

# Synthesis of Mixed Carbonates via a Three-Component Coupling of Alcohols, CO<sub>2</sub>, and Alkyl Halides in the Presence of K<sub>2</sub>CO<sub>3</sub> and Tetrabutylammonium Iodide

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**Abstract:** Various mixed carbonates can be conveniently prepared in good yields using the corresponding alcohols, alkyl halides under CO<sub>2</sub> atmosphere in the presence of potassium carbonate or sodium carbonate and tetrabutylammonium iodide.

**Keywords:** potassium carbonate; sodium carbonate, tetrabutylammonium iodide (TBAI); alcohols; carbonates.

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## Introduction

Organic carbonates have played very important roles in the area of Synthetic Organic Chemistry, as key intermediates or as novel protecting groups [1]. Common synthetic methods leading to carbonates can be categorized into five classes: 1) alcoholysis of phosgene or its derivatives [2]; 2) exchange of organic carbonates [3]; 3) alkylation of carbon dioxide [4]; and 5) alkylation of inorganic carbonate [5]. However, for the synthesis of mixed (unsymmetrical) alkyl carbonates [ROC(O)OR'], these methods all suffer from two main drawbacks: 1) low selectivity and low yield; (2) the limited scope and availability

of the substrates. The lack of facile synthetic methodologies for the preparation of mixed alkyl carbonates [6] promoted us to develop some efficient, convenient, and practical procedures for the synthesis of carbonates [7]. Recently, Jung *et. al.* reported a cesium carbonate ( $\text{Cs}_2\text{CO}_3$ ) and tetrabutylammonium iodide (TBAI) promoted O-alkylation of alcohols for the preparation of mixed alkyl carbonates under a  $\text{CO}_2$  atmosphere [8]. Herein, we wish to report the use of cheaper and more readily available potassium carbonate ( $\text{K}_2\text{CO}_3$ ) or sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) instead of cesium carbonate ( $\text{Cs}_2\text{CO}_3$ ) to synthesize the mixed alkyl carbonates via alkylation of carbon dioxide under mild conditions. This facile synthetic method provides a potentially practical way for the utilization of carbon dioxide, a cheap, environmentally benign, natural and abundant reagent, for the synthesis of mixed carbonates [9].

## Results and Discussion

First we sought to examine the best reaction conditions for the preparation of unsymmetrical carbonates under a  $\text{CO}_2$  atmosphere in the presence of  $\text{K}_2\text{CO}_3$  using benzyl alcohol and benzyl halides as the substrates (Scheme 1).

Scheme 1



In general, the reaction of benzyl alcohol and benzyl halides under a  $\text{CO}_2$  atmosphere with additives gave very poor yields of carbonate (Table 1, entry 1). In the presence of additives such as 18-crown-6, KI or tetrabutylammonium iodide (TBAI), the yields of carbonate can be increased to some extent (Table 1, entries 2-14). Potassium hydroxide (KOH) or DBU is not as good as potassium carbonate (Table 1, entry 7-9). Benzyl bromide gave a higher yield of carbonate than benzyl chloride (Table 1, entries 5-6). We found that when the reaction was carried out at 70 °C in the presence of a 5-fold excess of potassium carbonate as base and a 5-fold excess of TBAI as the additive in *N,N*-dimethylformamide (DMF) solution the yield of carbonate can reach 82% (Table 1, entry 13).

This represent the best reaction conditions found for the preparation of carbonates. Using sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) as a base under the same reaction conditions, the yields of carbonate are in general lower than those observed using  $\text{K}_2\text{CO}_3$  (Table 1, entries 12-14). Thus we have found a highly chemoselective, convenient, and efficient synthetic method for the preparation of carbonates in high yield through the three-component coupling reaction of alcohols, carbon dioxide, and halides. This synthetic method obviously has the potential for industrial use and for the preparation of mixed carbonates (unsymmetrical carbonates).

We next investigated the formation of carbonates using other alcohols and alkyl bromides as the substrates under the optimized conditions described above (Scheme 2).

