

Selective Conversion of Epoxides to *vic*-Halo Alcohols and Symmetrical or Unsymmetrical Dihalides by Triphenylphosphine/2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in the Presence of Quaternary Ammonium Halides

Nasser Iranpoor,* Habib Firouzabadi,* Ghasem Aghapour, and Azarmidokht Nahid

Chemistry Department, College of Sciences, Shiraz University, Shiraz 71454, Iran

Received July 29, 2003; E-mail: iranpoor@chem.susc.ac.ir

A new method is described for the efficient and selective conversion of epoxides to *vic*-halo alcohols or symmetrical and unsymmetrical dihalides using $PPh_3/DDQ/R_4NX$ (X = Cl, Br, I) as a mixed-reagent system.

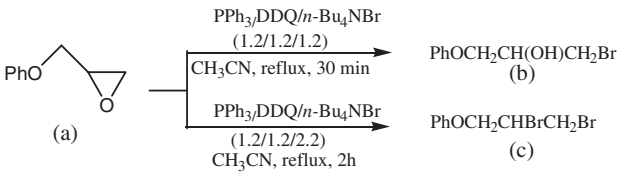
Epoxides are important intermediates in organic synthesis.[1] Their facile regio- and stereoselective ring-opening reactions with a wide variety of nucleophiles provide a powerful strategy in organic chemistry.[1–6] One of the useful nucleophilic reactions of epoxides is their conversion into their *vic*-halo alcohols.[7–11] In order to avoid the use of strongly acidic hydrogen halides for their synthesis,[12] different methodologies have been developed in recent years. Some of these methods are considered, such as the use of magnesium nitrate,[13] or ammonium cerium(IV) nitrate in the presence of halide ions,[14] phosphaferrocene as a catalyst with TMSCl,[15] silica gel in the presence of lithium halides,[16] 2-phenyl-2-(2-pyridyl)imidazolidine (PPI) in the presence of elemental halogens,[17] iron(III) trifluoroacetate with quaternary ammonium halides or their ammonium salts,[18] PPh_3/CBr_4,[19] phenylhydrazine in the presence of elemental halogens,[20] and crown ethers/elemental halogens.[21] The conversion of epoxides to symmetrical *vic*-dihalides as another important route for the preparation of halogenated compounds with reagents, such as PPh_3/CCl_4[22] and PPh_3/X_2 (X = Cl, Br),[23] are also reported in the literature.

Although there are reports concerning the preparation of unsymmetrical *vic*-dihalides from alkenes,[24–26] as far as we know there is only one method described in the literature about the preparation of unsymmetrical *vic*-dihalides from epoxides.[23] By this method, epoxide was firstly converted to its corresponding *vic*-halo alcohol under highly acidic conditions using HCl/THF, followed by a treatment with PPh_3/Br_2 to convert the hydroxy group into bromide.

In continuation of our recent work on the use of $PPh_3/DDQ/R_4NX$,[27] we now report on a new and highly selective method for the conversion of epoxides to either *vic*-halo alcohols and *vic*-symmetrical or unsymmetrical dihalides using this mixed-reagent system.

In this article, we report that epoxides in the presence of $PPh_3/DDQ/R_4NX$ (X = Cl, Br, I) can be converted to *vic*-halo alcohols or *vic*-dihalides, depending on the molar ratio of the reagents to the epoxides (Scheme 1).

We took oxiranylmethyl phenyl ether as an example, and optimized the reaction conditions for its conversion to *vic*-halo alcohols or *vic*-dibromides using different molar ratios of $PPh_3/DDQ/n\text{-}Bu_4NBr$ in refluxing acetonitrile. It was observed that the molar ratios of 1.2/1.2/1.2 and 1.2/1.2/2.2 of this mixed reagent system produced the highest yield of the corresponding *vic*-halo alcohol and *vic*-dibromide, respectively. The optimized reaction conditions are given in Table 1.



Scheme 1.

Table 1. Various Reaction Conditions for the Conversion of Oxiranylmethyl Phenyl Ether (a) with $PPh_3/DDQ/n\text{-}Bu_4NBr$ to Its *vic*-Bromo Alcohol (b) or *vic*-Dibromide (c) in Refluxing Acetonitrile

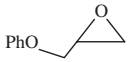
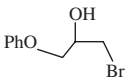
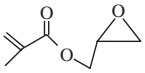
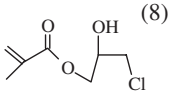
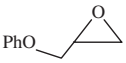
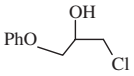
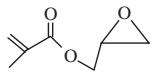
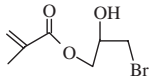
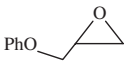
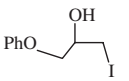
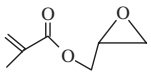
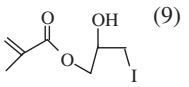
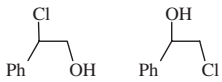
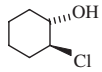
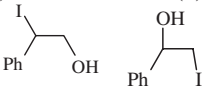
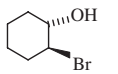
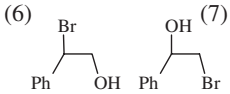
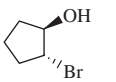
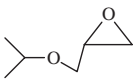
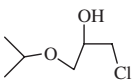
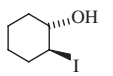
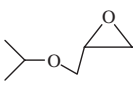
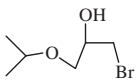
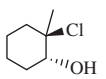
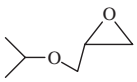
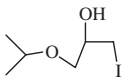
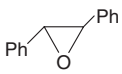
Entry	Time/h	Yield/%
1[i)]	0.5	20
2[ii)]	0.5	55 of (b) + 25 of (c)
3[iii)]	12	0
4[iv)]	3.75	95 of (b)
5[v)]	0.5	97 of (b)
6[vi)]	2.0	90 of (c)

