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One-Pot Formation of Carbonates from the Reactions of Carbonyl Compounds with Samarium Diiodide and Methyl Chloroformate

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Treatment of carbonyl compounds with SmI_2 and methyl chloroformate in the presence of molecular sieves provides the cyclic carbonates or biscarbonates of pinacols. This one-pot reaction proceeds rapidly even with aliphatic ketones. The stereochemistry obtained by this procedure is different from that of conventional pinacolic couplings.

INTRODUCTION

Reductive couplings of carbonyl compounds[1] to form vicinal diols are generally carried out with metals (particularly Mg)[2] or low-valent metal ions such as Ce(II),[3] Sm(II),[4] V(II)[5] and Ti(III)[6] ions. Pinacols are also obtained from electrolytic reduction of carbonyl compounds.[7] Intramolecular pinacolic couplings[1] of dicarbonyl compounds using metals, low-valent ions, or tributyltin hydride[8] have been reported. Aldehydes are converted to bis-silylated pinacols using zinc metal in the presence of Me_3SiCl.[9]

One-electron reductions of carbonyls with SmI_2 to produce samarium ketyl radical anions have generated a lot of attention.[10] On treating with SmI_2 in aprotic solvents, aromatic aldehydes, or aromatic ketones couple readily to give pinacols.[4a] Electrolyses of aromatic aldehydes or aromatic ketones in DMF or NMP by catalysis of $SmCl_3$ also give pinacols.[7b] However, SmI_2 is a slow reagent for the intermolecular couplings of aliphatic ketones. For example,[4a] twenty four hours is needed for completion of the pinacolic coupling of 2-heptanone on treating with SmI_2. Samarium dibromide is found to be a more efficient reagent for the pinacolic couplings of aliphatic ketones,[11] although the preparative procedure of $SmBr_2$ is tedious.

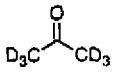
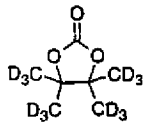
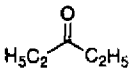
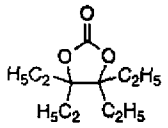
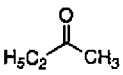
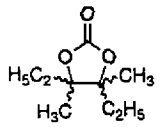
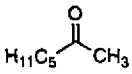
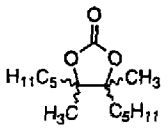
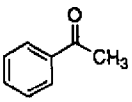
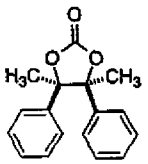
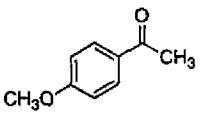
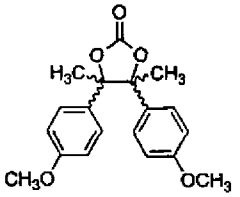
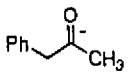
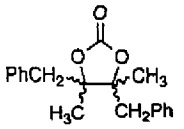
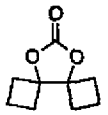
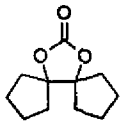
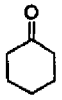
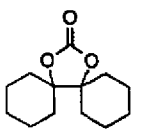
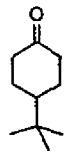
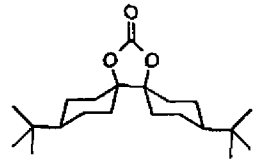
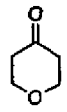
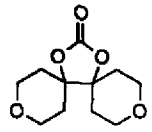
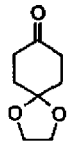
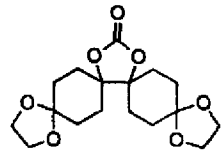
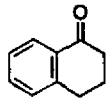
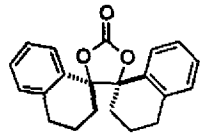
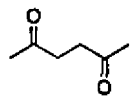
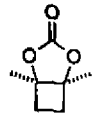
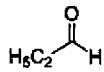
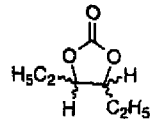
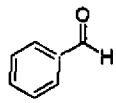
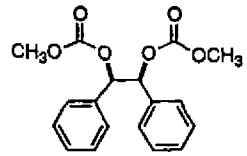
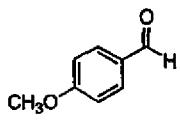
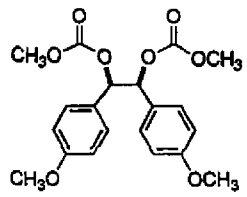
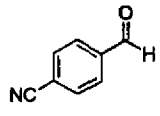
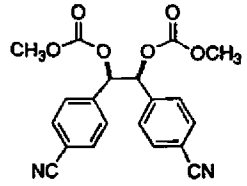
We report herein that various carbonyl compounds react with SmI_2 and $ClCO_2CH_3$ in the presence of molecular sieves to give the carbonates of pinacols. This one-pot method is expedient, converting even aliphatic ketones to cyclic carbonates within twenty minutes.

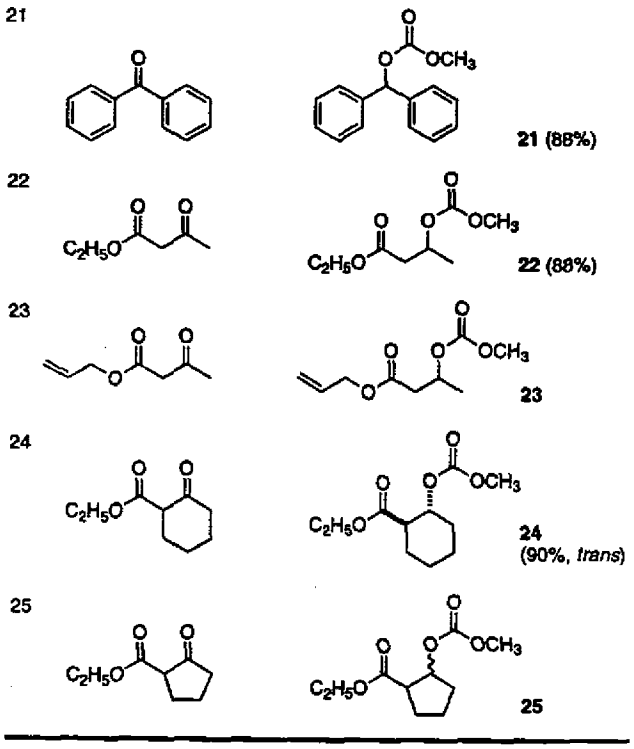
RESULTS AND DISCUSSION

A dark blue THF solution of SmI_2 (2 equiv) was prepared from samarium and 1,2-diiodoethane in the presence of molecular sieves. Methyl chloroformate (1 equiv) was added, followed by an appropriate carbonyl compound (1 equiv). After 10-20 minutes, the mixture was worked up to give the desired carbonates (Table 1). The reactions of ketones (entries 1-16) afforded cyclic carbonates **1-16**. The yields were roughly the same using 1 or 4 equiv of SmI_2. The use of molecular sieves[12] appeared to accelerate the reaction rates. For example, 2-heptanone was treated with SmI_2 and $ClCO_2CH_3$ in the presence of molecular sieves for 20 min to give the carbonate **5a** (83%). The pinacolic coupling of 2-heptanone was completed in 4 h using SmI_2 and molecular sieves, giving 6,7-dimethyl-6,7-dodecanediol **5b** in 80% yield, whereas the reaction requires 24 h in the absence of molecular sieves.[4a]

Pinacolic coupling of an unsymmetric ketone led to a product having two newly formed stereogenic centers. Carbonates **4**, **5a** and **8**, derived from the coupling reactions of unsymmetric ketones (entries 4, 5 and 8), existed as mixtures of diastereomeric isomers (1:1). The coupling reaction of 4-*tert*-butylcyclohexanone with $SmI_2/ClCO_2CH_3$ gave the cyclic carbonate **12** as a mixture of two isomers (87:13), out of three possible products.[13] The major isomer of **12** (*cis* configuration) was shown by an X-ray analysis to have two axial C-O bonds. The ^{13}C NMR spectrum of the major isomer showed seven signals, whereas that of the minor isomer (*trans* configuration) was complicated, indicating its unsymmetric nature with axial and equatorial C-O bonds. On treating with $SmI_2/ClCO_2CH_3$, 2,5-hexanedione cyclized to give a *cis* bicyclic carbonate **16**.[6b] The reaction of acetophenone with $SmI_2/ClCO_2CH_3$ occurred stereoselectively to form a *cis* carbonate **6a**, whereas the reaction of α-tetralone gave exclusively a *trans* carbonate **15**. The structures of **6a** and **15** were unambiguously determined by

