



A facile conversion of epoxides to halohydrins with elemental halogen using isonicotinic hydrazide (isoniazide) as a new catalyst

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Abstract

The regioselective ring opening halogenation of some epoxides using elemental iodine and bromine in the presence of a series of pyridine-containing groups has been studied. The epoxides were subject to cleavage by elemental halogen (I_2 and Br_2) in the presence of isonicotinic hydrazide (isoniazide) under mild reaction conditions in various solvents. In this study, reagents and conditions have been discovered with which the individual halohydrins can be synthesized in high yield and with more than 95% regioselectivity.

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Keywords: Ring opening; Epoxides; Halohydrin; Isonicotinic hydrazide (isoniazide)

1. Introduction

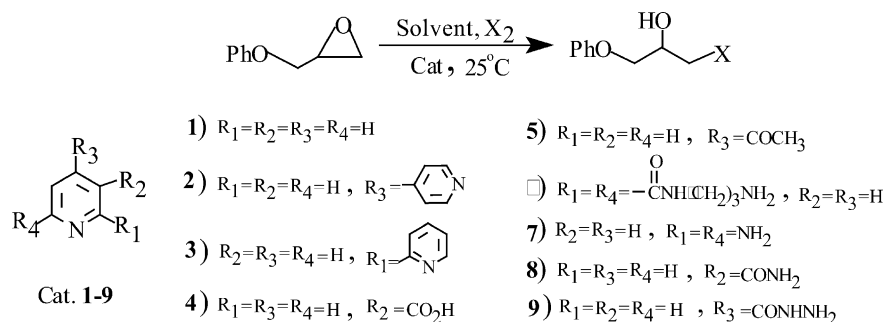
Isoniazide is an important drug and widely used for the chemotherapy of tuberculosis [1–3]. Vicinal halohydrins are useful compound in synthetic organic chemistry [4]. Although they are conveniently obtained by an addition of hypo halite–water to olefins [5], no regiospecific addition was observed. The regioselective conversion of epoxides to halohydrins is a useful tool for regiospecific synthesis of various synthons [6]. A great effort has been made in the last few years to find new mild procedures for converting epoxides into halohydrins. For example, silyl halides can be added to epoxides to give halohydrins [7]. In these cases, however, the primary reaction products are the *O*-silyl protected derivatives [7]. Other methods require the use of a halogen and triphenylphosphine [8], or disubstituted borane halogenides [9], β -bromo bis-(dimethylamino) borane [10], monochloro borane-dimethylsulfide [11], $Li_nM_nX_n$ ($M = Ni, Cu, Ti$) [12] and MX_n [13]. It has been found that epoxides also can be converted into halohydrin by means of elemental halogen [14], but this method has some limitations such as low regioselectivity, lengthy time, low yield and formation of acetones as byproducts in addition to the expected iodo adduct in acetone solution. In conjunction with ongoing

work in our laboratory on the synthesis and complex formation of heterocyclic compounds containing donor nitrogen atoms, with neutral molecules such as iodine and bromine [15], we introduce a very simple, mild, cheapness, facile workup, available and efficient method for the conversion of epoxides to β -halohydrins. In this paper, we would like to describe our successful results that led to a novel and extremely simple method for the transformation of epoxides into β -halohydrins with elemental iodine and bromine in the presence of catalytic amount of isoniazide (9).

2. Results and discussion

Epoxides of convenient volatility to allow GC analysis were chosen for study. As catalysts, pyridine (1), 4,4'-bipyridyl (2), 2,2'-bipyridyl (3), pyridine-3-carboxylic acid (4), methyl-4-pyridylketon (5), 2,6-bis(1-propanecarboxamido-3-amino)pyridine (6) [16], 2,6-diaminopyridine (7), nicotinamide (8) and isoniazide (9) according to Scheme 1 were selected. The results of the reaction of 1,2-epoxy-3-phenoxypropane with elemental iodine and bromine in the presence of the above catalysts are summarized in Table 1. In each case, cleavage of epoxide ring occurs, and upon thiosulfate workup, the corresponding iodohydrin and bromohydrin were obtained. The catalysts were easily recovered and could be reused several times. In comparison,

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Scheme 1.

