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Chemo- and Regioselective Reduction of Epoxides with Sodium Borohydride in Mixed Solvent Containing Methanol

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Mono- and *gem*-disubstituted epoxides were reduced to more substituted alcohols in good to high yields (73—100%) and in high regioselectivities (89—100:11—0) by sodium borohydride in a mixed solvent of *t*-butyl alcohol-methanol or 1,2-dimethoxyethane-methanol. The reaction of disubstituted epoxide depends on the steric hindrance and the position of the substituents. Trisubstituted epoxides were not reduced by the present reducing system. The reactivity order of epoxides by the present reducing system was mono->2,2-di->2,3-di-≫trisubstituted epoxides. The chemoselectivity of the present reducing system is excellent. Thus, epoxides were selectively reduced in the presence of such reducible groups as carbamoyl, carboxyl, nitro, cyano, and bromo.

Epoxides are important synthetic intermediates,[1a)] and their transformation reactions have been the subject of increasing interest in recent years.[1b)] Among the many types of reactions involving epoxides, the reduction to alcohols by metal hydrides is one of the most fundamental reactions.[1b,2)] Several kinds of metal hydrides[3)] such as lithium aluminum hydride ($LiAlH_4$), lithium 9,9-dibutyl-9-borabicyclo[3.3.1]-nonane,[3f)] lithium triethylhydroborate ($LiBHEt_3$)[4)] and aluminum hydride are known to reduce epoxides.[3a—c)] However, because of the poor chemoselectivities of most of these reducing agents, a selective reduction of epoxides can not usually be achieved in the presence of such reducible functional groups as carbamoyl, carboxyl, cyano, or halo. Regioselectivity and synthetic yield of lithium borohydride ($LiBH_4$) reduction of epoxides are low to moderate.[5)]

Sodium borohydride ($NaBH_4$) is a mild chemoselective reducing reagent for ketones and aldehydes. It is generally accepted, however, that the reduction rate of epoxides with $NaBH_4$ is very slow.[3a—c)] Exceptional epoxides, which are reported to be reduced with $NaBH_4$, contain neighboring functional groups which may in some way take part in the reduction.[6)] To the best of our knowledge, no systematic study has been reported on the selective reduction of epoxides with $NaBH_4$.

We have studied chemoselective[7,8)] and diastereoselective[9,10)] reductions using $NaBH_4$ in a mixed solvent containing MeOH as one component, and chemoselective[11)] and asymmetric[12)] reductions using $LiBH_4$. In this paper, we describe a chemo- and regioselective reduction of epoxides with $NaBH_4$ in a mixed solvent containing MeOH.

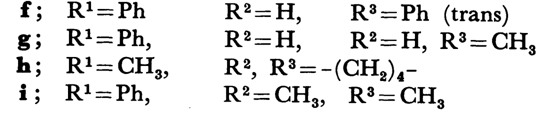
Results and Discussion

Table 1. Effect of the Solvent for the Reduction of 2-Phenyloxirane with $NaBH_4$

Entry	Solvent	Yield/%	Ratio[a)] **2a** : **2b**
1	MeOH	33	c)
2	*t*-BuOH	33	87 : 13
3	*t*-BuOH-MeOH[d)]	97	89 : 11
4	DME[b)]-MeOH[d)]	82	83 : 17
5	THF-MeOH[d)]	44	96 : 4
6	Hexane-MeOH[d)]	28	65 : 35
7	Benzene-MeOH[d)]	10	67 : 33

a) Determined by ^1H NMR. b) 1,2-Dimethoxyethane. c) Not determined. d) Molar ratio, 2-phenyloxirane : $NaBH_4$: MeOH = 1 : 2.5 : 12.

