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Notes

Metal-Catalyzed Dimethyl Carbonate Synthesis from Carbon Dioxide and Acetals

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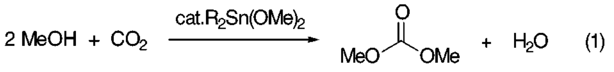
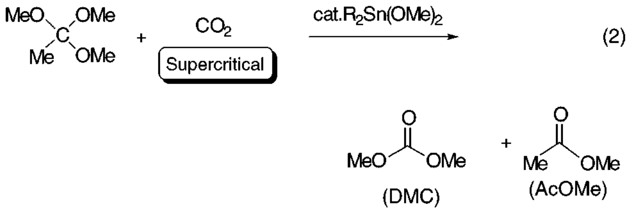
The transformation of carbon dioxide, an inexpensive and abundant C_1 building block, to useful compounds has been a challenge for synthetic chemists and is getting more important because of its environmentally friendly nature (nontoxic and nonflammable).[1] In particular, utilization as a phosgene alternative is quite fascinating. A significant synthetic target starting from CO_2 is dimethyl carbonate (DMC).[2] A considerable effort has already been devoted to the straightforward synthesis of DMC as shown in eq 1 using tin methoxides as a catalyst. However, the catalytic activity is still at the few turnovers level.[3] This poor yield is ascribed to the formation of water that decomposes both tin methoxide and DMC.



(1)

In a previous paper, we achieved improved catalytic efficiencies by reacting trimethyl orthoacetate (a dehydrated MeOH derivative) with supercritical CO_2 (eq 2).[4]



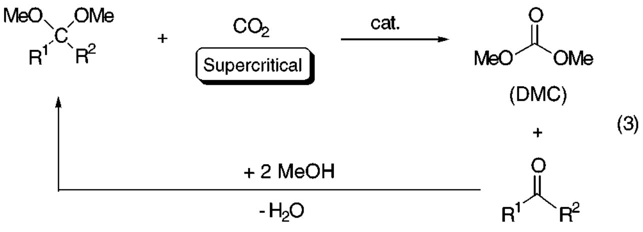
(2)

However, ortho esters are relatively expensive as an industrial raw material. In this paper, we wish to report the DMC synthesis from acetals and CO_2.[5] Note that acetals are much more inexpensive than ortho esters and easily regenerated from carbonyl compounds (eq 3). Hence, the reaction can be considered as a formal DMC synthesis from CO_2 and MeOH.

Table 1. DMC Synthesis from CO_2 and Dimethyl Acetals[a]

entry	R^1 (see eq 3)	R^2	metal complex	additive	yield[b] (%)	
1[c]	Me	Me	$Bu_2Sn(OMe)_2$	none	57	(3000)
2[d]	Et	Et	$Bu_2Sn(OMe)_2$	none	58	(3380)
3	Et	Et	$Bu_2Sn(OMe)_2$	none	26	(1530)
4	Ph	H	$Bu_2Sn(OMe)_2$	none	14	(790)
5	Ph	H	$Bu_2Sn(OMe)_2$	Bu_4PI	7	(430)
6	Ph	H	$Cp^*{}_2TiCl_2$	$Mg(OMe)_2$	8	(460)
7	Ph	H	$Mg(OMe)_2$	none	1	(65)
8[e]	Me	Me	$Bu_2Sn(OMe)_2$	none	88	(5180)

[a] Reaction conditions. Acetals (10 mmol), metal complex (0.17 mmol), additive (0.17 mmol), methanol (8.1 cm^3), CO_2 (300 atm), 180 °C, 24 h. $Mg(OMe)_2$ was added as a methanol solution (1.2 cm^3). [b] Based on acetals. Figures in parentheses are the yields based on metal. [c] After 96 h. [d] After 72 h. [e] CO_2 (2000 atm), 180 °C, 24 h.



