

Novel process for synthesis of 1,1,3,3-tetrabutyl-1-methoxy-3-isocyanatodistannoxane

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Abstract

A new process for synthesis of 1,1,3,3-tetrabutyl-1-methoxy-3-isocyanatodistannoxane (TBMI) from dibutyltin oxide (DSnO), methyl carbamate and methanol was proposed. The structure of the TBMI was confirmed by UV–Vis, elemental analyses, FTIR and HPLC. The effects of various conditions, such as reaction temperature, pressure, reaction time, molar ratio of the reactants and the stirring speed were investigated in the terms of TBMI yield. The experimental results indicated that the optimal reaction conditions were the molar ratio of methyl carbamate:DSnO of 2:1, the reaction time of 3 h, the reaction temperature of 433 K, the methanol:DSnO molar ratio of 2:1, the initial pressure of 0.4 MPa and the stirring speed of 1000 rpm, respectively. TBMI yield of 96.9% was obtained in the optimal reaction conditions. This process shows some advantages like easy to operate, higher yield, shorter reaction time and lower cost.

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Keywords: Organotin; Catalyst; Yield; Dimethyl carbonate

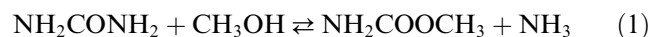
1. Introduction

Dimethyl carbonate (DMC) is a nontoxic organic synthetic intermediate [1,2]. Its molecule contains several active basic groups; as a result, DMC shows excellent reaction activity in carbonylation, carbomethoxylation and methylation, replacing toxic phosgene, dimethyl sulfate. DMC represents a viable alternative to acetate esters and ketones in most applications, from paints to adhesives, taking advantage of its good solvency power. In addition, it can also be used as a fuel additive for the enhancement of the octane number [3–8].

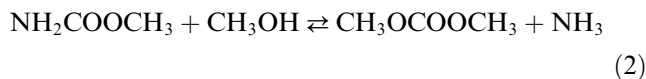
The DMC synthesis techniques reported mainly consist of phosgenation of methanol, oxidative carbonylation of methanol, transesterification of ethylene

carbonate with methanol [9–11]. Each of the aforementioned processes has either commercial or technical disadvantages which make it desirable in the industry to develop a new process which avoids such set backs. For example, the phosgenation is a complicated and expensive process, and phosgene is extreme toxicity. Oxidative carbonylation of methanol are the low production rate, high cost for the separation of ternary azeotrope, methanol–water–DMC, the need for corrosion resistant reactors. Transesterification of ethylene carbonate with methanol is operationally and economically unfavorable since the production of the DMC always entails the simultaneous production of a great deal of glycol.

Some researchers disclosed the new process that DMC can be synthesized in a two step reaction from urea and methanol via methyl carbamate (MC) intermediate [12–15].

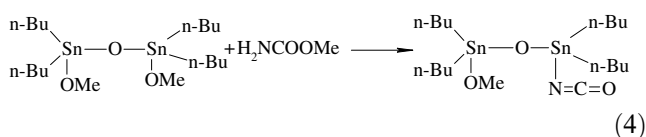
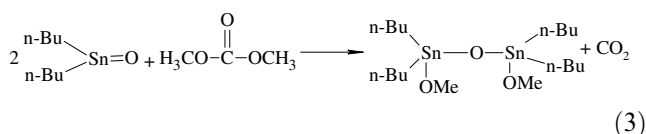


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The most active catalysts reported in the literature are organotin derivatives such as DSnO, dibutyldimethoxytin, dibutyldiisocyanatotin, dibutylisocyanatomethoxytin, 1,1,3,3-tetrabutyl-1,3-diisocyanatodistannoxane and TBMI. Dibutyldimethoxytin, dibutylisocyanatomethoxytin and TBMI have similar activity and are more active than dibutyloxotin for the synthesis of DMC. They are also suitable for various other applications such as transesterification, esterification and transamination [13–17].

TBMI was customarily synthesized quantitatively in a two-step process from DSnO using dimethyl carbonate in accordance with the equations set forth below [18]:



Because above-mentioned the synthetic route needs two steps, technological flow is relatively long, preparation and purification were complex. Moreover, it has high cost because of using expensive starting materials and a great deal of toxic toluene as solvent. Hence, it is necessary to develop one kind of low cost synthetic route to TBMI.

This paper presents a new process for the synthesis of TBMI from dibutyltin oxide, methyl carbamate and methanol with one step. The course of preparation and purification were simple. Low cost methanol was used in the new process, instead of DMC and toluene in above process. Proposed new routes shows some advantages such as easy to operate, higher yield, shorter reaction time and lower cost.

