Tetrahedron 66 (2010) 9675–9680

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Synthesis of carbonates directly from 1 atm CO_2 and alcohols using CH_2Cl_2

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ARTICLE INFO

Article history:
Received 29 September 2010
Received in revised form 15 October 2010
Accepted 18 October 2010
Available online 10 November 2010

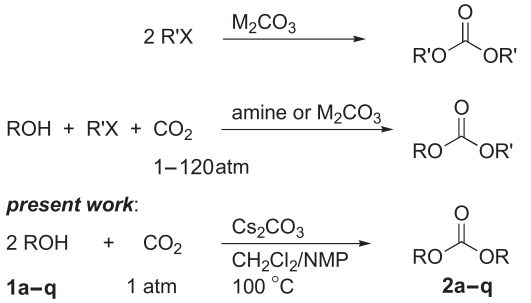
Keywords:
1 atm Carbon dioxide
Dichloromethane
Carbonate
Alcohol
Cesium carbonate

ABSTRACT

We introduced here a new one-pot, general procedure for the preparation of dialkyl carbonates from alcohols in a straightforward fashion under 1 atm pressure of CO_2 using Cs_2CO_3 and CH_2Cl_2 as key reagents.

1. Introduction

Recent interest in the utilization of carbon dioxide (CO_2) as a synthetic building block has inspired a number of investigations[1–5] of the preparation of dialkyl carbonates (RO(C═O)(OR))[1,4,5] from alcohols and CO_2. Carbonates have potential usage as neutral allylating,[6] alkylating,[7] and carbonylation[7] agents, as well as fuel additives, electrolyte solvents, etc., and in particular for poly(carbonate)s production.[1] In general, however, previous methods utilizing alcohols and CO_2, in the presence of heterogeneous or molecular catalysts,[4] accommodated rather drastic conditions including high pressure (>40 atm) and temperature (>150 °C), and concomitant removal of H_2O was a fatal event to overcome the thermodynamic disadvantage ($\Delta G >> 0$). In order to achieve carbonate synthesis under milder conditions including '1 atm CO_2', alkyl halides (R′Xs, Scheme 1) have been nicely adjusted, being an inevitable partner of CO_2 or its equivalents.[5] During an earlier attempt, R′Xs were used as electrophiles, wherein two molecules of an R′X underwent coupling with CO_3^- supplied from an alkaline metal carbonate (M_2CO_3; M═Na, K, Cs) ('inorganic carbonate alkylation', Scheme 1, top).[5b] Subsequently, a combined usage of R′X and alcohol, the former being used as an electrophile with the latter being a nucleophile, gave rise to either symmetrical or unsymmetrical dialkyl carbonates (Scheme 1, middle) in the absence or in the presence of CO_2 (1–120 atm) using more or less excess amount of base including a guanidine or M_2CO_3 as critical promoter.[5a, 5c–h] These two precedents were successfully implemented in demand for separately preparing R′Xs in advance from the corresponding alcohols. We report here a third synthetic method employing M_2CO_3 (M═Cs, Scheme 1, bottom), in which a range of carbonates was produced effectively upon simple exposure of a 1 atm pressure of CO_2 to alcohols in the presence of CH_2Cl_2.



Scheme 1. General scheme of carbonate synthesis: from alkaline metal carbonate (M_2CO_3) and alkyl halide (R′X) (top); from CO_2, alcohol (ROH) and R′X (middle); from CO_2 and alcohol (bottom).

2. Results and discussion

Our synthetic procedure for carbonates is very simple and straightforward: treatment of a CH_2Cl_2 (3.1 equiv)—NMP suspension of Cs_2CO_3 (2 equiv) with benzyl alcohol **1a** (1 equiv) under an atmosphere of CO_2 (1 atm) at 100 °C for 12 h gave, after column chromatography on silica gel, the corresponding dibenzyl carbonate (**2a**) in

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doi:10.1016/j.tet.2010.10.051

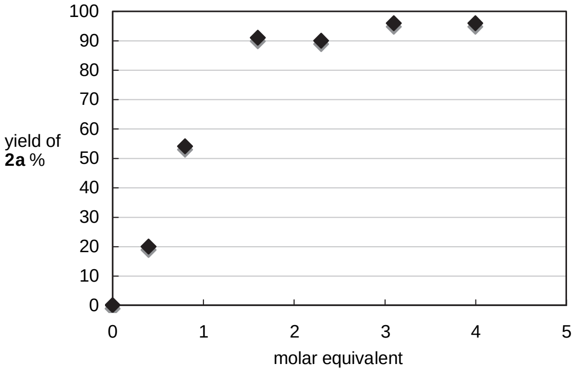
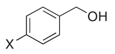
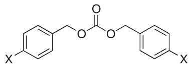
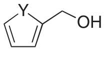
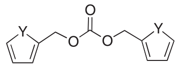
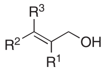
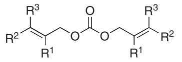
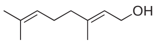
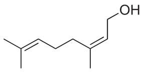
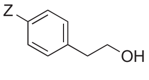
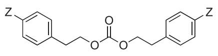
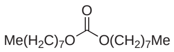


Fig. 1. NMR yield of **2a** as a function of molar equivalent of CH_2Cl_2 relative to molar amount of alcohol **1a**. 1,1,2,2-tetrachloroethane was used as an internal standard, which was added at 25 °C after the reaction time of 12 h.

an isolated yield of 96%. Smaller or larger amounts of CH_2Cl_2 were used to elucidate the relevance between molar equivalents of CH_2Cl_2 and yields of **2a** (Fig. 1).