(3)

The reaction of acetals takes place under conditions similar to the ortho ester reaction[4] (catalyzed by $Bu_2Sn(OMe)_2$, CO_2 300 atm, 180 °C, 24 h). Generally speaking, acetals derived from dialkyl ketones gave higher yields than aromatic acetals; the yields under the above conditions were in the order 2,2-dimethoxypropane (26%) = 3,3-dimethoxypentane (26%) > 1,1-dimethoxycyclohexane (23%) > dimethoxyphenylmethane (14%). Some typical results are summarized in Table 1. Since the 72 h reactions gave higher DMC yields compared with the 24 h reactions for the above acetals (e.g., entries 2 and 3), the relatively low yields of entries 3−7 are not due to thermodynamic limitations. A rather large MeOH/acetal molar ratio (e.g., 200/10) was effective to prevent the enol ether formation. This is probably related to the equilibrium between enol ethers and acetals.[6]

The effect of the catalyst structure is very significant. Although $Bu_2Sn(OMe)_2$ was a productive catalyst, $Bu_3Sn(OMe)$ was almost inactive. The same tendency was observed in the eq 1 and eq 2 reactions.[4] Other group 14 element dialkoxides such as $Me_2Ge(OMe)_2$ and Ph_2Si-

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[1] For recent reports for CO_2 conversion by homogeneous catalysis, see: (a) Jessop, P. G.; Ikariya, T.; Noyori, R. *Science* **1995**, *269*, 1065−1069. (b) Jessop, P. G.; Ikariya, T.; Noyori, R. *Chem. Rev.* **1995**, *95*, 259−272. (c) Leitner, W. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2207−2221. (d) Morgenstern, D. A.; LeLacheur, R. M.; Morita, D. K.; Borkowsky, S. L.; Feng, S.; Brown, G. H.; Luan, L.; Gross, M. F.; Burk, M. J.; Tumas, W. *Green Chemistry*; Anastas, P. T., Williamson, T. C., Eds.; ACS Symposium Series 626; American Chemical Society: Washington, DC, 1996; pp 132−151. (e) Cheng, M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **1998**, *120*, 11018−11019. (f) Darensbourg, D. J.; Holtcamp, M. W.; Struck, G. E.; Zimmer, M. S.; Niezgoda, S. A.; Rainey, P.; Robertson, J. B.; Draper, J. D.; Reibenspies, J. H. *J. Am. Chem. Soc.* **1999**, *121*, 107−116.

[2] (a) Pacheco, M. A.; Marshall, C. L. *Energy Fuels* **1997**, *11*, 2−29. (b) Aresta, M.; Quaranta, E. *CHEMTECH* **1997**, 30−40. (c) Shaikh, A.-A.; Sivaram, S. *Chem. Rev.* **1996**, *96*, 951−976.

[3] (a) Kizlink, J.; Pastucha, I. *Collect. Czech. Chem. Commun.* **1995**, *60*, 687−692. (b) Kizlink, J.; Pastucha, I. *Collect. Czech. Chem. Commun.* **1994**, *59*, 2116−2118. (c) Kizlink, J. *Collect. Czech. Chem. Commun.* **1993**, *58*, 1399−1402. (d) Yamazaki, N.; Nakahama, S.; Higashi, F. *Rep. Asahi Glass Found. Ind. Technol.* **1978**, *33*, 31−45.

[4] Sakakura, T.; Saito, Y.; Okano, M.; Choi, J.-C.; Sako, T. *J. Org. Chem.* **1998**, *63*, 7095−7096.

[5] A part of the work was presented at the 75th Annual Meeting of Japan Chemical Society, Sakakura, T.; Saito, Y.; Sako, T., Matsuyama, Japan, September 14−19, 1998; Japan Chemical Society; Abstract 1A604.

[6] Schostakowskii, M. F.; Graccheva, E. P.; Kul'bovskaia, N. K. *Zh. Obshch. Khim. (Engl. Transl.)* **1958**, *28*, 2344−2348.

