Direct condensation reaction of carbon dioxide with alcohols using trisubstituted phosphine–carbon tetrabromide–base system as a condensing agent

Jun-ichi Kadokawa,* Hideyuki Habu, Shinji Fukamachi, Masa Karasu, Hideyuki Tagaya and Koji Chiba

Department of Materials Science and Engineering, Faculty of Engineering, Yamagata University, Yonezawa 992-8510, Japan

This paper describes the preparation of carbonates by the direct condensation of CO_2 with alcohols using a trisubstituted phosphine–carbon tetrabromide–base system as a condensing agent. The yield of dibenzyl carbonate from CO_2 and benzyl alcohol was at most 90.7%. The reaction of CO_2 with the other primary alcohols such as methanol, ethanol, butan-1-ol, hexan-1-ol, allyl alcohol, and ethylene glycol also gave corresponding carbonates in relatively high yields, whereas yields of carbonates from CO_2 and secondary alcohols were low.

Introduction

Alkyl esters of carbonic acid (dialkyl carbonates), although not as widespread as the aromatic carbonates, *e.g.*, diphenyl carbonate, have found important applications in the field of industrial chemistry.[1] Dimethyl carbonate, especially, has grown in importance with numerous applications, such as a precursor for diphenyl carbonate.[2] Dialkyl carbonates are traditionally prepared by the reaction of phosgene, a highly toxic agent, with the appropriate alcohol or phenol in the presence of an acid acceptor.[3] Since aliphatic polycarbonates have been prepared by the reaction of CO_2 with epoxides,[4] the development of new synthetic methods for carbonates using CO_2 has attracted recently increasing interest from viewpoints not only of a new synthetic reaction, but also of the potential carbon source as well as the environmental aspects.[5] For example, the preparation of dialkyl carbonates from CO_2, alcohols, and alkyl halides has been reported under various conditions.[6] In the reactions, the carbonate anion, derived from CO_2 and an alcohol, acts as a nucleophile, whereas an alkyl halide has an electrophilic nature. Therefore, the reaction takes place *via* nucleophilic substitution of the carbonate anion with the alkyl halide to produce the dialkyl carbonate. However, the direct synthesis of carbonates from CO_2 and alcohols has not been well established so far. To our knowledge, only one clear direct condensation of CO_2 with alcohols to afford the corresponding dialkyl carbonates has previously been reported.[7] The reaction was achieved by using the triphenylphosphine–diethyl azodicarboxylate system as a condensing agent in THF solvent according to the manner of the Mitsunobu reaction. This situation concerning the previous investigations of the direct synthesis of carbonates should be compared with the preparation of urethanes and ureas using CO_2; those compounds have been prepared by direct condensation of CO_2 with an amine and an alcohol, and with amines, respectively, in the presence of an appropriate condensing agent.[5]

Very recently, we have found that the direct polycondensation of CO_2 with benzenedimethanols using a trisubstituted phosphine–carbon tetrabromide–2-cyclohexyl-1,1,3,3-tetramethylguanidine (CyTMG) system[8] as a condensing agent gave poly(oxycarbonyloxymethylenephenylenemethylene)s (Scheme 1).[9] This polymerization is the first example of the synthesis of a polycarbonate from CO_2 and a diol.

Here, we describe the scope and limitation of the direct condensation of CO_2 with alcohols using this type of condensing
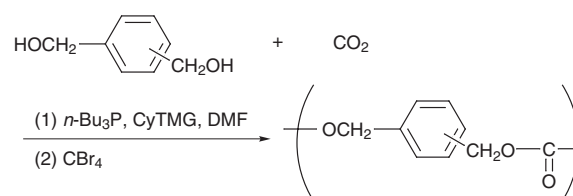
Scheme 1

agent consisting of trisubstituted phosphine, carbon tetrahalide, and base for formation of the corresponding carbonates (Scheme 2).
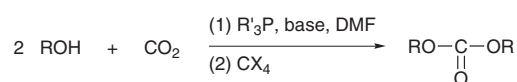
Scheme 2

