

## Atmospheric CO<sub>2</sub> Fixation by Unsaturated Alcohols Using *t*BuOI under Neutral Conditions

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CO<sub>2</sub> Fixation

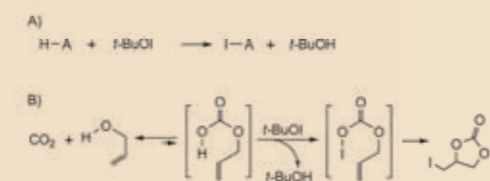
### Atmospheric CO<sub>2</sub> Fixation by Unsaturated Alcohols Using *t*BuOI under Neutral Conditions\*\*

Satoshi Minakata,\* Itsuro Sasaki, and Toshihiro Ide

Carbon dioxide is a significant contributor to environmental warming.<sup>1,2</sup> 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<sub>2</sub> and its subsequent use in producing valuable products is one possible approach to the effective utilization of CO<sub>2</sub>. Efforts to increase the use of CO<sub>2</sub> for the production of useful organic chemicals are needed. Unfortunately, CO<sub>2</sub> 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<sup>3</sup> are typically required to activate or capture carbon dioxide (Scheme 1A). 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<sub>2</sub> and alcohols (Scheme 1B), but such compounds have not been observed, owing to their instability.<sup>4</sup> 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<sub>2</sub>-expanded methanol.<sup>5</sup> Since the focus of the latter study was on evidence for the formation of alkylcarbonic acids from CO<sub>2</sub> and alcohols, CO<sub>2</sub> 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

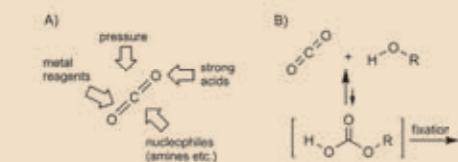
process would be interesting for chemical CO<sub>2</sub> fixation and would also reduce the requisite energy compared to conventional processes. In such a process, a carbonic acid monoester, generated spontaneously by the reaction of CO<sub>2</sub> with an alcohol, would result in its low-energy trapping. We previously reported that a proton of a weak acid such as an amide (HA) replaces the iodine of *tert*-butyl hypoiodite (*t*BuOI),<sup>6</sup> thus leading to the production of a reactive iodonium source (IA; Scheme 2A).<sup>7</sup> Using this unique phenomenon, if a weak acid, such as an alkylcarbonic acid derived from CO<sub>2</sub>, 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 2B). This strategy offers an innovative approach to the fixation of CO<sub>2</sub> to organic molecules.



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<sub>2</sub> fixation to unsaturated alcohols, using conventional procedures have been reported. The synthesis of cyclic iodocarbonates by the trapping of CO<sub>2</sub> with allyloxide and homoallyloxide ions was reported by Cardillo et al.<sup>8</sup> This procedure, however, requires a strong base, *n*BuLi, for the generation of the alkoxides. The incorporation of CO<sub>2</sub> into propargylic alcohols has also been reported,<sup>9</sup> but the procedure also requires high CO<sub>2</sub> 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<sub>2</sub>. The method takes advantage of the acidic character of the alkylcarbonic acid generated from CO<sub>2</sub> 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<sub>2</sub>-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.<sup>10</sup> Thus, the desired CO<sub>2</sub> fixation does not require the use of strong bases, environmentally unfriendly metal reagents, or pressurized conditions.



Scheme 1. A) Conventional routes for the activation of CO<sub>2</sub>. B) Utilization of an acidic environment generated from CO<sub>2</sub> and alcohols.

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The following is a comment on the published paper shown on the preceding page.

