Solar Energy Utilization

DOI: 10.1002/ange.201206166

Solar-Driven Incorporation of Carbon Dioxide into α-Amino Ketones[**]

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The recent manifestation of the potential risk inherent to nuclear technologies has incited a strong demand for exploration of innovative means to exploit energy from natural sources, thus increasing the need for research on sustainable energy in many scientific fields. Chemists can contribute by developing chemical systems to utilize solar light, which is undoubtedly the best source of sustainable energy available on the planet.[1] Another imperative issue is the establishment of carbon-neutral systems.[2] One synthetic approach to this issue is the incorporation of CO_2 into organic compounds as a chemical feedstock.[3] High-energy compounds suit energetically low CO_2 as the reaction partner. Under these circumstances, it presents a significant challenge to simultaneously tackle the two issues mentioned above. Thus, we tried to develop a reaction that is promoted by solar light and utilizes CO_2 as a chemical feedstock (Figure 1).

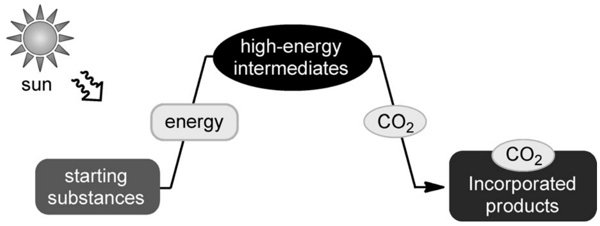
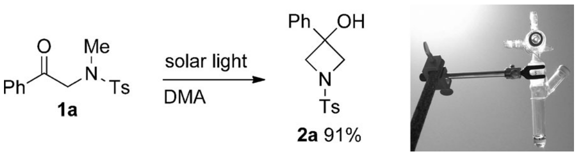


Figure 1. Solar-driven CO_2 incorporation.

We report herein a solar-driven process that incorporates CO_2 into α-methylamino ketones. The resulting amino-substituted cyclic carbonates are expected to be useful building blocks of pharmaceuticals and fuel additives.[4] Our attention was initially directed to a photochemical cyclization reaction observed with α-methylamino ketones.[5] Of note was that this photoreaction proceeded in an energetically uphill direction. A high-energy four-membered ring[6] was constructed through the insertion of a photo-excited carbonyl group into the carbon–hydrogen bond of a pendant methyl group on a nitrogen atom. In a formal sense, the intrinsically inert carbon–hydrogen bond was cleaved[7] and added across the carbon–oxygen double bond in a 4-*exo-trig* mode.[8] Although the reaction was originally reported to require irradiation with a mercury lamp, which used electricity,[5b] we discovered that natural solar light successfully effected this energetically uphill reaction; α-amino ketone **1a** cyclized at a reasonable rate upon exposure to solar light (Scheme 1).



Scheme 1. Solar-light-promoted cyclization of **1a**. On the right, the solution in the reaction vessel made of ordinary Pyrex glass is shown. Ts = toluenesulfonyl.

Furthermore, ordinary Pyrex glass, not quartz was suitable for the reaction vessel; light of wavelengths below 400 nm was required for the photoreaction, and Pyrex glass transmitted a sufficient amount of operative light even on a cloudy day. Thus, simply setting a Pyrex tube containing a solution of **1a** in *N,N*-dimethylacetamide (DMA) on a balcony or rooftop brought about the cyclization. The conversion was dependent upon the amount of solar radiation. We defined it as "sunny" when an hourly solar radiation over 0.4 $kW\,m^{-2}$ was observed, and as "cloudy" when it ranged from 0.1 to 0.4 $kW\,m^{-2}$. Typically, the total amount of solar radiation amounted to 5.5 $kWh\,m^{-2}$ in eight hours on a sunny day to cause full conversion of **1a** on a 0.1 mmol scale (0.10 $mmol\,L^{-1}$; Figure 2 A). The reaction mixture was subsequently applied to conventional column chromatography on silica gel and analytically pure azetidinol **2a** was isolated in 91 % yield. In contrast, an analogous experiment on a cloudy day produced **2a** in 54 % yield after eight hours (Figure 2 B), when the total amount of solar radiation reached 0.9 $kWh\,m^{-2}$. Thus, it turned out to be possible to transfer **1a** into the product[9] by using solar energy even on a cloudy day.

We next attempted to incorporate CO_2 into azetidinol **2a**, in which energy has been stored, by reacting it with CO_2, and a remarkably simple way was found; CO_2 was successfully incorporated upon exposure of a solution of **2a** in DMA to gaseous CO_2 in the presence of a base. For example, stirring a heterogeneous mixture of **2a** and Cs_2CO_3 (4.0 equiv) in DMA under an atmosphere of CO_2 (1 atm) at 60 °C for ten hours led to the quantitative production of the cyclic

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[**] This work was supported in part by a Grant-in-Aid for Scientific Research on Innovative Areas "Molecular Activation Directed toward Straightforward Synthesis" and Grant-in-Aid for Scientific Research (B) from MEXT and The Asahi Glass Foundation.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201206166.

