Silica gel modified with tetraalkylammonium halides as an available and efficient catalyst for the synthesis of cyclic organic carbonates from epoxides and CO_2

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Silica gel with the additives of tetraalkylammonium halides serves as an efficient catalyst for the solvent-free insertion of carbon dioxide into epoxides (10—56 atm of CO_2, 105—100 °C), leading to cyclic carbonates with quantitative conversion.

Key words: cyclic carbonates, silica gel, epoxides, carbon dioxide, carbon dioxide fixation.

Processing of carbon dioxide into practically significant organic compounds is an actual problem of modern chemistry.[1] This problem is not only environmentally substantiated, since CO_2 is one of the main components of greenhouse gas, but also interesting in practical terms because it is available and non-toxic. At the same time, CO_2 is characterized by high thermodynamic inertness with respect to the main classes of organic compounds, which complicates the development of the corresponding catalysts.[2] One of the most striking examples of the direct insertion of CO_2 into an organic molecule is its catalytic coupling with epoxides to form cyclic organic carbonates.[3,4] The latter are used as aprotic polar solvents, fuel additives, electrolytes for lithium-ion batteries, anti-caking agents, as well as monomers for the production of polycarbonates and polyurethanes.[5—8] Despite the industrial success of this reaction, the development of efficient inexpensive catalysts combining the ability to quickly complete the reaction at low temperatures and pressures of carbon dioxide continues. The catalysts for this reaction are very diverse,[9—19] for example, transition and non-transition metal complexes (including exotic ones based on Sc, Sm, Y, La, Re), modified carbon nanotubes, crown ether complexes, modified molecular sieves, ionic liquids based on ammonium, imidazolium, and phosphonium systems, as well as polyols.

In the present work, we show that cheap silica gel used for column chromatography and modified with tetraalkylammonium halide additives can efficiently and quantitatively convert different epoxides to carbonates.

Results and Discussion

For initial testing, we selected two types of silica gel for column chromatography as catalysts, differing in particle sizes (**SG1**, 0.06—0.2 mm; **SG2**, 0.04—0.063 mm). The silica gels were tested in the addition of CO_2 to cyclohexene oxide (**1**), which leads to cyclohexene carbonate (**2**) (Scheme 1). At an initial pressure of 56 atm and heating to 105 °C, the reaction, as it turned out, did not occur (Table 1, entries *1* and *2*). Taking into account the postulated reaction mechanism,[11] which requires the presence of a halide ion to ensure the occurrence of the process, we modified silica gel with the tetrabutylammonium iodide additives. In this case, both catalysts provided high conversion (entries *3* and *4*), with **SG2** silica gel with a smaller particle size being more efficient. Note that Bu_4NI itself in the absence of silica gel does not catalyze the process under the same conditions. When Bu_4NI was replaced with the more common bromide Bu_4NBr, the conversion was also high (*cf.* entries *4* and *5*). An increase in the content of the Bu_4NBr additive leads to even more complete conversion (*cf.* entries *5* and *6*). The study of the effect of CO_2 pressure on the rate of the process showed that its efficiency practically does not decrease at a pressure of 20 or even 10 atm (entries *7* and *8*). The use of Bu_4NCl as an additive gave a less acceptable result compared to the corresponding bromide or iodide, however, an increase in the content of chloride Bu_4NCl clearly had a positive effect on the rate of the process (entries *9* and *10*). The effect of Et_4NCl with shorter alkyl substituents is close to that of Bu_4NCl (entry *11*). Finally, for the Bu_4NBr • **SG2**

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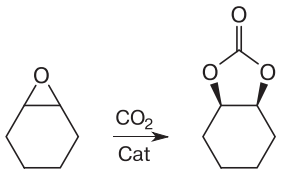
system a quantitative conversion of cyclohexene oxide (**1**) to carbonate **2** was achieved by a slight increase in temperature from 105 to 110 °C (entry *12*).

Scheme 1

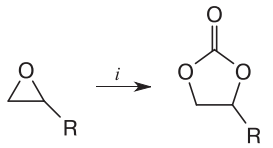


1 **2**

Cat is the catalyst.

Using this simple catalyst (Bu_4NBr • **SG2**) and the optimized conditions, we studied the addition of CO_2 to other epoxides **3a—h** (Scheme 2). In all the cases, the corresponding carbonates **4a—h** were obtained in quantitative yield.

Scheme 2



3a—h **4a—h** (100%)

R = CH_2Cl (**a**), CH_2F (**b**), CH_2CF_3 (**c**), $CH_2C_6F_5$ (**d**), CH_2OPh (**e**), CH_2NEt_2 (**f**), (morpholin-4-yl)methyl (**g**), Ph (**h**)

Reagents and conditions: *i*. CO_2 (initial pressure 56 atm), **3** (0.2 mL), NBu_4Br (6 mg), **SG2** (18 mg), 110 °C, 24 h.

Table 1. Insertion of CO_2 into the molecule of cyclohexene oxide (**1**)

Entry	Catalyst	*T*/°C	*P*/atm[a]	*t*/h	Conversion (%)
1	**SG1**	105	56	24	0
2	**SG2**	105	56	24	0
3	Bu_4NI^b • **SG1**	105	56	24	70
4	Bu_4NI^b • **SG2**	105	56	24	89
5	Bu_4NBr^b • **SG2**	105	56	24	86
6	Bu_4NBr^c • **SG2**	105	56	24	95
7	Bu_4NBr^c • **SG2**	105	20	24	93
8	Bu_4NBr^c • **SG2**	105	10	24	92
9	Bu_4NCl^b • **SG2**	105	56	24	35
10	Bu_4NCl^c • **SG2**	105	56	24	54
11	Et_4NCl^c • **SG2**	105	56	24	50
12	Bu_4NBr^c • **SG2**	110	56	24	100

[a] Initial pressure before heating.
[b] Alk_4NHal (3 mg)+ **SG1** or **SG2** (18 mg).
[c] Alk_4NHal (6 mg) + **SG2** (18 mg).

