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Reaction of Various Oxiranes and Carbon Dioxide. Synthesis and Aminolysis of Five-Membered Cyclic Carbonates

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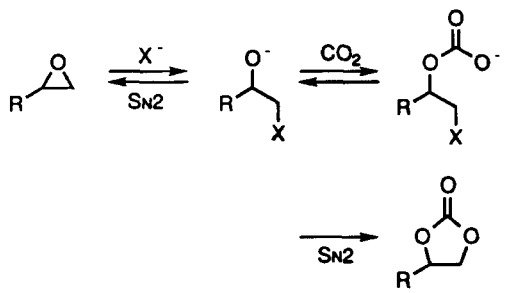
Various oxiranes reacted with carbon dioxide at 100 °C using lithium bromide as a catalyst under atmospheric pressure to afford the corresponding five-membered cyclic carbonates quantitatively. The rate of the reaction increased as the bulkiness of substituents on the oxirane ring was reduced or an electron-withdrawing group was introduced on the oxirane ring. The stereochemistry of the reaction of oxirane and carbon dioxide was retention without loss of optical purity. When substituted phenylethylene carbonates were reacted with benzylamine, the selectivity to afford secondary alcohol increased as the electron-withdrawing ability of the para-substituent increased.

Five-membered cyclic carbonates have many synthetic uses,[1,2] and have generally been synthesized from corresponding diols and phosgene or related compounds.[1—7] Although many phosgene-free methods to synthesize cyclic carbonates have been reported,[8—13] the reaction of oxirane with carbon dioxide[14—27] has received much attention because of its simple operation, high yield, and the harmless nature of the reagents. Further, the reaction is one of the most effective methods to incorporate carbon dioxide into organic molecules. Although the reaction of oxirane with carbon dioxide so far had been carried out at high pressure (> 50 atm), we have reported[26] recently that alkali metal or quaternary ammonium halides can be the effective catalysts for the reaction of oxiranes and carbon dioxide under atmospheric pressure. Catalytic activity of the salt increased when nucleophilicity of the halide anion and Lewis acidity of the cation increased. Although this simple and effective catalyst system has been applied to some oxiranes, its availability, especially stereochemical aspects, is not clear.

We have proposed that the reaction proceeds via the mechanism shown in Scheme 1,[26] and that the rate-determining step is the nucleophilic attack of the halide anion to the oxirane ring. Therefore, it is expected that the reactivity of the oxirane increases when the bulkiness of the substituent (R) on the oxirane ring decreases or the electron-withdrawing ability of R increases. Further, it is also expected that the oxirane and cyclic carbonate obtained will show the same stereochemistry because S_N2 inversion occurs twice during the conversion.

Among many synthetic uses of five-membered cyclic carbonate, we have been interested in its aminolysis[28—31] because of high chemoselectivity, facile reaction, and preparation of hydroxy urethane. However, there has been no effort to control the direction of ring-opening on the aminolysis (Scheme 2). It is expected that regioselective aminolysis can be performed by the introduction of sufficient substituent on the carbonate ring.

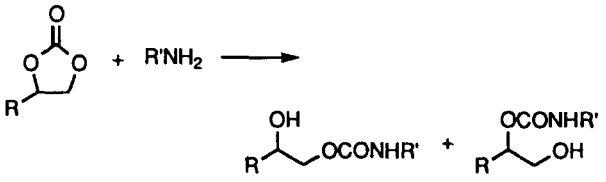


Scheme 1.

In this paper, we wish to report the reaction of various oxiranes with carbon dioxide catalyzed by alkali metal halides under atmospheric pressure. Electronic effects of the substituents on the oxirane ring will be discussed. Further, attempts to control the direction of ring-opening on the aminolysis of cyclic carbonate will also be discussed.

Results and Discussion

Reaction of Various Oxiranes with Carbon Dioxide. The reactions of various oxiranes with carbon dioxide were carried out at 100 °C in NMP under atmospheric pressure.



Scheme 2.

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Lithium bromide (5 mol%) was used as one of the most effective catalysts.[26] Results are summarized in Table 1 and Scheme 3.

Although most of the oxiranes gave the corresponding five-membered cyclic carbonates in high yields, the rate of the reaction decreased in the case of the oxiranes bearing more bulky substituents. Thus, it took 24 h to complete the reaction of **1c** and **1e** with carbon dioxide, and **1f** did not react with carbon dioxide even at 40 atm. Nucleophilic attack of bromide anion to highly bulky **1f** might not proceed.

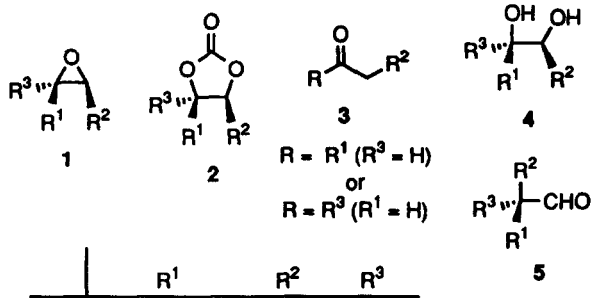
The reaction of an optically pure (2*R*)-**1a** with carbon dioxide was carried out. The alkaline hydrolysis of the resulting cyclic carbonate **2a** afforded optically pure diol (2*R*)-**4a** where optical purity was determined by the measurement of optical rotation (Scheme 4).[32] Thus, the optically active cyclic carbonate and/or diol can be easily synthesized from the corresponding optically active oxirane and carbon dioxide without any racemization.