A 2.3 or 1.6 equiv of CH_2Cl_2 was also satisfactory, giving comparable yields of **2a** (Table 1, entries 2 and 3), while the amounts of CH_2Cl_2 lower than 0.8 equiv afforded a significantly lower yield (**2a**: <54%) and without CH_2Cl_2, no reaction take place. The best yield of **2a** was saturated in using more than 3.1 equiv of CH_2Cl_2. Productivity was decreased significantly in use of a smaller amount of Cs_2CO_3, such as 1 and 0.4 equiv, which gave **2a** in 51% and 25% yield, respectively. Decreasing the reaction temperature to 80 °C or 60 °C again led to a decline in the carbonate yields (35% and 5%, respectively). Attempts to use 200 mol % each of K_2CO_3, Na_2CO_3, CsOH, $CsHCO_3$ or CsCl in place of Cs_2CO_3 resulted in almost no reaction (0–2%), while $CsHCO_3$+Cs_2CO_3 (100 mol % each) and $CsHCO_3$+Cs_2CO_3+CsCl (100 mol % each) showed fair reactivity, both

Table 1
Substrate scope in carbonate synthesis[a]

Entry	Alcohol **1**	Time [h]	Product **2**	Yield[b] [%]
1	 X = H (**1a**)	12	 **2a** (X = H)	96
2				90[c]
3				91[d]
4	X=OCH_3 (**1b**)	24	**2b** (X=OCH_3)	80 (19)
5	X=CH_3 (**1c**)	24	**2c** (X=CH_3)	87 (12)
6	X=Cl (**1d**)	24	**2d** (X=Cl)	99
7	X=CF_3 (**1e**)	48	**2e** (X=CF_3)	47
8	 Y = O (**1f**)	24	 **2f** (Y = O)	99
9	Y=S (**1g**)	24	**2g** (Y=S)	93
10	 $R^1 = R^2 = R^3 = H$ (**1h**)	24	 **2h** ($R^1 = R^2 = R^3 = H$)	58
11	R^1=CH_3; R^2=R^3=H (**1i**)	24	**2i** (R^1=CH_3; R^2=R^3=H)	61 (16)
12	R^1=H; R^2=R^3=CH_3 (**1j**)	24	**2j** (R^1=H; R^2=R^3=CH_3)	30 (69)
13	R^1=R^3=H; R^2=Ph (**1k**)	24	**2k** (R^1=R^3=H; R^2=Ph)	90 (7)
14	 (*E*)-**1l**)	12	(*E*)-**2l** (R^1=R^3=H; R^2=–$(CH_2)_2CH$=$C(CH_3)_2$)	49 (49)
15	 (*Z*)-**1l**)	12	(*Z*)-**2l** (R^1=R^2=H; R^3=–$(CH_2)_2CH$=$C(CH_3)_2$)	40 (47)
16	 Z = H (**1m**)	24	 **2m** (Z = H)	65 (33)
17	Z=OCH_3 (**1n**)	24	**2n** (Z=OCH_3)	60 (20)
18	Z=CH_3 (**1o**)	24	**2o** (Z=CH_3)	74 (8)
19	$Me(CH_2)_7OH$ (**1p**)	24	**2p**  $Me(H_2C)_7O-C(=O)-O(CH_2)_7Me$	42 (24)

[a] Cs_2CO_3/**1**/CH_2Cl_2=200:100:310 (mol %). Conditions: 100 °C, 12–48 h in NMP.

[b] Of isolated, purified products, corresponding to the conversion of alcohol. The values in parentheses are the isolated yields of **3**.

[c] Cs_2CO_3/**1**/CH_2Cl_2=200:100:230 (mol %).

[d] Cs_2CO_3/**1**/CH_2Cl_2=200:100:160 (mol %).

giving a considerably lower yield of **2a** (22%) under otherwise identical conditions. After carrying out the screening of solvent effects, it was shown that aprotic polar solvents (DMF, DMA or DMSO) were consistently better suited for rate enhancement (**2a**: 88%, 90% and 79%, respectively: 100 °C, 12 h), compared with less polar solvents (toluene or THF), which led to a very low conversion (**2a**: <2%). Without NMP, the reaction did not take place (**2a**: <1%). Scant reactivity (**2a**: <2%) was also obtained in the absence of CO_2, demonstrating that Cs_2CO_3 cannot be an alternative CO_2 source.

