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Reactions of epoxides and episulfides with electrophilic halogens

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Abstract—A novel method is described for the conversion of epoxides into β-bromoformates using Ph_3PBr_2, Ph_3P/*N*-bromosuccinimdes (NBS) and or Ph_3P/2,4,4,6-tetrabromo-2,5-cyclohexadiene-1-one (TABCO) in DMF. Epoxides in the presence of Ph_3P/I_2 were converted into olefins immediately in excellent yields. The application of NBS, NCS, and TABCO as compounds carrying electrophilic halogens for the highly selective alcoholysis of epoxides and dimerization or alcoholysis dimerization of episulfides are also described.

Epoxides and episulfides as special types of strained heterocycles play an increasingly pivotal role in organic synthesis as versatile synthetic intermediates. The inherent polarity and strain of their three-membered rings make them susceptible to reaction with a vast number of reagents, including nucleophiles, acids, bases, reducing and oxidizing agents, leading to a wide range of important and useful oxygenated and sulfurated synthons.[1–14] Episulfides are probably the most interesting class of cyclic sulfides both from theoretical and synthetic point of views. However, due to ready polymerization, their reactions are less studied compared to the epoxides. Although there are many catalysts or reagents reported in the literature for the nucleophilic ring opening of epoxides and episulfides, but reports on the selective ring opening of epoxides are rare[14e] and as far as we know, the selective ring opening reaction of episulfides has not been reported yet.

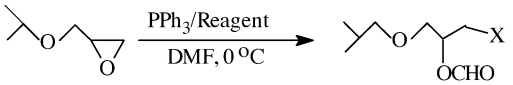
Recently, we have reported on some applications of molecular halogens and compounds carrying electrophilic halogens in organic synthesis.[15] Now, we report on the use of NBS, TABCO, Br_2 and I_2 in combination with Ph_3P as efficient systems for the conversion of epoxides into β-bromoformates or alkenes in DMF. Due to the importance of selectivity in organic synthesis, we introduced NBS, NCS, and TABCO for the selective alcoholysis of epoxides and dimerization or alcoholysis dimerization of episulfides.

1. Results and discussion

The combination of Ph_3P and halogens or *N*-halosuccinimides has found wide applications in the synthesis of different halogenated compounds.[16,17] The very different behavior of these mixed reagents in dry DMF, provided a useful method for the formylation of hydroxyl groups.[18,19] Wide applications of $POCl_3$[20] and $SOCl_2$[21] in dry DMF have also been reported for the formylation of hydroxyl groups as well as some activated aromatic rings. The reaction of ethylene oxide and some symmetrical cyclic epoxides with $[HC(NMe)_2POCl_2]Cl$ at 55–65°C with subsequent hydrolysis was also reported for the preparation of β-chloroformates.[22]

The use of Ph_3PBr_2 for the conversion of epoxides into bromohydrins and dibromides are reported.[23,24] However, as far as we know, the reaction of epoxides with the combination of Ph_3P and NBS, TABCO, NCS, trichloroisocyanuric acid (TCCA), Br_2 and I_2 in DMF has not been investigated. This is the focus of part of this study.

As a model compound, we first chose glycidyl-isopropylether and studied its reactions with NBS, NCS, TABCO, Br_2 and I_2 in the presence of Ph_3P. The results of this study are shown in Table 1 and Scheme 1. As it is demonstrated, the reaction of glycidyl-isopropylether with Ph_3P/Br_2 after 15 min produces the corresponding β-bromoformate in an excellent yield. When we replaced molecular bromine with NBS or TABCO as solid sources of electrophilic bromine, the same reaction occurred but considerably slower. The reaction of glycidyl-isopropylether with the combination of Ph_3P/NCS or Ph_3P/TCCA was not very successful and the corresponding β-chloroformate was obtained in only 30 and 3% yields, respectively, with some chlorohydrin as side products (Table 1).



Scheme 1. *Reagent*: Br_2, NBS, TABCO, NCS, TCCA. X=Br, Cl.

Keywords: alcoholysis dimerization; episulfides; electrophilic halogens; epoxide.