2. Experimental

2.1. Materials

MC and methanol were purchased from Xi'an Chemical Reagent of China. Dibutyltin oxide was purchased from Shanghai Chemical Reagent of China. All the chemicals were of analytical grade and were used without further purification. N_2 (>99.9%) was purchased from Xi'an Chemical Corporation of China. The standard sample MBTI was synthesized according to the literature [17].

2.2. Equipment and apparatus

The experiments were carried out in a stainless steel 750 ml autoclave with electric heating and dynamoelectric stirring. The scheme of reaction system is shown in Fig. 1. Dibutyltin oxide, MC and methanol were added to the autoclave in turn. The autoclave was firstly flushed with nitrogen to replace air within the reactor, then, the autoclave was pressurized with nitrogen to the desired initial pressure and was heated to the desired temperature with stirring. After the reaction was complete, the excess methanol was removed by distillation from the mixture at a temperature of 343–353 K. The mixture formed double layers, after cooling. The upper layer was excess MC, and under layer was TBMI. The TBMI was dried by vacuum at 333–343 K after it was obtained by separating funnel. The TBMI was crystallized on standing.

2.3. Analysis

The UV–Vis absorption spectra were completed by UV–Vis-1200 spectrophotometer, methanol as solvent. Nicolet Avatar 360 FT-IR spectrometer (using OMNIC sampler) was employed for IR studies. HPLC analyses were performed on a Shimadzu 10avp, high performance, liquid chromatograph, using a Hypersil C_{18} column ($L = 25$ cm, $D = 4.6$ mm, Film thickness = 5 μm), with mobile phase methanol, Flow: 1.0 ml min^{-1} , UV detector, wavelength: 345 nm, column temperature = 303 K. Elemental analyses were completed on Perkin–Elmer 2400. Analysis of the Sn content was completed by weight analysis. The external standard method was adapted to the quantitative analysis of the product.

2.4. Calculations

The yield of TBMI was calculated using following formula:

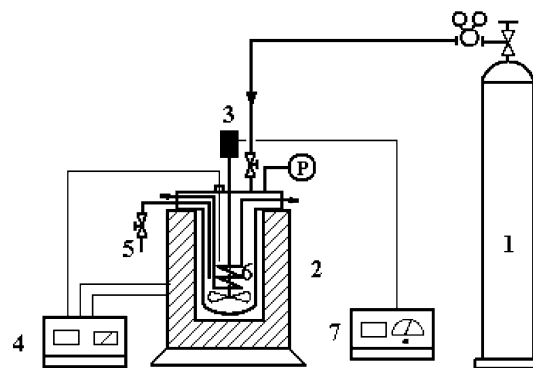


Fig. 1. Schematic diagram of the experimental apparatus: 1, N_2 cylinder; 2, autoclave; 3, stirrer; 4, temperature controller; 5, sampling port; 6, serpentine cooler; 7, stirring speed controller.

$$Y_{\text{TBMI}} = \frac{\text{Moles TBMI}}{\frac{1}{2} \text{Starting Moles Dibutyltin Oxide}} \times 100\% \quad (5)$$

3. Results and discussion

3.1. Structural analysis

In the experimental conditions, the product was obtained as a kind of semisolid white material, which can be crystallized on standing for some time. Its melting point was 397.6–400.5 K. It was analyzed by UV–Vis, IR elemental analysis and HPLC. Figs. 2 and 3 are UV–Vis and IR spectra, respectively.

From Fig. 2, it can be known that the product has no absorption within the range of visible light (400–800 nm) and has absorption within the range of ultraviolet (200–400 nm). This shows that the molecule of the product contains unsaturated group. The unsaturated group may be N=C=O.

From Fig. 3, the peaks of IR at 2203.64 and 1058.93 cm^{-1} are N=C=O, OMe, respectively. The IR data of the product is accord with TBMI's in the literature [13,16].

Elemental analysis: MW = 1110. Calc. for: $\text{C}_{36}\text{H}_{78}\text{N}_2\text{O}_6\text{Sn}_4$: C, 38.90; H, 7.03; O, 8.65; N, 2.52; Sn, 42.90%. Found: C, 38.96; H, 7.11; O, 8.15; N, 2.58; Sn, 41.69%.

HPLC analysis: the HPLC chromatogram of the product exhibited a single peak. The retention time was at 7.56 min.

At the same time, TBMI as standard sample was synthesized according to the literature [17], and was analyzed like the product obtained using this process. All analytical data of the compound compared with the standard sample. The results of comparison showed that all kinds of analytical data were as same as the standard sample.

