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Silanediol-Catalyzed Carbon Dioxide Fixation

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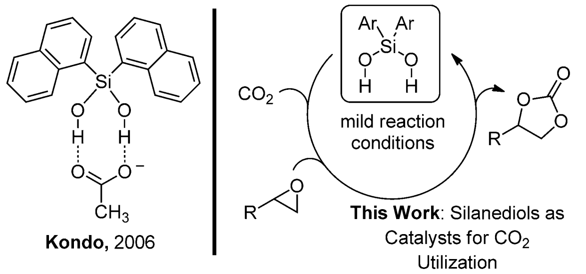
Carbon dioxide is an abundant and renewable C_1 source. However, mild transformations with carbon dioxide at atmospheric pressure are difficult to accomplish. Silanediols have been discovered to operate as effective hydrogen-bond donor organocatalysts for the atom-efficient conversion of epoxides to cyclic carbonates under environmentally friendly conditions. The reaction system is tolerant of a variety of epoxides and the desired cyclic carbonates are isolated in excellent yields.

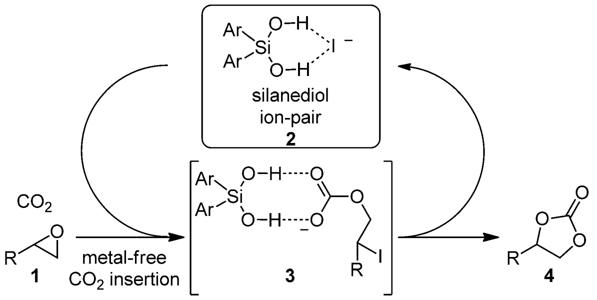
Carbon dioxide is an ideal renewable and environmentally friendly C_1 source.[1] Unfortunately, current research lacks appropriate processes to effectively utilize this reagent. As a highly oxidized, thermodynamically and kinetically stable molecule,[1] carbon dioxide traditionally requires harsh reaction conditions for chemical transformations, often involving high temperatures, high pressures, and transition-metal catalysis.[2] Mild, metal-free reaction conditions for the sustainable utilization of carbon dioxide remain in desirable, yet unmet, demand.

Hydrogen-bond donor (HBD) catalysis has emerged as a remarkable metal-free platform for the activation of organic molecules.[3] Despite its power, HBD catalysis has rarely been capitalized upon for controlling reactions of carbon dioxide. The lack of appropriate reactivity of conventional catalysts may be one reason HBDs have been slow to catch on in carbon dioxide fixation chemical technologies. One goal at the heart of our own research agenda is the design and application of enhanced HBD catalysts with the ability to influence reactivity patterns that are inaccessible to traditional catalysis.[4] Silanediols are one promising family of HBD catalysts under investigation in our laboratory in a number of reactions, including the fixation of carbon dioxide (Scheme 1). This Communication describes our discovery of silanediols as sustainable catalysts for ring-expansion reactions of epoxides in the presence of carbon dioxide.

Silanediols have excellent hydrogen-bonding capabilities. Kondo and co-workers demonstrated the power of silanediol hydrogen-bonds in the context of molecular recognition.[5] The hydrogen-bonding abilities of silanediols also enable the catalysis of reactions through either electrophile activation or anion-binding processes.[6] Their demonstrated catalytic abilities, as well as their molecular recognition properties, led us to hypothesize that silanediols would be ideal tools for catalyzing reactions of carbon dioxide (Scheme 2). Specifically, we envisioned a silanediol–halide ion pair (**2**) would affect a metal-free CO_2-insertion reaction into an epoxide, eventually giving rise to ring-expanded carbonate products **4** via proposed intermediate **3**. While our experience with silanediol catalysis encouraged our pursuit of this new approach toward carbon dioxide fixation, there was no evidence to support the compatibility of silanediols with carbon dioxide at the onset of our studies.[7,8]



Scheme 1. Silanediols as sustainable catalysts for mild fixation of CO_2.



Scheme 2. Proposed mode of action for silanediol co-catalyzed CO_2 activation.

Excited to test our hypothesis, we began investigating the 100% atom economical conversion of styrene oxide to cyclic carbonate **4a** (Table 1).[9] In general, cyclic carbonates are valuable intermediates in polymerization and pharmaceutical chemistry. They also function as polar aprotic solvents and can serve as electrolytic components of lithium batteries.[10] As described previously, the simple, albeit challenging, transformation of epoxides and carbon dioxide to cyclic carbonates often requires harsh conditions involving high temperatures and pressures of carbon dioxide and transition-metal catalysts for effective conversion. Less harsh conditions have been recently reported in a limited number of metal-free systems,[11] but a general organocatalytic system for the mild reaction of carbon dioxide and epoxides remains a challenge. We envi-

