

Factors Influencing the Nature of the Episulfonium Ion in Sulfenyl Chloride Addition to Terminal Olefins¹

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Abstract: Methane- and benzenesulfenyl chloride afforded predominantly anti-Markovnikov oriented adducts with terminal alkyl substituted olefins and vinyl chloride. This adduct selectivity increased with increasing bulkiness of the alkyl substituent of the substrate. These kinetically controlled adducts were found to readily undergo acid-catalyzed isomerization to the thermodynamically more stable Markovnikov adducts. Phenyl substituents on the olefin caused Markovnikov orientation of the kinetically controlled adducts. Exclusive *trans*-stereospecific addition to norbornene and acenaphthylene was established. The mechanism of such additions and, in particular, the factors influencing the transition state, *i.e.*, the ring opening of the episulfonium ion intermediate, are discussed.

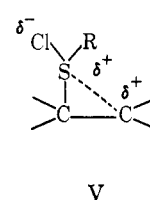
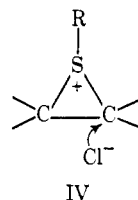
The addition of sulfenyl chlorides across double bonds has been known for many years and has received considerable attention.⁴⁻⁷ The molecule RSCl could, in theory, react in at least three distinct ways with an olefin: either as a source of electrophilic sulfur (I) or of chlorine (II), or as a source of free radicals by homolytic cleavage (III). Two of these possibilities, the occurrence of electrophilic sulfur as well as that of free radicals, have been recognized to date.



Most studies pertaining to the electrophilic addition mechanism have been conducted with 2,4-dinitrobenzenesulfenyl chloride, which was considered a convenient model reagent because of its outstanding stability. It was found that this particular reagent undergoes polarization in the sense of structure I and that there was no evidence that the reagent could become a source of chloronium ions.⁸ An investigation of the kinetics of the reaction of 2,4-dinitrobenzenesulfenyl chloride with styrene and cyclohexene revealed it to be second order.^{9,10} Enhanced rates were observed in more polar solvents. Comparison of relative rates of the reaction with *para*-substituted styrenes showed that the α -carbon is appreciably electron deficient in the transition state.⁹ More recently, an examination of the relative rates of the addition of several *para*-substituted, *o*-nitrobenzenesulfenyl chlorides to cyclohexene demonstrated the need to allow for an enhanced mesomeric electron release from *para* substituents by the use of σ^+ values.¹¹ All the kinetic data are consistent with,

but do not require, the general postulate of an episulfonium ion intermediate, IV.

Additional support in favor of such an intermediate is the almost exclusive *trans*-stereospecific addition observed with *cis*- and *trans*-2-butenes¹²⁻¹⁴ as well as



with norbornene.^{15,16} Particularly strong evidence against a nonrotating open carbonium ion has recently been supplied by the stereospecific integrity of this addition reaction over a wide range in temperature.¹⁷

The almost exclusive Markovnikov orientation¹⁸ reported for the reaction of 2,4-dinitrobenzenesulfenyl chloride with styrene and more significantly with propylene, however, reflects some carbonium ion character in the transition state.^{19,20} Additions of 2-haloalkanesulfenyl chlorides to terminal olefins have been also reported to be Markovnikov.^{21,22} These results seemed more compatible with an unsymmetrical episulfonium ion, V.

Our interest in the mechanism of sulfenyl chloride additions to olefins stems from the predominant anti-Markovnikov orientation observed with *O,O*-dimethylphosphorylsulfenyl chloride and terminal olefins.²³

(1) A preliminary account of part of this work has appeared: W. H. Mueller and P. E. Butler, *J. Am. Chem. Soc.*, **88**, 2866 (1966).

(2) To whom inquiries should be directed.

(3) Analytical Research Division.

(4) N. Kharasch in "Organic Sulfur Compounds," Vol. 1, N. Kharasch, Ed., Pergamon Press, Inc., New York, N. Y., 1961, pp 375-396.

(5) Reference 4, I. B. Douglass, pp 350-360.

(6) Reference 4, F. A. Drahowzal, pp 361-374.

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(22) C. Yu. Épshtein, I. A. Usov, and S. Z. Ivin, *J. Gen. Chem. USSR*, **34**, 2362 (1964).

(23) W. H. Mueller, R. M. Rubin, and P. E. Butler, *J. Org. Chem.*, **31**, 3537 (1966).

