Bull. Chem. Soc. Jpn., **72**, 1525—1531 (1999)

Schiff-Base Complexes of Metal(II) as New Catalysts in the High-Regioselective Conversion of Epoxides to Halo Alcohols by Means of Elemental Halogen

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(Received July 17, 1998)

The ring opening of epoxides with elemental iodine and bromine in the presence of some Schiff-base complexes of the first-row transition metal(II) as new catalysts affords vicinal iodo alcohols and bromo alcohols in high yields. This new procedure occurs regioselectively under mild conditions in various aprotic solvents. The catalysts are easily recovered and can be reused several times.

Vicinal halo alcohols have attained great significance in organic synthesis.[1,2] These compounds can be utilized for some useful synthetic transformations,[3] and are also key intermediates in the synthesis of halogenated marine natural products.[1a] The new methodologies for the regioselective ring opening of epoxides have been developed during the past three decades.[4,5] Although a variety of new and mild procedures to effect this transformation have been reported, most of them have some limitations.[1a,4,6] Early methods for converting epoxides to halo alcohols by electrophilic cleavage with aqueous hydrogen halides,[7,8] or Lewis acids, such as BF_3,[9] were limited by competing rearrangements and side reactions with other acid-sensitive functional groups. The ring opening of unsymmetrically substituted epoxides with $Li_2[NiBr_4]$,[10] Pyridine. HCl,[11] haloboran reagents,[12,13] Br_2/PPh_3,[14] Ti(O-i-pr)$_4$,[15] chlorosilanes,[16] [n-Bu_4N]Br/Mg$(NO_3)_2$,[17] Lewis acid metal halides,[1b,2,18] and Me_3SiBr[19] have been reported. However, these methods are not always fully satisfactory, and suffer from disadvantages, such as acidity, handling and in situ preparation of the reagent, the noncatalytic nature of the reagents and relatively long reaction times.[5,13a,15,20]

In conjunction with ongoing work in our laboratory on the synthesis and complex formation of Schiff base-metal complexes with neutral molecules, such as iodine and bromine,[21] we found that these complexes efficiently catalyzed the addition of elemental iodine and bromine to epoxides. Thus, some Schiff-base complexes of metal(II) were selected as catalysts in these reactions.

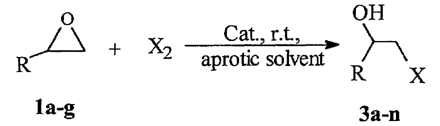
Here, we report on the reactions of some epoxides with elemental iodine and bromine in the presence of catalytic amounts of Schiff-base complexes of metal(II) with high yields and regioselectivity under mild conditions.

Results and Discussion

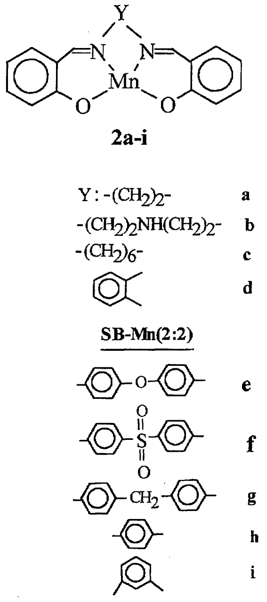
Recently, it has been found that although epoxides can be converted into iodo alcohols and bromo alcohols by means of elemental iodine and bromine,[22] this method has some limitations, such as low yields, long reaction times, the formation of isopropylidenedioxy compounds in addition to the expected iodoadduct in acetone solution (Entries 8, 9, and 22 in Table 3) and low regioselectivity. Furthermore, iodination does not occur in other aprotic solvents.

In this study, the reaction of styrene oxide with iodine and bromine in the presence of some Schiff-base (SB) complexes of Mn(II) were carried out. In order to examine the effects of ligands on the catalyst in the reaction, nine kinds of ligands were employed (Scheme 1). It should be noted that the Schiff bases of complexes **2e**—**i** behave as donor doubly-bidentate ligands, and form dinuclear complexes (SB–M, 2 : 2) with metal(II) ions.[23—25]

After a solution of styrene oxide and a catalyst in CH_2Cl_2 was stirred at room temperature, a solution of elemental halogen in CH_2Cl_2 was added dropwise. The amount of the complex catalyst was a 0.05 molar amount of the styrene oxide used. The reaction product was 2-halo-1-phenylethanol (**3a**, **3h**), and the yield was determined by GLC and TLC analyses. The results of the reactions of styrene oxide with elemental iodine and bromine in the presence of the above-mentioned catalysts are given in Table 1. In each case, cleavage of the epoxide ring occurs and, upon thiosulfate-workup, iodo alcohol and bromo alcohol are obtained. Two-valents metal salen complexes are well known to be oxidized to their three-valents complexes upon exposure to oxygen.[26] In order to find whether a three valents metal–salen complex is also formed in the reactions under our studies, the Mn(II)–salen complex was exposed to an excess of bromine for an appropriate time. Oxidation did not occur and the Mn(II)–salen complex was isolated intact. It therefore seems that the formation of three valents metal salen complexes in this condition is improbable. A comparison of the electronic absorption spectra of the recovered Mn(II)–salen complex from a reaction with Mn(II)–salen before the reaction, and Mn(III)–salen was also in accord with the above discussion. The catalysts are easily recovered and can be reused several



1a-g **3a-n**



2a-i

R of epoxide		R of halo alcohol	X: I	X: Br
Ph	**a**	Ph	**a**	**h**
$PhOCH_2$	**b**	$PhOCH_2$	**b**	**i**
p-Cl-$C_6H_4OCH_2$	**c**	p-Cl-$C_6H_4OCH_2$	**c**	**j**
p-Me-$C_6H_4OCH_2$	**d**	p-Me-$C_6H_4OCH_2$	**d**	**k**
i-$PrOCH_2$	**e**	i-$PrOCH_2$	**e**	**l**
n-Hex	**f**	n-Hex	**f**	**m**
Cyclohexene oxide	**g**	2-Halocyclohexanol	**g**	**n**

Scheme 1.