**Table 1.** Reactions of PhCH<sub>2</sub>OH (1.0 eq) with PhCH<sub>2</sub>X (1.0 eq) (X= Cl, Br) in the presence of additives (0.1 ~ 5.0 eq) under CO<sub>2</sub> atmosphere.

Entry	Base	Solvent	Time (d)	Temp[°C]	additive	PhCH <sub>2</sub> X	product (%) <sup>a</sup>	
							ester	ether
1	K <sub>2</sub> CO <sub>3</sub>	DMF	8	20	none	Br	trace	trace
2	K <sub>2</sub> CO <sub>3</sub>	DMF	8	20	18-crown-6 (0.1 eq)	Br	3.7	10.3
3	K <sub>2</sub> CO <sub>3</sub>	DMF	14	20	Bu <sub>4</sub> NBr (0.1 eq)	Br	11.5	trace
4	K <sub>2</sub> CO <sub>3</sub>	DMF	4	20	Bu <sub>4</sub> NI (1.0 eq)	Br	35	trace
5	K <sub>2</sub> CO <sub>3</sub>	DMF	4	20	Bu <sub>4</sub> NI (1.0 eq)	Cl	10	trace
6	K <sub>2</sub> CO <sub>3</sub>	toluene/hexane	4	20	Bu <sub>4</sub> NI/KI (1.0/0.1)	Cl	15	trace
7	KOH	DMF	4	20	Bu <sub>4</sub> NI (1.0 eq)	Br	trace	57.7
8	DBU	toluene/hexane	4	20	KI (0.1 eq)	Cl	25	trace
9	DBU	toluene/hexane	4	20	KI/18-crown-6 (0.1 eq)	Cl	30	trace
10	K <sub>2</sub> CO <sub>3</sub>	DMF	2	20	Bu <sub>4</sub> NI	Br	51	trace <sup>b</sup>
11	K <sub>2</sub> CO <sub>3</sub>	DMF	2	20	Bu <sub>4</sub> NI	Br	75	trace <sup>c</sup>
12	Na <sub>2</sub> CO <sub>3</sub>	DMF	2	20	Bu <sub>4</sub> NI	Br	26	trace <sup>b</sup>
13	K <sub>2</sub> CO <sub>3</sub>	DMF	2	60	Bu <sub>4</sub> NI	Br	82	trace <sup>c</sup>
14	Na <sub>2</sub> CO <sub>3</sub>	DMF	2	60	Bu <sub>4</sub> NI	Br	40	trace <sup>c</sup>

<sup>a</sup>)Isolated yields. <sup>b</sup>)Benzyl bromide (3.0 eq) and Bu<sub>4</sub>NI (3.0 eq).

<sup>c</sup>)Benzyl bromide (5.0 eq) and Bu<sub>4</sub>NI (5.0 eq).

### Scheme 2

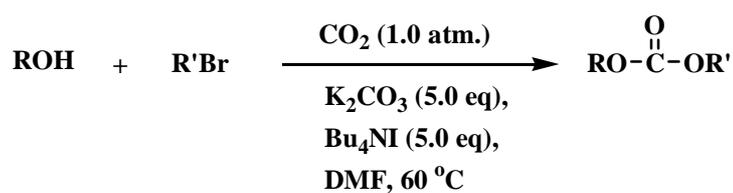
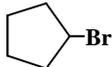


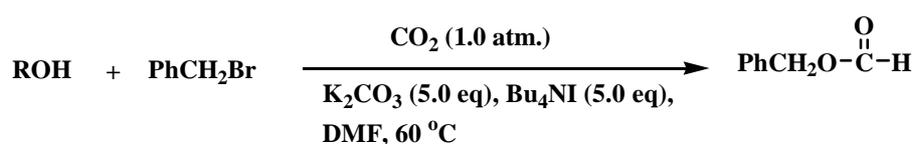
Table 2. Reactions of alcohols with different alkyl bromides under CO<sub>2</sub> atmosphere.