i) Epoxide (one equimolar) is added to the mixture of $PPh_3/DDQ/n\text{-}Bu_4NBr$ with molar ratio of 1.2/1.2/1.2 at room temperature. ii) Reaction is performed in refluxing acetonitrile. iii) Reaction is performed in the absence of PPh_3/DDQ. iv) $n\text{-}Bu_4NBr$ is gradually added to the refluxing mixture of Ph_3P/DDQ over 3.5 h and then refluxed for additional 0.5 h (see experimental section, method A). v) Reaction is carried out in the presence of 0.5 molar equivalent of water (see experimental section, method B). vi) This experiment is performed in refluxing acetonitrile, and the molar ratio of $PPh_3/DDQ/n\text{-}Bu_4NBr$ is 1.2/1.2/2.2.

As shown in Table 1, the reaction of oxiranylmethyl phenyl

Published on the web October 9, 2004; DOI 10.1246/bcsj.77.1885

Table 2. Conversion of Epoxides to *vic*-Halo Alcohols with PPh_3/DDQ/R_4NX (X = Cl, Br, I) (1.2/1.2/1.2) in Refluxing Acetonitrile[a)]

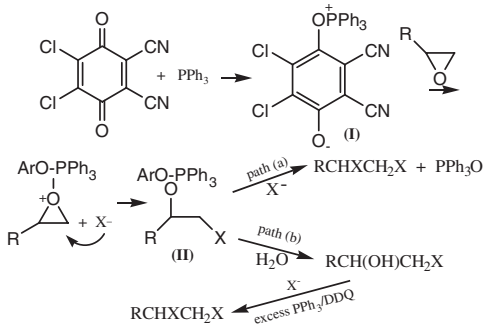
Entry	Substrate	Product[b)]	Yield[c)]/%	Entry	Substrate	Product[b)]	Yield[c)]/%
1		 (1)	95[d)]	10		 (8)	96[d)]
2		 (2)	75[d)]	11			87[d)]
3		 (3)	70[d)]	12		 (9)	90[d)]
4			75 (15)[e)]	13			88[d)]
5		 (4) (5)	65 (15)[d)]	14			78[d)]
6		 (6) (7)	60 (35)[c)]	15			80[d)]
7			94[d,e)]	16			95[d)]
8			87[d)]	17			78
9			95[d)]	18		*erythro*-PhCHOHCHBrPh	90[d)]

a) Method A is applied. b) All the products are known compounds[14,17,18,21,28] and are identified by their physical or spectral data. c) Isolated yield. d) Method B is used. Reaction time for all epoxides is 0.5 h except *trans*-stilbene and cyclopentene oxides which require 3 h. e) Yield is based on GC and NMR analysis.

ether (a) with a mixture of PPh_3/DDQ/*n*-Bu_4NBr at room temperature afforded 1-bromo-3-phenoxy-2-propanol (b) in only 20% after 0.5 h (Table 1, entry 1). However, in refluxing acetonitrile, the rate of the reaction was increased, and the desired product was obtained in 55% yield after 0.5 h, together with 1,2-dibromo-3-phenoxypropane (c) in 25% yield (Table 1, entry 2). A quantitative yield of the desired halo alcohol was obtained when the halide ion (1.2 mol. amt.) was gradually added into the reaction mixture of epoxide and PPh_3/DDQ (1.2:1.2) in refluxing acetonitrile over a period of about 3.5 h, and then refluxed for an additional 0.5 h. Under these conditions, 1-bromo-3-phenoxy-2-propanol (b) was obtained in 95% yield (Table 1, entry 4). Also, our studies showed that the addition of a 0.5 molar equivalent of water to a mixture of epoxide and PPh_3/DDQ/*n*-Bu_4NBr (1.2:1.2:1.2) in refluxing acetonitrile caused the reaction rate to increase, and the desired halo alcohol (Scheme 1, b) was obtained in 97% yield after 0.5 h (Table 1, entry 5). However, in the absence of PPh_3 and DDQ, the epoxide did not react with *n*-Bu_4NBr, even after 12 h of refluxing (Table 1, entry 3). By increasing the amount of *n*-Bu_4NBr from 1.2 molar amounts to 2.2, the corresponding *vic*-dibromide was produced in 90% yield (Scheme 1, c, Table 1, entry 6).