Table 1. Reaction of Styrene Oxide with Elemental Iodine and Bromine in the Presence of Various Catalysts in CH_2Cl_2 at Room Temperature

Entry	Catalyst	Iodination		Bromination	
		Time/h	Yield/%[a)]	Time/h	Yield/%[a)]
1	**2a**	0.25	> 95	Immed.	> 95
2	**2b**	0.4	92	0.3	95
3	**2c**	0.5	90	0.2	95
4	**2g**	1	80	0.5	85
5	**2f**	1	75	0.55	80
6	**2e**	1.5	80	0.7	83
7	**2d**	2	75	0.5	80
8	**2i**	2.5	60	1	75
9	**2h**	3.2	56	1.2	80
10[b)]	—	Several days	0	1	31[c)]

a) GC yield, based on epoxide. b) In the presence of excess of halogen (Ref. 22). c) The only one isomer, 2-bromo-2-phenylethanol was formed.

times.

In comparison, the cleavage behavior of styrene oxide with elemental iodine and bromine in the absence of a catalyst is given in Entry 10[22] (Table 1). As shown in Table 1, the yields of the reactions with this new method are quite fair, and the reaction time is very short. It is of great importance that the reaction is largely affected by the various ligands of the complexes. Catalysts **2a**, **2b**, and **2c** are the most effective ones in these reactions (Entries 1, 2 and 3). However, iodination of styrene oxide with excess elemental iodine in the absence of a catalyst did not occur, even under the reflux condition and an extension of the reaction time to several days, though the unreacted styrene oxide was completely recovered. In addition, the yield and regioselectivity of the bromination reaction are very low in the absence of catalysts.

Next, we studied the catalytic effect of the first-row transition metal(II) with the ligand of N,N'-ethylenedisalicylideneamine (or H_2salen) on the formation of 2-halo-1-phenylethanol (**3a**, **3h**), since it was found that H_2salen is the most effective ligand for the reaction. In all of the used catalysts, a halogenative cleavage of styrene oxide was carried out at room temperature. The corresponding results are summarized in Table 2. As can be seen, with Mn(II)–salen used as catalyst, iodo alcohol and bromo alcohol were formed in high yields and the reaction rate was much faster than other ones.

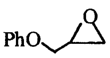
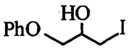
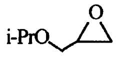
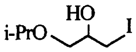
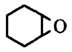
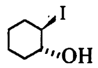
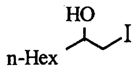
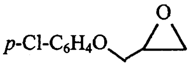
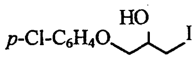
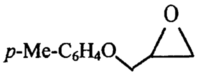
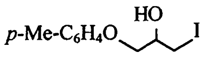
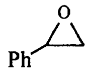
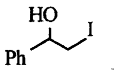
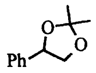
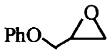
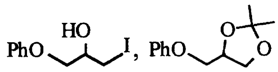
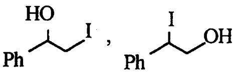
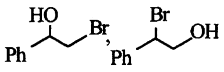
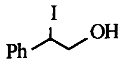
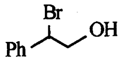
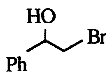
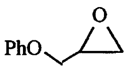
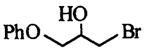
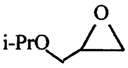
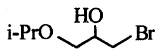
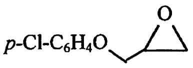
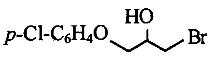
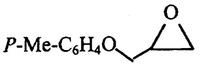
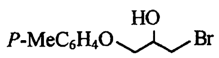
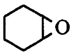
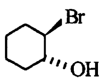
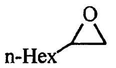
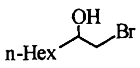
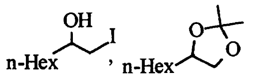
Furthermore, in order to ascertain the scope and limitation of the ring-opening reactions promoted by the above-mentioned complexes, reactions on various epoxides were carried out. The results of reactions with some representative epoxides in the presence of complex **2a** as the catalyst are summarized in Table 3. For a comparison, a number of other methods[5,17,13a,20a] for the conversion of oxiranes to the corresponding halo alcohols are given in Entries 10,11,12, 13 and 14 (Table 3). When epoxides were allowed to react in the presence of a catalyst, increases in the yield and regioselectivity were observed in all of the reactions studied. For all of the catalysts, the optimum amount of the catalyst was

Table 2. Reaction Times and the Yields of 2-Halo-1-phenylethanol in the Reactions of Styrene Oxide and Elemental Halogen in the Presence of Various Metal(II)–salen Complexes

Entry	Catalyst	Iodination		Bromination	
	M(II)–salen	Time/h	Yield/%[a)]	Time/h	Yield/%[a)]
1	Mn(II)	0.25	> 95	Immed	> 95
2	Fe(II)	0.7	93	0.3	> 95
3	Co(II)	1.25	90	0.5	92
4	Ni(II)	1.75	87	0.6	92
5	Cu(II)	2.5	87	0.75	90
6	Zn(II)	3	82	0.84	88

a) GC yield.