Results and discussion

Direct condensation of CO_2 with benzyl alcohol

In the direct condensation of CO_2 with benzyl alcohol, the optimum conditions were determined using the condensing agent consisting of various combinations of trisubstituted phosphine–carbon tetrahalide–base. Table 1 summarizes the yields of dibenzyl carbonate obtained by changing the reagents of the condensing agent and solvent. Previous studies had indicated that cyclic carbamates could be generated from CO_2 and amino alcohols using a triphenylphosphine–carbon tetrachloride–triethylamine system as condensing agent.[10] The possibility of carbonate formation from CO_2 and alcohol led us to consider the application of the above condensing agent. Carbonate, however, was not produced at all using this condensing agent (entry 8). Therefore, the other combinations of trisubstituted phosphines, carbon tetrahalides, and bases have been examined in the reaction of CO_2 with benzyl alcohol in DMF to give dibenzyl carbonate. A combination of trisubstituted phosphine, carbon tetrabromide, and a strong base gave dibenzyl carbonate (entries 3–7, 10, 11). Use of carbon tetrachloride did not give a carbonate at all (entries 1 and 9). Tributylphosphine was more suitable as a reagent for the condensing agent than was triphenylphosphine under the same reaction conditions (entries 3 and 10, 5 and 11). When various bases

Table 1 Direct condensation of CO_2 with benzyl alcohol using the condensing agent consisting of various combinations of R_3P–CX_4–base[a]

Entry	R_3P	CX_4	Base	Solvent	Yield (%)[b]
1	n-Bu$_3$P	CCl$_4$	DBU	DMF	0
2	n-Bu$_3$P	CBr$_4$	Pyridine	DMF	0
3	n-Bu$_3$P	CBr$_4$	DBU	DMF	21.8
4	n-Bu$_3$P	CBr$_4$	CyTMG	DMF	33.2
5[c]	n-Bu$_3$P	CBr$_4$	CyTMG	DMF	75.8
6	n-Bu$_3$P	CBr$_4$	CyTMG	DMSO	17.8
7	n-Bu$_3$P	CBr$_4$	CyTMG	NMP	27.4
8	Ph$_3$P	CCl$_4$	Triethylamine	DMF	0
9	Ph$_3$P	CCl$_4$	DBU	DMF	0
10	Ph$_3$P	CBr$_4$	DBU	DMF	8.9
11[c]	Ph$_3$P	CBr$_4$	CyTMG	DMF	56.6

[a] At room temperature for 2 h; [benzyl alcohol]:[R$_3$P]:[CX$_4$]:[base] = 2.0:1.0:5.0:2.0. [b] Determined by ^{1}H NMR spectra. [c] At room temperature for 15 h; [benzyl alcohol]:[R$_3$P]:[CBr$_4$]:[CyTMG] = 2.0:1.0:10.0:2.0.

Table 2 Effect of molar proportions of tributylphosphine–carbon tetrabromide–CyTMG on the yield of dibenzyl carbonate in the reaction of CO_2 with benzyl alcohol[a]

Entry	[Benzyl alcohol]: [n-Bu$_3$P]:[CBr$_4$]:[CyTMG]	Yield (%)[b]
1	2.0:1.0:2.0:2.0	23.8
2	2.0:1.5:2.0:2.0	90.7
3	2.0:1.0:5.0:2.0	33.2
4	2.0:1.0:10.0:2.0	59.5
5	2.0:1.0:10.0:1.0	50.3
6	2.0:1.5:10.0:2.0	88.8
7	2.0:2.0:10.0:2.0	54.3

[a] At room temperature for 2 h in DMF. [b] Determined by ^{1}H NMR spectra.

Table 3 Effect of reaction temperature and time on the yield of dibenzyl carbonate in the reaction of CO_2 with benzyl alcohol[a]

Entry	Temperature (T/ °C)[b]	Time (t/h)	Yield (%)[c]
1	0	2	16.3
2	rt	0.25	30.6
3	rt	2	90.7
4	rt	40	86.0
5	50	2	32.2

[a] The reaction was carried out in the presence of tributylphosphine, carbon tetrabromide, and CyTMG in DMF; [benzyl alcohol]:[n-Bu$_3$P]:[CBr$_4$]:[CyTMG] = 2.0:1.5:2.0:2.0. [b] rt = room temperature. [c] Determined by ^{1}H NMR spectra.

