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CO_2 Fixation

Atmospheric CO_2 Fixation by Unsaturated Alcohols Using *t*BuOI under Neutral Conditions**

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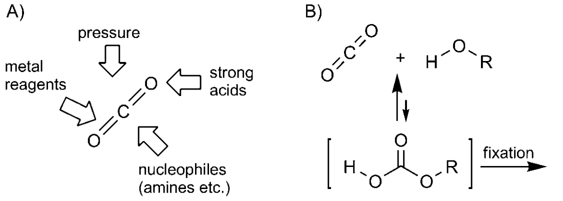
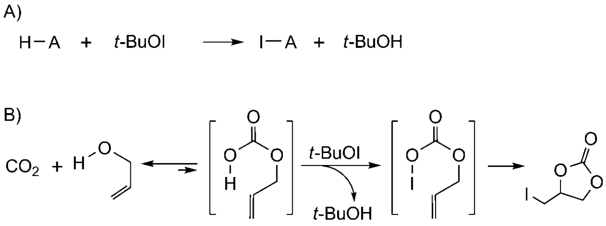
Carbon dioxide is a significant contributor to environmental warming.[1,2] The Kyoto Treaty, ratified in 1997, is intended to restrict the emission of greenhouse gases such as carbon dioxide. As a result, the development of methods for efficient consumption and storage of carbon dioxide would be highly desirable. The chemical fixation of CO_2 and its subsequent use in producing valuable products is one possible approach to the effective utilization of CO_2. Efforts to increase the use of CO_2 for the production of useful organic chemicals are needed. Unfortunately, CO_2 is a very stable compound; its carbon atom is in a highly oxidized state, thus imparting the compound with thermodynamic stability. Because of this stability, highly reactive metal catalysts or reagents, high pressures, strong acids, and strong nucleophiles or bases[3] are typically required to activate or capture carbon dioxide (Scheme 1 A). Clearly, a low-energy process is needed for capturing carbon dioxide and utilizing it in a chemical process. One possible solution is to take advantage of carbonic acid monoalkyl esters, which are thought to be generated from the equilibrium between CO_2 and alcohols (Scheme 1 B), but such compounds have not been observed, owing to their instability.[4] The most plausible evidence for their existence is a report describing the formation of methyl diphenylmethyl carbonate, which is produced by the reaction of diphenyldiazomethane in CO_2-expanded methanol.[5] Since the focus of the latter study was on evidence for the formation of alkylcarbonic acids from CO_2 and alcohols, CO_2 capturing efficiency was not addressed.

If a small amount of alkylcarbonic acid in the equilibrium mixture could be effectively trapped in some way, this new process would be interesting for chemical CO_2 fixation and would also reduce the requisite energy compared to conventional processes. In such a process, a carbonic acid monoester, generated spontaneously by the reaction of CO_2 with an alcohol, would result in its low-energy trapping. We previously reported that a proton of a weak acid such as an amide (HA) replaces the iodine of *tert*-butyl hypoiodite (*t*BuOI),[6] thus leading to the production of a reactive iodonium source (IA; Scheme 2 A).[7] Using this unique phenomenon, if a weak acid, such as an alkylcarbonic acid derived from CO_2, and an unsaturated alcohol were treated with *t*BuOI, an active species would be generated, and its subsequent intramolecular cyclization would displace the equilibrium to the right (the product side; Scheme 2 B). This strategy offers an innovative approach to the fixation of CO_2 to organic molecules.



Scheme 1. A) Conventional routes for the activation of CO_2. B) Utilization of an acidic environment generated from CO_2 and alcohols.



Scheme 2. A) Reaction of *tert*-butyl hypoiodite with weak acids. B) Strategy for trapping carbonic acids with *tert*-butyl hypoiodite.

Related transformations, such as CO_2 fixation to unsaturated alcohols, using conventional procedures have been reported. The synthesis of cyclic iodocarbonates by the trapping of CO_2 with allyloxide and homoallyloxide ions was reported by Cardillo et al.[8] This procedure, however, requires a strong base, *n*BuLi, for the generation of the alkoxides. The incorporation of CO_2 into propargylic alcohols has also been reported,[9] but the procedure also requires high CO_2 pressures, the use of strong bases, metal catalysts, and the application of heat.

Herein we report an extremely mild procedure for the fixation of CO_2. The method takes advantage of the acidic character of the alkylcarbonic acid generated from CO_2 and an unsaturated alcohol, in which iodination of the carbonic acid with *t*BuOI is a key reaction, which changes the position of the equilibrium of the initial CO_2-trapping reaction. The reagent, *t*BuOI, can be readily prepared in situ from commercially available *tert*-butyl hypochlorite (*t*BuOCl) and sodium iodide (NaI). The raw material *t*BuOCl is easily prepared from *tert*-butyl alcohol and commercial household bleach in the presence of acetic acid.[10] Thus, the desired CO_2 fixation does not require the use of strong bases, environmentally unfriendly metal reagents, or pressurized conditions.

