (5 mol %) was used as an antioxidant in the TBPB catalyzed ring opening reaction of epoxides with **11** (Table 3, entry1 and 4).



PGMEA: propylene glycol monomethyl ether-1,2-acetate

Scheme 3

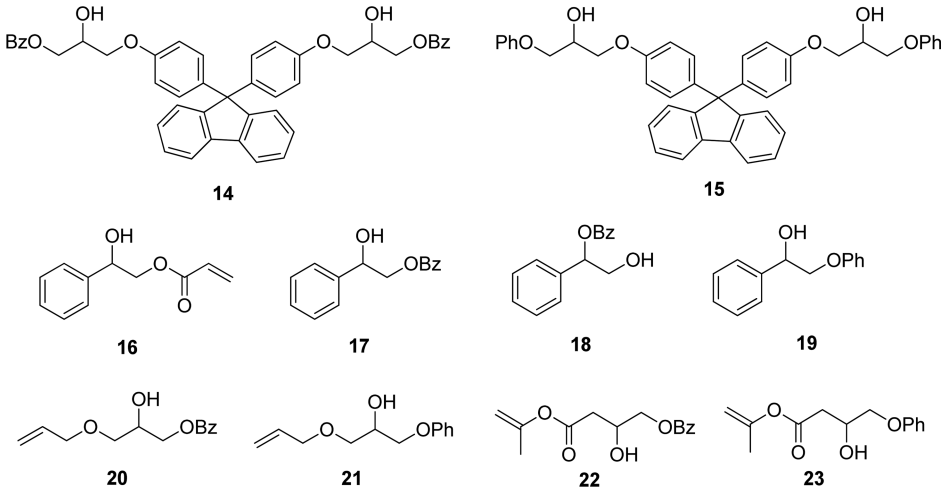


Figure 1. Products of TBPB catalyzed ring opening reactions of epoxides **5**, **7**-**9** with oxygen nucleophiles **10**-**12**.

Table 3. Ring opening reactions of epoxides **5** and **7**-**9** with oxygen nucleophilies **10**-**12** using 5 mol % TBPB at 110 °C for 5 h in toluene

Entry	Epoxide	Reagent (equiv.)	Product (% yield)
1	**7**	**10** (3.0 eq.)	**13** (100)[a]
2	**7**	**11** (3.0 eq)	**14** (99)[a]
3	**7**	**12** (1.6 eq)	**15** (95)[a]
4	**5**	**10** (1.5 eq.)	**16** (94)[a]
5	**5**	**11** (1.5 eq)	**17** (66)[b] + **18** (33)[b]
6	**5**	**12** (0.8 eq)	**19** (95)[a]
7	**8**	**11** (1.5 eq)	**20** (99)[a]
8	**8**	**12** (0.8 eq)	**21** (95)[b]
9	**9**	**11** (1.5 eq)	**22** (97)[a]
10	**9**	**12** (0.8 eq)	**23** (95)[a]

[a]Yields based on reacted epoxides. [b]Yield based on **12**.

The results, summarized in Table 3, show that TBPB catalyzed ring opening reactions of epoxides with oxygen nucleophiles to produce β-hydroxy esters and -ethers in a highly efficient manner. In addition, the processes were highly regioselective except in the case of reaction of styrene oxide with benzoic acid (entry 5), where a mixture of two regioisomeric adducts (**17** and **18**) was produced in a 3:1 ratio. When thermally less stable epoxides **8** and **9** along with **10** were utilized as reactants, reactions generated only polymeric substances rather than desired products.

Conclusion

We have developed a new protocol which utilizes quaternary ammonium and phosphonium halide salts as catalysts to promote epoxide ring opening reactions with various oxygen nucleophiles. The results show that the processes take place in excellent yields and that product purification can be readily accomplished. These observations point out the potentially advantageous features of applying epoxide ring opening reactions in synthetic organic chemistry.

Experimental Section

General Procedure. To a mixture of the epoxide (3 mmol) and a prescribed amount of the oxygen nucleophiles (1.5 eq. of **10** and **11**, 0.8 eq. of **12**) in toluene (10 mL) was added TBPB (5 mol %). When acrylic acid is used, di-*tert*-butyl *p*-cresol (5 mol %) was added to the mixture. The resulting mixture was stirred at 110 °C for 5 h and then, cooled to room temperature when TLC monitoring indicated that no further conversion of the reactants was taking place. The mixture was diluted with dichloromethane (30 mL), washed with saturated sodium bicarbonate solution (2 × 5 mL), dried over anhydrous magnesium sulfate, and concentrated in vacuo to give virtually pure products. In case of the reactions of epoxides with phenol **12**, the residues after the workup were subjected to silica gel column chromatography (EtOAc:Hex = 1:1) to remove remaining phenol.