We examined the effect of a solvent in the reduction of 2-phenyloxirane (**1a**) with $NaBH_4$. The reaction was carried out as follows. To a refluxing mixture of $NaBH_4$, **1a** and solvent, MeOH was added dropwise over a period of 1 h. Then, the reflux was continued for an additional 1 h. As shown in Table 1, the reaction in *t*-BuOH afforded 2-phenylethanol (**2a**) and 1-phenylethanol (**3a**) in 97% total yield with high regioselectivity (**2a**:**3a**=89:11). On the other hand, when a reduction was carried out in each single solvent (MeOH or *t*-BuOH), the yields of alcohols (**2a** and **3a**) dropped considerably to 33% (Table 1, Entries 1 and 2). Thus, the presence of a small amount of MeOH (about 5 molar equivalent to $NaBH_4$) in *t*-



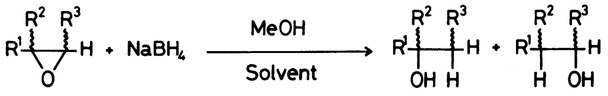
a;	R^1=Ph,	R^2=H,	R^3=H
b;	R^1=n-C_6H_{13},	R^2=H,	R^3=H
c;	R^1=Ph,	R^2=CH_3,	R^3=H
d;	R^1=H,	R^2, R^3=-$(CH_2)_4$-	
e;	R^1=Ph,	R^2=H,	R^3=Ph (cis)
f;	R^1=Ph	R^2=H,	R^3=Ph (trans)
g;	R^1=Ph,	R^2=H,	R^2=H, R^3=CH_3
h;	R^1=CH_3,	R^2, R^3=-$(CH_2)_4$-	
i;	R^1=Ph,	R^2=CH_3,	R^3=CH_3

BuOH was apparently effective to increase the chemical yields of **2a** and **3a**. 1,2-Dimethoxyethane (DME) was also a suitable co-solvent with MeOH for the reduction of **1a**. Reactions in such hydrocarbon solvents as benzene and hexane were very sluggish and showed low regioselectivities (Table 1, Entries 6 and 7).[13]

For one molar amount of monosubstituted oxirane, 2.5 molar amounts of $NaBH_4$ was sufficient to perform the reaction (Table 2, Entries 1—3). As to the amount of MeOH, about five molar amounts of MeOH to $NaBH_4$ were suitable for the reduction (Table 2, Entries 5—7). Thus, the optimum molar ratio was as follows: epoxide : $NaBH_4$: MeOH=1 : 2.5 : 12. Under the above conditions (in *t*-BuOH, molar ratio **1** : $NaBH_4$: MeOH=1 : 2.5 : 12), aromatic and aliphatic monosubstituted epoxides (**1a** and **1b**) were reduced to the corresponding alcohols in 96—97% yields (Table 2, Entries 1 and 8). The reduction of 2-methyl-2-phenyloxirane (**1c**) proceeded with high regioselectivity; 2-phenyl-1-propanol (**2c**) was obtained as the sole product in 73% yield (Table 2, Entry 9). The reaction with 2,3-disubstituted oxirane was slower than that with 2,2-disubstituted one. A long reaction time was required for the reduction of cyclohexene oxide (**1d**) (Table 2, Entry 10).

One of the characteristic features of the present reducing system is chemoselectivity. Chemoselective or competitive reductions of **1a** in the presence of other functional groups such as carbamoyl, carboxyl, nitro or cyano are shown in Table 3. **1a** was reduced in good to high yields while other functional groups were not reduced (Table 3, Entries 1—3). The reduction of 2-(4-bromophenyl)oxirane proceeded to

Table 2. Reduction of Various Types of Epoxides with $NaBH_4$ in a Mixed Solvent



1 2 3

Entry		1		Molar Ratio	Solvent	Time/h	Yield/%[a)]	Ratio[b)]
	R^1	R^2	R^3	**1** : $NaBH_4$: MeOH			2+3	2 : 3
1	Ph	H	H (**1a**)	1 : 2.5 : 12	*t*-BuOH	2.0	97	89 : 11
2		**1a**		1 : 1.5 : 7	*t*-BuOH	2.0	71	
3		**1a**		1 : 0.5 : 2.5	*t*-BuOH	2.0	49	
4		**1a**		1 : 2.5 : 20	*t*-BuOH	2.0	88	89 : 11
5		**1a**		1 : 2.5 : 6	THF	2.0	22	95 : 5
6		**1a**		1 : 2.5 : 12	THF	2.0	44	96 : 4
7		**1a**		1 : 2.5 : 20	THF	2.0	26	95 : 5
8	*n*-C_6H_{13}	H	H (**1b**)	1 : 2.5 : 12	*t*-BuOH	2.0	96	97 : 3[c)]
9	Ph	CH_3	H (**1c**)	1 : 5.0 : 25	*t*-BuOH	2.0	73	100 : 0
10	H	$-(CH_2)_4-$ (**1d**)		1 : 5.0 : 25	*t*-BuOH	9.5	72	
11	Ph	H	Ph(cis, **1e**)	1 : 5.0 : 25	*t*-BuOH	2.0	12	
12	Ph	H	CH_3 (**1g**)[d)]	1 : 5.0 : 25	*t*-BuOH	4.0	36(63)[e)]	68 : 32
13	CH_3	$-(CH_2)_4-$ (**1h**)		1 : 5.0 : 25	THF	2.0	0	
14	Ph	CH_3	CH_3 (**1i**)	1 : 5.0 : 25	*t*-BuOH	2.0	9	