Table 1. The Reaction of Carbonyl Compounds with SmI_2 (2 equiv)/$ClCO_2Me$ (1 equiv) in THF at Room Temperature

Entry	Substrate	Product (yield, ratio of isomers)
1		 1 (86%)
2		 2 (80%)
3		 3 (70%)
4		 4 (78%,1:1)
5		 5a (83%,1:1)
6		 6a (68%, *cis*)
7		 7 (83%, 3:1)
8		 8 (75%,1:1)
9		 9 (85%)
10		 10 (83%)
11		 11 (80%)
12		 12 (71%, 87:13)
13		 13 (67%)
14		 14 (80%)
15		 15 (53%, *trans*)
16		 16 (80%, *cis*)
17		 17 (75%,1:1)
18		 18a (82%, *meso*)
19		 19 (82%, *meso*)
20		 20 (74%, *meso*)



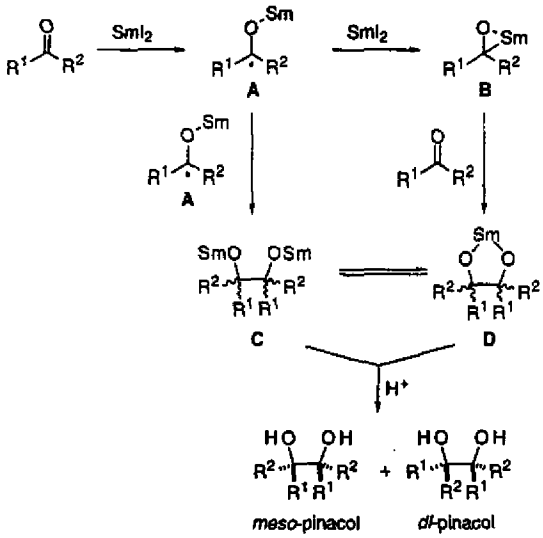
X-ray diffraction methods. The reaction of 4-methoxyacetophenone gave the carbonate **7** as a mixture of two isomers (3:1).

The reaction of propionaldehyde with SmI_2/$ClCO_2CH_3$ (entry 17) gave an isomeric mixture (1:1) of the cyclic carbonate **17**, whereas the reactions of benzaldehydes produced the biscarbonates **18a-20** in a stereospecific manner. Biscarbonate **18a** was saponified to give a product identical to *meso*-hydrobenzoin, showing the α′-H resonance at δ 4.80, whereas the corresponding protons of *dl*-hydrobenzoin occurred at a higher field, δ 4.67. A similar phenomenon was observed in the related cyclic carbonates **18c** and **18d** (see below). The α′-H of *trans* isomer **18d**, due to the shielding effect of the adjacent phenyl groups, exhibited at a higher field, δ 5.42, than the *cis*-isomer **18c** at δ 5.71. The biscarbonates **19** and **20**, obtained from the coupling reactions of 4-substituted benzaldehydes, were tentatively assigned to have *meso* configurations by analogy to that of **18a** as two compounds displayed their α′-protons at δ 5.81 and 5.90.

On treating with $SmI_2/ClCO_2CH_3$, benzophenone and 3-oxo esters were reduced and carbonated subsequently to give carbonates **21-25** (entries 21-25). Carbonates **23** and **25** were unstable on silica gel column and underwent decarbonation to give allyl crotonate and ethyl 1-cyclopentenecarboxylate, respectively. Carbonate **24** could be purified by chromatography on a silica gel column. The ^1H NMR spectrum of **24** indicated its *trans* configuration as the H-1 and H-2 exhibited a large coupling constant 10 Hz. Since H-1 and the carbonate group had a *cis* relationship, elimination of CH_3CO_2H *via* an E2 mechanism did not occur.

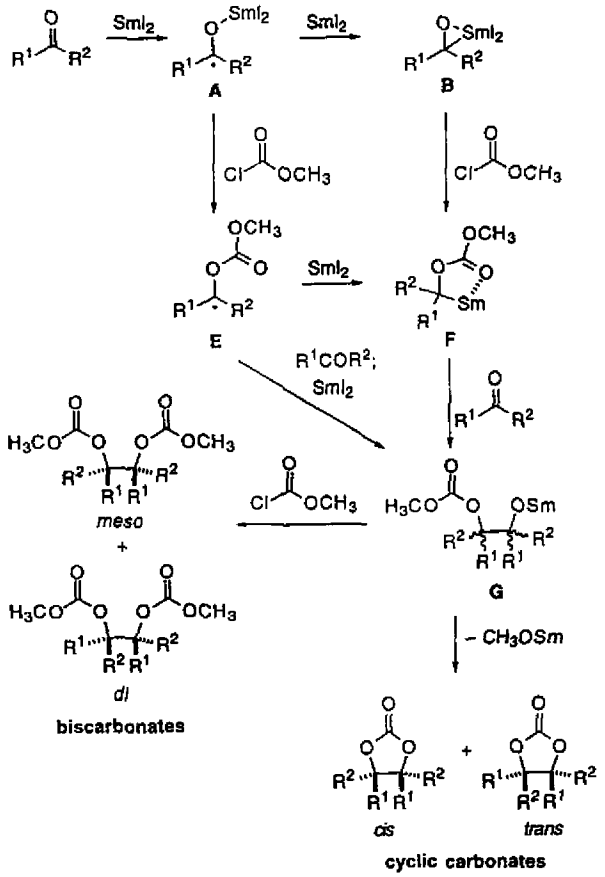
There are two possible pathways for the formation of pinacolates (Scheme I).[1] A carbonyl undergoes one-electron reduction with SmI_2 to give a ketyl radical **A**. In a nonpolar solvent, **A** might exist as tight ion pairs with oxygen-metal bonds to diminish the electrostatic repulsion on coupling to give the pinacolate **C**. Alternatively, the ketyl radical **A** might be further reduced by a second molecule of SmI_2 to give a samarium species **B**, which would add nucleophilically to the carbonyl to give the pinacolate **D**. The bis-coordinated pinacolate **C** and the chelated pinacolate **D** might also be interconvertible, and either pinacolate would lead to pinacols upon protonation. When a carbonyl compound is treated with SmI_2 in the presence of $ClCO_2CH_3$, the intermediates **A** or **B** can be trapped to give **E** or **F** (Scheme II). One-electron transfer from SmI_2 to the radical **E** can also afford the samarium species **F**. The carbonate intermediate **G** can be generated either by a nucleophilic addition of **F** to the carbonyl compound, or by a radical coupling between **E** and the carbonyl compound followed by a subsequent electron-transfer. Intramolecular cyclization of **G** would yield cyclic carbonates, but further reaction with a second molecule of $ClCO_2CH_3$ would furnish biscarbonates.

Scheme I



As shown in the example of 2-heptanone, the pinacolic coupling requires 24 h (giving **5b**), whereas the reaction in the presence of $ClCO_2CH_3$ and molecular sieves is completed in 20 min (giving **5a**). The great acceleration in formation of carbonate **5a** is attributable to trap of ketyl radical **A** with $ClCO_2CH_3$ to shift the equilibrium between the car-

Scheme II



bonyl compound and **A**.

Theoretically, formation of a biscarbonate (*e.g.* **18a**) requires 1 equiv of $ClCO_2CH_3$ (proportioned to the carbonyl compound), whereas formation of a cyclic carbonate (*e.g.* **6a**) only requires 0.5 equiv of $ClCO_2CH_3$. The reaction of benzaldehyde with SmI_2 (1 equiv) and $ClCO_2CH_3$ (0.5 equiv) in the presence of molecular sieves gave a *meso* biscarbonate **18a** (38%), a *meso* hydrobenzoin **18b** (37%) and a *cis* cyclic carbonate **18c** (11%). The inter- and intramolecular carbonations of the intermediate **G** (R^1, R^2 = H, Ph) appeared to be competitive. When 1 equiv of $ClCO_2CH_3$ was used (entry 18), the reaction gave exclusively the biscarbonate **18a**. Treatment of acetophenone (1 equiv) with SmI_2 (1 equiv) and $ClCO_2CH_3$ (0.5 equiv) in the presence of molecular sieves gave the cyclic carbonate **6a** in a lower yield (54%), by comparison with 68% in entry 6. In this case, no biscarbonated product was observed even when an excess of $ClCO_2CH_3$ (1 equiv) was employed. It seemed that the intermolecular biscarbonation of a congested intermediate **G** (R^1, R^2 = Me, Ph) was disfavored.

