

Letter

A novel catalyst for transesterification of dimethyl carbonate with phenol to diphenyl carbonate: samarium trifluoromethanesulfonate

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Abstract

Samarium trifluoromethanesulfonate ($\text{Sm}(\text{OTf})_3$) was found to be a novel catalyst for synthesis of diphenyl carbonate (DPC) by transesterification of dimethyl carbonate (DMC) with phenol. The best result was obtained by using $\text{Sm}(\text{OTf})_3$ catalyst. The TON reached 21.8 mol DPC/mol Sm when the reaction was carried out at 190 °C with the molar ratio of phenol-to-DMC 4:1 for 12 h. This catalyst could work in aqueous media and in air, and proved reusable. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Samarium trifluoromethanesulfonate; Transesterification; Diphenyl carbonate; Dimethyl carbonate

1. Introduction

Diphenyl carbonate (DPC) is an industrially important intermediate for the production of a lot of organic chemicals [1]. Recently, DPC is used for the synthesis of polycarbonate by melt polymerization process. Transesterification of dimethyl carbonate (DMC) with phenol is a phosgene-free method for manufacturing DPC. This method is proven to be effective and is now used in a pilot-plant [2].

The synthesis of DPC by transesterification of DMC with phenol are usually catalyzed by organometallic compounds containing titanium, aluminium and tin [3–8] and conventional Lewis acid catalysts such as aluminium chloride and zinc chloride [9,10]. Most of these catalysts are sensitive to water and air in the system, and can not be completely recovered after reaction. Lanthanide trifluoromethanesulfonates have

been used as catalysts in Michael addition, Diels–Alder reaction, Friedel–Crafts acylation and Aldol condensation for the purpose of overcoming the problems caused by the conventional Lewis acid catalysts [11–15]. We found that samarium trifluoromethanesulfonate ($\text{Sm}(\text{OTf})_3$) was also an effective catalyst for transesterification of DMC with phenol to synthesize DPC. To the best of our knowledge, it is the first time for this compound to be used in the catalytic synthesis of DPC (Scheme 1).

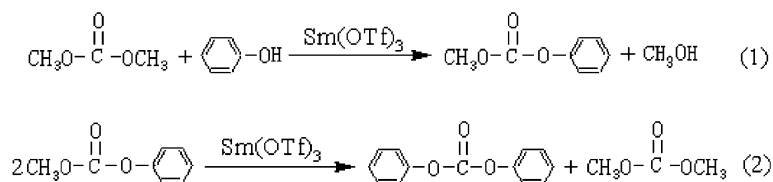
2. Experimental

2.1. Reagents

DMC (Ube Chemicals, Japan) was fractionally distilled and stored over molecular sieve (4 Å). Phenol was of laboratory reagent grade and subjected to drying and purification by standard procedure. Titanium butoxide (Shanghai Chemical Reagent Co., China),

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Scheme 1. Transesterification of DMC with phenol to DPC catalyzed by Sm(OTf)₃.

di-*n*-butyltin oxide (Fluka Chemical, Switzerland), aluminum chloride and zinc chloride were used as received. Sm(OTf)₃ was prepared from samarium oxide (Sm₂O₃) and trifluoromethanesulfonic acid according to literature [16].

2.2. Analysis

The distillates during reaction were analyzed by gas chromatography (GC) (HP 6890). The product DPC was characterized by NMR spectroscopy (Varian XL-200), IR spectroscopy (Impact-420, Nicolet) and mass spectroscopy (HP 5973). The melting points were determined for the products and compared with literature.

2.3. Procedure of synthesis

The reaction was carried out in a 250 ml three-necked round-bottomed flask equipped with a nitrogen inlet, a dropping funnel, and a fractionating column connected to a liquid dividing head. Under nitrogen gas, reagents and a catalyst were added to the flask, with stirring and slowly increasing temperature. The occurrence of reaction was indicated by attainment of temperature of 62–63 °C at the top of the column,

which corresponded to the 70:30 boiling azeotrope of methanol and DMC. This azeotrope was analyzed by GC one time per hour. The temperature was kept at 190 °C during the period of reaction. After filtration to recover the catalyst, the reaction mixture was distilled under 15 mmHg. The product was then recrystallized in absolute ethanol to obtain pure DPC.