Table 3. Reaction of Various Epoxides with Iodine and Bromine in the Presence of Catalyst **2a**

Entry	Epoxide **1a—g**	Conditions	Time/h	Yield/%[a]	Product(s) **3a—n**
1		I_2, **2a**, r.t., CH_2Cl_2	6	75 (71)	
2		"	9.5	62 (60)	
3		"	12	58 (55)	
4		"	7.2	65 (59)	
5		"	5	85 (81)	
6		"	6.2	80 (75)	
7		"	0.25	> 95 (92)	
8[b]	"	I_2, r.t., acetone	2	83	
9[b]		"	—	94 (53 : 47)	
10[c]	"	LiI, AcOH, THF, r.t.	1.3	87 (1 : 2)	
11[d]	"	$[n\text{-}Bu_4N]Br/Mg(NO_3)_2$, $CHCl_3$	5	78 (5 : 1)	
12[e]	"	$(Me_2N)_2BBr/CH_2Cl_2$, N_2 atm.	12	75 (1 : 4.5)	"
13[f]	"	HI, $CHCl_3$	0.25	> 99	
14[f]	"	HBr, $CHCl_3$	0.25	> 99	
15	"	Br_2, **2a**, r.t., CH_2Cl_2	Immed.	> 95 (94)	
16		"	1.5	95 (91)	
17		"	2.4	75 (73)	
18		"	0.5	95 (90)	
19		"	1.7	90 (86)	
20		"	2.8	75 (70)	
21		"	2.25	83 (76)	
22[b]	"	I_2, r.t., acetone	—	79 (1 : 4)	

a) GC yield, isolated product yields are given in parenthesis, based on epoxide. b) Ref. 22, c) Ref. 5, d) Ref. 17, e) Ref. 13a, f) Ref. 20a.

found to be 0.05 mol for 1 mol of epoxide and halogen.

However, the following factors can influence the yield and regioselectivity of the reactions: (1) the steric hindrance of epoxides (for example, compare Entry 3 vs. 4 and Entry 20 vs. 21 in Table 3), (2) the rate of admixing the reagents, (3) the order in which the reagents are combined, and (4) the nature of the solvent. In cases of the rate and order in which the reagents are combined, for example, if bromine before the catalyst is added to epoxide, two isomeric bromo alcohols are produced. However, if the epoxide is added to catalyst, and then bromine is added dropwise over a period of time, only one isomer is formed. Furthermore, the rapid addition of bromine reduced the regioselectivity.

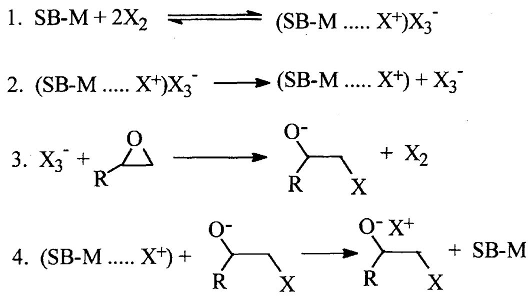
The results of a halogenative cleavage of styrene oxide with iodine and bromine by catalyst **2a** in various aprotic solvents are reported in Table 4. The order of the yields of these reactions is shown in which solvents can act as donor, such as THF; it is lower than those that can not. Thus, these reactions appeared to be heavily dependent on the nature of the solvent.

As shown in Table 3 (Entries 3 and 20), in which only the *trans* isomer is obtained, the reactions are completely *anti*-stereoselective. As for the regioselectivity, an attack of the nucleophile preferentially occurs at the less-substituted oxirane carbon. An *anti*-Markovnikov-type[27] regioselectivity is generally observed in these reactions. In many cases, this type of regioselectivity appears to be the opposite of that observed in ring opening of the same epoxides with aqueous hydrogen halides under classic acidic conditions[20a] (Entries 13 and 14, Table 3). The above-mentioned regiochemical mode can be viewed as occurring via a nucleophilic attack by a halide ion on the less sterically hindered oxirane carbon. This mechanism closely resembles the S_N2 model for aliphatic nucleophilic displacement. In conjunction with our previous studies on the complexation of Schiff base–Metal (SB–M) and other ligands with elemental halogens,[21,28,29] a four-step mechanism was suggested for the halogenative cleavage of epoxides, as in Scheme 2.

The first step involves the formation of a molecular complex between SB–M and elemental halogen as a contact ion pair. Evidence for the formation of such molecular complexes has been reported previously.[29] In the step (2), the X_3^- ion is released into the solution. Then, this ion is used as a nucleophile in the ring opening of epoxides (step 3).

Table 4. Halogenative Cleavage of Styrene Oxide in the Presence of 0.05 mol Catalyst **2a** in Various Solvents

Entry	Solvent	Iodination		Bromination	
		Time/h	Yield/%	Time/h	Yield/%
1	CH_2Cl_2	0.25	> 95	Immed.	> 95
2	$CHCl_3$	0.3	95	Immed.	> 95
3	C_6H_6	0.4	90	0.25	95
4	CH_3CN	0.7	85	0.4	90
5	DMSO	1.0	82	0.6	85
6	THF	1.25	65	0.8	75
7	CH_3COCH_3	1.7	60	1	70



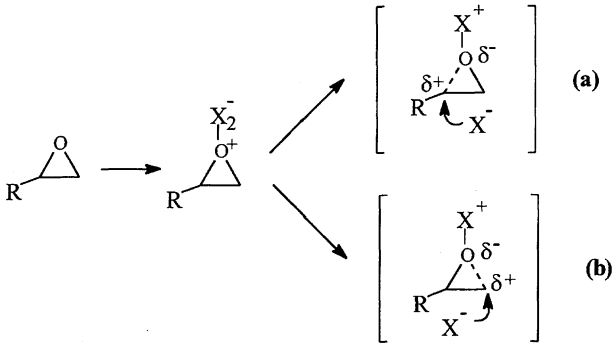
Scheme 2.

Finally, in step (4) the catalyst is reproduced and is used in the first step again. These step occur continuously until all of the epoxides and halogen are consumed. After work-up with thiosulfate, the catalyst can be easily recovered and halo alcohol obtained.