a) The values in parentheses were the yields of recovered **1**. b) Unless otherwise noted, the ratio was determined by ^1H NMR. c) Determined by GLC analysis. d) The ratio of cis/trans was 32/68. e) The ratio of cis/trans of recovered **1g** was 35/65.

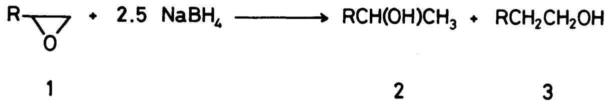
Table 3. Chemoselective or Competitive Reduction of Epoxide by $NaBH_4$-MeOH-*t*-BuOH System

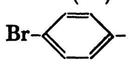
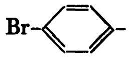
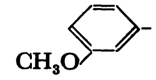
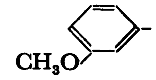
$$\mathbf{1a} + \mathbf{4} \xrightarrow[t\text{-BuOH-MeOH}]{NaBH_4} \mathbf{2} + \mathbf{3} + \mathbf{4}(\text{Recovery})$$

Entry[a)]	1	4	Yield/% 2+3	Ratio[b)] 2 : 3	Recovery/% 4
1[a)]	**1a**	$PhCONHCH_2CO_2H$	71	88 : 12[c)]	84
2[a)]	**1a**	$PhNO_2$	91	89 : 11[c)]	83
3[a)]	**1a**	PhCN	90	88 : 12[c)]	77
4[b)]	2-(4-Bromophenyl)oxirane		100	91 : 9[d)]	—

a) Molar ratio **1a** : **4** : $NaBH_4$ = 1 : 1 : 2.5—2.8. b) Molar ratio **1** : $NaBH_4$ = 1 : 2.5. c) Determined by GLC. d) Determined by ^1H NMR.

Table 4. Comparison of Regioselectivities in the Reduction of Epoxides



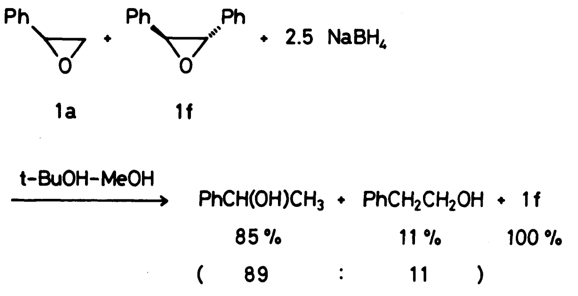
Entry	R	Reducing system	Yield/% **2**+**3**	Ratio **2** : **3**
1	Ph(**1a**)	$NaBH_4$-*t*-BuOH	33	87 : 13
2	Ph(**1a**)	$NaBH_4$-MeOH-*t*-BuOH	97	89 : 11
3[a)]	Ph(**1a**)	$LiBH_4$-Et_2O	66	56 : 44
4[a)]	Ph(**1a**)	$LiBH_4$-MeOH-Et_2O	99	65 : 35
5	Ph(**1a**)	KBH_4-MeOH-*t*-BuOH	18	100 : 0
6		$NaBH_4$-MeOH-*t*-BuOH	100	91 : 9
7[b)]		$LiBH_4$-Et_2O	66	84 : 16
8		$NaBH_4$-MeOH-*t*-BuOH	100	95 : 5
9[b)]		$LiBH_4$-Et_2O	63	77 : 23
10	*n*-C_6H_{13}-(**1b**)	$NaBH_4$-MeOH-*t*-BuOH	96	97 : 3

a) Data from Ref. 11. b) Data from Ref. 5.