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Table 1. Reaction of glycidyl-isopropylether with Br_2, NBS, TABCO, NCS, TCCA, and I_2 in the presence of Ph_3P in DMF

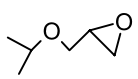
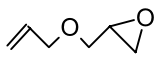
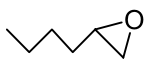
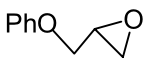
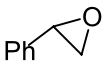
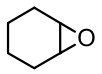
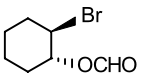
Reagent	Sub./Ph_3P/ Reagents	Product	Time (h)[a]	Yield (%)[b]
Br_2	1:1.5:1.4	$^{i}PrOCH_2CH(OCHO)CH_2Br$	0.25	81
NBS	1:3.2:3	$^{i}PrOCH_2CH(OCHO)CH_2Br$	3	80
TABCO	1:3.2:3	$^{i}PrOCH_2CH(OCHO)CH_2Br$	24	78
NCS	1:3.2:3	$^{i}PrOCH_2CH(OCHO)CH_2Cl$	24	30[c]
TCCA	1:3.2:3	$^{i}PrOCH_2CH(OCHO)CH_2Cl$	24	3[d,e]
I_2	1:2:2	$^{i}PrOCH_2CH{=}CH_2$	–[f]	100[e]

[a] The epoxide disappeared immediately at 0°C, with the formation of β-bromoformate as the major product together with some halohydrin. The reaction mixture was then stirred at room temperature until all the produced halohydrin was also converted into its β-bromoformate.
[b] Yield refers to the isolated product.
[c] The corresponding β-chlorohydrin (70%, GC yield) was also produced.
[d] The corresponding β-chlorohydrin (7%, GC yield) was also obtained.
[e] Yields are based on GC analysis.
[f] The reaction completed immediately.

We have proposed a general mechanism (Scheme 2) for this formylation reaction which is similar to the mechanism formerly proposed for the formylation of alcohols.[18b,c]

As it was shown in Table 1, the use of Ph_3P/I_2 in DMF resulted the conversion of glycidyl-isopropylether to its corresponding alkene in an excellent yield. However, the reported reaction of epoxides with Ph_3PCl_2 and Ph_3PBr_2 afforded the corresponding dihalides, which were dehalogenated by zinc powder to give the corresponding alkenes.[16h] Since the reaction of Ph_3PI_2 with glycidyl-isopropylether (Table 1) showed to be very suitable for deoxygenation of epoxides to alkenes, we used this reagent system for the direct and quantitative deoxygenation of different classes of epoxides. The results for the conversion of structurally different epoxides into their corresponding alkenes are shown in Table 3. We believe that this reaction

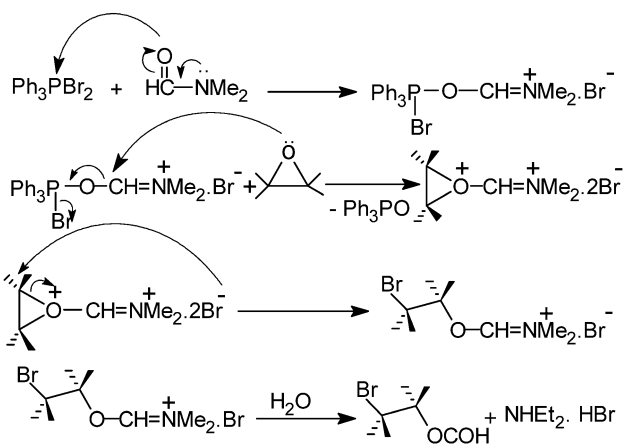
Table 2. Conversion of epoxides into β-bromoformates using the combination of Ph_3P with NBS or Br_2 in DMF

Entry	Epoxide	Ph_3P/Br_2		Ph_3P/NBS		Product[a]
		Time (min)	Yield (%)[a]	Time (h)	Yield (%)[b]	
1		15	85	3	84	$Me_2CHOCH_2CH(OCHO)CH_2Br$ (I)
2		30	82	2	83	$CH_2{=}CHCH_2OCH_2CH(OCHO)CH_2Br$ (II)
3		35	78	2	75	$Me(CH_2)_3CH(OCHO)CH_2Br$ (III)
4		120	80	5	82	$PhOCH_2CH(OCHO)CH_2Br$ (IV)
5		60	75	7	73	$ClCH_2CH(OCHO)CH_2Br$ (V)
6		30	57	0.5	54	$PhCH(Br)CH_2OCHO$ (VI)
7		30	50	1	51	

[a] For entries 1–5, the corresponding alkene was obtained in 8–10% yield. For entry 6, styrene (20%) and 2-bromo-2-phenyl ethanol (15%) were also obtained. 2-Bromo-2-phenyl ethanol contains a primary hydroxyl group, which cannot be formylated in the reaction mixture.[18b] For entry 7, cyclohexene (20%) and two other unknown products (20%) were also obtained.
[b] Yield refers to the isolated product.