Table I. Physical-Analytical Data of Methane- and Benzenesulfonyl Chloride-Olefin Adducts

Olefin	Sulfonyl chloride	Isomeric adducts, summary formula	Bp, ^a °C (mm)	Calcd, %			Found, %		
				C	H	S	C	H	S
Ethylene	CH ₃ SOCl	C ₂ H ₅ SOCl	51 (30)	32.58	6.38	28.99	32.41	6.33	29.14
Propylene	CH ₃ SOCl	C ₃ H ₇ SOCl	58–60 (25)	38.55	7.22	25.70	38.62	7.26	26.16
	C ₆ H ₅ SOCl	C ₉ H ₁₁ SOCl	117–118 (5)	57.89	5.93	17.17	58.02	5.86	17.69
Isobutylene	CH ₃ SOCl	C ₄ H ₉ SOCl	68 (27)	43.31	8.00	23.12	43.60	8.15	23.50
3-Methylbutene	CH ₃ SOCl	C ₅ H ₁₁ SOCl	72–73 (17)	47.84	7.31	21.26	47.66	7.23	20.56
	C ₆ H ₅ SOCl	C ₁₁ H ₁₅ SOCl	62–64 (2 × 10 ⁻³)	61.52	7.04	14.93	61.31	7.11	14.95
3,3-Dimethylbutene	CH ₃ SOCl	C ₇ H ₁₅ SOCl	78 (12)	50.43	9.07	19.23	50.63	9.13	19.33
Styrene	CH ₃ SOCl	C ₉ H ₁₁ SOCl	128–129 (10)	57.89	5.93	17.17	57.95	5.87	17.19
Acenaphthylene	CH ₃ SOCl	C ₁₂ H ₁₁ SOCl	Dec	66.51	4.72	13.66	66.43	5.01	13.48
Norbornene	CH ₃ SOCl	C ₈ H ₁₃ SOCl	56–58 (1)	54.37	7.42	18.15	54.20	7.35	18.23
	C ₆ H ₅ SOCl	C ₁₃ H ₁₇ SOCl	102–103 (5 × 10 ⁻³)	65.39	6.33	13.43	65.44	6.68	13.60
Vinyl chloride	CH ₃ SOCl	C ₃ H ₅ SOCl ₂	Dec	24.84	4.17	22.10	24.52	4.05	21.93

^a Uncorrected.

It was conceivable that in this special case one was dealing with a sulfonyl chloride which may tend to polarize in the sense of II owing to the phosphoryl group. Similarly it could be argued that 2,4-dinitrobenzenesulfonyl chloride represents the opposite extreme since one can envision additional stabilization of a positive charge on sulfur by the *o*-nitro group.

Therefore, it was desirable to study the addition of several diverse sulfonyl chlorides to terminal olefins. These model sulfonyl chlorides should possess high reactivity toward double bonds, that is, add spontaneously via an ionic mechanism. With the above considerations in mind methane- and benzenesulfonyl chloride, the simplest representatives of aliphatic and aromatic sulfonyl chlorides, were chosen as model addends. A variety of alkyl-substituted terminal olefins designed to emphasize steric effects of the olefins' substituent on the adduct orientation were employed as substrates. Vinyl chloride and styrene having chlorine or phenyl substituents on the terminal olefins, which are known to support a positive charge on the α -carbon atom, were used to study electronic effects on the adduct orientation.

Results

Methane- or benzenesulfonyl chloride was slowly added to *ca.* 30% solutions of the respective olefin in methylene chloride containing a small amount of calcium carbonate²⁴ suspended in it. With the exception of 1-propene (−78°), the reaction temperatures were maintained at −20 to −25° during the additions. The reaction was in each case spontaneous and exothermic. Upon completion of the addition most of the methylene chloride was removed at −10° and reduced pressure. The initial isomer distribution was obtained by immediate nmr analysis. In general, analytical samples, *i.e.*, mixtures of the two isomers, were obtained by distillation *in vacuo* (Table I).

An *in situ* determination of the adduct isomer ratio had become mandatory since the tendency of certain β -halomercaptides to isomerize has been recognized.²⁴ Initial attempts to use gas chromatography for this purpose proved futile due to the facile rearrangement of the product. Thus, nuclear magnetic resonance spectroscopy became the method of choice.