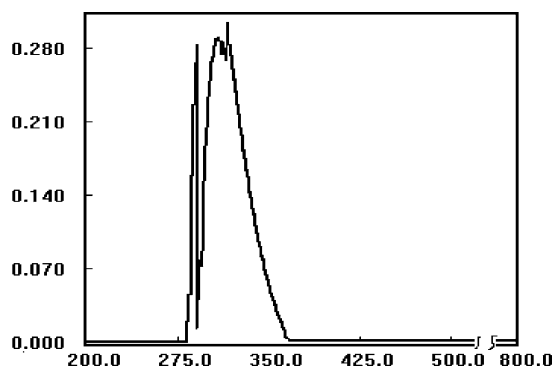


Fig. 2. UV–Vis absorption spectra of the product.

From above analysis, it can be known that the product obtained adopting this process is real TBMI.

3.2. Effect of MC:DSnO molar ratio on TBMI yield

The effect of MC:DSnO molar ratio on TBMI yield is shown in Fig. 4. It can be known from this figure, TBMI yield increased with the increasing of the molar ratio in MC:DSnO, however, it increased slightly after the molar ratio of MC:DSnO exceeded 2:1. MC:DSnO molar ratio 2:1 thus was selected. The TBMI yield reached 96.9% in this case.

3.3. Effect of reaction time on TBMI yield

Fig. 5 shows the effect of reaction time on TBMI yield. From Fig. 5, it can be observed that TBMI yield increased rapidly before 3 h and reached the maximum in 3 h. Then, the TBMI yield gradually decreased. For longer reaction times, TBMI was hydrolyzed due to water formed in course of reaction. At the same time, the TBMI was getting brown-red color as a result its quality went bad at long reaction time. Thus, the optimal reaction time is about 3 h.

3.4. Effect of reaction temperature on TBMI yield

The reaction temperature can affect TBMI synthesis reaction very favorably as shown in Fig. 6. It was apparent that TBMI yield rapidly increased in a range of 393–433 K. TBMI yield decreased when reaction temperature exceeded 433 K. Very higher reaction temperature can cause thermal decomposition of MC, and TBMI color to strengthen. It can be known that 433 K is the optimal reaction temperature for the synthesis of TBMI. The reaction pressure in the autoclave was 2.1 MPa at 433 K.

3.5. Effect of the methanol:DSnO molar ratio on TBMI yield

Fig. 7 shows the effect of the methanol:DSnO molar ratio on TBMI yield. From Fig. 7, it can be known that TBMI yield increased with the increasing of feed rate for fresh methanol. The change of TBMI yield was slight when the methanol:DSnO molar ratio exceeded 2:1. Thus, the methanol:DSnO molar ratio 2:1 was selected in this process.

3.6. Effect of the initial pressure on TBMI yield

Fig. 8 shows the effect of the initial pressure on TBMI yield. From Fig. 8, it can be observed that TBMI yield increased with the increasing of the initial pressure. TBMI yield changed slightly after the initial pressure exceeded 0.4 MPa. The methanol is both a reactant and a

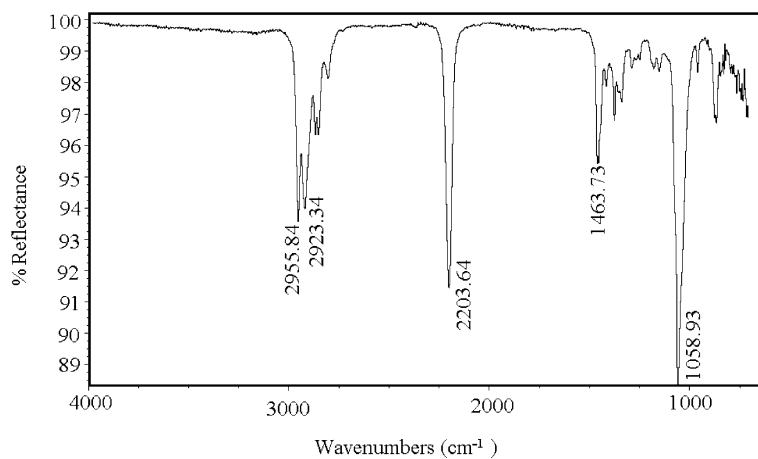


Fig. 3. IR spectra of the product.

