CHEMISTRY LETTERS, pp. 749-752, 1981.

A FACILE PREPARATION OF DIALKYL CARBONATES FROM POTASSIUM CARBONATE AND ALKYL BROMIDES BY USING ORGANOSTANNYL COMPOUND AS A CATALYST

Tatsuo FUJINAMI, Shinichi SATO, and Shizuyoshi SAKAI
Department of Industrial Chemistry, Faculty of Engineering,
Shizuoka University, Hamamatsu 432

Dialkyl carbonates were easily prepared by the heterogeneous reaction of solid potassium carbonate with alkyl bromides in dimethylformamide or dimethylsulfoxide in the presence of organostannyl compound such as hexabutyldistannoxane or chlorotributylstannane. Mixed catalytic system consisting of a tributylstannyl compound and 18-Crown-6 was much effective even in less polar solvents.

Carbonic acid esters have been usually synthesized from phosgene and alcohols. Carbonylation of alcohols with carbon monooxide1) and transesterification of ethylene carbonate with alcohols2) or their derivatives3) have been increasingly attractive as preparative methods without using poisonous phosgene.

On the other hand, little is known about transformation of inorganic carbonates to organic carbonates, except the reaction of silver carbonate with alkyl iodide4). This may be due to insolubilities of inorganic carbonates in any aprotic organic solvents. During the recent developement of solid-liquid phase reaction promoted by phase transfer catalyst, it has been found that potassium and sodium carbonates can act as strong bases for generation of ylide5) or carbanions6) in the presence of a phase transfer catalyst. In addition, a new synthetic route to a polycarbonate from potassium carbonate and α,α′-dibromo-*p*-xylene by using a crown ether was reported7). But simple dialkyl carbonates have not been easily obtained from alkali carbonates. We report here the convenient method for preparation of dialkyl carbonates from potassium carbonate and alkyl bromides by using organostannyl compound as a catalyst.

$$K_2CO_3 \quad + \quad 2RBr \xrightarrow{\text{Organostannyl catalyst}} (RO)_2C{=}O \quad + \quad 2KBr$$

At first, we estimated the catalytic activities of various compounds in the heterogeneous reaction of potassium carbonate with 1,2-dibromoethane to afford ethylene carbonate. Commercially available potassium carbonate (1.66 g, 12 mmol) which had been dried at about 300°C before use, 1,2-dibromoethane (1.88g, 10 mmol), and a catalyst (10 or 5 mol%) were stirred with a magnetic stirrer in dimethylformamide (10 ml) under moistureless conditions for 3 h at 80°C. Conversion of 1,2-dibromoethane to ethylene carbonate was determined by NMR spectrum of the supernatant solution after the reaction. The results are summarized in Table 1.

Table 1. Catalytic activities in the reaction of potassium carbonate with 1,2-dibromoethane to afford ethylene carbonate(EC)[a)]

Catalyst	Yield of EC (%)[b)]	Catalyst	Yield of EC (%)[b)]	Catalyst	Yield of EC (%)[b)]
None	3	$(Me_3Sn)_2S$[c)]	62	$Bu_3SnOSiMe_3$[c)]	36
18-Crown-6	9	Bu_3SnCl	72	$Me_3SiOSiMe_3$[c)]	4
$(PhCH_2)Et_3N^+Cl^-$	5	Ph_3SnCl	65	Ph_2BCl	19
Bu_4Sn	3	Bu_2SnCl_2	2	$SnCl_4$	5
$(Bu_3Sn)_2O$[c)]	70	Bu_2SnO	2	$TiCl_4$	5
$(Bu_3Sn)_2S$[c)]	73	Bu_2SnS	2	$AlCl_3$	12

a) Potassium carbonate (12 mmol), 1,2-dibromoethane (10 mmol), and a catalyst (1 mmol) were stirred in dimethylformamide (10 ml) for 3 h at 80°C. b) Yields were determined by NMR spectra. c) The amount of the dimetallo catalyst was 0.5 mmol.

Well known phase transfer catalyst such as 18-Crown-6 or benzyltriethylammonium chloride was slightly effective but not sufficient for this heterogeneous reaction. We found that the reaction was distinctly accelerated by the addition of triorganostannyl, especially tributylstannyl compounds, while tetrabutyl- and dibutylstannyl compounds were not active at all. Trimethylsilyl and diphenylboryl compounds, or inorganic metal chlorides were also ineffective.