3,3'-(4,4'-(9*H*-Fluorene-9,9-diyl)bis(4,1-phenylene))bis-(oxy)bis(2-hydroxypropane-3,1-diyl) Diacrylate 13[21]**:** ^{1}H-NMR ($CDCl_3$) δ 7.74 (2H, d, *J* = 7.2 Hz), 7.36-7.22 (6H, m), 7.11 (4H, d, *J* = 8.4 Hz), 6.75 (4H, d, *J* = 8.7 Hz), 6.43 (2H, d, *J* = 17.4 Hz), 6.17-6.08 (2H, dd, *J* = 17.4 Hz) 5.84 (2H, d, *J* = 10.2 Hz), 4.42-4.20 (6H, m), 4.00-3.88 (4H, m); ^{13}C-NMR ($CDCl_3$) δ 166.4, 157.1, 151.6, 140.0, 131.8, 129.3, 127.9, 127.5, 126.0, 125.6, 120.3, 144.2, 68.6, 68.5, 65.5, 64.2; HRMS (FAB) *m/z* 606.2255 (M^+, $C_{37}H_{34}O_8$ requires 606.2254).

3,3'-(4,4'-(9*H*-Fluorene-9,9-diyl)bis(4,1-phenylene))bis-(oxy)bis(2-hydroxy propane-3, 1-diyl) Dibenzoate 14: ^{1}H-NMR ($CDCl_3$) δ 8.03 (4H, d, *J* = 7.8 Hz), 7.75 (2H, d, *J* = 7.5 Hz), 7.57 (2H, t, *J* = 7.8 Hz), 7.44 (4H, t, *J* = 7.8 Hz), 7.35 (4H, t, *J* = 7.6 Hz), 7.27 (2H, d, *J* = 7.5 Hz), 7.13-7.09 (4H, m), 6.77 (4H, d, *J* = 8.7 Hz), 4.51-4.49 (4H, m), 4.33 (2H, q, *J* = 5.1 Hz), 4.09-3.99 (4H, m), 2.72 (2H, br); ^{13}C-NMR ($CDCl_3$) δ 166.5, 162.1, 156.8, 151.3, 139.7, 138.6, 133.1, 129.5, 129.0, 128.2, 127.5, 125.7, 119.9, 113.9, 68.4, 68.3, 65.5, 63.8; HRMS (FAB) *m/z* 706.2569 (M^+, $C_{45}H_{38}O_8$ requires 706.2567).

3,3'-(4,4'-(9*H*-Fluorene-9,9-diyl)bis(4,1-phenylene))bis-(oxy)bis(1-Phenoxypropan-2-ol) 15: ^{1}H-NMR ($CDCl_3$) δ 7.75 (2H, d, *J* = 7.2 Hz), 7.37-7.21 (12H, m), 7.12 (4H, d. *J* = 8.4 Hz), 6.91 (4H, d, *J* = 8.7 Hz), 6.78 (4H, d, *J* = 8.4 Hz), 4.35 (2H, q, *J* = 4.8 Hz), 4.11-4.08 (8H, m), 2.60 (2H, d, *J* = 4.8 Hz); ^{13}C-NMR ($CDCl_3$) δ 158.4, 151.6, 140.0, 138.8, 129.6, 129.3, 127.8, 127.5, 126.0, 121.3, 120.3, 114.5, 114.2, 68.8, 68.5, 64.2; HRMS (EI) *m/z* 650.2665 (M^+, $C_{43}H_{38}O_6$ requires 650.2668).

2-Hydroxy-2-phenylethyl Acrylate 16[22]**:** ^{1}H-NMR ($CDCl_3$) δ 7.36-7.28 (5H, m), 6.44 (1H, d, *J* = 17. 4 Hz), 6.19-6.10 (1H, m), 5.85 (1H, d, *J* = 10.2 Hz), 4.96 (1H, d, *J* = 5.7 Hz), 4.35-4.18 (2H, m), 2.97 (1H, br); ^{13}C-NMR ($CDCl_3$) δ 166.4, 139.9, 131.7, 128.7, 128.3, 128.0, 126.3, 72.4, 69.4; HRMS (FAB) *m/z* 193.0863 ($M+H^+$, $C_{11}H_{13}O_3$ requires 193.0865).

2-Hydroxy-2-phenylethyl Benzoate 17[23]**:** ^{1}H-NMR ($CDCl_3$) δ 8.05 (2H, d, *J* = 8.1 Hz), 7.57 (1H, t, *J* = 6.9 Hz), 7.46-7.30 (7H, m), 5.12-5.08 (1H, dd, *J* = 3.3 Hz), 4.54-4.38 (2H, m); ^{13}C-NMR ($CDCl_3$) δ 139.9, 133.3, 129.8, 128.7, 128.5, 128.4, 126.3, 72.6, 69.9; HRMS (FAB) *m/z* 243.1024 ($M+H^+$, $C_{15}H_{15}O_3$ requires 243.1017).

