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Selective 1,2-Reduction of α,β-Unsaturated Carbonyl Compounds with $LnCpCl_2(THF)_3/NaBH_4$

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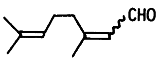
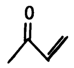
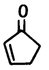
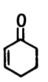
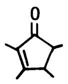
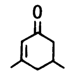
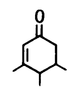
Synopsis. Highly selective 1,2-reduction of conjugated α,β-unsaturated carbonyl compounds such as enones and unsaturated aldehydes has been achieved by $NaBH_4/LnCpCl_2(THF)_3$ (Ln=Sm and Er) in MeOH under ambient conditions.

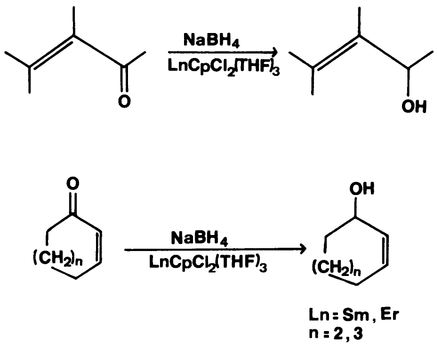
Utilization of organolanthanoid reagents to organic reactions has been recently attracting growing attention.[1] Although lanthanoid compounds are now available in large quantities and in very pure form, their chemical uses are still very limited. Luche et al. reported lanthanoid ion-promoted reduction of enones to allylic alcohol with $NaBH_4$,[2] which is of interest, since the regio- and chemoselectivity is in sharp contrast to the reduction promoted by $NaBH_4$ in the presence of late transition metal complexes as well as to the reduction with $NaBH_4$ in pyridine.[2,3] We now report the highly chemo- and regioselective 1,2-reduction of conjugated unsaturated carbonyl compounds with $NaBH_4$ assisted by organolanthanide complexes, $LnCpCl_2(THF)_3$ (Ln=Sm and Er)[4] in methanol.

Table 1 summarizes the results of selective reduction of α,β-unsaturated carbonyl compounds with $NaBH_4/LnCpCl_2(THF)_3$. When a half-molar amount of $NaBH_4$ per substrate was added into a 4:1 mixture of crotonaldehyde and $SmCpCl_2(THF)_3$ (**1**) in methanol at room temperature, crotyl alcohol was selectively obtained in an almost quantitative yield. Cinnamaldehyde was also reduced cleanly to cinnamyl alcohol. Only slight amounts of saturated alcohols and 1,4-reduction products were formed in these reactions. The present selective reduction is also applicable to various alicyclic and cyclic enones such as methyl vinyl ketone, cyclopentenone and cyclohexenone, to give corresponding allylic alcohols in

Table 1. Reduction of α,β-Unsaturated Ketones and Aldehydes with $NaBH_4/LnCpCl_2(THF)_3$[a)]

Substrate	Complex	Yield/%[b)]	Product ratio/%[c)] A	B	C
	**1**	97.7	100	0	0
	2	95.6	100	0	0
	**1**	90.2	92.4	0	7.6
	2	95.2	96.6	0	3.4
	**1**	91.9	100	0	0
	2	93.3	99.9	0	0.1
	**1**	97.3	100	0	0
	2	97.3	99.5	0	0.5
	**1**	95.3	98.8	0	1.2
	2	82.7	100	0	0
	**1**	98.8	97.9	0	2.1
	2	98.8	97.8	0	2.2
	**1**	No reaction			
	2	No reaction			
	**1**	87.0	90.7	1.3	8.0
	**1**	75.1	73.0	0	27.0

a) In methanol (1.0 cm³) at room temperature for 6 h. The ratio of substrate, $NaBH_4$, and $LnCpCl_2(THF)_3$ used was 4.4:2.2:1. b) Yields are based on the starting substrates by GLC. c) A: Allylic alcohol, B: saturated ketone, C: saturated alcohol.