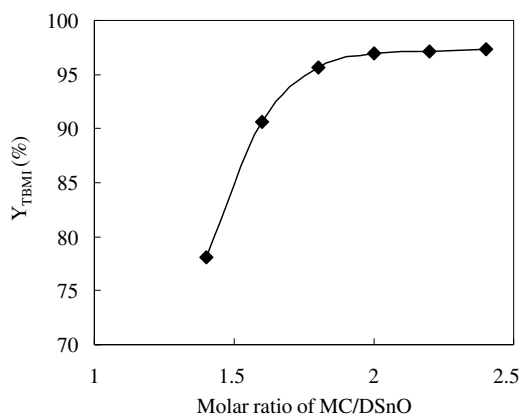


Fig. 4. The effect of methanol:urea molar ratio on TBMI yield. Reaction time: 3 h; reaction temperature: 433 K; methanol:DSnO = 2:1; the initial pressure: 0.4 MPa, the stirring speed: 1000 rpm.

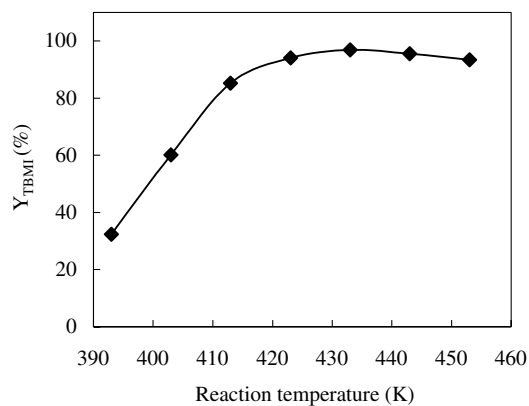


Fig. 6. The effect of reaction temperature on TBMI yield. MC:DSnO molar ratio: 2:1; reaction time: 3 h; methanol:DSnO = 2:1; the initial pressure: 0.4 MPa; the stirring speed: 1000 rpm.

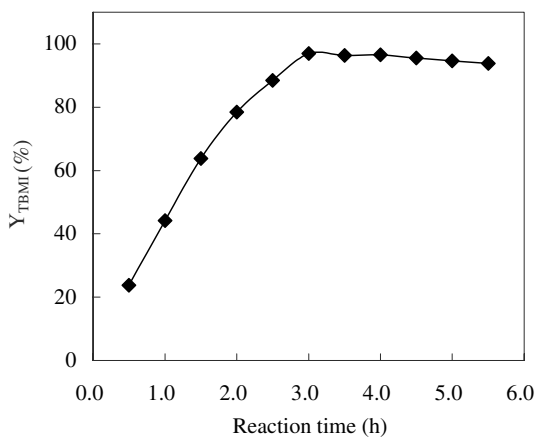


Fig. 5. The effect of reaction time on TBMI yield. MC:DSnO molar ratio: 2:1; reaction temperature: 433 K; methanol:DSnO = 2:1; the initial pressure: 0.4 MPa; the stirring speed: 1000 rpm.

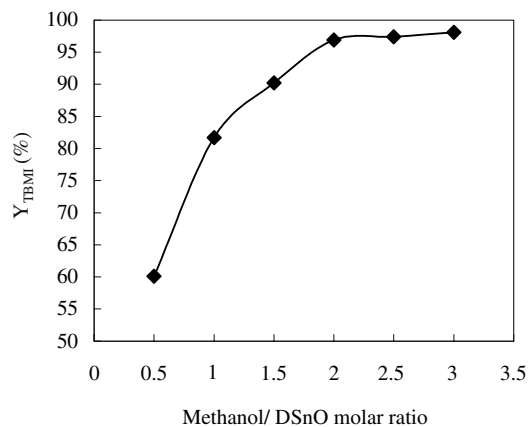


Fig. 7. The effect of the flow rate of fresh methanol on TBMI yield. MC:DSnO molar ratio: 2:1; reaction time: 3 h; reaction temperature: 433 K; the initial pressure: 0.4 MPa; the stirring speed: 1000 rpm.

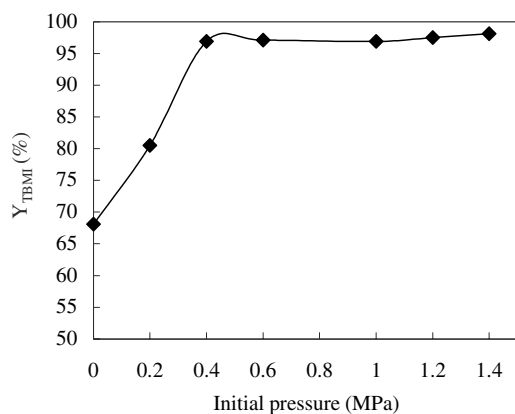


Fig. 8. The effect of the initial pressure on TBMI yield. MC:DSnO molar ratio: 2:1; reaction time: 3 h; reaction temperature: 433 K; methanol:DSnO = 2:1; the stirring speed: 1000 rpm.

