Photoinduced Reduction of *gem*-Dichlorocyclopropanes with SmI_2 and Benzenethiol

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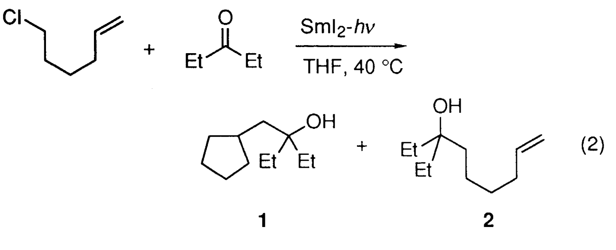
Upon irradiation with visible light, *gem*-dichlorocyclopropanes undergo reductive dechlorination with samarium diiodide and benzenethiol to provide the corresponding cyclopropanes in good yields. The reaction may proceed via the hydrogen abstraction from PhSH by cyclopropyl radicals formed in situ by the reduction with SmI_2.

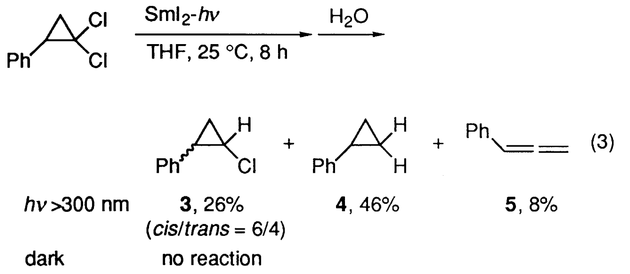
Samarium diiodide (SmI_2) is widely employed as a useful one-electron reducing agent in organic synthesis.[1] For example, the reductive dehalogenation of organic halides is well-known as a representative reaction using SmI_2, in which organic iodides and bromides can easily be reduced to the corresponding hydrocarbons.[2] On the other hand, the reduction of organic chlorides with SmI_2 alone is difficult, and excess amounts of HMPA are required to accomplish this reduction.[3] On the contrary, we have recently revealed that, upon irradiation with visible light, the reduction of organic chlorides with SmI_2 can take place even in the absence of HMPA.[4,5] In this reduction, both radical and organosamarium species are expected to form as key intermediates (eq 1). It is therefore of great interest from the viewpoint of synthetic organic chemistry to control these two species.

$$\text{R-Cl} \xrightarrow{SmI_2\text{-}h\nu} \text{R}\bullet \xrightarrow{SmI_2} \text{RSmI}_2 \xrightarrow{H^+} \text{R-H} \qquad (1)$$

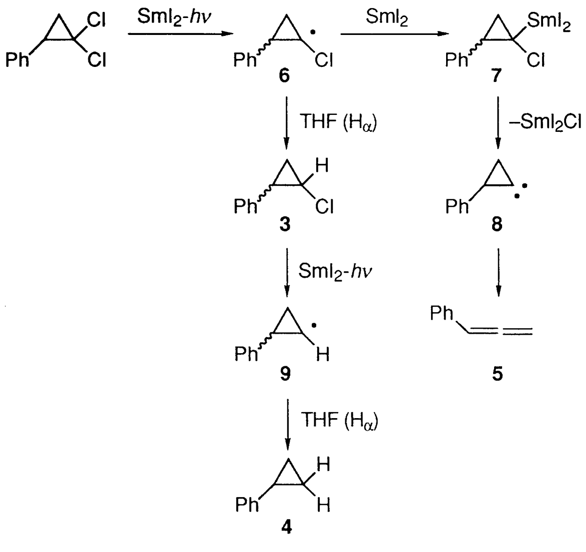
In the SmI_2-HMPA system, the first bimolecular rate constants for the reduction of R• (primary alkyl radicals) to $RSmI_2$ is estimated to be $0.5\text{~}7.0 \times 10^6\ M^{-1}s^{-1}$.[6] However, it is unclear whether this value can be applied directly to the SmI_2-*hv* reduction system. Thus, we first examined the SmI_2-mediated Barbier reaction of 5-hexenyl chloride (0.1 M) with diethyl ketone under irradiation with visible light (eq 2). The reaction afforded the cyclic and acyclic Barbier adducts (**1** and **2**) with the ratio of 29/71. As the rate constant (k_c) for cyclization of 5-hexenyl radical is $4.19 \times 10^5\ s^{-1}$ (at 40 °C),[7] the bimolecular rate constant for the reduction of R• with SmI_2-*hv* is roughly estimated to be $10^5\ M^{-1}s^{-1}$ (at 40 °C).



With these kinetic consideration in mind, we next examined the reduction of geminal dichlorocyclopropanes with a SmI_2-*hv* system.[8] Upon irradiation through Pyrex with tungsten lamp (>300 nm), the reaction of 1,1-dichloro-2-phenylcyclopropane with SmI_2 (4 equiv) in THF was conducted at 25 °C for 8 h (eq 3). After treatment with aqueous workups, 1-chloro-2-phenylcyclopropanes **3**, phenylcyclopropanes **4**, and phenylallene **5** were obtained in 26%, 46%, and 8% yields, respectively. In the dark, no reaction took place, indicating that the visible-light-irradiation is essential for this dechlorination.[9]



To elucidate the reaction pathway, a deuterium trapping experiment was examined. Quenching of the reaction mixture with D_2O instead of H_2O afforded a mixture of **3**, **4**, and **5** with a similar product ratio as the case of the H_2O quench, but the formation of deuterized products was not detected at all. This suggests the possibility that, before quenching with H_2O, in situ formed cyclopropyl radicals abstract hydrogen from solvent (THF).