We then applied the optimized reaction conditions of Table 1 (entries 4 or 5, methods A or B respectively, see experimental section), for the conversion of structurally different epoxides to their corresponding *vic*-halo alcohols. The results are given in Table 2.

Under these reaction conditions, the ethereal bonds, ester groups, and carbon–carbon double bonds as functional groups that are present in the epoxide molecules remained intact. Except for the case of styrene oxide, which produced two regioisomers (Table 2, entries 4–6), the reaction of other unsymmetrical epoxides occurred with high regioselectivity, and the halide anion attacked at the less-hindered side of the epoxide ring due to the combination of steric and electronic factors. The reaction of *trans*-stilbene oxide (Table 2, entry 18) as an example of a hindered disubstituted epoxide completed after 3 h and *erythro*-2-bromo-1,2-diphenylethanol[28] was obtained in 90% yield. The reaction of cyclopentene oxide was also found to be slower than the reaction of cyclohexene oxide (Table 2, entry 15).



Scheme 2.

In order to obtain *vic*-dihalides, epoxides were reacted with a mixture of PPh_3/DDQ/*n*-R_4NX (R = Bu, X = Br, I; R = Hex, X = Cl) using the optimized molar ratio of 1.2/1.2/2.2 in refluxing acetonitrile. The use of bromide and chloride anions in this method offers the possibility of having *vic*-dichlorides and dibromides under mild and neutral reaction conditions. In contrast with reagents such as PPh_3/Br_2 or PPh_3/CCl_4, our reagent system does not produce any electrophilic halogen in the reaction mixture. This gives the advantage that activated aromatic rings and double bonds remain intact during the reaction, and only the epoxide ring reacts. For preparing *vic*-dichlorides from epoxides, in addition to *n*-Hex_4NCl, hydrated *n*-Bu_4NCl can also be used as the source of halide anion, but due to the presence of water in the reaction mixture, which can destroy the adduct (**I**, Scheme 2), the required amounts of PPh_3 and DDQ are increased (see experimental section, method B). The results of this investigation are given in Table 3.

However, the preparation of *vic*-diiodide was not successful. This observation is in accordance with the literature data,[29] which show that alkene formation is favored due to the easy elimination of molecular iodine from their corresponding diiodides. In all of the reactions with I^-, the alkene formation was the major pathway and the corresponding alkenes were obtained in high yields. For example, the addition of oxiranylmethyl phenyl ether to the mixture of PPh_3/DDQ/*n*-Bu_4NI (1.2:1.2:2.2) in refluxing acetonitrile produced allyl phenyl ether as the major product (90%) after 0.5 h. Therefore, the use of a PPh_3/DDQ mixture in the presence of *n*-Bu_4NI offers a new mixed-reagent system for the deoxygenation of epoxides into their corresponding alkenes.

In order to overcome the problems of using the highly acidic conditions reported for the conversion of epoxides to *vic*-dihalides,[27] and to introduce a mild and novel method for this transformation, we decided to apply our procedure for this preparation by a successive use of two different halide ions. For this purpose, first, oxiranylmethyl phenyl ether was added to a mixture of PPh_3/DDQ/*n*-$Bu_4NCl \cdot H_2O$ with a stoichiometry ratio of (1.2:1.2:1.2). Then, the reaction mixture was refluxed to produce 1-chloro-3-phenoxy-2-propanol (2). When all of the epoxide was consumed, the mixture was poured to another mixture containing (PPh_3/DDQ/*n*-Bu_4NBr (2.3:2.3:1.2) in acetonitrile and refluxed for another 0.5 h. After completion of the reaction, 2-bromo-1-chloro-3-phenoxypropane (13) was obtained in 81% yield (Table 4, entry 1) and its structure was confirmed by its ^1H, ^{13}C NMR and mass spectral data. Since this attempt was successful, we applied it to the preparation of unsymmetrical *vic*-dihalides from other epoxides. By using proper halide anions in each step, we cauld easily control the formation of *vic*-dihalides with high regioselectivity. The results obtained for this study are given in Table 4.

In these reactions, as we expected, in the first step, the primarily used halide ion attacks the epoxide ring from its less-hindered side, similar to the formation of *vic*-halo alcohols. In the second step, the resulting halo alcohol reacts with the mixture of PPh_3/DDQ in the presence of the second halide anion to displace the hydroxy group to produce the desired unsymmetrical dihalide. It was observed that, when one of the nucleophiles was iodide, due to the possibility of the elimination of IX; (X = Cl, Br), alkene formation was a competing pathway, which lowered the yield of *vic*-dihalides considerably (Table 4, entries 3 and 6).

