

References

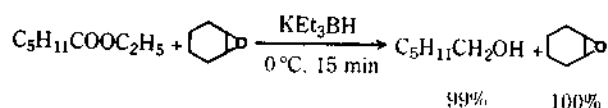
1. J. R. Reynolds, P. A. Poropatic, and R. L. Toyooka, *Macromolecules*, **20**, 958 (1987).
2. M. Nechtschen *et al.*, *Synth. Met.*, **15**, 59 (1987).
3. R. M. Penner and C. R. Martin, *J. Electrochem. Soc.*, **133**, 310 (1986).
4. T. Ikeshoji, *J. Electroanal. Chem.*, **201**, 409 (1986).
5. J.-D. Kim, K.-J. Kim, and J.-K. Chon, *Bull. Korean Chem. Soc.*, **8**, 362 (1987).
6. Y. Ikariyama and W. R. Heineman, Proc. of the 2nd. Int. meeting on chemical sensors, Bordeaux, 1986, p. 669, and references therein.
7. W. R. Heineman, H. J. Wieck, and A. M. Yacynych, *Anal. Chem.*, **52**, 345 (1980).

Chemoselective Reduction of Lactones with Potassium Tri-*s*-butylborohydride

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Carboxylic acids esters are readily reduced to the corresponding alcohols with lithium aluminum hydride¹ (LiAlH₄), diisobutylaluminum hydride² (DIBAH), and lithium triethylborohydride³ (LiEt₃BH). However these are so strong reducing agents that the chemoselectivity of ester function in the presence of other functionalities can not be expected. Recently we have found that potassium triethylborohydride (KEt₃BH) is an excellent chemoselective reducing agent for esters⁴ in the presence of epoxides, nitriles or amides.



These results intrigued us to explore the chemoselectivity of potassium tri-*s*-butylborohydride⁵ (Ks-Bu₃BH), a bulkier borohydride, towards organic functionalities. We now wish to report such chemoselectivity of the reagent for lactones in the presence of other functional groups.

Chemoselective reduction of lactones with Ks-Bu₃BH was studied by competitive reaction. Thus an equimolar mixture of a lactone and other substrate containing more common functional groups such as ester, epoxide, amide etc. was reacted with 2.1 mole equivalents of Ks-Bu₃BH at 0°C for 5 min. The results are excellent as shown in Table 1.

Table 1. Chemoselective Reduction of Lactones with Ks-Bu₃BH in Tetrahydrofuran at 0°C^a

entry	compounds	product	yield ^b (%)
1	γ-butyrolactone	1,4-butanediol	99
	ethyl caproate	ethyl caproate	96
2	γ-butyrolactone	1,4-butanediol	100
	ethyl benzoate	ethyl benzoate	95
3	γ-valerolactone	1-methyl-1,4-butanediol	93.2
	ethyl benzoate	ethyl benzoate	90
4	α-methyl-γ-butyrolactone	2-methyl-1,4-butanediol	96

5	ethyl benzoate	ethyl benzoate	92
	δ-valerolactone	1,5-pentanediol	96.3
6	ethyl benzoate	ethyl benzoate	93.4
	phthalide	phthalyl alcohol	100
7 ^c	ethyl benzoate	ethyl benzoate	99
	γ-butyrolactone	1,4-butanediol	88
8 ^d	ethyl benzoate	ethyl benzoate	86
	γ-butyrolactone	benzyl alcohol	10
	ethyl benzoate	1,4-butanediol	30
	ethyl benzoate	ethyl benzoate	74
9	γ-butyrolactone	benzaldehyde	10.3
	styrene oxide	benzyl alcohol	18.5
10	γ-butyrolactone	1,4-butanediol	99
	cyclohexene oxide	styrene oxide	100
11	γ-butyrolactone	1,4-butanediol	99.8
	N,N-dimethylcaproamide	1,4-butanediol	99
12	γ-butyrolactone	N,N-dimethylcaproamide	99
	capronitrile	1,4-butanediol	99
13	γ-butyrolactone	1,4-butanediol	99.8
	1-chlorooctane	1,4-butanediol	99
14	γ-butyrolactone	1-chlorooctane	99
	decene	1,4-butanediol	97
		decene	100

^aA mixture of one mmol each of lactone and other substrate was reacted with 2.1 mmol of Ks-Bu₃BH at 0°C for 5 min. ^bYields were estimated by GLC. ^cReaction with KEt₃BH. ^dReaction with DIBAH.

As shown in entry 1 and 2, γ-butyrolactone can be selectively reduced in the presence of either aliphatic ester (*i.e.* ethyl caproate) or aromatic ester (*i.e.* ethyl benzoate). And other representative lactones such as γ-valerolactone, α-methyl-γ-butyrolactone, δ-valerolactone and phthalide are also reduced with excellent chemoselectivity (entry 3-6). To the best of our knowledge, there have been no report of such selective reduction. We also undertook the competitive re-

duction between γ -butyrolactone and ethyl benzoate, using KEt_3BH and DIBAH in the place of $\text{Ks-Bu}_3\text{BH}$ for comparison. The results are far less satisfactory as shown in entry 7 and 8. Other chemoselectivities were examined using γ -butyrolactone as a representative. Thus the terminal epoxide (*i.e.*, styrene oxide) and *cis*-epoxide (*i.e.*, cyclohexene oxide) are both intact during the quantitative reduction of lactone (entry 9, 10), and as shown in entry 11-14, the same is true for amides, nitriles, primary chlorides and olefins.

The reduction of γ -butyrolactone in the presence of ethyl caproate is representative. To an equimolar mixture of γ -butyrolactone (1 mmol) and ethyl caproate (1 mmol) containing 0.5 mmol of dodecane (as an internal standard) in THF (2 ml) was added 4.2 ml (2.1 mmol) of $\text{Ks-Bu}_3\text{BH}\cdot\text{THF}$ solution at 0 °C. After 5 min, the reaction was quenched with 0.5 ml of water and oxidized with $\text{H}_2\text{O}_2\text{-NaOH}$ for 2 h at 30 °C. After drying with anhydrous K_2CO_3 , the THF layer was subjected to GLC to analyze the unreacted ethyl caproate (96%). And then, 2.5 ml of pyridine, 1.6 ml of hexamethyldisilazane and 1 ml of trimethylsilyl chloride were added to the solution. After stirred for 1 h, the supernatant liquid was subjected to GLC analysis to provide 99% of 1,4-butanediol.

In conclusion, $\text{Ks-Bu}_3\text{BH}$ is a remarkable chemoselective

reducing agent for lactones.

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References

1. N. G. Gaylord, *Reduction with Complex Metal Hydride*, Wiley Interscience, New York, 1956.
2. (a) E. Winterfeldt, *Synthesis* 617 (1975); (b) N. M. Yoon and Y. S. Gyoung, *J. Org. Chem.*, **50**, 2443 (1985).
3. H. C. Brown, S. C. Kim and S. Krishnamurthy, *J. Org. Chem.*, **45**, 1 (1980).
4. (a) N. M. Yoon, H. S. Yang and Y. S. Hwang, *Bull. Korean Chem. Soc.*, **8**, 285 (1987); (b) For the chemoselective reduction of esters; N. M. Yoon, H. S. Yang and Y. S. Hwang, *Bull. Korean Chem. Soc.*, submitted for publication.
5. (a) C. A. Brown, *J. Am. Chem. Soc.*, **95**, 4100 (1973); (b) Y. S. Hwang and N. M. Yoon, The study of the reaction of $\text{Ks-Bu}_3\text{BH}$ with representative organic compounds has been completed, and the manuscript is in preparation.