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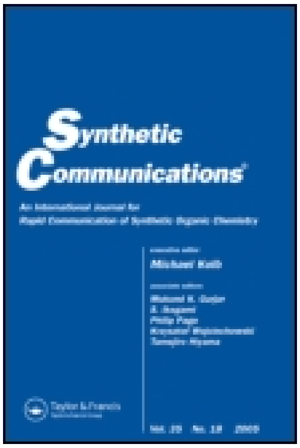

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Abstract: Catalyzed by ytterbium(III) triflate, asymmetrical carbonate can be chemoselectively synthesized from alcohols and dimethyl carbonate (DMC) in moderate to good yield under the mild conditions.

Keywords: carbonate interchange reaction, dimethyl carbonate, ytterbium triflate

Organic carbonates and carbamates play an important role in the agrochemical, pharmaceutical, polymer, and plastic industries.[1] The traditional method for the preparation of carbonates uses the toxic phosgene or its derivatives.[2,3] Hence, several efforts have been made to prepare the title compounds using nontoxic reagents, such as dimethyl carbonate (DMC).[4] DMC has been found extensive applications in carbonylation and methylation instead of toxic phosgene and dimethyl sulfate.[5,6] DMC also has been used to synthesize asymmetrical carbonates. As reports mentioned previously, carbonylation technology has been used to generate symmetrical monomeric dialkyl carbonates. Very few asymmetrical carbonate syntheses are available commercially. Asymmetrical carbonates should be generated in two steps. Although a variety of efficient catalysts have been chosen for this purpose,[7,8] most of procedures were performed either in high temperature

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or lower selectivity. Furthermore, Lewis acids such as $ZnCl_2/Et_3N$,[9] p-$CH_3C_6H_4SO_3H$,[10] and $YbCl_3$[11] have been tested. The symmetrical carbonates were the main product under high temperature; few asymmetrical carbonates were obtained.

As a novel Lewis acid, ytterbium(III) triflate has been used widely in organic synthesis.[12–16] Recently, Curini et al.[17] reported that $Yb(OTf)_3$ can promote the preparation of asymmetrical carbamates from amines and dimethyl carbonate in solvent-free conditions. In our laboratory, we have reported that metal triflate can catalyze many organic synthetic reactions.[18] We investigated the ester interchange reaction of dimethyl carbonate with alcohols for the preparation of asymmetrical carbonates using $Yb(OTf)_3$ as a catalyst.

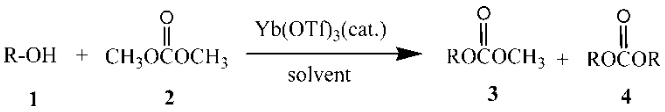
Our first attempt was performed with benzyl alcohol (**1a**) as substrate. To investigate suitable conditions for the ester interchange reaction (Scheme 1), a series of experiments was tested (Table 1).

As shown in Table 1, when **1a** was treated with 1 equiv. of DMC in CH_2Cl_2 or CH_3CN catalyzed by ytterbium triflate, no product was detected; in the case of chloroform, only 17% of the corresponding product **3a** was obtained. When the reaction was carried out in 1,2-dichloroethane under reflux conditions, **3a** was obtained in moderate yield (65%), accompanied by 11% of the symmetrical carbonate **4a** (Table 1, entry 4). Thus, the following reactions were performed in 1,2-dichloroethane.

The amount of $Yb(OTf)_3$ and the ratio of alcohols with DMC were studied carefully. According to Table 1, 10 mol% of $Yb(OTf)_3$ was enough and efficiently promoted the interchange reaction. Increasing the amount of catalyst did not obviously increase the yield (Table 1, entry 5). When the ratio of alcohols with DMC was 1:2 (Table 1, entry 7), **3a** was the main product. The symmetrical product **4a** becomes the main product if the ratio of alcohols with DMC is up to 2:1. Under this optimal condition (Table 1, entry 7), methyl phenyl carbonate (**3a**) can be obtained in 73% yield.

To explore the scope of our method, a variety of alcohols were investigated to react with DMC catalyzed by ytterbium triflate, and the results are summarized in Table 2.