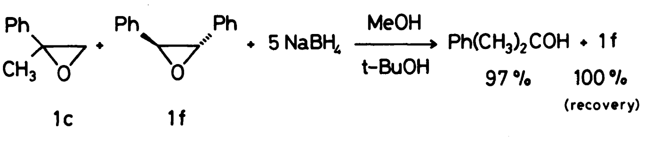
afford 2-(4-bromophenyl)ethanols in 100% yield (Table 3, Entry 4).

Another feature is high regioselectivity. Results are summarized in Table 4. Both aromatic and aliphatic epoxides were reduced with high regioselectivities (89—97:11—3) by $NaBH_4$-*t*-BuOH-MeOH (Table 4, Entries 2, 6, 8, and 10). The regioselectivities of $NaBH_4$ were higher than those of $LiBH_4$ (Entries 3, 4, 7, and 9). The regioselectivity was excellent in the reduction of **1a** with potassium borohydride (KBH_4)-MeOH-*t*-BuOH, although the chemical yield was low. The addition of MeOH caused an increace in the chemical yield and regioselectivity (Entries 1—4).

Though many reports have appeared regarding reductions of epoxide to alcohol, most of them (for example, $LiAlH_4$,[14] $LiBEt_3H$,[15] $LiAlH_4$-$AlCl_3$,[14]) reduce epoxides exceedingly rapidly, regardless of the structure of epoxide. In the competitive reduction of **1a** and *trans*-2,3-diphenyloxirane (**1f**) by a $NaBH_4$-*t*-BuOH-MeOH reducing system, **1a** was selectively reduced to **2a** and **3a** in 96% total yield, while **1f** was in 100% recovered. Thus, the present method can differentiate the structure of epoxides.



Furthermore, a competitive reduction between disubstituted epoxides was also performed. 2-Methyl-2-phenyloxirane (**1c**) was selectively reduced to 2-phenyl-2-propanol in 97% yield, while *trans*-2,3-disubstituted (**1f**) was quantitatively recovered.



Conclusion

The reduction of epoxides with $NaBH_4$ in a mixed solvent containing MeOH is of practical utility. The unique characteristic features of the present reducing system are exemplified by the regioselective and chemoselective reductions of epoxide in the presence of carbamoyl, carboxyl, nitro, cyano, bromo, and methoxyl groups and/or a structure selective reduction of the terminal epoxide in the presence of an internal one. A small amount of MeOH caused an increase in the reducing ability of $NaBH_4$ and the use of $NaBH_4$ in a *t*-BuOH-MeOH mixed solvent enabled the above-mentioned unique selective reduction.

Experimental

Melting and boiling points were uncorrected. IR spectra were recorded with a Hitachi 260-10 spectrophotometer. ^1H NMR spectra (60 MHz) were recorded using either a JEOL JNM-PMX-60 NMR spectrometer or a JEOL-PMX 60 SI NMR spectrometer. GLC analyses were carried out with a Shimadzu Gas Chromatograph (either model GC-4A or model GC-4C). All of the reactions were run under an argon atmosphere. Organic extracts were dried over anhydrous sodium sulfate.

Materials Methanol and ethanol were stored, respectively, over 3A and 4A molecular sieves. *t*-Butyl alcohol (Kanto), sodium borohyride (Nakarai), potassium borohydride (Nakarai), and lithium borohydride (Wako) were used without further purification. 2-Phenyloxirane, *trans*-2,3-diphenyloxirane, α-methylstyrene and cyclohexene oxide were purchased from Aldrich. 2-Methyl-3-phenyloxirane was prepared by the method of Eliel et al.[14] Bp 49 °C/1.5 mmHg (lit,[14] 62 °C/2.3 mmHg)(1 mmHg=133.322 Pa). 2-(4-bromophenyl)oxirane and 2-(3-methoxyphenyl)-oxirane were prepared from the corresponding phenacyl bromide according to a procedure from the literature.[4] Other epoxides were synthesized by an oxidation of the corresponding olefin with *m*-chloroperbenzoic acid.[16] *trans*-2,3-Diphenyloxirane: Mp 68.2—70.0 °C (lit,[17] 65—67 °C). *cis*-2,3-Diphenyloxirane: Mp 38.2—39.0 °C (lit,[18] 37—38 °C). 1-Methylcyclohexene oxide: Bp 58.0—58.4 °C/20 mmHg (lit,[18] 136—137 °C). 2-Methyl-3-phenyloxirane: Bp 115 °C/39 mmHg (bath temp). This oxirane was identified by ^{1}H NMR, compared to those of an authentic sample;[19] the ratio of cis/trans was determined by a GLC analysis.

