JOC Article

Chemical Fixation of Carbon Dioxide by NaI/PPh_3/PhOH

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In the presence of catalytic amounts of sodium iodide, triphenylphosphine, and phenol, carbon dioxide can efficiently react with epoxides to give the corresponding five-membered cyclic carbonates in high yields. The mechanism of this reaction was disclosed by ^{31}P NMR spectroscopic data and deuterium labeling experiments.

Introduction

Conversion of carbon dioxide to industrially useful compounds has been a challenge for synthetic chemists and has recently attracted much interest in view of the so-called "sustainable society"[1] and "green chemistry" concepts.[2] One of the most attractive synthetic goals starting from carbon dioxide is the five-membered cyclic carbonates system because five-membered cyclic carbonates have many synthetic uses and have generally been synthesized from the corresponding diols and phosgene or related compounds.[3] In the past decades of the twentieth century, numerous catalytic systems using harmless oxiranes with CO_2 have been developed for this transformation,[4−6] while the advances have been significant, all suffer from either low catalyst stability/reactivity, air sensitivity, the need for cosolvent, or catalysts requiring special structures.

Herein, we wish to report an extremely simple and ecologically safer route to cyclic carbonate from the reactions of epoxide with carbon dioxide in the presence of catalytic amounts of sodium iodide, triphenylphosphine, and phenol without organic solvent.

Results and Discussion

During our investigations on the reaction of propylene oxide with CO_2 in the presence of catalytic amounts of triphenylphosphine (0.5 mol %) and phenol (0.5 mol %),[7] we found that only a trace amount of the corresponding cyclic carbonate **1a** was obtained. However, if epichlorohydrin was used as the substrate under the same reaction conditions, the cyclic carbonate **1b** was formed almost quantitatively (Scheme 1). This drastically different result caused us to believe that the additional chlorine atom in epichlorohydrin played a crucial role in this reaction. A plausible mechanism for this reaction was shown in Scheme 2. The ylide (A^+Cl^-) produced from the reaction of epichlorohydrin with triphenylphosphine acted as a catalyst in this reaction. The chlorine ion of ylide (A^+Cl^-) opens the epoxy ring, which is activated by phenol through hydrogen bonding, to give the intermediate **B**.[7] Then, it further reacts with CO_2 to give the corresponding cyclic carbonate **1b** and regenerate the ylide (A^+Cl^-) (Scheme 2).

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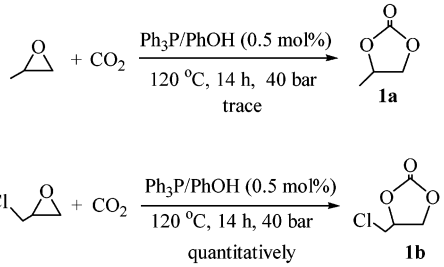
SCHEME 1. Reaction of Epoxide with CO_2 in the Presence of Triphenylphosphine and Phenol



SCHEME 2. Plausible Mechanism for the Reaction of Epichlorohydrin with CO_2

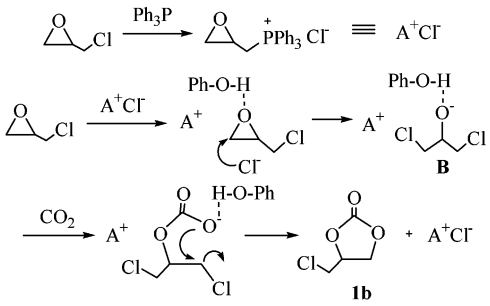
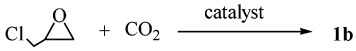


TABLE 1. Reactions of Epichlorohydrin with CO_2 in the Presence of Phenol and Different Trisubstituted Phosphines



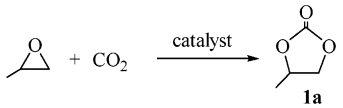
entry[a]	catalyst	temp (°C)	time (h)	yield (%)[b]
1	Ph_3P/PhOH	80	14	93
2	Bu_3P/PhOH	80	14	86
3	Me_3P/PhOH	120	12	20
4	Ph_3P/PhOH	80	12	87
5	Ph_3P/PhOH	60	10	52
6	Ph_3P/PhOH	120	14	100
7	Ph_3P	120	14	65
8	Ph_3P	120	48	100
9	Bu_3P	120	48	100

[a] All reactions were carried out under 40 bar initial pressure of CO_2 with 0.5 mol % catalyst. [b] Isolated yield.