As shown in Table 2, most of aliphatic alcohols can provide the corresponding products with good yields, and the catalyst could be reused several times without any loss of activity. However, when alcohol contains the bulky group, no product was detected, possibly because of the high hindrance (Table 2, entry 16). As for the less active phenol, no product was found under similar conditions. Finally, diols were tested in our experiment;



$$\underset{\mathbf{1}}{\text{R-OH}} + \underset{\mathbf{2}}{CH_3O\overset{O}{\overset{\|}{C}}OCH_3} \xrightarrow[\text{solvent}]{Yb(OTf)_3\text{(cat.)}} \underset{\mathbf{3}}{RO\overset{O}{\overset{\|}{C}}OCH_3} + \underset{\mathbf{4}}{RO\overset{O}{\overset{\|}{C}}OR}$$

Scheme 1.

Table 1. Preparation of methyl benzyl carbonate (**3a**) under different conditions catalyzed by Yb(OTf)$_3$[a]

Entry	Ratio of ROH/DMC	Cat. equiv.	Solvent	Time (h)	Yield (**3a**)[b]	Yield (**4a**)[a]
1	1:1	0.1	CH_2Cl_2	24	ND[c]	ND[c]
2	1:1	0.1	CH_3CN	24	ND[c]	ND[c]
3	1:1	0.1	$CHCl_3$	12	17	Trace
4	1:1	0.1	$ClCH_2CH_2Cl$	8	65	11
5	1:1	0.2	$ClCH_2CH_2Cl$	8	68	15
6	1:1	0.05	$ClCH_2CH_2Cl$	12	45	Trace
7	1:2	0.1	$ClCH_2CH_2Cl$	8	73	Trace
8	1:4	0.1	$ClCH_2CH_2Cl$	8	75	Trace
9	2:1	0.1	$ClCH_2CH_2Cl$	8	25	53
10	4:1	0.1	$ClCH_2CH_2Cl$	8	11	60

[a] The reaction was carried out in 5 ml of solvent under reflux condition.

[b] Isolated yields based on alcohols.

[c] No product was detected.

to our surprised, the five-membered ring 1,3-dioxolan-2-one was obtained with lower yields (Scheme 2).

In summary, an efficient and mild method for the chemoselective synthesis of asymmetrical carbonate from the carbonate interchange reaction was developed. Compared to previously reported methodologies, the advantages of the present method are high chemoselectivity, simple operation, and mild reaction conditions with good yield.

Table 2. Preparation of asymmetrical carbonate from alcohols with DMC catalyzed by Yb(OTf)$_3$[a]

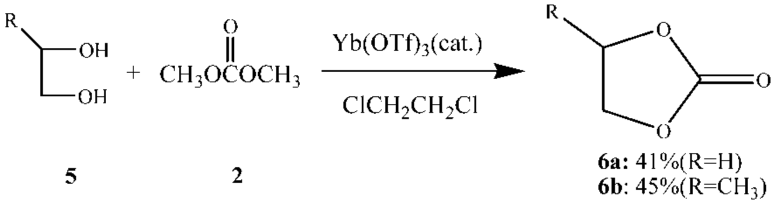
Entry	R	Product	Reaction time (h)	Product (**3**)[b]
11	$PhCH_2$ (**1a**)	**3a**	8	73
12	$CH_3(CH_2)_6CH_2$ (**1b**)	**3b**	8	75
13	$PhCH_2CH_2$ (**1c**)	**3c**	8	65
14	*m*-$O_2NC_6H_4CH_2$ (**1d**)	**3d**	12	78
15	*p*-$CH_3C_6H_4CH_2$ (**1e**)	**3e**	8	75, 74, 73[c]
16	$(C_6H_5)_2CH$ (**1f**)	—	24	ND[d]
17	C_6H_5 (**1g**)	—	24	ND[d]

[a] 2 mmol of alcohols, 4 mmol of DMC, 0.2 mmol of Yb(OTf)$_3$ and 5 ml of 1,2-dichloroethane were used, and the reaction was carried out under reflux temperature.

[b] Isolated yields based on alcohols.

[c] The recovered catalyst was used.

[d] No product was detected.



Scheme 2.

