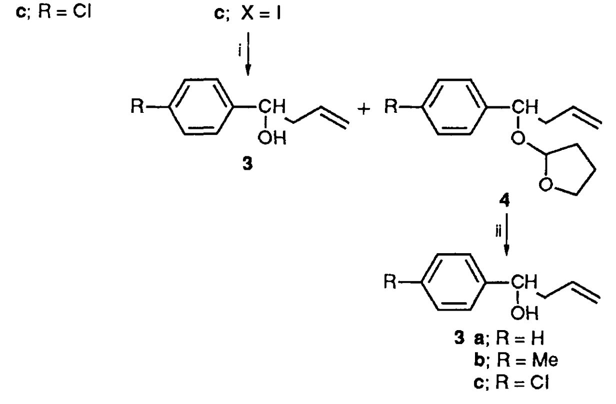
Lanthanide(II) Iodide Catalysed Photochemical Allylation of Aldehydes with Allylic Halides

Teruyuki Kondo, Motohiro Akazome and Yoshihisa Watanabe*

Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606, Japan

Lanthanide(II) iodides such as SmI_2 and YbI_2 show high catalytic activity for the photochemical allylation of aldehydes with allylic halides to give the corresponding homoallylic alcohols.

Since lanthanide or actinide elements have 4f or 5f atomic orbitals, many intriguing reactions mediated by them which cannot be achieved by d-block transition metal compounds are expected to occur.[1] Especially, low valent lanthanide complexes such as Sm^{II} compounds have been used as one-electron transfer reagents in various organic syntheses.[2] However, almost all of these reactions require use of stoichiometric and/or excess amount of Sm^{II} compounds and except for the hydrogenation,[3] polymerization[1b,4] and isomerization[5] reactions, little is known of lanthanide complex catalysis.



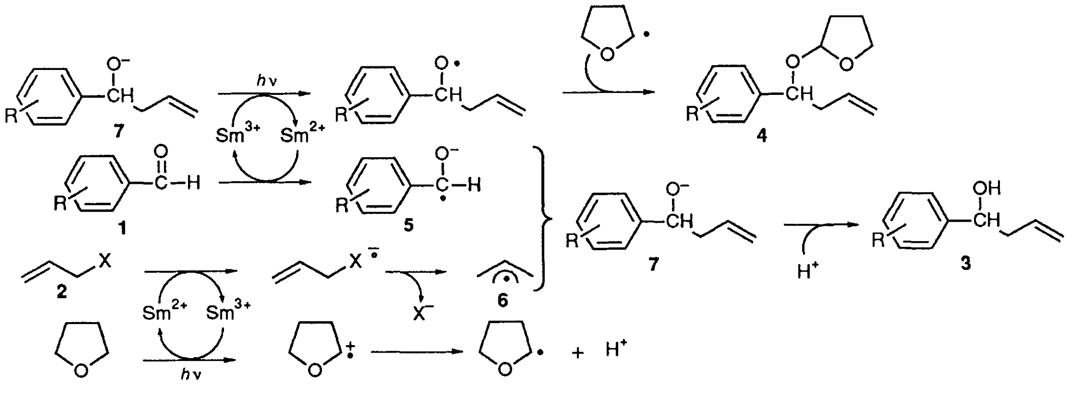
Scheme 1 Reagents and conditions (see Table 1); i, SmI_2 (catalyst), K_2CO_3, THF; ii, 3% H_2SO_4 aq.

Recently, much attention has been paid to lanthanide catalysed reactions. Marks *et al.* reported $[(C_5Me_5)_2LnH]_2$[6] and $(C_5Me_5)_2Sm(THF)_2$[7] catalysed intramolecular hydroamination of alkenes and Lu *et al.* reported SmI_2 catalysed addition reaction of perfluoroalkyl iodides to alkenes or alkynes.[8] Leonard *et al.* reported $SmCl_3$ catalysed electrochemical coupling reaction between aldehydes and ketones,[9] and Ishida *et al.* reported hydroxymethylation of 1,3-dimethyluracil using the photoredox system of Eu^{3+}/Eu^{2+} in methanol.[10]

In this communication, we report the novel lanthanide(II) iodides catalysed photochemical allylation of aldehydes with allylic halides (Scheme 1).

When aromatic aldehydes were treated with allylic halides in the presence of a catalytic amount of lanthanide(II)iodide under photo-irradiation, the corresponding homallyl alcohols **3** were generally obtained together with the generation of ethers **4** (Scheme 1). After quantitative hydrolysis of **4** with 3% H_2SO_4 aq. to **3**, homoallyl alcohols **3** were isolated by medium pressure column chromatography and fully characterized. Representative results are summarized in Table 1.