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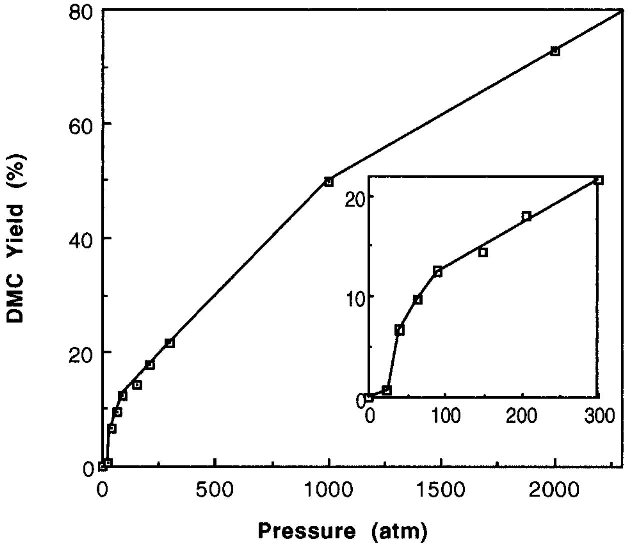
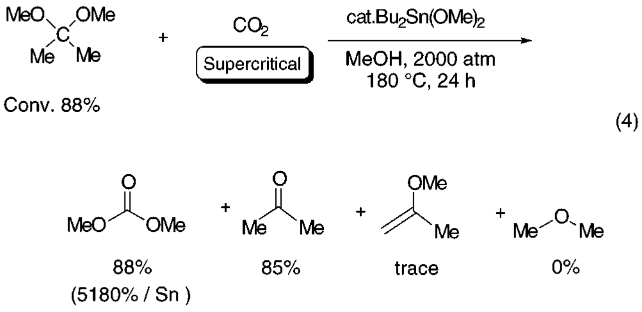


Figure 1. Pressure effect on the $Bu_2Sn(OMe)_2$-catalyzed DMC synthesis from CO_2 and acetal. Reaction conditions: 1,1-dimethoxycyclohexane (10 mmol), $Bu_2Sn(OMe)_2$ (0.17 mmol), MeOH (8.1 cm^3), 180 °C, 24 h.

$(OMe)_2$ did not show catalytic activities. Interestingly, titanocene dichloride coupled with $Mg(OMe)_2$ also promoted the catalysis (entries 6 and 7). Onium salts such as Bu_4PI, which remarkably accelerate the ortho ester reaction, did not promote the present catalysis (entry 5).

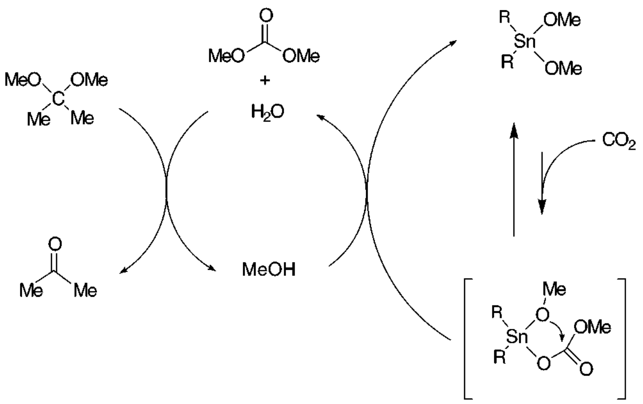
The reaction is also highly dependent on the CO_2 pressure, as shown in Figure 1: the pressures described below correspond to the total pressure of the reaction mixtures at 180 °C. DMC yield increased fairly steadily with the increase in pressure, and the change was especially significant in the region up to 100 atm. The yield finally reached 88% in 24 h at 2000 atm using 2,2-dimethoxypropane as a substrate (entry 8). The entire consequence of this reaction is outlined in eq 4. The amount of DMC was almost the same as that of acetone to give a good material balance. The formation of dimethyl ether, a major byproduct in the ortho ester reaction, was negligible.