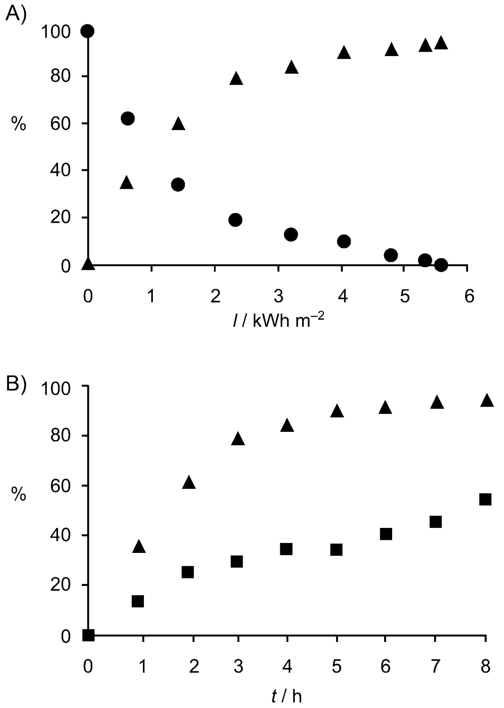
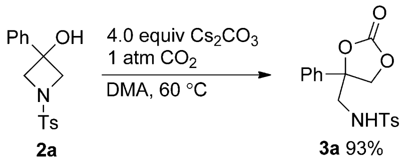


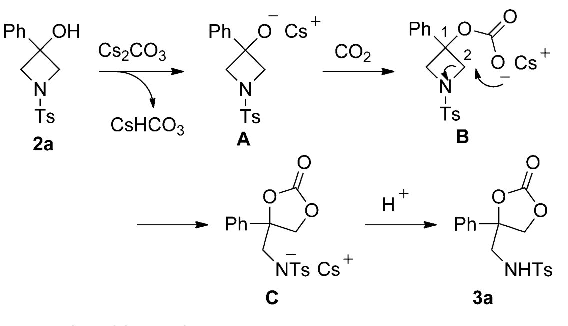
Figure 2. Solar-light-promoted cyclization of **1a**. The reactions were conducted on a 0.1 mmol scale. A) Residual ratio of **1a** (●) and yield of **2a** (▲) during solar radiation. B) Yield of **2a** over time on sunny (▲) and cloudy (■) days.

carbonate **3a**, which was isolated in 93% yield after purification by chromatography (Scheme 2). Organic bases, such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), also afforded **3a**, albeit in a lower yield (56%).



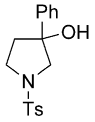
Scheme 2. CO_2 incorporation.

The formation of **3a** is explained by assuming the pathway depicted in Scheme 3.[4] Azetidinol **2a** is initially deprotonated by Cs_2CO_3 to produce alkoxide anion **A**, which subsequently adds to CO_2 to afford carbonate anion **B**. The following nucleophilic attack of the anionic oxygen onto the 2-carbon atom prompts displacement of the tosylamide anion through a 5-*exo-tet* process.[8] Thus, the four-membered ring is opened, thereby releasing the energy originating from sun. Finally, protonation of **C** affords **3a**.



Scheme 3. Plausible mechanism.

For comparison, pyrrolidinol **4** was subjected to the identical reaction conditions. Unlike the four-membered counterpart **2a**, the five-membered compound **4** failed to react and was recovered unchanged. The contrasting results observed with **2a** and **4** lend support to the explanation that the major driving force for the CO_2-capturing reaction is the release of the energy stored in the form of the strained four-membered ring.



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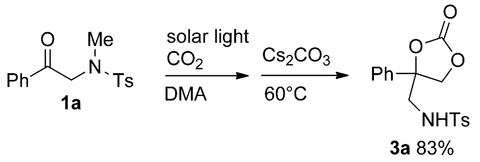
The experimental procedures for both the photochemical cyclization reaction and the CO_2-capturing reaction are so simple that it is possible to carry them out in a single flask (Scheme 4). Initially, a DMA solution of **1a** in an atmosphere of CO_2 (1 atm) was irradiated with solar light outside. After completion of the photoreaction, Cs_2CO_3 was simply added to the reaction mixture, which was then heated at 60 °C for ten hours in a fume hood. Isolation by chromatography afforded the analytically pure cyclic carbonate **3a** in 83% yield based on **1a**.

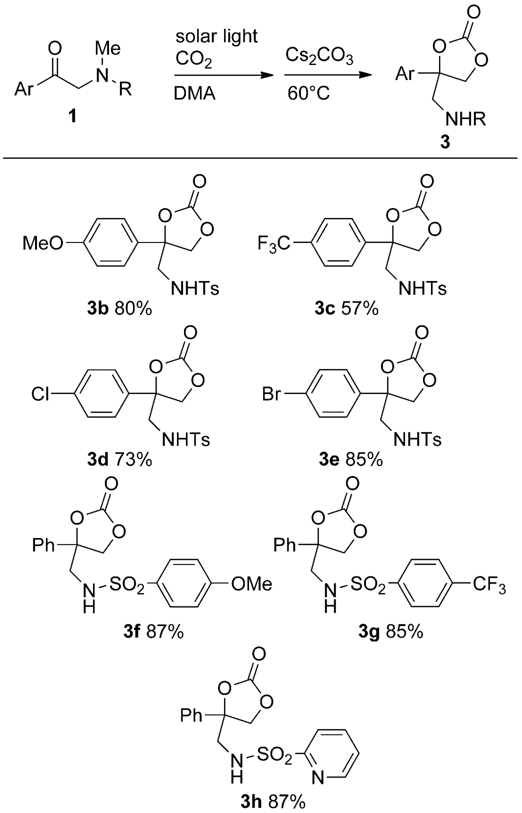


Scheme 4. Solar-driven CO_2 incorporation into α-amino ketone **1a**.

