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Effective synthesis of dialkyl carbonate from CO_2 and alcohols using dibutyltin(IV) oxide catalyst and dehydrating agents

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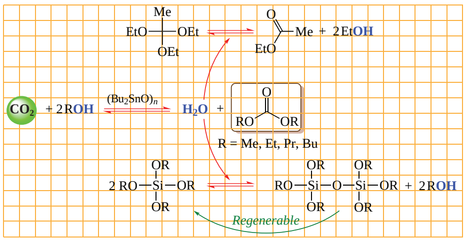
The combination of a dibutyltin(IV) oxide catalyst with an ortho ester as the dehydrating agent exhibited high activity for the direct synthesis of diethyl carbonate from CO_2 and ethanol in 78% yield. With water as a by-product limiting the reaction, a recoverable dehydrating agent is required. When alkoxysilanes were employed for this purpose, various dialkyl carbonates were obtained in yields of 33–45%.



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Dialkyl carbonates such as dimethyl carbonate (DMC), diethyl carbonate (DEC), di-*n*-propyl carbonate (DPrC), dibutyl carbonate (DBC) are of interest due to their ‘green properties’[1] as well as their applications in chemical synthesis,[2] polymer synthesis,[3] battery electrolytes[4] and fuel additives.[5] Dialkyl carbonates have been commercially synthesized by the Bayer phosgenation process,[6] ENIChem alcohol oxycarbonylation process,[7] UBE alkyl nitrate carbonylation process,[8] and the Asahi–Kasei process comprising indirect trans-esterification of alcohols.[9,10] The use of CO_2 for the synthesis of dialkyl carbonates is an appealing greener alternative to conventional procedures. Dialkyl carbonates can be in principle directly obtained from CO_2 and alcohols, however this reaction is inhibited by water generated as the by-product. Therefore, an appropriate combination of the catalyst and dehydrating agent (DA) is required to overcome the equilibrium limitations.

Organometallic complexes based on metal alkoxides have been known to form metal alkoxy carbonates in the presence of CO_2, making them good candidates for catalysts in the synthesis of dialkyl carbonates. To date, $Ti(OR)_4$,[11] $Zr(OR)_4$,[12] $Nb(OR)_5$,[13] $VO(OR)_3$,[14] $R_2Sn(OR)_2$,[15] *etc*. [Figure 1(*a*)] have been reported for catalyzing the direct synthesis of dialkyl carbonates. Among them, Sn-based catalysts, *e.g*. $Bu_2Sn(OMe)_2$ and $Sn(OR)_4$, have been extensively studied for DMC synthesis.[16–18] For example, Sakakura *et al*. found that the addition of Bu_4PI to $Bu_2Sn(OMe)_2$ significantly enhances the yield of DMC.[19] Onaka *et al*. reported that the combination of $Sn(OBu^t)_4$ with C_6F_5OH and pyridine as the additives was the most effective for the direct synthesis of