The reaction conditions were optimized. Tributylphosphine and trimethylphosphine also can catalyze this reaction, while triphenylphosphine gave the best result under the same conditions (Table 1, entries 1−3). The reaction temperature and time have significant effects on the yield of cyclic carbonate **1b**. Using the same catalysts, the reaction of CO_2 with epichlorohydrin gave a higher yield of **1b** at 120 °C for 14 h than at 60 or 80 °C within a shorter reaction time (Table 1, entries 4−6). Phenol has the effect of accelerating the reaction rate because **1b** was obtained in 65% yield under the same conditions without phenol (Table 1, entry 7). In the absence of phenol, a prolonged reaction time is required in order to get the higher yield of **1b** (Table 1, entries 8 and 9).

These excellent results led us to believe that the combination of triphenylphosphine, phenol, and halide ion can catalyze the reaction of other epoxides with CO_2. As expected, we found that by addition of a catalytic amount of sodium iodide, propylene oxide can react with CO_2 smoothly to give the corresponding cyclic carbonate in high yield (Table 2, entry 1). Further studies revealed that the combination of triphenylphosphine and phenol with many other nucleophiles such as Br^-, Cl^-, AcO^-, and PhO^-, etc., also have catalytic abilities for this reaction. The results were summarized in Table 2. Sodium iodide is the best ionic or nucleophilic source for this reaction (Table 2, entries 1−7). This catalytic system on chemical fixation of CO_2 is very efficient. The scope and limitations of catalysts and reaction conditions have been carefully examined. The ammonium salt, the combination of NaI/P(O)Ph_3/PhOH, and imidazole (organic base) are less effective than the mixed catalyst NaI/PPh_3/PhOH (Table 2, entries 7−10 and 11). Phosphonium salt ($Ph_3P^+MeI^-$) itself has poor catalytic activity for this reaction (Table 2, entry 11), while in the presence of a catalytic amount of phenol, this transformation also proceeded smoothly to give **1a** in high yield (Table 2, entry 13). We also tested other alcoholic substances such as methanol or water (H-bond donor)[7] and $Ph_3P^+MeI^-$ in this catalytic reaction. As a result, we found that they also can cocatalyze this reaction under the same conditions but not as effectively as phenol (Table 2, entries 14 and 15).

TABLE 2. Reactions of Propylene Oxide with CO_2 in the Presence of Various Catalysts



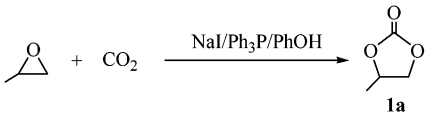
entry[a]	catalyst	temp (°C)	time (h)	yield (%)[b]
1	NaI/PPh_3/PhOH	120	4	100
2	NaI/PPh_3/PhOH	120	4	96
3	NaBr/PPh_3/PhOH	120	4	90
4	NaCl/PPh_3/PhOH	120	4	26
5	PhONa/PPh_3/PhOH	120	48	100
6	AcONa/PPh_3/PhOH	120	48	100
7	EtONa/PPh_3/PhOH	120	24	none
8	ButOK/PPh_3/PhOH	120	24	none
9	Bu4N$^+$I$^-$/PhOH	120	8	81
10	NaI/P(O)Ph_3/PhOH	120	9	6
11	imidazole	120	40	19
12	$Ph_3P^+MeI^-$	120	9	9
13	$Ph_3P^+MeI^-$/PhOH	120	4	95
14	$Ph_3P^+MeI^-$/PhOH	120	4	63
15	$Ph_3P^+MeI^-$/H_2O	120	4	56

[a] All reactions were carried out under 40 bar initial pressure of CO_2 with 2.0 mol % catalyst. [b] Isolated yield.