(24) D. N. Hall, private communication; it was found that small amounts of CaCO₃ prevent isomerization of certain β -halomercaptides.

In general, protons α or β to chlorine are considerably deshielded relative to those α or β to sulfur.^{25,26} The nmr parameters compiled during the present study (Table II) show relative differences in chemical shift for the signals of such α -methylene- or -methine protons on the order of 0.7–1 ppm. Protons β and γ to the center of substitution are still influenced by the nature of the substituent, but to a lesser degree. The respective chemical shift differences observed for β - and γ -hydrogens were *ca.* 0.15–0.30 ppm and 0.01–0.1 ppm. The signals for the α -hydrogens obtained on a 60-Mc instrument were in most cases quite complex particularly since spectra of mixtures of both possible adduct isomers had to be analyzed. However, the previously reported complete analysis of the 100-Mc spectrum of the acetylthiosulfonyl chloride-propylene adduct isomers²⁷ served as a convenient model for the elucidation of the systems encountered during the present study. In every case it was possible to compute the isomer distribution within the desired accuracy from the relative intensity of nonoverlapping signals.

The initial adduct isomer mixture obtained from alkyl-substituted terminal olefins and methane- or benzenesulfonyl chloride contained predominantly the anti-Markovnikov product (Table III). With increasing size of the substituent on the double bond (*e.g.*, going from methyl as in propylene to isopropyl and *t*-butyl as in 3-methylbutene) with 3,3-dimethylbutene higher selectivity for the anti-Markovnikov-oriented product was observed. This selectivity ranged from *ca.* 80 to 95% with methanesulfonyl chloride and was somewhat less with benzenesulfonyl chloride. Two methyl groups *vs.* one methyl substituent on the olefin (*e.g.*, isobutylene *vs.* propylene) did not significantly influence the adduct selectivity using methanesulfonyl chloride.

The initial isomer distribution remained constant if the product was stored over a small amount of CaCO₃ and preferentially at temperatures below 0°. Without the presence of CaCO₃ or a similar base, slow isomerization to the corresponding Markovnikov-oriented products took place. In general, the rearranged isomer ratio contained *ca.* 90% of the Markovnikov product at

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Table II. Nmr Parameters of Sulfinyl Chloride-Olefin Adducts