the cleavage behavior of 1,2-epoxy-3-phenoxypropane with elemental iodine and bromine in the absence of catalyst is given in Table 3, entries 2 and 5. As shown in Table 1 yields of both iodination and bromination with this new methodology are quite good. Catalyst (9) is the most effective, and reactions occur in the presence of this catalyst (Table 1, entry 10). In the presence of other catalysts (1–8), the yields of products for iodination and bromination at room temperature are in the range 20–70% and 30–75%, respectively. The results of ring opening of 1,2-epoxy-3-phenoxypropane in the presence of isoniazide (9) in various solvents are summarized in Table 2. The iodination and bromination reactions proceed most cleanly in THF, while those performed in chloroform, dichloromethane, HMPA, diethylether, DMSO and CH₃CN lead to a lower yield of β-halohydrins.

The results obtained with some representative epoxides in the presence of isoniazide (9) as catalyst are summarized in Table 3 and are compared with the corresponding results obtained in the reaction of the same epoxides in the absence of catalyst (entries 2, 3, 5, 8, 9, 13 and 18). On the other hand, for comparison, some other methods for conversion of epoxides to the corresponding halohydrins are given in Table 3 (entries 10, 14, 15 and 22). When epoxides were

allowed to react in the presence of our catalyst, increases in yield and regioselectivity were observed in all of the reactions studied. The increase appeared to be largely dependent on the type and amount of catalyst (Table 1). Generally, the optimum amount of the catalyst was found to be 0.1 mol for 1 mol of epoxides and halogen.

However, other factors can exert a controlling influence, such as (1) steric hindrance of epoxides; (2) the nature of solvent; (3) the rate of admixing the reagents; and (4) the order in which the reagents are combined. Each one can have a pronounced effect on the observed ratio of β-halohydrins isomers and overall yield.

A comparison of the reaction of epoxides with elemental bromine or iodine in the presence of catalyst (9) indicates that an increase in steric hindrance at the epoxide ring results in a general decrease in the rate of halohydrin formation (for example, compare Table 3, entry 7 with entry 20).

The order and rate in which the reagents are combined were found to exert a subtle influence on yield and regioselectivity in both bromohydrin and iodohydrin formation. For example, if bromine added to epoxide before catalyst is added, two bromohydrin isomers are produced, but if the epoxide is added to catalyst and then bromine is added dropwise over a period of time, only one isomer is formed. Furthermore, fast addition of bromine reduced regioselectivity, too (Table 3, entry 6). The reactions are completely anti-stereoselective as shown for cyclohexene oxide (Table 3,

Table 1

Halogenative cleavage of 1,2-epoxy-3-phenoxypropane in the presence of various pyridine-containing groups in THF at 25 °C

Entry	Solvent	Catalyst	Iodination		Bromination	
			Time (h)	Yield ^a (%)	Time (h)	Yield ^a (%)
1	THF	1 (0.1 mol)	24	30	20	40
2	THF	2 (0.1 mol)	24	40	20	45
3	THF	3 (0.1 mol)	24	20	20	30
4	THF	4 (0.1 mol)	24	20	20	30
5	THF	5 (0.1 mol)	24	40	20	45
6	THF	6 (0.1 mol)	24	70	20	75
7	THF	7 (0.1 mol)	24	55	20	60
8	THF	8 (0.1 mol)	24	45	20	50
9	THF	9 (0.2 mol)	4	75	2	80
10	THF	9 (0.1 mol)	4	75	2	80
11	THF	9 (0.05 mol)	4	60	2	65
12	THF	9 (0.025 mol)	4	55	2	58

^a Isolated yield.

Table 2

Halogenative reaction of 1,2-epoxy-3-phenoxypropane in the presence of isoniazide (9) in various solvents at 25 °C

Entry	Solvent	Catalyst (0.1 mol)	Iodination		Bromination	
			Time (h)	Yield ^a (%)	Time (h)	Yield ^a (%)
1	THF	9	4	75	2	80
2	Et ₂ O	9	25	20	18	25
3	CH ₂ Cl ₂	9	29	20	20	30
4	CHCl ₃	9	35	30	30	35
5	DMSO	9	24	15	20	20
6	CH ₃ CN	9	15	40	12	55
7	HMPA	9	38	25	24	30
8	Dioxane	9	8	55	6	60

^a Isolated yield.

