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Reactions of Dichlorocarbene and Arenesulfenyl Chlorides with 3,4-Epoxy-1-butene and Vinylethylene Carbonate

T. G. Mannafov, E. A. Berdnikov, and Ya. D. Samuilov

Kazan State University, ul. Kremlevskaya 18, Kazan, 420008 Tatarstan, Russia
e-mail: airatz@auz.kcn.ru

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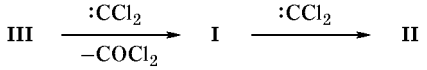
Abstract—Reaction of 3,4-epoxy-1-butene with dichlorocarbene is accompanied by deoxygenation and yields a mixture of 1,1-dichloro-2-vinylcyclopropane, 2,2,2′,2′-tetrachlorobicyclopropyl, and 2,2-dichlorocyclopropyloxirane. Arenesulfenyl chlorides react with 3,4-epoxy-1-butene to afford both Markownikoff and anti-Markownikoff addition products, whereas vinylethylene carbonate gives rise exclusively to the anti-Markownikoff adducts.

The high and versatile reactivity of large-scale unsaturated epoxy derivatives determines their great synthetic potential. Reactions of nucleophilic reagents [1] with 3,4-epoxy-1-butene, which involve opening of the oxirane ring, have been studied in sufficient detail. Much less information is available on reactions of 3,4-epoxy-1-butene with electrophiles. It is known that chlorine, bromine, and methyl hypochlorite add across the double bond of 3,4-epoxy-1-butene and that methyl hypochlorite gives rise to a mixture of adducts formed according to and against the Markownikoff rule [2]. Reactions of 3,4-epoxy-1-butene with dihalocarbenes and sulfenyl chlorides were not studied.

The present communication reports on the results of our study on reactions of 3,4-epoxy-1-butene and vinylethylene carbonate (which is readily accessible from 3,4-epoxy-1-butene and carbon dioxide [3]) with dichlorocarbene and arenesulfenyl chlorides. We also endeavored to compare the effects of the oxirane and 2-oxo-1,3-dioxolane fragments on the reactivity of the double bond in 3,4-epoxy-1-butene toward electrophilic reagents.

The reaction of 3,4-epoxy-1-butene with dichlorocarbene was carried out in the system chloroform–aqueous sodium hydroxide in the presence of benzyltriethylammonium chloride (following the known Makosza procedure). According to the GLC data, the reaction mixture contained a number of products together with unreacted 3,4-epoxy-1-butene. By fractional distillation we succeeded in isolating three products: 1,1-dichloro-2-vinylcyclopropane (**I**), *meso*-2,2,2′,2′-tetrachlorobicyclopropyl (**II**), and diastereoisomeric 2,2-dichlorocyclopropyloxiranes (**III**) (Scheme 1). The overall yield of the identified products was 39%.

The structure of compounds **I**–**III** was confirmed by the ^{1}H and ^{13}C NMR spectra (Table 1). As a rule, dichlorocarbene reacts with olefins through addition at the double bond. In our case, substituted oxirane **III** can be regarded as such a common addition product. The formation of compounds **I** and **II** may be explained in terms of the known ability of carbenes to deoxygenate oxirane ring [4]:



In fact, treatment of both oxirane **III** and dichlorocyclopropane **I** with excess dichlorocarbene leads to formation of diastereoisomeric tetrachlorobicyclopropyls **II**; only the *meso* form of **II** was isolated in the pure state.

Scheme 1.

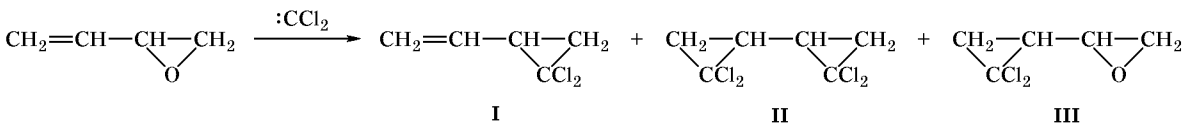


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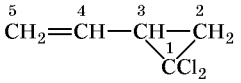
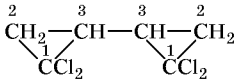
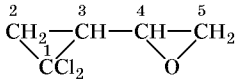
Table 1. ^{1}H and ^{13}C NMR spectra of dichlorocyclopropane derivatives **I**–**III** in $CDCl_3$