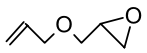
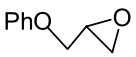
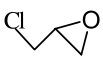
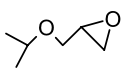
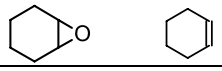
The reaction of Ph_3P/I_2 with glycidyl-isopropylether was very different from other reagents and gave exclusively the corresponding alkene in a quantitative yield (Table 1). On the basis of these findings, we studied the reaction of different epoxides with Ph_3P/Br_2 and Ph_3P/NBS for the preparation of β-bromoformates and the reaction of epoxides with Ph_3PI_2 for the preparation of alkenes.

The conversion of epoxides carrying electron-donating or electron-withdrawing groups to their corresponding β-bromoformates was achieved by the use of Ph_3P/Br_2 or Ph_3P/NBS in DMF at room temperature. However, the yields of bromoformates obtained from the reaction of the epoxides carrying electron-withdrawing groups were found to be higher than styrene and cyclohexene oxides (Table 2).



Scheme 2. Proposed mechanism for the conversion of epoxides into β-bromoformates.

Table 3. Immediate conversion of epoxides to alkenes by Ph_3P/I_2 in DMF at room temperature

Entry	Epoxide	Product	% Conversion[a]
1		$CH_2{=}CHCH_2OCH_2CH{=}CH_2$	100
2		$PhOCH_2CH{=}CH_2$	100
3		$ClCH_2CH{=}CH_2$	100
4		$(CH_3)_2CHOCH_2CH{=}CH_2$	100
5		$C_4H_9CH{=}CH_2$	100
6		$PhCH{=}CH_2$	91
7			85

The molar ratio of epoxide to Ph_3P to I_2 was 1:2:2.
[a] Conversion was based on GC analysis using internal standard.

occurs through the formation of the corresponding unstable di-iodides followed by the rapid dehalogenation to their alkenes.

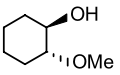
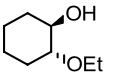
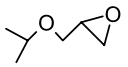
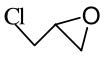
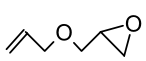
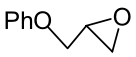
In the other part of this work, we employed TABCO, NBS and NCS as mild and highly selective catalysts for the alcoholysis of epoxides having alkyl or aryl substituents in the presence of those carrying electron-withdrawing groups (Table 4). We also used successfully these compounds as efficient catalysts for the selective ring opening of styrene and cyclohexene oxides in presence of epoxides such as epichlorohydrin, glycidyl-isopropylether and also 1,2-hexene oxide.

We also used NBS, NCS and TABCO in alcohols and aqueous acetonitrile for the efficient conversion of episulfides into their corresponding β,β′-dialkoxy- or dihydroxydisulfides, respectively. Excellent selectivity was again observed between episulfides substituted with alkyl or phenyl groups and those carrying electron-withdrawing substituents (Table 5).

In comparison with the reaction of epoxides, the reaction of episulfides with NBS, NCS, or TABCO in protic solvents occurs immediately. The faster reaction of episulfides could be due to the better interaction of electrophilic halogens with sulfur atom of the episulfide ring rather than oxygen of the epoxide.

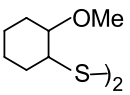
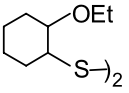
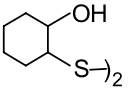
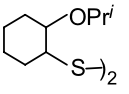
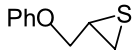
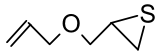
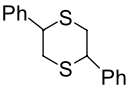
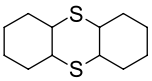
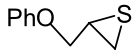
The reaction of episulfides in non-nucleophilic solvents such as dichloromethane furnished the corresponding substituted 1,4-dithianes in good yields. Here again, high selectivity was observed and episulfides carrying electron-withdrawing substituents were remained unreacted (Table 5).