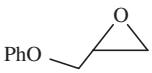
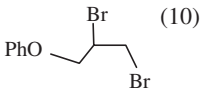
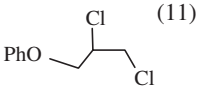
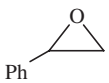
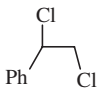
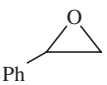
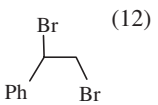
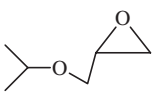
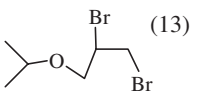
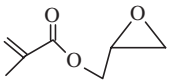
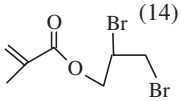
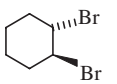
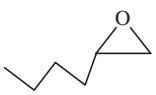
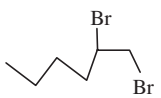
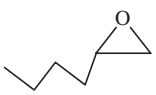
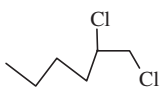
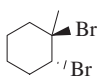
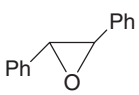
Although, the exact mechanism of these reactions is not clear, we may suggest that at first, a positively charged adduct **I** is formed from the reaction of PPh_3 with DDQ[27] (Scheme 2). This positively charged adduct can then activate the epoxide ring through an interaction with its oxygen atom so that halide ion can attack this activated ring and produce the intermediate **II**. The attack of another halide ion could convert the intermediate **II** into the desired symmetrical or unsymmetrical *vic*-dihalide (path a). The hydrolysis of **II** in the workup procedure produces triphenylphosphine oxide and the corresponding *vic*-halo alcohol (path b). Also, in the case of using hydrated quaternary ammonium halides (method B), the hydrated water hydrolyzes the intermediate (II) to halo alcohol (path b). In this case, for converting the produced halo alcohol to *vic*-dihalides, excess PPh_3 and DDQ are required, since the adduct (I) which is produced in this stage can be partly hydrolyzed with the hydrated water.

As shown in Table 4, entries 2, 4, when the first nucleophile used was bromide, a mixture of two regio-isomers were obtained. It is assumed that in these cases, the intermediate **I** can release $OPPh_3$ through the anchimeric assistance of bromide to form the bromonium ion **II** which can be equilibrated with **III** (Scheme 3). Attacking the second nucleophile to either side of **II** can produce a mixture of two regio-isomers.

This phenomenon can also be observed in the conversion of cyclohexene oxide to *trans*-1,2-dibromocyclohexane instead of its *cis*-isomer (Table 3, entry 7). Cyclohexene oxide in the first step can interact with the adduct complex of PPh_3/DDQ to form the intermediate **I**. The attack of Br^- to **I** produces the *trans*-intermediate **II**. The attack of the second Br^- converts the intermediate **II** to the corresponding *cis*-*vic*-dibromides (path a). However, our observation showed that the actual pathway of reaction is path (b). This is evidenced by the formation of *trans*-*vic*-dibromide, which can occur through the bromonium ion intermediate **III** (Scheme 4).

In summary, the present investigation has demonstrated that the use of the PPh_3/DDQ/R_4NX system offers a simple, novel, and convenient method for the selective conversion of epoxides to either their corresponding *vic*-halo alcohols or symmetrical *vic*-dihalides. Also, *vic*-dihalides containing two different types of halides with the desired regiochemistry can be produced easily by the use of this mixed-reagent system.

Table 3. Conversion of Epoxides to *vic*-Dihalides by PPh_3/DDQ in the Presence of R_4NX (R = *n*-Bu or *n*-Hex, X = Cl, Br)[a)]

Entry	Substrate	Product[b)]	Isolated and (conversion)[c)] Yield/%
1		 (10)	80 (90)
2		 (11)	78 (97)
3			70 (85)
4		 (12)	77 (92)
5		 (13)	85 (90)
6		 (14)	74 (85)
7			70 (83)
8			67 (93)[d)]
9			72 (88)
10			(80)
11			84 (93)
12		*erythro*-PhCHBrCHBrPh	86 (94)[d)]

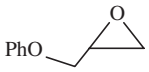
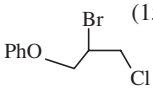
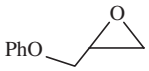
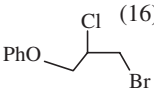
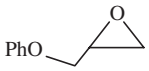
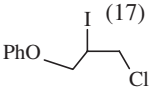
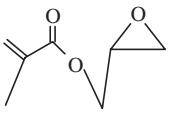
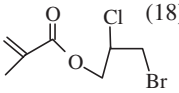
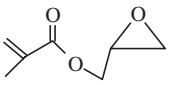
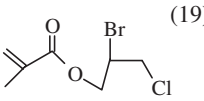
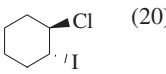
a) Methods A and B are used for the preparation of dibromides and dichlorides respectively. b) The products of entries 7–12 are known compounds.[28] c) Conversion yield is based on GC and NMR analysis using internal standard. (d) Reaction times for *trans*-stilbene and cyclopentene oxides are more than other epoxides (see experimental section).

Experimental

Solvents, reagents, and chemicals were obtained from Merck (Germany) Fluka (Switzerland) Chemical Companies. Infrared spectra were recorded on a Perkin Elmer 781 spectrophotometer. Nuclear magnetic resonance spectra were recorded on Hitachi R-245 and Brucker Avance DPX-250 spectrometers. Mass spectra were determined on a Shimadzu GCMS-QP 1000 EX at 70 eV.