2-Hydroxy-1-phenylethyl Benzoate 18[23a]**:** ^{1}H-NMR ($CDCl_3$) δ 8.11 (2H, d, *J* = 7.2 Hz), 7.57 (1H, t, *J* = 7.5 Hz), 7.47-7.25 (7H, m), 6.12-6.09 (1H, dd, *J* = 3.9 Hz), 4.07-3.91 (2H, m); ^{13}C-NMR ($CDCl_3$) δ 165.9 137.5, 133.7, 130.2, 129.1, 128.9, 127.0, 66.6; HRMS (FAB) *m/z* 243.1023 ($M+H^+$, $C_{15}H_{15}O_3$ requires 243.1017).

2-Phenoxy-1-phenylethanol 19[24]**:** ^{1}H-NMR ($CDCl_3$) δ 7.36-7.28 (5H, m), 7.20 (2H, t, *J* = 7.5 Hz), 6.92-6.86 (3H, m), 5.29-5.25 (1H, dd, *J* = 3.0 Hz), 3.95-3.79 (2H, m), 2.32 (1H, br); ^{13}C-NMR ($CDCl_3$) δ 158.1, 138.2, 129.9, 129.2, 128.6, 126.7, 121.6, 116.3, 81.5, 68.0; HRMS (EI) *m/z* 214.0991 (M^+, $C_{14}H_{14}O_2$ requires 214.0994).

3-(Allyloxy)-2-hydroxypropyl Benzoate 20[5b]**:** ^{1}H-NMR ($CDCl_3$) δ 8.04 (2H, d, *J* = 7.2 Hz), 7.55 (1H, t, *J* = 6.9 Hz), 7.42 (2H, t, *J* = 7.2 Hz), 5.96-5.82 (1H, m), 5.30-5.17 (2H, m), 4.43-4.34 (2H, m), 4.16 (1H, s), 4.04-4.02 (2H, m), 3.63-3.52 (2H, m), 3.13 (1H, s); ^{13}C-NMR ($CDCl_3$) δ 166.7, 134.3, 133.2, 129.9, 129.8, 129.7, 128.5, 117.6, 72.4, 71.0, 68.9, 66.1; HRMS (FAB) *m/z* 237.1131 ($M+H^+$, $C_{13}H_{17}O_4$ requires 237.1127).

1-(Allyloxy)-3-phenoxypropan-2-ol 21[25]**:** ^{1}H-NMR ($CDCl_3$) δ 7.27 (2H, t, *J* = 7.8 Hz), 6.97-6.89 (3H, m), 5.96-5.83 (1H, m), 5.30-5.17 (2H, m), 4.17 (1H, s), 4.03-4.00 (4H, m), 3.65-3.54 (2H, m), 2.93 (1H, s); ^{13}C-NMR ($CDCl_3$) δ 158.3, 134.1, 129.3, 120.8, 117.2, 114.3, 72.2, 70.8, 68.8, 68.6; HRMS (EI) *m/z* 208.1104 (M^+, $C_{12}H_{16}O_3$ requires 208.1099).

Hydroxy-4-oxo-4-(prop-1-en-2-yloxy)butyl Benzoate 22: ^{1}H-NMR ($CDCl_3$) δ 8.06-8.03 (2H, m), 7.61-7.55 (1H, m), 7.47-7.42 (2H, m), 6.16 (1H, s), 5.62 (1H, t, *J* = 1.5 Hz), 4.49-4.26 (5H, m), 2.82 (1H, s), 1.95 (3H, s); ^{13}C-NMR ($CDCl_3$) δ 167.5, 166.7, 162.4, 135.8, 133.4, 129.8, 128.5, 126.6, 68.5, 65.8, 65.6, 18.4; HRMS (FAB) *m/z* 265.1079 ($M+H^+$, $C_{14}H_{17}O_5$ requires 265.1076.

Prop-1-en-2-yl 3-hydroxy-4-phenoxybutanoate 23: ^{1}H-NMR ($CDCl_3$) δ 7.31-7.25 (2H, m), 7.00-6.90 (3H, m), 6.15 (1H, s), 5.61 (1H, t, *J* = 1.5 Hz), 4.36-4.35 (2H, m), 4.31-4.26 (1H, m), 4.09-3.99 (2H, m), 2.84 (1H, d, *J* = 4.2 Hz), 1.95 (3H, s); ^{13}C-NMR ($CDCl_3$) δ 168.3, 159.0, 136.6, 130.3, 127.1, 122.1, 115.2, 69.3, 66.4, 19.1; HRMS (EI) *m/z* 236.1053 (M^+, $C_{13}H_{16}O_4$ requires 236.1049).

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