Table 4 Direct condensation of CO_2 with various alcohols using tributylphosphine–carbon tetrabromide–CyTMG system as a condensing agent[a]

Entry	Alcohol	Yield[b]/Isolated yield[c] (%)
1	Benzyl alcohol	90.7
2[d]	Benzyl alcohol	76.3/67.3
3	Methanol	86.1
4	Ethanol	77.3
5	Propan-1-ol	70.2
6	Propan-2-ol	22.0
7	Butan-1-ol	54.4
8[d]	Butan-1-ol	43.9/37.1
9	Butan-2-ol	14.2
10	Hexan-1-ol	63.1
11[e]	Hexan-1-ol	38.3/24.2
12	Cyclohexanol	trace
13	Allyl alcohol	64.1
14[f]	Ethylene glycol	78.1

[a] At room temperature for 2 h in DMF; [alcohol]:[n-Bu$_3$P]:[CBr$_4$]:[CyTMG] = 2.0 mmol:1.5 mmol:2.0 mmol:2.0 mmol. [b] Determined by ^{1}H NMR spectra. [c] Isolated yield by column chromatography. [d] [alcohol]:[n-Bu$_3$P]:[CBr$_4$]:[CyTMG] = 10 mmol:7.5 mmol:10 mmol:10 mmol. [e] [alcohol]:[n-Bu$_3$P]:[CBr$_4$]:[CyTMG] = 20 mmol:15 mmol:20 mmol:20 mmol. [f] [ethylene glycol]:[n-Bu$_3$P]:[CBr$_4$]:[CyTMG] = 1.0 mmol:1.5 mmol:2.0 mmol:2.0 mmol.

were used for the reaction, CyTMG, a strong, hindered, non-nucleophilic and highly polarizable base, was more effective than other bases such as DBU (entries 3 and 4).[11] The yield was higher when the reaction was carried out in DMF solvent compared with other solvents such as DMSO and 1-methyl-2-pyrrolidone (NMP) (entries 4, 6 and 7).

Then, the optimum molar proportions of tributylphosphine, carbon tetrabromide, and CyTMG were examined at room temperature for 2 h to give dibenzyl carbonate in higher yield (Table 2). When the molar proportions of benzyl alcohol, tributylphosphine, carbon tetrabromide, and CyTMG were 2.0:1.5:2.0:2.0, the yield of dibenzyl carbonate was highest (90.7%) (entry 2). When a larger amount of each reagent of the condensing agent was used, the yields decreased. When the reaction temperature and time were changed from room temperature and 2 h, respectively, the yields decreased in all cases (Table 3). A larger scale reaction of CO_2 with benzyl alcohol (10.0 mmol) under conditions identical to those of entry 2 in Table 3 also gave dibenzyl carbonate in 76.3% yield, and which was isolated by column chromatography on silica gel (cyclohexane–ethyl acetate = 50:1 v/v) in 67.3% yield (entry 2 in Table 4). The structure was determined as dibenzyl carbonate by ^{1}H NMR and IR spectra (see Experimental section). Furthermore, thin-layer chromatographic (TLC) data of the isolated product were identical with those of an authentic sample. In this reaction system, a weight increase corresponding to *ca.* 10.0 mmol of CO_2 was observed by adding CO_2 for 15 min to a mixture of benzyl alcohol (10.0 mmol) and CyTMG (10.0 mmol) in DMF. This result indicated that sufficient CO_2 for the reaction was introduced in the reaction mixture.