The ratios of NaI (2.0 mol %), PPh_3 (2.0 mol %), and PhOH (2.0 mol %) on this reaction have been investigated (Table 3). From these studies, it appears that triphenylphosphine is essential for this process and the coexistence of phenol must be required in order to reduce the reaction time (Table 3, entries 1−6), The best combination of this mixed catalytic system is sodium iodide/triphenylphosphine/phenol = 1/1/1 in this reaction (Table 3, entries 5 and 6).

Under the optimized reaction conditions (NaI/PPh_3/PhOH, 40 bar CO_2, 120 °C, 4 h), we examined the reactions of other epoxides with carbon dioxide (Table 4). We found that, using 2 mol % NaI, PPh_3 and PhOH as catalysts, many monosubstituted terminal epoxides can be transferred to the corresponding cyclic carbonates in high yields within 4 h (Table 4, entries 1−5).

TABLE 3. Reactions of Propylene Oxide with CO_2 in the Presence of Different Ratios of Sodium Iodide, Triphenylphosphine, and Phenol

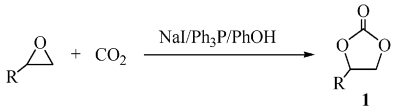


1a

entry[a]	NaI/Ph_3P/PhOH	temp (°C)	time (h)	yield (%)[b]
1	0/1/1	120	48	trace
2	1/0/1	120	12	trace
3	1/1/0	120	6	64
4	1/1/1	80	4	62
5	1/1/1	120	2	95
6	1/1/1	120	4	100

[a] All the reactions were carried out under 40 bar initial pressure of CO_2 with 2.0 mol % of catalyst. [b] Isolated yield.

TABLE 4. Reactions of Epoxide with CO_2 in the Presence of Sodium Iodide, Triphenylphosphine, and Phenol



1

entry[a]	R	temp (°C)	time (h)	yield (%)[b]
1	$ClCH_2$	120	4	**1b**, 100
2	Et	120	4	**1c**, 99
3	*n*-Bu	120	4	**1d**, 97
4	C_6H_5	120	4	**1e**, 85
5	$ClCH_2C_6H_4$	120	4	**1f**, 75

[a] All reactions were carried out under 40 bar initial pressure with 2.0 mol % catalyst. [b] Isolated yield.

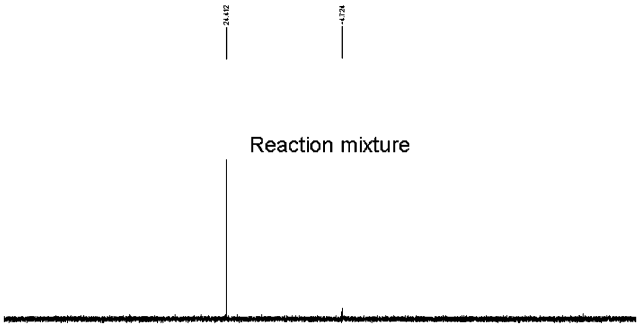
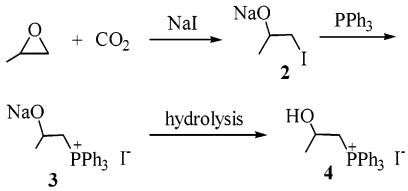


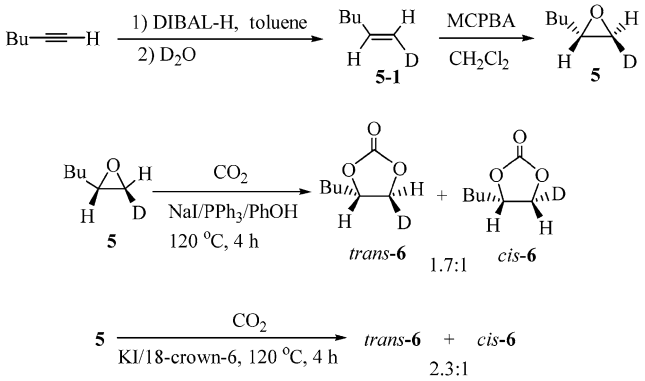
FIGURE 1. ^{31}P NMR spectrum of the reaction mixture.