Given the optimal conditions accommodating 96% yield of **2a**, (Cs_2CO_3 (200 mol %), CH_2Cl_2 (310 mol %) in NMP at 100 °C) other representative alcohols **1a**–**p** were applied in this carbonate synthesis and the results are listed in Table 1. This synthetic protocol showed substrate generality with respect to benzylic, allylic, phenylethyl, and saturated alcohols **1a**–**p** (entries 1–19), but in some cases, was contaminated with different carbonates **3** (Fig. 2). In a series of benzylic alcohols **1a**–**g**, substrates **1f** and **1g** with heterocyclic ring systems were well suited for this procedure (entries 8 and 9). The reaction proceeded as well no matter how electron-withdrawing or -donating groups were attached to the aromatic ring; however, substitution by the nitro group at the *para*-position (X=NO_2) almost prohibited the reaction from proceeding. The more electron-donating the X group, the more increased the formation of **3** (entries 4 and 5).

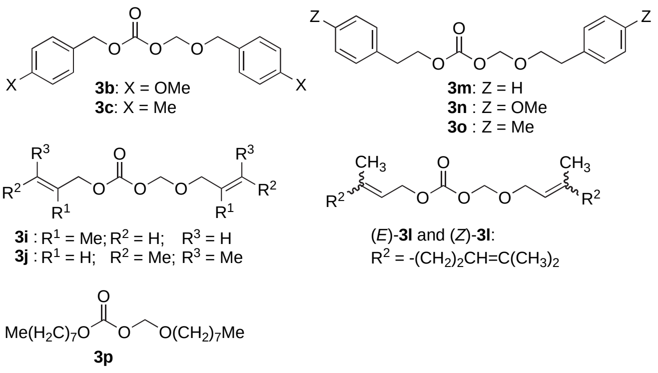
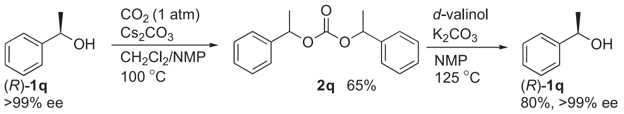


Fig. 2. A series of by-products **3**.

In a series of allylic alcohols **1h**–**l**, the allylic olefins vicinal to the OH group, were tolerated and remained essentially unreacted (entries 10–15). The *E* and *Z* geometry of these olefins in **1k** and **1l** was well preserved to give retention of the configuration.

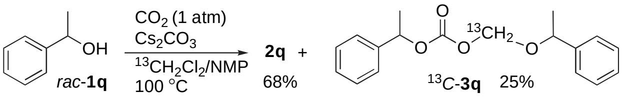
The substitution by a phenyl group at the β-position of hydroxy groups (**1m**–**o**) (Table 1, entries 16–18) did not prevent from the formation of the carbonates except with relatively lower yields of **2m**–**o**, accompanied by considerable amounts of **3m**–**o**. A great difficulty in carbonate formation was observed using phenol, but instead the formation of the acetal ($PhOCH_2OPh$)[8] predominated. This alternative pathway could be interpreted by direct reaction of 2 equiv of the phenoxide (CsOPh) with 1 equiv of CH_2Cl_2 that prevailed over the incorporation of CO_2. CsF is also known to promote the O-alkylation of phenol with CH_2Cl_2.[9] In contrast, diphenyl carbonate[1e,f] was synthesized in low yields (~20%) by treatment of a high pressure of CO_2 (40 atm) with phenol, CCl_4, and K_2CO_3 in the presence of a stoichiometric amount of $ZnCl_2$ at 120 °C.[10]

In order to gain further insights into the rather complicated multi-steps that should be involved during the carbonate formation from CO_2, we carried out a set of model experiments separately. Did alcohols act as nucleophiles or electrophiles? To verify this point, optically pure (*R*)-α-phenylethyl alcohol **1q** (>99% ee) was used under the optimized conditions, which gave a mixture of **2q** and **3q** in >90% total yields (Scheme 2; **3q** was omitted). Subsequently isolated **2q** was degradated by a β-aminoalcohol[11] into the parent alcohol **1q**, which was recovered in 80% yield with complete preservation of the *R* configuration, ascertained by chiral HPLC analysis.[12] This suggests that alcohol should merely react as nucleophile, although we could not fully rule out the mechanistic scenario, in which alcohol worked as electrophile undergoing double inversion or retention pathway.



Scheme 2. Carbonate formation and subsequent degradation. Cs_2CO_3/(*R*)-**1q**/CH_2Cl_2=200:100:310 (mol %).

When CH_2Cl_2 was replaced by $^{13}CH_2Cl_2$, **3q** was obtained in a comparable yield with $^{13}CH_2$ fully incorporated into the structure of **3q** (Scheme 3).



Scheme 3. Incorporation of ^{13}C into carbonate **3q**. Cs_2CO_3/*rac*-**1q**/$^{13}CH_2Cl_2$=200:100:310 (mol %).

We therefore envisioned that either one of $\mathbf{I_A}$ and $\mathbf{I_B}$ (Fig. 3) would be formed as *meta*-stable intermediates upon reaction of CH_2Cl_2 with alkoxide (CsOR) or carboxylate (CsO(C=O)OR, derived from Cs_2CO_3+ROH+CO_2), respectively, so that chloromethyl ether **4** was used to see whether this could afford carbonate **2a** in a reasonable yield (Scheme 4). Although the reaction fairly brought about **2a**, its yield was significantly lower, suggesting that more reactive intermediate $\mathbf{I_B}$ is highly likely to be responsible for promoting a major pathway. Unfortunately, intermediate $\mathbf{I_B}$ was too reactive to be detected or isolated. In addition, formaldehyde was unable to be trapped by chemical reagents during any attempts exerted so far. Nevertheless, we wish to emphasize that the present protocol using CO_2, alcohol and CH_2Cl_2 is attractive from several notable viewpoints: e.g., productivity, substrate generality, functional group tolerance, preservation of chirality, straightforwardness and practicality at least in lab-scale experiments.