Olefin	RSCl, R	Group assignments					Chemical shifts, ^a ppm					Coupling constants, ^b cps	
		1	2	3	4	5	1	2	3	4	5		
Ethylene	CH ₃	ClCH ₂	CH ₂	SCH ₃			3.67m ^o	2.82m ^o	2.15s				
Propylene	CH ₃	ClCH ₂	CH	(SCH ₃)	CH ₃		3.36 ^c 3.78	2.83qdd	2.11s	1.35d		$J_{1,2} = 9.5, 4.3; J_{1e} = 10.6; J_{2,4} = 6.3$	
		CH ₃ S	CH ₂	CH(Cl)	CH ₃		2.13s	2.68 ^c 2.98	4.18qdd	1.58d		$J_{2,3} = 8.3, 5.8; J_{2g} = 14.0; J_{3,4} = 6.5$	
		ClCH ₂ C ₆ H ₅ S	CH CH ₂	(SC ₆ H ₅) CH(Cl)	CH ₃ CH ₃		3.0-3.9m 7.25m	2.97 ^c 3.37	7.35m 4.05qdd	1.31d ^d 1.46d		$J_{1,4} \neq 0$ $J_{2,3} = 9.0, 5.3; J_{2g} = 14.0; J_{3,4} = 6.5$	
Isobutylene	CH ₃	ClCH ₂ CH ₃ S	C(SCH ₃) CH ₂ C	(CH ₃) ₂ (CH ₃) ₂			3.59s 2.21s	2.03s 2.91s	1.33s 1.64s				
3-Methylbutene	CH ₃	ClCH ₂	CH	(SCH ₃)	CH	(CH ₃) ₂	3.57 ^c 3.84	2.62ddd	2.13s	2.15m ^e		$J_{1,2} = 8.5, 6.3; J_{1e} = 11.2; J_{2,4} = 3.5$	
		CH ₃ S	CH ₂	CH(Cl)	CH	(CH ₃) ₂	2.15s	2.87d	4.06dt	2.15m ^e		$J_{4,5} = 6.7$ $J_{2,3} = 7.3; J_{3,4} = 3.3; J_{4,5} = 6.7$	
		ClCH ₂	CH	(SC ₆ H ₅)	CH	(CH ₃) ₂	3.57 ^f	3.24m	7.25m	2.39dh		$J_{2,4} = 3.4; J_{4,5} = 6.8$	
		C ₆ H ₅ S	CH ₂	CH(Cl)	CH	(CH ₃) ₂	7.30m	3.08 ^c 3.36	3.97ddd	2.23dh		$J_{2,3} = 8.0, 6.3; J_{2g} = 14.3; J_{4,5} = 6.7$	
3,3-Dimethylbutene	CH ₃	ClCH ₂	CH	(SCH ₃)	C(CH ₃) ₃		3.54 ^c 3.94	2.43dd	2.17s	1.04s		$J_{1,2} = 7.5, 4.8; J_{1g} = 11.5$	
		CH ₃ S	CH ₂	CH(Cl)	C(CH ₃) ₃		2.13s	2.61 ^c 3.01	3.82dd	1.02s		$J_{2,3} = 10.0, 3.3; J_{2g} = 14.5$	
												$J_{2,3} = 6.5$ $J_{2,3} = 6.3$	
Vinyl chloride	CH ₃	ClCH ₂ CH ₃ S	CH CH ₂	(SCH ₃) CH	Cl (Cl) ₂		3.94d 2.22s	5.23t 3.23d	2.28s 5.88t			$J_{2,3} = 6.5$ $J_{2,3} = 6.3$	
Styrene	CH ₃	CH ₃ S	CH ₂	CH(Cl)	C ₆ H ₅		1.78s	2.93 ^c 3.19	4.91dd	7.23m		$J_{2,3} = 8.3, 6.8; J_{2g} = 14.0$	
		ClCH ₂	CH	(SCH ₃)	C ₆ H ₅		3.83 ^f		1.77s	7.23m			
1,1-Diphenyl-ethylene ^a	CH ₃	CH ₃ S	CH ₂	C	(C ₆ H ₅) ₂		1.62s	3.60s		7.24m			
		ClCH ₂	C	(SCH ₃)	(C ₆ H ₅) ₂		4.33s		1.63s				

^a Abbreviations used: s, singlet; d, doublet; t, triplet; q, quartet; dd, double doublet; qdd, quartets of double doublet; ddd, doublets of double doublet; dt, double triplet; dh, double heptet. ^b g = geminal. ^c Protons 1 and 2 (or 2 and 3) form the AB part of an ABX system; the chemical shifts are approximated from a first-order analysis of the pair of overlapping quartets. ^d Protons 1, 2, and 4 form a virtually coupled ABCX₂ system ($J_{1,4} = 0$); the methyl group appears as a doublet with additional interior lines. ^e The signal for this group is obscured by other peaks. ^f Protons 1 and 2 form the ABC part of an ABCX_n system; the chemical shifts are estimated from the center of the multiplet. ^g Protons from an AA'BB' type system. ^h Spectra were obtained at -30°.

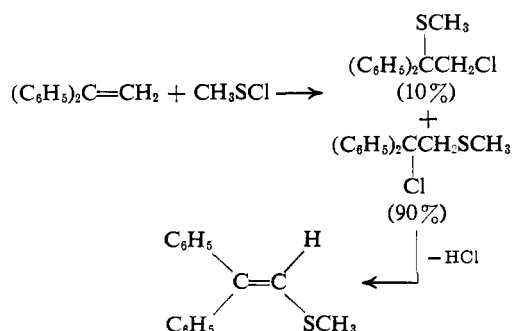
Table III. Methane- and Benzenesulfonyl Chloride-Olefin Adducts

Reactants		% adduct ratio ^a			
		Initial		Rearranged	
		CH ₂ -C< Cl SR	CH ₂ -C< SR Cl	CH ₂ -C< Cl SR	CH ₂ -C< SR Cl
CH ₂ =CHCH ₃	CH ₃ SCl	82	18	12	88
CH ₂ =C(CH ₃) ₂	CH ₃ SCl	80	20	17	83
CH ₂ =CHCH(CH ₃) ₂	CH ₃ SCl	94	6	10	90
CH ₂ =CHC(CH ₃) ₃	CH ₃ SCl	95	5	11	89
CH ₂ =CHCH ₃	C ₆ H ₅ SCl	68	32	15	85
CH ₂ =CHCH(CH ₃) ₂	C ₆ H ₅ SCl	87	13	15	85
CH ₂ =CHC ₆ H ₅	CH ₃ SCl	2	98		
CH ₂ =C(C ₆ H ₅) ₂	CH ₃ SCl	10	90		
CH ₂ =CHCl	CH ₃ SCl	77	23		

^a The adduct ratio was calculated from the relative intensity of their characteristic nmr signals.