Alcohol	Alkyl bromide	Carbonate	Yields (%) <sup>a</sup>
n-BuOH	PhCH <sub>2</sub> Br	n-BuOCO <sub>2</sub> CH <sub>2</sub> Ph	56
n-Heptanol	PhCH <sub>2</sub> Br	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> OCO <sub>2</sub> CH <sub>2</sub> Ph	82
PhCH <sub>2</sub> OH	PhCH <sub>2</sub> Br	PhCH <sub>2</sub> OCO <sub>2</sub> CH <sub>2</sub> Ph	60
PhCH <sub>2</sub> OH		PhCH <sub>2</sub> OCO <sub>2</sub> 	42
PhCH <sub>2</sub> OH	n-C <sub>16</sub> H <sub>33</sub> Br	PhCH <sub>2</sub> OCO <sub>2</sub> C <sub>16</sub> H <sub>33</sub>	76
PhCH <sub>2</sub> OH	(CH <sub>3</sub> ) <sub>2</sub> CH(CH <sub>2</sub> ) <sub>2</sub> Br	PhCH <sub>2</sub> OCO <sub>2</sub> (CH <sub>2</sub> ) <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	52
PhCH <sub>2</sub> OH	n-C <sub>8</sub> H <sub>17</sub> Br	PhCH <sub>2</sub> OCO <sub>2</sub> C <sub>8</sub> H <sub>17</sub>	60
PhCH <sub>2</sub> OH	n-C <sub>4</sub> H <sub>9</sub> Br	PhCH <sub>2</sub> OCO <sub>2</sub> C <sub>4</sub> H <sub>9</sub>	87
n-Heptanol	n-C <sub>4</sub> H <sub>9</sub> Br	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> OCO <sub>2</sub> C <sub>4</sub> H <sub>9</sub>	58
n-BuOH	n-C <sub>4</sub> H <sub>9</sub> Br	BuOCO <sub>2</sub> C <sub>4</sub> H <sub>9</sub>	70
PhCH <sub>2</sub> OH	n-C <sub>6</sub> H <sub>13</sub> Br	PhCH <sub>2</sub> OCO <sub>2</sub> C <sub>6</sub> H <sub>13</sub>	67
PhCH <sub>2</sub> OH	PhCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Br	PhCH <sub>2</sub> OCO <sub>2</sub> (CH <sub>2</sub> ) <sub>3</sub> Ph	69

<sup>a</sup>) Isolated yields.

The results are summarized in Table 2. As can be seen, we found that C<sub>4</sub>–C<sub>7</sub> alcohols and benzyl alcohol can react efficiently with various alkyl bromides under a CO<sub>2</sub> atmosphere to give the corresponding carbonates in moderate to good yields. In addition, we also found that in the reaction of n-propylalcohol, isopropylalcohol, 1-dodecanol and 1-tetradecanol with benzyl bromide under the same reaction conditions, the mixed carbonates were obtained in very low yield and major product was PhCH<sub>2</sub>OCHO, which is derived from a Vilsmeier-Haack salt [9] in the reaction of benzyl bromide with DMF [8] (Scheme 3).

### Scheme 3



R = C<sub>3</sub>H<sub>7</sub>, i-C<sub>3</sub>H<sub>7</sub>, C<sub>12</sub>H<sub>25</sub>, C<sub>14</sub>H<sub>29</sub>.

It should be emphasized that using  $C_4H_9Br$  or  $C_8H_{17}Br$  as the electrophile, the mixed carbonate is formed exclusively without the formation of the corresponding  $ROCHO$  ( $R = C_4H_9$  or  $C_8H_{17}$ ).

## Conclusions

In summary, we have disclosed a highly efficient three-component coupling reaction using alcohols, carbon dioxide, and alkyl halides as the starting materials in the presence of potassium carbonate and TBAI and leading to the exclusive synthesis of mixed alkyl carbonates. This synthetic method has potential future industrial use as potassium carbonate, a much cheaper and more easily available inorganic base than cesium carbonate, is utilized as the base.