When catalyst is not present, the cleavage of epoxides can occur via two limiting mechanistic pathways, either an electrophilic attack by halogen, behaving as a Lewis acid, giving the more-stable carbenium ion-like transition state **a**, or via nucleophilic attack by a halide ion on the epoxide–halogen complex, giving the more-stable transition state **b** (Scheme 3).

The regiochemistry of the cleavage can be selective depending on the choice of the Lewis acid and reaction conditions. The reaction conditions which provide the most Lewis acidic, namely with titanium halides, foster electrophilic opening of the epoxide ring to yield transition state **a**. Conversely, when weaker Lewis acids are employed, such as molecular halogen, nucleophilic attacks by the generated halide ions should be fostered, and transition state **b** may be expected to be lower in energy. In this case, a mixture of secondary and primary alcohols are produced. The variation in the yield and rate of cleaving styrene oxide by elemental halogen in the presence of various catalysts (Table 1) can be satisfactory rationalized in terms of the suggested mechanism.

In support of this mechanism, the electronic absorption spectra of iodine (1), catalyst **2c** (2), complex formation between iodine and catalyst **2c** (3) and complex formation of iodine with all of the used Schiff base–Mn(II) complexes in dichloromethane solution at 25 °C are shown in Figs. 1 and 2, respectively. As can be seen from Fig. 1, while none of the initial reactants show any measurable absorption in the



Scheme 3.

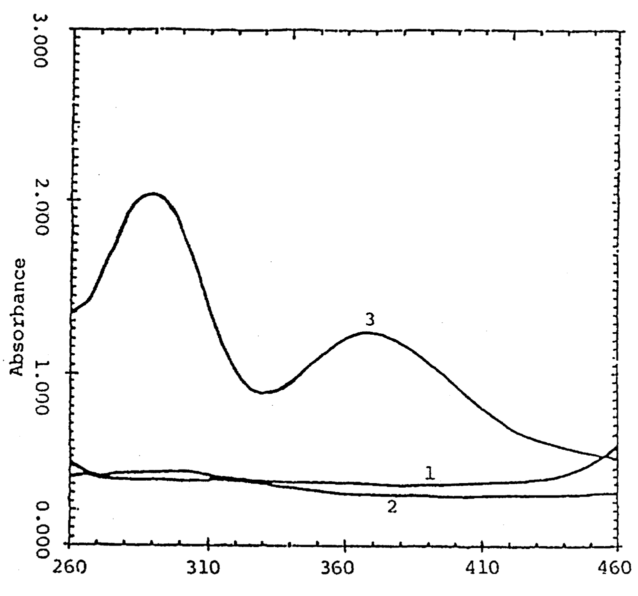


Fig. 1. Absorption spectra of: (1) 1.36×10^{-3} mol dm^{-3} iodine; (2) 1.21×10^{-4} mol dm^{-3} catalyst **2c**; (3) catalyst **2c** : I_2 with molar ratio 1.42 : 1 in dichloromethane solution.

260—460 nm region, the addition of the Schiff base–Mn to iodine results in two strong absorption bands at 292 and 364 nm, presumably due to the complex formation of iodine with Schiff base–Mn. It should be noted that the bands of 292 and 364 nm are characteristic for the formation of the triiodide ion, I_3^-, in the process of complex formation between iodine and different electron-pair donor ligands.[30—35]

As shown in Fig. 2, in all cases a characteristic band in 364 nm is well known to be specific for the formation of triiodide ion, I_3^-.[28,29] In the case of catalysts **2a**, **2b**, and **2c**, this band appeared immediately and clarified the much faster complexation of iodine with these catalysts.

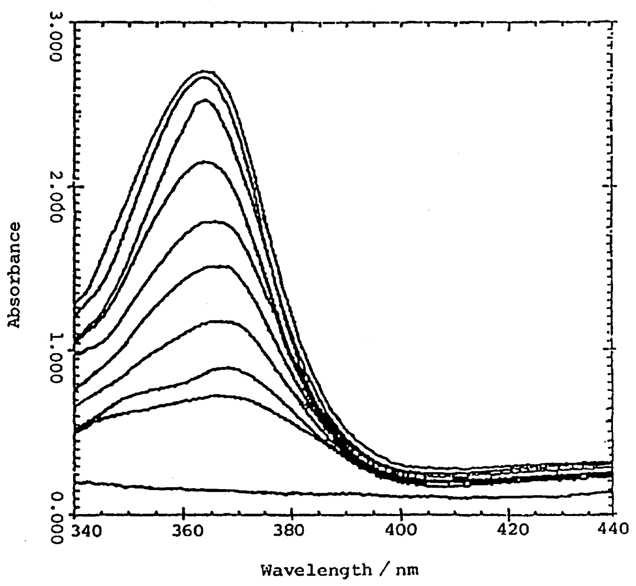


Fig. 2. Absorption spectra of complexes between iodine and the used Schiff base–Mn(II) complexes in dichloromethane solution. Spectra from the bottom to the top refer to 1.36×10^{-3} mol dm^{-3} iodine and catalyst **2h**, **2i**, **2d**, **2e**, **2f**, **2g**, **2c**, **2b**, **2a** : iodine complexes (molar ratio for all of the complexes is 1.54 : 1).

The decrease of regioselectivity that results by merely reversing the order of mixing of epoxide and halogen, namely the slow addition of epoxide to bromine or the fast addition of bromine to epoxide, before the catalyst being added, can be readily understood from the model. When the initial epoxide is introduced (in the absence or presence of catalyst), it would encounter an excess amount of bromine, and electrophilic attack by bromine can occur at the oxygen of epoxide. Then, the bromide anion will attack the more substituted carbon.[2] On the other hand, the slow addition of bromine to the mixture of catalyst and epoxide foster the previous-mentioned four-step mechanism in which elemental bromine is converted to the tribromide ion, Br_3^- by the catalyst; it then attacks the less-substituted carbon selectively. This ion is produced in the process of complex formation between bromine and different electron donors.[36—38]

In conclusion, we have found that epoxides are cleaved regioselectively under neutral and mild conditions by elemental halogens in the presence of some Schiff-base complexes of metal(II) as catalyst. This methodology can be applied for acid-sensitive substrates in aprotic solvents. In these reactions, halo alcohols were obtained in high yields, and the catalysts were easily recovered and could be reused several times. An extension of this methodology toward other Schiff bases with other metals is under investigation.