General Procedure for the Conversion of Epoxides to *vic*-Halo Alcohols. Method A: To a flask containing of PPh_3

Table 4. Conversion of Epoxides to Unsymmetrical *vic*-Dihalides by PPh_3/DDQ and Quaternary Ammonium Salts of Different Halides

Entry	Substrate	Product	Yield[a)]/%
1		 (15)	81
2		 (16)	65[b)]
3		 (17)	40
4		 (18)	63[b)]
5		 (19)	72
6		 (20)	55

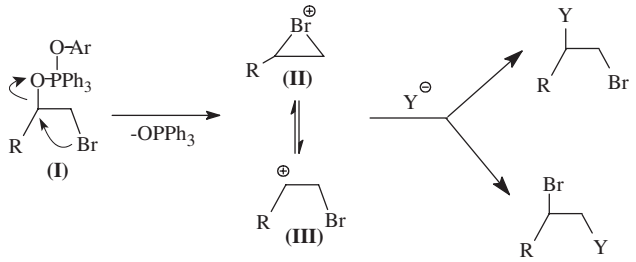
a) Isolated yield. b) The other isomeric product was formed about 20% yield in this case.

(1.2 mmol) and DDQ (1.2 mmol) in refluxing acetonitrile (7 mL) was added epoxide (1 mmol). Then, a solution of quaternary ammonium halide (1.2 mmol) in acetonitrile (5 mL) was gradually added to the reaction mixture over a period of 3.5 h. TLC or GC analysis showed completion of the reaction after 4 h. The solvent was evaporated. Pure *vic*-halo alcohol was obtained in 70–96% yields after column chromatography of the crude mixture on silica gel using petroleum ether/ethyl acetate as an eluent (Table 2).

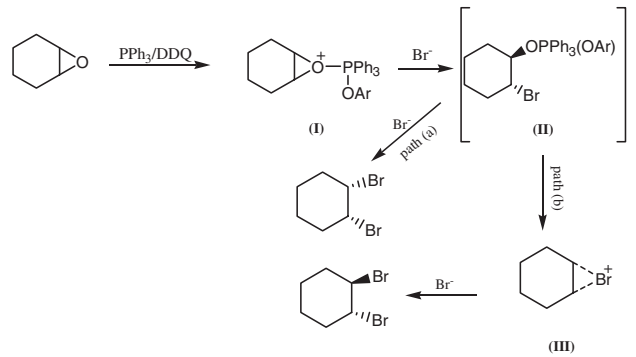
Method B: Quaternary ammonium halide (1.2 mmol) and H_2O (1 mmol) were added to a flask containing of PPh_3 (1.2 mmol) and DDQ (1.2 mmol) in refluxing acetonitrile (10 mL), respectively. Then, epoxide (1 mmol) was added to the reaction mixture. TLC monitoring showed completion of the reaction after 30 min. The solvent was evaporated. The corresponding *vic*-halo alcohol was obtained in good to excellent yields after column chromatography of the crude product on silica gel using petroleum ether/ethyl acetate as an eluent (Table 2).

General Procedure for the Conversion of Epoxides to Symmetrical *vic*-Dihalides. Method A: Anhydrous quaternary ammonium halide (2.2 mmol) was added to a flask containing of PPh_3 (1.2 mmol) and DDQ (1.2 mmol) in refluxing acetonitrile (15 mL). Then, epoxide (1 mmol) was added to the reaction mixture. TLC or GC analysis showed completion of the reaction after 2 h (in the case of *trans*-stilbene and cyclopentene oxides, the reaction mixtures were refluxed for 9 and 4 h, respectievly). After evaporation of the solvent, the crude mixture was purified by column chromatography using petroleum ether as an eluent to give *vic*-dihalide in 65–85% yield (Table 3).

Method B: PPh_3 (1.2 mmol) was added to a flask containing



Scheme 3.



Scheme 4.

of DDQ (1.2 mmol) in refluxing acetonitrile (15 mL). Quaternary ammonium halide monohydrate (2.2 mmol) and epoxide (1 mmol) were added to this reaction mixture. A TLC or GC analysis showed the completion of the conversion of epoxide to *vic*-halo alcohol after 30 min. Then, the reaction mixture was transferred to another mixture containing PPh_3 (2.3–2.8 mmol) and DDQ (2.3–2.8 mmol) in acetonitrile (10 mL) and refluxed for 0.5 h to produce *vic*-dihalide. The solvent was then evaporated. *vic*-Dihalide was obtained after column chromatography of the crude mixture using petroleum ether as an eluent in 65–85% yield (Table 3).