Table 3

Reaction of epoxides with elemental iodine and bromine in the presence of isoniazide (**9**) at 25 °C

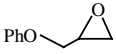
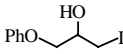
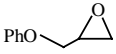
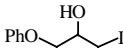

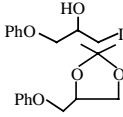
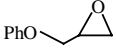
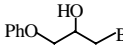

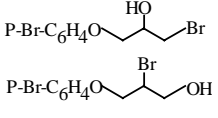

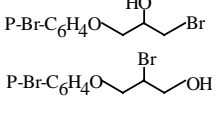







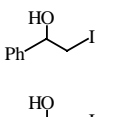

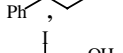

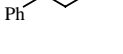

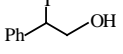

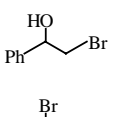

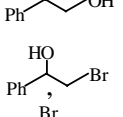

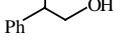

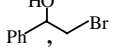
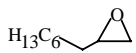
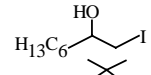
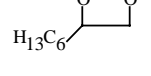
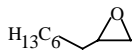
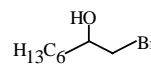

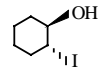

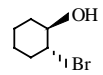

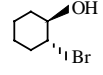
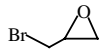
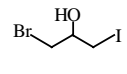
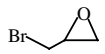
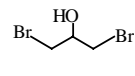
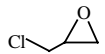
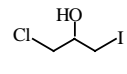
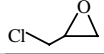
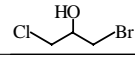
Entry	Epoxide	Catalyst	Condition	Time (h)	Yield ^a (%)	Product(s)	Ref.
1		9	I ₂ /RT/THF	4	75		
2		–	I ₂ /RT/THF	Several days	20		
3		–	I ₂ /RT/acetone	–	94 (1:1)		[14]
4		9	Br ₂ /RT/THF	2	80		
5		–	Br ₂ /RT/THF	–	67(10:1)		[14]
6		9	Br ₂ /RT/THF	2	77(12:1)		
7		9	I ₂ /RT/THF	0.66	95		
8		–	I ₂ /RT/acetone	2	83		[14]
9		–	THF/I ₂ (excess)	Several days	30		[14]
10		–	LiI/AcOH/THF/RT	1.3	87 (1:2)		[13a]
11		–	HI/CHCl ₃	0.25	>99		[19]
12		9	Br ₂ /RT/THF	0.25	97		
13		–	Br ₂ /RT/CH ₂ Cl ₂	1	31		[14]
14		–	<i>n</i> -Bu ₄ NBr/Mg(NO ₃) ₂ /CHCl ₃	5	78 (5:1)		[47]
15		–	(Me ₂ N) ₂ BBr/CH ₂ Cl ₂ /N ₂	12	75 (1:4.5)		[10]
16		–	HBr/CHCl ₃	0.25	>99		[19]
17		9	I ₂ /RT/THF	2	80		

Table 3 (Continued)

Entry	Epoxide	Catalyst	Condition	Time (h)	Yield ^a (%)	Product(s)	Ref.
18		–	I ₂ /acetone	–	79 (1:4)	 	[14]
19		9	Br ₂ /RT/THF	0.33	85		
20		9	I ₂ /RT/THF	0.83	85		
21		9	Br ₂ /RT/THF	0.25	90		
22		–	LiBr/RT/AcOH/THF	5	90		[13a]
23		9	I ₂ /RT/THF	4	85		
24		9	Br ₂ /RT/THF	0.33	90		
25		9	I ₂ /RT/THF	4	75		
26		9	Br ₂ /RT/THF	0.33	80		