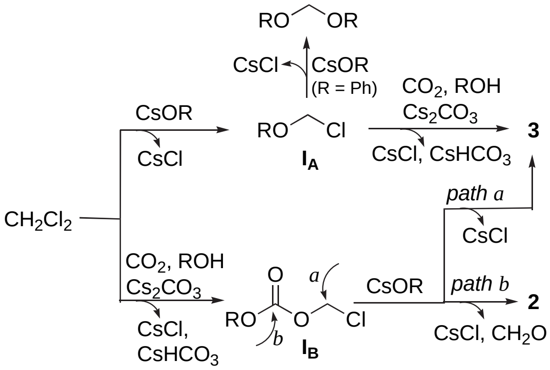
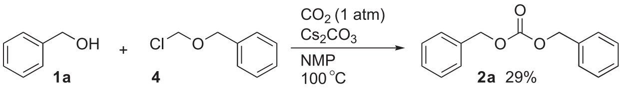


Fig. 3. Possible reaction intermediates and pathways.



Scheme 4. Reaction of **1a** with chloromethyl ether **4** under 1 atm pressure of CO_2. Cs_2CO_3/**1a**/**4**=200:100:100 (mol %).

Bearing the above working hypothesis in mind, the reaction conditions were further optimized to obtain **2** as a sole carbonate. During such attempts, it was revealed that addition of water or rather acidic environments ($pH=5\pm0.02$) adjusted by an aqueous buffer (citric acid/NaOH) at 125 °C, facilitated the decomposition of **2** and **3** into CO_2 and **1**. Finally, exactly the same reaction conditions (100 °C) described in Table 1 for each substrate (first step) were followed by addition of Na_2SO_4 (50 mol % with respect to the molar amount of starting alcohol) and subsequently raising the temperature to 125 °C under argon (second step) uniformly increased the yield of **2** (Table 2). As a few exceptions, no improvement was observed with alcohols **1b** and **1o** having a more electron-donating group (entries 1 and 7). In all attempts, undesirable carbonate **3** was converted not only into respective **2**, but also into CO_2 and the parent alcohol **1** even after such an effort to re-optimize the conditions. In contrast, when the reaction of (*E*)-**1l** with CO_2 was started at 125 °C (as the first step), which was kept through the end (12 h), the yield of (*E*)-**2l** (57%) was better than that in Table 1 (entry 12) but worse than in Table 2 (entry 4); formation of (*E*)-**3l** was not observed in this case.

Table 2
Improved one-pot preparation of carbonate **2**[a]

Entry	Alcohol **1**	Yield[b] [%] of **2** (**3**)	Product **2**[c]	Yield[d] of **2** [%]	Recovery[e] of **1** [%]
1	**1b**	80 (19)	**2b**	66	33
2	**1i**	61 (16)	**2i**	63	36
3	**1j**	30 (69)	**2j**	74	25
4	(*E*)-**1l**	49 (49)	(*E*)-**2l**	79	19
5	(*Z*)-**1l**	40 (47)	(*Z*)-**2l**	66	33
6	**1m**	65 (33)	**2m**	67	32
7	**1n**	60 (20)	**2n**	25	74
8	**1o**	74 (8)	**2o**	77	22
9	**1p**	42 (24)	**2p**	60	39

[a] Cs_2CO_3/**1**/CH_2Cl_2=200:100:310 (mol %). Conditions: first step: 100 °C, 12–24 h in NMP as in Table 1, then; second step: the mixture being further reacted for 6 h at 125 °C under Ar after adding Na_2SO_4 (50 mol %).

[b] Of the first step, the same values as in Table 1.

[c] Of the second step.

[d] Of isolated, purified products obtained after the total (first and second) steps, based on the conversion % of **1**.

[e] Determined by ^1H NMR using 1,1,2,2-tetrachloroethane as an internal standard.

3. Conclusions

In summary, we introduced a new one-pot procedure for the preparation of carbonates from alcohols in a straightforward fashion under 1 atm pressure of CO_2 using Cs_2CO_3 and CH_2Cl_2. A set of multi-steps involving $\mathbf{I_B}$, and another set of distinct steps involving $\mathbf{I_A}$, might be involved in the overall process, both affording carbonates. The reaction was demonstrated to preserve *E* or *Z* geometry of the olefin of allylic alcohols as well as a stereogenic center of alcohol. By contrast, in use of alkyl halides (R′X, Scheme 1) previously reported,[5] these aspects were not necessarily guaranteed. To be emphasized is that separately preparing RX from the corresponding ROH is not needed. The more detailed reaction mechanism, as well as a possibility of replacement of the CH_2Cl_2 by other reagents that mimic a potential function of CH_2Cl_2, are to be addressed in a next improvement. In addition, an attempt to expand the substrate scope to the autoclave synthesis of more important classes of low molecular weight carbonates, such as dimethyl carbonate (DMC)[7] is now underway in our laboratory.