Direct condensation of CO_2 with the other alcohols

To survey the scope and limitations of the condensation reaction using the condensing agent composed of tributylphosphine, carbon tetrabromide, and CyTMG, the reaction of CO_2 with various alcohols was carried out under conditions similar to those of entry 3 in Table 3. The yields were directly analyzed by ^{1}H NMR analyses. As the results in Table 4 show, the reaction using primary alcohols gave the corresponding carbonates in relatively high yields (entries 3–5, 7, 10 and 13). Formation of the carbonates was confirmed further by TLC analyses of the reaction mixtures in comparison with the corresponding authentic samples. The organic solvent-extractable carbonates with high boiling points such as dibutyl carbonate and dihexyl carbonate were prepared by larger scale reactions under the same conditions and were isolated by silica gel column chromatography in 37.1 and 24.2% yield, respectively (entries 8 and 11). The yields of carbonates from secondary alcohols such as propan-2-ol and butan-2-ol were not high, and cyclohexanol, a secondary alcohol with a bulky side-group, gave only a trace of dicyclohexyl carbonate (entries 6, 9, and 12). When ethylene glycol was used as a hydroxy compound, ethylene carbonate was obtained in 78.1% yield by cyclization (entry 14).

Mechanism of the reaction

In the ^{31}P and ^{1}H HMR spectra of the reaction mixture obtained under the conditions of entry 3 in Table 3, the

formation of tributylphosphine oxide and bromoform was confirmed. Moreover, the peak due to phosphonium species in the ^{31}P NMR spectrum was detected when the reaction of CO_2 with benzyl alcohol was followed by NMR spectroscopy. On the basis of the above observations, the following mechanism is proposed to explain the present reaction using the tributylphosphine–carbon tetrabromide–CyTMG system (Scheme 3);

Scheme 3
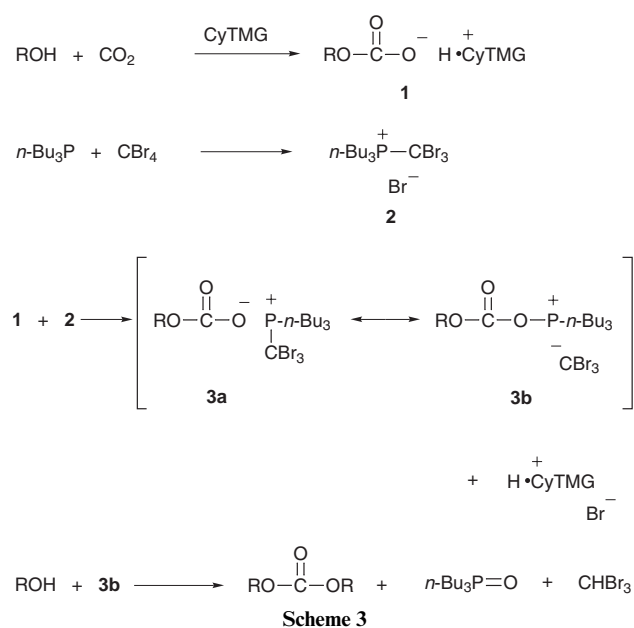
a similar mechanism was suggested to be involved in the formation of cyclic urethanes from amino alcohols and CO_2 using the triphenylphosphine–carbontetrachloride–triethylamine system.[10] The first step is the formation of carbonate anion **1** by the reaction of alcohol with CO_2 in the presence of CyTMG. On the other hand, the reaction of tributylphosphine with carbon tetrabromide takes place to form the (tribromomethyl)-phosphonium bromide **2**. Then an ion-exchange reaction between these two species **1** and **2** occurs, giving rise to phosphonium intermediate **3a**, which is probably in equilibrium with **3b**. A phosphoniumoxy group in **3b** is a good leaving group; the nature of anion **1** can be changed from nucleophilic to electrophilic by the conversion into **3b** having this leaving group. Therefore, nucleophilic attack of the alcohol onto the carbonyl carbon of **3b** can occur, followed by Arbuzov-type reaction to lead to a carbonate, tributylphosphine oxide, and bromoform.

Although the present condensing agent has traditionally been used as a halogenating agent of alcohols,[8] the formation and participation of alkyl halides in the present reaction systems were excluded since benzyl bromide was not detected in the ^1H NMR spectrum of the reaction mixture from benzyl alcohol and CO_2. Furthermore, benzyl bromide was totally recovered from the reaction mixture, and the yield of dibenzyl carbonate was the same as that of entry 1 in Table 4, when the reaction of benzyl alcohol with CO_2 was carried out in the presence of an equimolar amount of benzyl bromide.

