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Paper in journals : this is the first page of a paper published in *Angewandte Chemie International Edition*. [*Angewandte Chemie International Edition*] 49, 1309-1311 (2010)

Angewandte
Chemie

DOI: 10.1002/anie.200906352

CO₂ Fixation

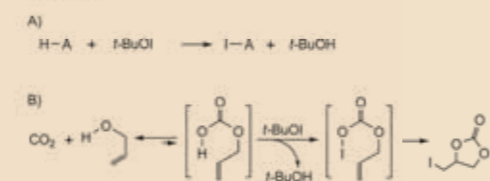
Atmospheric CO₂ Fixation by Unsaturated Alcohols Using *t*BuOI under Neutral Conditions**

Satoshi Minakata,* Itsuro Sasaki, and Toshihiro Ide

Carbon dioxide is a significant contributor to environmental warming.^{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 CO₂ and its subsequent use in producing valuable products is one possible approach to the effective utilization of CO₂. Efforts to increase the use of CO₂ for the production of useful organic chemicals are needed. Unfortunately, CO₂ 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 bases³ 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 CO₂ and alcohols (Scheme 1B), 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 CO₂-expanded methanol.⁵ Since the focus of the latter study was on evidence for the formation of alkylcarbonic acids from CO₂ and alcohols, CO₂ 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

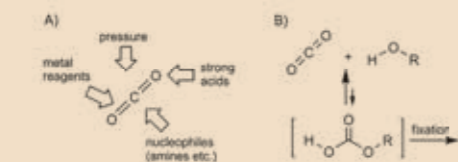
process would be interesting for chemical CO₂ fixation and would also reduce the requisite energy compared to conventional processes. In such a process, a carbonic acid monoester, generated spontaneously by the reaction of CO₂ with an alcohol, would result in its low-energy trapping. We previously reported 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 2A).⁷ Using this unique phenomenon, if a weak acid, such as an alkylcarbonic acid derived from CO₂, 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 CO₂ 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 CO₂ fixation to unsaturated alcohols, using conventional procedures have been reported. The synthesis of cyclic iodocarbonates by the trapping of CO₂ 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 CO₂ into propargylic alcohols has also been reported,⁹ but the procedure also requires high CO₂ pressures, the use of strong bases, metal catalysts, and the application of heat.

Herein we report an extremely mild procedure for the fixation of CO₂. The method takes advantage of the acidic character of the alkylcarbonic acid generated from CO₂ 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 CO₂-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 CO₂ 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 CO₂. B) Utilization of an acidic environment generated from CO₂ and alcohols.

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[**] This work was partially supported by Japan Science and Technology Agency.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.200906352>.

Angew. Chem. Int. Ed. 2010, 49, 1309–1311

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

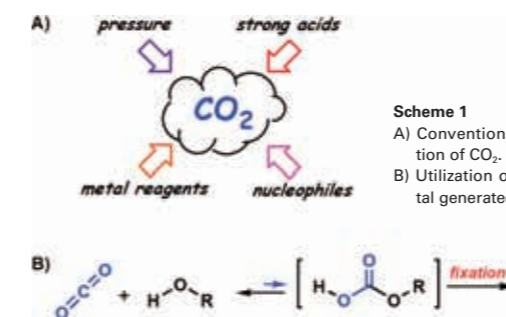
A New Process for Chemical CO₂ Fixation: Utilization of Weak Interaction with Alcohols

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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 CO₂ and its subsequent use in producing valuable products is one possible approach to the effective utilization of CO₂. Efforts to increase the use of CO₂ for the production of useful organic chemicals are needed. Unfortunately, CO₂ 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 CO₂ 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 CO₂-expanded methanol [3]. Since the focus of the latter study was on evidence for the formation of alkylcarbonic acids from CO₂ and alcohols, CO₂ capturing efficiency was not addressed.



Scheme 1
A) Conventional routes for the activation of CO₂.
B) Utilization of an acidic environment generated from CO₂ and alcohols.

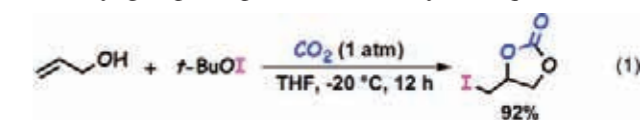
Strategy

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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂ to organic molecules. Based on this concept, an extremely mild procedure for the fixation of CO₂ is described in this paper.

CO₂ 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 CO₂ 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 CO₂ 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.