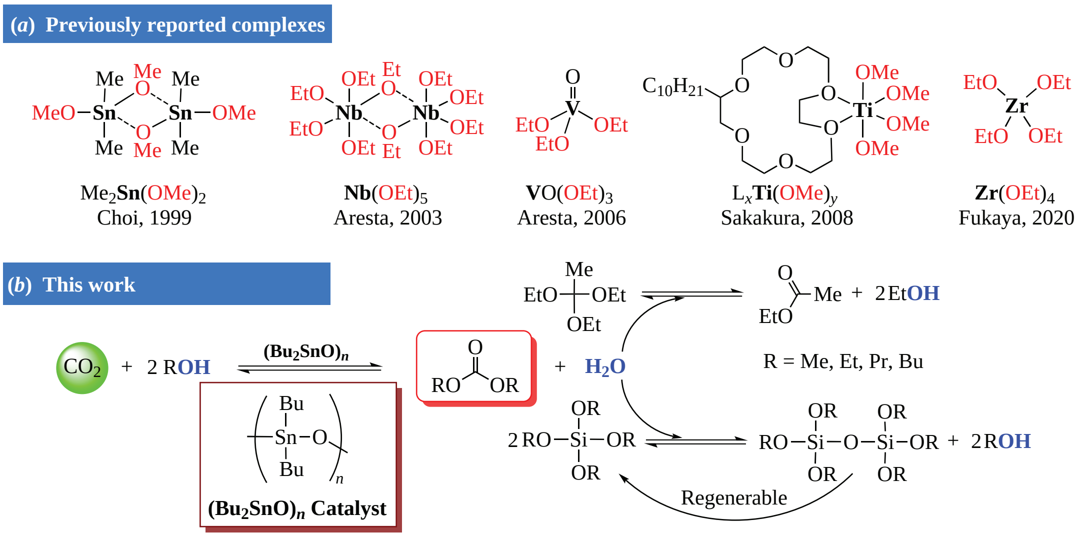
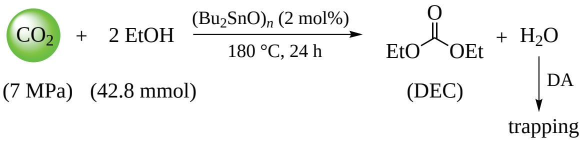


Figure 1 (*a*) Metal alkoxide complexes containing Sn, Nb, V, Ti, and Zr; (*b*) dialkyl carbonate synthesis using $(Bu_2SnO)_n$ and ortho ester or alkoxysilane as the DA.



Scheme 1

Table 1 Effect of DA on the direct synthesis of DEC using $(Bu_2SnO)_n$ catalyst.

Entry	DA	EtOH/DA molar ratio	DEC/ mmol	GC yield (%) based on		By-product
				EtOH	DA	
1	2,2-diethoxy-propane	1 : 0.25	1.51	7	14	acetone
2	1,1-diethoxy-cyclohexane	1 : 0.25	0.26	1	2	cyclo-hexanone
3	$Si(OEt)_4$	1 : 0.25	2.46	11	45	$[(EtO)_3Si]_2O$
4	$Si(OEt)_4$	1 : 0.50	2.68	13	25	$[(EtO)_3Si]_2O$
5	$MeC(OEt)_3$	1 : 0.25	7.81	36	68	$MeCO_2Et$

DMC.[20] In this work, we report the direct synthesis of dialkyl carbonates from CO_2 and alcohols using dibutyltin(IV) oxide $(Bu_2SnO)_n$ as the catalyst and a suitable DA without additives [Figure 1(*b*)].

The DA played an important role in the direct synthesis of dialkyl carbonates from CO_2 and alcohols (Scheme 1). The results shown in Table 1 clearly indicate that the reactivity of the DA in the synthesis of DEC follows the order acetals (entries 1 and 2) < alkoxysilane (entries 3 and 4) < ortho ester (entry 5). This trend was also observed by Sakakura *et al*. who demonstrated that an ortho ester was the most reactive DA in DMC synthesis.[19] Moreover, the EtOH/DA ratio remarkably affected the outcome of DEC formation. Increasing the EtOH/DA mole ratio increased the amount of DEC formed, *i.e*., 2.46 and 2.68 mmol for ratios of 1 : 0.25 and 1 : 0.5, respectively, when tetraethyl orthosilicate $Si(OEt)_4$ was used as the DA (entries 3 and 4). To compare the productivity of $Si(OEt)_4$ and $MeC(OEt)_3$ for DEC formation, the reaction progress was monitored based on the activity profiles (Figure 2).