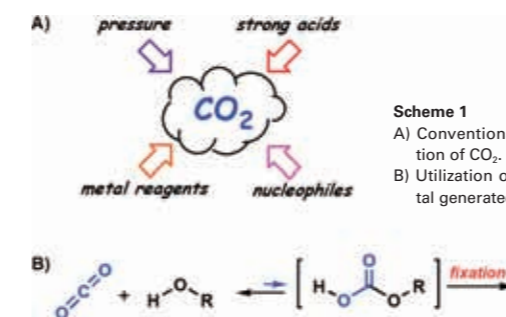
## A New Process for Chemical CO<sub>2</sub> Fixation: Utilization of Weak Interaction with Alcohols

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### Introduction

Carbon dioxide as a greenhouse gas significantly contributes to warming of the earth. 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 efficiently consuming and storing carbon dioxide would be highly desirable. The chemical fixation of CO<sub>2</sub> and its subsequent use in producing valuable products is one possible approach to the effective utilization of CO<sub>2</sub>. Efforts to increase the use of CO<sub>2</sub> for the production of useful organic chemicals are needed. Unfortunately, CO<sub>2</sub> is a very stable compound, in that it is in a highly oxidized state and is thermodynamically stable. Because of this, highly reactive metal catalysts or reagents, high pressures, strong acids, and strong nucleophiles or bases [1] are typically required to activate or capture carbon dioxide (Scheme 1A). 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<sub>2</sub> and alcohols (Scheme 1B), but such compounds have not been observed, due to their instability [2]. The most plausible evidence for their existence is the report describing the formation of methyl diphenylmethyl carbonate, which is produced by the reaction of diphenyldiazomethane in CO<sub>2</sub>-expanded methanol [3]. Since the focus of the latter study was on evidence for the formation of alkylcarbonic acids from CO<sub>2</sub> and alcohols, CO<sub>2</sub> capturing efficiency was not addressed.



Scheme 1  
A) Conventional routes for the activation of CO<sub>2</sub>.  
B) Utilization of an acidic environment generated from CO<sub>2</sub> and alcohols.

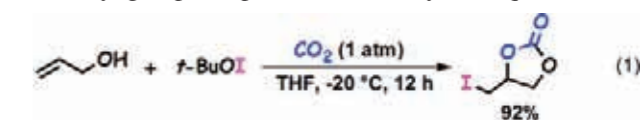
### Strategy

If a small amount of alkylcarbonic acid in the equilibrium mixture could be effectively trapped in some way, this would represent an interesting new process for chemical CO<sub>2</sub> 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<sub>2</sub> with an alcohol,

would result in its low energy trapping. We previously reported that a proton of a weak acid such as an amide (H-A) replaces the iodine of *tert*-butyl hypoiodite (*t*-BuOI), leading to the production of a reactive iodonium source (I-A) [4]. Using this unique phenomenon, if a weak acid, such as an alkylcarbonic acid derived from CO<sub>2</sub> and an unsaturated alcohol were reacted with *t*-BuOI, an active species would be generated and its subsequent intramolecular cyclization would displace the equilibrium to the right (the product side). This strategy offers an innovative approach to the fixation of CO<sub>2</sub> to organic molecules. Based on this concept, an extremely mild procedure for the fixation of CO<sub>2</sub> is described in this paper.

### CO<sub>2</sub> Fixation with Alkenyl Alcohols

To test the concept, when the simplest allyl alcohol was treated with *t*-BuOI (2 equiv) under an atmospheric pressure of CO<sub>2</sub> in THF at -20 °C, a five-membered cyclic carbonate containing an iodomethyl group was produced in 92% yield (equation 1).



We explored the scope of the reaction with respect to substrate (Figure 1). The reaction was not grossly affected by substituents at the allylic position. A β-branched allyl alcohol was smoothly and efficiently converted into the cyclic carbonate. 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. Allyl alcohols containing rigid, cyclic olefins were also applicable to the reaction. Hydroxyl, ester, and silyl groups were also compatible with this CO<sub>2</sub> fixation reaction. Homoallyl alcohols were also converted into six-membered cyclic carbonates in good yields. These complete 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.