To clarify the reaction mechanism, after reaction, we carried out the ^{31}P NMR (85% H_3PO_4, $CDCl_3$) measurement of the reaction mixture (Figure 1). We found a new signal at δ 24.41 along with the signal of PPh_3 at δ −4.72. This observation suggests that PPh_3 has been transferred to another product. By careful isolation of the reaction mixture with Sephadex LH-20 and detailed spectroscopic and microanalysis analysis (see Supporting Information), we confirmed that β-hydroxy phosphonium iodide **4**, which is conceivably derived from its precursor sodium salt **3** as shown in Scheme 3, was produced. In a control experiment, we found that **4** treated with NaH can effectively catalyze the reaction of propylene oxide with CO_2 to give the corresponding cyclic carbonate in high yield and that no cyclic carbonate can be formed by treatment of **3** or **4** itself under a CO_2 atmosphere (see Supporting Information). Since NaI itself and NaI/phenol

SCHEME 3. Formation Route of β-Hydroxy Phosphonium Salt 4



SCHEME 4. Reaction of *trans*-1-Deuterio-2-butyl-oxirane 5 with CO_2 in the Presence of 2 Mol % NaI/PPh_3/PhOH and KI with 18-Crown-ether



cannot efficiently catalyze the reaction of epoxide with CO_2, we believe that the real active species is phosphonium iodide **3**.

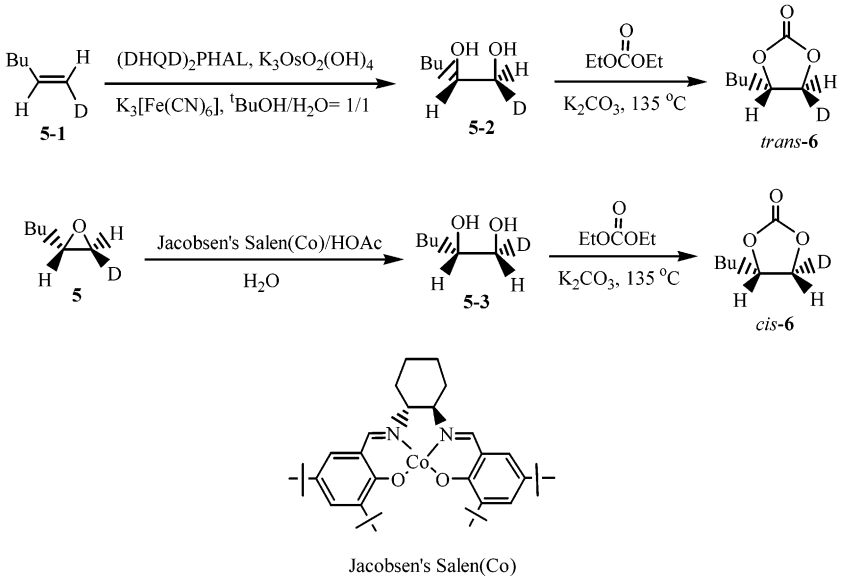
To demonstrate the mechanism of ring-opening reaction of epoxides, we synthesized *trans*-1-deuterio-1,2-hexene oxide **5** according to the literature and utilized it as the substrate in the presence of 2.0 mol % sodium iodide, triphenylphosphine, and phenol (1/1/1) to react with CO_2 (Scheme 4). The deuterated hexene carbonate formed was analyzed with the authentic samples prepared as shown in Scheme 5 according to the literature (their spectral charts were shown in Supporting Information). As a result, we obtained a mixture of 1-deuterio-2-butyl-cyclic carbonate **6** with a trans/cis ratio of 1.7:1 in ^1H NMR spectroscopic data (Scheme 4). A similar trans/cis ratio of 2.3:1 was also observed in the KI and 18-crown-6-catalyzed reaction of **5** with CO_2, which is a typical ring-opening reaction of epoxide by iodine ion (I^-) (Scheme 4).[4c] On the basis of these results, we can conclude that this reaction is involved with a ring-opening reaction of epoxide by iodide ion. The partial conversion of configuration can be explained by the presence of an iodide−iodide ion exchange process (Scheme 6).