Table 4. Alcoholysis of epoxides using NBS, NCS, and TABCO as catalyst at room temperature

Entry	Epoxide	Solvent	NBS		NCS		TABCO		Product[a]
			Time (h)	Yield (%)	Time (h)	Yield (%)	Time (h)	Yield (%)	
1		MeOH	0.7	90	5.4	95	2	95	$PhCH(OMe)CH_2OH$
2		EtOH	2.8	90	–	–	8	93	$PhCH(OEt)CH_2OH$
3		^{i}PrOH	24	91	–	–	20[b]	97	$PhCH(OPr^{i})CH_2OH$
4		MeOH	1.4	95	24	5	4.5	93	
5		EtOH	30	93[b]	–	–	28	90	
6		MeOH	3	94	–	–	20	93	Mixture of isomers[c]
7		MeOH	24	0			24	0	No reaction
8		MeOH	24	30			24	28	$ClCH_2CH(OH)CH_2OMe$
9		MeOH	24	0			24	0	No reaction
10		MeOH	24	0			24	0	No reaction

The molar ratio of epoxide to NBS, NCS or TABCO was 1:0.2.
[a] Isolated yield.
[b] The reaction was performed under reflux.
[c] Mixture of 2-methoxy-1-hexanol and 1-methoxy-2-hexanol was obtained in the ratio of 70:30.

Table 5. Reaction of episulfides with NBS, NCS or TABCO in alcohols, aqueous acetonitrile and dichloromethane at room temperature

Entry	Episulfide	Solvent	NBS		NCS		TABCO		Product
			Time (min)	Yield (%)	Time (min)	Yield (%)	Time (min)	Yield (%)	
1		MeOH	3	85	3	85	4	85	$PhCH(OMe)CH_2S-)_2$
2		EtOH	3	70	3	75	4	78	$PhCH(OEt)CH_2S-)_2$
3		CH_3CN/H_2O	3	75	3	75	4	85	$PhCH(OH)CH_2S-)_2$
4		^{i}PrOH	5	53	4	50	6	60	$PhCH(OPr^i)CH_2S-)_2$
5		MeOH	3	92	3	80	4	92	
6		EtOH	3	85	3	79	4	86	
7		CH_3CN/H_2O	3	90	3	85	4	92	
8		^{i}PrOH	5	64	5	60	5	72	
9		MeOH	60	0	60	0	60	0	No reaction
10		MeOH	60	0	60	0	60	0	No reaction
11		CH_2Cl_2	20	77	15	70	20	75	
12		CH_2Cl_2	5	80	5	80	5	82	
13		CH_2Cl_2	60	0	60	0	60	0	No reaction

The molar ratio of episulfide to NBS, NCS or TABCO in protic solvents was 1:0.55. For the reactions of entries 11 and 12, the ratio of episulfide to the reagents were 1:0.2 and 1:0.5, respectively.

2. Conclusion

In this study, we have introduced the uses of Ph_3P in the presence of Br_2, NBS and TABCO in DMF for the conversion of epoxides into their β-bromoformates in good to high yields. We have also presented the application of Ph_3P/I_2 system for the direct conversion of epoxides into their corresponding alkenes with excellent yields. The use of NBS, NCS, and TABCO as efficient catalysts provides highly selective methods for alcoholysis of epoxides carrying alkyl or phenyl substituents. Immediate dimerization or alcoholysis dimerization of episulfides were also observed using NBS, NCS, and TABCO.

3. Experimental

Chemicals were either prepared in our laboratories or were purchased from Fluka and Merck chemical companies. The purity determination of the products was accomplished by GC on a Shimadzu model GC-14A instrument or by TLC on silica gel polygram SIL G/UV 254 plates. Mass spectra were run on a Shimadzu GC-Mass-QP 1000 EX at 20 eV. The IR spectra were recorded on a Perkin–Elmer 781 spectrophotometer. The NMR spectra were recorded on a Bruker advance DPX 250 MHz spectrometer.

3.1. General procedure for the conversion of epoxides to β-bromoformates by Ph_3PBr_2 in DMF

To a solution of Ph_3P (1.5 mmol, 393 mg) in dry DMF (2 ml) at 0°C under nitrogen was added bromine (1.4 mmol, 0.07 ml) in DMF (2 ml) dropwise. After 10 min, the epoxide (1 mmol) was added. GC and TLC analysis using *n*-hexane/EtOAc (3:1) as eluent monitored the progress of the reaction. Epoxide was disappeared immediately with

formation of the corresponding β-bromoformate as the major product together with some halohydrin. The reaction mixture was then stirred at room temperature for 15–180 min (Table 2), until the complete conversion of halohydrin into its β-bromoformate was observed (except styrene oxide, which its halohydrin has a primary hydroxyl group and cannot be formylated[18b]). The reaction mixture was then poured into saturated brine and the product was extracted by ether (2×30 ml) and washed by water (2×15 ml). The combined organic layers were dried over anhydrous Na_2SO_4. Filtration and evaporation of the solvent followed by column chromatography on silica gel using *n*-hexane/EtOAc (20:1) gave the corresponding β-bromoformate (Table 2). All the obtained β-bromoformates gave satisfactory elemental analysis. Their spectral data are shown below.