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## Experimental

### General

MPs were obtained with a Yanagimoto micro melting point apparatus and are uncorrected.  $^1H$ -NMR spectra were recorded on a Bruker AM-300 spectrometer for solution in  $CDCl_3$  with tetramethylsilane (TMS) as internal standard; J-values are in Hz. Mass spectra were recorded with a HP-5989 instrument and HRMS was measured by a Finnigan MA+ mass spectrometer. Organic solvents were dried by standard methods when necessary. Analyzed solid compounds reported in this paper gave satisfactory CHN microanalyses using a Carlo-Erba 1106 analyzer. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC using Huanghai GF<sub>254</sub> silica gel coated plates. Flash column chromatography was carried out using 200-300 mesh silica gel.

*Representative Experimental Procedure.* To benzyl alcohol (216 mg, 2.0 mmol) in anhydrous *N,N*-dimethylformamide (10 mL) were added potassium carbonate (1.38 g, 10 mmol, 5.0 eq.) and tetrabutylammonium iodide (3.7 g, 10.0 mmol, 5.0 eq.). Carbon dioxide gas was flushed into the reaction mixture three times, and then alkyl bromide (10 mmol, 5.0 equiv.) was added into suspension. The reaction was carried out under carbon dioxide atmosphere for 48 h, during which time the starting material was consumed. The reaction mixture was then poured into water (30 mL) and extracted with EtOAc (3 x 30 mL). The organic layer was washed with water (2 x 30 mL) and brine (30 mL) and dried over anhydrous sodium sulfate. Evaporation of solvent followed by flash column chromatography (eluent: hexane-EtOAc, 20:1) afforded the carbonate as a colorless oil.

*Carbonic acid dibenzyl ester (PhCH<sub>2</sub>OCO<sub>2</sub>CH<sub>2</sub>Ph)*. A colorless liquid; 277 mg, 60%; IR (CHCl<sub>3</sub>)  $\nu$  1745 cm<sup>-1</sup> (C=O); <sup>1</sup>H-NMR:  $\delta$  5.17 (4H, s, CH<sub>2</sub>), 7.35-7.41 (10H, m, Ph); MS (EI) m/z 197 (M<sup>+</sup>-45); [Calc. for C<sub>15</sub>H<sub>14</sub>O<sub>3</sub>: requires M, 242.0943. Found: 243.1024 (M<sup>+</sup>)].

*Dibenzyl ether (PhCH<sub>2</sub>OCH<sub>2</sub>Ph)*. A colorless liquid; 217 mg, 16%; IR (CHCl<sub>3</sub>)  $\nu$  1600, 1445 cm<sup>-1</sup>; <sup>1</sup>H-NMR:  $\delta$  4.56 (4H, s, CH<sub>2</sub>), 7.25-7.39 (10H, m, Ph); MS (EI) m/z 197 (M<sup>+</sup>-1); [Calc. for C<sub>14</sub>H<sub>14</sub>O: requires M, 198.1045. Found: 198.1041 (M<sup>+</sup>)].

*Carbonic acid benzyl ester hexadecyl ester (PhCH<sub>2</sub>OCO<sub>2</sub>C<sub>16</sub>H<sub>33</sub>)*. A colorless liquid; 543 mg, 76%; IR (CHCl<sub>3</sub>)  $\nu$  1737 cm<sup>-1</sup> (C=O); <sup>1</sup>H-NMR:  $\delta$  0.90 (3H, t, J = 6.9 Hz, CH<sub>3</sub>), 1.22-1.33 (28H, m, CH<sub>2</sub>), 1.51-1.60 (2H, m, CH<sub>2</sub>), 4.17 (2H, t, J = 6.7 Hz, CH<sub>2</sub>), 5.12 (2H, s, CH<sub>2</sub>), 7.37-7.42 (5H, m, Ph); MS (EI) m/z 152 (M<sup>+</sup>-224); [Calc. for C<sub>24</sub>H<sub>40</sub>O<sub>3</sub>: requires M, 376.2979. Found: 376.2966 (M<sup>+</sup>)].

