

Short communication

Transesterification of dimethyl carbonate and phenol to diphenyl carbonate catalyzed by samarium diiodide

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Received 9 May 2006; received in revised form 16 June 2006; accepted 23 June 2006

Available online 4 August 2006

Abstract

Samarium diiodide was found to be a novel and efficient catalyst for the transesterification of phenol and DMC. Compared with other catalysts, samarium diiodide can reach high activity with a very low catalyst amount. When the reaction was carried out between 150 and 180 °C, with a molar ratio of phenol to DMC of 1:1, a reaction time 10 h, a catalyst amount 0.2% (molar ratio to phenol), the conversion of phenol was 52.8%, the yield of MPC and DPC was 26.5% and 22.8%, respectively.

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

1. Introduction

Polycarbonates (PCs) are achieving great importance due to their promising mechanical, optical, heat, engineering and electronic properties [1,2]. Diphenyl carbonate (DPC) has been regarded as a potential substitute material for highly toxic phosgene in the synthesis of PCs [3–5]. Several non-phosgene methods for the synthesis of DPC have been proposed, including oxidative carbonylation of phenol and transesterification between dimethyl carbonate (DMC) and phenol. Though the oxidative carbonylation is an attractive method for the production of DPC due to the cheap and easily available materials, the noble catalysts and the low yield of DPC limit its commercial utilization [6]. The best method as of now appears to be through the transesterification between DMC and phenol in spite of the fact that this reaction is slow and possesses unfavorable equilibrium and thermodynamics [7,8] (Scheme 1).

Various different catalysts have been studied for the transesterification reaction, including homogeneous catalysts such as Lewis acids [9], organometallic compounds [10–14] and heterogeneous catalysts such as TiO₂/SiO₂ [15], MoO₃/SiO₂ [16], Pb–Zn double oxides [6] and so on [17,18]. Though heteroge-

neous catalysts are easy to separate and recover for reuse, their low catalytic activities and selectivities impede their industrialization. And homogeneous catalysts are used in commercial production. Unfortunately, these homogeneous catalysts require a large amount in the transesterification reaction to reach the maximum catalytic activity, which, to some extent, may impair their values in commercial applications. Consequently, the development of more efficient catalysts is desirable.

First introduced by Kagan and co-workers [19], samarium diiodide (SmI₂) has rapidly become a well-established reagent in organic chemical community due to its stability, reactivity, and availability [20]. SmI₂ is air sensitive but tolerant of water and some organic solvents and can be handled with standard techniques. At the same time, it is commercially available and can be conveniently prepared in THF solution at room temperature by the reaction of samarium metal and 1,2-diiodoethane [21]. Samarium diiodide has strong oxophilicity, high reduction potential, and high electropositivity and can be used as Lewis acids or as a powerful one electron-donating reagent. Therefore, most of substrates containing oxygen, halide or p-electrons are active toward SmI₂ [22]. Many important individual reactions found useful in organic synthesis have been promoted by SmI₂ [23], but up to now, to the best of our knowledge, samarium diiodide has not been used as a catalyst for the transesterification of DMC and phenol. Herein, we report our preliminary findings of samarium diiodide in this reaction.

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Scheme 1.

2. Experimental

2.1. Chemical reagents

Ti(OBu)₄, BuSnO₂ and samarium diiodide were purchased from Aldrich Chemical Co. and used as received. Dimethyl carbonate, phenol, ZnCl₂ and FeCl₃ were obtained from local manufactures and were of laboratory reagent grade.

2.2. General procedure

The reaction was carried out in a 100-mL three-neck round-bottomed flask, equipped with a magnetic stirring bar, a nitrogen inlet, a dropping funnel, and a fractionating column connected to a liquid dividing head. Under nitrogen gas, phenol and a catalyst were introduced into the flask. After the mixture was heated to 160 °C, DMC was added drop-wise. The reaction temperature was kept between 150 and 180 °C. During the reaction, a distillate of DMC and methanol was collected slowly in a receiver flask attached to the liquid dividing head for analysis. After the reaction, the mixture was cooled to room temperature and then analyzed by gas chromatograph.