4. Experimental

4.1. General

All reactions were carried out under argon atmosphere and in dried up glassware by means of standard Schlenk techniques unless otherwise noted. All reagents were purchased from Aldrich, Wako, TCI, Kanto and used without further purification except for benzyl alcohol, which is simply distilled under reduced pressure. Column chromatography was performed using silica gel (silica gel 60, 230–400 mesh, Merck). TLC was performed using pre-coated silica gel plate (silica gel 60 F_{254}, Merck) and products were observed under UV light or with either phosphomolybdic acid reagent. ^1H NMR and ^{13}C NMR spectra were recorded on a JEOL ECA-600 spectrometer, operating in $CDCl_3$ at 600 MHz. Chemical shifts and coupling constants are presented in parts per million δ relative to tetramethylsilane and hertz, respectively. High resolution mass spectra was obtained on JEOL JMS-700. Chiral high performance liquid chromatography analysis was conducted using Shimadzu LC-10AD coupled with photo diode array-detector SPD-M20A and chrial column of CHIRALCEL OD-H (Daicel chemical industries, LTD.). **2a**, **2c**, **2d**, **2f**, **2h**, **2i**, **2k**, **2m**, **2n**, **2o**, and **2q** are all known compounds (For references, see Electronic Supplementary data). The available spectral and analytical data for all new compounds are shown below.

4.2. Typical procedure: the synthesis of carbonate 2a (Table 1)

To an anhydrous 1-methyl-2-pyrrolidinone (NMP) (1 mL) solution of benzyl alcohol (**1a**) (217 mg, 2 mmol) were added cesium carbonate (1303 mg, 4 mmol) and dichloromethane (400 μL, 6.2 mmol) under argon atmosphere at room temperature. A 1 L balloon charged with CO_2 gas was equipped to the reaction tube, and the mixture was subjected to the freeze (−196 °C)–thaw (25 °C) cycle (×3) to replace the argon atmosphere by CO_2 (filled in 1 L balloon). The mixture was stirred for 12 h at 100 °C in a closed system. The reaction mixture was quenched with saturated aq NH_4Cl (10 mL), and then the mixture was extracted with EtOAc (10 mL×3). The organic layer was dried over Na_2SO_4 and filtered. Evaporation of the filtrate solvents followed by flash column chromatography on silica gel (eluent: hexane/EtOAc, 10:1) afforded **2a** (232.5 mg, 0.96 mmol, 96%) as a colorless oil.

4.3. Typical procedure: the improved synthesis of carbonate (*E*)-2l (Table 2)

To an anhydrous 1-methyl-2-pyrrolidinone (NMP) (1 mL) solution of geraniol ((*E*)-**1l**) (351 μL, 2 mmol) were added cesium carbonate (1303 mg, 4 mmol) and dichloromethane (400 μL, 6.2 mmol) under argon atmosphere at room temperature. A 1 L balloon charged with CO_2 gas was equipped to the reaction tube, and the mixture was subjected to the freeze (−196 °C)–thaw (25 °C) cycle (×3) to replace the argon atmosphere by CO_2 (filled in 1 L balloon). The mixture was stirred at 100 °C in this closed system. After stirring for 12 h, The CO_2 gas in balloon was replaced by argon gas, followed by the addition of anhydrous Na_2SO_4 (142 mg, 1 mmol) to the reaction mixture. The resulting mixture was stirred at 125 °C for 6 h. The reaction was quenched with saturated aq NH_4Cl (10 mL), and then the mixture was extracted with EtOAc (10 mL×3). The organic layer was dried over Na_2SO_4 and filtered. Evaporation of the filtrate solvents followed by flash column chromatography on silica gel (eluent: hexane/EtOAc, 10:1) afforded (*E*)-**2l** (264 mg, 0.79 mmol, 79%) as a colorless oil.

*4.3.1. Bis((4-methoxyphenyl)methyl) carbonate (**2b**).* R_f (17% EtOAc/hexane) 0.37; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.29 (d, J=8.8 Hz, 2H), 6.86 (d, J=8.8 Hz, 2 H), 5.07 (s, 2H), 3.76 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.7, 155.0, 130.1, 127.3, 113.8, 69.3, 55.1. HRMS (FAB) calcd for $C_{17}H_{18}O_5$ ($M+Na^+$): 325.1046. Found m/z=325.1048.

*4.3.2. 4-Methoxybenzyl (4-methoxybenzyloxy)methyl carbonate (**3b**).* R_f (10% EtOAc/hexane) 0.31; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.34 (d, J=8.3 Hz, 2H), 7.25 (d, J=8.6 Hz, 2 H), 6.90 (d, J=8.5 Hz, 2H), 6.87 (d, J=8.5 Hz, 2H), 5.32 (s, 2H), 5.12 (s, 2H), 4.64 (s, 2H), 3.81 (s, 3H), 3.80 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.9, 159.5, 154.5, 130.4, 129.7, 128.6, 127.1, 114.0, 114.0, 90.9, 71.3, 69.6, 55.3, 55.2. HRMS (FAB) calcd for $C_{18}H_{20}O_4$ ($M+Na^+$): 355.1158. Found *m*/*z*=355.1148.

