SYNTHESIS OF DIMETHYL CARBONATE FROM CARBON DIOXIDE AND METHANOL IN THE PRESENCE OF ORGANOTIN COMPOUNDS

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The effect of a series of organotin(II) compounds of the formulae Bu_2SnX_2 (X = OMe, OEt, OBu, Cl, Br, OPh, OOCMe, $OOC(CH_2)_{10}Me$, $SSNEt_2$; X_2 = O, (OH, Cl)) and $Bu_2XSnOSnXBu_2$ (X = Cl, Br, OOCMe, OBu, n-Bu) in the synthesis of dimethyl carbonate by the title reaction was studied. It was found that the most efficient compounds of the series were the tin alkoxides $Bu_2Sn(OR)_2$ (R = Me, Et, Bu) which afforded the carbonate in up to 160 mole % yields (with respect to the tin compound) under convenient reaction conditions (low CO_2 pressure, 130 – 190 °C, 6 h).

Dimethyl carbonate is an important methylating agent, substituting at present toxic agents such as dimethyl sulfate, methyl halides and lately also phosgene. It is used for preparing the higher carbonates, carbaminates and also as fuel additive. The widely used method of its preparation is the oxidative carbonylation of methanol with the use of copper(II) or palladium(II) catalysts[1 – 3].

Of interest is also the formation of the carbonate by the reaction of carbon dioxide with methanol in the presence of organotin(IV) compounds, especially dialkyltin dialkoxides[4 – 6], tin(IV) tetraalkoxides[6], and also titanium(IV) tetraalkoxides[6]. The use of some other systems, such as a mixture of palladium(II) chloride and copper(II) acetate[7] or of thallium(I) hydroxide and alkali metal iodides[8], has been also reported. The reaction requires usually the elevated temperatures (100 – 150 °C), the carbon dioxide pressure of 0.5 – 1.0 MPa and the reaction time of 12 to 27 h.

However, data on the above reaction are still scarse and mainly the subject of patent literature. Comparison of the properties of organotin compounds under similar conditions has not yet been made. For this reason, in the present work we performed such a study using a broad series of organotin compounds of the type Bu_2SnX_2 (X = OMe, OEt, OBu, Cl, Br, OPh, OOCMe, $OOC(CH_2)_{10}Me$, $SSNEt_2$; X_2 = O, (OH, Cl)) and $Bu_2XSnOSnXBu_2$ (X = Cl, Br, OOCMe, OBu, n-Bu). With the aim to shorten reaction times, dry ice has been used in place of gaseous carbon dioxide.

EXPERIMENTAL

Chemicals. Dimethyl carbonate, 99% (Aldrich, Germany), methanol (p.a. 99.8%, 0.2% water; Lachema, Brno) dried over Na_2SO_4. Dibutyltin oxide (97%, m.p. above 300 °C) and bis(tributyltin) oxide (96%), both Schering, Germany, dibutyltin dichloride (97%, BDH, England), dibutyltin dimethoxide (97%, Metal and Thermit, U.S.A.) were commercial samples. Dibutyltin diethoxide was prepared by reported procedure[9], dibutyltin dibutoxide was obtained either from dibutyltin dichloride[10,11] (m.p. 113 – 115 °C) or from dibutyltin oxide[12] (m.p. 114 – 116 °C). Dibutyl(chloro)tin hydroxide[13] (m.p. 106 – 108 °C) and bis(dibutyl-(acetate)tin oxide[14] (m.p. 51 – 53 °C) were prepared as reported. Bis(dibutylhalogenidotin) oxides were prepared by reported procedure[15], yielding the chloro derivative $Bu_2ClSnOSnClBu_2$ melting at 112 – 114 °C and the bromo compound melting at 104 – 106 °C. The properties of the above tin oxides are given in several studies[16 – 18].

Instruments. All experiments were carried out in a stainless steel Rotamag (STU-made) 250 ml autoclave provided with a frictional magnetic stirring and an electric heating. GLC analyses were made with the use of Chrom 4 instrument equipped with CI-100 integrator (both Laboratorní přístroje, Praha) under the following conditions: FID detector, column temperature 60 °C, injection port temperature 200 °C, 2 m column (4 mm i.d.) packed with 10% silicone elastomer SE-30 on Chromaton N-AW-DMCS (0.100 – 0.125 mm particle size), nitrogen as a carrier gas.

Procedure. The cooled pressure vessel was charged with 150 ml (120 g, 3.75 mol) of cold methanol, then 10 mmol of the tin compound were added, along with 44 g (1.0 mol) of dry ice. The autoclave was closed, warmed up to the reaction temperature and kept at that temperature for required time (from 6 to 12 h). After the reaction was completed, the reaction mixture was cooled to ambient temperature, filtered off and then condensed by distillation to the half volume. The samples of the so obtained mixtures were analyzed gas chromatographically, using toluene as an internal standard.