On the basis of all these experimental results, we proposed a reasonable mechanism for the formation of cyclic carbonate in Scheme 7. The initially formed phosphonium salt **3** (B^+I^-) in the catalytic system of NaI/PPh_3/PhOH catalyzes the reaction of epoxide with CO_2 by ring-opening reaction of epoxide with iodide ion in **3**, which further reacts with CO_2 to produce cyclic carbonate and regenerate the catalyst (B^+I^-).

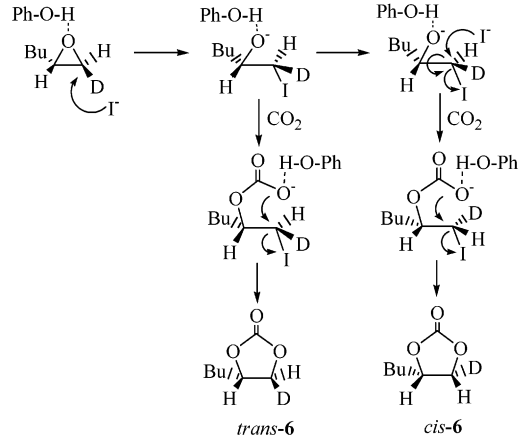
Conclusion

In conclusion, we found that cyclic carbonate **1** can be obtained in very high yield from the reaction of epoxide

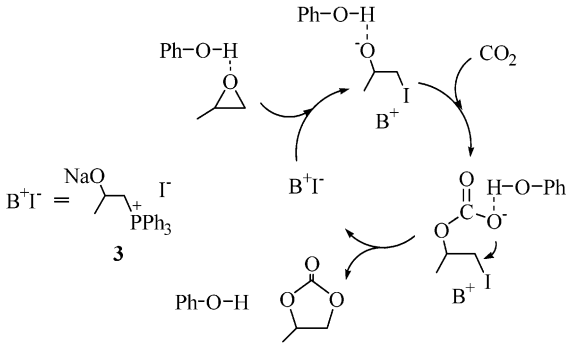
SCHEME 5. Preparation of Authentic Samples of *trans*-6 and *cis*-6



SCHEME 6. Partial Conversion of Configuration in the Deuterium-Labeled Experiments



SCHEME 7. Plausible Reaction Mechanism



with carbon dioxide in the presence of catalytic amounts of sodium iodide, triphenylphosphine, and phenol without using any organic solvent. In this reaction, the phosphonium salt **3** derived from the reaction of epoxide with NaI and PPh_3 is the active catalyst and phenol acted as a Br*ϕ*nsted acid to accelerate the ring-opening reaction of epoxide through hydrogen bonding. Efforts are underway to elucidate the further mechanistic details of this reaction and to identify systems enabling the similar carboxylation of other substrates and subsequent transformation thereof.

Experimental Section

Representative Procedure for the Reactions of Epoxides with Carbon Dioxide. A 100 mL stainless pressure reactor was charged with propylene oxide (2.6 g, 45 mmol), sodium iodide (135 mg, 0.9 mmol), triphenylphosphine (235 mg, 0.9 mmol), and phenol (84 mg, 0.9 mmol). The reaction vessel was placed under a constant pressure (40 bar) of carbon dioxide for 5 min to allow the system to equilibrate and then heated to 120 °C for 4 h. The vessel was then cooled to ambient temperature and the pressure released, and the contents were transferred to a round-bottom flask. Unreacted substrate and solvent were removed in a vacuum, and the residue was purified by silica gel column chromatography (eluent: petroleum ether/EtOAc = 1/4) to give the cyclic carbonate as a colorless liquid.