*4.3.3. 4-Methylbenzyl (4-methylbenzyloxy)methyl carbonate (**3c**).* R_f (10% EtOAc/hexane) 0.29; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.31–7.13 (m, *J*=8H), 5.34 (s, 2 H), 5.15 (s, 2H), 4.67 (s, 2H), 2.36 (s, 3H), 2.34 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.5, 138.5, 137.8, 133.5, 132.0, 129.3, 129.2, 128.6, 128.1, 91.1, 71.5, 69.7, 21.2, 21.2. HRMS (FAB) calcd for $C_{18}H_{20}O_4$ ($M+Na^+$): 323.1259. Found *m*/*z*=323.1256.

*4.3.4. Bis(4-(trifluoromethyl)benzyl) carbonate (**2e**).* R_f (33% EtOAc/hexane) 0.63; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.63 (d, *J*=7.9 Hz, 4H), 7.50 (d, *J*=7.9 Hz, 4 H), 5.23 (s, 4H); ^{13}C NMR ($CDCl_3$, 400 MHz) δ 154.8, 139.0, 130.9, 130.6, 128.3, 127.8, 125.7, 125.7, 125.6, 125.6, 125.4, 125.3, 122.6, 68.9. HRMS (FAB) calcd for $C_{17}H_{12}F_6O_3$ ($M+Na^+$): 401.0588. Found *m*/*z*=401.0579.

*4.3.5. Bis(thiophen-2-ylmethyl) carbonate (**2g**).* R_f (10% EtOAc/hexane) 0.61; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.35 (dd, *J*=5.3, 1.0 Hz, 2H), 7.15 (d, *J*=3.3 Hz, 2H), 7.00 (dd, *J*=3.6, Hz, 2H), 5.33 (s, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.3, 137.4, 129.5, 127.9, 127.5, 64.4. HRMS (FAB) calcd for $C_{11}H_{20}O_3S_2$ ($M+Na^+$): 276.9969. Found *m*/*z*=276.9965.

*4.3.6. 2-Methylallyl (2-methylallyloxy)methyl carbonate (**3i**).* R_f (17% EtOAc/hexane) 0.60; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 5.32 (s, 2H), 5.02 (d, *J*=8.6 Hz, 2H), 4.95 (d, *J*=9.6 Hz, 2H), 4.58 (s, 2H), 4.11 (s, 2H), 1.79 (s, 3H), 1.75 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.5, 140.8, 139.2, 113.7, 113.3, 91.3, 73.8, 71.2, 19.4, 19.3. Desirable HRMS (FAB) peak sets data were unable to be obtained due to strong instability of **3i** under a range of HRMS measurement conditions.

*4.3.7. Bis(3-methylbut-2-enyl) carbonate (**2j**).* R_f (17% EtOAc/hexane) 0.77; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.37 (t, *J*=7.3 Hz, 2H), 4.64 (d, *J*=7.1 Hz, 4H), 1.76 (s, 6H), 1.72 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.4, 139.8, 118.2, 64.5, 25.8, 18.1. HRMS (FAB) calcd for $C_{11}H_{18}O_3$ ($M+Na^+$): 221.1154. Found *m*/*z*=221.1158.

*4.3.8. 3-Methylbut-2-enyl (3-methylbut-2-enyloxy)methyl carbonate (**3j**).* R_f (17% EtOAc/hexane) 0.66; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 5.42–5.26 (m, 2H), 5.29 (s, 2H), 4.66 (d, *J*=7.3 Hz, 2H), 4.19 (d, *J*=6.9 Hz, 2H), 1.77 (s, 3H), 1.76 (s, 3H), 1.73 (s, 3H), 1.68 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.7, 140.2, 138.8, 119.6, 117.9, 91.0, 66.2, 64.7, 25.8, 18.1, 18.0. HRMS (FAB) calcd for $C_{12}H_{20}O_4$ ($M+Na^+$): 251.1259. Found *m*/*z*=251.1251.

*4.3.9. Cinnamyl cinnamyloxymethyl carbonate (**3k**).* R_f (17% EtOAc/hexane) 0.11; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.41–7.22 (m, 10H), 6.67 (t, *J*=15.8 Hz, 2H), 6.35–6.21 (m, 2H), 5.39 (s, 2H), 4.81 (dd, *J*=6.6, 1.3 Hz, 2H), 4.38 (dd, *J*=6.3, 1.3, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.5, 136.3, 136.0, 135.1, 133.6, 128.6, 128.6, 128.2, 127.9, 126.7, 126.6, 124.3, 122.1, 91.2, 70.6, 68.5. HRMS (FAB) calcd for $C_{20}H_{20}O_4$ ($M+Na^+$): 347.1259. Found *m*/*z*=347.1259.

*4.3.10. Bis((E)-3,7-dimethylocta-2,6-dienyl) carbonate ((E)-**2l**).* R_f (17% EtOAc/hexane) 0.68; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.38 (t, *J*=6.4 Hz, 2H), 5.08 (t, *J*=5.4 Hz, 2 H), 4.65 (d, *J*=7.1 Hz, 4H), 2.10–2.05 (m, 8H), 1.71 (s, 6H), 1.68 (s, 6H), 1.60 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.4, 143.0, 131.9, 123.7, 117.8, 64.6, 39.5, 26.2, 25.7, 17.7, 16.5. HRMS (FAB) calcd for $C_{21}H_{34}O_3$ ($M+Na^+$): 357.2406. Found *m*/*z*=357.2402.