2.3. Product analysis

The azeotrope of DMC and methanol and the reaction mixture were analyzed by gas chromatograph equipped with a SE-30 capillary column (30 m) and a flame ionization detector (FID). Identification analysis of the reaction mixture was conducted on a 6890/5973 GC–mass spectrometer.

3. Results and discussion

3.1. The catalytic activity of samarium diiodide

Conventional Lewis acid catalysts have played important roles in the transesterification of DMC and phenol. SmI₂ is a kind of Lewis acid and can work in aqueous media or in organic solvents, so we thought that SmI₂ should be suitable for this reaction. At the same time, Sm₂O₃ [24] and Sm(OTf)₃ [17] have been reported as catalysts for the transesterification of DMC and

phenol. In addition, SmI₂ has strong oxophilicity, so we thought it might coordinate with the oxygen atom and thus accelerate the reaction rate. Taking all these into consideration, we decided to explore the catalytic behavior of SmI₂ in the transesterification between DMC and phenol.

Lewis acid, tetrabutyl titanate and dibutyltin oxide are traditionally used as catalysts for the transesterification of DMC and phenol. For comparison, the catalytic activities of samarium diiodide, Lewis acids, Ti(OBu)₄ and Bu₂SnO were tested in a refluxing batchwise reactor. As shown in Table 1, the activities of FeCl₃ and ZnCl₂ were very low when the catalyst amount was only 0.2%. Ti(OBu)₄ and Bu₂SnO had higher activities than Lewis acids. Among all these tested catalysts, SmI₂ had the highest activity though a small quantity of by product, anisole, was formed. Mei et al. [18] reported that when the reaction was carried out at 190 °C with the molar ratio of phenol-to-DMC 4:1, the molar ratio of Sm-to-DMC 1:70 for 12 h, the conversion of DMC was 34.4%. It is obvious that the catalytic activity of SmI₂ was also much higher than that of Sm(OTf)₃. The high activity of SmI₂ might ascribe to its strong oxophilicity. SmI₂ might coordinate with oxygen atom in the reactant molecule and thus accelerate the reaction rate.

3.2. The effect of catalyst amount on the transesterification reaction

The effect of catalyst amount on the transesterification of DMC and phenol was studied. As shown in Table 2, the conversion of phenol increased rapidly when the molar ratio of SmI₂/phenol was below 0.002. When the molar ratio of SmI₂/phenol was above 0.002, the conversion of phenol kept almost unchanged while the yield of anisole kept increasing, so the optimal catalyst amount might be 0.002. The data also showed that SmI₂ could reach its high catalytic activity with a very low catalyst amount, while other catalysts including titanium esters and BuSnO₂ required a large amount in this reaction to reach the maximum catalytic activity (usually the catalyst amount was 1–5% of phenol or DMC) [7,8]. Therefore, SmI₂ is an economic and efficient catalyst for the transesterification of DMC and phenol.

3.3. The effect of molar ratio of phenol/DMC on the transesterification reaction

The effect of molar ratio of phenol/DMC on the transesterification reaction was also studied. As shown in Table 3, when

Table 1
Transesterification of phenol and DMC catalyzed by SmI₂ and some other catalysts

Catalyst	Conversion of phenol (%)	Yield of MPC (%)	Yield of DPC (%)	Yield of AN (%)	Transesterification selectivity (%)
SmI ₂	47.7	26.0	18.7	2.3	93.7
Bu ₂ SnO	21.4	14.7	6.7	–	100
Ti(OBu) ₄	40.4	21.2	17.5	–	95.8
FeCl ₃	4.5	3.6	0.6	Trace	93.3
ZnCl ₂	6.7	5.1	1.4	Trace	97.0

MPC: methyl phenyl carbonate; DPC: diphenyl carbonate; AN: anisole. Reaction condition: temperature: 150–180 °C, the molar ratio of phenol/DMC: 1, the molar ratio of catalyst/phenol: 0.2%, reaction time: 8 h, the mole of phenol: 0.2 mol.

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