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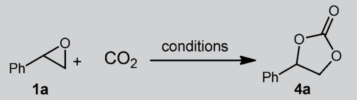
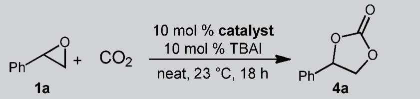
Table 1. Optimization of reaction conditions.[a]

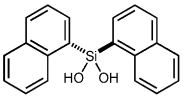
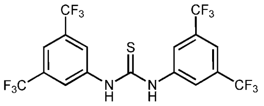
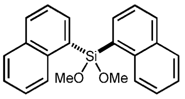
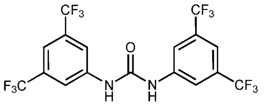
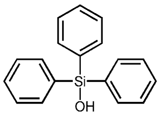
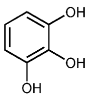
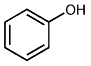


Entry	Loading of **5** [mol %]	TBAX[b]	Solvent	*T* [h]	*T* [°C]	Yield[c] [%]
1	10	TBAB	PhMe	24	60	89
2	10	TBAB	neat	14	60	95
3	10	TBAB	neat	18	23	49
4	10	TBAI	neat	18	23	93
5	5	TBAI	neat	24	23	83
6	10	TBAI	PhMe	18	40	91
7	10	TBAI	EtOAc	18	40	70
8	10	TBAI	MEK	18	40	85
9	10	TBAI	acetone	18	40	88

[a] All reactions performed using a balloon of CO$_2$ at 1 bar. [b] 1:1 mol% loading as catalyst **5**. [c] Isolated yield.

Table 2. Hydrogen-bond donor catalyst screen.[a]



Catalyst	Yield[b] [%]	Catalyst	Yield[b] [%]
5 	93	**9** 	58[c]
6 	1[c]	**10** 	38[c]
7 	60	**11** 	87
8 SiO$_2$ (10 wt%)	34	**12** 	82

[a] All reactions performed using a balloon of CO$_2$ at 1 bar. [b] Isolated yield. [c] ^{1}H NMR yield using mesitylene as an internal standard.

sioned that our silanediols would be able to affect this transformation under mild reactions conditions while simultaneously accommodating a variety of reactant epoxides.

We were pleased early on to find that our dinaphthyl silanediol **5** was indeed compatible with carbon dioxide. Styrene oxide afforded 89% yield of **4a** with 10 mol% of catalyst **5** under an atmosphere of carbon dioxide in 2 M toluene using tetrabutylammonium bromide (TBAB) as a co-catalyst (entry 1, Table 1). Determined to find more environmentally friendly conditions, further optimization of the reaction conditions was investigated. We first observed that solvent was often unnecessary for the reaction: neat conditions at 60 °C increased the yield to 95% (entry 2). After our initial disappointment that temperatures below 60 °C did not provide high yields (entry 3), we discovered that switching to tetrabutylammonium iodide (TBAI) as co-catalyst afforded excellent yields of **4a** at 23 °C (entry 4). Lowering the loading of silanediol catalyst **5** from 10 to 5 mol% resulted in a small loss in yield (entry 5). A variety of green solvents (5 M) afforded excellent conversions albeit at slightly increased temperature (entries 6–9).[12]

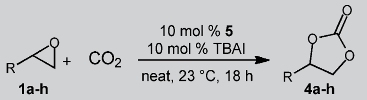
A family of catalysts was then tested under our optimized reactions conditions found in entry 4 of Table 1. Dimethoxysilane **6**, a catalyst that cannot donate hydrogen- bonds, provided no conversion to the desired carbonate product and confirmed the necessity of the hydrogen-bonding functionality (Table 2). Triphenylsilanol **7** provided only 60% yield of the carbonate product suggesting that the dual hydrogen-bonding capabilities of **5** is a key factor in the success of the reaction. Phenols have been shown to affect the conversion of epoxides to cyclic carbonates as HBD catalysts,[11d,g,13] but were not as effective under our reaction conditions (catalysts **11** and **12**). Interestingly, traditional 1,3-bis(3,5-bis(trifluoromethyl)phenyl)urea **9** and thiourea **10** HBD catalysts did not operate well under these reaction conditions. This suggests that silanediol catalysts are uniquely suited for the activation of epoxides. Control experiments resulted in a 1% ^{1}H NMR yield in the absence of a HBD catalyst; without the presence of the co-catalyst, no conversion to the desired product was observed.