*4.3.11. (E)-3,7-Dimethylocta-2,6-dienyl ((E)-3,7-dimethylocta-2,6-dienyloxy)methyl carbonate ((E)-**3l**).* R_f (17% EtOAc/hexane) 0.59; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.39 (t, *J*=6.4 Hz, 1H), 5.33 (t, *J*=6.1 Hz, 1H), 5.29 (s, 2H), 5.09–5.06 (m, 2H), 4.68 (d, *J*=7.3 Hz, 2H), 4.22 (d, *J*=6.8 Hz, 2H), 2.11–2.05 (m, 8H), 1.72 (s, 3H), 1.68 (s, 9H), 1.60 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.6, 143.3, 142.0, 131.8, 131.7, 123.8, 123.6, 119.2, 117.5, 90.9, 66.1, 64.8, 39.5, 39.5, 26.2, 26.2, 25.6, 17.6, 16.5, 16.4. HRMS (FAB) calcd for $C_{22}H_{36}O_4$ ($M+Na^+$): 387.2511. Found *m*/*z*=387.2493.

*4.3.12. Bis((Z)-3,7-dimethylocta-2,6-dienyl) carbonate ((Z)-**2l**).* R_f (17% EtOAc/hexane) 0.69; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 5.38 (t, *J*=6.9 Hz, 2H), 5.09 (t, *J*=5.6 Hz, 2H), 4.61 (d, *J*=7.3 Hz, 4H), 2.16–1.99 (m, 8H), 1.76 (s, 6H), 1.68 (s, 6H), 1.60 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.3, 143.0, 132.2, 123.5, 118.8, 64.2, 32.1, 26.6, 25.6, 23.5, 17.6. HRMS (FAB) calcd for $C_{21}H_{34}O_3$ ($M+Na^+$): 357.2406. Found *m*/*z*=357.2395.

*4.3.13. (Z)-3,7-Dimethylocta-2,6-dienyl ((Z)-3,7-dimethylocta-2,6-dienyloxy)methyl carbonate ((Z)-**3l**).* R_f (17% EtOAc/hexane) 0.62; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 5.47–5.30 (m, 2H), 5.28 (s, 2H), 5.10–5.09 (m, 2H), 4.64 (d, *J*=7.3 Hz, 2H), 4.10–4.05 (m, 2H), 2.09–2.08 (m, 8H), 1.75 (s, 3H), 1.69 (s, 3H), 1.67 (s, 3H), 1.60 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.6, 143.5, 140.0, 132.5, 130.9, 128.8, 124.4, 123.6, 121.2, 120.2, 66.0, 63.6, 32.2, 31.9, 26.6, 26.5, 25.7, 25.6, 23.5, 23.4, 17.6. HRMS (FAB) calcd for $C_{22}H_{36}O_4$ ($M+Na^+$): 387.2511. Found *m*/*z*=387.2493.

*4.3.14. Phenethoxymethyl phenethyl carbonate (**3m**).* R_f (17% EtOAc/hexane) 0.55; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.19–7.32 (m, 10H), 5.24 (s, 2H), 4.34 (t, *J*=7.2 Hz, 2H), 3.86 (t, *J*=6.9 Hz, 2H), 2.97 (t, *J*=6.9 Hz, 2H), 2.89 (t, *J*=7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.3, 139.0, 137.9, 129.7, 129.7, 129.3, 129.2, 127.5, 127.1, 93.0, 72.1, 69.2, 36.9, 35.8. HRMS (FAB) calcd for $C_{18}H_{20}O_4$ ($M+Na^+$): 323.1259. Found *m*/*z*=323.1256.

*4.3.15. Bis(4-methoxyphenethyl) carbonate (**2n**).* R_f (10% EtOAc/hexane) 0.49; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.15–7.10 (m, 4H), 6.87–6.81 (m, 4H), 4.28 (t, *J*=7.2 Hz, 4H), 3.78 (s, 6H), 1.26 (t, *J*=7.2 Hz, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.4, 155.1, 129.9, 129.2, 114.0, 113.8, 68.5, 55.2, 34.3. HRMS (FAB) calcd for $C_{19}H_{22}O_5$ ($M+Na^+$): 353.1365. Found *m*/*z*=353.1356.

*4.3.16. (4-Methoxyphenethoxy)methyl 4-methoxyphenethyl carbonate (**3n**).* R_f (10% EtOAc/hexane) 0.29; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.16–7.12 (m, 2H), 7.12–7.09 (m, 2H), 6.86–6.83 (m, 2H), 6.82–6.80 (m, 2H), 5.25 (s, 2H), 4.30 (t, *J*=7.2 Hz, 2H), 3.83 (t, *J*=6.9 Hz, 2H), 3.76 (s, 6H), 2.91 (t, *J*=7.2 Hz, 2H), 2.83, (t, *J*=6.9 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.3, 158.1, 154.4, 130.1, 129.8, 129.8, 129.0, 113.9, 113.8, 92.2, 71.5, 68.5, 55.1, 35.1, 34.1. Desirable HRMS (FAB) peak sets data were unable to be obtained due to strong instability of **3n** under a range of HRMS measurement conditions.