Conclusions

Direct condensation of CO_2 with alcohols was achieved using the tributylphosphine–carbon tetrabromide–CyTMG system as a condensing agent. The reaction of CO_2 with primary alcohols gave the corresponding carbonates in high or relatively high yields. From CO_2 and secondary alcohols, however, the carbonates were produced in only low yields. In the reaction of CO_2

with ethylene glycol, cyclization took place to produce ethylene carbonate in 78.1% yield.

Experimental

Materials and methods

Carbon dioxide from a gas cylinder was dried through a silica gel tube. Alcohols and DMF were purified by distillation. CyTMG was prepared according to the literature.[12] Other reagents were used without further purification. ^1H NMR spectra were recorded on a Varian Mercury 200 spectrometer. J-Values are given in Hz. IR spectra were recorded on a Horiba FT-200 spectrometer.

The identities and purities of dialkyl carbonates $(RO)_2CO$ were confirmed by TLC analysis on silica gel 60 with n-pentane–diethyl ether = 5 : 1 (R = Me and Et) or cyclohexane–ethyl acetate = 5 : 1 (other carbonates) solvent system as follows (R/R_f): Me/0.63; Et/0.81; n-Pr/0.34; i-Pr/0.30; n-Bu/0.34; s-Bu/0.34; n-hexyl/0.55; cyclohexyl/0.71; allyl/0.53; benzyl/0.69; –CH_2CH_2–/0.24; column chromatography was performed on (Wakogel C-200) silica gel.

Reaction of CO_2 with benzyl alcohol

To a stirred solution of benzyl alcohol (0.216 g, 2.00 mmol), tributylphosphine (0.303 g, 1.50 mmol) and CyTMG (0.394 g, 2.00 mmol) in DMF (2.00 cm^3) was added CO_2 at room temperature. After 15 min, carbon tetrabromide (0.663 g, 2.00 mmol) was added to the mixture, and the reaction system was sealed and stirred for 2 h. Then, the reaction mixture was diluted with ethyl acetate, washed successively with 0.5 mol dm^{-3} aqueous HCl and saturated aqueous $NaHCO_3$, and dried over Na_2SO_4. Diphenylmethanol as an internal standard was added to the organic solution and the yield of dibenzyl carbonate was determined by the integrated ratio between a methylene peak of the carbonate and a methine peak of diphenylmethanol in the ^1H NMR spectrum of the ethyl acetate solution. Dibenzyl carbonate, prepared by a larger scale reaction of CO_2 with benzyl alcohol (1.08 g, 10.0 mmol), was isolated by column chromatography (cyclohexane–ethyl acetate = 50 : 1) in 67.3% yield (0.816 g), δ_H(200 MHz) 5.17 (4H, s, CH_2), 7.30–7.43 (10H, m, C_6H_5); ν_{max}(NaCl)/cm^{-1} 1747 (C=O), 1260 (C–O).

Reaction of CO_2 with methanol, ethanol, propan-1-ol, propan-2-ol allyl alcohol and ethylene glycol

The reaction was started according to the experimental procedure used in synthesis of dibenzyl carbonate, and the reaction system was sealed and stirred for 2 h. The yields of the lower boiling and/or water-soluble carbonates from those alcohols were directly determined by the integrated ratio between the following characteristic peaks due to the methylene or methine protons neighboring the OC=O group and the methine peak of diphenylmethanol as an internal standard of the ^1H NMR spectra of the reaction mixtures; δ_H 3.79 (dimethyl carbonate), 4.18 (diethyl carbonate), 4.09 (dipropyl carbonate), 4.87 (diisopropyl carbonate), 4.64 (diallyl carbonate), and 4.59 (ethylene carbonate).

Reaction of CO_2 with hexan-1-ol

Procedure was as described in synthesis of dibenzyl carbonate. The yield of dihexyl carbonate was determined by the integrated ratio of the peak at δ 4.11 due to methylene protons neighboring OC=O and the methine peak of diphenylmethanol as an internal standard of the ^1H NMR spectrum of the reaction mixture. Dihexyl carbonate, prepared by the larger-scale reaction of CO_2 with hexan-1-ol (20.4 g, 20.0 mmol), was isolated by column chromatography (cyclohexane–ethyl acetate = 50 : 1) in 24.2% yield (0.557 g), δ_H(200 MHz) 0.89 (6H, t,

J 6.4, CH$_3$), 1.26–1.37 [12H, m, CH$_3$(CH_2)$_3$], 1.60–1.70 (4H, m, CH_2CH$_2$O), 4.12 (4H, t, J 6.6, CH$_2$O); v_{max}(NaCl)/cm^{-1} 1745 (C=O), 1255 (C–O).