Table 1. The Reaction of Oxiranes with Carbon Dioxide Catalyzed by Lithium Bromide[a)]

$$\mathbf{1} + CO_2 \xrightarrow[\text{NMP, 1 atm, 100 °C}]{\text{LiBr (5 mol\%)}} \mathbf{2}\ (+\mathbf{3})$$

Oxirane	Time/h	Product (Yield/%)
1a	3	**2a** (91)
1b	3	**2b** (88)
1c	3	**2c** (87)
1c	24	**2c** (94)
1d	3	**2d** (87)
1e	3	**2e** (62)
1e	24	**2e** (89)
1f	24	No reaction
1f	24[b)]	No reaction
1g	24	**2g** (40), **3g** (18)
1h	24	**2h** (31), **3h** (3), **1i** (2)
1i	24	**2i** (3), **2h** (40), **3i** (3), **1h** (36)

a) Reactions were carried out under an atmospheric pressure with 5 mol% of lithium bromide in NMP (1 mol dm^{-3}). b) At 40 atm.

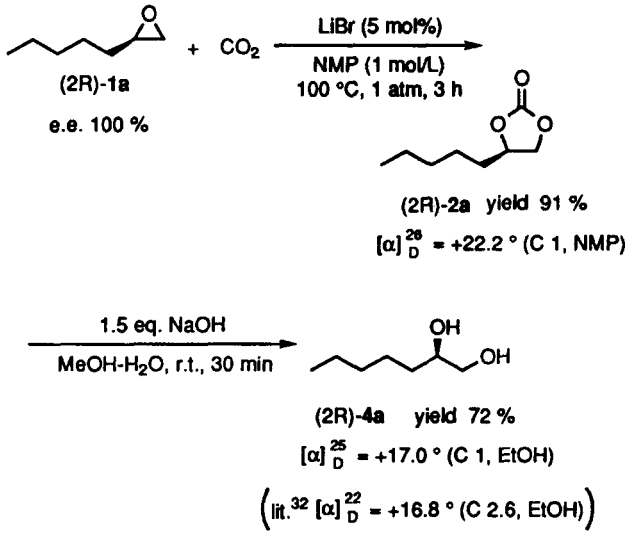


	R^1	R^2	R^3
a	$-(CH_2)_4CH_3$	H	H
b	$-(CH_2)_5CH_3$	H	H
c	Ph	H	H
d	$-CH_2OPh$	H	H
e	$-CH_2OCH_2Ph$	H	CH_3
f	Ph	H	Ph
g	$-(CH_2)_4-$		H
h	H	Ph	Ph
i	Ph	Ph	H
j	$-C_6H_4$-p-NO_2	H	H
k	$-C_6H_4$-p-CN	H	H
l	$-C_6H_4$-p-Cl	H	H
m	$-C_6H_4$-p-CH_3	H	H
n	$-C_6H_4$-p-OCH_3	H	H

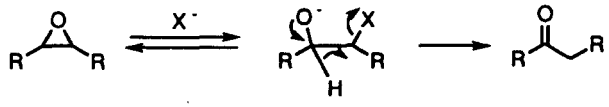
Scheme 3.

The reactions of *vic*-disubstituted oxiranes with carbon dioxide were rather complex. The reaction of **1g** afforded *cis*-carbonate **2g** in 40% yield and ketone **3g** in 18% yield, respectively, while neither *trans*-carbonate nor aldehyde **5g** was detected. This stereospecificity can be easily explained by double S_N2 inversion. Although it has been reported[33—35] that the Lewis acid-catalyzed isomerization of **1g** afforded aldehyde **5g**, only ketone **3g** was obtained as an isomerization product in this case. We have already reported[26] similar isomerization of **1d** to phenoxyacetone (**3d**) catalyzed by halide salts. The isomerization of an oxirane to the corresponding ketone is considered to proceed via hydride migration of the alkoxide intermediate, as shown in Scheme 5. Although the isomerization of **1d** to **3d** was not observed in the presence of carbon dioxide, the isomerization of **1g** did occur even in the presence of carbon dioxide. Thus, the ring-closure step to afford **2g** is slower than that to afford **2d** because secondary the alkyl halide is less reactive than the primary one.

The reactions of stilbene oxides **1h** and **1i** were more complicated. From *trans*-oxirane **1h**, *trans*-carbonate **2h**, cis-oxirane **1i**, and ketone **3h** were obtained in 31, 2, and 3% yields, respectively. The stereospecificity of the formation of cyclic carbonate was also observed. The isomerization of **1h** to **3h** might proceed via the hydride migration of alkoxide intermediate, as discussed above. At the present time, however, the mechanism of the epimerization of **1h** to form **1i** is mysterious. One of the possibilities is that ring-opening of



Scheme 4.



Scheme 5.