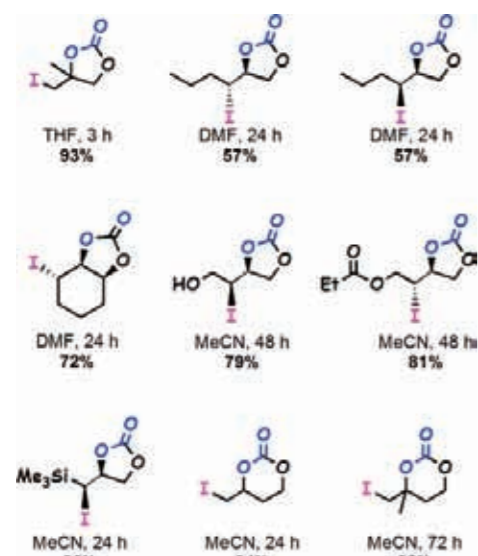
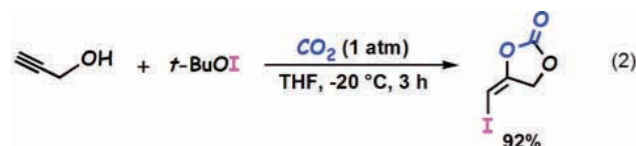


Fig.1 CO₂ fixation with (homo)allyl alcohols and *t*-BuOI.

CO₂ Fixation with Acetylenic Alcohols

The successful transformation of allyl and homoallyl alcohols to cyclic carbonates through CO₂ 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 CO₂ 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 CO₂ 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 CO₂ to propargyl alcohols in conventional methods [5]. However, such substrates could be readily employed in the present system.

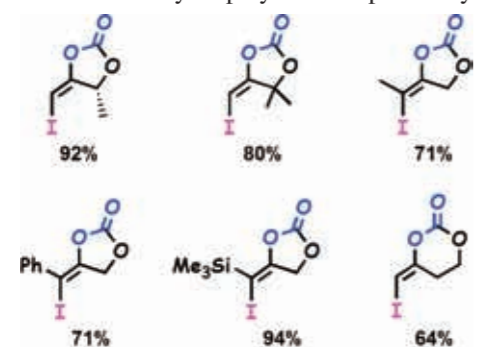
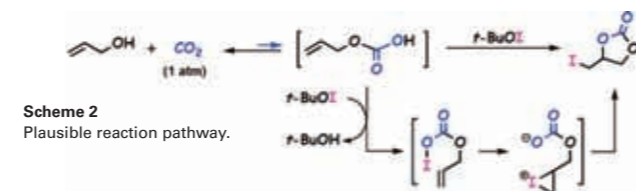


Fig.2 CO₂ fixation with acetylenic alcohols and *t*-BuOI.

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 CO₂. NMR spectra indicated that *t*-BuOCl did not react with either the alcohol or CO₂ 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 CO₂) reacts first. To address this, the reaction of allyl alcohol and *t*-BuOI was monitored by ¹H NMR, and small signals, assigned to H₂C=CHCH₂OI 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 I₂ was exposed to CO₂, 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 CO₂ was then monitored by means of NMR (¹H and ¹³C), IR and ESIMS, but no reaction was observed. Therefore, as expected initially, CO₂ 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.



Scheme 2
Plausible reaction pathway.

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 CO₂. 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 sp³ and sp² carbons are versatile functional groups for organic synthesis. We conclude that the results described herein describe an innovative CO₂ 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

Paper in journals : this is the first page of a paper published in *Journal of the American Chemical Society*.
[*Journal of the American Chemical Society*] **132**, 2538-2539 (2010)

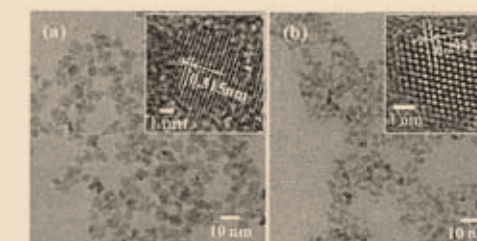


Figure 1. TEM images of ZrO₂ nanocrystals grown in the (a) TMAHC/TMAH and the (b) KHCO₃/KOH systems. Each respective inset shows an HRTEM image of an isolated nanocrystal.

In this communication, we demonstrate for the first time a selective growth of single-crystalline pure monoclinic and tetragonal ZrO₂ nanocrystals of <10 nm diameter, driven by controlling their surface energy. The growth of metal oxide nanocrystals with a well-organized crystalline phase is of fundamental and technological interest because in this way it is possible to tune their size-dependent unique properties,^{1,2} and thus establish their potential application in chemistry, electronics, optics, magnetics, and mechanics. ZrO₂ is a case in point, with a phase-dependent potential application in a number of technologies. Monoclinic ZrO₂ is important for catalysis,³ gate dielectrics,⁴ and bioactive coatings on bone implants,⁵ while tetragonal and cubic ZrO₂ are promising candidates for fuel cell electrolytes,⁶ oxygen sensors,⁷ and phase-transformation-toughened structural materials.⁸

