

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

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Received January 26, 1994

Accepted June 7, 1994

Dibutyltin dialkoxides react with methanol and carbon dioxide to give dimethyl carbonate in 60 to 220 mole % yields with respect to the organotin compound. The higher yields of the carbonate (150 up to 330 mole %) have been achieved with the use of chemical scavengers of the reaction water.

In the preceding study<sup>1</sup> the synthesis of dimethyl carbonate by the title reaction<sup>2</sup> was effected in the presence of a series of organotin compounds. Their effectiveness has been compared with the use of solid carbon dioxide (dry ice) as one of the reaction components. As the relatively low yields of dimethyl carbonate obtained by this way might result from the moisture introduced by the dry ice, in the present work the dimethyl carbonate synthesis was carried out with the use of gaseous carbon dioxide and in the presence of chemical scavengers of water<sup>3,4</sup>.

### EXPERIMENTAL

*Chemicals.* Methanol (p. a., 99.8% and 0.2% H<sub>2</sub>O, Lachema Brno, The Czech Republic) was dried over sodium sulfate and calcium hydride and distilled through a column filled with sodium, yielding the product containing max. 0.01% H<sub>2</sub>O. Pressurized carbon dioxide (pure, min. 98.5%, max. 0.5% H<sub>2</sub>O, Tetragas Sala, The Slovak Republic) was used as obtained. The water content in both reagents was determined by the Fischer method. Dicyclohexylcarbodiimide (DCC) and trimethyl phosphate (TMP) (both chemical purity grade, min. 99%, Aldrich, U.K.) were used as chemical scavengers of water. The other chemicals were the same as in our previous work<sup>1</sup>.

*Procedure.* All the experiments were carried out in a 150 ml-stainless steel autoclave equipped with magnetic stirring. The reactor was immersed into the electrically heated and temperature controlled silicone bath. The autoclave was charged with 40 ml (32 g, 1 mol) of methanol, followed by 10 mmol of organotin compound, 8 g of drying agent (Na<sub>2</sub>SO<sub>4</sub>, MgSO<sub>4</sub>, molecular sieve and others), eventually by 5 mmol of iodine as the initiator or 50 mmol of the water scavenger (DCC or TMP). After purging with carbon dioxide, the autoclave was pressurized to 0.5 MPa, warmed up to 150 °C (by which the pressure increased to 2.5 MPa), and the reaction mixture was stirred at this temperature for 20 h. After that, the reaction mixture cooled to room temperature was filtered and analyzed by GLC, using toluene as the internal standard. Chromatographic analyses were carried out under the

same conditions as in the previous work<sup>1</sup> (SE-30, SE-31, SE-30I, and Reoplex-400 as stationary phases). The results are presented in Table I.

## RESULTS AND DISCUSSION

The inspection of data presented in Table I shows that when compared to our previous work<sup>1</sup> the use of gaseous carbon dioxide, the lower pressure and the longer reaction time results in the dimethyl carbonate yields greater by 30 to 50 per cent, and that in

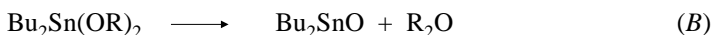
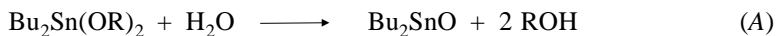
TABLE I  
Activity of organotin compounds in the reaction of carbon dioxide with methanol to give dimethyl carbonate

Compound	Addend <sup>a</sup>	(MeO) <sub>2</sub> CO yield <sup>b</sup> , %
150 °C, 2.5 MPa (total pressure), 20 h		
Bu <sub>2</sub> Sn(OMe) <sub>2</sub>	none	81
	TMP	103
	DCC	118
Bu <sub>2</sub> Sn(OEt) <sub>2</sub>	none	115
	TMP	118
	DCC	170
Bu <sub>2</sub> Sn(OPr) <sub>2</sub>	none	90
	TMP	130
	DCC	170
Bu <sub>2</sub> Sn(OBu) <sub>2</sub>	none	220
	TMP	180
	DCC	317
180 °C, 2.8 MPa (total pressure), 20 h		
Bu <sub>2</sub> Sn(OMe) <sub>2</sub>	none	100
Bu <sub>2</sub> Sn(OEt) <sub>2</sub>	none	133
Bu <sub>2</sub> Sn(OPr) <sub>2</sub>	none	110
	TMP	140
	DCC	177
Bu <sub>2</sub> Sn(OBu) <sub>2</sub>	none	222
	TMP	235
	DCC	333

<sup>a</sup> TMP, DCC, 50 mmol of each, the reaction activated by adding 5 mmol of iodine as the activator.

<sup>b</sup> Expressed as mole % per mol of organotin compound. The dibutyl tin alkoxide is partially decomposed to Bu<sub>2</sub>SnO (Eq. (A)) during the reaction.

the 60 to 220 mole % range with respect to the organotin compound. Nevertheless, the yields are still lower compared to those reported earlier by other authors<sup>2</sup>. The use of iodine as the initiator turned out to be advantageous also in the present reaction (for further compounds see ref.<sup>1</sup>). The favourable effect of increased temperature<sup>1</sup> was here less pronounced. The formation of alcohols by the decomposition of dibutyltin dialkoxides by water (Eq. (A)) was within the range 16 to 55 mole % for dibutyltin diethoxide, 17 to 62 mole % for the dipropoxide, and 22 to 77 mole % for the dibutoxide. Besides formation of dimethyl carbonate, any other thermal decomposition of dibutyltin dialkoxides such as formation of the ethers according to Eq. (B) has not been observed.



The main problem of the synthesis is the removal of the reaction water. Of the inorganic drying agents,  $\text{MgSO}_4$  proved to be suitable, the less so  $\text{Na}_2\text{SO}_4$  and molecular sieves of different types (Calsit, Nalsit, Potasit). Calcium oxide induced a considerable decomposition of the dimethyl carbonate formed. The yields of dimethyl carbonate can however be significantly increased in the presence of chemical scavengers of the reaction water. The best ones turned out to be trimethyl phosphate (TMP), giving 100 up to 230 mole % yields (also with added cation exchanger) and especially dicyclohexylcarbodiimide (DCC), with 160 up to 330 mole % yields (Table I). These water scavengers should be used in at least twofold molar excess with respect to the organotin compound. The fivefold amount of the scavengers has not any additional favourable effect. The water content in the reaction mixture after completion of the reaction was 0.05 to 0.10 wt.% with the use of inorganic drying agents, while the above scavengers reduced it to max. 0.05% with TMP and to max. 0.02% with DCC. By this way of water removal, the results comparable with – and in some respects even better than – those reported earlier by other authors<sup>2</sup> have been achieved in the present study.

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Translated by J. Heflejš.