Reduction of 2-Phenyloxirane (1a): To a refluxing mixture of $NaBH_4$ (0.095 g, 2.5 mmol) and **1a** (0.120 g, 1.0 mmol) in *t*-BuOH (4.0 ml), MeOH (0.5 ml) was added over a period of 1 h. After the reflux was continued for an additional 1 h, water and satd. aq. ammonium chloride were added to quench the reaction. Most of the solvent was evaporated under reduced pressure at an ambient temperature, and the residue was extracted with ether. An ethereal extract was dried, evaporated on a rotary evaporator and the residual oil was purified on silica gel TLC (dichloromethane–MeOH (10:1) as a developing solvent). A mixture of 1- and 2-phenylethanol was obtained in 93% yield (0.114 g).

Reduction of 2-Methyl-3-phenyloxirane (1g): Methanol (1.08 ml) was added dropwise to a refluxing mixture of 2-methyl-3-phenyloxirane (0.1465 g, 1.08 mmol), sodium borohydride (0.205 g, 5.42 mmol) and *t*-BuOH (6 ml) over a period of 1.5 h and the reflux was continued for additional 2.5 h. After cooling the mixture to room temperature, water, satd. aq ammonium chloride and ether were added. An organic layer was separated and an aq layer was extracted with dichloromethane. The combined organic layer was dried and evaporated. The residue was purified on silica-gel TLC (chloroform as developing solvent) to afford 1- and 2-phenylpropanols (**2g** and **3g**, 0.053 g, 36%). The recovery of **1g** was 63%. A GLC analysis showed that the ratio of alcohol (**2g**:**3g**) was 68:32. Analytical conditions were as follows; Shimadzu Gas chromatograph GC-4C model, OV-1 50 m capillary column, column temperature 120 °C, retention time, *trans*-**1g** (17.0 min), *cis*-**1g** (15.9 min); SE-30 25 m capillary column, column temp 95 °C, retention time, **2g** (7.1 min), **3g** (7.8 min).

Selective Reduction of 2-Phenyloxirane (1a) in the Presence of Nitrobenzene: Methanol (0.5 ml) was added dropwise to a mixture of **1a** (0.120 g, 1 mmol), nitrobenzene (0.123 g, 1 mmol), sodium borohydride (0.095 g, 2.5 mmol), and *t*-BuOH (4 ml) over a period of 1 h. The mixture was refluxed for an additional 1 h, cooled to room temperature, followed by the addition of water and MeOH. After evaporating most of the MeOH under reduced pressure, the mixture was extracted with dichloromethane. The extract was then dried and evaporated in vacuo. The residue was purified on silica-gel TLC (dichloromethane as developing solvent) to afford 1-phenyl- and 2-phenylethanol (0.111 g, 91% yield) and nitrobenzene (0.102 g, 83% recovery). A GLC analysis showed that the ratio of **2a** and **3a** was 89:11.

Structural Selective Reduction of 2-Phenyloxirane (1a) in the Presence of *trans*-2,3-Diphenyloxirane (1f): To a refluxing mixture of **1a** (0.118 g, 0.98 mmol), **1f** (0.193 g, 0.98 mmol), sodium borohydride (0.093 g, 2.46 mmol) and *t*-BuOH (6 ml), MeOH (0.5 ml) was added dropwise over a period of 1 h and the mixture was refluxed for additional 1 h. After quenching the reaction by the addition of water and satd. aq. ammonium chloride, the mixture was extracted with dichloromethane. The extract was dried and evaporated under reduced pressure. Purification on silica-gel TLC (benzene–chloroform=3:1 as developing solvent) afforded a mixture of **2a** and **3a** (0.115 g, 96% yield). ^{1}H NMR analyses of the mixture showed that the ratio of **2a** to **3a** was 89:11.

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