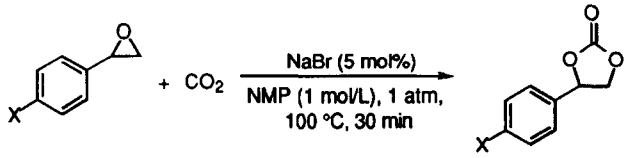
oxirane ring proceeded via S_N1 mechanism in the case of **1h**. However, if the reaction had proceeded via S_N1 mechanism, an aldehyde **5h** would be obtained as a by-product.[33] The fact that only **3h** was obtained as an isomerization product ruled out the possibility of S_N1 mechanism. Another possibility is the epimerization by the halogen exchange reaction of the β-haloalkoxide intermediate with lithium bromide. We could not rule out this possibility. From *cis*-oxirane **1i**, expected *cis*-carbonate **2i**, *trans*-carbonate **2h**, *trans*-oxirane **1h**, and ketone **3i** (**3h**) were obtained in 3, 40, 36, and 3% yield, respectively. *trans*-Carbonate **2h**, which was the main product in this case, was obviously formed from *trans*-oxirane **1h** produced by the epimerization of *cis*-oxirane **1i** during the reaction. In the case of **1i**, epimerization was more rapid than the reaction with carbon dioxide, while the reaction with carbon dioxide was superior to the epimerization in the case of **1h**. Epimerization of **1i** to the thermodynamically more stable **1h** occurred easily. Although it seemed that the stereospecificity was lost in the case of **1i**, the reaction of oxirane and carbon dioxide itself is speculated to be stereospecific.

Electronic Effect on the Reaction of Oxirane and Carbon Dioxide. To examine the electronic effect of substituent on the oxirane ring, the reaction of a series of *para*-substituted styrene oxides and carbon dioxide was carried out. Sodium bromide, which showed moderate catalytic activity,[26] was used as a catalyst. The reaction was carried out at 100 °C for 30 min in NMP; results are summarized in Table 2.

As the electron-withdrawing ability of *para*-substituent increased, the yield increased. Assuming that the reaction is first order with respect to the concentration of oxirane,[26] relative ratios of apparent rate constant k's are plotted against the Hammett's σ values of *para*-substituents,[36] to produce a simple linear relationship as shown in Fig. 1. Therefore, it was confirmed that introduction of electron-withdrawing group on oxirane ring increased the reactivity of oxirane to carbon dioxide. It has been reported[33] that the rate of the addition of nucleophile to the styrene oxides, which is the rate-determining step of the reaction of oxirane and carbon dioxide, was also related to Hammett's σ value.

The reaction for 24 h gave the corresponding cyclic carbonates quantitatively, except for *p*-nitro derivative **1j**. In the case of **1j**, carbonate **2j** and isomerization product **3j** were obtained in 60 and 40% yields, respectively (Scheme 6). Since β-haloalkoxide intermediate was stabilized by nitro group, its higher concentration in the reaction system increased to facilitate the isomerization. Indeed, when **1j** was treated with 5 mol% of sodium bromide at 100 °C under argon atmosphere in NMP for 3 h, **3j** was obtained in 7% yield, while **1c** did not react at all under the same condition. In conclusion, the electron-withdrawing group introduced on oxirane ring accelerates not only the reaction with carbon dioxide but also isomerization, because both reactions proceed via the same intermediate, β-haloalkoxide.

Table 2. The Reaction of *para*-Substituted Styrene Oxides with Carbon Dioxide Catalyzed by Sodium Bromide



Oxirane	–X	Yield/%
1c	–H	18
1j	$-NO_2$	57
1k	–CN	48
1l	–Cl	38
1m	$-CH_3$	12
1n	$-OCH_3$	11

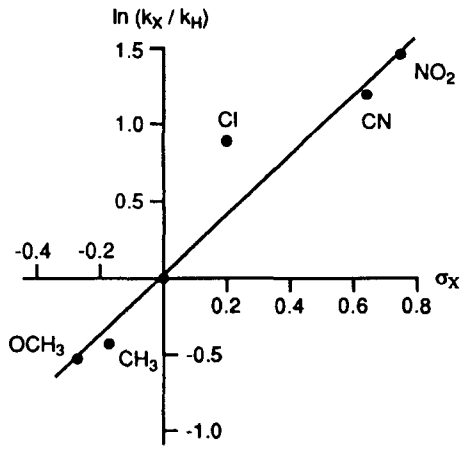
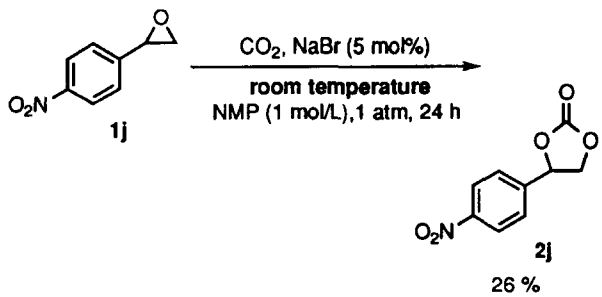


Fig. 1. Hammett plot of the reaction of *p*-substituted styrene oxides with carbon dioxide.

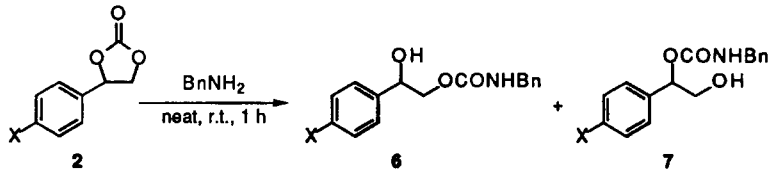
Since **1j** was the most reactive oxirane examined, **1j** was reacted with carbon dioxide at room temperature using sodium bromide as a catalyst. As expected, **2j** was obtained in 26% yield. The isomerization to **3j** could not be observed. This is the first example that a simple oxirane reacted with carbon dioxide at room temperature.[25] Indeed, **1c** did not react at all in the same condition.