From these results, preparation of various dialkyl carbonates from potassium carbonate and alkyl halides was easily attained by the similar procedure using tributylstannyl catalyst as mentioned above. The yields of dialkyl carbonates isolated by distillation are shown in Table 2. Dimethylformamide and dimethylsulfoxide were good solvents for this reaction and either of these solvents was separable from the dialkyl carbonate by distillation.

Alkyl bromides were more favorable reagents than the corresponding chlorides and iodides. The yield of dimethyl carbonate in Table 2 is remarkably lower than expected from high reactivity of methyl iodide in bimolecular nucleophilic substitution reactions. A rational reason for this fact may be deactivation of the catalyst caused by preferential interaction of the organostannyl compound with iodide ion which is formed as potassium iodide during the reaction with methyl iodide. Actually, the yield (73%) of ethylene carbonate was decreased into 34 and 3% by the addition of 5 and 50 mol% of potassium iodide, respectively, in the reaction of potassium carbonate with 1,2-dibromoethane catalyzed by hexabutyldistannthiane in dimethylformamide for 3 h at 80°C.

IR spectrum showed that chlorotriorganostannane reacted with potassium carbonate to form bis(triorganostannyl) carbonate, $(R_3Sn)_2CO_3$, and its decarboxylation product, $(R_3Sn)_2O$. Hexabutyldistannthiane is an efficient catalyst although its Sn-S bond is more stable than the corresponding Sn-O bond[8)]. Therefore, effective catalytic species must consist of bis(triorganostannyl) derivative such as $(Bu_3Sn)_2O$ or $(Bu_3Sn)_2S$. We assume that these distannyl compounds interact with carbonate ion to form a soluble intermediate, as shown in Scheme 1, acting as a solid-liquid phase transfer catalyst. Even if such interaction has not been established, it will be

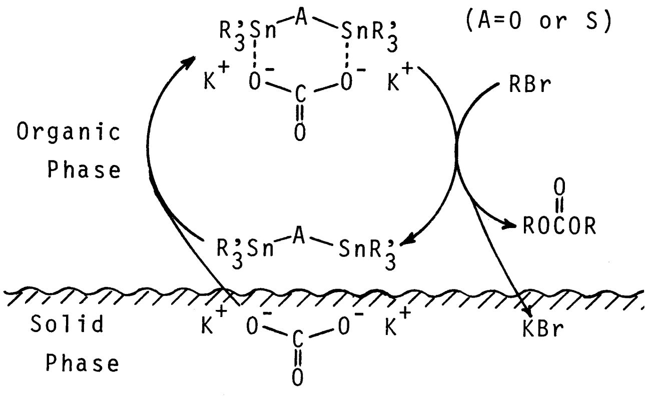
Table 2. Yields of dialkyl carbonates from potassium carbonate and alkyl halides[a)]

Alkyl halide	Catalyst	Solvent	Temperature (°C)	Time (h)	Yield[b)] (%)
MeI	Bu_3SnCl	DMF	40	16	11
EtBr	$(Bu_3Sn)_2O$[c)]	DMF	40	80	89
n-PrBr	Bu_3SnCl	DMSO	60	30	69
i-PrBr	Bu_3SnCl	DMSO	60	30	29
n-BuBr	$(Bu_3Sn)_2O$[c)]	DMF	100	10	51
$PhCH_2Br$	Bu_3SnCl	DMF	40	8	57
$BrCH_2CH_2Br$	$(Bu_3Sn)_2O$[c)]	DMF	100	1	80
$ClCH_2CH_2Cl$	Bu_3SnCl	DMF	60	8	8
$BrCH_2CH_2CH_2Br$	Bu_3SnCl	DMF	60	8	66[d)]

a) Alkyl halide (50-200 mmol), potassium carbonate (two equivalents), catalyst (10 mol%), and solvent (0.6 ml/mmol of potassium carbonate) were used. b) Isolated yield. c) 5 mol%. d) Product, trimethylene carbonate, was partially polymerized during distillation.

supported by NMR observation in which δ_{CH_3} of hexamethyldistannthiane, $(Me_3Sn)_2S$, was shifted from 0.41 to 0.37 ppm and $J_{^{119}Sn-CH}$[9)] from 57.6 to 59.6 Hz by the addition of cesium carbonate (25 mmol/l) in methanol. Furthermore, hexabutyldistannoxane makes potassium carbonate slightly soluble (0.4 mmol/l concentration) in dimethylformamide at 60°C.