To sum up, we have proposed the most available at present catalyst for the synthesis of cyclic carbonates from the corresponding epoxides. The catalyst consists of widely used column chromatography silica gel and available quaternary ammonium salt Bu_4NBr. Note that this simplest catalytic system allows one to carry out the reaction without solvent, providing quantitative conversion of epoxides to carbonates, regardless of the steric and electronic factors of the starting substrates.

Experimental

^1H, ^{13}C and ^{19}F NMR spectra were recorded on Bruker Avance 400 spectrometer (400.13, 100.61, and 376.5 MHz). Silica gel **SG1** (0.06—0.2 mm, 60 Å, Acros Organics), **SG2** (0.04—0.063 mm, 60 Å, Merck), cyclohexene oxide (**1**), 2-(chloromethyl)oxirane (**3a**), 2-(phenoxymethyl)oxirane (**3e**), and 2-phenyloxirane (**3h**) are commercially available reagents. 2-(Fluoromethyl)oxirane (**3b**), 2-(2,2,2-trifluoroethyl)oxirane (**3c**), 2-[(pentafluorophenyl)methyl]oxirane (**3d**), 2-(*N*,*N*-diethylaminomethyl)-oxirane (**3f**), and 4-(oxirane-2-ylmethyl)morpholine (**3g**) were obtained according to procedures described earlier.[20—24]

Synthesis of carbonates 2 and 4a—h from epoxides. The corresponding silica gel (18 mg), tetraalkylammonium halide (3—6 mg) (see Table 1 and Scheme 2) were placed in a 10-mL autoclave, followed by the addition of epoxide **1** or **3a—h** (0.2 mL). The autoclave was filled with CO_2 (initial pressure 10, 20, or 56 atm) and heated to the required temperature in a thermostat. After completion of the reaction, the autoclave was cooled, decompressed, and opened, dichloromethane (2 mL) was added to the residue, the mixture was filtered through a short layer of silica gel, the solvent was evaporated, and the reaction mixture was analyzed by NMR. The spectral characteristics of carbonates **2** and **4a**,**b**,**e—h** correspond to the literature data.[10,22,25,26]

4-(2,2,2-Trifluoroethyl)-1,3-dioxolan-2-one (4c). A white powder, m.p. 63 °C. Found (%): C, 35.26; H, 3.04. $C_5H_5F_3O_3$. Calculated (%): C, 35.31; H, 2.96. ^1H NMR ($CDCl_3$), δ: 2.51—2.64 (m, 1 H); 2.74—2.87 (m, 1 H); 4.25 (t, 1 H, *J* = 8.0 Hz); 4.68 (t, 1 H, *J* = 8.0 Hz); 4.98—5.05 (t, 1 H). ^{13}C NMR ($CDCl_3$), δ: 38.06 (q, *J* = 29.0 Hz); 68.78 (s); 70.50 (q, *J* = 3.0 Hz); 124.45 (q, *J* = 277.15 Hz); 153.74. ^{19}F NMR ($CDCl_3$), δ: −63.84.

4-[(Pentafluorophenyl)methyl]-1,3-dioxolan-2-one (4d). A white powder, m.p. 133 °C. Found (%): C, 44.71; H, 1.96. $C_{10}H_5F_5O_3$. Calculated (%): C, 44.79; H, 1.88. ^1H NMR (400.13 MHz, $CDCl_3$), δ: 3.12—3.27 (m, 2 H); 4.25 (t, 1 H, *J* = 8.0 Hz); 4.62 (t, 1 H, *J* = 8.0 Hz); 4.92—4.98 (m, 1 H). ^{13}C NMR (75.5 MHz, $CDCl_3$), δ: 26.83 (CH_2); 68.62 (CH_2—O); 74.53 (CH—O); 107.99 (dt, *ipso*-C, $^2J_{C-F}$ = 18.3 Hz, $^3J_{C-F}$ = = 3.8 Hz); 137.69 (ddddd, *m*-C—F, $^1J_{C-F}$ = 253.8 Hz, $^2J_{C-F}$ = 17.4 Hz, $^2J_{C-F}$ = 12.7 Hz, $^3J_{C-F}$ = 4.9 Hz, $^4J_{C-F}$ = = 1.9 Hz); 140.90 (dtt, *p*-C—F, $^1J_{C-F}$ = 254.8 Hz, $^2J_{C-F}$ = 13.3 Hz, $^3J_{C-F}$ = 5.4 Hz); 145.45 (dddd, 2 *o*-C—F, $^1J_{C-F}$ = 247.6 Hz, $^2J_{C-F}$ = 15.6 Hz, $^3J_{C-F}$ = 8.1 Hz, $^3J_{C-F}$ = 3.0 Hz); 153.92 (C=O). ^{19}F NMR (376.50 MHz, $CDCl_3$), δ: −(160.87—160.67) (m, 2 F); −153.56 (t, 1 F, *J* = 22.6 Hz); −141.92 (dd, 2 F, *J* = 7.53 Hz, *J* = 22.6 Hz).

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