Direction of Ring-Opening on the Aminolysis of Five-Membered Cyclic Carbonates. Control of regioselectivity of the ring-opening in the aminolysis of five-membered cyclic carbonates was carried out using series of aryl-substituted cyclic carbonates. Thus, **2c**, **2j**, and **2m** were treated with benzylamine at room temperature. The reactions were completed within 1 h to give hydroxy urethanes **6** and **7** quantitatively. The results are summarized in Table 3. As the electron-withdrawing ability of the *para*-substituent in-



Scheme 6.

Table 3. Aminolysis of Aryl-Substituted Cyclic Carbonates by Benzylamine



2 **6** **7**

Carbonate	–X	Yield of urethane/%	**6** / **7**
2c	–H	93	59 : 41
2j	$-NO_2$	95	77 : 23
2m	$-CH_3$	92	54 : 46

creased, the selectivity of secondary alcohol **6** increased.

When **7j** was treated with a catalytic amount of triethylamine in chloroform, **6j** could not be detected, indicating that the selectivity between **6** and **7** was kinetically controlled. When the rates of the ring-opening of tetrahedral intermediate to form **6** and **7**, which are functions of *para*-substituent X, are denoted as k_{6X} and k_{7X}, respectively, the ratio of the yield of **6** and **7** equals k_{6X}/k_{7X}. Since k_6 and k_7 are the function of acidity or leaving ability of alcohol **6** and **7**, the following equations can be formulated[36] using Hammett's σ values:

$$\log\left(\frac{k_{6X}}{k_{6H}}\right) = \rho\cdot\sigma_X, \quad (1)$$

$$\log\left(\frac{k_{7X}}{k_{7H}}\right) = \rho'\cdot\sigma_X, \quad (2)$$

thus

$$\log\left(\frac{k_{6X}}{k_{7X}}\right) = (\rho-\rho')\cdot\sigma_X + \log\left(\frac{k_{6H}}{k_{7H}}\right). \quad (3)$$

Based on Eq. 3, log (yield of **6**/yield of **7**) values were plotted against σ_X values. As shown in Fig. 2, a linear relationship was observed as expected. The slope of the line, $\rho-\rho'$, was positive because the inductive effect of the electron-withdrawing group to increase acidity of hydroxy group decreased as the distance between electron-withdrawing group and hydroxy group increased. In conclusion, the direction of the ring-opening of the cyclic carbonate by aminolysis can be controlled by the electronic effect of substituent introduced on the carbonate ring.

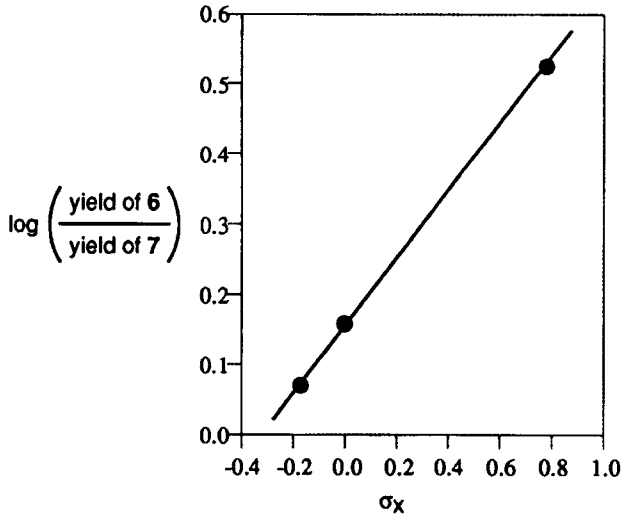


Fig. 2. Plots of the yield of **6** and **7** against σ_X value.

Experimental

1,2-Epoxyheptane, 1,2-epoxyoctane, styrene oxide, 2,3-epoxypropyl phenyl ether, cyclohexene oxide, *N*-methyl-2-pyrrolidinone (NMP), benzylamine, and hexamethyldisiloxane were used after distilation on CaH_2. 2,2-Diphenyloxirane[37,38] and 2-benzyloxymethyl-2-methyloxirane[39] were prepared according to the literature. Other chemicals were reagent grade, and were used without further purification.

2-(4-Nitrophenyl)oxirane (1j). A solution of 25.40 g (0.12 mol) of trimethylsulfonium iodide, 6.76 g (0.12 mol) of potassium hydroxide, and 2.33 g (0.12 mol) of water in 200 mL of acetonitrile was allowed to stand at 55 °C for 15 min. After the addition of 16.67 g (0.11 mol) of 4-nitrobenzaldehyde, the reaction mixture was allowed to stand for 3 h. The reaction mixture was filtered off through celite, and the filtrate was evaporated. The crude oxirane was chromatographed on silica-gel (eluent: ether/petroleum ether 1/1 v/v) to give 9.50 g (48%) of **1j** as a pale yellow crystal. Mp 84.0—85.0 °C (toluene–hexane, lit,[40] 84.2—85.4 °C). ^{1}H NMR (90 MHz, $CDCl_3$) δ = 7.34—7.57 (4H, m), 3.97 (1H, dd, J = 2.4, 4.1 Hz), 3.23 (1H, dd, J = 4.1, 5.5 Hz), 2.78 (1H, dd, J = 2.4, 5.5 Hz). ^{13}C NMR (22.5 MHz, $CDCl_3$) δ = 145.4, 126.3, 123.8, 51.7, 51.5. IR (KBr) 1604, 1520, 1344, 848, 750 cm^{-1}. Anal. Calcd for $C_8H_7NO_3$: C, 58.18; H, 4.27; N, 8.48%. Found: C, 58.21; H, 4.34; N, 8.47%.

