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Convenient Reduction of C-C Multiple Bonds Conjugated with Aromatic Rings by PhYbI Complex or Yb Metal†

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A variety of C-C multiple bonds conjugated with aromatic rings are smoothly reduced by the PhYbI/MeOH or Yb/MeOH systems under very mild conditions to give the corresponding saturated products in excellent yields. This reaction provides a novel convenient method for reduction of multiple bonds conjugated with aromatic rings.

C-C multiple bonds are reduced both by catalytic hydrogenation and by alkali metals in liquid ammonia. However, in systems of conjugated double bonds catalytic hydrogenation usually gives a mixture of all possible products and with alkali metals in systems containing aromatic rings, nuclear reduction will accompany the reduction of the side unsaturated bonds.1) In continuation of our study on the organolanthanoid chemistry,2) we have found that PhYbI complex or Yb metal can selectively reduce the C-C multiple bonds conjugated with aromatic rings and leave the aromatic rings unaffected. We now report the lanthanoid-mediated facile reduction of the C-C multiple bonds conjugated with aromatic rings to give the corresponding saturated products.

Table 1 summarizes the results of the reactions of (*E*)-stilbene under various reaction conditions. One can see from the table that reaction of PhYbI with the olefin in THF gives bibenzyl(**1**), the reduction product in 18% yield (run 1) and that when some amounts of MeOH are added as a hydrogen source, **1** is formed in high yield (run 2). As a hydrogen source, H_2O is not suitable to this reaction (run 3). Furthermore, Yb metal which is activated with a trace of MeI also shows high reducing ability (runs 4 and 5).

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† Dedicated to Professor T. Mukaiyama on the occasion of his 60th birthday.

Table 1. Reduction of (*E*)-stilbene by PhYbI or Yb[a)]

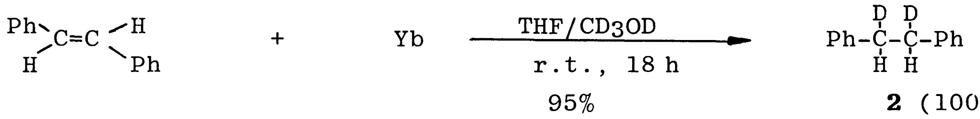
$$(E)\text{-PhCH=CHPh} \xrightarrow{\text{Reducing agent}} \underset{\mathbf{1}}{\text{PhCH}_2\text{CH}_2\text{Ph}}$$

Run	Reducing agent (mmol)	Hydrogen source[b)]	Yield of 1/%[c)]
1	PhYbI (1.5)[d)]	-	18
2	PhYbI (1.5)[d)]	MeOH	87
3	PhYbI (1.5)[d)]	H_2O[e)]	11
4	Yb (1.0)	MeOH	66
5	Yb (1.5)	MeOH	95[f)]

a)PhCH=CHPh: 0.5 mmol, THF: 4 ml, room temperature, 18 h. b)MeOH: 0.5 ml. c)NMR yield based on PhCH=CHPh. d)Yb:PhI=2.0:1.5. e)H_2O: 0.1 ml. f)Isolated yield.

Reactions of a variety of substrates with the lanthanoid reducing agents are summarized in Table 2. It is clear that besides stilbene a lot of C-C multiple bonds conjugated with aromatic rings can be reduced selectively by Yb metal or PhYbI complex. Three equivalent amounts of Yb metal reduce styrene to ethylbenzene quantitatively (run 2) in marked contrast to the case of alkali metals.[3)] In the case of 1-decene (run 5), no reaction occurred, indicating that isolated C-C double bonds cannot be reduced by Yb under the present reaction conditions. Diphenylacetylene is reduced by 3 equiv. of Yb to a mixture of 1 and stilbenes (run 6). However, further excess of the Yb metal gave only bibenzyl(1), the completely reduced product, in high yield (run 7). Reduction of (*E*,*E*)-1,4-diphenyl-1,3-butadiene gave 1,4-diphenyl-2-butene as a final product whose C-C double bond could not be further reduced (run 8). The metal could not reduce naphthalene under the present conditions, showing its different reactivity compared with alkali metals[4)] and Yb in liquid ammonia.[5)] Furthermore, that the naphthalene ring does not suffer the reduction, enables it to reduce acenaphthylene into acenaphthene selectively (runs 10 and 11). Cerium (Ce) and samarium (Sm) were found to be inactive for the reaction under the same conditions (runs 12 and 13). Either samarium diiodide or ytterbium diiodide was also inert toward the olefin (runs 14 and 15).

It was also found that in the case of (*E*)-stilbene, if CD_3OD was used instead of CH_3OH, the deuterated reduction product(2) was obtained almost quantitatively (Eq. 1).