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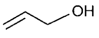
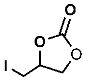
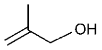
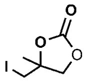
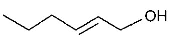
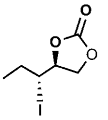
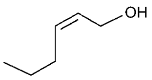
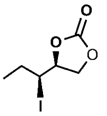
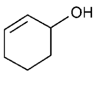
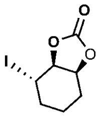
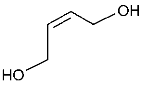
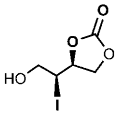
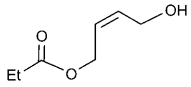
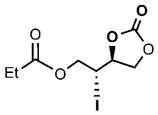
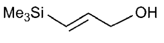
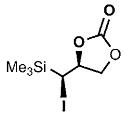
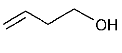
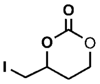
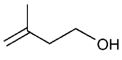
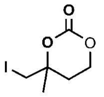
To test the concept, when the simplest allyl alcohol was treated with *t*BuOI (2 equiv) under 1 atm of CO_2 in acetonitrile at room temperature, a five-membered cyclic carbonate containing an iodomethyl group was produced in 50% yield. To improve the efficiency of the reaction, a variety of solvents and temperature were screened. The use of tetrahydrofuran (THF) as a solvent and a reaction temperature of −20°C resulted in the formation of the desired carbonate in 92% yield (Table 1, entry 1). Although the reaction proceeded even with the use of one equivalent of *t*BuOI, the yield of the product was rather low (78% yield). To confirm the superiority of the system, we tested other representative iodinating reagents (bis(pyridine)iodine tetrafluoroborate (IPy_2BF_4), *N*-iodosuccinimide (NIS), I_2, and a combination of I_2 and triethylamine), which failed to provide the desired product. The reason that *t*BuOI is the most appropriate iodinating reagent can be attributed to the liberation of the relatively weak acid (*t*BuOH) during the reaction of allylcarbonic acid and *t*BuOI.

Table 1: CO_2 fixation with (homo)allyl alcohols and *t*BuOI.[a]

Entry	Alcohol	Solvent [mL]	*t* [h]	Carbonate		Yield [%]
1		THF (3)	12		**1**	92
2		THF (3)	3		**2**	93
3		DMF (2)	24		**3**	57
4		MeCN (3)	48		**4**	78
5		DMF (3)	24		**5**	72
6		MeCN (3)	48		**6**	79
7		MeCN (3)	48		**7**	81
8		MeCN (3)	24		**8**	86
9		THF (3)	24		**9**	84
10		MeCN (3)	72		**10**	92

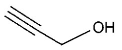
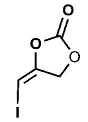
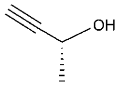
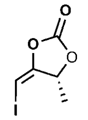
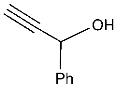
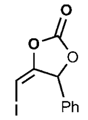
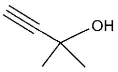
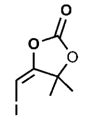
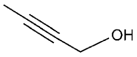
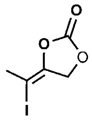
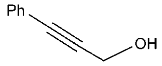
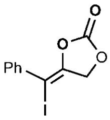
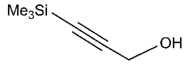
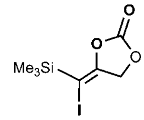
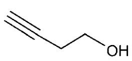
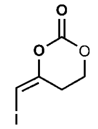
[a] Reaction conditions: CO_2 (1 atm), alcohols (0.5 mmol), *t*BuOI (1 mmol), −20°C.

Having identified the suitable reagents, we explored the scope of the reaction with respect to substrate (Table 1). Solvent and the concentration of reactants affected the efficiency of CO_2 fixation to unsaturated alcohols. A β-branched allyl alcohol was smoothly and efficiently converted into the cyclic carbonate (Table 1, entry 2). Both *E*- and *Z*-allyl alcohols were transformed to the corresponding carbonates. It is noteworthy that, when geometric isomers were used, complete stereoselectivity as well as stereospecificity was observed in the reactions (Table 1, entries 3 and 4). Allyl alcohols containing rigid, cyclic olefins were also applicable to the reaction (Table 1, entry 5). Hydroxy, ester, and silyl groups were also compatible with this CO_2 fixation reaction (Table 1, entries 6 to 8). Homoallyl alcohols were also converted into six-membered cyclic carbonates in good yields (Table 1, entries 9 and 10). These completely stereospecific and stereoselective cyclizations are consistent with a reaction pathway involving a cyclic iodonium intermediate. The resulting carbonates containing an iodomethyl group represent synthetically valuable building blocks, because they can be readily converted into epoxy alcohols and triols.[11]