The activity profile using $Si(OEt)_4$ illustrates that DEC is obtained in 45% yield after 24 h processing. Subsequently, no increase in yield was observed even after prolonging the reaction to 72 h, which is probably due to the equilibrium limitations. With growth of DEC concentration, it might react with the disiloxane by-product $[(EtO)_3Si]_2O$ to form the initial $Si(OEt)_4$, causing the reaction to shift to the left-hand side.[12] In contrast, the use of ortho ester resulted in a higher yield of 65% for DEC after 24 h reaction time, which gradually increased to 78% after 72 h reaction time. This indicates that the ortho ester can effectively remove water from the reaction even at lower concentrations since the ethyl acetate by-product is formed irreversibly. For all screened reaction parameters, such as reaction time (see Figure 2), temperature (see Online Supplementary Materials, Figure S1), and pressure (Figure S2), the use of an ortho ester as a DA provided higher DEC yield than that obtained with $Si(OEt)_4$, clearly suggesting that the ortho ester demonstrates higher affinity toward water than does $Si(OEt)_4$. Although the use of ortho ester resulted in higher yields of DEC, an efficient process to regenerate the ortho ester from the corresponding ester by-product remains a formidable challenge. On the other hand, we have developed a simple method to obtain $Si(OR)_4$ from SiO_2[21] or disiloxane (see Online Supplementary Materials, Scheme S1, *a*), which allowed us to regenerate herein the $Si(OR)_4$ from the corresponding $[(RO)_3Si]_2O$ (see Scheme S1, *b*). Therefore, $Si(OR)_4$ was the DA of choice for direct synthesis of various dialkyl carbonates from CO_2 and alcohols, using $(Bu_2SnO)_n$ catalyst (Scheme 2).

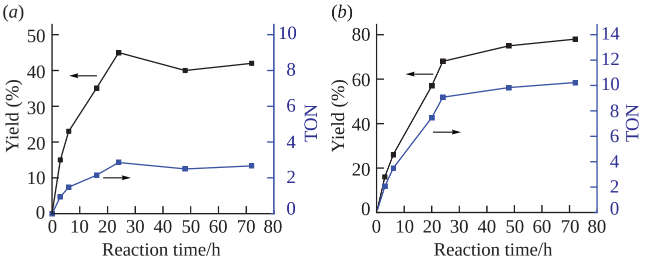
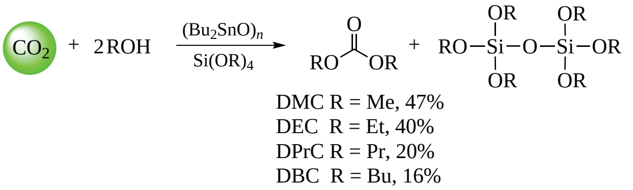


Figure 2 DEC yield and turnover number (TON) as a function of reaction time for (*a*) $Si(OEt)_4$ and (*b*) $MeC(OEt)_3$ as DAs. Reaction conditions: EtOH (42.8 mmol), DA (10.7 mmol), CO_2 (7 MPa), $(Bu_2SnO)_n$ catalyst (0.86 mmol), 180 °C. GC yield with internal standard based on DA.



Scheme 2 *Reagents and conditions*: ROH (42.8 mmol), CO_2 (initial pressure at room temperature 5 MPa), $(Bu_2SnO)_n$ (0.86 mmol), $Si(OR)_4$ (10.7 mmol), 180 °C, 24 h. Yield of dialkyl carbonates are calculated based on $Si(OR)_4$.

Alcohols with longer chain lengths tend to give lower yields (yield drop from 47 to 16% on Me→Bu moving, see Scheme 2), suggesting that the alcohol reactivity decreases with an increase in the alkyl chain lengths.[22] However, different results were obtained when the CO_2 pressure at 180 °C was set to 7 MPa (Table S7). The yield for all dialkyl carbonates was in the range of 33–45%, indicating that the CO_2 pressure remarkably influenced the yield.

In conclusion, we have reported the use of $(Bu_2SnO)_n$ as the catalyst for the direct synthesis of dialkyl carbonates. The DEC yield strongly depended on the alcohol/DA ratio, as well as the type of DA employed. Under all the screened reaction conditions, the ortho ester gave higher DEC yields than did $Si(OEt)_4$. Although the ortho ester was found to be the most effective DA, the use of $Si(OR)_4$ is more favorable, because the latter can be regenerated from the corresponding disiloxane by-product. The combination of the $(Bu_2SnO)_n$ catalyst and $Si(OR)_4$ allowed for the direct synthesis of dialkyl carbonates.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.01.017.

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