4-Methyl-[1,3]-dioxolan-2-one 1a. This is a known compound.[5d] IR (neat): ν 1800 (C═O) cm^{-1}. ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ 1.51 (3H, d, J = 6.2 Hz, CH_3), 4.04 (1H, t, J = 8.1 Hz, CH), 4.57 (1H, t, J = 8.1 Hz), 4.84−4.91 (1H, m, CH). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 19.3, 70.8, 73.9, 155.3 (C═O).

4-Chloromethyl-[1,3]-dioxolan-2-one 1b. IR (neat): ν 1801 (C═O) cm^{-1}. ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ 3.71−3.82 (2H, m, CH_2), 4.43 (1H, dd, J = 8.6, 5.5 Hz, CH), 4.61 (1H, t, J = 8.6 Hz, CH), 4.94−5.02 (1H, m, CH). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 44.1, 66.6, 74.3, 154.4 (C═O). MS (EI): m/z 136 (M^+). HRMS (EI): calcd for $C_4H_5ClO_3$ (M), 135.9927; found (M^+), 135.9915.

4-Ethyl-[1,3]-dioxolan-2-one 1c. IR (neat): ν 1798 (C═O) cm^{-1}. ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ 1.0 (3H, t, J = 7.1 Hz, CH_3), 1.74−1.95 (2H, m, CH_2), 4.14 (1H, dd, J = 8.1, 7.1 Hz, CH), 4.54 (1H, t, J = 8.1 Hz, CH), 4.64−4.78 (1H, m, CH). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 9.2, 27.6, 69.8, 78.8, 155.9 (C═O). MS (EI): m/z 117 ($M^+ + 1$). HRMS (EI): calcd for $C_5H_8O_3$ (M), 116.0473; found (M^+), 116.0465.

4-Butyl-[1,3]-dioxolan-2-one 1d. IR (neat): ν 1800 (C═O) cm^{-1}. ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ 0.95 (3H, t, J = 7.1 Hz, CH), 1.20−1.54 (4H, m, CH_2), 1.60−2.0 (2H, m, CH_2), 4.09 (1H, dd, J = 8.1, 7.4 Hz, CH), 4.54 (1H, t, J = 8.1, CH), 4.65−4.80 (1H, m, CH). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 14.0, 22.5, 26.6, 33.7, 69.7, 77.4, 155.5 (C═O). MS (EI): m/z 144 (M^+). HRMS (EI): calcd for $C_7H_{12}O_3$ (M), 144.0786; found (M^+), 144.0789.

4-Phenyl-[1,3]-dioxolan-2-one 1e. Mp: 50−51 °C.[7] IR (neat): ν 1814 (C═O) cm^{-1}. ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ 4.36 (1H, t, J = 8.6 Hz, CH), 4.82 (1H, t, J = 8.6 Hz, CH), 5.68 (1H, t, J = 8.6 Hz, CH), 7.27−7.46 (5H, m, Ar). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 71.1, 125.8, 129.1, 129.6, 135.7, 154.8 (C═O). MS (EI): m/z 164 (M^+). Anal. Calcd for $C_9H_8O_3$: C, 65.85; H, 4.88. Found: C, 65.91; H, 5.02.

4-(3-Chloromethyl-phenyl)-[1,3]-dioxolan-2-one and 4-(4-Chloromethyl-phenyl)-[1,3]-dioxolan-2-one 1f. IR (neat): ν 1801 (C═O) cm^{-1}. ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ 4.36 (1H, dd, J = 8.6, 8.0 Hz, CH), 4.62 (1H, s, CH_2), 4.84 (1H, dd, J = 8.6, 8.0 Hz, CH), 5.71 (1H, t, J = 8.0 Hz, CH), 7.40−7.48 (5H, m, Ar). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 43.0, 71.3, 77.8, 126.1, 130.1, 136.2, 138.9, 177.8 (C═O). MS (EI): m/z 212 (M^+). HRMS (EI): calcd for $C_{10}H_9ClO_3$ (M), 212.0240; found (M^+), 212.0241.