*Carbonic acid benzyl ester butyl ester (n-BuOCO<sub>2</sub>CH<sub>2</sub>Ph)*. A colorless liquid; 221 mg, 56%; IR (CHCl<sub>3</sub>)  $\nu$  1718 cm<sup>-1</sup> (C=O); <sup>1</sup>H-NMR:  $\delta$  0.90 (3H, t, J = 6.9 Hz, CH<sub>3</sub>), 1.37-1.44 (2H, m, CH<sub>2</sub>), 1.64-1.69 (2H, m, CH<sub>2</sub>), 4.12 (2H, t, J = 6.7 Hz, CH<sub>2</sub>), 5.18 (2H, s, CH<sub>2</sub>), 7.36-7.42 (5H, m, Ph); MS (EI) m/z 208 (M<sup>+</sup>); [Calc. for C<sub>12</sub>H<sub>16</sub>O<sub>3</sub>: requires M, 208.1100. Found: 208.1105 (M<sup>+</sup>)].

*Carbonic acid benzyl ester hexadecyl ester [CH<sub>3</sub>(CH<sub>2</sub>)<sub>5</sub>CH<sub>2</sub>OCO<sub>2</sub>CH<sub>2</sub>Ph]*. A colorless liquid; 301 mg, 60%; IR (CHCl<sub>3</sub>)  $\nu$  1716 cm<sup>-1</sup> (C=O); <sup>1</sup>H-NMR:  $\delta$  0.89 (3H, m, CH<sub>3</sub>), 1.29-1.32 (8H, m, CH<sub>2</sub>), 1.66 (2H, m, CH<sub>2</sub>), 4.15 (2H, t, J = 6.0 Hz, CH<sub>2</sub>), 5.16 (2H, s, CH<sub>2</sub>), 7.35-7.45 (5H, m, Ph); MS (EI) m/z 250 (M<sup>+</sup>); [Calc. for C<sub>15</sub>H<sub>22</sub>O<sub>3</sub>: requires M, 250.1570. Found: 250.1576 (M<sup>+</sup>)].

*Carbonic acid benzyl ester cyclopentyl ester [PhCH<sub>2</sub>OCO<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>]*. A colorless liquid; 167 mg, 40%; IR (CHCl<sub>3</sub>)  $\nu$  1736 cm<sup>-1</sup> (C=O); <sup>1</sup>H-NMR:  $\delta$  1.56-1.93 (8H, m, CH<sub>2</sub>), 5.01-5.10 (1H, m, CH), 5.12 (2H, s, CH<sub>2</sub>), 7.31-7.45 (5H, m, Ph); MS (EI) m/z 219 (M<sup>+</sup>-1); [Calc. for C<sub>13</sub>H<sub>16</sub>O<sub>3</sub>: requires M, 220.1100. Found: 220.1094 (M<sup>+</sup>)].

*Carbonic acid benzyl ester 3-methylbutyl ester [PhCH<sub>2</sub>OCO<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>]*. A colorless liquid; 219 mg, 52%; IR (CHCl<sub>3</sub>)  $\nu$  1742 cm<sup>-1</sup> (C=O); <sup>1</sup>H-NMR:  $\delta$  0.94 (6H, d, J = 6.7 Hz, CH<sub>3</sub>), 1.59 (2H, q, J = 6.9 Hz, CH<sub>2</sub>), 1.69-1.76 (1H, m, CH), 4.20 (2H, t, J = 6.9 Hz, CH<sub>2</sub>), 5.18 (2H, s, CH<sub>2</sub>), 7.34-7.42 (5H, m, Ph); MS (EI) m/z 222 (M<sup>+</sup>); [Calc. for C<sub>13</sub>H<sub>18</sub>O<sub>3</sub>: requires M, 222.1256. Found: 222.1244 (M<sup>+</sup>)].