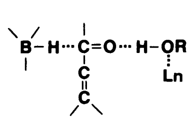


high yields as well as in high selectivity.

Although the reaction products were determined after 6 h, the reduction was actually completed after 5 min. On the other hand, reduction of 2,3,4,5-tetramethylcyclopentenone failed. Selectivity and the yields of 1,2-reduction products decrease when methyl and methoxycarbonyl substituents are placed on the cyclic enone ring. Steric effect may be important in these reduction process. Similar selective 1,2-reduction of α,β-unsaturated carbonyl compounds was also performed by using $ErCpCl_2(THF)_3$ (**2**).

Limitation of the present reduction to other organic substances was determined. Reductions of allyl phenyl ether, cyclohexene oxide, cyclohexene, allyl bromide, methyl acrylate, and crotonic acid have failed. The results demonstrate the high chemoselectivity of the reaction. Thus, the reduction of citral (neral:geranial=37:63) with **1** or **2** gave quantitative yields of a mixture of nerol and geraniol in 37:63 ratio.

Table 2 shows the reduction of 2-cyclohexen-1-one in various solvents. Polar and protonic solvent such as methanol seems to be the best for the reduction. A considerable amount of dimethoxymethane (31.2 mol%/Sm) was detected in the reduction of crotonaldehyde, suggesting participation of methanol during the reduction. An analogous mechanism proposed by Luche[2] involving solvent assisted intermediate seems to be operative.



Present results are considered to be complement to the Luche's selective reduction of enones with lanthanoid metal salts.[2]

Table 2. Solvent Effect on the Reduction of 2-Cyclohexen-1-one with $NaBH_4/SmCpCl_2(THF)_3$[a)]

Solvent	Yield/%	Product ratio/%[b)]		
		A	B	C
Hexane	0.1	0	100	0
Benzene	0.1	0	100	0
CH_2Cl_2	0.1	0	100	0
Et_2O	1.9	84.2	15.8	0
THF	24.8	93.5	0.5	6.0
DMSO	78.2	92.9	2.8	4.3
MeOH	98.8	97.8	0	2.2
EtOH	66.9	81.6	0.8	17.6
i-PrOH	98.2	88.3	0	11.7

a) Solvent = 1.0 cm^3. At room temperature for 6 h. Yields are based on 2-cyclohexen-1-one. The ratio of substrate, $NaBH_4$, and **1** was 4.4:2.2:1. b) A: 2-Cyclohexen-1-ol, B: cyclohexanone, C: cyclohexanol.

Experimental

General. All the reactions were carried out under nitrogen. Solvents were dried by usual procedure, distilled, and stored under nitrogen. Enones and unsaturated aldehydes were used after distillation of commercially available materials. $SmCpCl_2(THF)_3$ were prepared according to the literature methods.[4]

Reduction of α,β-Unsaturated Carbonyl Compounds. Typical procedure of the reduction is described below: To a homogeneous solution of a mixture of 2-cyclohexen-1-one (0.240 mmol) and $SmCpCl_2(THF)_3$ (0.057 mmol) in methanol(1.0 cm^3), $NaBH_4$ (0.120 mmol) was added at room temperature. After 6 h a quantitative yield of 2-cyclohexenol (0.232 mmol) was detected by GLC analysis. A small amount of 2-cyclohexan-1-ol (0.005 mmol) was also formed. Other experiments were carried out similarly and the results are listed in Tables 1 and 2.

References

1) T. J. Marks and I. L. Fragala, "Fundamental and Technological Aspects of Organo-f-Element Chemistry," Reidel Publishing Company, Dordrecht (1984) and references cited therein.

2) J.-L. Luche, *J. Am. Chem. Soc.*, **100**, 2226 (1978); J.-L. Luche and A. L. Gemal, *ibid.*, **101**, 5848 (1979); **103**, 5454 (1981).

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4) S. Manastyrskyj, R. E. Maginn, and M. Dubeck, *Inorg. Chem.*, **2**, 904 (1963).