In particular, the growth of pure monoclinic ZrO₂ nanocrystals of <10 nm diameter is a challenging task in the selective growth of the different phases, since a high-temperature tetragonal phase is stable at room temperature as the consequence of the dominance of the surface energy contribution to the Gibbs free energy of formation in this size range.⁹ A report by Zhang et al. suggests that the surface energy of oxides can be controlled by capping the surface with an organic substance.¹⁰ They successfully grow the unstable (001) faceted CeO₂ by capping with decanoic acid. Although surface capping-assisted growth using similar anionic substances was also applied to ZrO₂, the resulting nanocrystals of <10 nm diameter still chiefly exhibited a tetragonal phase.^{11,12} Herein, we report the facile selective growth route of pure monoclinic and tetragonal ZrO₂ nanocrystals of <10 nm diameter, with and without a cationic capping agent, N(CH₃)₄⁺.

In a typical procedure, a Zr⁴⁺ precursor (ZrOCl₂·8H₂O, 0.01 mol) was dissolved in a basic aqueous solution (pH ≈ 10.5) containing a mixture of either N(CH₃)₄HCO₃ (tetramethyl-ammonium hydrogen carbonate; TMAHC)/N(CH₃)₄OH (tetramethyl-ammonium hydroxide; TMAH) or KHCO₃/KOH. The clear solution of dissolved precursor was transferred into a 50 mL, Teflon-lined, stainless steel autoclave and heat treated at 150 °C. The products were obtained as well-dispersed colloidal solutions. ZrO₂ nanocrystals in the solution were purified by washing ten times with deionized water using ultrafiltration, with a molecular weight cutoff of 3000 for subsequent characterizations. The yield of ZrO₂ nanocrystals was almost 100% in both TMAHC/TMAH and KHCO₃/KOH systems. The ZrO₂ nanocrystals were characterized by transmission electron microscopy (TEM; JEOL JEM-2100F) with an accelerating voltage of 200 kV, X-ray diffraction (XRD; JEOL JDX-3530M) with Cu Kα radiation (λ = 0.154178 nm) at 40 kV and 40 mA, Raman spectroscopy (Horiba Jobin Yvon LabRAM ARAMIS) at room temperature with 532 nm excitation line of a diode-pumped solid state laser, and UV-vis adsorption spectroscopy (Shimadzu, UV-2450) with a double-beam recording spectrometer using 1 cm quartz cells.

Figure 1 shows TEM images of ZrO₂ nanocrystals grown in the TMAHC/TMAH and KHCO₃/KOH systems. These images clearly

indicate that both nanocrystals consist entirely of crystals of a uniform size of <10 nm diameter. The inset shows the high-resolution TEM (HRTEM) image of an isolated nanocrystal, indicating the single-crystalline nature of the nanocrystals grown in both systems. The lattice spacing is 0.315 and 0.295 nm, corresponding to (-111) of monoclinic and (111) of tetragonal ZrO₂ for the nanocrystals grown in the TMAHC/TMAH and the KHCO₃/KOH systems, respectively. Figure S-1 (Supporting Information) shows the size distribution of the ZrO₂ nanocrystals in the aqueous solution measured by dynamic light-scattering method, showing the nanocrystals almost perfectly dispersed in the aqueous solution by taking into account that the hydrodynamic diameter overestimates by several nanometers the real size.¹³

The XRD patterns of the powdered nanocrystals shown in Figure 2 further confirm that the respective phases observed in the HRTEM images represent the entire nanocrystals in both systems. The peaks are relatively broad, supporting the very small crystalline size. The sizes estimated by Scherrer's formula using full width of half maxima of (-111) for monoclinic and (111) for tetragonal phases were almost the same at 5.4 and 5.2 nm, respectively. The inset of Figure 2 shows the Raman spectra recorded for colloidal solutions of ZrO₂ nanocrystals. For the nanocrystals grown in the TMAHC/TMAH system, the purely monoclinic structure is confirmed by the observation of 13 Raman modes of the 18 (9A_g + 9B_g) expected by symmetry analysis,¹⁴ which provides evidence that the growth of monoclinic ZrO₂ nanocrystals shown above was driven by the surface capping with N(CH₃)₄⁺ (denoted as TMA⁺ in the following text), and not by the surface energy reduction through agglomeration by drying. The broad Raman band for the tetragonal ZrO₂ nanocrystals indicates that they involve highly disordered lattice defects.¹⁴

Optical absorption spectra of the colloidal ZrO₂ solutions shown in Figure 3 provide information relating to the lattice defects. Two absorption shoulders are clearly observed at around 5.2 and 5.7 eV for the ZrO₂ nanocrystals grown in the TMAHC/TMAH system. These are almost identical to the optical band gaps of bulk monoclinic ZrO₂,¹⁵ indicating less defective lattices.¹⁶ The tetrago-

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