I



II



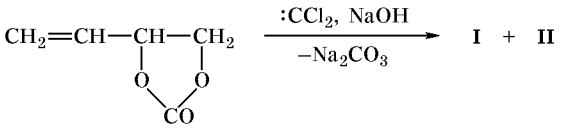
III

Compound no.	^{1}H NMR spectrum, δ, ppm (*J*, Hz)
I	1.42 d.d (1H, CH_2CCl_2, $^2J_{2,2}$ = 7.0, $^3J_{trans\text{-}2,3}$ = 7.8), 1.79 d.d (1H, CH_2CCl_2, $^2J_{2,2}$ = 7.0, $^3J_{cis\text{-}2,3}$ = 10.4), 2.28 d.d.d (1H, $CHCCl_2$, $^3J_{cis\text{-}2,3}$ = 10.4, $^3J_{trans\text{-}2,3}$ = 7.8, $^3J_{3,4}$ = 7.9), 5.25 d.d (1H, CH_2=, $^2J_{5,5}$ = 1.2, $^3J_{cis\text{-}4,5}$ = 10.0), 5.32 d.d (1H, CH_2=, $^2J_{5,5}$ = 1.2, $^3J_{trans\text{-}4,5}$ = 17.0), 5.58 d.d.d (1H, CH=, $^3J_{trans\text{-}4,5}$ = 17.0, $^3J_{cis\text{-}4,5}$ = 10.0, $^3J_{3,4}$ = 7.9)
II	*erythro*: 1.51 m (4H, $2CH_2$), 1.86 m (2H, 2CH) *threo*: 1.49 m (4H, $2CH_2$), 1.85 m (2H, 2CH)
III	*erythro*: 1.45 d.d (1H, CH_2CCl_2, $^2J_{2,2}$ = 7.1, $^3J_{trans\text{-}2,3}$ = 7.5), 1.55 d.d (1H, CH_2CCl_2, $^2J_{2,2}$ = 7.1, $^3J_{cis\text{-}2,3}$ = 10.3), 1.79 d.d.d (1H, $CHCCl_2$, $^3J_{cis\text{-}2,3}$ = 10.3, $^3J_{trans\text{-}2,3}$ = 7.5, $^3J_{3,4}$ = 3.5), 2.58 d.d (1H, CH_2O, $^2J_{5,5}$ = 4.9, $^3J_{trans\text{-}4,5}$ = 2.6), 2.85 d.d (1H, CH_2O, $^2J_{5,5}$ = 4.9, $^3J_{cis\text{-}4,5}$ = 4.2), 3.08 d.d.d (1H, CHO, $^3J_{trans\text{-}4,5}$ = 2.6, $^3J_{cis\text{-}4,5}$ = 4.2, $^2J_{3,4}$ = 3.5) *threo*: 1.50 m (2H, CH_2CCl_2), 1.88 m (1H, $CHCCl_2$), 2.67 d.d (1H, CH_2O, $^2J_{5,5}$ = 4.7, $^3J_{trans\text{-}4,5}$ = 2.6), 2.84 d.d (1H, CH_2O, $^2J_{5,5}$ = 4.7, $^3J_{cis\text{-}4,5}$ = 4.7), 2.91 m (1H, CHO)

Compound no	^{13}C NMR spectrum, δ_C, ppm ($^1J_{C,H}$, Hz)				
	C^1	C^2	C^3	C^4	C^5
I	60.86 s	27.70 t	34.05 d	134.00 d	118.96 t
II-*erythro* (*meso*)	59.65 s	27.42 t (165.8)	31.12 d (166.6)	–	–
II-*threo*	58.40 s	26.43 t (163.2)	30.71 d (166.0)	–	–
III-*erythro*	58.50 s	23.10 t (166.9)	31.46 d (166.0)	49.12 d (177.1)	45.96 t (176.4)
III-*threo*	58.62 s	24.36 t (166.4)	31.76 d (166.0)	51.46 d (177.0)	45.64 t (176.4)

Under similar conditions, the reaction of dichlorocarbene with vinylethylene carbonate afforded a complex mixture of products. Only two of them were isolated in the pure state by distillation. These were compounds **I** and **II** which were identical to those obtained by reaction of 3,4-epoxy-1-butene with dichlorocarbene. The overall yield was as low as 27%. Presumably, the reaction is accompanied by decomposition of the 2-oxo-1,3-dioxolane ring (decarboxylation and deoxygenation) by the action of alkali and dichlorocarbene (Scheme 2).