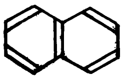
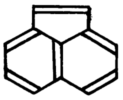
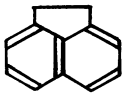
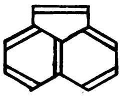
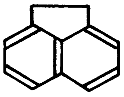


$$\overset{\text{Ph}}{\underset{\text{H}}{}}\!\text{C=C}\!\overset{\text{H}}{\underset{\text{Ph}}{}} + \text{Yb} \xrightarrow[\text{r.t., 18 h}]{\text{THF/CD}_3\text{OD}} \text{Ph-}\overset{\text{D}}{\underset{\text{H}}{\text{C}}}\text{-}\overset{\text{D}}{\underset{\text{H}}{\text{C}}}\text{-Ph} \quad (1)$$

95%

2 (100%D)

Table 2. Reduction of C-C multiple bonds by PhYbI or lanthanoid metals$^{a)}$

Run	Substrate (mmol)	Reducing agent (mmol)	Product$^{b)}$	Yield/%$^{c)}$
1	$Ph_2C=CH_2$ (0.5)	PhYbI (1.0)$^{d,e)}$	Ph_2CHCH_3	$(94)^{f)}$
2	$PhCH=CH_2$ (1.0)	Yb (3.0)$^{e,g)}$	$PhCH_2CH_3$	(98)
3	$Ph(CH_3)C=CH_2$ (0.5)	Yb (1.5)	$PhCH(CH_3)_2$	54
4	$Ph(CH_3)C=CH_2$ (0.5)	Yb (2.0)	$PhCH(CH_3)_2$	78
5	$n\text{-}C_8H_{17}CH=CH_2$ (1.0)	Yb (2.0)	no reaction	
6	PhC≡CPh (0.5)	Yb (1.5)$^{e)}$	$PhCH_2CH_2Ph$ Z-PhCH=CHPh E-PhCH=CHPh	47 $11^{g)}$ $20^{g)}$
7	PhC≡CPh (0.5)	Yb (3.0)$^{e)}$	$PhCH_2CH_2Ph$	(87)
8	E,E-PhCH=CHCH=CHPh (0.5)	Yb (2.0)	$PhCH_2CH=CHCH_2Ph$	(92)
9	 (0.5)	Yb (1.0)	no reaction	
10	 (0.5)	Yb (1.0)		53
11	 (0.5)	Yb (2.0)		73
12	PhCH=CHPh (0.5)	Sm (1.5)	no reaction	
13	PhCH=CHPh (0.5)	Ce (2.0)	no reaction	
14	PhCH=CHPh (0.5)	YbI_2 (1.0)	no reaction	
15	PhCH=CHPh (0.5)	SmI_2 (1.0)	no reaction	

a)THF: 4 ml, room temperature, 18 h. b)Products were identified by NMR spectra and by comparison of GC retention time. The reactions were very clean and only a little byproducts could be detected except the unreacted starting materials. c)NMR yield based on the substrate. d)PhYbI was prepared using Yb (1.5 mmol) and PhI (1.0 mmol) as described previously.$^{2a)}$ e)HMPA (hexamethylphosphoric triamide, 2 ml) was also used as a cosolvent. f)Numbers in parentheses are isolated yields. g)Determined by GC.

A typical experiment (run 5, Table 1) is carried out as follows. To 260 mg of 40-mesh Yb metal (1.5 mmol) was dropped 2 µl of CH_3I under nitrogen atmosphere and the metal was then warmed slightly with a dryer. Addition of 2 ml of THF gave a colored solution to which 90 mg (0.5 mmol) of (*E*)-stilbene with THF (2 ml) and MeOH (0.5 ml) were introduced by a syringe. The mixture was then stirred at room temperature for 18 h and finally a dark slury was obtained. Usual work-up followed by chromatographic purification (silica gel) gave the reduction product, bibenzyl

(1) (86.5 mg, 95% yield). The reaction system must be completely anhydrous and deoxygenated to obtain reproducible results.

Studies on reduction of other substrates with lanthanoid-based reducing agents are under progress.

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References

1) M. Hudlicky, "Reductions in Organic Chemistry," Ellis Horwood, West Sussex (1984).

2) a)T. Fukagawa, Y. Fujiwara, K. Yokoo, and H. Taniguchi, Chem. Lett., 1981, 1771; b)T. Fukagawa, Y. Fujiwara, and H. Taniguchi, ibid., 1982, 601; c)K. Yokoo, Y. Yamanaka, T. Fukagawa, H. Taniguchi, and Y. Fujiwara, ibid., 1983, 1301; d)K. Yokoo, Y. Fujiwara, T. Fukagawa, and H. Taniguchi, Polyhedron, 2, 1101 (1983); e)K. Yokoo, T. Fukagawa, Y. Yamanaka, H. Taniguchi, and Y. Fujiwara, J. Org. Chem., 49, 3237 (1984); f)K. Yokoo, Y. Kijima, Y. Fujiwara, and H. Taniguchi, Chem. Lett., 1984, 1321; g)K. Yokoo, N. Mine, H. Taniguchi, and Y. Fujiwara, J. Organomet. Chem., 279, C19 (1985); h)Z. Hou, N. Mine, Y. Fujiwara, and H. Taniguchi, J. Chem. Soc., Chem. Commun., 1985, 1700; i)N. Mine, Y. Fujiwara, and H. Taniguchi, Chem. Lett., 1986, 357.

3) For example, reaction of styrene with lithium in methylamine afforded a mixture of 25% of 1-ethylcyclohexene and 18% of ethylcyclohexane. See R. A. Benkeser, C. Arnold, Jr., R. F. Lambert, and O. H. Thomas, J. Am. Chem. Soc., 77, 6042 (1955).

4) A. J. Birch, A. R. Murray, and H. Smith, J. Chem. Soc., 1951, 1945.

5) J. D. White and G. L. Larson, J. Org. Chem., 43, 4555 (1978).

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