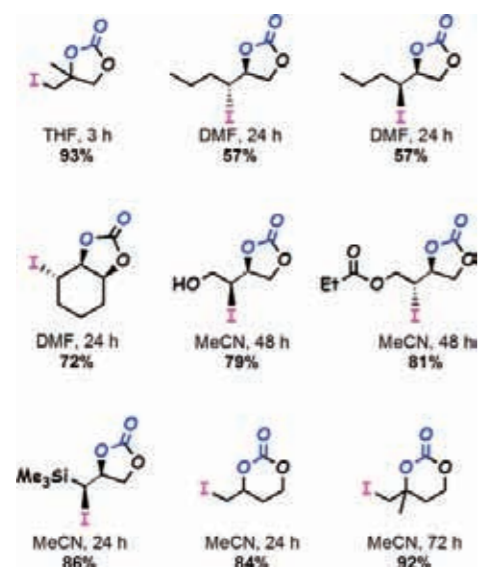


Fig.1 CO<sub>2</sub> fixation with (homo)allyl alcohols and *t*-BuOI.

### CO<sub>2</sub> Fixation with Acetylenic Alcohols

The successful transformation of allyl and homoallyl alcohols to cyclic carbonates through CO<sub>2</sub> fixation under extremely mild conditions prompted us to investigate the use of acetylenic alcohols as substrates (Figure 2). An unsubstituted propargyl alcohol was subjected to the above CO<sub>2</sub> fixation reaction to afford a five-membered cyclic carbonate containing an iodomethylene group in high yield as a sole *E*-isomer (equation 2).

Propargyl alcohols having a variety of substituents at the propargylic position also trapped CO<sub>2</sub> to give the corresponding carbonates. 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 resulted in a highly efficient reaction. Butynyl alcohols were also applicable to the reaction, yielding six-membered cyclic carbonates. Substituents at the propargylic position are required for the fixation of CO<sub>2</sub> to propargyl alcohols in conventional methods [5]. However, such substrates could be readily employed in the present system.

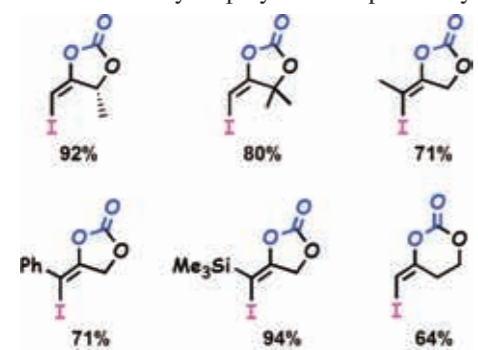
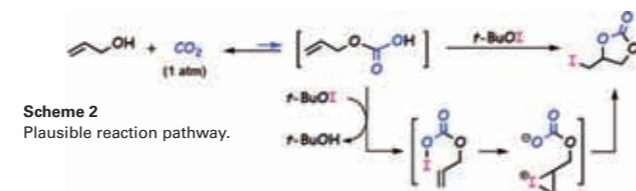


Fig.2 CO<sub>2</sub> fixation with acetylenic alcohols and *t*-BuOI.

### Proposed Mechanism

Although the precise mechanism of the reaction is unclear at present, the proposed mechanism shown in Scheme 2 is supported by the following experimental findings. In the reaction,

*t*-BuOCl is added to a solution of the alcohol and NaI under an atmosphere of CO<sub>2</sub>. NMR spectra indicated that *t*-BuOCl did not react with either the alcohol or CO<sub>2</sub> 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 (an saturated alcohol, *t*-BuOI and CO<sub>2</sub>) reacts first. To address this, the reaction of allyl alcohol and *t*-BuOI was monitored by <sup>1</sup>H NMR, and small signals, assigned to H<sub>2</sub>C=CHCH<sub>2</sub>OI was 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 from the reaction of sodium allyloxide and I<sub>2</sub> was exposed to CO<sub>2</sub>, 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, the corresponding oxidation product, an α,β-unsaturated aldehyde was obtained. The reaction of *t*-BuOI and CO<sub>2</sub> was then monitored by means of NMR (<sup>1</sup>H and <sup>13</sup>C), IR and ESIMS, but no reaction was observed. Therefore, as expected initially, CO<sub>2</sub> fixation appears to proceed through an allyl carbonic acid intermediate, as shown in Scheme 2. 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.