EXPERIMENTAL

Melting points were recorded on a WRS-1B digital melting-point apparatus and are uncorrected. IR spectra were recorded using KBr pellets on an Avatar 370 FI-infrared spectrophotometer. ^1H NMR spectra was recorded on a Varian Mercury Plus-400 instrument using $CDCl_3$ as the solvent with TMS as an internal standard. Mass spectra were measured with Thermo Finnigan LCQ-Advantage (EI). $Yb(OTf)_3$ was prepared from ytterbium oxide and trifluoromethanesulfonic acid and recovered according to the literature.[19] All reagents are commercially available and used without further purification.

General Procedure for the Preparation of Asymmetrical Products

A mixture of alcohols (2 mmol), dimethyl carbonate (4 mmol), and $Yb(OTf)_3$ (0.2 mmol) in 1,2-dicholoroethane (5 ml) was stirred under reflux temperature. The reaction was controlled by thin-layer chromatography (TLC). After stirring for the time given in Table 2, the reaction was quenched with water (5 ml). Then organic layer was washed with brine and dried over $MgSO_4$. After solvent was reduced in vacuo, the residue was purified by preparative TLC to obtain **3**. The aqueous layer was concentrated in vacuo to give white crystals $[Yb(H_2O)_9](OTf)_3$ and then heated at 190°C for 4 h in vacuo to give 112 mg of $Yb(OTf)_3$ (90.3%).

Data

3a: oil (lit.[20]). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.35–7.31$ (m, 5 H, ArH), 5.13 (s, 2 H, CH_2), 3.74 (s, 3 H, CH_3). IR (neat): 3033, 2957, 2856, 1749, 1498, 1446, 790, 751, 698 cm^{-1}.

3b: oil (lit.[21]). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 4.14$ (t, 2 H, $J = 7.0$ Hz, CH_2), 3.78 (s, 3 H, CH_3), 1.36–1.28 (m, 12 H, CH_2), 0.88 (t, 3 H, $J = 6.6$ Hz, CH_3). IR (neat): 2956, 2927, 2856, 1751 cm^{-1}.

3c: oil (lit.[22]). ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.31-7.22$ (m, 5 H, ArH), 4.34 (t, 2 H, $J = 7.6$ Hz, CH_2), 3.76 (s, 3 H, CH_3), 2.98 (t, 2 H, $J = 7.2$ Hz, CH_2). IR (neat): 3031, 2957, 2905, 1751, 1447, 794, 761, 697 cm^{-1}.

3d: Solid mp 60.9–61.3°C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 8.26$ (s, 1 H, ArH), 8.21 (d, 1 H, $J = 8.0$ Hz, ArH), 7.74 (d, 1 H, $J = 8.0$ Hz, ArH), 7.57 (t, 1 H, $J = 8.0$ Hz, ArH), 5.26 (s, 2 H, CH_2), 3.83 (s, 3 H, CH_3). ^{13}C NMR (400 MHz, $CDCl_3$) $\delta = 55.1$, 67.9, 122.8, 123.3, 129.6, 133.8, 137.2, 138.3, 155.3. MS: m/z 212 (15%, $M^+ + 1$), 150 (35%), 135 (100%). IR (KBr) 3027, 2967, 2926, 2859, 1749, 1528, 1444, 790, 728, 670 cm^{-1}.

3e: oil (lit.[23]). ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.38$ (d, 2 H, $J = 7.6$ Hz, ArH), 7.27 (d, 2 H, $J = 7.6$ Hz, ArH), 5.22 (s, 2 H, CH_2), 3.88 (s, 3 H, CH_3), 2.45 (s, 3 H, CH_3). IR (neat): 2956, 2923, 1749, 1515, 1445, 846, 795 cm^{-1}.

6a: oil (lit.[24]). ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 4.52$ (s, 4 H, CH_2). IR (neat): 2927, 1773 cm^{-1}.

6b: oil (lit.[25]). ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 4.90$ (m, 1 H, CH), 4.59 (t, 1 H, $J = 8.0$ Hz, CH_2), 4.05 (t, 1 H, $J = 8.0$ Hz, CH_2), 1.48 (d, 3 H, $J = 3.0$ Hz, CH_3). IR (neat): 2928, 2835, 1710 cm^{-1}.

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