Most pinacolic couplings of aldehydes or unsymmetric ketones result in two diastereomers.[14] For example,[4a] the SmI_2-mediated pinacolic coupling of benzaldehyde gives hydrobenzoin containing *meso*- and *dl*-isomers (44:56).[4a] The *meso/dl* ratio increased to 7:3 when the pinacolic coupling was conducted in the presence of molecular sieves. The stereochemical outcome may be considered as the competition between dipolar and chelate transition states **H-K** (Fig. 1). The transition states **I** and **J** (Z = Sm) are disfavored due to the steric effects between the two large groups (L). The transition state **H** of the dipolar mode would give the *erythro* pinacolate, and hence the *meso*-pinacol upon protonation. On the other hand, the transition state **K** of the chelate mode would give the *threo* pinacolate and lead to the *dl*-pinacol upon protonation. When the SmI_2-mediated reaction is conducted in the presence of $ClCO_2CH_3$, the chelate transition state **K'** with the seven-membered ring would not be so favorable as **K** with the five-membered ring. However, the dipolar transition state **H'** (Z = CO_2CH_3) is preferable and leads to the formation of the *meso* biscarbonate **18a**. In this case, the *meso* selectivity may also account

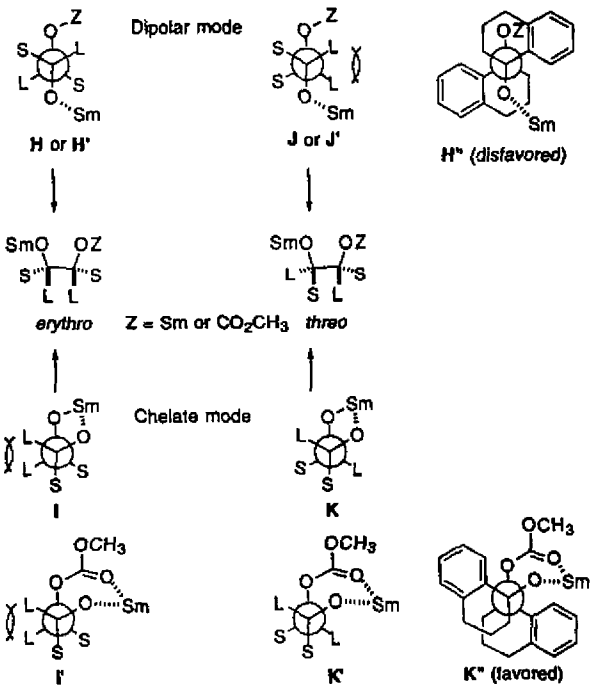


Fig. 1. The stereochemistry in pinacolic couplings (Z = Sm) and the related C-C bond forming reactions (Z = CO_2CH_3). The transition states **I**, **I'**, **J** or **J'** are disfavored due to the steric effect between two large groups (L). The transition state **H** (or **H'**) of dipolar mode leads to *erythro* pinacolate, *cis* cyclic carbonate and *meso* biscarbonate, whereas the transition state **K** (or **K'**) of chelate mode leads to *threo* pinacolate, *trans* cyclic carbonate and *dl* biscarbonate.

for the transition state **I'** (L = Ph) which exerts a π-π interaction[15] instead of a steric effect. If benzaldehyde was treated with SmI_2-molecular sieves in THF for 20 min, and then $ClCO_2CH_3$ (1 equiv) was added to trap the resulting pinacolates, *meso* biscarbonate **18a** and *trans* cyclic carbonate **18d** were obtained in a ratio of 7:3 (same as the *meso/dl* ratio of pinacolic coupling). The stereoselectivity increased (**18a/18d** = 9:1) when equimolar amounts of benzaldehyde and $ClCO_2CH_3$ were premixed prior to addition to the suspension of SmI_2 and molecular sieves in THF. If $ClCO_2CH_3$ was added prior to benzaldehyde (entry 18), the reaction gave the *meso* product **18a** exclusively. The reactions of 4-methoxybenzaldehyde and 4-cyanobenzaldehyde also showed the *meso*-selectivity.

The reactions of unsymmetric aliphatic ketones (entries 4, 5, and 8) are not stereoselective. The reaction of acetophenone (entry 6) gave a *cis* cyclic carbonate **6a**, whereas the reaction of α-tetralone (entry 15) gave a *trans* cyclic carbonate **15**. The *cis* selectivity for **6a** may be attributable to a reason similar to that described for **18a** *via* transition states **H'** and **I'** (L = Ph). By examining the transition states for the reaction of tetralone, one can see that the carbonate and OSm groups are displayed in the rings of the dipolar transition state **H"**, which may be disfavored by severe steric effects. The transition state **K"**, leading to the observed *trans* carbonate **15**, is less congested and procures a stabilization by chelation.

Alcohols, including diols, are often protected or activated as carbonates for applications in polymerization and organic synthesis.[16] We have demonstrated an efficient one-pot method for preparation of carbonates from a variety of carbonyl compounds in a short reaction time, even with the substrates of aliphatic carbonyls. Methyl chloroformate not only functioned as a carbonating agent, it played an important role in acceleration of the coupling reactions. Reactions conducted under such conditions showed different stereochemistry from pinacolic couplings using more traditional methods.

Crystal Data

Molecular structures of five compounds, **6a**, **8-*trans***, **12-major**, **12-minor**, and **15**, were determined by single

Table 2. Crystal Data of Compounds **6a**, **8-*trans***, **12-major**, **12-minor** and **15**

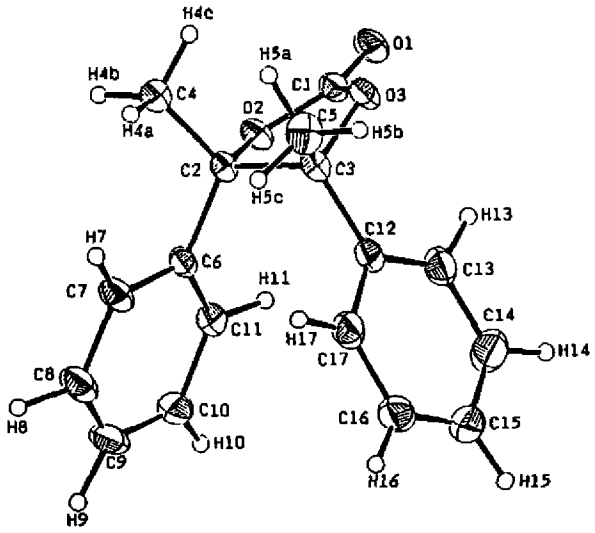
Compound	**6a**	**8-*trans***	**12-major**	**12-minor**	**15**
Space group	$P2_1/n$	C2/c	$P2_1/c$	$P2_1/c$	$P2_1/n$
a, Å	13.602(4)	9.721(3)	25.195(6)	9.878(3)	8.494(4)
b, Å	7.015(3)	16.361(5)	6.6690(2)	7.975(4)	16.849(4)
c, Å	15.040(4)	10.606(3)	12.224(3)	25.940(7)	11.357(2)
β, deg	96.90(3)	107.35(2)	91.60(2)	96.26(2)	90.56(3)
V, $Å^3$	1424.6(8)	1610.2(8)	2053.2(9)	2031(1)	1625.2(9)
Z	4	4	4	4	4
D(calc), $g.cm^{-3}$	1.251	1.223	1.089	1.100	1.309
λ(Å)	1.5418	1.5418	1.5418	0.7707	1.5418
F(000)	570	634	746	744	682
unit cell detn; #, (2θ range)	25, (35-52 deg.)	25, (33-47 deg.)	25, (26-46 deg.)	25, (17-23 deg)	25, (39-53 deg.)
scan type	**θ/2θ**	**θ/2θ**	**θ/2θ**	**θ/2θ**	**θ/2θ**
2θ scan width, deg	2(0.75+0.15tanθ)	2(0.9+0.15tanθ)	2(1.0+0.15tanθ)	2(0.6+0.35tanθ)	2(0.7+0.15tanθ)
2θ max, deg	140.0	149.0	120.0	50.0	140.0
mμ, cm^{-1}	8.164	5.971	5.201	0.665	6.545
Crystal size, mm	0.4 × 0.5 × 0.6	0.4 × 0.5 × 0.6	0.05 × 0.05 × 0.5	0.25 × 0.25 × 0.3	0.32 × 0.4 × 0.4
Temperature, K	298	298	298	298	298
No. of unique reflns	2529	1657	3013	3563	3050
No. of obs reflns (I >2σ<(I))	2101	1169	1418	1599	2269
R_f, R_w*	0.054; 0.056	0.047; 0.040	0.086; 0.092	0.046; 0.042	0.104; 0.103
GOF	2.97	1.98	1.80	1.53	3.85
Minimized function	$\Sigma w\|F_o-F_c\|^2$	$\Sigma w\|F_o-F_c\|^2$	$\Sigma w\|F_o-F_c\|^2$	$\Sigma w\|F_o-F_c\|_2$	$\Sigma w\|F_o-F_c\|^2$
g(second. ext. coeff.) × 10^4	3.00(4)	0.059(8)	0.31(2)	0.71(6)	0.33(4)
$(\Delta/\sigma)_{max}$	0.0045	0.0079	0.0028	0.0002	0.0011
$(\Delta\rho)_{max, min}$ $eÅ^{-3}$	-0.20; 0.25	-0.12; 0.19	-0.31; 0.24	-0.14; 0.14	-0.29; 0.89