(4)

The phase behavior of the reaction was investigated using an autoclave with sapphire windows. Two phases were observed at or below 150 atm, while the reaction mixture was homogeneous above 300 atm. These phenomena and the enhancement of DMC yield at high pressures are presumably attributable to the increase in CO_2 density. Thus, the densities of pure CO_2 at 180 °C are calculated to be 0.200, 0.417, and 1.025 g/cm^3 under 150, 300, and 2000 atm, respectively.[7]

Scheme 1. Possible Catalytic Cycle



A possible catalytic cycle of the tin-based system is shown in Scheme 1. The insertion of carbon dioxide into $R_2Sn(OMe)_2$ afforded $R_2Sn(OMe)(OCO_2Me)$, and the formation of DMC upon thermolysis of the resulting carbonate complex has already been confirmed.[8] The carbonate complex formed from $R_2Sn(OMe)_2$ and CO_2 easily loses CO_2 under a N_2 atmosphere even at room temperature to give the starting dialkoxide. In addition, the equilibrium between the dialkoxide and the carbonate complex should shift in the direction of CO_2 release at higher temperatures. Hence, at the reaction temperature (180 °C), high pressure would be required to generate the carbonate complex at a fair concentration.

From a mechanistic viewpoint, the following observations are also informative and suggest a mechanism moderately different from that for the ortho ester reaction. (i) Onium salts do not improve the catalytic activity. (ii) The addition of MeOH is needed to obtain DMC. (iii) A byproduct is the enol ether rather than dimethyl ether. Presumably, the major role of the acetals is to remove water from the system in order to prevent catalyst decomposition and DMC hydrolysis.

In summary, we have achieved the catalytic formal DMC synthesis from CO_2 and methanol. This work demonstrates the promising prospect of using carbon dioxide, especially under supercritical conditions, as a phosgene substitute in molecular catalysis.

Experimental Section

General Comments. 2,2-Dimethoxypropane, 1,1-dimethoxycyclohexane, dimethoxyphenylmethane, dibutyltin dimethoxide, tributyltin methoxide, bis(pentamethylcyclopentadienyl)titanium dichloride, and magnesium dimethoxide (methanol solution) were purchased from Aldrich Chemical Co. (Milwaukee, WI). Carbon dioxide (Showa Tansan Co., Kawasaki, purity over 99.9%, water content less than 0.01%) was used without further purification. 3,3-Dimethoxypentane[9] and tetrabutylphosphonium iodide[10] were synthesized according to the literature methods. Reaction products were analyzed by GC using capillary columns: J & W Science DB-1 (60 m) and GL Science TC-WAX

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[7] CO_2 densities were calculated according to the literature method; see: Huang, F.-H.; Li, M.-H.; Lee, L. L.; Starling, K. E.; Chung, F. T. H. *J. Chem. Eng. Jpn.* **1985**, *18*, 490−495.

[8] Choi, J.-C.; Sakakura, T.; Sako, T. *J. Am. Chem. Soc.*, in press. See also: Sakai, S.; Fujinami, T.; Yamada, T.; Furusawa, S. *Nippon Kagaku Kaishi* **1975**, 1789−1794.

[9] Napolitano, E.; Fiaschi, R.; Mastrorilli, E. *Synthesis* **1986**, 122−125.

[10] Kline, E. R.; Kraus, C. A. *J. Am. Chem. Soc.* **1947**, *69*, 814−816.

(60 m) on a Shimadzu GC-9A or GC-17A gas chromatograph equipped with a flame ionization detector (FID) using 1,3,5-trimethylbenzene as the internal standard. All the volatile products were also characterized with GC−MS using a HP-5890 gas chromatograph connected to a HP-5971A mass spectrometer (EI 70 eV).

General Procedure. All manipulations were carried out under purified argon. In a stainless steel autoclave (20 cm^3 inner volume), carbon dioxide (liquid, 65 atm) was added to a mixture of dimethyl acetal (10 mmol), a metal alkoxide (0.17 mmol), additive (0.17 mmol), and methanol (8.1 cm^3) at room temperature. The autoclave was heated in an oil bath, and the initial pressure was adjusted to 300 atm at 180 °C. After cooling, 1,3,5-trimethylbenzene (50 μL) was added to the reaction mixture as the internal standard in order to determine product yields by GC. Products were further identified using GC−MS by the comparison of the retention times and fragmentation patterns with the authentic samples.

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