The lanthanide complexes, divalent samarium and ytterbium iodides showed the highest catalytic activity (Runs 1,2). However, the catalytic activity of trivalent lanthanide chlorides was moderate to low (Runs 3,4). In the present reaction, both continuous photo-irradiation and addition of K_2CO_3 were essential for catalytic activity. Without photo-irradiation (only reflux in THF) or in the absence of K_2CO_3, homoallyl alcohol **3** was not obtained and when the UV light was removed, the reaction ceased completely. Furthermore, addition of galvinoxyl as a radical scavenger inhibited the



Scheme 2

Table 1 Lanthanide catalysed photochemical allylation of aldehydes with allylic halides[a]

Run	Aldehyde 1	Allylic halide 2	Catalyst	Product 3	Yield/%[b]
1[c]	a	a	SmI_2	a	51
2	a	a	YbI_2	a	43
3	a	a	$SmCl_3 \cdot 6H_2O$	a	33
4	a	a	$EuCl_3 \cdot 6H_2O$	a	34
5[d]	a	a	SmI_2	a	0
6	b	a	SmI_2	b	19
7	c	a	SmI_2	c	18
8	a	b	SmI_2	a	10
9	a	c	SmI_2	a	5

[a] A mixture of aldehyde (5.0 mmol), allylic halide (10 mmol), K_2CO_3 (3 mmol) and SmI_2–THF solution (0.040 mol dm^{-3}, 10 ml) was irradiated in a Pyrex flask using a 200 W high pressure mercury lamp for 10 h at room temperature under an argon atmosphere. [b] Determined by GLC based on the amount of aldehyde. [c] SmI_2–THF solution (0.020 mol dm^{-3}, 10 ml) was used. [d] Galvinoxyl (1.0 mmol) was added.

present reaction completely (Run 5) and these results suggest that the present reaction would include the non-chain radical mechanism (see below). *p*-Tolualdehyde and *p*-chlorobenzaldehyde also reacted with allyl bromide, but the yields of the corresponding homoallyl alcohols were low (Runs 6,7). Aliphatic aldehydes such as heptanal and cinnamaldehyde, however, did not react with allyl bromide under the present reaction conditions.

Among the allylic compounds, allyl bromide gave the best result (Run 1) and allyl iodide, allyl chloride (Runs 8,9) and allyl phenyl ether were less reactive. Furthermore, when benzyl halides instead of allyl halides were employed in the present reaction, similar benzylation of aldehyde also ensued.

By considering both effects of photo-irradiation and radical scavenger, a tentative catalytic cycle for the generation of **3** and **4** is depicted in Scheme 2. Since samarium(II) iodide is a strong one-electron donor ($Sm^{3+}/Sm^{2+} = -1.55$ V),[11] the first step of the present reaction is the formation of an anion radical **5** from aldehyde **1**. Allylic halide **2** is also reduced by SmI_2 to give an allyl radical **6**.[†] The coupling reaction between **5** and **6** would give an anion **7**, which could immediately abstract a proton to give the corresponding homoallyl alcohol **3**. For the recyclization of generated Sm^{III} species to active Sm^{II} species,[‡] continuous photo-irradiation is essential and ether **4** is thought to be generated in this recycling step. Mechanistic study and application of the present reaction are now in progress.

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[†] If the allyl radical **6** exists as a free radical, both propene, which would be generated from abstraction of a proton by the allyl radical **6**, and 1,5-hexadiene, which would be generated from self-coupling of the allyl radical **6**, should be obtained in the reaction mixture. However, only 12 μmol of propene was detected and 1,5-hexadiene was not detected. These results show that the radical **6** as well as the anion radical **5** should strongly interact with the samarium in the coordination sphere and this would also be the reason why the radical **6** could effectively combine with the anion radical **5** even in low concentration.

[‡] In order to investigate the reaction mechanism, absorption spectroscopy was employed in the stoichiometric reaction. The SmI_2 solution employed in the present reaction was an intense blue–green and showed absorption bands at 282, 349, 418, 557 and 618 nm.[12] When SmI_2–THF [0.040 mol dm^{-3}, 25 ml (1.0 mmol)] solution was added to a mixture of benzaldehyde (1.0 mmol), allyl bromide (1.0 mmol), and K_2CO_3 (1.0 mmol), the colour of the solution immediately turned yellow. This yellow solution showed no absorption band at > 300 nm. After irradiation for 5 h, however, the solution showed two absorption bands at 295 and 366 nm, which suggests the generation of an active samarium species.