*$R_f = [S|F_o-F_c|/F_o]$

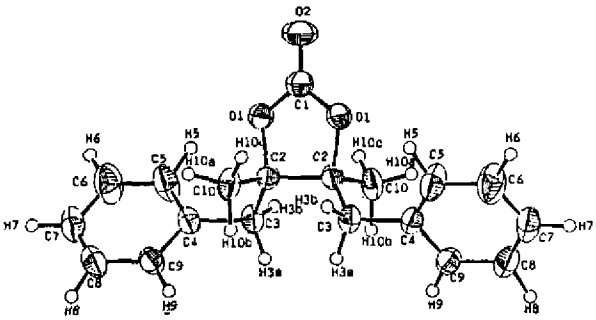
R_w = Sqrt[$\Sigma w|F_o-F_c|^2/\Sigma w|F_o|^2$]

GOF = Sqrt[$\Sigma w|F_o-F_c|^2$/(No. of reflns - No. of params.)]

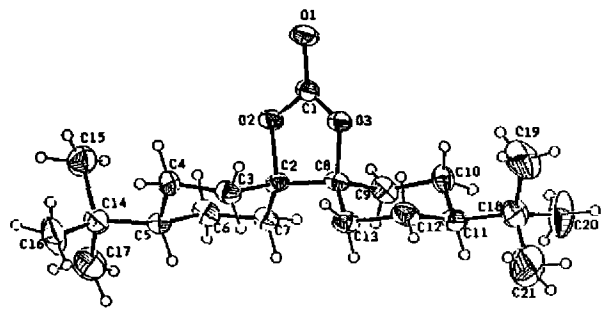
crystal X-ray diffraction. The data were collected on a CAD 4 diffractometer using CuK_α or MoK_α radiation. The relevant experimental conditions as well as the essential crystal data and final results of the least squares refinement are all given in Table 2. The ORTEP drawing of each compound is displayed and the stereochemistries are clearly indicated. All bond distances and bond angles are as expected.



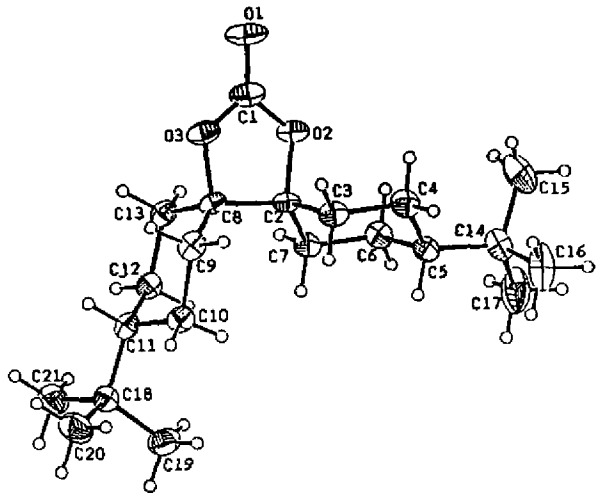
ORTEP Drawing of Compound **6a**



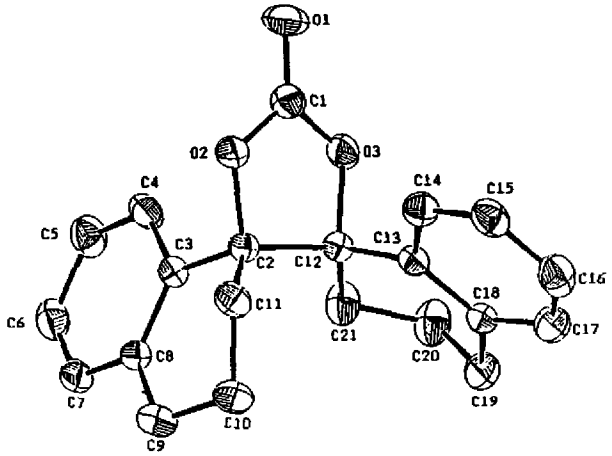
ORTEP Drawing of Compound **8-*trans***



ORTEP Drawing of Compound **12-major**



ORTEP Drawing of Compound **12-*minor***



ORTEP Drawing of Compound **15**

EXPERIMENTAL

Melting points are uncorrected. ^1H NMR spectra were recorded at 200 or 300 MHz; ^{13}C NMR spectra were recorded at 50 or 75 MHz. $CHCl_3$ ($\delta = 7.24$ ppm) was used as an internal standard in ^1H NMR spectra. Mass spectra were recorded at an ionizing voltage of 70 or 20 eV. Merck silica gel 60F sheets were used for analytical thin-layer chromatography. Column chromatography was performed on silica gel (70-230 mesh) or alumina (neutral); gradients of EtOAc and *n*-hexane were used as eluents. HPLC was performed on a Hibar Lichrosorb Si 60 (7 μm) column (25 cm × 1 cm i.d.) with the indicated eluent of a 5 mL/min flow rate. THF was distilled from sodium benzophenone ketyl under N_2.

General Procedure for the Preparation of Carbonates

In an oven-dried round-bottomed flask (50 mL) was

placed samarium metal (668.2 mg, 4.44 mmol), 1,2-diiodoethane (1.25 g, 4.44 mmol) and molecular sieves (4 Å, 200 mg). The air was evacuated by pump. The flask was inflated with argon and capped with septum. Anhydrous THF (12 mL) was added *via* syringe. The mixture was vigorously stirred at room temperature (30 °C) for 15-20 min to give a deep blue suspension. The formed suspension was stirred for 20 additional min and used readily for the coupling reaction.

Methyl chloroformate (0.16 mL, 2.12 mmol) was added *via* syringe. The mixture was stirred for 2-3 min, an appropriate carbonyl compound (2.12 mmol) in THF (2 mL) was added dropwise over a period of 2 min. The reaction occurred exothermically, the deep blue suspension changed to yellowish green color after stirring for 10-20 min. The septum was removed, and the mixture was stirred for 10 additional min in the air to become a yellow suspension. The mixture was filtered and rinsed with CH_2Cl_2 (2 × 25 mL), and the filtrate was concentrated by rotary evaporation. The residue was passed through a short column packed with alumina (neutral, 20-25 g), and eluted with EtOAc to give the desired carbonate products.

2,3-Dimethyl-2,3-butanediol cyclic carbonate (1)[17]

The reaction of acetone (123 mg, 2.12 mmol) with $SmI_2/ClCO_2CH_3$ according to the general procedure gave the title carbonate (132 mg, 86%). White solid; mp 99-100 °C; TLC (EtOAc/hexane (5:95)) R_f = 0.3; IR (KBr) 1770 (carbonate) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.35 (12 H, s); ^{13}C NMR ($CDCl_3$) δ 22.2 (4 C), 85.9 (2 C), 153.8; MS *m/z* (rel intensity) 144 (1, M^+), 85 (25), 59 (100).

Perdeuterio 2,3-dimethyl-2,3-butanediol cyclic carbonate (2)

The reaction of perdeuterioacetone (136 mg, 2.12 mmol) with $SmI_2/ClCO_2CH_3$ according to the general procedure gave the title carbonate (133 mg, 80%). White solid; mp 124-125 °C; TLC (EtOAc/hexane (15:85)) R_f = 0.14; ^{13}C NMR ($CDCl_3$) δ 20.4, 20.7, 20.9, 21.2, 21.5, 21.7, 21.9, 85.6, 153.8.