In a less polar solvent such as benzene or acetonitrile, tributylstannyl catalyst was not effective. We found a marvelous effect in combination of tributylstannyl compound with 18-Crown-6 but not with a quaternary ammonium salt. Thus the yield of ethylene carbonate in the reaction of potassium carbonate with 1,2-dibromoethane catalyzed by hexabutyldistannthiane in acetonitrile or benzene was dramatically increased by the addition of 18-Crown-6 as shown in Table 3. In this mixed catalytic system, it is interesting to note that the organostannyl catalyst acts as a Lewis acid to interact with carbonate ion and the crown ether is a Lewis base to associate with potassium ion.



Scheme 1 Formation of dialkyl carbonate from potassium carbonate and alkyl bromide

In a successful experiment without solvent, diethyl carbonate was prepared in 90% yield by the reaction of potassium carbonate with ethyl bromide for 40 h at 100°C in a glass autoclave using 0.25 mol% of hexabutyldistannthiane and 0.5 mol% of 18-Crown-6.

Table 3. Mixed catalytic systems[a)]

Catalyst (mol%)	Yield of ethylene carbonate (%)[b)] in CH_3CN	in C_6H_6
None	trace	0
$(Bu_3Sn)_2S$ (5)	5	0
18-Crown-6 (10)	2	0
$(Bu_3Sn)_2S$ (5) + 18-Crown-6 (10)	93	64
$(Bu_3Sn)_2S$ (5) + $(PhCH_2)Et_3N^+Cl^-$ (10)	19	0

a) Reaction conditions: 1,2-dibromoethane(10 mmol), potassium carbonate(15 mmol), and solvent(10 ml); for 10 h at 80°C. b) Yields were determined by NMR spectra.

This work was supported by the Grant-in-Aid for Scientific Research No. 565282 from the Ministry of Education, Science and Culture.

References

1) a) T. Saegusa, T. Tsuda, K. Isayama, and K. Nishijima, *Tetrahedron Lett.*, 1968, 831.
b) T. Saegusa, T. Tsuda, and K. Isayama, *J. Org. Chem.*, 35, 2976(1970).
c) M. Graziani, P. Uguagliati, and G. Cartrun, *J. Organometal. Chem.*, 27, 275 (1971).
d) D. M. Fenton and P. J. Steinwand, *J. Org. Chem.*, 39, 701(1974).
e) K. Kondo, N. Sonoda, and S. Tsutsumi, *Tetrahedron Lett.*, 1971, 4885.
f) K. Kondo, N. Sonoda, and H. Sakurai, *Bull. Chem. Soc. Jpn.*, 48, 108(1975).
2) a) L. K. Frevel and J. A. Gilpin, U. S. Patent 3642858(1972); *Chem. Abstr.*, 76, 99140z(1972).
b) S. Sakai, K. Fujitani, and T. Fujinami, 36th Annual Meeting of the Chemical Society of Japan, April, 1977, Abstr. No. 2C32.
3) S. Sakai, S. Furusawa, H. Matsunaga, and T. Fujinami, *J. Chem. Soc., Chem. Commun.*, 1975, 265.
4) Beilsteins Handbuch, 3, 5.
5) R. M. Boden, *Synthesis*, 1975, 784.
6) M. Fedorynski, K. Wojiciechowski, Z. Matacz, and M. Makosza, *J. Org. Chem.*, 43, 4682(1978).
7) K. Soga, S. Hosoda, and S. Ikeda, *J. Polym. Sci., Polym. Lett. Ed.*, 15, 611(1977).
8) H. Schumann and I. Schumann-Ruidisch, "Organotin Compounds", ed by A. K. Sawyer, Marcel Dekker, Inc., New York(1971), Vol. 2, Chap. 6.
9) J. R. Holmes and H. D. Kaesz, *J. Am. Chem. Soc.*, 83, 3903(1961).

(Received March 23, 1981)