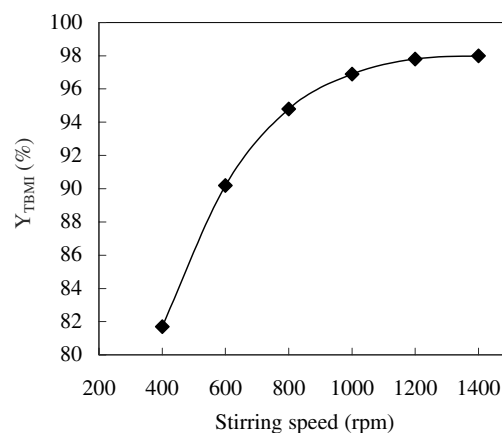


Fig. 9. The effect of the Stirring speed on TBMI yield. MC:DSnO molar ratio: 2:1; reaction time: 3 h; reaction temperature: 433 K; methanol:DSnO = 2:1; the initial pressure: 0.4 MPa.

solvent. The saturated vapor pressure of methanol is 1.744 MPa at 433 K. If the reaction pressure is lower than the saturated vapor pressure of methanol at the reaction temperature, methanol will be vaporized from reaction system. Thus, TBMI yield is low at low initial pressure. The reaction pressure was 2.1 MPa under this reaction condition, when the initial pressure was 0.4 MPa.

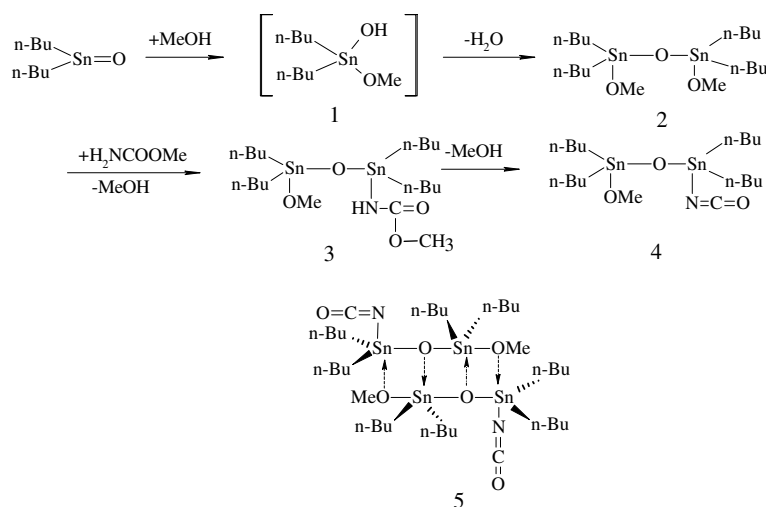
3.7. Effect of the stirring speed on TBMI yield

The stirring speed on MC yield is shown in Fig. 9. With the increasing of the stirring speed, TBMI yield was increased. Because this reaction is heterogeneous phase reaction, the higher stirring speed results the higher reaction rate. However, TBMI yield increased slightly

after the stirring speed exceeded 1000 rpm. In this process, the stirring speed 1000 rpm was selected.

3.8. Reaction mechanism

Scheme 1 is reaction mechanism for the formation of TBMI. Firstly, the intermediate dibutyltin methoxyl-hydroxyl, **1**, is produced under the reaction of DsnO with methanol. Then, dibutyltin methoxyl-hydroxyl dehydrates to form 1,1,3,3-tetrabutyl-1,3-dimethoxydis-tannoxane, **2**, via intermolecular dehydration. The reaction of the compound **2**, with MC yields tetrabutyl-methoxycarbamate, **3**. Finally, TBMI, **4** is formed via the compound **3** in intramolecular eliminating one mole MeOH. TBMI is known to exist as dimer, **5**, bound via pentacoordinated tin atoms [19,20].



Scheme 1. Proposed reaction mechanism for the formation of TBMI.

4. Conclusions

1,1,3,3-tetrabutyl-1-methoxy-3-isocyanatodistannoxane from dibutyltin oxide, methyl carbamate and methanol was synthesized with one step. The structure of this compound was confirmed by UV–Vis, elemental analyses, FTIR, and HPLC. The UV–Vis spectrogram was first given. The molar ratio of methyl carbamate/dibutyltin oxide, the reaction time, the reaction temperature, the methanol:dibutyltin oxide molar ratio, the initial pressure and the stirring speed can affect TBMI yield. This process has easy to operate, higher yield, shorter reaction time and lower cost.

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