*Carbonic acid benzyl ester octyl ester (n-C<sub>8</sub>H<sub>17</sub>OCO<sub>2</sub>CH<sub>2</sub>Ph)*. A colorless liquid; 301 mg, 60%; IR (CHCl<sub>3</sub>)  $\nu$  1745 cm<sup>-1</sup> (C=O); <sup>1</sup>H-NMR:  $\delta$  0.88 (3H, t, J = 6.9 Hz, CH<sub>3</sub>), 1.27-1.43 (10H, m, 5CH<sub>2</sub>), 1.62-1.69 (2H, m, CH<sub>2</sub>), 4.15 (2H, t, J = 6.9 Hz, CH<sub>2</sub>), 5.16 (2H, s, CH<sub>2</sub>), 7.33-7.41 (5H, m, Ar); MS (EI) m/z 264 (M<sup>+</sup>); [Calc. for C<sub>16</sub>H<sub>24</sub>O<sub>3</sub>: requires M, 264.1726. Found: 264.1725 (M<sup>+</sup>)].

*Carbonic acid benzyl ester hexyl ester (n-C<sub>6</sub>H<sub>13</sub>OCO<sub>2</sub>CH<sub>2</sub>Ph).* A colorless liquid; 300 mg, 67%; IR (CHCl<sub>3</sub>)  $\nu$  1744 cm<sup>-1</sup> (C=O); <sup>1</sup>H-NMR:  $\delta$  0.88-0.90 (3H, m, CH<sub>3</sub>), 1.31-1.41 (6H, m, CH<sub>2</sub>), 1.61-1.71 (2H, m, CH<sub>2</sub>), 4.10- (2H, t, J = 6.9 Hz, CH<sub>2</sub>), 5.16 (2H, s, CH<sub>2</sub>), 7.33-7.41 (5H, m, Ar); MS (EI) m/z 236 (M<sup>+</sup>); [Calc. for C<sub>14</sub>H<sub>20</sub>O<sub>3</sub>: requires M, 236.1412. Found: 236.1372 (M<sup>+</sup>)].

*Carbonic acid benzyl ester 3-phenylpropyl ester [Ph(CH<sub>2</sub>)<sub>3</sub>OCO<sub>2</sub>CH<sub>2</sub>Ph].* A colorless liquid; 291 mg, 69%; IR (CHCl<sub>3</sub>)  $\nu$  1723 cm<sup>-1</sup> (C=O); <sup>1</sup>H-NMR:  $\delta$  1.98-2.07 (2H, m, CH<sub>2</sub>), 2.71-2.78 (2H, m, CH<sub>2</sub>), 4.17-4.23 (2H, m, CH<sub>2</sub>), 5.19 (2H, s, CH<sub>2</sub>), 7.21-7.40 (5H, m, Ar); MS (EI) m/z 208 (M<sup>+</sup>-60); [Calc. for C<sub>17</sub>H<sub>18</sub>O<sub>3</sub>: requires M, 270.1256. Found: 270.1245 (M<sup>+</sup>)].

*Carbonic acid benzyl ester heptyl ester (n-C<sub>7</sub>H<sub>15</sub>OCO<sub>2</sub>C<sub>4</sub>H<sub>9</sub>).* A colorless liquid; 238 mg, 58%; IR (CHCl<sub>3</sub>)  $\nu$  1744 cm<sup>-1</sup> (C=O); <sup>1</sup>H-NMR:  $\delta$  0.86-0.96 (6H, m, CH<sub>3</sub>), 1.25-1.50 (10H, m, CH<sub>2</sub>), 1.60-1.68 (4H, m, CH<sub>2</sub>), 4.10-4.16 (4H, m, CH<sub>2</sub>); MS (EI) m/z 215 (M<sup>+</sup>-1); [Calc. for C<sub>12</sub>H<sub>24</sub>O<sub>3</sub>: requires M, 216.1726. Found: 216.1722 (M<sup>+</sup>)].