Experimental

IR spectra were obtained on a Perkin–Elmer 781 spectrophotometer and an Impact 400 Nickolet FTIR spectrophotometer. NMR spectra were recorded in $CDCl_3$ with a Brucker Avance DPX-250 (^{1}H NMR 250 MHz and ^{13}C NMR 62.9 MHz) spectrometer using TMS as an internal standard. UV-vis spectra were obtained with a Philips PU8750 spectometer. The purity determination of the substrates and reactions monitoring were accomplished by TLC on silica-gel polygram SILG/UV 254 plates or GLC on a Shimadzu GC-10A instrument with a flame-ionization detector using a column of 15% carbowax 20 M chromosorb W acid washed 60—80 mesh; temperature, 20 °C below the boiling point of each compound. Some epoxides and other chemical materials were purchased from Fluka and Merck in high purity. The Schiff-base complexes were prepared by reported procedures, and their spectroscopic and physical data were compared with the literature.[23,25,39—42] Epoxides **1c** and **1d** were synthesized[43] and characterized. The yields refer to isolated pure products after column chromatography.

General Procedure for the Reaction of Epoxides with Halogen: Epoxide (1 mmol) in CH_2Cl_2 (5 ml) was added to a stirred solution of catalyst (0.05 mmol) in CH_2Cl_2 (5 ml) at room temperature. Then a solution of elemental halogen (1 mmol) in CH_2Cl_2 (5 ml) was added dropwise (15 min) to the above-mentioned mixture. The progress of the reaction was monitored by GLC and TLC. After the complete disappearance of the starting material, the reaction mixture was washed with 10% aqueous $Na_2S_2O_3$ (2×10 ml) and water (2×10 ml). The aqueous layer was further extracted with CH_2Cl_2 (2×10 ml). The combined organic layer was dried over $MgSO_4$ and evaporated to give a crude alcohol-catalyst. The crude products were purified by crystallyzation in diethyl ether. After cooling, the catalyst was filtered off and washed with cold ether. The solvent was evaporated and pure halo alcohol was obtained. The halo alcohols were identified by a comparison with authentic samples prepared in accordance with literature procedures.[5,18b,20a,44,45]

***p*-Chlorophenyl 2,3-Epoxypropyl Ether (1c):** ^{1}H NMR δ = 2.56 (dd, 1H, J_1 = 4.9 Hz, J_2 = 2.25 Hz), 2.72 (dd, 1H, J_1 = 4.35 Hz, J_2 = 3.8 Hz), 3.14—3.19 (m, 1H), 3.76 (dd, 1H, J_1 = 5.6 Hz, J_2 = 1.45 Hz), 4.03 (dd, 1H, J_1 = 11.0 Hz, J_2 = 2.85 Hz), 6.71 (dd, 2H, J_1 = 8.8 Hz, J_2 = 2.22 Hz), 7.11 (dd, 2H, J_1 = 6.93 Hz, J_2 = 1.85 Hz); IR (neat) 635 (m), 664 (s), 686 (m), 767 (s), 825 (s), 862 (m), 914 (s), 971 (m), 1006 (s), 1032 (s), 1094 (s), 1131 (m), 1172 (s), 1244 (s), 1286 (s), 1348 (m), 1409 (m), 1430 (m), 1455 (m), 1495 (s), 1582 (s), 1598 (s), 2873 (m), 2928 (s), 2996 (m), 3059 (m), 3158 (m) cm^{-1}.

2,3-Epoxypropyl *p*-Tolyl Ether (1d): ^{1}H NMR δ = 2.11 (s, 3H), 2.46 (d, 1H, J = 5 Hz), 2.63 (dd, 1H, J_1 = 5 Hz, J_2 = 2.6 Hz), 3.03—3.09 (m, 1H), 3.71 (dd, 1H, J_1 = 10.9 Hz, J_2 = 5.35 Hz), 3.89 (dd, 1H, J_1 = 10.9 Hz, J_2 = 3.5 Hz), 6.57 (d, 2H, J = 7.0 Hz), 6.84 (d, 2H, J = 7.5 Hz; IR (neat) 662 (m), 715 (w), 742 (m), 769 (m), 816 (s), 838 (m), 862 (m), 913 (s), 1036 (s), 1109 (m), 1176 (m), 1249 (s), 1289 (s), 1345 (m), 1452 (m), 1512 (s), 1536 (m), 1614 (s), 2865 (m), 2920 (s), 2995 (m), 3025 (m), 3052 (m) cm^{-1}.

2-Iodo-1-phenylethanol (3a): ^{1}H NMR δ = 2.02 (s, 1H), 3.76 (d, 2H, J = 5.5 Hz), 4.78 (t, 1H, J = 5.0 Hz), 7.17—7.35 (m, 5H); ^{13}C NMR δ = 54.96, 66.90, 128.22, 129.10, 129.21, 138.17; IR (neat) 748 (m), 915 (m), 1032 (s), 1121 (w), 1243 (s), 1365 (m), 1492 (m), 1602 (s), 2885 (m), 2930 (s), 3061 (m), 3398 (br, s) cm^{-1}.