General Procedure for the Conversion of Epoxides to Unsymmetrical *vic*-Dihalides. A mixture of PPh_3 (1.2 mmol) and DDQ (1.2 mmol) was prepared in refluxing acetonitrile (10 mL). Then, quaternary ammonium halide monohydrate (1.2 mmol) and epoxide (1 mmol) were added to this mixture. TLC or GC analysis showed the conversion of the epoxide to the corresponding *vic*-halo alcohol after 0.5 h. The reaction mixture was then transferred to another flask containing PPh_3 (2.8 mmol), DDQ (2.8 mmol) and the tetraalkylammonium salt of the desired halide anion (1.2 mmol) in acetonitrle (15 mL) and refluxed for 0.5 h to produce *vic*-dihalide. After evaporation of the solvent, *vic*-dihalide was obtained in 40–81% yield by column chromatography of the crude mixture using petroleum ether as an eluent (Table 4).

All of the new products gave satisfactory elemental analysis. The spectral data of some of the products are shown below:

1-Bromo-3-phenoxy-2-propanol (1): ^{1}H NMR ($CDCl_3$, 250 MHz) δ 2.59–2.61 (d, 1H, $J = 5$ Hz), 3.58–3.69 (m, 2H), 4.07–4.10 (m, 2H), 4.14–4.23 (m, 1H), 6.90–7.10 (m, 3H), 7.26–7.54 (m, 1H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 35.04, 69.50, 70.27, 114.54, 121.45, 129.59, 158.13; Mass spectra *m/e*: 232 (M + 2, 33.1%), 230 (M, 35.6%), 151 (M − Br, 20.3%).

1-Chloro-3-phenoxy-2-propanol (2): ^{1}H NMR ($CDCl_3$, 250 MHz) δ 2.64–2.66 (d, 1H, $J = 5$ Hz), 3.68–3.81 (m, 2H), 3.98–4.08 (m, 2H), 4.12–4.22 (m, 1H), 6.89–7.01 (m, 3H), 7.24–7.32

(m, 2H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 46.37, 68.79, 70.29, 114.94, 121.86, 130.01, 158.08; Mass spectra *m/e*: 188 (M + 2, 34.9%), 186 (M, 100%), 169 (M − OH).

1-Iodo-3-phenoxy-2-propanol (3): ^{1}H NMR ($CDCl_3$, 250 MHz) δ 2.57 (s, 1H), 3.38–3.50 (m, 2H), 3.97–4.0 (m, 1H), 4.05–4.1 (m, 2H), 6.90–7.01 (m, 3H), 7.25–7.33 (m, 2H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 9.15, 69.55, 70.29, 114.58, 121.46, 129.60, 158.16; Mass spectra *m/e*: 278 (M, 25.7%), 151 (M − I, 6.7%), 133 (M − (I + H_2O), 27.1%).

2-Iodo-2-phenylethanol (4): ^{1}H NMR ($CDCl_3$, 250 MHz) δ 2.04 (s, 1H), 3.92 (s, 1H), 4.09 (s, 1H), 5.17–5.23 (t, 1H, J = 7.5 Hz), 7.25–7.44 (m, 5H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 35.78, 68.62, 127.91, 128.61, 129.0, 142.4; Mass spectra *m/e*: 248 (M, 0.1%), 231 (M − OH, 22.2%), 121 (M − I, 100%).

2-Iodo-1-phenylethanol (5): ^{1}H NMR ($CDCl_3$, 250 MHz) δ 2.50 (s, 1H), 3.36–3.52 (m, 2H), 4.82–4.85 (m, 1H), 7.36 (s, 5H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 15.78, 74.45, 126.14, 128.79, 129.11, 141.5; Mass spectra *m/e*: 248 (M, 0.5%), 231 (M − OH, 1.9%), 121 (M − I, 9.3%).

2-Bromo-2-phenylethanol (6): ^{1}H NMR ($CDCl_3$, 250 MHz) δ 2.08 (s, 1H), 3.93–4.10 (m, 2H), 5.02–5.08 (t, 1H, J = 7.5 Hz), 7.25–7.43 (m, 5H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 56.95, 67.53, 127.92, 128.90, 128.99, 138.21; Mass spectra *m/e*: 202 (M + 2, 5.2%), 200 (M, 0.9%), 183 (M − OH, 27.4%), 121 (M − Br, 100%).

2-Bromo-1-phenylethanol (7): ^{1}H NMR ($CDCl_3$, 250 MHz) δ 2.66 (s, 1H), 3.50–3.66 (m, 2H), 4.94 (s, 1H), 7.37–7.38 (s, 5H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 40.65, 74.22, 126.37, 128.89, 129.1; Mass spectra *m/e*: 202 (M + 2, 0.6%), 200 (M, 0.4%), 183 (M − OH, 2.8%), 121 (M − Br, 4.1%).

3-Chloro-2-hydroxypropyl Methacrylate (8): ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.96 (s, 3H), 2.94 (s, 1H), 3.57–3.71 (m, 2H), 4.09–4.17 (m, 1H), 4.28–4.31 (d, 2H, J = 7 Hz), 5.62 (s, 1H), 6.15 (s, 1H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 18.29, 46.02, 65.48, 69.65, 126.55, 135.72, 167.44; Mass spectra *m/e*: 178 (M, 0.9%), 143 (M − Cl, 1.2%).