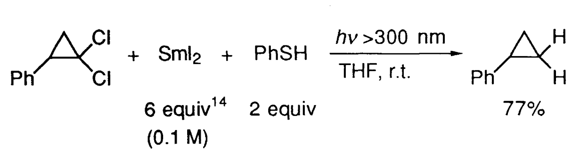


Scheme 1. A possible reaction path.

Scheme 1 presents a mechanistic model for interpreting these observations. Photoinduced one electron transfer from SmI_2 to 1,1-dichloro-2-phenylcyclopropane forms α-chlorocyclopropyl radical **6**. If the radical **6** undergoes further reduction with SmI_2 to generate samarium species **7**, the α-elimination of SmI_2Cl from **7**, followed by the rearrangement of carbene species **8** may lead to phenylallene.[10] On the other hand, if the radical

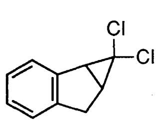
6 abstracts hydrogen from THF, monochlorocyclopropane **3** is produced. Moreover, **3** may undergo a similar reduction/ hydrogen abstraction sequence, giving phenylcyclopropane **4**.

The rate constant for the hydrogen abstraction of primary alkyl radicals from THF is reported to be 6.0 x 10^3 $M^{-1}s^{-1}$ (25 °C).[11] As described already, the rate constant for the electron transfer of SmI_2 to alkyl radicals is estimated to be 10^5 $M^{-1}s^{-1}$ (40 °C). Accordingly, to improve the product selectivity, the use of excellent hydrogen donors is promising. We selected diethyl phosphite[12] and benzenethiol as the hydrogen atom source. When the photoinduced reduction of 1,1-dichloro-2-phenylcyclopropane with SmI_2 was carried out in the presence of diethyl phosphite, the formation of allene **5** was suppressed entirely. However, the undesired reduction of the phosphite with SmI_2 took place competitively. On the other hand, the rate constant for the hydrogen abstraction of primary alkyl radicals from PhSH is determined to be 9.2 x 10^7 $M^{-1}s^{-1}$ (25 °C).[13] A similar reduction in the presence of PhSH led to selective formation of phenylcyclopropane successfully, as indicated in eq 4.



(4)

The procedure can be employed with substates bearing 3,5-fused rings and sterically bulky substituents (**10** and **11**, respectively). The corresponding dechlorinated cyclopropanes are formed in 70% and 46% yields, respectively.



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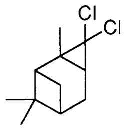

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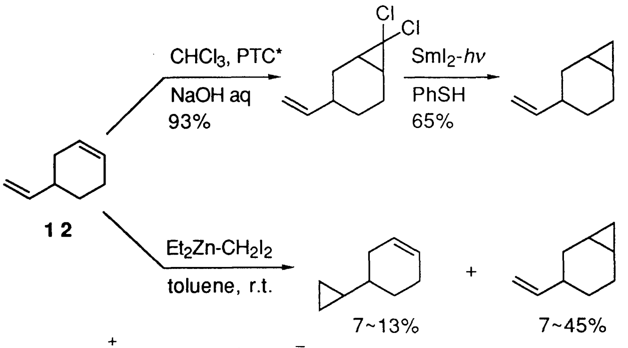
Simmons-Smith reaction is accepted as one of the most useful methods for the construction of cyclopropane rings from alkenes.[15]



*PTC: $Bz\overset{+}{N}Me_2CH_2CH_2OH\ OH^-$.

Scheme 2. Regioselective cyclopropanation.

In this reaction, electronic effects have a weak influence, with a small preference for electron-rich alkenes, but steric effects often play a dominant role. Contrary to this, the addition of dichlorocarbenes to olefins is governed mainly by electronic effects (preferring electron-rich alkenes). For example, Simmons-Smith cyclopropanation of 4-vinylcyclohexene **12** took place at both terminal and inner olefinic positions,[16] whereas dichlorocarbene adds to the cyclohexene unit of **12** predominantly (Scheme 2).[17] Subsequent dechlorination with SmI_2-*hν*-PhSH provides a regioselective synthesis of bicyclic cyclopropanes.

In conclusion, we have developed a new reduction system, *i.e.*, SmI_2-*hν*-PhSH, which is useful for the selective dechlorination of *gem*-dichlorocyclopropanes.[18]

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14 In principal, 4 equiv of SmI_2 is essential for the dechlorination of *gem*-dichlorocyclopropanes, because PhS• (formed in situ via the hydrogen abstraction by cyclopropyl radicals) is reduced by SmI_2 to form $PhSSmI_2$. In order to avoid a lowering of the concentration of SmI_2 at the latter half of the reaction, we use excess SmI_2.

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