The broad generality of this consecutive process was verified by application to various acetophenone derivatives (Scheme 5). Both an electron-donating methoxy group and an electron-withdrawing trifluoromethyl group were allowed at the *para*-position of the benzoyl group, and the corresponding products **3b** and **3c** were isolated in reasonable total yields. The presence of possibly photoactive bromo and chloro groups[10] had essentially no effect on the reaction (**3d** and **3e**). Sulfonyl groups other than a *p*-toluenesulfonyl group were also suitable as the substituent on the nitrogen atom (**3f–h**).

In summary, we have developed the unique solar-driven transformation of α-amino ketones. CO_2 is incorporated to afford amino-substituted cyclic carbonates, which are potentially useful ingredients in industry.

Although photosynthesis is a complex assembly of a number of elementary reactions, it can be divided into two major reactions; the light reaction and the dark reaction. In the former reaction, solar energy is captured to promote an energetically uphill process with production of high-energy molecules (adenosine triphosphate (ATP) and nicotinamide adenine dinucleotide phosphate (NADPH)). The dark reaction is an energetically downhill process that does not require light. ATP and NADPH, which have chemically stored solar



Scheme 5. Scope of solar-driven CO_2 incorporation into α-amino ketone **1**. Overall yields of isolated products are given. Reactions were conducted on a 0.2 mmol scale with the following reagents and conditions: **1** (0.20 mmol), DMA (1.0 mL), solar light, ambient temperature, CO_2 (1 atm); then Cs_2CO_3 (0.80 mmol), 60 °C. See the Supporting Information for full experimental details.

energy during the former reaction, assist in the fixation of CO_2, which is intrinsically low in energy. Photosynthesis as a whole reduces CO_2 into carbohydrates. Although the present consecutive process does not involve CO_2 reduction, its mechanistic profile of energy resembles that of photosynthesis and presents a simple model of the chemical utilization of solar energy for CO_2 incorporation.

Experimental Section

A typical procedure for the one-pot reaction of α-amino ketone **1a** with carbon dioxide: α-Amino ketone **1a** (30.3 mg, 0.10 mmol) was placed in a Pyrex tube. The vessel was subsequently filled with CO_2 (1 atm) by vacuum–refill cycles (three times), and *N,N*-dimethylacetamide (1.0 mL) was added therein. The mixture was exposed to solar light outside for eight hours. After completion of the photochemical reaction, Cs_2CO_3 (130 mg, 0.40 mmol) was added to the reaction mixture, which was then stirred at 60 °C in a fume hood. After ten hours, the reaction mixture was treated with HCl aq. (2.0 M) and the aqueous layer was extracted with Et_2O (three times). The combined organic layer was washed with water (three times) and brine (once), dried over $MgSO_4$, and concentrated. The residue was purified by preparative thin-layer chromatography on silica gel (hexane/ethyl acetate = 3:1) to afford the analytically pure carbonate **3a** (28.8 mg, 0.083 mmol, 83 % yield). ^{1}H NMR: $\delta = 2.40$ (s, 3H), 3.30 (dd, $J = 14.4$, 5.6 Hz, 1H), 3.40 (dd, $J = 14.4$, 8.8 Hz, 1H), 4.54 (d, $J = 8.4$ Hz, 1H), 5.08 (d, $J = 8.4$ Hz, 1H), 5.70 (dd, $J = 8.4$ Hz, 5.6 Hz, 1H), 7.26–7.32 (m, 4H), 7.34–7.43 (m, 3H), 7.69–7.73 ppm (m, 2H); ^{13}C NMR: $\delta =$ 21.5, 50.3, 72.4, 85.0, 124.2, 126.9, 129.2, 129.9, 136.5, 138.1, 143.9, 154.2 ppm; HRMS (ESI$^+$): Calcd for $C_{17}H_{18}NO_5S$, $[M+H]^+$ 348.0900, found *m/z* 348.0892. Elemental analysis calcd for $C_{17}H_{18}NO_5S$: C, 58.78; H, 4.93; N, 4.03; O, 23.03; S, 9.23; found: C, 58.71; H, 4.96; N, 3.89; O, 22.84; S, 9.32; IR (ATR): 3261, 1773, 1435, 1319, 1045 cm^{-1}.

Received: August 1, 2012

Keywords: C–H activation · carbon dioxide · photochemistry · photosynthesis · strained molecules

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