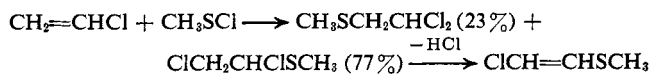
equilibrium.²⁸ At ambient temperature equilibration had usually taken place after *ca.* 200 hr. Catalytic amounts of acids (*e.g.*, mineral acid or acetic acid) were found to accelerate this rearrangement by a factor of 5 to 10. The initial adduct mixtures from benzenesulfonyl chloride isomerized at a considerably slower rate than those obtained from methanesulfonyl chloride.

Predominantly Markovnikov-oriented adducts were obtained from phenyl-substituted terminal olefins and methanesulfonyl chloride. This adduct selectivity was 98% with styrene and 90% with 1,1-diphenylethylene. The styrene adduct did not show any tendency to rearrange at ambient temperature. Partial rearrangement to the anti-Markovnikov adduct could only be achieved under more stringent conditions such as heat and acid catalysis. The major adduct from 1,1-diphenylethylene had only limited stability even at temperatures below -20°. At ambient temperature spontaneous dehydrohalogenation took place.



Thus, its propensity for rearrangement could not be established.

The anti-Markovnikov adduct was formed in 77% selectivity upon reaction of methanesulfonyl chloride with vinyl chloride. Little tendency for post isomerization of the adduct was observed on standing at ambient temperature. However, slow loss of hydrogen chloride took place, *i.e.*,

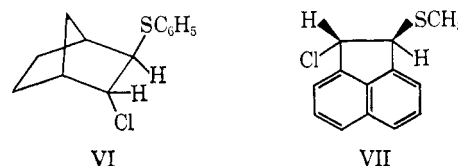


It was felt that the observed rearrangement of the initial adducts made it necessary to reexamine the stereo-

(28) Pure 1-methylmercapto-2-chloropropane was obtained from free-radical addition of methylmercaptan to 2-chloropropene. It isomerized to an identical 12:88% isomer ratio as obtained from rearrangement of the "initial" methanesulfonyl chloride-propylene adduct.

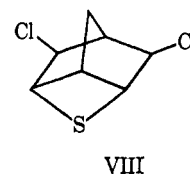
chemistry of such additions. With the choice of proper model substrates nmr spectroscopy provided a useful tool for the important *in situ* determination of the adducts' stereochemistry. This was particularly warranted since the previous support for the *trans* configuration of the adducts was indirect and did not preclude isomerization prior to the stereochemical analysis.^{12,16}

Exclusive *trans* addition to both norbornene and acenaphthylene (VI and VII) has been confirmed during the present study. Nmr spectra and parameters in

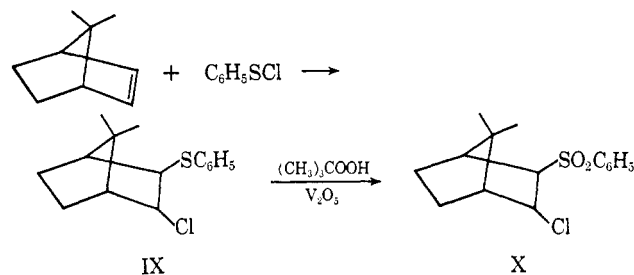


support of the structure assignment of both adducts have been published previously.^{1,27}

The exclusive *exo* position of the mercapto group on VI is in contrast to the reported *endo*-sulfide VIII which had been obtained from norbornadiene and sulfur dichloride.²⁹ Therefore, it was of interest to see if



endo-mercaptides would result from sulfonyl chloride additions to 7,7-dimethylnorbornene.³⁰ Benzenesulfonyl chloride and 7,7-dimethylnorbornene afforded the *exo*-phenylmercapto-*endo*-chloro derivative IX in *ca.* 85% selectivity. Gas chromatography of the product revealed several minor by-products with similar glpc retention time, presumably isomers of IX.