2-Hydroxy-3-iodopropyl Methacrylate (9): ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.96 (s, 3H), 2.73 (s, 1H), 3.24–3.39 (m, 2H), 3.90–3.92 (m, 1H), 4.27–4.29 (m, 2H), 5.63 (s, 1H), 6.15 (s, 1H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 9.02, 18.35, 67.23, 69.35, 126.59, 135.72, 167.37.

1,2-Dibromo-3-phenoxypropane (10): ^{1}H NMR ($CDCl_3$, 250 MHz) δ 3.78–3.91 (m, 2H), 4.31–4.43 (m, 3H), 6.91–7.01 (m, 3H), 7.21–7.32 (m, 2H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 31.74, 46.71, 68.0, 113.81, 120.63, 128.57, 156.91; Mass spectra *m/e*: 296 (M + 4, 16.2%), 294 (M + 2, 41.7%), 292 (M, 14.1%), 203 (M + 4 − PhO, 3.2%), 201 (M + 2 − PhO, 8.7%), 199 (M − PhO, 5.3%).

1,2-Dichloro-3-phenoxypropane (11): ^{1}H NMR ($CDCl_3$, 250 MHz) δ 3.86–4.00 (m, 2H), 4.26–4.41 (m, 3H), 6.91–7.02 (m, 3H), 7.24–7.33 (m, 2H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 45.02, 57.30, 68.09, 114.72, 121.66, 129.62, 157.94.

1,2-Dibromo-1-phenylethane (12): ^{1}H NMR ($CDCl_3$, 250 MHz) δ 4.01–4.11 (m, 2H), 5.11–5.17 (dd, 1H, J = 10, 5 Hz), 7.35–7.39 (br, s, 5H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 35.00, 50.86, 127.64, 128.85, 129.17, 138.6; Mass spectra *m/e*: 266 (M + 4, 0.4%), 264 (M + 2, 0.5%), 262 (M, 0.4%), 185 (M + 4 − Br, 1.3%), 183 (M − Br, 1.2%).

1,2-Dibromo-3-isopropyloxypropane (13): ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.17–1.20 (m, 6H), 3.64–3.87 (m, 5H), 4.20–4.25 (m, 1H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 22.04, 33.48, 49.78, 68.63, 72.62.

2,3-Dibromopropyl 2-Methacrylate (14): ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.89 (s, 3H), 3.71–3.74 (d, 2H, J = 7.5 Hz), 4.17–4.26 (m, 1H), 4.33–4.46 (m, 2H), 5.56 (s, 1H), 6.09 (s, 1H); Mass spectra *m/e*: 288 (M + 4, 2.1%), 286 (M + 2, 2.5%), 284 (M, 1%), 207 (M + 4 − Br, 9%), 205 (M − Br, 10%).

2-Bromo-1-chloro-3-phenoxypropane (15): ^{1}H NMR ($CDCl_3$, 250 MHz) δ 3.92–4.02 (m, 2H), 4.25–4.39 (m, 3H), 6.83–7.07 (m, 3H), 7.23–7.33 (m, 2H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 45.01, 48.10, 68.26, 114.79, 121.66, 129.61, 157.92; Mass spectra *m/e*: 252 (M + 4, 8.7%), 250 (M + 2, 29.3%), 248 (M, 24%), 171 (M + 2 − Br and M + 4 − Br, 7.2%), 169 (M + 2 − Br and M − Br, 12.9%).

1-Bromo-2-chloro-3-phenoxypropane (16): ^{1}H NMR ($CDCl_3$, 250 MHz) δ 3.77–3.95 (m, 2H), 4.25–4.37 (m, 3H), 6.91–7.02 (m, 3H), 7.23–7.33 (m, 2H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 33.36, 57.40, 69.29, 115.18, 122.09, 130.04, 158.37; Mass spectra *m/e*: 250 (M + 2, 0.8%), 248 (M, 0.4%), 169 (M + 2 − Br and M − Br, 7%).

1-Chloro-2-iodo-3-phenoxypropane (17): ^{1}H NMR ($CDCl_3$, 250 MHz) δ 3.90–4.05 (m, 2H), 4.26–4.36 (m, 3H), 6.91–7.02 (m, 3H), 7.24–7.33 (m, 2H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 29.70, 45.02, 68.10, 114.71, 121.67, 129.62, 158.02; Mass spectra *m/e*: 298 (M + 2, 9.2%), 296 (M, 26.3%), 261 (M − Cl, 5.4%), 169 (M − I, 15.3%).

3-Bromo-2-chloropropyl Methacrylate (18): ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.97 (s, 3H), 3.66–3.91 (m, 2H), 4.32–4.58 (m, 3H), 5.64 (s, 1H), 6.18 (s, 1H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 18.61, 32.45, 56.85, 65.70, 126.95, 135.72, 167.40.