Reaction of CO$_2$ with butan-1-ol and butan-2-ol

The reaction was carried out as described in synthesis of dimethyl carbonate. Then, the reaction mixture was diluted with methylene dichloride, washed successively with 0.5 mol dm^{-3} aqueous HCl and saturated aqueous NaHCO$_3$, and dried over Na$_2$SO$_4$. Diphenylmethanol as an internal standard was added to the organic solution. The yields of carbonates were determined by the integrated ratio of the peaks at δ 4.13 (dibutyl carbonate) or 4.68 [di(s-butyl)carbonate] due to the methylene or methine protons, respectively, neighboring OC=O and the methine peak or diphenylmethanol as an internal standard of the ^{1}H NMR spectra of the reaction mixtures. Dibutyl carbonate, prepared by a larger-scale reaction of CO$_2$ with butan-1-ol (0.740 g, 10.0 mmol), was isolated by column chromatography (cyclohexane–ethyl acetate = 50:1) in 37.1% yield (0.323 g), δ_H(200 MHz) 0.94 (6H, t, J 7.4, CH$_3$), 1.31–1.50 (4H, m, CH$_3$CH_2), 1.59–1.73 (4H, m, CH_2CH$_2$O), 4.13 (4H, t, J 6.4, CH$_2$O); v_{max}(NaCl)/cm^{-1} 1745 (C=O), 1257 (C–O).

References

1 E. Abrams, *Kirl-Othmer Encyclopedia of Chemical Technology*, Wiley, New York, 1978, 4th edn.

2 For example: *US Pat.* 4 554 110, 1985 (*Chem. Abstr.*, 1986, **104**, 50647c).

3 For example: I. F. Fieser and M. Fieser, *Reagents for Organic Chemistry*, Wiley, New York, 1967, vol. 1, p. 856.

4 S. Inoue, H. Koinuma and T. Tsurata, *J. Polym. Sci., Part B: Polym. Lett.*, 1969, **7**, 287; S. Inoue, H. Koinuma and T. Tsuruta, *Makromol. Chem.*, 1969, **130**, 210.

5 S. Inoue and N. Yamazaki, *Organic and Bio-organic Chemistry of Carbon Dioxide*, Kodansha, Tokyo, 1981.

6 For example: S. Oi, Y. Kuroda, S. Matsuno and Y. Inoue, *Nippon Kagaku Kaishi*, 1993, 985 (*Chem. Abstr.*, 1993, **119**, 228475v); W. McGhee and D. Riley, *J. Org. Chem.*, 1995, **60**, 6205.

7 W. A. Hoffman III, *J. Org. Chem.*, 1982, **47**, 5209.

8 A similar system has traditionally been used for the preparation of alkyl halides from alcohols. V. R. Appel, *Angew. Chem.*, 1975, **87**, 963 (*Angew. Chem., Int. Ed. Engl.*, 1975, **14**, 801).

9 J. Kadokawa, H. Habu, S. Fukamachi, M. Karasu, H. Tagaya and K. Chiba, *Macromol. Rapid Commun.*, 1998, **19**, 657.

10 Y. Kubota, M. Kodaka, T. Tomohiro and H. Okuno, *J. Chem. Soc., Perkin Trans. 1*, 1993, 5.

11 Previously, it was reported that CyTMG was very effective for the preparation of carbonates from alcohols, CO$_2$ and alkyl halides.[6]

12 H. Bredereck and K. Bredereck, *Chem. Ber.*, 1961, **94**, 2278; D. H. R. Barton, J. D. Elliott and S. D. Gero, *J. Chem. Soc., Perkin Trans. 1*, 1982, 2085.

Paper 9/00483A