2-(4-Methylphenyl)oxirane (1m). In a flask fitted with septum rubber was placed 1.80 g (0.046 mol) of 60% sodium hydride in mineral oil; the contents were washed three times with petroleum ether by swirling and decantating the liquid portion. The flask was evacuated and a nitrogen atmosphere was introduced. After the addition of 50 ml of DMSO, 10.05 g (0.044 mol) of trimethyloxosulfonium iodide was added slowly. After the evolution of hydrogen ceased, 5.01 g (0.042 mol) of 4-methylbenzaldehyde was dropwise added. The reaction mixture was allowed to stand at room temperature for 20 min, and at 60 °C for an additional 2.5 h. After addition of 100 mL of ice water, the reaction mixture was extracted three times by 30 mL of ether. The organic layer was washed with brine, dried over anhydrous magnesium sulfate, and evaporated. The crude oxirane was chromatographed on silica-gel (eluent: ether/petroleum ether 1/3 v/v) to give 1.61 g (27%) of **1m** as a colorless oil, which was used after further distillation.

Bp 85—87 °C/5 mmHg (lit,[41] 33—35 °C/0.001 mmHg) (1 mmHg = 133.322 Pa). ^{1}H NMR (90 MHz, $CDCl_3$) δ = 7.14 (4H, s), 3.80 (1H, dd, J = 2.7, 4.1 Hz), 3.09 (1H, dd, J = 4.1, 5.5 Hz), 2.76 (1H, dd, J = 2.7, 5.5 Hz), 2.33 (3H, s). ^{13}C NMR (22.5 MHz,

$CDCl_3$) δ = 137.9, 134.6, 129.2, 125.5, 52.3, 51.0, 21.2. IR (Neat) 881, 817 cm^{-1}. Anal. Calcd for $C_9H_{10}O$: C, 80.56; H, 7.51%. Found: C, 80.34; H, 7.85%.

2-(4-Cyanophenyl)oxirane (1k).[42] **1k** was synthesized from 4-cyanobenzaldehyde in 26% yield as described above. Bp 111 °C/2 mmHg. ^{1}H NMR (90 MHz, $CDCl_3$) δ = 7.20—7.77 (4H, m), 3.91 (1H, dd, J = 2.4, 4.2 Hz), 3.20 (1H, dd, J = 4.2, 5.5 Hz), 2.75 (1H, dd, J = 2.4, 5.5 Hz). ^{13}C NMR (22.5 MHz, $CDCl_3$) δ = 143.3, 132.3, 126.2, 118.6, 111.9, 51.6, 51.6. IR (Neat) 2229, 877, 839 cm^{-1}. Anal. Calcd for C_9H_7NO: C, 74.47; H, 4.86; N, 9.65%. Found: C, 74.34; H, 4.94; N, 9.62%.

2-(4-Methoxyphenyl)oxirane (1n). **1n** was synthesized from 4-methoxybenzaldehyde in 37% yield as described above. Bp 97—98 °C/3 mmHg (lit,[41] 51 °C/0.001 mmHg). ^{1}H NMR (90 MHz, $CDCl_3$) δ = 6.81—6.94 (4H, m), 3.74—3.83 (4H, m), 3.09 (1H, dd, J = 3.9, 5.4 Hz), 2.78 (1H, dd, J = 2.6, 5.4 Hz). ^{13}C NMR (22.5 MHz, $CDCl_3$) δ = 159.8, 129.5, 126.8, 114.0, 55.3, 52.2, 50.9. IR (Neat) 1614, 1516, 1248, 879, 833, 808 cm^{-1}. Anal. Calcd for $C_9H_{10}O_2$: C, 71.98; H, 6.71%. Found: C, 72.23; H, 6.87%.

2-(4-Chlorophenyl)oxirane (1l). To a solution of 24.74 g (0.14 mol) of *m*CPBA in 300 mL of chloroform was added a solution of 15.90 g (0.11 mol) of 4-chlorostyrene in 40 mL of chloroform at 0 °C. After stirring for 24 h, a large amount of white crystal of *m*-chlorobenzoic acid was precipitated and complete consumption of 4-chlorostyrene was confirmed by TLC. The reaction mixture was filtered, and the filtrate was washed with 20% aqueous solution of sodium hydrogensulfite, 10% aqueous solution of sodium hydrogencarbonate, followed by brine. The organic layer was dried over anhydrous magnesium sulfate and evaporated. The crude oxirane was distilled in reduced pressure to give 14.24 g (84%) of **1l** as a colorless oil. Bp 79—80 °C/2 mmHg (lit,[43] 102—103 °C/10 mmHg). ^{1}H NMR (90 MHz, $CDCl_3$) δ = 7.12—7.37 (4H, m), 3.81 (1H, dd, J = 2.6, 4.0 Hz), 3.12 (1H, dd, J = 4.0, 5.5 Hz), 2.73 (1H, dd, J = 2.6, 5.5 Hz). ^{13}C NMR (22.5 MHz, $CDCl_3$) δ = 136.3, 133.9, 128.7, 126.9, 51.7, 51.2. IR (Neat) 1478, 1089, 878, 832 cm^{-1}. Anal. Calcd for C_8H_7ClO: C, 62.15; H, 4.56%. Found: C, 62.10; H, 4.68%.