3,4-Diethyl-3,4-hexanediol cyclic carbonate (3)

The reaction of diethyl ketone (182 mg, 2.12 mmol) with $SmI_2/ClCO_2CH_3$ according to the general procedure gave the title carbonate (148 mg, 70%). Oil; TLC (EtOAc/hexane (5:95)) R_f = 0.35; IR (neat) 1789 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.95 (12 H, t, J = 7.7 Hz), 1.73-1.88 (8 H, m); ^{13}C NMR ($CDCl_3$) δ 8.2, 24.4, 91.2, 154.0; MS *m/z* (rel intensity) 201 (3, M^+ + 1), 127 (14), 87 (29), 57 (100); HRMS Calcd for $C_{11}H_{21}O_3$: 201.1491. Found: 201.1495.

3,4-Dimethyl-3,4-hexanediol cyclic carbonate (4)

The reaction of methyl ethyl ketone (153 mg, 2.12 mmol) with $SmI_2/ClCO_2CH_3$ according to the general procedure gave the title carbonate (143 mg, 78%) as a mixture of two isomers (1:1). Oil; TLC (EtOAc/hexane (5:95)) R_f = 0.31; IR (neat) 1779 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.99 (6 H, t, J = 7.4 Hz), 1.33 (6 H, s), 1.52-1.66 (2 H, m), 1.77-1.92 (2 H, m); ^{13}C NMR ($CDCl_3$) δ 8.1/8.2, 18.0/18.8, 27.0/27.9, 88.6/88.7, 154.1; MS *m/z* (rel intensity) 173 (56, M^+ + 1), 143 (56), 73 (100), 56 (77); HRMS Calcd for $C_9H_{16}O_3$: 173.1177. Found: 173.1180.

6,7-Dimethyl-6,7-dodecanediol cyclic carbonate (5a)

The reaction of 2-heptanone (242 mg, 2.12 mmol) with $SmI_2/ClCO_2CH_3$ according to the general procedure gave the title carbonate (225 mg, 83%) as a mixture of two isomers (1:1). Oil; TLC (EtOAc/hexane (5:95)) R_f = 0.6; IR (KBr) 1796 (carbonate) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.87 (6 H, m), 1.22-1.38 (12 H, m), 1.32 (6H, s), 1.40-1.58 (2H, m), 1.70-1.77 (2 H, m); ^{13}C NMR ($CDCl_3$) δ 13.9, 18.8/19.4, 22.4, 23.4/23.5, 32.1, 34.3/34.9, 88.4, 154.1; MS *m/z* (rel intensity) 257 (100, M^+ + 1), 195 (68); HRMS Calcd for $C_{15}H_{29}O_3$: 257.2117. Found: 257.2119.

2,3-Diphenyl-2,3-butanediol cyclic carbonate (6a)

The reaction of acetophenone (254.7 mg, 2.12 mmol) with $SmI_2/ClCO_2CH_3$ according to the general procedure gave the title carbonate (194 mg, 68%), which had the *cis* configuration as shown by an X-ray analysis. White solid; mp 105-106 °C; TLC (EtOAc/hexane (10:90)) R_f = 0.43; IR (KBr) 1791 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.94 (6 H, s), 6.87-6.92 (4 H, m), 7.03-7.10 (6 H, m); ^{13}C NMR ($CDCl_3$) δ 22.5, 90.3, 124.9, 127.8, 138.4, 154.3; MS *m/z* (rel intensity) 268 (71, M^+), 224 (87), 209 (30), 181 (24), 121 (29), 104 (100); HRMS Calcd for $C_{17}H_{16}O_3$: 268.1099. Found: 268.1111.

2,3-Bis(4-methoxyphenyl)-2,3-butanediol cyclic carbonate (7)

The reaction of 4'-methoxyacetophenone (292.6 mg, 2.12 mmol) with $SmI_2/ClCO_2CH_3$ according to the general procedure gave the title carbonate (288 mg, 83%) as a mixture of two isomers (3:1). White solid; mp 88-89 °C; TLC (EtOAc/hexane (30:70)) R_f = 0.31; IR (KBr) 1797 cm^{-1}; ^1H NMR ($CDCl_3$, major/minor = 3:1) δ 1.30 (s)/1.38 (s), 3.82 (s)/3.79 (s), 6.92 (d, J = 8.2 Hz)/6.81 (d, J = 8.2 Hz), 7.29 (d, J = 8.2 Hz)/7.08 (d, J = 8.2 Hz); ^{13}C NMR ($CDCl_3$, major/minor) δ 24.8/22.6, 55.3/55.1, 89.9/90.3, 113.8/113.1, 126.4/126.2, 129.8/130.6, 147.9, 159.6/159.0; MS *m/z* (rel intensity) 328 (23, M^+), 241 (23), 134 (100); HRMS Calcd for $C_{19}H_{20}O_5$: 328.1310. Found: 328.1310.

2,3-Dibenzyl-2,3-butanediol cyclic carbonate (8)

The reaction of benzyl methyl ketone (284.5 mg, 2.12 mmol) with $SmI_2/ClCO_2CH_3$ according to the general procedure gave the title carbonate (253.3 mg, 75%) as a mixture of two isomers (1:1). White solid; mp 95.5-96.5 °C; TLC (EtOAc/hexane (10:90)) R_f = 0.5; IR (KBr) 1785 cm^{-1}; ^1H

NMR ($CDCl_3$, *cis/trans*) δ 1.23 (3 H, s)/1.30 (3 H, s), 2.64/2.75 (2 H, d, J = 14.0 Hz), 3.25/3.38 (2 H, d, J = 14.0 Hz), 7.26-7.31 (10 H, m); ^{13}C NMR ($CDCl_3$) δ 18.9/19.0, 40.2/40.6, 88.1, 127.2, 128.4, 130.5/130.7, 134.7, 153.6; MS *m/z* (rel intensity) 296 (11, M^+), 205 (100), 161 (96), 91 (37); HRMS Calcd for $C_{19}H_{20}O_3$: 296.1412. Found: 296.1414. Anal. Calcd for $C_{19}H_{22}O_5$: C, 77.0, H. 6.80. Found: C, 76.8, H, 6.70. The *trans* isomer, mp 90-91 °C, was obtained by recrystallization from $CHCl_3/Et_2O$, and the configuration was confirmed by an X-ray analysis.

Bis(cyclobutyl)-1,1′-diol cyclic carbonate (9)

The reaction of cyclobutanone (148.6 mg, 2.12 mmol) with $SmI_2/ClCO_2CH_3$ according to the general procedure gave the title carbonate (131.3 mg, 85%). White solid; mp 68-69 °C; TLC (EtOAc/hexane (5:95)) R_f = 0.5; IR (KBr) 1781 (carbonate) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.59-1.78 (2 H, m), 1.94-2.11 (2 H, m), 2.44 (8 H, t, J= 7.8 Hz); ^{13}C NMR ($CDCl_3$) δ 12.6, 29.6, 87.5, 153.0; MS *m/z* (rel intensity) 169 (4, M^+ + 1), 152 (20), 96 (100), 68 (74), 55 (46); Anal. Calcd for $C_9H_{12}O_3$: C, 64.27; H, 7.19. Found: C, 64.26; H, 6.91.

Bis(cyclopentyl)-1,1′-diol cyclic carbonate (10)

The reaction of cyclopentanone (178.3 mg, 2.12 mmol) with $SmI_2/ClCO_2CH_3$ according to the general procedure gave the title carbonate (172.4 mg, 83%). White solid; mp 77.5-78.5 °C; TLC (EtOAc/hexane (5:95)) R_f = 0.53; IR (KBr) 1777 (carbonate) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.69-1.99 (16 H, m); ^{13}C NMR ($CDCl_3$) δ 22.7, 33.7, 95.9, 154.0; MS *m/z* (rel intensity) 197 (5, M^+ + 1), 124 (20), 111 (77), 97 (46), 84 (100), 67 (46), 55 (78); HRMS Calcd for $C_{11}H_{17}O_3$: 197.1177. Found: 197.1169.

Bis(cyclohexyl)-1,1′-diol cyclic carbonate (11)

The reaction of cyclohexanone (208 mg, 2.12 mmol) with $SmI_2/ClCO_2CH_3$ according to the general procedure gave the title carbonate (190 mg, 80%). White solid; mp 167-168 °C; TLC (EtOAc/hexane (5:95)) R_f = 0.53; IR (KBr) 1758 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.09-1.34. (4 H, m), 1.53-1.76 (12 H, m), 1.87-1.95 (4 H, m); ^{13}C NMR ($CDCl_3$) δ 21.8, 24.9, 30.4, 87.2, 154.1; MS *m/z* (rel intensity) 224 (M^+, 100); Anal. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.67; H, 9.02.