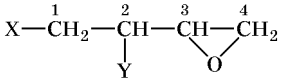
Scheme 2.



Reactions of 3,4-epoxy-1-butene and vinylethylene carbonate with arenesulfenyl chlorides were more selective. *p*-Toluenesulfenyl chloride readily adds to 3,4-epoxy-1-butene in carbon tetrachloride, affording the corresponding 1:1 adduct (according to the data of elemental analysis) in high yield (Scheme 3). Gas chromatographic–mass spectrometric analysis of the product showed that it is a mixture of four isomers with close retention times. Their mass spectra were also very similar. Each isomer showed in the mass spectrum strong molecular ion peak $[M]^+$ with *m*/*z* 228/230. The spectra of two isomers contained fragment ion peaks with *m*/*z* 179 $[M-CH_2Cl]$, which were absent in the spectra of the two other isomers.

In the ^{13}C NMR spectrum (Table 2) we also observed four sets of signals (total of 16) belonging to CHO and CH_2O groups (4 signals per group) and

Table 2. ^{13}C NMR spectra (δ_C, ppm, $^1J_{C,H}$, Hz) of oxiranes **IV**–**VI** in $CDCl_3$



Compound no.	X	Y	C^1	C^2	C^3	C^4	CH_3
IV	*p*-$CH_3C_6H_4S$	Cl	38.68 t (144.0)	61.07 d (155.0)	54.47 d (177.0)	46.92 t (177.0)	21.18 q (127.0)
			40.75 t (144.0)	60.11 d (155.0)	53.94 d (177.0)	48.22 t (177.0)	21.18 q (127.0)
IVa	Cl	*p*-$CH_3C_6H_4S$	45.14 t (155.0)	52.71 d (144.0)	52.52 d (177.0)	48.32 t (177.0)	21.30 q (127.0)
			44.51 t (165.0)	53.27 d (144.0)	52.71 d (177.0)	47.21 t (177.0)	21.30 q (127.0)
V	*o*-$NO_2C_6H_4S$	Cl	37.10 t	60.11 d	54.39 d	46.50 t	–
			38.03 t	59.10 d	54.02 d	47.42 t	–
Va	Cl	*o*-$NO_2C_6H_4S$	44.62 t	51.98 d	50.50 d	47.75 t	–
			44.19 t	52.54 d	50.82 d	46.50 t	–
VI[a]	*p*-$CH_3C_6H_4SO_2$	Cl	63.57 t	55.40 d	55.30 d	46.96 t	21.54 q

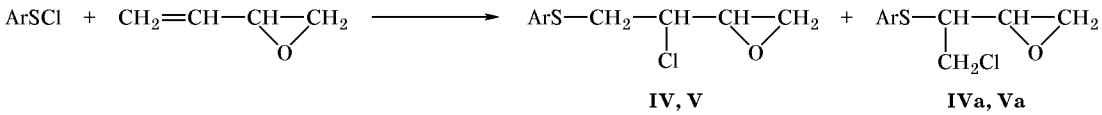
[a] Aromatic carbon signals, δ_C, ppm: 142.30 s, 139.99 s, 130.33 d, 124.18 d.

CHCl, CH_2Cl, CHS, and CH_2S groups (2 signals per group). Taking into account published data on carbon chemical shifts of addition products of *p*-toluenesulfenyl chloride to 3,3-dimethyl-1-butene [5], we came to the conclusion that the obtained mixture of four 1:1 adducts consists of two diastereoisomeric pairs formed by addition of *p*-toluenesulfenyl chloride to 3,4-epoxy-1-butene according to the Markownikoff rule (**IV**) and against it (**IVa**). Our conclusion was based on the signal multiplicities and experimental direct coupling constants $^1J_{C,H}$ typical of the oxirane ring [6], as well as on the known carbon chemical shifts of substituted oxiranes [7]. Likewise, *o*-nitrobenzenesulfenyl chloride reacted with 3,4-epoxy-1-butene, yielding two diastereoisomeric pairs **V** and **Va** (Scheme 3, Table 2).

Oxidation of mixture **IV**/**IVa** with hydrogen peroxide in acetic acid resulted in formation of a complex mixture of products from which only one pure diastereoisomer, sulfone **VI** (Table 2) was isolated in 12.4% yield.

Vinylethylene carbonate also readily takes up arenesulfenyl chlorides in carbon tetrachloride or chloroform. According to the ^1H and ^{13}C NMR data (Table 3), in this case only anti-Markownikoff adducts **VII** and **VIII** were formed, each being a mixture

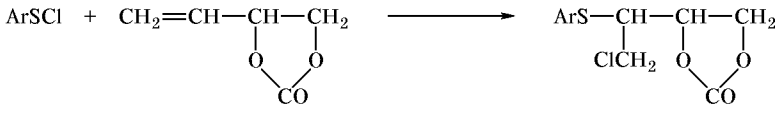
Scheme 3.



IV, V **IVa, Va**

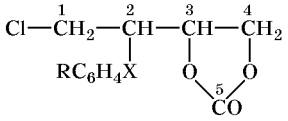
IV, **IVa**, Ar = *p*-$CH_3C_6H_4$; **V**, **Va**, Ar = *o*-$O_2NC_6H_4$.

Scheme 4.



VII, VIII

Table 3. ^1H and ^{13}C NMR spectra of ethylene carbonate derivatives **VII**–**X**



Compound no.	X	R	^1H NMR spectrum, δ, ppm (*J*, Hz)
VII-*threo*[a]	S	*p*-CH_3	3.22 d.d.d (1H, CHS, $^3J_{1,2}$ = 10.6, $^3J_{1,2}$ = 5.0, $^3J_{2,3}$ = 2.3), 3.82 d.d (1H, CH_2Cl, $^2J_{1,1}$ = 11.4, $^3J_{1,2}$ = 10.6), 3.87 d.d (1H, CH_2Cl, $^2J_{1,1}$ = 11.4, $^3J_{1,2}$ = 5.0), 4.58 d.d (1H, CH_2O, $^2J_{4,4}$ = 8.5, $^3J_{trans\text{-}3,4}$ = 6.7), 4.62 d.d (1H, CH_2O, $^2J_{4,4}$ = 8.5, $^3J_{cis\text{-}3,4}$ = 8.5), 5.32 d.d.d (1H, CHO, $^3J_{cis\text{-}3,4}$ = 8.5, $^3J_{trans\text{-}3,4}$ = 6.7, $^3J_{2,3}$ 2.3)
VII-*erythro*[a]	S	*p*-CH_3	3.40 m (1H, CHS), 3.78 m (2H, CH_2Cl), 4.34 d.d (1H, CH_2O, $^2J_{4,4}$ = 8.6, $^3J_{trans\text{-}3,4}$ = 7.3), 4.60 d.d (1H, CH_2O, $^2J_{4,4}$ = 8.6, $^3J_{cis\text{-}3,4}$ = 8.6), 4.83 d.d.d (1H, CHO, $^3J_{cis\text{-}3,4}$ = 8.6, $^3J_{trans\text{-}3,4}$ = 7.3, $^3J_{2,3}$ = 7.0)
VIII-*threo*[b]	S	*o*-NO_2	4.02 d.d (1H, CH_2Cl, $^2J_{1,1}$ = 11.4, $^3J_{1,2}$ = 13.2), 4.05 d.d (1H, CH_2Cl, $^2J_{1,1}$ = 11.4, $^3J_{1,2}$ = 1.6), 4.16 d.d.d (1H, CHS, $^3J_{1,2}$ = 13.2, $^3J_{1,2}$ = 1.6, $^3J_{2,3}$ = 3.2), 4.59 d.d (1H, CH_2O, $^2J_{4,4}$ = 8.8, $^3J_{trans\text{-}3,4}$ = 6.6), 4.83 d.d (1H, CH_2O, $^2J_{4,4}$ = 8.8, $^3J_{cis\text{-}3,4}$ = 8.6), 5.53 d.d.d (1H, CHO, $^3J_{cis\text{-}3,4}$ = 8.6, $^3J_{trans\text{-}3,4}$ = 6.6, $^3J_{2,3}$ 3.2)
VIII-*erythro*[b]	S	*o*-NO_2	4.10 d.d (1H, CH_2Cl, $^2J_{1,1}$ = 11.4, $^3J_{1,2}$ = 7.6), 4.11 d.d (1H, CH_2Cl, $^2J_{1,1}$ = 11.4, $^3J_{1,2}$ = 2.6), 4.35 d.d.d (1H, CHS, $^3J_{1,2}$ = 7.6, $^3J_{1,2}$ = 2.6, $^3J_{2,3}$ = 7.0), 4.50 d.d (1H, CH_2O, $^2J_{4,4}$ = 8.8, $^3J_{3,4}$ = 6.6), 4.78 d.d (1H, CH_2O, $^2J_{4,4}$ = 8.8, $^3J_{cis\text{-}3,4}$ = 8.6), 5.24 d.d.d (1H, CHO, $^3J_{trans\text{-}3,4}$ = 6.6, $^3J_{cis\text{-}3,4}$ = 8.6, $^3J_{2,3}$ = 7.0)
IX-*threo*[a]	SO_2	*p*-CH_3	3.73 d.d.d (1H, $CHSO_2$, $^3J_{1,2}$ = 7.3, $^3J_{1,2}$ = 4.7, $^3J_{2,3}$ = 3.3), 3.86 d.d (1H, CH_2Cl, $^2J_{1,1}$ = 12.1, $^3J_{1,2}$ = 7.3), 4.01 d.d (1H, CH_2Cl, $^2J_{1,1}$ = 12.1, $^3J_{1,2}$ = 4.7), 4.69 d.d (1H, CH_2O, $^2J_{4,4}$ = 9.4, $^3J_{trans\text{-}3,4}$ = 6.7), 4.73 d.d (1H, CH_2O, $^2J_{4,4}$ = 9.4, $^3J_{cis\text{-}3,4}$ = 10.1), 5.37 d.d.d (1H, CHO, $^3J_{trans\text{-}3,4}$ = 6.7, $^3J_{cis\text{-}3,4}$ = 10.1, $^3J_{2,3}$ = 3.3)
X-*threo*[b]	SO_2	*o*-NO_2	4.10 m (2H, CH_2Cl), 4.20 m (1H, $CHSO_2$), 4.89 d.d (1H, CH_2O, $^2J_{4,4}$ = 9.1, $^3J_{trans\text{-}3,4}$ = 6.6), 4.98 d.d (1H, CH_2O, $^2J_{4,4}$ = 9.1, $^3J_{cis\text{-}3,4}$ = 8.1), 5.51 d.d.d (1H, CHO, $^3J_{trans\text{-}3,4}$ = 6.6, $^3J_{cis\text{-}3,4}$ = 8.1, $^3J_{2,3}$ = 6.1)

Compound no.	^{13}C NMR spectrum, δ_C, ppm				
	C^1	C^2	C^3	C^4	C^5
VII-*threo*[a]	43.58	54.95	74.25	67.18	154.37
VII-*erythro*[a]	44.21	54.26	74.69	67.97	154.38
VIII-*threo*[b]	44.43	52.68	75.76	68.20	154.79
VIII-*erythro*[b]	45.31	52.52	76.02	68.20	154.83
IX-*threo*[a]	37.05	72.62	66.52	66.18	154.41
X-*threo*[b]	37.51	75.36	68.34	64.22	154.82

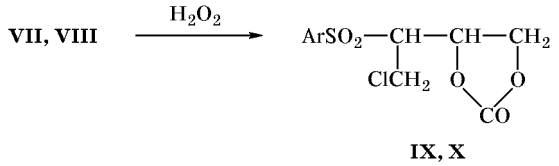
[a] In $CDCl_3$.

[b] In acetone-d_6.

of diastereoisomers (Scheme 4). We succeeded in separating a part of the *threo* isomers, and they were characterized as individual compounds (Tables 3, 4); pure *erythro* isomers were not obtained. Oxidation of *threo*-sulfides **VII** and **VIII** with 30% hydrogen peroxide in acetic acid smoothly yields sulfones **IX** and **X** (Scheme 5).

Comparison of the behavior of 3,4-epoxy-1-butene and vinylethylene carbonate in electrophilic addition reactions with arenesulfenyl chlorides leads us to conclude that the 2-oxo-1,3-dioxolane group is a stronger acceptor that the oxirane moiety. According to [8], the oxiranyl group is assumed to be a fairly weak π-donor.

Scheme 5.



VII, **IX**, Ar = *p*-$CH_3C_6H_4$; **VIII**, **X**, *o*-$NO_2C_6H_4$.

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were recorded on a Varian-200 spectrometer in $CDCl_3$ or acetone-d_6 using HMDS as internal reference. The mass spectra were run on an INCOS-50 GC–MS system.

Reaction of 3,4-epoxy-1-butene with dichlorocarbene. To a solution of 35 g (0.5 mol) of 3,4-epoxy-1-butene and 2 g (8.8 mmol) of benzyltriethylammonium chloride (BTEAC) in 140 ml of chloroform we added dropwise with stirring a solution of 142 g (3.55 mol) of sodium hydroxide in 142 ml of water over a period of 2 h, maintaining the temperature at 35–40°C. The mixture was then stirred for 10 h at 40°C, the precipitate was filtered off, and the organic phase was separated and dried over magnesium sulfate. Products **I**–**III** were isolated by fractional distillation.

1,1-Dichloro-2-vinylcyclopropane (I). Yield 6.17 g (9%). bp 123–124°C, n_D^{20} 1.4730. Found, %: C 43.94; H 4.64. $C_5H_6Cl_2$. Calculated, %: C 43.83; H 4.41.

2,2,2′,2′-Tetrachlorobicyclopropyl (II) (a mixture of *meso* and *threo* isomers). Yield 27.5 g (25%). bp 90–94°C (12 mm). On cooling to 0°C, 11.2 g (10.2%) of the *meso* form precipitated. mp 78–79°C (from hexane); published data [9]: mp 76°C. Found, %: C 33.18; H 2.80. $C_6H_6Cl_4$. Calculated, %: C 32.77; H 2.75. The liquid obtained after separation of *meso*-**II** was a mixture of *meso*-**II** and *threo*-**II**, the latter prevailing (Table 1).

2,2-Dichlorocyclopropyloxirane (III) (a mixture of diastereoisomers). Yield 15.2 g (20%). bp 72–75°C (12 mm), n_D^{20} 1.4831. Found, %: C 39.62; H 3.61. $C_5H_6Cl_2O$. Calculated, %: C 39.25; H 3.95.

Reactions of oxirane III with dichlorocarbene. The reaction was carried out following the above procedure with 7.65 g (0.05 mol) of compound **III**, 0.3 g (1.3 mmol) of BTEAC, 15 ml of chloroform, and a solution of 12 g (0.3 mol) of sodium hydroxide in 12 ml of water. We isolated 9.3 g (85%) of **II** as a mixture of diastereoisomers (Table 1). bp 90–94°C (12 mm). On cooling, 3.1 g (28%) of *meso*-**II** was separated. mp 78–79°C (from hexane).

Reaction of compound I with dichlorocarbene. The reaction was carried out following the above procedure with 11 g (0.08 mol) of compound **I**, 0.32 g (1.4 mmol) of BTEAC, 15 ml of chloroform, and a solution of 3.3 g (0.082 mol) of sodium hydroxide in 3.4 ml of water. We isolated 15.7 g (89%) of **II** as a mixture of diastereoisomers (Table 1). On cooling, 5.8 g (32.8%) of *meso*-**II** was separated. mp 78–79°C (from hexane).

Reaction of vinylethylene carbonate with dichlorocarbene. The reaction was carried out following the above procedure with 11.4 g (0.1 mol) of vinylethylene carbonate, 0.8 g (3.5 mmol) of BTEAC, 80 ml of chloroform, and a solution of 40 g (1 mol) of sodium hydroxide in 40 ml of water. We isolated 1.7 g (12.5%) of compound **I**, bp 123–124°C, n_D^{20} 1.4733, and 3.1 g (14%) of *meso*-**II**, mp 78–79°C (from hexane).

(1-Chloro-2-*p*-tolylthioethyl)oxirane (IV) and (2-chloro-1-*p*-tolylthioethyl)oxirane (IVa). To a solution of 7 g (0.1 mol) of 3,4-epoxy-1-butene in 50 ml of carbon tetrachloride we added dropwise (with stirring and cooling by water) a solution of 15.8 g (0.1 mol) of *p*-tolylsulfenyl chloride in 30 ml of carbon tetrachloride. The solvent was removed under reduced pressure, and the residue was distilled. Yield 20.1 g (88%), bp 135–138°C (1 mm), n_D^{20} 1.5740.