Reaction of Oxiranes with Carbon Dioxide. In a two-necked flask equipped with septum rubber and a balloon filled with carbon dioxide was placed 8.7 mg (0.1 mmol, 5 mol%) of lithium bromide. After the atmosphere was replaced with carbon dioxide, 2 mmol of oxirane was introduced with 2.0 mL of NMP using a syringe through the septum rubber. After the salt was dissolved, the solution was allowed to stand at 100 °C with continuous stirring for the period mentioned. The reaction mixture was poured into 30 ml of water and was extracted with 3×10 ml of ether. The organic layer was combined, washed with brine, and dried over anhydrous magnesium sulfate before evaporation to obtain the crude carbonate. Hexamethyldisiloxane was weighed and added to the crude product. Yields of carbonate were estimated by the integration of ^{1}H NMR signals of trimethylsilyl group and cyclic carbonate group. The products were purified by column chromatography using silica-gel.

2a: ^{1}H NMR (90 MHz, $CDCl_3$) δ = 4.35—4.90 (2H, m), 3.89—4.19 (1H, m), 0.70—1.98 (11H, m). ^{13}C NMR (22.5 MHz, $CDCl_3$) δ = 155.1, 77.1, 69.4, 33.8, 31.3, 24.1, 22.4, 13.9. IR (Neat) 1799, 1172, 1062, 775 cm^{-1}. Anal. Calcd for $C_8H_{14}O_3$: C, 60.74; H, 8.92%. Found: C, 60.82; H, 8.91%.

2b: ^{1}H NMR (90 MHz, $CDCl_3$) δ = 4.41—4.90 (2H, m), 3.88—4.30 (1H, m), 0.69—1.95 (13H, m). ^{13}C NMR (22.5 MHz, $CDCl_3$) δ = 155.2, 77.2, 69.5, 33.9, 31.6, 28.9, 24.4, 22.5, 14.0. IR (Neat) 1801, 1172, 1066, 775 cm^{-1}. Anal. Calcd for $C_9H_{16}O_3$: C, 62.77; H, 9.36%. Found: C, 62.68; H, 9.41%.

2c: Mp 50.0—53.0 °C (lit,[44] 56.3 °C). ^{1}H NMR (90 MHz, $CDCl_3$) δ = 7.26—7.49 (5H, m), 5.67 (1H, dd, J = 7.9, 8.1 Hz), 4.79 (1H, dd, J = 8.1, 8.6 Hz), 4.32 (1H, dd, J = 7.9, 8.6 Hz). ^{13}C NMR (22.5 MHz, $CDCl_3$) δ = 154.8, 135.9, 129.7, 129.2, 125.9, 78.0, 71.2. IR (KBr) 1780, 1170, 1055, 760, 700 cm^{-1}. Anal. Calcd for $C_9H_8O_3$: C, 65.85; H, 4.91%. Found: C, 65.80; H, 4.89%.

2d: Mp 101.0—103.0 °C (lit,[26] 98.5—99.5 °C). ^{1}H NMR (90 MHz, $CDCl_3$) δ = 6.84—7.40 (5H, m), 4.89—5.14 (1H, m), 4.01—4.69 (4H, m). ^{13}C NMR (22.5 MHz, $CDCl_3$) δ = 157.8, 154.7, 129.6, 121.9, 114.6, 74.1, 66.9, 66.2. IR (KBr) 1805, 1249, 1167, 1091, 760 cm^{-1}. Anal. Calcd for $C_{10}H_{10}O_4$: C, 61.85; H, 5.19%. Found: C, 62.27; H, 5.21%.

2e: ^{1}H NMR (90 MHz, $CDCl_3$) δ = 7.31 (5H, s), 4.57 (2H, s), 4.45 (1H, d, J = 8.3 Hz), 4.03 (1H, d, J = 8.3 Hz), 3.62 (1H, d, J = 10.4 Hz), 3.37 (1H, d, J = 10.4 Hz), 1.44 (3H, s). ^{13}C NMR (22.5 MHz, $CDCl_3$) δ = 154.6, 137.2, 128.5, 128.4, 128.0, 127.6, 82.3, 73.6, 71.8, 21.8. IR (Neat) 1803, 1122, 1068 cm^{-1}. Anal. Calcd for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35%. Found: C, 64.79; H, 6.58%.

2g: ^{1}H NMR (90 MHz, $CDCl_3$) δ = 4.54—4.82 (2H, m), 1.12—2.11 (10H, m). ^{13}C NMR (22.5 MHz, $CDCl_3$) δ = 155.4, 75.6, 26.7, 19.1. IR (KBr) 1803, 1140, 1033 cm^{-1}. Anal. Calcd for $C_7H_{10}O_3$: C, 59.14; H, 7.09%. Found: C, 58.46; H, 7.06%.