Bis(4-*tert*-butylcyclohexyl)-1,1′-diol cyclic carbonate (12)

The reaction of 4-*tert*-butylcyclohexanone (327 mg, 2.12 mmol) with $SmI_2/ClCO_2CH_3$ according to the general procedure gave the title carbonate (253 mg, 71%) as a mixture of two isomers (87:13) as shown by the ^1H NMR analysis. Two isomers were separated by HPLC with elution of EtOAc/hexane (5:95). The configuration of the major isomer was determined to have two axial C-O bonds by an X-ray analysis. **Major isomer**: White solid; mp 171-172 °C; t_R 9 min; IR (KBr) 1768 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.81 (3 H, s), 0.83-0.98 (1 H, m), 1.28-1.42 (4 H, m), 1.69-1.74 (2 H, m), 1.93-1.98 (1 H, m); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 22.8, 27.4, 30.9, 32.3, 47.0, 86.7, 154.1. **Minor isomer**: White solid; mp 175-176 °C; t_R 11 min; IR (KBr) 1774 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.83 (3 H, s), 1.02-1.45 (2 H, m), 1.38-1.77 (12 H, m), 2.05-2.25 (4 H, m); ^{13}C NMR ($CDCl_3$) δ 22.9 23.9, 27.4, 31.6, 32.2, 32.4, 32.7, 46.4, 47.0, 86.9, 153.8; MS *m/z* (rel intensity) 336 (1, M^+), 280 (100); HRMS Calcd for $C_{21}H_{36}O_3$: 336.2664. Found: 336.2663.

Bis(tetrahydro-4*H*-pyranyl)-1,1′-diol cyclic carbonate (13)

The reaction of tetrahydro-4*H*-pyranone (212.3 mg, 2.12 mmol) with $SmI_2/ClCO_2CH_3$ according to the general procedure gave the title carbonate (164 mg, 67%). White solid; mp 199-200 °C; TLC (EtOAc/hexane (10:90)) R_f = 0.47; IR (KBr) 1774 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.72-1.77 (8 H, m), 3.69-3.77 (4 H, m), 3.94-3.97 (4 H, m); ^{13}C NMR ($CDCl_3$) δ 30.6, 63.4, 84.2, 152.7; MS *m/z* (rel intensity) 228 (9, M^+), 166 (23), 140 (54), 101 (36), 84 (100), 56 (58); HRMS Calcd for $C_{11}H_{16}O_5$: 228.0997. Found: 228.0996.

Bis[(4-ethylenedioxy)cyclohexyl]-1,1′-diol cyclic carbonate (14)

The reaction of 1,4-cyclohexanedione mono-ethylene ketal (331.1 mg, 2.12 mmol) with $SmI_2/ClCO_2CH_3$ according to the general procedure gave the title carbonate (289 mg, 80%). White solid; mp 227-228 °C; TLC (EtOAc/hexane (10:90)) R_f = 0.31; IR (KBr) 1789 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.65-1.96 (16 H, m), 3.88-3.97 (8 H, m); ^{13}C NMR ($CDCl_3$) δ 28.2, 30.3, 64.1, 64.3, 85.6, 107.1, 153.3; MS *m/z* (rel intensity) 340 (60, M^+), 310 (21), 181 (36), 99 (100); Anal. Calcd for $C_{17}H_{24}O_7$: C, 59.99; H, 7.11. Found: C, 59.95: H, 7.36.

Bis[3,4-dihydro-1(2*H*)-naphthyl]-1,1′-diol cyclic carbonate (15)

The reaction of α-tetralone (310 mg, 2.12 mmol) with $SmI_2/ClCO_2CH_3$ according to the general procedure gave the title carbonate (180 mg, 53%), which had the *trans* configuration as shown by an X-ray analysis. White solid; mp 217.5-218 °C; TLC (EtOAc/hexane (5:95)) R_f = 0.28; IR (KBr), 1775 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.36-1.64 (4 H, m), 1.64-1.96 (4 H, m), 2.63-2.80 (4 H, m), 7.24 (2 H), 7.26-7.32 (4 H, m), 7.45-7.49 (2 H, m); ^{13}C NMR ($CDCl_3$) δ 18.6, 28.7, 33.2, 88.5, 126.1, 127.2, 128.8, 129.3, 134.2, 138.0, 155.1; MS *m/z* (rel intensity) 320 (25, M^+), 276 (32), 130 (100); HRMS Calcd for $C_{21}H_{20}O_3$: 320.1412. Found: 320.1409.

1,2-Dimethyl-1,2-cyclobutanediol cyclic carbonate (16)

The reaction of 2,5-hexanedione (242 mg, 2.12 mmol) with $SmI_2/ClCO_2CH_3$ according to the general procedure gave a *cis* carbonate **16** (241 mg, 80%). White solid; mp 110-111 °C; TLC (EtOAc/hexane (5:95)) R_f = 0.23; IR (KBr) 1786 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.40 (6 H, s), 2.04-2.15 (2 H, m), 2.36-2.47 (2 H, m); ^{13}C NMR ($CDCl_3$) δ 18.2, 30.5, 86.5, 153.6; MS *m/z* (rel intensity) 114 (54, M^+ - 28), 97 (65), 83 (61), 55 (100); Anal. Calcd for $C_7H_{10}O_3$: C, 59.14; H, 7.09. Found: C, 59.53; H, 7.09.

3,4-Hexanediol cyclic carbonate (17)

The reaction of propionaldehyde (123.1 mg, 2.12 mmol) with $SmI_2/ClCO_2CH_3$ according to the general procedure gave the title carbonate (115 mg, 75%) as a mixture of two isomers (1:1). Oil; TLC (EtOAc/hexane (10:90)) R_f = 0.28; IR (neat) 1780 (carbonate) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.04 (3 H, t, J = 7.2 Hz), 1.54-1.78 (4 H, m), 4.52/4.56 (2 H, t, J = 6.2 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 8.7, 26.9, 82.5, 154.7; MS *m/z* (rel intensity) 145 (6, M^+ + 1), 129 (22), 85 (36), 59 (100); HRMS Calcd for $C_7H_{13}O_3$: 145.0864. Found: 145.0868.

1,2-Diphenylethane-1,2-diyl dimethyl dicarbonate (18a) and 1,2-Diphenyl-1,2-ethanediol cyclic carbonate (18c)

The reaction of benzaldehyde (225 mg, 2.12 mmol) with $SmI_2/ClCO_2CH_3$ (1 equiv) according to the general procedure gave a *meso* biscarbonate **18a** (287 mg, 82%), which yielded *meso*-1,2-diphenyl-1,2-ethanediol (**18b**) upon saponification (saturated aqueous NaOH, MeOH). If equimolar amounts of benzaldehyde and $ClCO_2CH_3$ were premixed and subjected to the reaction with SmI_2 according to the general procedure, **18a** (72%) and a trans cyclic carbonate **18d** (8%) were obtained. The reaction of benzaldehyde (225 mg, 2.12 mmol) with $SmI_2/ClCO_2CH_3$ (0.5 equiv) according to the general procedure gave **18a** (177 mg, 38%), *meso* pinacol **18b** (111 mg, 37%) and *cis* cyclic carbonate **18c** (37.3 mg, 11%).

18a: White solid; mp 176.5-177 °C; TLC (EtOAc/hexane (5:95)) R_f = 0.2; HPLC (EtOAc/hexane (5:95)) t_R = 7 min; IR (KBr) 1743 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.69 (6 H, s, OCH_3), 5.91 (2 H, s), 7.16-7.30 (10 H, m); ^{13}C NMR ($CDCl_3$) δ 55.0, 80.2 ,127.6, 128.1, 128.7, 134.9, 154.7; MS *m/z* (rel intensity) 330 (0.3, M^+), 254 (19, $M^+ - CH_3OCO_2H$), 165 (100), 121 (74); HRMS Calcd for $C_{18}H_{18}O_6$: 330.1103. Found: 330.1113.

18c: White solid; mp 95.5-96.5 °C; HPLC (EtOAc/hexane (5:95)) t_R = 9 min; IR (KBr) 1815 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.71 (2 H, s), 7.42-7.59 (10 H, m); ^{13}C NMR ($CDCl_3$) δ 85.3, 126.0, 129.2, 129.8, 134.8, 153.6; MS *m/z* (rel intensity) 240 (65, M^+), 195 (35), 167 (50), 90 (100); HRMS Calcd for $C_{15}H_{12}O_3$: 240.0786. Found: 240.0771.