3.1.1. Formic acid 1-bromomethyl-2-isopropyl-ethyl ester (I). IR (neat): 4433, 2933, 2892, 2808, 1668, 1350, 1266, 1250, 1000, 800 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ (ppm)=8.04 (s, 1H), 5.09–5.17 (m, 1H), 3.44–3.57 (m, 5H), 1.08–1.12 (d, 6H, J=9 Hz); ^{13}C NMR (63 MHz, $CDCl_3$): δ (ppm)=160.4, 72.9, 71.8, 67.1, 30.8, 22.3. Anal. Calcd for $C_7H_{13}BrO_3$: C, 37.35; H, 5.82. Found: C, 37.24; H, 5.90.

3.1.2. Formic acid 1-bromomethyl-2-vinyloxy-ethyl ester (II). IR (neat): 3421, 3072, 2994, 2904, 2857, 1714, 1642, 1421, 1345, 1149, 927 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ (ppm)=8.03 (s, 1H), 5.76–5.87 (m, 1H), 5.12–5.25 (m, 3H), 3.95 (d, 2H, J=1.2 Hz), 3.48–3.62 (m, 4H); ^{13}C NMR (63 MHz, $CDCl_3$): δ (ppm)=160.3, 134.3, 118.1, 72.8, 71.0, 69.0, 30.5; MS (20 eV), *m/e* (%): 167 (23.6), 165 (23), 123 (3.0), 121 (3.0), 97 (26.5), 71 (42.9), 57 (28.3), 41 (100). Anal. Calcd for $C_7H_{11}BrO_3$: C, 37.69; H, 4.97. Found: C, 37.80; H, 4.72.

3.1.3. Formic acid 1-bromomethyl-penthyl ester (III). IR (neat): 3442, 2958, 2917, 2875, 1733, 1183 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ (ppm)=8.13 (s, 1H), 5.11–5.2 (m, 1H), 3.44–3.58 (m, 2H), 1.64–1.78 (m, 2H), 1.34 (m, 4H), 0.92 (t, 3H); ^{13}C NMR (63 MHz, $CDCl_3$): δ (ppm)=160.6, 72.7, 34.0, 32.5, 27.4, 22.7, 14.2; MS (20 eV), *m/e* (%): 163 (1.5), 165 (1.5), 129 (14.1), 83 (21.2), 55 (42.3), 57 (33.9), 43 (100), 41 (92.1). Anal. Calcd for $C_7H_{13}BrO_2$: C, 40.21; H, 6.27. Found: C, 40.34; H, 6.20.

3.1.4. Formic acid 1-bromomethyl -2-phenoxy-ethyl ester (IV). IR (neat): 3431, 3078, 3065, 3036, 2931, 2869, 1714, 1598, 1490, 1239, 1145, 753 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ (ppm)=8.05 (s, 1H), 7.17–7.25 (m, 2H), 6.82–6.94 (m, 3H), 5.37 (m, 1H), 4.09–4.15 (m, 2H), 3.54–3.64 (m, 2H); ^{13}C NMR (63 MHz, $CDCl_3$): δ (ppm)=160.2, 158.4, 130.0, 122.0, 115.0, 70.9, 66.9, 30.2; MS (20 eV), *m/e* (%): 260 (4), 258 (4), 167 (96.2), 165 (100), 133 (23.5), 94 (32.3), 57 (31.4). Anal. Calcd for $C_{10}H_{11}BrO_3$: C, 46.36; H, 4.28. Found: C, 46.50; H, 4.14.

3.1.5. Formic acid 1-bromomethyl-2-chloro-ethyl ester (V). IR (neat): 3446, 2975, 2909, 2888, 1645, 1300, 1194, 978, 807 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ (ppm)=8.08 (m, 1H), 3.72 (dd, 2H, J=5.17 Hz), 3.56 (dd, 2H, J=5.31 Hz); ^{13}C NMR (63 MHz, $CDCl_3$): δ (ppm)=159.8, 71.4, 43.4, 30.2; MS (20 eV), *m/e* (%): 158 (10.8), 154 (35.7), 156 (46.3), 123 (57.8), 121 (25.6), 77 (24), 75 (70.8), 43 (100), 41 (20.8). Anal. Calcd for $C_4H_6BrClO_2$: C, 23.85; H, 3.00. Found: C, 23.92; H, 2.90.