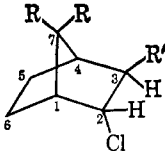


(29) F. Lautenschlaeger, *J. Org. Chem.*, **31**, 1679 (1966).

(30) A sample of 7,7-dimethylnorbornene was graciously supplied by Professor H. C. Brown.

The structure assignment of compound IX is based mainly on characteristic nmr signals observed for the methine hydrogens adjacent to chlorine (H_2) and to sulfur (H_3). The spectral parameters of IX and those of the corresponding sulfone X and the norbornene adduct VI are summarized in Table IV. In each case a double triplet at *ca.* 4 ppm appears for H_2 . Its *exo* position is determined by the observed coupling of H_2 with H_1, H_3 and H_{6-exo} .²⁷ The *endo* position of H_3 in norbornane systems is manifested in its coupling with only H_2 and H_{7-anti} . Thus, a double doublet appears for H_3 of the norbornane adduct VI and only a doublet for H_3 of the 7,7-dimethylnorbornane analogs IX and X.

Table IV. Nmr Parameters of Benzenesulfonyl Chloride-Norbornene and -7,7-Dimethylnorbornane Adducts^a



VI, R = H; R' = SC₆H₅
 IX, R = CH₃; R' = SC₆H₅
 X, R = CH₃; R' = SO₂C₆H₅

Compd	Chemical shifts, ppm		Coupling constants, cps			
	H ₂	H ₃	J _{1,2}	J _{2,3}	J _{2,6-exo}	J _{3,7-anti}
VI	3.98dt	3.04dd	4.1	3.9	1.0	2.6
IX	4.08dt	3.69d	4.3	4.7	0.9	...
X	3.95dt	4.37d	4.5	5.2	0.9	...

^a Notation as in Table II; samples were run as 50% solutions in deuteriochloroform.

Hydrogen H_3 (3.69 ppm) in adduct IX is considerably deshielded in comparison to H_3 (3.04 ppm) of the norbornene adduct VI. Therefore, it was felt necessary to verify its assignment by oxidation of IX to its corresponding sulfone X. As expected, the signal for H_3 (4 ppm) of the sulfone experiences a paramagnetic shift while the position of the signal for H_2 was relatively unaffected.

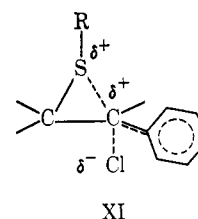
Comparison of the coupling constants $J_{1,2}$ and $J_{2,3}$ of compounds VI, IX, and X (Table IV) shows clearly an increase in magnitude with the presence of methyl groups in the 7 position of the norbornane system and a further increase with the change of the phenylmercapto group to the sulfone. Apparently steric interaction of the 7-methyl substituent with the *exo*-phenylmercapto group distorts the bond angles of the norbornane structure which changes the relative spacial arrangement of the hydrogens in question. This becomes even more evident in case of the more bulky sulfone.

Discussion

An examination of the results obtained in the present study and consideration of previously reported work on this topic clearly show that no single mechanistic picture can accommodate all the data. It is apparent that the nature of the substituents on both the olefin and on the sulfonyl chloride itself significantly influences the course of such a reaction.

The high selectivity for the anti-Markovnikov-oriented products observed with alkyl-substituted terminal olefins and, in particular, the increase of this selectivity with the size of the alkyl substituent demonstrates that steric factors can control the ring opening of the episulfonium ion intermediate. This finding appears to be unambiguous evidence for a bridged episulfonium ion IV and is completely consistent with the expectation of a nucleophilic attack of the chloride ion on the episulfonium ion intermediate. In analogy to S_N2 displacement reactions on alkyl halides, steric requirements of alkyl substituents on the carbons involved in an episulfonium ion were expected to be of importance.