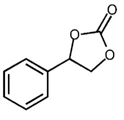
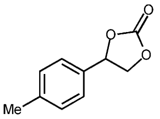
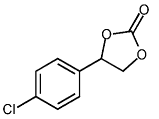
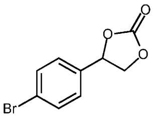
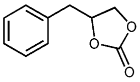
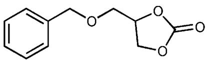
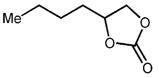
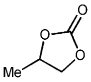
A variety of epoxide substrates were tested under our optimal reaction conditions (Table 3). A wide range of aromatic epoxides was well tolerated in the system providing excellent yields of cyclic carbonates **4a**–**4d** (73–97%). The epoxide derived from allylbenzene operated well in the reaction system, giving rise to **4e** in 96% yield. 2-(Benzyloxy)methyloxirane gave rise to an excellent yield of product **4f**. Alkyl epoxides also underwent ring expansion within this reaction system and gave rise to good yields of products **4g** and **4h**. It is worthwhile to mention that the best reactivity of volatile alkyl epoxides, such as propylene oxide, is achieved in the presence of solvent. At this time, the reaction system is limited to monosubstituted epoxides as poor conversion was observed with several disubstituted epoxides tested; efforts are underway in our laboratory to enable reactions with these substrates.

Taking into account previous mechanistic investigations on related systems[7,11c, g,13,14] and our own experimental observations, a proposed reaction pathway is depicted in Scheme 3. Initial activation of the epoxide by dual hydrogen-bonding with the silanediol yields **I**. The epoxide then undergoes ring-opening upon nucleophilic attack of the iodide co-catalyst[15] to yield hydrogen-bond-stabilized alkoxide **II**.[16] The addition of **II** to carbon dioxide generates silanediol-stabilized intermediate **III**. The completion of the catalytic cycle occurs upon intramolecular ring closure of **III** to generate the cyclic carbonate **4**, iodide, and silanediol **5**.

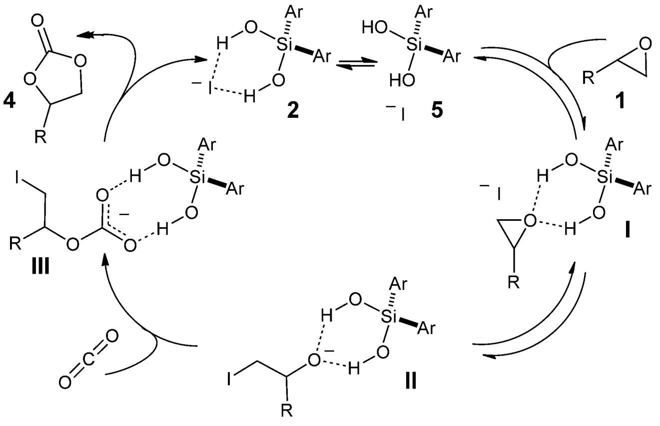
To gain insight into the proposed reaction pathway, optically pure (*R*)-styrene oxide was tested under our optimized conditions to determine if chirality would transfer from the epoxide.

Table 3. Substrate scope.[a]

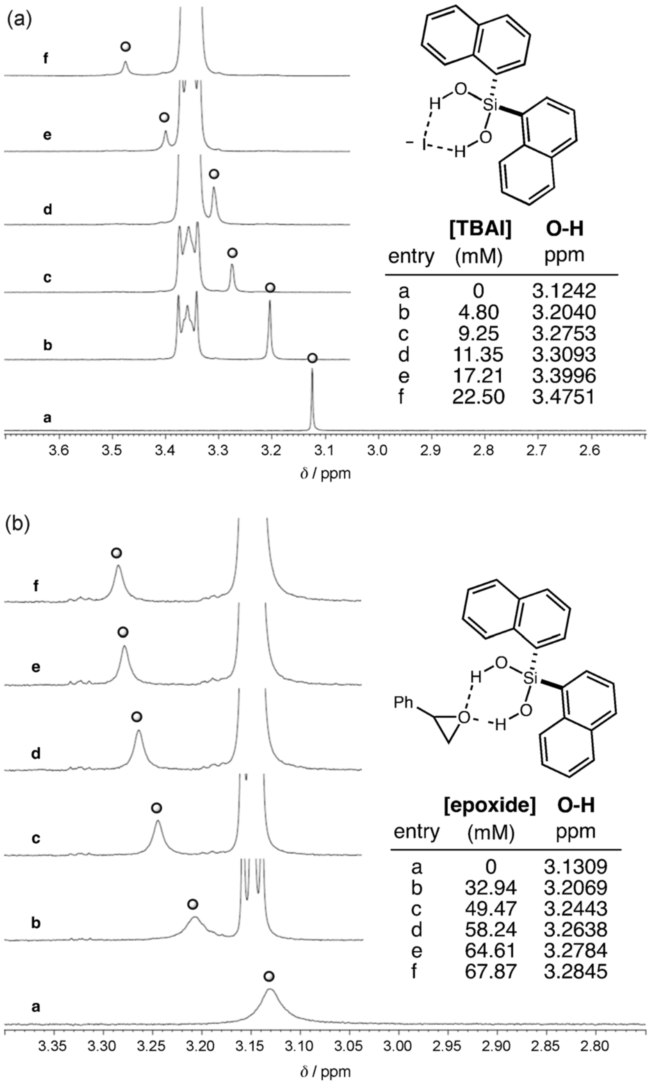


Carbonate product	Yield[b] [%]	Carbonate product	Yield[b] [%]
4a 	93	**4b** 	97
4c 	88	**4d**[c] 	73
4e 	96	**4f** 	96
4g 	82	**4h**[c] 	74