3.1.6. Formic acid 2-bromo-2-phenyl-ethyl ester (VI). IR (neat): 3421, 3059, 3027, 2927, 2873, 1714, 1452, 1138, 756, 703 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ (ppm)=8.06 (s, 1H), 7.17–7.35 (m, 5H), 5.05 (t, 1H, J=7.3 Hz), 4.49–4.66 (m, 2H); ^{13}C NMR (63 MHz, $CDCl_3$): δ (ppm)=160.4, 138.1, 129.4, 129.2, 127.0, 67.1, 49.6; MS (20 eV), *m/e* (%): 184 (9.0), 182 (9.6), 171 (9.2), 169 (9.2), 149 (49.2), 121 (100), 103 (81.7), 91 (17), 77 (14.2). Anal. Calcd for $C_9H_9BrO_2$: C, 47.19; H, 3.96. Found: C, 47.24; H, 3.90.

3.1.7. *trans*-Formic acid 2-bromo-cyclohexyl ester (VII). IR (neat): 3419, 2928, 2857, 1711, 1447, 1369, 1245, 1154, 1109, 1002, 860, 762 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ (ppm)=8.03 (s, 1H), 4.89–4.98 (m, 1H), 3.87–3.97 (m, 1H), 2.28 (m, 1H), 2.1 (m, 1H), 1.63–1.84 (m, 3H), 1.29–1.41 (m, 3H); ^{13}C NMR (63 MHz, $CDCl_3$): δ (ppm)=160.3, 76.1, 52.5, 35.9, 31.4, 25.8, 23.6; MS (20 eV), *m/e* (%): 193 (10.1), 191 (10.4), 127 (13.4), 99 (20.4), 97 (20.9), 81 (100), 57 (66.7). Anal. Calcd for $C_7H_{11}BrO_2$: C, 40.60; H, 5.35. Found: C, 40.72; H, 5.40.

3.2. General procedure for the alcoholysis of epoxides

Either of the catalysts, TABCO, NBS or NCS (0.2 mmol,) was added to a solution of epoxide (1 mmol) in alcohol (2 ml). The mixture was stirred for 15 min–48 h at room temperature or under reflux condition (Table 4). GC and TLC monitored the progress of reaction. After the completion of the reaction, 10% aqueous solution of NaOH (20 ml) was added to the mixture. The product was then extracted with diethyl ether (2×20 ml) and washed with water (2×10 ml). The organic layer was separated and dried with anhydrous Na_2SO_4. Filtration and evaporation of the solvent followed by purification on a short column of silica gel produced the desired product (0–97%). All the products are known compounds and were identified by comparison of their spectral data with known samples reported in the literature.[12,14a–c,e,f]

3.3. General procedure for the conversion of episulfides into bis(2-alkoxy ethane)disulfides with NBS

To a solution of episulfide (1 mmol), in alcohol (3 ml), NBS (0.55 mmol, 0.098 g) was added and the mixture was stirred at room temperature for the appropriate time (Table 5). After completion of reaction, the solvent was evaporated and then 10% aqueous solution of NaOH (20 ml) was added to the mixture. The product was extracted by ether (2×30 ml) and the combined organic layers were dried on anhydrous Na_2SO_4. The solution was filtered and evaporated. The product was purified by column chromatography on silica-gel using petroleum ether/ethyl acetate (80:20) as eluent. The pure product was obtained in 20–93% yield (Table 5). All the products are known compounds and were identified by comparison of their spectral data with those of known samples reported in the literature.[14d]

3.4. General procedure for dimerization of episulfides into 1,4-dithianes with NBS

To a solution of episulfides (1 mmol), in dichloromethane (2 ml), NBS (0.2 mmol, 0.04 g) was added and the mixture was stirred at room temperature for the appropriate time (Table 5). After completion of the reaction, 10% aqueous solution of NaOH (20 ml) was added to the reaction mixture. The product was extracted by ether (2×30 ml) and the combined organic layers were dried on anhydrous Na_2SO_4. After filtration and evaporation of the solvent, the product was purified by column chromatography on silica-gel using petroleum ether/ethyl acetate (80:20) as eluent. The pure product was obtained in 75–80% yield (Table 5). The spectral data of the products were compared with those of known samples.[14d]

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