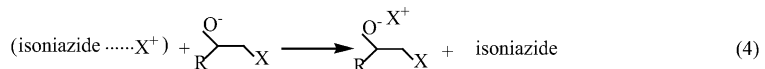
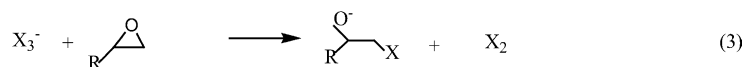
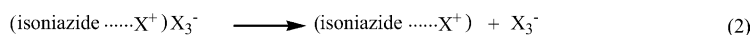
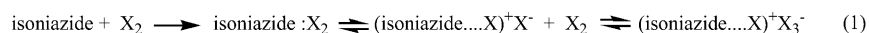
^a Isolated yield.

entries 20 and 21), in which only the *trans* isomers were detected. A contra-Markovnikov-type [17,18], regioselectivity is generally observed in these reactions. Interestingly, in many cases, this type of regioselectivity appears to be opposite of that observed in ring opening of the same epoxides with aqueous hydrohalogenic acids, under classic conditions [19] (entries 11 and 16).

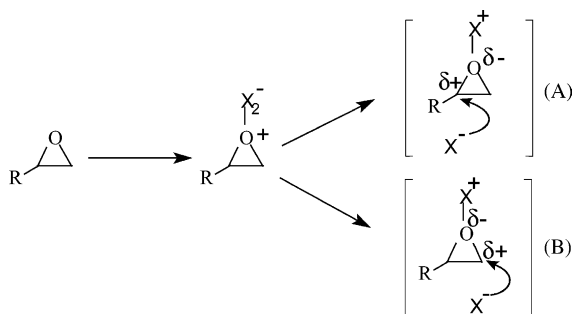
The regiochemical mode of epoxide cleavage by elemental iodine or bromine in the presence of pyridine-containing group's catalyst can be viewed as occurring via nucleophilic attack by halide ion on the less sterically hindered epoxide carbon. This mechanism closely resembles the S_N2 model for aliphatic nucleophilic displacement. On the basis of our

study on the complexation of isoniazide and other works reported on the different ligands [14,20] with elemental halogen, halogenative cleavage of epoxides occurs according to the following four-step mechanism (Scheme 2).

The first step involves the formation of a 1:1 molecular complex between isoniazide (**9**) and elemental halogen, in which halogen ion (X₃[−]) exists as a contact ion pair. In the second step this complex is further decomposed to release X₃[−] ion into solution. Therefore, in this way, molecular iodine or bromine is converted to a nucleophilic halogen species in the presence of a isoniazide (**9**) and, in the third step, this ion participates in the ring opening reaction of epoxides. These steps occur continuously until all of the



Scheme 2.

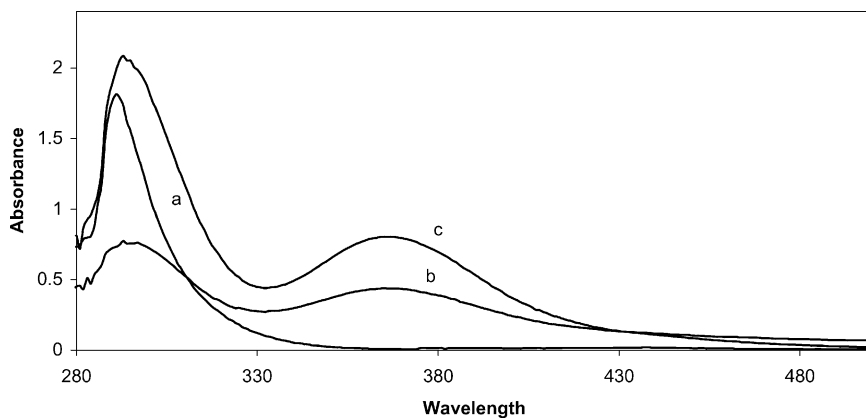
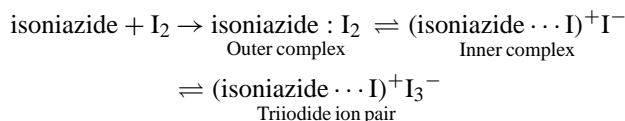


Scheme 3.