2h: Mp 111.0—112.0 °C (EtOH). ^{1}H NMR (90 MHz, $CDCl_3$) δ = 7.16—7.55 (10H, m), 5.43 (2H, s). ^{13}C NMR (22.5 MHz, $CDCl_3$) δ = 154.1, 134.9, 129.3, 126.1, 85.4. IR (KBr) 1819, 1035 cm^{-1}. Anal. Calcd for $C_{15}H_{12}O_3$: C, 74.99; H, 5.03%. Found: C, 75.17; H, 5.17%.

2j: Mp 105.0—106.5 °C (EtOH). ^{1}H NMR (90 MHz, $CDCl_3$) δ = 8.27—8.37, 7.52—7.62 (4H, m), 5.81 (1H, dd, J = 7.9, 8.1 Hz), 4.90 (1H, dd, J = 8.1, 8.6 Hz), 4.32 (1H, dd, J = 7.9, 8.6 Hz). ^{13}C NMR (22.5 MHz, $CDCl_3$) δ = 154.1, 142.8, 126.6, 124.5, 124.5, 76.4, 70.7. IR (KBr) 1797, 1521, 1352, 1182, 1072 cm^{-1}. Anal. Calcd for $C_9H_7NO_5$: C, 51.68; H, 3.37; N, 6.70%. Found: C, 51.79; H, 3.48; N, 6.71%.

2k: Mp 90.5—91.5 °C. ^{1}H NMR (90 MHz, $CDCl_3$) δ = 7.39—7.89 (4H, m), 5.80 (1H, dd, J = 7.9, 8.1 Hz), 4.90 (1H, dd, J = 8.1, 8.5 Hz), 4.32 (1H, dd, J = 7.9, 8.5 Hz). ^{13}C NMR (22.5 MHz, $CDCl_3$) δ = 154.3, 141.1, 133.1, 126.4, 118.0, 113.5, 76.7, 70.8. IR (KBr) 2231, 1788, 1182, 1070 cm^{-1}. Anal. Calcd for $C_{10}H_7NO_3$: C, 63.49; H, 3.73; N, 7.40%. Found: C, 63.37; H, 3.80; N, 7.41%.

2l: Mp 68.0—69.0 °C. ^{1}H NMR (90 MHz, $CDCl_3$) δ = 7.24—7.49 (4H, m), 5.67 (1H, dd, J = 7.9, 8.1 Hz), 4.80 (1H, dd, J = 8.1, 8.5 Hz), 4.30 (1H, dd, J = 7.9, 8.5 Hz). ^{13}C NMR (22.5 MHz, $CDCl_3$) δ = 154.5, 135.8, 134.4, 129.5, 127.2, 77.2, 71.0. IR (KBr) 1793, 1180, 1167, 1053 cm^{-1}. Anal. Calcd for $C_9H_7ClO_3$: C, 54.43; H, 3.55%. Found: C, 54.61; H, 3.53%.

2m: Mp 43.0—44.0 °C. ^{1}H NMR (90 MHz, $CDCl_3$) δ = 7.25 (4H, s), 5.64 (1H, dd, J = 7.9, 8.1 Hz), 4.77 (1H, dd, J = 8.1, 8.5 Hz), 4.33 (1H, dd, J = 7.9, 8.5 Hz), 2.38 (3H, s). ^{13}C NMR (22.5 MHz, $CDCl_3$) δ = 160.0, 139.8, 129.9, 126.1, 78.1, 71.1, 21.2. IR (KBr) 1792, 1180, 1170, 1055 cm^{-1}. Anal. Calcd for $C_{10}H_{10}O_3$: C, 67.41; H, 5.66%. Found: C, 67.91; H, 5.90%.

2n: ^{1}H NMR (90 MHz, $CDCl_3$) δ = 6.89—7.02 (4H, m), 5.62 (1H, dd, J = 7.9, 8.1 Hz), 4.75 (1H, dd, J = 8.1, 8.5 Hz), 4.33 (1H, dd, J = 7.9, 8.5 Hz), 3.82 (3H, s). ^{13}C NMR (22.5 MHz, $CDCl_3$) δ = 160.8, 154.9, 127.9, 127.5, 114.7, 78.2, 71.1, 55.5. IR (Neat) 1793, 1614, 1518, 1253, 1170, 1072 cm^{-1}. Anal. Calcd for $C_{10}H_{10}O_4$: C, 61.85; H, 5.19%. Found: C, 61.99; H, 5.23%.

(2*R*)-1,2-Heptanediol (4a). Into a solution of 0.372 g (9.31 mmol) of sodium hydroxide in 2 mL of water and 2 mL of methanol was dissolved 0.994 g (6.29 mmol) of (2*R*)-**2a**. The mixture was

allowed to stand at room temperature for 30 min before the addition of 30 mL of brine and extraction by 3×10 mL of dichloromethane. The organic layer was dried over anhydrous magnesium sulfate and evaporated. The residue was distilled in a glass tube oven at 2 mmHg to obtain 0.595 g (72%) of (2*R*)-**4a**[32] as a colorless distillate at 150 °C. ^{1}H NMR (60 MHz, $CDCl_3$) δ = 3.26—3.92 (5H, m), 0.64—1.70 (11H, m). IR (Neat) 3362, 2930, 2860, 1072, 1032 cm^{-1}. $[\alpha]_D^{25}$ = +17.0° (*c* 1, EtOH).