*4.3.17. Bis(4-methylphenethyl) carbonate (**2o**).* R_f (17% EtOAc/hexane) 0.63; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.10 (s, 10H), 4.28 (t, *J*=7.2 Hz, 4H), 2.92 (t, *J*=7.2 Hz, 4H), 2.32 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.1, 136.2, 135.2, 134.3, 134.1, 129.2, 128.8, 68.4, 34.7, 21.0. HRMS (FAB) calcd for $C_{19}H_{22}O_3$ ($M+Na^+$): 321.1467. Found *m*/*z*=321.1472.

*4.3.18. (4-Methylphenethoxy)methyl 4-methylphenethyl carbonate (**3o**).* R_f (17% EtOAc/hexane) 0.54; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 5.24 (s, 2H), 4.32 (t, *J*=7.2 Hz, 2H), 3.85 (t, *J*=6.9 Hz, 2H), 2.9 (t, *J*=7.3 Hz, 2H), 2.86 (t, *J*=6.9 Hz, 2H), 2.31 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.5, 136.2, 135.8, 135.0, 134.0, 129.2, 129.1, 128.8, 128.7, 92.2, 74.1, 71.4, 68.5, 35.6, 34.6. HRMS (FAB) calcd for $C_{20}H_{24}O_4$ ($M+Na^+$): 351.1572. Found *m*/*z*=351.1561.

*4.3.19. Dioctyl carbonate (**2p**).* R_f (10% EtOAc/hexane) 0.75; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 4.12 (t, *J*=6.6 Hz, 4H), 1.66 (septet, *J*=6.6 Hz, 4H), 1.42–1.22 (m, 20H), 0.87 (t, *J*=6.3 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.5, 68.1, 31.8, 29.20, 29.16, 28.7, 25.7, 22.6, 14.1. HRMS (FAB) calcd for $C_{17}H_{34}O_3$ ($M+Na^+$): 309.2406. Found *m*/*z*=309.2407.

*4.3.20. Octyl octyloxymethyl carbonate (**3p**).* R_f (10% EtOAc/hexane) 0.65; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 5.28 (s, 2H), 4.16 (t, *J*=6.6 Hz, 2H), 3.66 (t, *J*=6.6 Hz, 2H), 1.75–1.53 (m, 4H), 1.46–1.17 (m, 20H), 0.88 (t,

J=6.3 Hz, 6H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 154.7, 92.3, 70.8, 68.3, 31.80, 31.77, 29.5, 29.3, 29.22, 29.18, 29.16, 28.6, 25.9, 25.7, 22.65, 22.63, 14.1 (2C). HRMS (FAB) calcd for $C_{18}H_{36}O_4$ (M+Na$^+$): 339.2511. Found m/z=339.2522.

*4.3.21. (1-Phenylethoxy)methyl 1-phenylethyl carbonate (**3q**).* R_f (10% EtOAc/hexane) 0.16; ^{1}H NMR (CDCl$_3$, 270 MHz) δ 7.37–7.25 (m, 10H), 5.74–5.70 (m, 1H), 5.38 (dd, J=6.3, 11.2 Hz, 1H), 5.01 (dd, J=6.3, 15.5 Hz, 1H), 4.81–4.78 (m, 1H), 1.61–1.44 (m, 6H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 153.9, 142.3, 140.9, 128.5, 128.5, 128.1, 127.8, 126.3, 126.0, 90.0, 76.7, 76.5, 23.7, 22.2. When $^{13}CH_2Cl_2$ was reacted with **1q** and CO$_2$, the ^{13}C NMR signal of **3q**-d_2 at 90.0 ppm showed significantly strong intensity. HRMS (FAB) calcd for $C_{18}H_{20}O_4$ (M+Na$^+$): 323.1259. Found m/z=323.1251. Data of chiral HPLC analysis of 1-phenylethenol (**1q**): chiral column: OD-H; eluent: hexane:*i*-PrOH=20:1; retention time: t_R=11.8 min ((*R*)-isomer); t_R=13.1 min ((*S*)-isomer) at a flow rate of 1.0 mL/min.

Acknowledgements

This work was supported by a Grant-in-Aid for Basic Research (B) and Scientific Research on Priority Areas ‘Advanced Molecular Transformations of Carbon Resource’ from the Ministry of Education, Culture, Science, Sports and Technology of Japan, and by funds from Asahi Glass, Asahi Kasei Chemicals, Daiso, Kuraray, Mitsubishi Chemical, Mitsui Chemicals, Nissan Chemical Ind., and Sumitomo Chemical. SS also greatly appreciates Prof. R. Noyori (Nagoya University & RIKEN) for his valuable suggestions and fruitful discussions.

Supplementary data

Supplementary data including ^{1}H and ^{13}C NMR spectra of all new compounds for this article is available. Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2010.10.051. These data include MOL files and InChIKeys of the most important compounds described in this article.

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12. See the Experimental section.