The successful transformation of allyl and homoallyl alcohols to cyclic carbonates through CO_2 fixation under extremely mild conditions prompted us to investigate the use of acetylenic alcohols as substrates (Table 2). An unsubstituted propargyl alcohol was subjected to the above CO_2 fixation reaction to afford a five-membered cyclic carbonate containing an iodomethylene group in high yield as a sole *E*-isomer (Table 2, entry 1). Propargyl alcohols having a variety of substituents at the propargylic position also trapped CO_2 to give the corresponding carbonates (Table 2, entries 2 to 4). Internal acetylenic alcohols were employed in the reaction, giving cyclic carbonates containing a tetrasubstituted olefin moiety. It is noteworthy that a silyl group directly attached to an acetylenic carbon atom resulted in a highly efficient reaction (Table 2, entries 5 to 7). Butynyl alcohols were also applicable to the reaction, yielding six-membered cyclic carbonates (Table 2, entry 8). Substituents at the propargylic position are required for the fixation of CO_2 to propargyl alcohols in conventional methods.[9] However, substrates without substituents at the propargylic position could be readily employed in the present system.

Although the precise mechanism of the reaction is unclear at present, the proposed mechanism shown in Scheme 2B is supported by experimental findings. In the reaction, *t*BuOCl is added to a solution of the alcohol and NaI under an atmosphere of CO_2. NMR spectra indicated that *t*BuOCl does not react with either the alcohol or CO_2 under these conditions. Thus, it is likely that *t*BuOCl reacts rapidly with NaI, leading to the production of *t*BuOI. Thus, the question arises as to which two reagents of the three present (a saturated alcohol, *t*BuOI, and CO_2) react first. To address this issue, the reaction of allyl alcohol and *t*BuOI was monitored by ^1H NMR spectroscopy, and small signals assigned to $H_2C{=}CHCH_2OI$ were observed (most of the starting allyl alcohol remained unreacted). The *O*-iodinated allyl alcohol could be considered as an active intermediate, so the species prepared

Table 2: CO_2 fixation with acetylenic alcohols and *t*BuOI.[a]

Entry	Alcohol	THF [mL]	*t* [h]	Carbonate		Yield [%]
1		3	3		**11**	92
2		3	24		**12**	92
3		5	24		**13**	90
4		5	24		**14**	80
5		5	24		**15**	71
6		5	24		**16**	70
7		3	24		**17**	94
8		2	24		**18**	64

[a] Reaction conditions: CO_2 (1 atm), alcohols (0.5 mmol), *t*BuOI (1 mmol), −20 °C.

from the reaction of sodium allyloxide and I_2 was exposed to CO_2, but the desired reaction did not occur. Instead, the formation of acrolein was observed. In fact, when the efficiency of the reaction is less than ideal (for example, Table 1, entry 3), the corresponding oxidation product, an α,β-unsaturated aldehyde, was obtained. The reaction of *t*BuOI and CO_2 was then monitored by means of NMR (^1H and ^{13}C) and IR spectroscopy and electrospray ionization mass spectrometry (ESI-MS), but no reaction was observed. Therefore, as expected initially, CO_2 fixation appears to proceed through an allyl carbonic acid intermediate, as shown in Scheme 2B. The very low concentration of allyl carbonic acid would react with *t*BuOI, leading to an *O*-iodinated species, which acts as an iodonium source, and a cyclic iodonium intermediate is formed by reaction with carbon–carbon unsaturated moieties. The generation of a cyclic iodonium intermediate explains the complete stereoselectivity observed in these reactions.

To assess the scope of this method, a gram-scale reaction was carried out. Allyl alcohol (1.16 g, 0.02 mol) was treated with *t*BuOI prepared from *t*BuOCl (4.3 g, 0.04 mol) and NaI (6 g, 0.04 mol) under 1 atm of CO_2 in THF (0.12 L) at −20 °C, producing the corresponding cyclic carbonate **1** in 82 % yield (3.8 g). This result indicates that the present system should be applicable to larger-scale process.

From the results of the present study and on the basis of the proposed main reaction pathway, a non-metal, non-basic, non-pressurized method was developed, representing a new, low-energy process for the chemical fixation of CO_2. The simple methodology has a very broad scope in terms of both olefinic and acetylenic alcohols, thus allowing access to a wide range of cyclic carbonates. Moreover, iodo substituents attached to sp^3- and sp^2-hybridized carbon atoms are versatile functional groups for organic synthesis. We conclude that the results herein describe an innovative CO_2 fixation process that involves simple and convenient chemical manipulation and proceeds under extremely mild conditions.

Experimental Section

Typical procedure for CO_2 fixation: *t*BuOCl (108.5 mg, 1.0 mmol) was added to a mixture of NaI (150 mg, 0.5 mmol) and an unsaturated alcohol (0.5 mmol) in an appropriate solvent under 1 atm of CO_2 at −20 °C. The mixture was stirred in the dark for the indicated time and quenched with aqueous $Na_2S_2O_3$ (0.5 M, 5 mL), and the solution was extracted with diethyl ether (4 × 20 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated under vacuum to give the crude product. Purification by flash column chromatography (silica gel; ethyl acetate/hexane 2:8) gave a cyclic carbonate (for example, compound **1**: 105 mg, 92 %).

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