Aminolysis of Five-Membered Cyclic Carbonates. A mixture of 0.5 mmol of five-membered cyclic carbonate and 0.55 mmol of benzylamine was stirred at room temperature for 1 h. Hydroxy urethanes were purified by silica-gel column chromatography eluted by ethyl acetate/hexane (1/1 v/v).

6j: Yield 73%. ^{1}H NMR (90 MHz, $CDCl_3$) δ = 7.37—7.58, 8.11—8.20 (4H, m), 7.26 (5H, s), 5.35 (1H, t, *J* = 5.9 Hz), 4.91—5.17 (1H, m), 3.96—4.50 (4H, m), 3.54—3.95 (1H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.8, 147.6, 147.3, 137.8, 128.8, 127.7, 127.5, 127.0, 123.7, 72.3, 69.8, 45.2. IR (Neat) 3360, 3269, 1689, 1520, 1261, 742, 696 cm^{-1}. Anal. Calcd for $C_{16}H_{16}N_2O_5$: C, 60.76; H, 5.10; N, 8.86%. Found: C, 60.74; H, 5.08; N, 8.85%.

7j: Yield 22%. ^{1}H NMR (90 MHz, $CDCl_3$) δ = 7.06—7.69, 8.07—8.36 (9H, m), 5.86 (1H, t, *J* = 5.0 Hz), 5.06—5.41 (1H, m), 4.38 (2H, d, *J* = 5.9 Hz), 3.86 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 155.6, 147.7, 144.9, 137.8, 128.8, 127.8, 127.6, 127.3, 123.8, 76.6, 65.9, 45.3. IR (Neat) 3414, 1701, 1521, 1348, 1257, 856, 700 cm^{-1}. Anal. Calcd for $C_{16}H_{16}N_2O_5$: C, 60.76; H, 5.10; N, 8.86%. Found: C, 60.71; H, 5.10; N, 8.82%.

6c: Yield 55%. Mp 112.0—113.0 °C. ^{1}H NMR (90 MHz, $CDCl_3$) δ = 7.32 (5H, s), 7.27 (5H, s), 5.18—5.51 (1H, m), 4.78—5.05 (1H, m), 3.97—4.45 (4H, m), 3.09—3.49 (1H, m). ^{13}C NMR (22.5 MHz, $CDCl_3$) δ = 156.9, 140.0, 138.2, 128.7, 128.5, 128.0, 127.5, 126.2, 72.8, 70.1, 45.1. IR (KBr) 3425, 3331, 1689, 1545, 1452, 1273, 1140, 746, 704 cm^{-1}. Anal. Calcd for $C_{16}H_{17}NO_3$: C, 70.83; H, 6.32; N, 5.16%. Found: C, 70.70; H, 6.18; N, 5.12%.

7c: Yield 38%. Mp 90.0—91.0 °C. ^{1}H NMR (90 MHz, $CDCl_3$) δ = 7.30 (5H, s), 7.25 (5H, s), 5.77 (1H, t, *J* = 5.5 Hz), 5.29—5.60 (1H, m), 4.29 (2H, d, *J* = 5.9 Hz), 3.77 (2H, d, *J* = 5.5 Hz), 2.58—3.13 (1H, m). ^{13}C NMR (22.5 MHz, $CDCl_3$) δ = 156.4, 138.3, 137.5, 128.6, 128.5, 128.2, 127.5, 126.5, 77.7, 66.3, 45.1. IR (KBr) 3360, 3263, 1691, 1537, 1454, 1286, 1265, 1145, 1039, 696 cm^{-1}. Anal. Calcd for $C_{16}H_{17}NO_3$: C, 70.83; H, 6.32; N, 5.16%. Found: C, 70.66; H, 6.34; N, 5.09%.

6m: Yield 50%. Mp 88.0—89.0 °C. ^{1}H NMR (90 MHz, $CDCl_3$) δ = 7.00—7.48 (9H, m), 5.26—5.57 (1H, m), 4.70—4.94 (1H, m), 4.03—4.40 (4H, m), 3.33—3.58 (1H, m), 2.30 (3H, s). ^{13}C NMR (22.5 MHz, $CDCl_3$) δ = 156.9, 138.3, 137.6, 137.1, 129.1, 128.6, 127.5, 126.1, 72.5, 70.0, 45.1, 21.1. IR (KBr) 3562, 3306, 1682, 1537, 1263, 1089, 696 cm^{-1}. Anal. Calcd for $C_{17}H_{19}NO_3$: C, 71.56; H, 6.71; N, 4.91%. Found: C, 71.30; H, 6.74; N, 4.87%.

7m: Yield 42%. Mp 122.0—123.0 °C. ^{1}H NMR (90 MHz, $CDCl_3$) δ = 7.05—7.41 (9H, m), 5.75 (1H, t, *J* = 5.9 Hz), 5.19—5.47 (1H, m), 4.31 (2H, d, *J* = 5.9 Hz), 3.78 (2H, d, *J* = 5.7 Hz) 2.28 (3H, s). ^{13}C NMR (22.5 MHz, $CDCl_3$) δ = 156.4, 138.3, 138.1, 134.5, 129.2, 128.7, 127.5, 126.5, 77.8, 66.4, 45.2. IR (KBr) 3358, 1691, 1548, 1288, 1263, 1145, 1049, 1037, 698 cm^{-1}. Anal. Calcd for $C_{17}H_{19}NO_3$: C, 71.56; H, 6.71; N, 4.91%. Found: C, 71.32; H, 6.73; N, 4.96%.

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