[a] All reactions performed using a balloon of CO_2 at 1 bar. [b] Isolated yield. [c] Experiment reacted in 5 M toluene for 18 h at 40 °C.



Scheme 3. Proposed reaction pathway for cyclic carbonate formation.



entry	[TBAI] (mM)	O-H ppm
a	0	3.1242
b	4.80	3.2040
c	9.25	3.2753
d	11.35	3.3093
e	17.21	3.3996
f	22.50	3.4751

entry	[epoxide] (mM)	O-H ppm
a	0	3.1309
b	32.94	3.2069
c	49.47	3.2443
d	58.24	3.2638
e	64.61	3.2784
f	67.87	3.2845

Figure 1. Binding titrations with silanediol **5**: (a) Tetrabutylammonium iodide-silanediol binding and (b) styrene oxide-silanediol binding.

We isolated the carbonate product in 95% enantiomeric excess (*ee*), providing evidence for the ring opening of the epoxide by the iodide ion.[13b-d] This environmentally friendly method provides access to enantioenriched aromatic carbonate products with minimal racemization from the initial epoxide.[12]

Qualitative ^{1}H NMR titration studies demonstrated silanediol recognition of both the epoxide and iodide through proposed hydrogen-bonding interactions (Figure 1). Upon addition of tetrabutylammonium iodide to the silanediol catalyst, downfield shifting of the silanediol O–H chemical signal was observed (Figure 1 a). Similarly, the addition of styrene oxide to the silanediol caused downfield shifting of the O–H peak (Figure 1 b).[12]

In conclusion, silanediols operate as a sustainable class of catalysts for the reaction of carbon dioxide with epoxides under mild reaction conditions. A variety of epoxides are transformed into their corresponding cyclic carbonates with excellent yields under environmentally friendly conditions using only an atmosphere of carbon dioxide. With this mild methodology, chirality of aromatic epoxides is transferred to the corresponding cyclic carbonate product with minimal loss in enantioenrichment. The demonstration of the compatibility of silanediol catalysis and carbon dioxide provides a new platform for the development of innovative reactivity patterns previously unattainable with traditional hydrogen-bond donor catalysts.

Experimental Section

Procedure for preparation of **4a**: A dry, screw-capped reaction vial containing a magnetic stir bar was charged with silanediol **5** (27.6 mg, 0.087 mmol, 0.1 equiv.), tetrabutylammonium iodide (32.3 mg, 0.087 mmol, 0.1 equiv.) and styrene oxide **1a** (100 μL, 0.874 mmol, 1 equiv.). The vial was fitted with a cap and septa and degassed with carbon dioxide. The vial was put under a positive pressure with a balloon of carbon dioxide and allowed to stir at room temperature for 18 h. After the reaction time, mesitylene (40.5 μL, 0.291 mmol, 0.33 equiv.) and $CDCl_3$ were added to the vial and stirred for 1 min. A ^1H NMR sample was taken to determine the yield with mesitylene as the internal standard. The NMR sample and the reaction vial were combined, and the carbonate product isolated via flash column chromatography using silica gel (5:95 diethyl ether/hexanes to 50:50 diethyl ether/hexanes). The isolated yield of carbonate products correlated with the yield determined by ^1H NMR spectroscopy using the internal standard. All isolated carbonate products matched reported characterization data.[12]

4-phenyl-1,3-dioxolane-2-one (**4a**): Isolated as a white solid. ^1H NMR yield: 95%. Isolated yield: 93%. $R_f = 0.20$ (40:60 diethyl ether/hexanes). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.47$–7.42 (m, 3H); 7.38–7.35 (m, 2H); 5.67 (apparent t, $J = 8$ Hz, 1H); 4.79 (apparent t, $J = 8.4$ Hz, 1H); 4.36–4.32 ppm (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 154.8$, 135.8, 129.7, 129.2, 125.8, 77.9, 71.1 ppm. All other spectroscopic data matched that previously reported. See the Supporting Information for characterization data of other compounds reported.

Acknowledgements

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Keywords: carbon dioxide · cyclic carbonate · hydrogen-bond donors · metal-free catalysis · silanediol

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[12] See the Supporting Information for additional experimental details involving reaction conditions, silanediol catalyst, and product isolation.

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