epoxides and halogen are consumed, and after workup, the catalyst can be recovered easily. On the other hand, when catalyst is not present, cleavage of epoxides can occur via two limiting mechanistic pathways, either electrophilic attack by molecular halogen, behaving as Lewis acid, giving the more stable carbonium ion-like transition state A, or via nucleophilic attack by halide ion on the epoxide or epoxide–halogen complex, giving the more stable transition state B (Scheme 3). Most Lewis acidic compounds, such as titanium halides, foster electrophilic opening of the epoxide ring to yield transition state A. When weaker Lewis acids are employed, namely bromine or iodine, nucleophilic attack, by the halide ions generated should be fostered and transition state B may be expected to be lower in energy. In this case, the cleavage leads to a mixture of secondary alcohol and primary alcohol products [18]. The variation in yield and rate of cleaving epoxides by elemental iodine or bromine in the presence of different catalysts (1–9) can be satisfactory rationalized in terms of the suggested mechanism. The isoniazide (9) is the most active catalyst in these reactions. According to the mechanism, in isoniazide (9) complexation with I_2 and, hence, elaboration of I_3^- occurred much faster than with other catalysts. In support of this mechanism, reaction of catalyst with iodine was followed by UV spectroscopy (Fig. 1). Fig. 1 shows the characteristic UV band for I_2 –isoniazide (9) at 364 nm. This band is well known to be specific for the formation

of triiodide ion, I_3^- , in the complex formation process between iodine and different electron-pair-donating ligands [21–23]. Especially in the case of isoniazide (9) this band appeared immediately and clarified the much faster complexation of I_2 with isoniazide (9) and consequently formation of I_3^- .

Molecular charge-transfer complexes (C.T.) play an important role in quantitative and qualitative analysis of different pharmaceutical compounds. The energy of C.T. complex depends upon the ionization potential of the donor and the electron affinity of the acceptor and contributes to the spectral absorption characteristics of the molecular complex where a new absorption maximum is formed at considerably longer wavelength in the visible region. Such band is not found in the absorption spectra of both donor and acceptor and can be considered as the basis for the identification of the C.T. complex, particularly when such complex could not be isolated [24]. Isoniazide is an important, widely used tuberculostatic drug. It contains three nitrogen atoms, thus is an electron-rich compound, which reacts with iodine to give product with characteristic charge-transfer absorption spectra. Isoniazide more soluble in water, THF, and 1,1,2,2-tetrachloroethane and insoluble in other halogenated solvents. Iodine molecule reacts with THF and generated of triiodide, therefore, we cannot study the stoichiometry of isoniazide–iodine system in this solvent. This suggested the use of 1,1,2,2-tetrachloroethane for dissolving the isoniazide and charge-transfer complex formation of iodine. Mixing the isoniazide and iodine in 1,1,2,2-tetrachloroethane media resulted in a change on the violet color of iodine to yellowish purple depending on the isoniazide concentration. This interaction is a charge-transfer complexation reaction between n-donor isoniazide and σ -electron acceptor iodine followed by formation of a triiodide ion according to the following suggested routes:

Fig. 1. Absorption spectra in THF solution: (a) isoniazide; (b) I_2 ; and (c) I_2 –isoniazide.

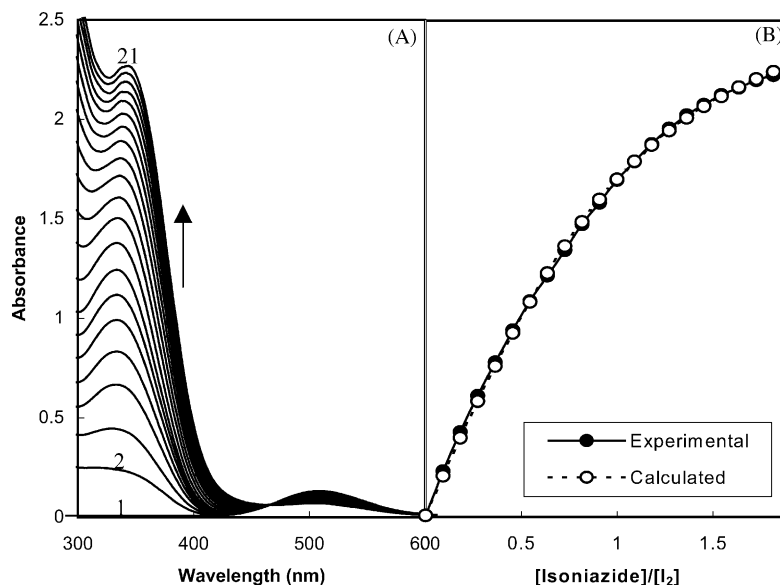


Fig. 2. (A) Absorption spectra of the isoniazide-iodine system. No. 1 contains 7.22×10^{-4} M iodine, nos. 2–21 contains increasing in concentrations from 6.55×10^{-5} – 1.31×10^{-3} M of isoniazide. (B) Mole ratio plot at 342 nm (solid line: experimental values and point line: calculated values).