2-Bromo-3-chloropropyl Methacrylate (19): ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.97 (s, 3H), 3.79–3.91 (m, 2H), 4.30–4.36 (m, 1H), 4.47–4.56 (m, 2H), 5.64 (s, 1H), 6.17 (s, 1H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 18.25, 44.72, 47.34, 64.58, 126.60, 135.61, 167.43; Mass spectra *m/e*: 242 (M + 2, 0.4%), 205 (M − Cl, 0.9%), 161 (M − Br, 2.7%), 155 (M − CH_2=C(CH_3)CO_2, 5.5%), 85 (M − $CH_2CHBrCH_2Cl$, 16.6%).

1-Chloro-2-iodocyclohexane (20): ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.47–1.54 (m, 2H), 1.70–1.96 (m, 4H), 2.17–2.30 (m, 2H), 3.82 (s, 1H), 4.66 (s, 1H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 22.59, 23.09, 25.20, 34.45, 35.33, 64.25; Mass spectra *m/e*: 246 (M + 2, 3.7%), 244 (M, 10.3%), 117 (M − I, 13.4%).

We acknowledge the support of this work by Shiraz University Research Council and Iran TWAS Chapter Based at ISMO.

References

1 C. H. Behrens, S. Y. Ko, K. B. Sharpless, and F. J. Walker, *J. Org. Chem.*, **50**, 5687 (1985).

2 W. A. Nugent, *J. Am. Chem. Soc.*, **114**, 2768 (1992).

3 M. Tokunaga, J. F. Larrow, F. Kakiuchi, and E. N. Jacobsen, *Science*, **227**, 936 (1997).

4 C. R. Bonini and G. Righi, *Synthesis*, **1994**, 225.

5 J. G. Smith, *Synthesis*, **1984**, 629.

6 J. Yamada, M. Yumoto, and Y. Yamamoto, *Tetrahedron Lett.*, **30**, 4255 (1989).

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

8 E. J. Corey and J. Das, *Tetrahedron Lett.*, **23**, 4217 (1982).

9 Y. Ueda and S. C. Maynard, *Tetrahedron Lett.*, **29**, 5197 (1988).

10 H. R. Nace and G. A. Crosby, *J. Org. Chem.*, **44**, 3105

(1979).
11 A. J. Sisti and A. C. Vitale, *J. Org. Chem.*, **37**, 4090 (1972).
12 C. A. Stewart and C. A. Vanderwerf, *J. Am. Chem. Soc.*, **76**, 1259 (1954).
13 Y.-G. Suh, B. A. Koo, J.-A. Ko, and Y.-S. Cho, *Chem. Lett.*, **1993**, 1907.
14 N. Iranpoor, F. Kazemi, and P. Salehi, *Synth. Commun.*, **27**, 1247 (1997).
15 C. E. Garrett and G. C. Fu, *J. Org. Chem.*, **62**, 4534 (1997).
16 H. Kotsuki, T. Shimanouchi, R. Ohshima, and S. Fujiwara, *Tetrahedron*, **54**, 2709 (1998).
17 H. Sharghi and H. Naeimi, *Synlett*, **1998**, 1343.
18 N. Iranpoor and H. Adibi, *Bull. Chem. Soc. Jpn.*, **73**, 675 (2000).
19 D. Diaz, T. Martin, and V. S. Martin, *J. Org. Chem.*, **66**, 7231 (2001).
20 H. Sharghi and M. M. Eskandari, *Synthesis*, **2002**, 1519.
21 H. Sharghi, A. R. Massah, H. Eshghi, and K. Niknam, *J. Org. Chem.*, **63**, 1455 (1998).
22 N. S. Isaacs and D. Kirkpatrick, *Tetrahedron Lett.*, **13**, 3869 (1972).
23 P. E. Sonnet and J. E. Oliver, *J. Org. Chem.*, **41**, 3279 (1976).
24 R. C. Cambie, W. I. Noall, G. J. Potter, P. S. Rutledge, and P. D. Woodgate, *J. Chem. Soc., Perkin Trans. 1*, **1977**, 226.
25 J. Barluenga, J. M. Gonzalez, P. J. Campos, and G. Asensio, *Angew. Chem., Int. Ed. Engl.*, **24**, 319 (1985).
26 C. H. Robinson, L. Finckenor, E. P. Oliveto, and D. Gould, *J. Am. Chem. Soc.*, **81**, 2191 (1959).
27 N. Iranpoor, H. Firouzabadi, G. Aghapour and A. R. Vaezzadeh, *Tetrahedron*, **58**, 8689 (2002).
28 a) D. R. Dalton, J. B. Henderickson, and D. Jones, *Chem. Commun.*, **1966**, 591. b) R. E. Buckles and J. W. Long, *J. Am. Chem. Soc.*, **73**, 998 (1951). c) E. Baciocchi and R. Ruzziconi, *J. Org. Chem.*, **49**, 3395 (1984). d) M. Mousseron and F. Winternitz, *Compt. Rend.*, **219**, 132 (1944). e) M. Mousseron, R. Jacquier, R. Henry, and M. Mousseron-Canet, *Bull. Soc. Chim. Fr.*, **1953**, 628.
29 Z. Paryzek and R. Wydra, *Tetrahedron Lett.*, **25**, 2601 (1984).