RESULTS AND DISCUSSION

The results presented in Table I show that dimethyl carbonate is formed from carbon dioxide and methanol in the presence of such organotin compounds which make formation of $R_2Sn(OMe)(OCOOMe)$ (R is usually n-butyl) possible. Thermal decomposition of this substance gives dimethyl carbonate with re-formation of the starting organotin compound, as depicted in the Scheme 1.

$$\underset{\mathbf{A}}{Bu_2Sn(OMe)_2} + CO_2 \longrightarrow \underset{\mathbf{B}}{Bu_2Sn(OCOOMe)(OMe)} \xrightarrow{+\ 2\ MeOH}$$

$$\longrightarrow \underset{\mathbf{A}}{Bu_2Sn(OMe)_2} + (MeO)_2CO + H_2O$$

SCHEME 1

Another route proposed[5] involves the insertion of carbon dioxide molecule to the Sn–O bond of the tin alkoxide, the methanolysis of the product by methanol to afford dimethyl carbonate and dialkyltin dihydroxide of the type $R_2Sn(OH)_2$ which is subsequently esterified by methanol to give the starting organotin(IV) compound.

The reaction is accompanied by partial reesterification[16,17]. This was observed especially with $Bu_2Sn(OBu)_2$ where n-butanol was formed during the reaction. The higher efficiency of the tin dibutoxide when compared to the other alkoxides tested (Table I) could also be explained by transient formation of $Bu_2Sn(OBu)(OCOOBu)$, this being decomposed by methanol to give dimethyl carbonate and butanol. The alternative formation of dibutyl carbonate has not been detected.

The low activity of $Bu_2Sn(OPh)_2$ may be due to steric reasons[18]. Worthy of mentioning is the poor effectiveness of dibutyltin dilaurate, considered by some authors as a convenient reagent for the synthesis of diethyl carbonate[19]. Tributyltin methoxide formed by the reaction of $Bu_3SnOSnBu_3$ with methanol is ineffective likely due to the presence of only one alkoxy group[18].

When compared to previous studies[14,15] in which 260 mole % of dimethyl carbonate (with respect to the molar amount of the tin compound) were obtained at 15 °C with gaseous carbon dioxide after 24 h (the mentioned experiments were made however with

TABLE I
Effect of organotin compounds in the reaction of carbon dioxide with methanol to give dimethyl carbonate (150 °C, total pressure 6.6 MPa, 6 h)

Tin compound, 10 mmol	Additive 5 mmol	Yield[a] of	
		BuOH	$(MeO)_2CO$
Bu_2SnO	–	0	16
$Bu_2Sn(OMe)_2$	–	0	32
$Bu_2Sn(OEt)_2$	–	0	36
$Bu_2Sn(OBu)_2$	–	62	80
Bu_2SnX_2 (X = Cl, Br, OPh, OOCMe, $OOC(CH_2)_{10}Me$,	–	0	0
$SSCNEt_2$)	–		
$Bu_2Sn(OH)Cl$	–	0	0
$Bu_2XSnOSnXBu_2$ (X = Cl, Br, OOCMe)	–	0	0
$Bu_2(BuO)SnOSn(BuO)Bu_2$	–	83	10
$Bu_3SnOSnBu_3$	–	0	0
$Bu_2Sn(OBu)_2$	NaBr	50	85
	NaI	44	78
	MeI	62	88
	I_2	60[b]	103[b]
	I_2	70[c]	118[c]
	I_2	55[d]	122[d]
	I_2	62	145[c, d]

[a] Mole % of $(MeO)_2CO$ per mole % of the Sn compound. [b] 77% BuOH and 135% $(MeO)_2CO$ after 12 h. [c] 200 °C. [d] Na_2SO_4 used as dehydration agent, 66% BuOH and 160% $(MeO)_2CO$ obtained after 12 h.

microquantities needed for GLC analysis), even on using the higher carbon dioxide pressures (up to ten times) at the same reaction temperature, only 80 – 100 mole % and 135 mole % yields of dimethyl carbonate were obtained after 6 and 12 h, respectively. The use of different initiators (iodine, alkali metal halides, methyl iodide) does increases the yields, but only by approximately 10% (Table I), similarly as the higher reaction temperature (up to 200 °C) which is believed[20] to make decomposition of the intermediate easier (the increase by about 15%, see Table I). As already observed[5], the water formed has negative effect on the yield of the reaction. This is confirmed also by the results obtained in this study. The removal of the water of reaction by suitable agents, such as sodium sulfate, zerolite and others, results in the increased dimethyl carbonate yields by about 20%. The pure dimethyl carbonate can be obtained from the reaction mixture by extractive distillation.

Summarizing, the results obtained in the present study indicate that even the choice of relatively broad series of organotin compounds did not overcome limits of the title reaction.

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