### Conclusion

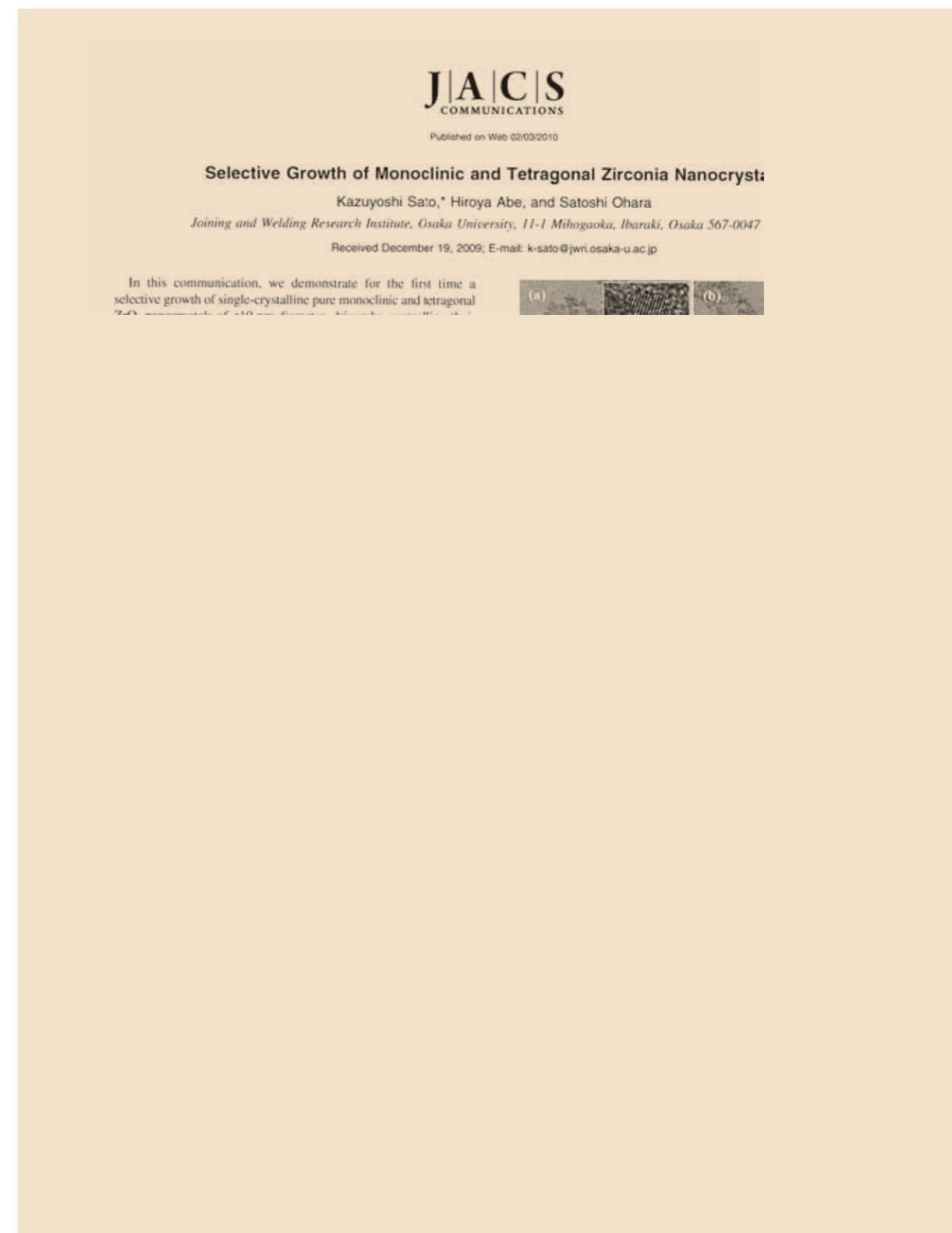
From the results of the present study and on the basis of the proposed main reaction pathway, a non-metal, non-basic, non-pressurized method was achieved, representing a new, low energy process for the chemical fixation of CO<sub>2</sub>. The simple methodology has a very broad scope in terms of both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

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### Selective Growth of Monoclinic and Tetragonal Zirconia Nanocrystals

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