Phenyl substituents on the olefin, however, cause reversal of the direction of ring opening, *i.e.*, Markovnikov adduct orientation. This may be explained by a lower transition-state energy of XI relative to that arising from attack of the chloride on the terminal carbon. Stabilization of the transition state XI is due to π -bond



overlap of the p orbital of the electron-deficient α -carbon with the phenyl ring's π cloud. The factors influencing the ring opening are again reminiscent of those invoked for displacement reactions on benzylic halides.^{31a}

The observed *trans*-stereospecific addition to norbornene is also consistent with a bridged episulfonium ion. The result with this model, however, may not reflect the degree of bridging or the occurrence of a carbonium ion when a benzylic carbon is involved as in the case of styrene. Therefore, only the observed *trans*-stereospecific addition to acenaphthylene validates our mechanistic interpretation as expressed by XI. The decreased selectivity for the Markovnikov adduct with 1,1-diphenylethylene also supports the attack of chloride on a bridged rather than on an open ion. In this case two geminal phenyl groups cause some competition between the steric requirements and the electronic factors which would be less likely for a S_N1-type reaction.

The well-recognized dual role that chlorine may play in the stabilization (destabilization) of an electron-deficient center rendered interest in the course of the methanesulfonyl chloride addition to vinyl chloride. Predominant anti-Markovnikov orientation of the resultant adduct indicates that overlap of the central p orbital of the α -carbon with a p orbital of the adjacent chlorine (similar to XI) does not significantly contribute to lowering the energy of the transition-state resonance hybrid. In fact, destabilization of an electron-deficient α -carbon by the electron withdrawal, along with possible steric hindrance to attack by the incoming chloride, explains our result. Again our finding on the ring opening of this episulfonium ion is

(31) Andrew Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962: (a) pp 13-15; (b) p 25.

paralleled by the previously reported retardation of displacement rates by α -chloro substituents.^{31b}

The nature of the R group on the sulfenyl chloride has an equally important influence on the adduct orientation as the above-discussed substituents of the olefinic substrates. This can be most dramatically demonstrated with the addition of several diverse sulfenyl chlorides to isobutylene (Table V).

Table V. Influence of R on the Episulfonium Ion

$\text{XV} \rightleftharpoons \text{XVI} \rightleftharpoons \text{XVII}$
 $\text{XV} \xrightarrow{\text{Z}^-} \text{XII}$
 $\text{XVI} \xrightarrow{\text{Z}^-} \text{XIII}$
 $\text{XVII} \xrightarrow{\text{Z}^-} \text{XIV}$

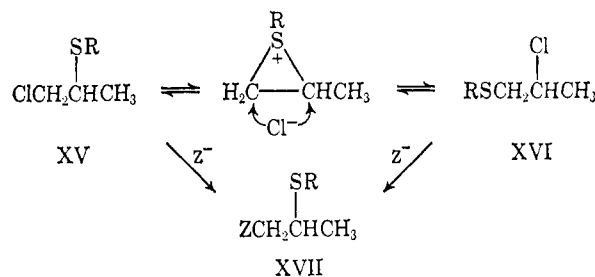
R	~% product distribution~		
	XII	XIII	XIV
CH ₃	80	20	0
CH ₃ C(O)S	32	68	0
(CH ₃ O) ₂ P(O)	19	57	21

As expected, the adduct distribution from methanesulfenyl chloride and isobutylene shows little difference from that of propylene. However, the electron-withdrawing effect of the acetyl group when R is CH₃(CO)S tends to destabilize the positive charge on the sulfur atom in the episulfonium ion, thus contributing to the development of an electron-deficient center on the substituted carbon atom. This results in predominant Markovnikov addition to isobutylene. Although no evidence for a true carbonium ion intermediate had been detected in an extensive study with acetylthiosulfenyl chloride additions to a variety of unsaturates,³² it appears that in the case of isobutylene the transition state must closely resemble a carbonium ion in order to receive stabilization by the methyl substituents.

The effect of an electron-withdrawing R group on the mechanism of sulfenyl chloride additions to olefins becomes even more apparent with O,O-dimethylphosphorylsulfenyl chloride.²³ In contrast to acetylthiosulfenyl chloride, here the electronegative phosphoryl group is directly bonded to the sulfur atom participating in the episulfonium ion. This apparently impairs the sulfur's bridging ability sufficiently to allow for the formation of olefin XIV in the case of isobutylene. The expulsion of a proton and formation of product XIV is strongly reminiscent of the disciplines observed in carbonium ion chemistry, particularly since no indication for its formation *via* dehydrohalogenation of XIII had been found.

Further evidence for the important influence of R on the sulfur atom participating in the episulfonium ion stems from the differing propensity for rearrangement of the kinetically controlled (initial) adducts XV to the thermodynamically more stable Markovnikov products XVI, *e.g.*

(32) W. H. