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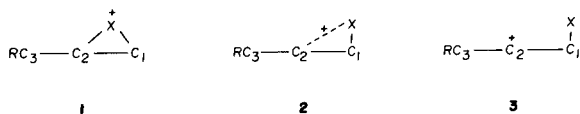
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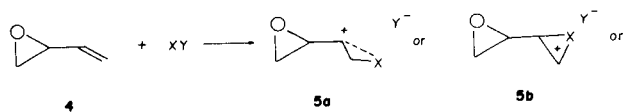
Ionic reactions of bromine, chlorine, methyl hypochlorite or *N*-bromosuccinimide with butadiene monoxide (4) give only 1,2-addition products. The Markownikoff (1-halo-2-methoxy-3,4-epoxybutane) and anti-Markownikoff (2-halo-1-methoxy-3,4-epoxybutane) product ratios for ionic reaction of methyl hypochlorite and *N*-bromosuccinimide in methanol with 4 are similar to those obtained with 1-hexene. These data indicate that a rather symmetrical halonium ion is formed in the ionic halogenation of 4. Free radical reaction of bromine, chlorine, or trichloramine to 4 does not give ring-opened products as one might expect for formation of an epoxy carbonyl intermediate. The mechanistic implications from these observations are discussed.

J. Heterocyclic Chem., 20, 229 (1983).

Reaction of halogens with alkenes to give halonium ions is well documented (1). The ionic intermediates from halogenation of terminal alkenes can be symmetrical (1), unsymmetrical (2), or open-ion intermediates (3). The type of intermediate depends on the substituent on carbon-3. For example, addition of halogens to 1-hexene gives a



rather symmetrical intermediate (2), while addition to vinylcyclopropanes (3) gives an open-ion intermediate. When the number 3-carbon is unsaturated, as with styrenes (4) or dienes (5), a weakly bridged or open intermediate may be formed.



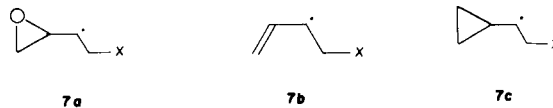
4

5a

5b

In this study we report on the addition of halogens and some halogen systems to butadiene monoxide (4). Our goal is to compare data from addition to 4 with our previous studies on vinylcyclopropane (3) butadienes (5) and 1-hexene (2). Unsymmetrical (5a) or open-ion (6a,b) intermediates from addition to 4 will give only Markownikoff (M) and/or rearranged products similar to those reported from vinylcyclopropane (3). A symmetrical intermediate (5b) should give both Markownikoff (M) and *anti*-Markownikoff (aM) products and no rearranged products.

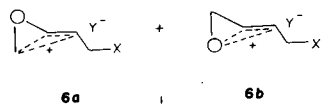
Ionic additions of halogens to 4 have the advantage that reactions can be carried out in solvents similar to solvolysis conditions (methanol) or in less polar aprotic solvents. Also, halogens can be forced to react with alkenes by a radical pathway (6). Thus we can observe the effects of a carbon radical adjacent to an epoxide (7) substituent 7a, and compare these results with vinyl and cyclopropyl substituents derived from radical addition of halogens to butadiene (8) and vinylcyclopropane (3) as indicated by 7b and 7c, respectively.



7a

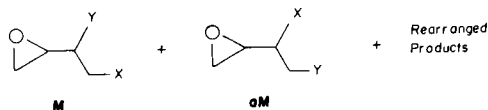
7b

7c



6a

6b



M

aM

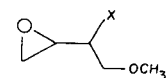
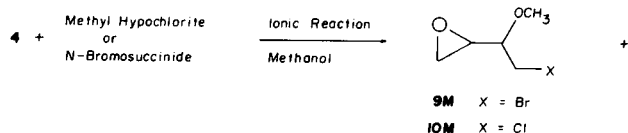
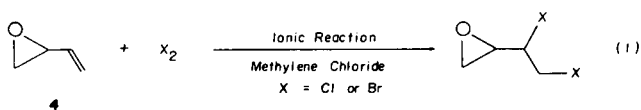
Rearranged Products

Results and Discussion.

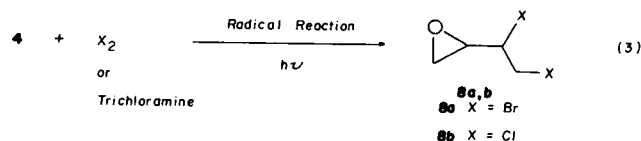
Reaction of chlorine and bromine with 4 under ionic conditions in methylene chloride did not give ring-opened products (equation 1). Compound 4 reacted with methyl hypochlorite and *N*-bromosuccinimide in methanol as solvent to produce both Markownikoff (9M) and *anti*-Markownikoff (9aM) products (equation 2); the data in Table I show that the latter is formed in approximately 40%. Therefore, the halonium ions from addition of halogens

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and halogen systems to butadiene monoxide **4** are rather symmetrical and similar to the intermediates reported for addition of bromine chloride, (2a) bromine in methanol (9a), and methyl hypobromite (9b) to 1-hexene (Table). A symmetrically bridged thiiranium ion was also indicated for reaction of 4-chlorobenzenesulfonyl chloride with 1-hexene (10) (Table). These results are in contrast to those reported for oxymercuration-demercuration of butadiene monoxide (11a) and 1-hexene (11b) were Markownikoff products are greatly preferred.



We observed that only 1,2-products are formed in the photochemical (radical) addition of chlorine, bromine and trichloramine (12) to **4** (equation 3). We did not anticipate this result since only ring-opened products were reported when **4** was treated with alkyl radicals (7), and ring-opened and 1,4-products are formed in large amount from radical addition of halogens to vinylcyclopropanes (3) and butadienes (13). Presumably the chain-transfer step in our halogenation reaction is a low energy process and thereby faster than rearrangement of **10** to **11** (Scheme). On the other hand, only rearranged products are found when **4** is treated with alkyl radicals because rearrangement of **12** to **13** is faster than hydrogen abstraction by **12** (Scheme).



EXPERIMENTAL

General.

(2) Butadiene monoxide (**4**) was purchased from the Aldrich Chemical Company. Methyl hypochlorite (14) and trichloramine (15) were prepared as described in the literature. All other reagents and solvents were obtained commercially. Reactions were performed on 70 to 500 mg of **4** with the halogen system as limiting reagent (20-50 percent completion). Yields were determined by nmr analysis on the crude reaction mixture using benzene as an internal standard. Product percentages were obtained by vapor phase chromatograph. Experiments confirmed that the pro-

Scheme

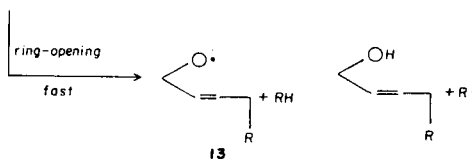
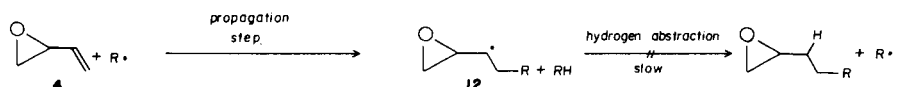
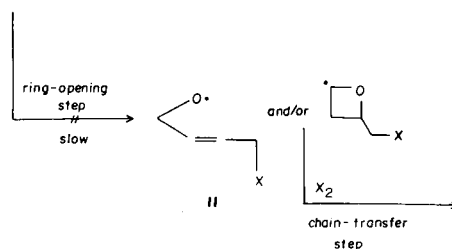
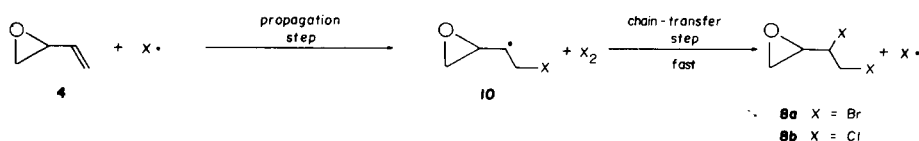
Reaction of Halogen Atoms (X·) and Alkyl Radicals (R·)
With Butadiene Monoxide **4**

Table
Ionic Addition of Electrophiles to Terminal Alkenes

Electrophile	Alkene	Solvent	Percent Products (a) (M)	Reference (aM)
Chlorine	4	Methylene Chloride	100	(b)
Bromine	4	Methylene Chloride	100	(b)
Methyl Hypochlorite	4	Methanol	66	34 (b)
N-bromosuccinimide	4	Methanol	55	45 (b)
Bromine	Propane	Methanol	81	19 (c)
Bromine	1-hexene	Methanol	80	20 (d)
Bromine Chloride	1-hexene	Carbon Tetrachloride	61	39 (e)
Iodine Monochloride	1-hexene	Carbon Tetrachloride	57	43 (f)
4-Chlorobenzenesulfonyl chloride	1-hexene	Tetrachloroethane	32	68 (g)

(a) M = Markownikoff products; aM = anti-Markownikoff product. (b) This work. (c) Product mixture contained 39 percent dibromoproducts. See J. E. Dubois and J. R. Chretien, *J. Am. Chem. Soc.*, **100**, 3506 (1978). (d) Product mixture contained 31 percent dibromo products; see reference 9a. (e) Reference 2a. (f) Reference 2b. (g) Reference 10.

ducts were stable under reaction and isolation conditions. Preparative vapor phase chromatography was accomplished with a Perkin-Elmer 800 chromatograph. The following columns were used: Column A (SS) 8' × ¼", 5% DNP on 80-100 mesh Chromosorb W; Column B (glass) 12' × 6 mm (O.D.) 7% DNP on 80-100 Chromosorb W. Infrared and nuclear magnetic resonance spectra were obtained on a Perkin-Elmer 337 spectrophotometer and a Varian T-60A spectrometer, respectively. Mass Spectra were obtained on a Varian EM 600 spectrometer at 70eV. The compounds isolated in this study were unstable liquids and turn light yellow after several days. Analyses reported below represent the best data we could obtain (16).

Ionic Halogenation Procedure.

Ionic reactions were done in the dark with butadiene monoxide 0.02 mole fraction relative to the solvent (Table). Oxygen was used as a radical inhibitor and it was bubbled into the reaction mixture for ca. three minutes before addition of the halogen. A positive pressure of oxygen was maintained throughout the reaction. Bromine was diluted with 1-2 ml methylene chloride and then added to the reaction mixture. Chlorine and methyl hypochlorite were added as 1.0 M solutions in methylene chloride. N-Bromosuccinimide was added as a solid. Reactions were run at 0° for 3 hours except for the N-bromosuccinimide system which required 5 hours at 25° for completion. Water was added to the mixture and the products extracted with methylene chloride, dried over anhydrous magnesium sulfate, and concentrated.

Radical Addition of Chlorine, Bromine and Trichloramine.

The halogen reagent was added to neat 4 under nitrogen at 0°. Oxygen was removed by bubbling nitrogen through 4 before the reaction. Bromine was added neat while chlorine and trichloramine were added as 1.0 M and 0.35 M solutions, respectively, in methylene chloride. Ultraviolet illumination was provided with a 275-W sunlamp. Reactions were immediate.

1,2-Dibromo-3,4-epoxybutane (8a).

1,2-Dibromo-3,4-epoxybutane was produced in 65% yield under ionic conditions as a mixture of diastereomers with retention times on Column A at 100° of 44 and 52 minutes formed in 39 and 61 percent, respectively. Radical addition of bromine gave a 50% yield with a similar mixture of diastereomers (47:53). The isomers were isolated by preparative vpc and had the following spectra: 44 minutes; ir (carbon tetrachloride): 3060 (17), 2980 and 2940 (C-H), 1255 (18), 875 and 855 (18) cm⁻¹; nmr (carbon tetrachloride): δ 2.67 (dd, J = 4.8 Hz and J = 2.0 Hz, 1H) 2.82 (dd, J = 4.8 Hz and J = 4.0 Hz, 1H), 3.10-3.50 (m, 2H), 3.60-3.90 (m, 2H); 52 minutes; ir (carbon tetrachloride): 3060 (17), 2980, 2930 (C-H), 1260, 1230 (18), 865 (18) cm⁻¹; nmr (carbon tetrachloride): δ 2.80 (dd, J = 4.8 Hz and

J = 2.0 Hz, 1H); 2.95 (dd, J = 4.8 Hz and J = 4.0 Hz, 1H), 3.00-3.40 (m, 2H), 3.72-4.05 (m, 2H).

Anal. (mixture of both isomers) Calcd. for C₄H₆Br₂O: C, 20.90; H, 2.63. Found: C, 20.77; H, 2.59.

1-Bromo-2-methoxy-3,4-epoxybutane (9M) and 2-Bromo-1-methoxy-3,4-epoxybutane (9aM).

Reaction of N-bromosuccinimide with 4 in methanol produced 1-bromo-2-methoxy-3,4-epoxybutane and 2-bromo-1-methoxy-3,4-epoxybutane in a ratio of 55:45 as a mixture of diastereomers (98% yield). The regio- and stereoisomers were isolated by preparative vpc on column B at 95°. The 2-bromo-1-methoxy-3,4-epoxybutanes had retention times of 20 and 36 minutes and were formed in 22 and 23 percent, respectively. These anti-Markownikoff products had the following spectra: 36 minutes; ir (carbon tetrachloride): 3060 (17), 3010, 2970, 2940 and 2840 (C-H), 1250 (18), 1120, and 860 (18) cm⁻¹; nmr (carbon tetrachloride): δ 2.63 (dd, J = 4.8 Hz and 2.4 Hz, 1H), 2.83 (dd, J = 4.8 Hz and J = 3.5 Hz, 1H), 2.95-3.20 (m, 2H), 3.35 (s, 3H), 3.55-3.65 (m, 2H); characteristic mass spectral fragments are m/e (relative intensity) 151 (12), 149 (9), 139 (35), 137 (46), 101 (50), 45 (100), 43 (66); 20 minutes; ir (carbon tetrachloride): 3060 (17), 3000, 2940, and 2840 (C-H), 1250 (18), 1190, 850, and 840 (18) cm⁻¹; nmr (carbon tetrachloride): δ 2.53 (dd, J = 4.8 Hz and J = 2.2 Hz, 1H), 2.78 (dd, J = 4.8 Hz, J = 4.0 Hz, 1H), 2.90-3.40 (m, 2H), 3.40 (s, 3H), 3.40-4.00 (m, 2H); mass spectrum: m/e (relative intensity) 139 (3), 137 (3), 45 (15), 43 (25), 15 (100). The 1-bromo-2-methoxy-3,4-epoxybutanes had

retention times of 30 and 34 minutes and were formed in 29 and 23 percent, respectively. These Markownikoff products had the following spectra: 34 minutes; ir (carbon tetrachloride): 3060 (17), 3010, 2960, 2940 and 2840 (C-H), 1248 (18), 1120 and 860 (18) cm⁻¹ nmr (carbon tetrachloride): δ 2.60-3.00 (m, 2H), 3.00-3.30 (m, 1H), 3.00-3.50 (s at δ 3.40 superimposed on mult, 6H); characteristic mass spectral fragments are m/e (relative intensity) 182 (3), 180 (4), 139 (100), 137 (100), 95 (7), 93 (8), 87 (67), 43 (70); 30 minutes; ir (carbon tetrachloride): 3060 (17), 3010, 2940, and 2840 (C-H), 1250 (18), 1115, 870 (18) cm⁻¹; nmr (carbon tetrachloride): δ 2.50 (dd, J = 4.4 Hz and J = 2.2 Hz, 1H), 2.60-3.44 (m, 5H), 3.46 (s, 3H); mass spectrum: m/e (relative intensity) 139 (86), 137 (91), 95 (10), 93 (12), 43 (100).

Anal. (mixture of four isomers) (16) Calcd. for C₅H₈BrO₂: C, 33.17; H, 5.01. Found: C, 32.53; H, 4.93.

1,2-Dichloro-3,4-epoxybutane (8b).

1,2-Dichloro-3,4-epoxybutane was produced in 80% yield under ionic conditions as a mixture of diastereomers with retention times of 10 and 12 minutes formed in 45 and 55 percent, respectively. Radical reactions gave the following data: chlorine (60% yield) ratio fo 10:12 minute

isomers 43:57; trichloramine (80% yield) ratio of 10:12 minute isomers 41:59. The dichlorides were isolated by preparative vpc and had the following spectra: 10 minutes; ir (carbon tetrachloride): 3080 (17), 2970, 2940 (C-H), 1255 (18), 860, and 840 (18) cm^{-1} ; nmr (carbon tetrachloride): δ 2.66 (dd, $J = 5.8$ Hz and $J = 2.4$ Hz, 1H), 2.82 (dd, $J = 5.8$ Hz and $J = 4.0$ Hz, 1H), 3.18 (ddd, $J = 6.8$ Hz, $J = 4.0$ Hz, and $J = 2.4$ Hz, 1H), 3.40-4.00 (m, 3H); 12 minutes; ir (carbon tetrachloride): 3070 (17), 3010, 2950 (C-H), 1295, 1250 (18), 940, 905, 870 and 840 (18) cm^{-1} ; nmr (carbon tetrachloride): 2.75 (dd, $J = 4.8$ Hz and $J = 2.2$ Hz, 1H), 2.85 (dd, $J = 4.4$ Hz and 4.0 Hz, 1H), 3.10 (seven peak multiplet, 1H), 3.50-3.80 (m, 3H). *Anal.* (mixture of both isomers) (16) Calcd. for $\text{C}_5\text{H}_8\text{ClO}_2$: C, 34.07; H, 4.29; Cl, 50.29. Found: C, 33.23; H, 4.22; Cl, 50.65.

1-Chloro-2-methoxy-3,4-epoxybutane (**10M**) and 2-Chloro-1-methoxy-3,4-epoxybutane (**10aM**).

Reaction of methyl hypochlorite with **4** in methanol produced 1-chloro-2-methoxy-3,4-epoxybutane and 2-chloro-1-methoxy-3,4-epoxybutane in a ratio of 66:34 as a mixture of diastereomers (90% yield). Only one stereoisomer of each regioisomer could be isolated pure by preparative vpc on column B at 80°. The one stereoisomer of 2-chloro-1-methoxy-3,4-epoxybutane had a retention time of 38 minutes and was found to be 19 percent of the product mixture. This anti-Markownikoff product had the following spectra; ir (carbon tetrachloride): 3060 (17), 3000, 2940, 2910 and 2840 (C-H), 1260 (18), 1220, 875 and 810 (18) cm^{-1} ; nmr (carbon tetrachloride): δ 2.60-2.80 (m, 2H), 2.84-3.20 (m, 1H), 3.35 (s, 3H), 3.50-3.82 (m, 3H); the mass spectrum had a base peak at $m/e = 45$ ($\text{CH}_2 = \text{OCH}_3$). The one stereoisomer of 1-chloro-2-methoxy-3,4-epoxybutane had a retention time of 34 minutes and was 30 percent of the product mixture. This Markownikoff product had the following spectra: ir (carbon tetrachloride): 3080 (17), 2960, 2930 and 2850 (C-H), 1250 (18), 1120, 870, and 855 (18) cm^{-1} ; nmr (carbon tetrachloride): δ 2.67 (m, 2H), 2.80-3.10 (m, 1H), 3.36 (s, 3H), 3.40-3.68 (m, 3H); characteristic mass spectral fragments were m/e (relative intensity) 100 (13) $\text{P} - \text{HCl}$ not present in the anti-Markownikoff isomer; isotope cluster 95 (34), 97 (100); 51 (7) and 49 (11), $\text{CH}_2 = ^*\text{Cl}$ not present in the anti-Markownikoff isomer; 43 (79). Products with retention times of 27 and 29 minutes were collected as a mixture formed in 15 and 36 percent respectively; ir (carbon tetrachloride): 3060 (17), 3000, 2940, 2910 and 2840 (C-H), 1250 (18), 880, 850 and 830 (18) cm^{-1} ; nmr: 2.40-3.30 (m, 4H), 3.38-3.70 (m, 5H); mass spectrum: m/e (relative intensity) parent ions 138 (2), 136 (5), P-14 124 (6), 122 (18), P-43 95 (35) and 93 (100), and $\text{CH}_2 = \text{Cl}^+$ 51 (7), 49 (9).

Anal. (mixture of all four isomers) (16) Calcd. for $\text{C}_5\text{H}_8\text{ClO}_2$: C, 43.97; H, 6.64. Found: C, 42.47; H, 6.29.

Acknowledgements.

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(16) Repeated analysis on the unstable liquids did not give acceptable results. The results reported represent the purity of the sample after some decomposition during shipment to the commercial laboratory where the analyses were performed.

(17) The C-H stretching vibration of epoxides is above 3000 cm^{-1} and is characteristic for strained three-membered rings. See M. Arvam and G. H. D. Mateescu, "Infrared Spectroscopy", Wiley-Interscience, New York, 1972, pp 283-285.

(18) The absorption band at 1230-1280 cm^{-1} is typical of epoxides. Monosubstituted epoxides have a band of 806-877 cm^{-1} , see reference 17.