Table 4. Yields, melting points, and elemental analyses of compounds **VIIa**–**X**

Compound no.	Yield, %	mp, °C	Found, %		Formula	Calculated, %	
			C	H		C	H
VIIa	32	78–79	52.99	4.40	$C_{12}H_{13}ClO_3S$	52.84	4.80
VIIIa	35	134–135	43.58	3.24	$C_{11}H_{10}ClO_5NS$	43.51	3.32
IX	75	145–147	47.41	4.20	$C_{12}H_{13}ClO_5S$	47.29	4.29
X	69	148–150 (decomp.)	39.19	3.10	$C_{11}H_{10}ClO_7NS$	39.35	3.00

Found, %: C 57.40; H 5.71. $C_{11}H_{13}ClOS$. Calculated, %: C 57.46; H 5.73.

(1-Chloro-2-*o*-nitrophenylthioethyl)oxirane (V) and (2-chloro-1-*o*-nitrophenylthioethyl)oxirane (Va). To a solution of 19 g (0.1 mol) of *o*-nitrobenzenesulfenyl chloride in 80 ml of chloroform we added 7 g (0.1 mol) of 3,4-epoxy-1-butene. After 2 days, the solvent was removed under reduced pressure to leave an undistillable oily liquid. Found, %: C 45.70; H 3.48. $C_{10}H_{10}ClO_3NS$. Calculated, %: C 46.24; H 3.88.

(1-Chloro-2-*p*-tolylsulfonylethyl)oxirane (VI). To a solution of 2.29 g (0.01 mol) of a mixture of sulfides **IV** and **IVa** in 100 ml of acetic acid we added 10 ml of 30% hydrogen peroxide. After 2 days, the mixture was diluted with water and extracted with chloroform (2 × 30 ml). The extract was washed with water, dried over magnesium sulfate, and evaporated under reduced pressure. The precipitate was filtered off and recrystallized from benzene. Yield 0.32 g (12.4%). mp 135°C. Found, %: C 50.47; H 5.12. $C_{11}H_{13}ClO_3S$. Calculated, %: C 50.67; H 5.02.

(2-Chloro-1-*p*-tolylthioethyl)-1,3-dioxolan-2-one (VIIa). A solution of 7.93 g (0.05 mol) of *p*-toluenesulfenyl chloride and 5.7 g (0.05 mol) of vinylethylene carbonate in 40 ml of carbon tetrachloride was kept for 4 days. The solvent was removed under reduced pressure, and the precipitate was filtered off and recrystallized from hexane. The crystalline product and the liquid phase were characterized by ^1H and ^{13}C NMR spectra (Table 3).

4-(2-Chloro-1-*o*-nitrophenylthioethyl)-1,3-dioxolan-2-one (VIIIa). A solution of 5.79 g (0.03 mol) of *o*-nitrobenzenesulfenyl chloride and 3.42 g (0.03 mol) of vinylethylene carbonate in 100 ml of carbon tetrachloride was kept for 7 days. The precipitate was filtered off and recrystallized from acetonitrile. The filtrate was evaporated under reduced pressure to obtain an oily liquid. The solid and liquid products were characterized by ^1H and ^{13}C NMR spectra (Table 3).

4-(2-Chloro-1-*p*-tolylsulfonylethyl)-1,3-dioxolan-2-one (IX). To a solution of 0.97 g (3.56 mmol) of compound **VII** in 50 ml of acetic acid we added 4 ml of 30% hydrogen peroxide. After 2 days, the mixture was diluted with water, and the precipitate was filtered off and recrystallized from benzene–acetonitrile.

4-(2-Chloro-1-*o*-nitrophenylsulfonylethyl)-1,3-dioxolan-2-one (X). The reaction was performed in a similar way with 0.9 g (3 mmol) of compound **VII** and 4 ml of 30% hydrogen peroxide. The product was recrystallized from benzene–acetonitrile.

The yields, melting points, and elemental analyses of compounds **VIIa**, **VIIIa**, **IX**, and **X** are collected in Table 4.

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