1-(Triphenyl-λ^5-phosphanyl)-propan-2-ol, Iodide Salt 4. After reaction, dichloromethane CH_2Cl_2 was added into the reaction mixture; the sodium iodide was precipitated and removed by filtration. The filtrates were passed through a short path column (SiO_2) to get rid of the formed cyclic carbonate (eluent: ethyl acetate). The residue in silica gel column chromatography was isolated by washing with methanol. The methanol was removed under reduced pressure; the residue was purified by a Sephadex LH-20 column with methanol, and the corresponding phosphonium iodide **4** was obtained as a colorless solid. Isolated yield: 3.6% (based on the NaI used). Mp: 119−121 °C. IR (neat): ν 3311, 1588, 1485, 1438, 1112 cm^{-1}. ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ 1.51 (dd, J = 5.7, 2.4 Hz, 3H, CH_3), 3.46 (ddd, J = 15.3, 12.6, 2.7 Hz, 1H, CH_2), 3.81 (ddd, J = 21.0, 15.3, 10.5 Hz, 1H, CH_2), 4.05 (d, J = 6.6 Hz, OH), 4.20−4.33 (m, 1H, CH), 7.64−7.83 (m, 15H). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 25.5 (d, J_{C-P} = 14.0 Hz, CH_3), 32.6 (d, J_{C-P} = 51.4 Hz, CH_2), 62.7 (d, J_{C-P} = 6.2 Hz, CH), 118.6 (d, J_{C-P} = 86.4 Hz, C), 130.1 (d, J_{C-P} = 12.6 Hz, CH), 133.9 (d, J_{C-P} = 10.4 Hz, CH), 134.7 (d, J_{C-P} = 2.8 Hz, CH). Anal. Calcd for $C_{21}H_{22}IOP$: C, 56.27; H, 4.95; I, 28.31. Found: C, 55.83; H, 5.19; I, 28.14.

***trans*-1-Deuterio-1-hexene 5-1** and ***trans*-1-deuterio-2-butyloxirane 5** were prepared according to the literature.[8]

***erythreo*-1-Deuterio-1,2-hexanediol 5-2.** This compound was prepared from *trans*-1-deuterio-1-hexene **5-1** using Sharpless dihydroxylation reaction.[9] To a solution of $K_3Fe(CN)_6$ (2.96 g, 9.0 mmol), K_2CO_3 (1.24 g, 9.0 mmol), $MeSO_2NH_2$ (285 mg, 3.0 mmol), $(DHQD)_2PHAL$ (23 mg, 0.03 mmol), and $K_2OsO_2(OH)_4$ (4 mg, 0.011 mmol) in $^tBuOH-H_2O$ (1:1) (30 mL) was added *trans*-1-deuterio-1-hexene (255 mg, 3.0 mmol) at 0 °C, and the mixture was vigorously stirred for 11 h at 0 °C. The reaction was quenched by slow addition of Na_2SO_3 (4.2 g, 33.3 mmol). After stirring for 0.5 h at room temperature, the reaction mixture was filtered. The solvent was removed from the filtrate under reduced pressure, and the residue was extracted with EtOAc. The extracted organic layer was washed with 5% H_2SO_4 and brine and then dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography (eluent: petroleum ether/EtOAc = 2/1) to give the corresponding diol **5-2** as a colorless oil, 280 mg (79%). IR (neat): ν 3369, 2931, 2151, 1466, 1061 cm^{-1}. ^1H NMR (300 MHz, TMS, $CDCl_3$): δ 0.91 (3H, t, J = 6.9 Hz, CH_3), 1.25−1.43 (6H, m, $-CH_2CH_2CH_2-$), 2.50 (1H, br, s, OH), 3.41 (1H, d, CHD, J = 7.5 Hz), 3.72 (1H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.0, 22.7, 27.8, 32.7, 66.2 (t, J_{C-D} = 20.18 Hz), 72.2. MS (EI): *m/e* 87 (M^+ − HCDOH) (34).