*Carbonic acid dibutyl ester (n-C<sub>4</sub>H<sub>9</sub>OCO<sub>2</sub>C<sub>4</sub>H<sub>9</sub>).* A colorless liquid; 231 mg, 70%; IR (CHCl<sub>3</sub>)  $\nu$  1745 cm<sup>-1</sup> (C=O); <sup>1</sup>H-NMR:  $\delta$  0.88 (6H, t, J = 6.9 Hz, CH<sub>3</sub>), 1.20-1.40 (4H, m, CH<sub>2</sub>), 1.50-1.65 (4H, m, CH<sub>2</sub>), 4.05 (4H, t, J = 6.7 Hz, CH<sub>2</sub>); MS (EI) m/z 175 (M<sup>+</sup>+1); [Calc. for C<sub>9</sub>H<sub>18</sub>O<sub>3</sub>: requires M, 174.1256. Found: 174.1263 (M<sup>+</sup>)].

*Formic acid benzyl ester [PhCH<sub>2</sub>OC(O)H].* A colorless liquid; 217 mg, 60%; IR (CHCl<sub>3</sub>)  $\nu$  1724 cm<sup>-1</sup> (C=O); <sup>1</sup>H-NMR:  $\delta$  5.12 (2H, s, CH<sub>2</sub>), 7.33-7.41 (5H, m, Ar), 8.14 (1H, s, CH); MS (EI) m/z 136 (M<sup>+</sup>); [Calc. for C<sub>8</sub>H<sub>8</sub>O<sub>2</sub>, M 136.1749: requires C, 70.57; H, 5.92. Found: C, 70.12; H, 6.21].

## References

1. For comprehensive reviews on organic carbonates, see: (a) Hegarty, A. F. In *Comprehensive Organic Chemistry*; Sutherland, I. O., Ed; Pergamon: London, **1979**; Vol. 2, p.1067. (b) Shaikh, A. A. G; Sivaram, S. *Chem. Rev.*, **1996**, *96*, 951.
2. Burk, R. M.; Roof, M. B. *Tetrahedron Lett.*, **1993**, *34*, 395.
3. Bertolini, G.; Pavich, G.; Vergani, B. *J. Org. Chem.*, **1998**, *63*, 6031.
4. McGhee, W.; Riley, D. *J. Org. Chem.*, **1995**, *60*, 6025.
5. Cella, J. A.; Bacon, S. W. *J. Org. Chem.*, **1984**, *49*, 1122.
6. (a) Eckert, H.; Forster, B. *Angew. Chem., Int. Ed. Engl.*, **1987**, *26*, 894. (b) Burk, R. M.; Roof, M. B. *Tetrahedron Lett.*, **1993**, *34*, 395. (c) Bertolini, G.; Pavich, G.; Vergani, B. *J. Org. Chem.*, **1998**, *63*, 6031.
7. (a) McGhee, W.; Riley, D. *J. Org. Chem.*, **1995**, *60*, 6025. (b) Sakakura, T.; Saito, Y.; Okano, M.; Choi, J.-C.; Sako, T. *J. Org. Chem.*, **1998**, *63*, 7095. (c) Casadei, M. A.; Cesa, S.; Feroci, M.; Inesi, A.; Rossi, L.; Moracci, F. M. *Tetrahedron Lett.*, **1997**, *53*, 167. (d) Darensbourg, D. J.; Niezgoda, S.

- A.; Drapper, J. D.; Reibenspies, J. H. *J. Am. Chem. Soc.*, **1998**, *120*, 4690. (e) Cheng, M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.*, **1998**, *120*, 11018.
8. (a) Chu, F.; Dueno, E. E.; Jung, K.W. *Tetrahedron Lett.*, **1999**, *40*, 1847. (b) Kim, S. I.; Chu, F.; Dueno, E. E.; Jung, K. M. *J. Org. Chem.*, **1999**, *64*, 4578.
9. (a) Barluenga, J.; Campos, P. J.; Gonzalez-Nunez, E.; Asensio, G. *Synthesis*, **1985**, 426. (b) Caputo, R.; Ferreri, C.; Palumbo, G. *Synth. Commun.*, **1987**, *17*, 1629.

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