18d: White solid; mp 97.5-98.0 °C; HPLC (EtOAc/hexane (5:95)) t_R = 13 min; IR (KBr) 1817 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.42 (2 H, s), 7.28-7.43 (10 H, m); ^{13}C NMR ($CDCl_3$) δ 85.3, 126.0, 129.2, 129.7, 134.8, 154.0.

1,2-Bis(4-methoxyphenyl)ethane-1,2-diyl dimethyl dicarbonate (19)

The reaction of *p*-anisaldehyde (289 mg, 2.12 mmol) with $SmI_2/ClCO_2CH_3$ according to the general procedure gave the title carbonate (389 mg, 82%) as a single isomer. White solid; mp 173.5-174 °C; TLC (EtOAc/hexane (10:90)) R_f = 0.33; IR (KBr) 1739 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.67 (6 H, s, OCH_3), 3.76 (6 H, s, OCH_3), 5.81 (2 H, s), 6.79 (4 H, d, J = 8.4 Hz), 7.12 (4 H, d, J = 8.5 Hz); ^{13}C NMR ($CDCl_3$) δ 54.9, 55.1, 79.9, 113.5, 127.2, 129.0, 154.7, 159.7; MS *m/z* (rel intensity) 390 (17, M^+), 314 (17), 271 (40), 195 (100), 151 (92); HRMS Calcd for $C_{20}H_{22}O_8$: 390.1315. Found: 390.1316.

1,2-Bis(4-cyanophenyl)ethane-1,2-diyl dimethyl dicarbonate (20)

The reaction of 4-cyanobenzaldehyde (278 mg, 2.12 mmol) with $SmI_2/ClCO_2CH_3$ according to the general procedure gave the title carbonate (298 mg, 74%) as a single isomer. White solid; mp 194.5-195.5 °C; TLC (EtOAc/hexane (10:90)) R_f = 0.4; IR (KBr) 1749 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.73 (6 H, s), 5.90 (2 H, s), 7.27 (4 H, d, J = 8.4 Hz), 7.59 (4 H, d, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$) δ 55.4, 78.8, 113.0, 128.0 130.3, 132.2, 139.4, 154.3; MS *m/z* (rel intensity) 380 (7, M^+), 190 (26), 146 (100); HRMS Calcd for $C_{20}H_{16}O_6N_2$: 380.1008. Found: 380.1000.

Diphenylmethyl methyl carbonate (21)

The reaction of benzophenone (386 mg, 2.12 mmol) with $SmI_2/ClCO_2CH_3$ according to the general procedure gave the title carbonate (451 mg, 88%). White solid; mp 65-66 °C; TLC (EtOAc/hexane (15:85)) R_f = 0.6; IR (KBr) 1711 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.85 (3 H, s, OCH_3), 4.28 (1 H, s), 7.32-7.45 (10 H, m); ^{13}C NMR ($CDCl_3$) δ 53.5, 81.0, 127.3, 127.9, 128.0, 141.8, 174.9; MS *m/z* (rel intensity) 242 (1, M^+), 183 (100); HRMS Calcd for $C_{15}H_{14}O_3$: 242.0942. Found: 242.0941.

(2-Ethoxycarbonyl-1-methyl)ethyl methyl carbonate (22)

The reaction of ethyl acetoacetate (276 mg, 2.12 mmol) with $SmI_2/ClCO_2CH_3$ according to the general procedure gave the title carbonate (354 mg, 88%). Oil; TLC (EtOAc/hexane (30:70)) R_f = 0.27; IR (neat) 1738 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.23 (3 H, t, J = 7.2 Hz), 1.34 (3 H, d, J = 7.4 Hz), 2.49 (1 H, dd, J = 16.0, 5.8 Hz), 2.69 (1 H, dd, J = 16.0, 7.2 Hz), 3.75 (3 H, s, OCH_3), 4.13 (2 H, q, J = 7.2 Hz), 5.1 (1 H, m); ^{13}C NMR ($CDCl_3$) δ 14.0, 19.8, 40.7, 54.6,

60.6 ,71.3, 154.9, 169.9; MS *m/z* (rel intensity) 191 (3, M^+ + 1), 145 (34), 114 (54), 69 (100); HRMS Calcd $C_8H_{14}O_5$: 190.0841. Found: 190.0847.

(2-Alloxycarbonyl-1-methyl)ethyl methyl carbonate (23) and Allyl crotonate (26)

The reaction of allyl acetoacetate (301 mg, 2.12 mmol) with $SmI_2/ClCO_2CH_3$ according to the general procedure gave the title carbonate **23**, which was unstable and yielded **26** (214 mg, 80%) on silica gel column or in $CDCl_3$ solution. **23**: ^1H NMR ($CDCl_3$) δ 1.14-1.15 (3 H, m), 2.49-2.67 (2 H, m), 3.65 (3 H, s), 4.47-4.57 (2 H, m), 5.05-5.27 (3 H, m), 5.74-5.84 (1 H, m). ^{13}C NMR ($CDCl_3$) δ 19.6, 40.4, 54.6, 65.3, 71.1, 118.3, 131.5, 154.8, 169.7. **26**: MS *m/z* (rel intensity) 126 (15, M^+), 85 (20), 77 (21), 69 (100), 59 (82); HRMS Calcd for $C_7H_{10}O_2$: 126.0681. Found: 126.0690.

(2-Ethoxycarbonyl)cyclohex-1-yl methyl carbonate (24)

The reaction of ethyl 2-oxo cyclohexanecarboxylate (361 mg, 2.12 mmol) with $SmI_2/ClCO_2CH_3$ according to the general procedure gave the title carbonate (439 mg, 90%). Oil; TLC (EtOAc/hexane (20:80)) R_f = 0.45; IR (KBr) 1792, 1731 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.16 (3 H, t, J = 7.4 Hz) 1.22-1.47 (4 H, m), 1.52-1.82 (2 H, m), 1.90-2.12 (2 H, m), 2.44 (1 H, dt, J = 10.0, 4.0 Hz), 3.68 (3 H, s), 4.00-4.12 (2 H, m), 4.78 (1 H, dt, J = 10.0, 4.4 Hz); ^{13}C NMR ($CDCl_3$) δ 13.9, 23.5, 24.2, 28.3, 30.5, 48.2, 54.4, 60.4, 76.6, 154.8, 173.1; MS *m/z* (rel intensity) 231 (100, M^+ + 1), 230 (30, M^+), 185 (32), 155 (67); HRMS Calcd for $C_{11}H_{18}O_5$: 230.1154. Found: 230.1144.

(2-Ethoxycarbonyl)cyclopent-1-yl methyl carbonate (25) and Ethyl 1-cyclopentenecarboxylate (27)

The reaction of methyl 2-oxocyclopentanecarboxylate (331 mg, 2.12 mmol) with $SmI_2/ClCO_2CH_3$ according to the general procedure gave the title compound **25** as a mixture of isomers, which were unstable and yielded **27** (228 mg, 77%) on silica gel column or in $CDCl_3$ solution. **25**: Oil; TLC (EtOAc/hexane (20:80)) R_f = 0.31; IR (neat) 1789, 1746 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.16-1.26 (3 H, m), 1.73-2.14 (6 H, m), 2,44-2.58 (1 H, m), 3.70/3.72 (3 H, s), 3.97-4.09 (2 H, m), 5.12-5.13 (1 H, m); ^{13}C NMR ($CDCl_3$) δ 13.9, 23.1, 32.1, 37.7, 50.1, 54.3, 60.4, 81.6, 154.9, 173.5; MS *m/z* (rel intensity) 217 (44, M^+ + 1), 141 (96), 95 (92), 67 (100), 55 (68); HRMS Calcd for $C_{10}H_{16}O_5$: 216.0997. Found: 216.0998. **27**: Oil; TLC (EtOAc/hexane (30:70)) R_f = 0.7; IR (KBr) 1774 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.23 (3 H, t, J = 7.4 Hz), 1.92 (2 H, m), 2.40-2.54 (4 H, m), 4.13 (2 H, q, J = 7.4 Hz), 6.71 (1 H, m); ^{13}C NMR ($CDCl_3$) δ 14.2, 23.0, 31.2, 33.2, 59.9, 136.7, 143.4, 165.3; MS *m/z* (rel intensity) 140 (8, M^+), 95 (6), 84 (100); HRMS Calcd for $C_8H_{12}O$: 140.0837. Found: 140.0846.

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Samarium diiodide; Carbonates; Molecular sieves; Stereochemistry.

