Pergamon

Tetrahedron Letters, Vol. 38, No. 52, pp. 9017-9018, 1997
© 1997 Elsevier Science Ltd
All rights reserved. Printed in Great Britain
0040-4039/97 $17.00 + 0.00

PII: S0040-4039(97)10409-9

Novel Enhancement of the Reducing Ability of Ytterbium Diiodide by Irradiation with Near-UV Light

Akiya Ogawa,* Syoji Ohya, Yukihito Sumino, Noboru Sonoda,† and Toshikazu Hirao*
Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan
†*Department of Applied Chemistry, Faculty of Engineering, Kansai University, Suita, Osaka 564, Japan*

Abstract: *Irradiation with near-UV light dramatically enhances the reducing ability of ytterbium diiodide* (*YbI_2*). *Organic bromides, iodides, tosylates, and tellurides are reduced efficiently by a YbI_2-hv system, while these can not be reduced with YbI_2 in the dark.* © 1997 Elsevier Science Ltd.

Samarium diiodide (SmI_2) has attracted considerable attention during the last two decades in view of its importance as a one-electron reducing agent and a source for the synthesis of other samarium reagents in organic synthesis.[1] In contrast, ytterbium diiodide (YbI_2), which can be prepared easily from ytterbium metal and diiodoethane in THF similarly as SmI_2,[2] has far fewer applications, probably because of its lower reducing potential and lower solubility in common organic solvents. In practice, hitherto known reactions of YbI_2 as a one-electron reducing agent are limited to the following:[3] YbI_2-induced reduction of conjugated C=C double bonds of cinnamic acid and its ethyl ester,[2] reductive cyclization of 2-(ω-iodoalkyl)cycloalkanones by a YbI_2-cat. Fe(III) system,[4] YbI_2-catalyzed photochemical allylation of aldehydes with allylic halides,[5] and deoxygenative coupling of amides by a YbI_2-Yb system.[6]

As indicated in Fig.1, YbI_2 exhibits its absorption maximum in near ultraviolet regions, *i.e.*, λ_{max} = 307 nm, 342 nm, and 390 nm, which can be identified as a $4f^{14}\rightarrow4f^{13}5d^1$ transition.[7] Surprisingly, we have found that irradiation with near-UV light leads to pronounced enhancement of the reducing ability of YbI_2 (eq 1).[8]

$$\text{R-Br} + \text{YbI}_2 \xrightarrow[\text{THF, 30 °C}]{h\nu} \text{R-H} \qquad (1)$$

R = $^n C_{12}H_{25}$		
	>300 nm	85%
	300~420 nm	60%
	>500 nm	trace

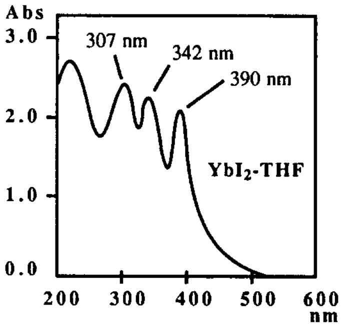


Fig. 1 UV-visible spectrum of YbI_2 in THF (4.0×10^{-5} mol/L)

Although the reduction of dodecyl bromide with YbI_2 in THF does not take place at all in the dark, irradiation with a tungsten

Table 1. Photoinduced Reduction with YbI_2[a]

$$^nC_{12}H_{25}X + YbI_2 \xrightarrow{h\nu} {}^nC_{12}H_{26}$$

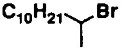
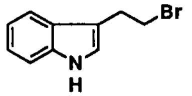
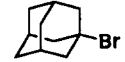
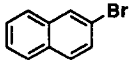
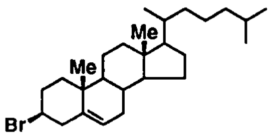
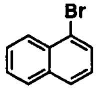
Entry	X	Yield, %		Entry	X	Yield, %	
		hv	dark			*hv*	dark
1	I	73	4	4	OTs	73	trace
2	Br	99	trace	5	SePh	25	no reaction
3	Cl	27	no reaction	6	Te-α-naphthyl[b]	40[c]	7

[a] Substrate (0.5 mmol), YbI_2 (4.0 mmol), THF (20 mL), 60 °C, 8 h. [b] $^nC_{11}H_{23}TeC_{10}H_7$-α was employed. [c] Both undecane and naphthalene were formed in 40% and 20% yields, respectively.

lamp through Pyrex causes efficient debromination giving dodecane in a quantitative yield (Table 1, entry 2).