1-Iodo-3-phenoxy-2-propanol (3b): ^{1}H NMR δ = 3.1 (s, 1H), 3.48 (d, 2H, J = 5.0 Hz), 4.06 (tt, 1H, J_1 = 7.0 Hz, J_2 = 5.0 Hz), 4.13 (d, 2H, J = 5.6 Hz), 6.78—6.9 (m, 3H), 7.36 (m, 2H); ^{13}C NMR δ = 67.18, 69.67, 70.01, 114.98, 116.87, 121.79, 129.89, 132.86; IR (neat) 650 (w), 678 (w), 760 (m), 823 (m), 1038 (s), 1113 (w), 1240 (s), 1375 (m), 1494 (s), 1588 (s), 2877 (m), 2927 (s), 3050 (m), 3418 (br, s) cm^{-1}.

1-(*p*-Chlorophenoxy)-3-iodo-2-propanol (3c): ^{1}H NMR δ = 2.25 (s, 1H), 3.38 (d, 2H, J = 5.1 Hz), 3.86 (q, 1H, J = 1.8 Hz), 4.41 (d, 2H, J = 6.4 Hz), 7.22 (d, 2H, J = 8.7 Hz), 7.61 (d, 2H, J = 6.92 Hz); IR (neat) 632 (w), 648 (w), 667 (s), 694 (m), 742 (m), 818 (s), 893 (m), 936 (m), 1004 (s), 1088 (m), 1167 (s), 1239 (s), 1282 (s), 1374 (w), 1456 (m), 1488 (s), 1580 (m), 1593 (m), 2869 (m), 2925 (s), 2952 (m), 3412 (br, s) cm^{-1}.

1-Iodo-3-(*p*-tolyloxy)-2-propanol (3d): ^{1}H NMR δ = 2.15 (s, 1H), 2.49 (s, 3H), 3.02 (d, 2H, J = 4.1 Hz), 3.46 (q, 1H, J = 2.6 Hz), 4.16 (d, 2H, J = 5.6 Hz), 6.95 (d, 2H, J = 8.5 Hz), 7.23 (d, 2H, J = 8.2 Hz); IR (neat) 665 (s), 743 (w), 814 (m), 1015 (s), 1072 (w), 1123 (s), 1240 (s), 1286 (m), 1378 (w), 1462 (m), 1512 (s), 1586 (m), 1611 (m), 2875 (m), 2928 (s), 2962 (m), 3038 (m), 3422 (br, s) cm^{-1}.

1-Iodo-3-isopropyloxy-2-propanol (3e): ^{1}H NMR δ = 1.15 (d, 6H, J = 4.0 Hz), 2.92 (s, 1H), 3.38—3.59 (m, 5H), 3.79 (m, 1H); ^{13}C NMR δ = 22.78, 36.2, 67.3, 69.8, 72.5; IR (neat) 743 (w), 923 (m), 1050 (s), 1085 (s), 1128 (s), 1375 (m), 1467 (m), 2870 (m), 2926 (m), 2975 (s), 3472 (br, s) cm^{-1}.

1-Iodo-2-octanol (3f): ^{1}H NMR δ = 0.89 (t, 3H, J = 7.0 Hz), 1.26—1.58 (m, 10H), 2.24 (s, 1H), 3.24—3.55 (m, 3H); ^{13}C NMR δ = 14.09, 16.45, 22.62, 25.56, 29.12, 31.70, 36.89, 70.91; IR (neat) 725 (m), 1015 (br, s), 1105 (m), 1130 (m), 1185 (s), 1385 (s), 1425 (s), 1465 (s), 1475 (s), 2870 (vs), 2940 (vs), 2970 (s), 3400 (br, s) cm^{-1}.

2-Iodocyclohexanol (3g): ^{1}H NMR δ = 1.26—1.44 (m, 3H), 1.75—1.95 (m, 3H), 2.15—2.3 (m, 1H), 2.3—2.35 (m, 1H), 2.72 (s, 1H), 3.58—3.62 (m, 1H), 3.9—4.0 (m, 1H); ^{13}C NMR δ = 24.51, 26.56, 32.75, 35.40, 59.84, 71.59; IR (neat) 690 (s), 790 (w), 870 (m), 948 (s), 1038 (w), 1082 (br, s), 1123 (m), 1189 (s), 1372 (m), 1462 (s), 2882 (s), 2960 (br, s), 3425 (br, s) cm^{-1}.

2-Bromo-1-phenylethanol (3h): ^{1}H NMR δ = 1.98 (s, 1H), 4.01 (m, 2H), 4.98 (t, 1H, J = 5.0 Hz), 7.19—7.39 (m, 5H); ^{13}C NMR δ = 57.39, 67.97, 128.32, 129.30, 129.37, 138.98; IR (neat) 689 (m), 766 (m), 823 (m), 1036 (s), 1115 (w), 1233 (s), 1375 (m), 1494 (m), 1600 (s), 2875 (m), 2935 (s), 3064 (m), 3405 (br, s) cm^{-1}.

1-Bromo-3-phenoxy-2-propanol (3i): ^{1}H NMR δ = 2.75 (s, 1H), 3.61 (d, 2H, J = 5.3 Hz), 4.03 (tt, 1H, J_1 = 7.1 Hz, J_2 = 5.0 Hz), 4.11 (d, 2H, J = 7.0 Hz), 6.78 (d, 1H, J = 5.0 Hz), 6.94 (d, 2H, J = 8.0 Hz), 7.35 (m, 2H); ^{13}C NMR δ = 69.58, 69.77, 69.93, 115.01, 116.82, 121.86, 129.99, 132.79; IR (neat) 641 (w), 688 (m), 756 (m), 823 (m), 1038 (s), 1112 (w), 1239 (s), 1375 (m), 1494 (s), 1588 (s), 2878 (m), 2925 (s), 3059 (m), 3415 (br, s) cm^{-1}.