This was postulated on the basis of the molar ratio of isoniazide to iodine 1:1 and consideration of previous reports on similar reactions in the literature [25–30]. The measurable species is the triiodide ion pair. The electronic absorption spectra of the isoniazide-iodine reaction product (Fig. 2(A)) show a high absorption bands with a maximum at 272 nm and a lower band with a maximum at 342 nm that are characteristic of n-donor-iodine charge-transfer complex leading to radical ion formation in 1,1,2,2-tetrachloroethane. The final reaction product is assumed to be a triiodide ion pair, as confirmed by the slight modification of the absorption of triiodide ion with the accompanying cation and the variation in λ_{\max} [25,26,31–33]. Regarding the third step in the above scheme, iodide alone does not absorb at the wavelength of maximum absorption, hence the stoichiometry will show only the iodide ion released as a result of 1 mol of iodine being consumed in the second step. Moreover, the single isosbestic point located between free and complexed iodine bands at 469 nm lends additional support for the 1:1 estimated ratio [33]. Association constant and molar absorptivity of the charge-transfer complex were determined by measuring the absorbance at 357 nm for a series of solutions with varying concentration of isoniazide (6.55×10^{-5} – 1.31×10^{-3} M) and constant iodine concentration (7.22×10^{-4} M) in 1,1,2,2-tetrachloroethane (Fig. 2(A)) by non-linear curve fitting using Microsoft excel solver. The values of 3.89×10^4 l mol $^{-1}$ cm $^{-1}$ and 5.35×10^4 calculated for the molar absorptivity and association constant, respectively (Fig. 2(B)).

Especially in the case of isoniazide (9) this band appeared immediately and clarified the much faster complexation of I $_2$ with isoniazide (9) and consequently formation of I $_3^-$. The decrease in regioselectivity that results by merely reversing the order of mixing of epoxide and halogen, namely

the slow addition of epoxide to bromine or fast addition of bromine to epoxide, before catalyst was added, can readily be understood from the model. When the initial epoxide was introduced (in the absence or presence of catalyst), it would encounter an excess amount of bromine; electrophilic attack by bromine can then occur, giving the transition state A, and bromine anions will attack the more substituted carbon. On the other hand, slow addition of bromine to the mixture of catalyst and epoxide fosters the four-step mechanism presented above in which all of the elemental bromine is converted to Br $_3^-$ by the catalyst and it then attacks the less substituted carbon selectively. In conclusion, we have found that isoniazide (9) can catalyze the regioselective ring opening of epoxides by elemental iodine and bromine under neutral conditions. Especially noteworthy is the compatibility of these reaction conditions with a variety of sensitive functional groups, which make this synthetic technique highly useful. In additions, the advantages such as high regio- and stereoselectivity of the reactions, stability, high yield, very simple, mild and facile workup make this method a useful addition to the present methodologies in organic syntheses.

3. Experimental

All products are known compounds and yields refer to isolated yields, NMR spectra were recorded in CDCl $_3$ on a Bruker Advanced Dpx-250 (1 H NMR 250 MHz and 13 C NMR 62.9 MHz) spectrophotometer using TMS as internal standard. An Ultrospec 3000 (Pharmacia Biotech, England), UV-Vis spectrophotometer, with matched, stoppered quartz cells of 10 mm path length at a scan speed of 6000 nm min $^{-1}$ was used for recording the spectral and absorbance measurements. The swift (II) software prepared by Pharmacia

Biotech Company was used to collect the absorbance data in a spreadsheet. GC spectra were recorded on a Shimadzu GC-14A. Infrared spectra were recorded on a Perkin-Elmer IR-157G and a Perkin-Elmer 781 spectrometer.