REFERENCES

1. For reviews, see (a) Kahn, B. E.; Rieke, R. D. *Chem. Rev.* **1988**, *88*, 733. (b) Robertson, G. M. in *Comprehensive Organic Synthesis*, Trost, B. M.; Fleming, I. Eds. Pergamon: Oxford, 1991, Vol. 3, pp 563-611. (c) Pons, J.-M.; Santelli, M. *Tetrahedron* **1988**, *44*, 4295. (d) Wirth, T. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 61. (e) Molander, G. A.; Harris, C. R. *Chem. Rev.* **1996**, *96*, 307.
2. Fürstner, A.; Csuk, R.; Rohrer, C.; Weidmann, H. *J. Chem. Soc., Perkin Trans 1* **1988**, 1729 and the references cited therein.
3. Imamoto, T.; Kusumoto, T.; Hatanake, Y.; Yokoyama, M. *Tetrahedron Lett.* **1982**, *23*, 1353.
4. (a) Namy, J. L.; Souppe, J.; Kagan, H. B. *Tetrahedron Lett.* **1983**, *24*, 765. (b) Souppe, J.; Danon, L.; Namy, J. L.; Kagan, H. B. *J. Organomet. Chem.* **1983**, *250*, 227. (c) Namy, J. L.; Collin, J.; Zhang, J.; Kagan, H. B. *J. Organomet. Chem.* **1987**, *328*, 81. (d) Molander, G. A.; Kenny, C. *J. Am.. Chem. Soc.* **1989**, 111, 8236, and the references cited therein. (e) Chiana, J. L.; Cabri, W.; Hanessian, S. *Tetrahedron Lett.* **1991**, *32*, 1125. (f) Uenishi, J.; Masuda, S.; Wakabayashi, S. *Tetrahedron Lett.* **1991**, *32*, 5097. (g) Csuk, R.; Hu, Z.; Abdou, M.; Kratky, C. *Tetrahedron* **1991**, *47*, 7037. (h) Hou, Z.; Miyano, T.; Yamazaki, H.; Wakatsuki, Y. *J. Am. Chem. Soc.* **1995**, *117*, 4421. (i) Nomura, R.; Matsuno, T.; Endo, T. *J. Am. Chem. Soc.* **1996**, *118*, 11666.
5. (a) Konstantatos, J.; Vrachnou-Astra, E.; Katsaros, N.; Katakis, D. *J. Am. Chem. Soc.* **1980**, *102*, 3035. (b) Konradi, A. W.; Kemp, S. J.; Pedersen, S. F. *J. Am. Chem. Soc.* **1994**, *116*, 1316 and the references cited therein.
6. (a) Mukaiyama, T.; Sato, T.; Hanna, J. *Chem. Lett.* **1973**, 1041. (b) Corey, E. J.; Danheiser, R. L.; Chan-

drasekaran, S. *J. Org. Chem.* **1976**, *41*, 260. (c) Chen, T. H.; Shaven, A. *J. Organomet. Chem.* **1984**, *268*, C1. (d) Clerici, A. *J. Org. Chem.* **1983**, 48, 1690. (e) Cleric, A.; Porta, O. *Tetrahedron Lett.* **1982**, *23*, 3517. (f) Nakayama, J.; Yamaoka, S.; Hoshino, M. *Tetrahedron Lett.* **1988**, *29*, 1399. (g) Handa, Y.; Inanaga, J. *Tetrahedron Lett.* **1987**, *28*, 5717. (h) Clerici, A.; Clerici, L.; Porta, O. *Tetrahedron Lett.* **1996**, *37*, 3035.

7. (a) Schäfer, H. J. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 911. (b) Léonard, E.; Duñach, E.; Périchon, J. *J. Chem. Soc., Chem. Commun.* **1989**, 276.
8. (a) Hays, D. S.; Fu, G. C. *J. Am. Chem. Soc.* **1995**, *117*, 7283. (b) Hiyama, T.; Obayashi, M.; Mori, I.; Nozaki, H. *J. Org. Chem.* **1983**, 48, 912.
9. So, J.-H.; Park, M.-K.; Boudjouk, P. *J. Org. Chem.* **1988**, *53*, 5871.
10. For reviews on SmI_2, see: (a) Kagan, H. B; Namy, J. L. *Tetrahedron* **1986**, *42*, 6573. (b) Inanaga, J. *J. Syn. Org. Chem.* **1989**, *47*, 200. (c) Soderquist, J. A. *Aldrich. Acta* **1991**, *24*, 15. (d) Molander, G. A. *Chem. Rev.* **1992**, *92*, 29. (e) Brandukova, N. E.; Vygodskii, Y. S.; Vinogradova, S. V. *Russ. Chem. Rev.* **1994**, *63*, 345. (f) Mblander, G. A.; Harris, C. R. *Chem. Rev.* **1996**, *96*, 307.
11. Lebrun, A.; Namy, J.-L.; Kagan, H. B. *Tetrahedron Lett.* **1993**, *34*, 2311.
12. Advantageous use of molecular sieves in organic reactions, see: (a) Hanson, R. M.; Sharpless, K. B. *J. Org. Chem.* **1986**, *51*, 1922. (b) Narasaka, K.; Inoue, M.; Yamada, T. *Chem. Lett.* **1986**, 1967. (c) Mikami, K.; Terada, M.; Nakai, T. *J. Am. Chem. Soc.* **1989**, *111*, 1940.
13. The SmI_2-promoted Barbier-type reaction of 4-*tert*-butylcyclohexanone with (2-bromoethyl)benzene gives the major addition product having an axial hydroxyl group (*cis* to the *t*-Bu group). The SmI_2-mediated coupling of 4-*tert*-butylcyclohexanone with styrene gives the major product having an equatorial hydroxyl group (*trans* to the *t*-Bu group). See, (a) Inanaga, J.; Ojikawa, O.; Handa, Y.; Otsub, K.; Yamaguchi, M. *J. Alloys Compounds* **1993**, *192*, 197. (b) Inanaga, J.; Katsuki, J.; Ujikawa, O.; Yamaguchi, M. *Tetrahedron Lett.* **1991**, *32*, 4921.
14. For the stereochemistry of pinacolic couplings, see: Taniguchi, N.; Kaneta, N.; Uemura, M. *J. Org. Chem.* **1996**, *61*, 6088 and the references cited therein.
15. (a) Stocker, J. H.; Kern, D. H. *J. Org. Chem.* **1968**, *33*, 1270. (b) Perkle, W.; Sikkenga, D. *J. Org. Chem.* **1975**, *40*, 3430. (c) Trost, B. M.; Curran, D. P. *J. Am. Chem. Soc.* **1980**, *102*, 5699. (d) Whitesell, J. K.; Battacharaya, A.; Aguilar, D. A.; Henke, K. *J. Chem. Soc., Chem. Commun.* **1982**, 988. (e) Evans, D. A.; Chapman, K. T.; Bisaha, J. *J. Am. Chem. Soc.* **1988**, *110*, 1238. (f) Solladie-Cavallo, A. *Tetrahedron* **1991**, *47*, 249.
16. (a) Greene, T. W.; Wuts, P. G. N. *Protective Groups in Organic Synthesis*, 2nd ed., Wiley: New York, p. 104. (b) Burk, R. M.; Roof, M. B. *Tetrahedron Lett.* **1993**, *34*, 395. (c) Kang, S.-K.; Jeon, J.-H.; Nam, K.-S.; Park, C.-H.; Lee, H.-W. *Synth. Commun.* **1994**, *24*, 305 and the references cited therein. (d) Myers, A. G.; Widdowson, K. L. *Tetrahedron Lett.* **1988**, 29, 6389. (e) Teranishi, K.; Nakao, H.; Komoda, A.; Hisamatsu, M.; Yamada, T. *Synthesis* **1995**, 176. (f) Scholl, M.; Lim, C.-K.; Fu, G. C. *J. Org. Chem.* **1995**, *60*, 6229. (g) Kundu, B.; Shukla, M.; Shukla, S. *J. Chem. Res. (S)* **1994**, 427. (h) Ghosh, A. K.; Duong, T. T.; Mckee, S. P. *Tetrahedron Lett.* **1991**, *32*, 4251. (i) McGhee, W.; Riley, D. *J. Org. Chem.* **1995**, *60*, 6205.
17. Budzikiewicz, H.; Djerassi, C.; Williams, D. H. *Mass Spectrometry of Organic Compounds* Holden-Day, Inc.: San Francisco, 1967, p. 494.