1-Bromo-3-(*p*-chlorophenoxy)-2-propanol (3j): ^{1}H NMR δ = 2.21 (s, 1H), 3.42 (d, 2H, J = 5.0 Hz), 3.81 (q, 1H, J = 2.5 Hz), 4.39 (d, 2H, J = 6.2 Hz), 7.26 (d, 2H, J = 8.25 Hz), 7.65 (d, 2H, J = 6.5 Hz); IR (neat) 649 (m), 664 (m), 695 (m), 743 (m), 768 (w), 821 (m), 938 (m), 1005 (s), 1132 (s), 1245 (m), 1282 (m), 1318 (w), 1449 (m), 1492 (s), 1581 (m), 1596 (m), 1615 (m), 2858 (m), 2928 (s), 2956 (m), 3406 (br, s) cm^{-1}.

1-Bromo-3-(*p*-tolyloxy)-2-propanol (3k): ^{1}H NMR δ = 2.12 (s, 1H), 2.53 (s, 3H), 3.16 (d, 2H, J = 5.0 Hz), 3.47 (q, 1H, J = 2.1 Hz), 4.11 (d, 2H, J = 7.0 Hz), 6.93 (d, 2H, J = 8.8 Hz), 7.19 (d, 2H, J = 7.5 Hz); IR (neat), 659 (s), 819 (m), 1016 (s), 1075 (w), 1123 (s), 1242 (s), 1285 (m), 1381 (w), 1458 (m), 1512 (s), 1585 (m), 1613 (m), 2875 (m), 2927 (s), 2962 (m), 3035 (m), 3425 (br, s) cm^{-1}.

1-Bromo-3-isopropyloxy-2-propanol (3l): ^{1}H NMR δ = 1.16 (d, 6H, J = 4.0 Hz), 2.78 (s, 1H), 3.42—3.65 (m, 5H), 3.92 (m, 1H); ^{13}C NMR δ = 22.34, 35.40, 69.59, 70.40, 72.70; IR (neat) 675 (m), 798 (w), 923 (m), 1051 (s), 1085 (s), 1125 (s), 1375 (m), 1467 (m), 2871 (m), 2925 (m), 2972 (s), 3435 (br, s) cm^{-1}.

1-Bromo-2-octanol (3m): ^{1}H NMR δ = 0.89 (t, 3H, J = 6.5 Hz), 1.25—1.63 (m, 8H), 1.86 (q, 2H, J = 7.1 Hz), 2.22 (s, 1H), 3.42 (d, 2H, J = 7.1 Hz), 3.75—3.84 (m, 1H); ^{13}C NMR δ = 14.01, 22.52, 25.58, 29.14, 31.68, 35.05, 40.73, 71.02; IR (neat) 720 (m), 830 (m), 1050 (s), 1075 (s), 1125 (m), 1225 (m), 1265 (m), 1385 (m), 1425 (m), 1470 (s), 2860 (vs), 2935 (vs), 2970 (vs), 3380 (br, s) cm^{-1}.

2-Bromocyclohexanol (3n): ^{1}H NMR δ = 1.26—1.42 (m, 3H), 1.78—1.98 (m, 3H), 2.18—2.32 (m, 1H), 2.32—2.38 (m, 1H), 2.68 (s, 1H), 3.58—3.64 (m, 1H), 3.82—3.92 (m, 1H); ^{13}C NMR δ = 24.48, 27.02, 33.95, 36.59, 62.13, 75.66; IR (neat) 690 (s), 793 (w), 865 (m), 960 (s), 1038 (m), 1075 (br, s), 1123 (m), 1189 (s), 1372 (m), 1460 (s), 2882 (s), 2960 (br, s), 3425 (br, s) cm^{-1}.

We gratefully acknowledge the support of this work by the Shiraz University Research Council and Professor H. Firouzabadi for his helpful comments.

References

1 a) C. Bonini and G. Righi, *Synthesis*, **1994**, 225. b) M. Shimizu, A. Yoshida, and T. Fujisawa, *Synlett*, **1992**, 204.

2 J. J. Eisch, Z. -R. Liu, X. Ma, and G. -X. Zheng, *J. Org. Chem.*, **57**, 5140 (1992).

3 a) Y. Ueda and S. C. Maynard, *Tetrahedron Lett.*, **29**, 5197

(1988). b) J. P. Konopelski, M. A. Boehler, and T. M. Tarasow, *J. Org. Chem.*, **54**, 4966 (1989).

4 R. C. Larock, "Comprehensive Organic Transformations," VCH, New York (1989), p. 508.

5 J. S. Bajwa and R. C. Anderson, *Tetrahedron Lett.*, **32**, 3021 (1991).

6 Fieser and Fieser, "Reagent for Organic Synthesis," ed by J. G. Smith and M. Fieser, John Wiley, New York (1990), looking for: Halohydrins and Derivatives.

7 C. A. Stewart and C. A. Van der Werf, *J. Am. Chem. Soc.*, **76**, 1259 (1954).

8 S. Winstein and L. L. Ingraham, *J. Am. Chem. Soc.*, **74**, 1160 (1952).

9 J. N. Coxon, M. P. Hartshorn, and W. J. Rae, *Tetrahedron*, **26**, 1091 (1970).

10 R. D. Dawe, T. F. Molinski, and J. V. Turner, *Tetrahedron Lett.*, **25**, 2061 (1984).

11 M. A. Loreto, L. Pellacani, and P. A. Tardella, *Synth. Commun.*, **11**, 287 (1981).

12 a) Y. Guindon, M. Therien, Y. Girard, and C. Yoakim, *J. Org. Chem.*, **52**, 1680 (1987); b) N. N. Joshi, M. Srebnik, and H. C. Brown, *J. Am. Chem. Soc.*, **110**, 6246 (1988).

13 a) T. W. Bell and J. A. Ciaccio, *Tetrahedron Lett.*, **27**, 827 (1986). b) A. K. Mandal, N. R. Soni, and K. R. Ratnam, *Synthesis*, **1985**, 274.