Similar conditions can be employed with alkyl iodides and tosylates (entries 1 and 4), but the reduction of dodecyl chloride and dodecyl phenyl selenide gives rise to poor yields of dodecane (entries 3 and 5). The reduction of undecyl α-naphthyl telluride resulted in the formation of both undecane and naphthalene (entry 6). Unambiguously, these results indicate that, upon irradiation with the light of wavelength over 300 nm, YbI_2 exhibits a similar reducing power as that of samarium diiodide in THF.

Table 2. Photoinduced Reductive Debromination with YbI_2[a]

Entry	Substrate	Yield, %	Entry	Substrate	Yield, %
1		88	5		81
2		58			
3		74	6		80[b]
4		76			

[a] Reaction conditions: substrate (0.5 mmol), YbI_2 (4.0 mmol), THF (20 mL), 67 °C, 8 h. [b] 11 h.

Table 2 represents examples of the photoinduced reduction of functionalized bromides. The present debromination procedure can be employed with secondary and tertiary alkyl bromides (entries 1-2), aryl bromides (entries 3-4), and a heterocyclic bromide (entry 5). Cholesteryl bromide undergoes debromination efficiently (entry 6).

To enhance the synthetic utility of YbI_2-$h\nu$, we further examined the catalytic use of YbI_2 in the reduction of organic bromides. Since the reduction potential of YbI_2 (Yb^{3+}/Yb^{2+}) is estimated to be –1.15 eV,[2] co-reductants bearing a moderate reducing power look like a very favorable choice. Thus, the YbI_2-catalyzed reduction of dodecyl bromide was conducted by using excess amounts of aluminum (Al^{3+}/Al^0 = –1.66 eV) as a co-reductant. The catalytic reaction proceeded successfully, giving dodecane in a 88% yield (eq 2).[9] In the absence of a catalytic amount of YbI_2 (or in the dark), the present reduction did not occur at all.

$$\underset{1\ \text{mmol}}{{}^{n}C_{12}H_{25}Br} \quad + \quad \underset{4\ \text{mmol}}{Al} \quad \xrightarrow[\text{THF, 67 °C, 40 h}]{10\ \text{mol\%}\ YbI_2\text{-}h\nu} \quad \underset{88\%}{{}^{n}C_{12}H_{26}} \qquad (2)$$

In summary, this paper discloses a novel photoactivation of YbI_2 in the reduction of organic bromides, iodides, tosylates, and tellurides. Further investigation along these lines is now in progress.

Acknowledgments. This research was supported by a Grant-in-Aid for Scientific Research on Priority Areas "New Development of Rare Earth Complexes" No. 08220243 from the Ministry of Education, Science and Culture, Japan.

References and Notes

1. Kagan, H. B.; Namy, J. L. *Tetrahedron* **1986**, *42*, 6573; Inanaga, J. *Rev. Heteroat. Chem.* **1990**, *3*, 75; Imamoto, T. *Lanthanides in Organic Synthesis*; Academic Press: London, 1994; pp21-62; Molander, G. A. *Org. React.* **1994**, *46*, 211.
2. Girard, P.; Namy, J. L.; Kagan, H. B. *J. Am. Chem. Soc.* **1980**, *102*, 2693.
3. For $YbBr_2$, see: Taniguchi, Y.; Kuno, T.; Nakahashi, M.; Takaki, K.; Fujiwara, Y. *Appl. Organomet. Chem.* **1995**, *9*, 491.
4. Molander, G. A.; Etter, J. B. *J. Org. Chem.* **1986**, *51*, 1778.
5. Kondo, T.; Akazome, M.; Watanabe, Y. *J. Chem. Soc., Chem. Commun.* **1991**, 757.
6. Ogawa, A.; Nanke, T.; Takami, N.; Sekiguchi, M.; Kambe, N.; Sonoda, N. *Appl. Organomet. Chem.* **1995**, *9*, 461.
7. Namy, J. L.; Girard, P.; Kagan, H. B. *Nouv. J. Chim.* **1981**, *5*, 479.
8. For SmI_2-$h\nu$, see: Ogawa, A.; Sumino, Y.; Nanke, T.; Ohya, S.; Sonoda, N.; Hirao, T. *J. Am. Chem. Soc.* **1997**, *119*, 2745.
9. Takaki, K.; Nagase, K.; Beppu, F.; Fujiwara, Y. *Chem. Lett.* **1991**, 1665 and 1669.

(*Received in Japan* 16 *September* 1997; *accepted* 17 *October* 1997)