3. Results and discussion

Although conventional Lewis acid catalysts have played important roles in modern organic synthesis, a small amount of water or oxygen in the reaction system could decompose or deactivate the catalysts. Kobayashi and co-workers demonstrated that lanthanide trifluoromethanesulfonate could substitute conventional Lewis acid catalysts in Michael addition, Diels–Alder reaction, Friedel–Crafts acylation and Aldol condensation [11–15], and could be used in aqueous media and in the presence of oxygen. Because Lewis acids can catalyze the synthesis of DPC by transesterification of DMC with phenol and lanthanide trifluoromethanesulfonate is a kind of Lewis acid, it should be suitable for this reaction. In addition, Yoshisato and Yoshitomi used

Table 1
Transesterification of DMC with phenol catalyzed by Sm(OTf)₃, Sn, Ti, Al and Zn compounds

Catalyst	Molar ratio catalyst-to-DMC	Conversion of DMC (%)	Yield of DPC (%)	Yield of MPC (%)	Yield of Anisole (%)	Selectivity to DPC (%)	TON mol DPC/mol catalyst
Sm(OTf) ₃	1:70	34.4	31.1	2.1	1.2	90.4	21.8
<i>n</i> -Bu ₂ SnO	1:60	37.6	33.3	4.3	Trace	88.6	20.0
Ti(OC ₄ H ₉) ₄	1:60	31.2	26.0	5.2	Trace	83.3	15.6
AlCl ₃	1:10	18.2	15.0	2.2	1.0	82.4	1.5
ZnCl ₂	1:10	13.7	11.0	1.5	1.2	80.3	1.1

Reaction conditions: molar ratio of phenol-to-DMC 4:1; 12 h; temperature 190 °C. DPC yield was based on the amount of charged DMC. MPC: methyl phenyl carbonate.

Table 2
Recycling of Sm(OTf)₃ in transesterification of DMC with phenol

Times of catalyst used	DMC conversion (%)	DPC yield (%)	Recovery of catalyst (%)	DMC conversion calculated (%)
1	34.4	31.1	95	–
2	32.4	29.3	92	32.7
3	31.3	28.3	89	31.7

Reaction conditions: molar ratio of phenol-to-DMC 4:1; 12 h; temperature 190 °C. Recovery of catalyst was determined by the ratio of the isolated amount of Sm(OTf)₃ based on the initial amount of Sm(OTf)₃. DMC conversions calculated are determined as follows: $34.4 \times 95(\%) = 32.7$, $34.4 \times 92(\%) = 31.7$.

La[OCH(CH₃)₂]₃ and Sm₂O₃ as catalysts for transesterification of DMC with phenol to DPC and methyl phenyl carbonate [17,18]. Taking these into considerations, we explored the potential of Sm(OTf)₃ for a catalyst in the transesterification. For comparison, tin, titanium, aluminum and zinc compounds are also tested as catalysts for the transesterification of DMC with phenol. The results are shown in Table 1.

The reactions (1) and (2) are endothermic [19]. The increase in temperature is favorable for reactions thermodynamically and kinetically. Thus, the yield of DPC will increase with increasing of temperature. The yield of DPC decreases when temperature is over 190 °C. The reason is that when temperature is too high, catalysts deactivate and reactants, especially DMC, will easily escape from the reaction system due to its low boiling point (90.5 °C). Because the equilibrium constant for reaction (1) is 3.0×10^{-4} at 453 K [20], the reactions (1) and (2) are slow and thermodynamically unfavorable. Therefore, it is necessary to discharge the by-product CH₃OH to shift the equilibrium in the direction of DPC formation and shorten the reaction time. From reactions (1) and (2), it is evident that the excess of phenol is favorable for producing DPC. We found that the molar ratio of phenol-to-DMC 4:1, reaction time 12 h and temperature 190 °C are the optimized reaction conditions.

As shown in Table 1, Ti(OC₄H₉)₄ has high activity, but it is hydrolyzed to TiO₂ in the presence of aqueous media and can not be recovered at all. AlCl₃ and ZnCl₂ can be used as catalyst for this reaction, but they are also easily hydrolyzed and the turnover number is very low. The compound *n*-Bu₂SnO is found to be effective and insensitive to air and water, but the obtained DPC shows greyish color due to the contamination of tin. Sm(OTf)₃ has the highest turnover number and no

samarium is detected in the product DPC. It can work in aqueous media or organic solvent.

After filtration from reaction mixture and drying, Sm(OTf)₃ is reusable. The results of recycling of catalyst are shown in Table 2. From the data in Table 2, it is found that the catalytic activities of the recovered catalyst are almost the same as that of fresh catalyst. The decreases in DMC conversion of the second run and the third run are caused by the loss of catalyst during the physical treatment, filtration of catalyst from the reaction mixture.

4. Conclusions

In summary, a novel catalyst Sm(OTf)₃ for facile synthesis of DPC by transesterification of DMC with phenol in the presence of Sm(OTf)₃ has been found. At the optimized conditions, the molar ratio of phenol-to-DMC 4:1, 12 h and 190 °C, the TON reaches 21.8 mol DPC/mol Sm. In comparison to the other conventional catalysts, Sm(OTf)₃ gives higher TON and can be used in aqueous media and in air, and recycled without significant decrease in the catalytic activity. Further study on the detail of this novel catalyst for the transesterification is under way in this laboratory.

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