***threo*-1-Deuterio-1,2-hexanediol 5-3.** This compound was prepared from *trans*-1-deuterio-1,2-hexene oxide **5** using Jacobsen's reaction.[10] To a solution of racemic Salen(Co) (15 mg, 0.025 mmol), HOAc (6.0 μL, 0.1 mmol), and *trans*-1-deuterio-1,2-hexene (325 mg, 3.2 mmol) was added H_2O (90 μL, 5.0 mmol) in one portion at 0 °C, and the mixture was vigorously stirred for 16 h at 0 °C. The organic product was extracted with ether. The extracted organic layer was washed with water and brine and then dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography (eluent: petroleum ether/EtOAc = 2/1) to give the corresponding diol **7** as a colorless oil, 309 mg (81%). IR (neat): ν 3317, 2932, 2169, 1466, 1085 cm^{-1}. ^1H NMR (300 MHz, TMS, $CDCl_3$): δ 0.91 (3H, t, J = 6.9 Hz, CH_3), 1.26−1.47 (6H, m, $-CH_2CH_2CH_2-$), 2.67 (2H, br, s, OH), 3.64 (1H, m, CHD, J = 7.5 Hz), 3.70 (1H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.0, 22.7, 27.8, 32.8, 66.3 (t, J_{C-D} = 21.0 Hz), 72.3. MS (EI): *m/e* 87 (M^+ − HCDOH) (30.71).

***trans*-4-Butyl-5-deuterio-[1,3]-dioxolane-2-one 6.** *erythreo*-1-Deuterio-1,2-hexanediol **5-2** (238 mg, 2.0 mmol), K_2CO_3 (28 mg, 0.2 mmol), and $(EtO)_2C$═O (15 mL) were heated to reflux (at 135 °C) for 5 h. The excess $(EtO)_2C$═O was removed under reduced pressure, and the residue was purified by silica gel column chromatography (eluent: petroleum ether/EtOAc = 6/1) to give the corresponding *trans*-4-butyl-5-deuterio-[1,3]-dioxolane-2-one **6** as a colorless oil, 192 mg (66%). IR (neat): ν 1801 (C═O) cm^{-1}. ^1H NMR (300 MHz, TMS, $CDCl_3$): δ 0.93 (3H, t, J = 7.2 Hz, CH_3), 1.33−1.45 (4H, m, $-CH_2CH_2-$), 1.68−1.85 (2H, m, CH_2), 4.07 (1H, d, J = 6.9 Hz, CHD), 4.72 (1H, m, CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.8, 22.2, 26.4, 33.5, 69.2 (t, J_{C-D} = 23.78 Hz), 77.1, 155.2 (C═O). MS (EI): *m/e* 145 (M^+) (0.93). HRMS (EI): calcd for $C_7H_{11}DO_3$ (M), 145.0848; found (M^+), 145.0910.

***cis*-4-Butyl-5-deuterio-[1,3]-dioxolane-2-one 6.** This compound was prepared in the same manner as that described above from **5-3** a colorless oil, 190 mg (65%). IR (neat): ν 1801 (C═O) cm^{-1}. ^1H NMR (300 MHz, TMS, $CDCl_3$): δ 0.92 (3H, t, J = 7.2 Hz, CH_3), 1.33−1.44 (4H, m, $-CH_2CH_2-$), 1.68−1.85 (2H, m, CH_2), 4.52 (1H, dt, J = 7.8, 1.2 Hz, CHD), 4.69 (1H, m, CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.6, 22.1, 26.3, 33.3, 69.1 (t, J_{C-D} = 22.95 Hz), 77.1, 155.2 (C═O). MS (EI): *m/e* 146 (M^+ + 1) (3.36). HRMS (EI): calcd for $C_7H_{11}DO_3$ (M), 145.0848; found (M^+), 145.0910.

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Supporting Information Available: ^{13}C NMR spectra of the cyclic carbonates **1a**−**f** and β-hydroxy phosphonium salt **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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