4. Association constant and molar absorptivity

The association constant and molar absorptivity of the resulting charge-transfer complex between isoniazide and iodine in 1,1,2,2-tetrachloroethane were determined at 25 °C by measurements, at λ_{\max} 342 nm of solutions in which varying concentration of isoniazide (6.55×10^{-5} – 1.31×10^{-3} M) were added to a fixed concentration of iodine (7.22×10^{-4} M) in 1,1,2,2-tetrachloroethane. The association constant and molar absorptivity were determined by non-linear curve fitting using Microsoft excel solver.

4.1. General procedure for conversion of epoxides to β -halohydrins

Epoxide (1 mmol) in THF (5 ml) was added to a stirred solution of catalyst (0.1 mmol) in THF (5 ml) at room temperature. Next, a solution of elemental halogen (1 mmol) in THF (5 ml) was added portion wise (15 min) to the above mixture. GLC and TLC monitored the progress of the reaction. After complete disappearance of the starting material, the reaction was poured to the 10% aqueous $\text{Na}_2\text{S}_2\text{O}_3$ (20 ml) and extracted with CH_2Cl_2 (2×10 ml). The organic layer was washed with water (2×10 ml) and dried over MgSO_4 and evaporated to give crude alcohol-catalyst. The crude products were purified by crystallization in diethyl ether. After cooling the catalyst was filtered off and washed with cold ether. The solvent was evaporated and pure halohydrin was obtained. The halohydrins were identified by comparison with authentic samples prepared in accordance with literature procedures [12c,13,14,34,36].

4.1.1. 2-Iodo-1-phenylethanol

White crystal; mp 33–35 °C ([35], 34 °C); yield = 90%; spectroscopic data identical to that reported in the literature [15].

4.1.2. 2-Bromo-1-phenylethanol

Liquid; bp 110–111 °C (4.2 mm) ([36], 120–123 °C (5 mm)); yield = 95%; spectroscopic data identical to that reported in the literature [15].

4.1.3. 1-Bromo-2-octanol

Liquid; bp 115–117 °C (15 mm) ([37], 111–112 °C (10 mm)); yield = 75%; spectroscopic data identical to that reported in the literature [34].

4.1.4. 1-Iodo-2-octanol

Yellow liquid; yield = 70%; spectroscopic data identical to that reported in the literature [34].

4.1.5. 2-Iodocyclohexanol

White crystal; mp 41.5–43 °C ([38], 41.5–42.5 °C); yield = 80%; spectroscopic data identical to that reported in the literature [34].

4.1.6. 2-Bromocyclohexanol

Liquid; bp 84–86 °C (1 mm) ([39], 88–90 °C (7 mm)); yield = 87%; spectroscopic data identical to that reported in the literature [34].

4.1.7. 1-Bromo-3-phenoxy-2-propanol

Odorless liquid; bp 160–161 °C (1 mm) ([40], 167–169 °C (16 mm)); yield = 75%; spectroscopic data identical to that reported in the literature [15].

4.1.8. 1-Iodo-3-phenoxy-2-propanol

Odorless liquid; bp 176–180 °C (16 mm) ([40], 177–181 °C (16 mm)); yield = 70%; spectroscopic data identical to that reported in the literature [15].

4.1.9. 1,3-Dibromo-2-propanol

Yellow liquid; bp 103–106 °C (15 mm) ([41], 105 °C (16 mm)); yield = 65%; spectroscopic data identical to that reported in the literature [42].

4.1.10. 1-Bromo-3-chloro-2-propanol

Liquid; bp 96–98 °C (15 mm) ([43], 95–98 °C (15 mm)); yield = 75%; spectroscopic data identical to that reported in the literature [44].

4.1.11. 1-Bromo-3-iodo-2-propanol

Yellow liquid; yield = 58%; spectroscopic data identical to that reported in the literature [45].

4.1.12. 1-Chloro-3-iodo-2-propanol

Liquid; bp 53–55 °C (0.2 mm) ([46], 52–54 °C (0.2 mm)); yield = 63%; spectroscopic data identical to that reported in the literature [45].

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