14 G. Palumbo, C. Ferreri, and R. Caputo, *Tetrahedron Lett.*, **24**, 1307 (1983).

15 E. Alvarez, M. t. Nunez, and V. S. Martin, *J. Org. Chem.*, **55**, 3429 (1990).

16 G. C. Andrews, T. C. Grawford, and L. G. Contilio, Jr., *Tetrahedron Lett.*, **22**, 3803 (1981).

17 Y. G. Suh, B. A. Koo, J. A. Ko, and Y. S. Cho, *Chem. Lett.*, **1993**, 1907.

18 a) C. Bonini, G. Righi, and G. Sotgiu, *J. Org. Chem.*, **56**, 6206 (1991); b) N. Iranpoor, F. Kazemi, and P. Salehi, *Synth. Commun.*, **27**, 1247 (1997).

19 H. R. Kricheldorf, G. Morber, and W. Regel, *Synthesis*, **1981**, 383.

20 a) M. Chini, P. Crotti, C. Gardelli, and F. Macchia, *Tetrahedron*, **48**, 3805 (1992); b) L. X. Gao, H. Saitoh, F. Feng, and A. Murai, *Chem. Lett.*, **1991**, 1787.

21 H. Naeimi, Ph. D. Thesis, Shiraz University, Shiraz, Iran, 1997.

22 M. I. Konaklieva, M. L. Dahi, and E. Turos, *Tetrahedron Lett.*, **33**, 7093 (1992).

23 a) G. Mohan, R. C. Sharma, and R. K. Parashar, *Pol. J. Chem.*, **66**, 929 (1992). b) B. B. Mahapatra and D. Panda, *Transition Met. Chem.*, **9**, 280 (1984).

24 K. H. Reddy and Y. Sreenivasulu, *Pol. J. Chem.*, **67**, 637 (1993).

25 a) B. B. Mahapatra, M. K. Raval, A. K. Behera, and A. K. Das, *J. Indian Chem. Soc.*, **72**, 161 (1995). b) A. Ramachandraiah, P. N. Rao, and M. Ramaiah, *Indian J. Chem.*, *Sect. A*, **28A**, 309 (1989).

26 a) S. J. E. Titus, W. M. Barr, and L. T. Taylor, *Inorg. Chim. Acta*, **32**, 103 (1979). b) C. J. Boreham and B. Chiswell, *Inorg. Chim. Acta*, **24**, 77 (1977).

27 P. B. D. De La Mare and R. Bolton, "Electrophilic Addition to Unsaturated Systems," Elsevier Scientific, Amsterdam (1996), p. 132.

28 A. Semnani and M. Shamsipur, *J. Chem. Soc., Dalton Trans.*, **1996**, 2215.

29 Y. A. Serguchev and T. I. Petrenko, *Teor. Eksp. Khim.*, **13**, 705 (1977).

30 H. P. Hopkins, D. V. Jahagirdar, and F. Windler, *J. Phys. Chem.*, **82**, 1254 (1978).

31 E. M. Nour and L. A. Shahada, *Spectrochim. Acta, Part A*, **44A**, 1277 (1988).

32 E. M. Nour, *Spectrochim. Acta, Part A*, **47A**, 473 (1991).

33 R. P. Lang, *J. Phys. Chem.*, **78**, 1657 (1974).

34 L. J. Andrews, E. S. Prochaska, and A. Loewenschuss, *Inorg. Chem.*, **19**, 463 (1980).

35 M. Mizuno, J. Tanaka, and I. Harada, *J. Phys. Chem.*, **85**, 1789 (1981).

36 H. D. Spivey and T. Shedlovsky, *J. Phys. Chem.*, **71**, 2165 (1967).

37 E. Shchori and J. J. Grodzinski, *J. Am. Chem. Soc.*, **94**, 7957 (1972).

38 R. E. Buckles and J. P. Yuk, *J. Am. Chem. Soc.*, **75**, 7043 (1953).

39 a) J. Csaszar, *Acta Phys. Chem.*, **28**, 135 (1982). b) P. Pfeiffer, Th. Hesse, H. Pfitzner, W. Scholl, and H. Thielert, *J. Prakt. Chem.*, **149**, 217 (1937).

40 a) T. Matsushita, T. Yarino, I. Mosuda, T. Shomo, and K. Shinra, *Bull. Chem. Soc. Jpn.*, **46**, 1712 (1972). b) G. L. Johnson and W. D. Beveridge, *Inorg. Nucl. Chem. Lett.*, **3**, 323 (1967).

41 C. A. McAuliffe, R. V. Parish, F. M. Ashmawy, R. M. Issa, and S. A. Amer, *J. Chem. Soc., Dalton Trans.*, **1987**, 2009.

42 a) B. Mabad, P. Cassoux, J. P. Tuchagues, and D. N. Hendrickson, *Inorg. Chem.*, **25**, 1420 (1986). b) S. R. Edmondson, R. H. Niswander, and L. T. Taylor, *J. Coord. Chem.*, **7**, 113 (1977).

43 T. Kida, M. Yokota, A. Masuyama, Y. Nakatsuji, and M. Okahara, *Synthesis*, **1993**, 487.

44 a) H. Masuda, K. Takase, M. Nishio, A. Hasegawa, Y. Nishiyama, and Y. Ishii, *J. Org. Chem.*, **59**, 5550 (1994). b) C. O. Guss and R. Rosenthal, *J. Am. Chem. Soc.*, **77**, 2549 (1955).

45 a) P. Pfeiffer and K. Bauer, *Chem. Ber.*, **80**, 7 (1947). b) S. M. Naqvi, J. P. Horwitz, and R. Filler, *J. Am. Chem. Soc.*, **79**, 6283 (1957). c) Z. Ailian and W. Yuanliu, *Youji Huaxue*, **13**, 616 (1993).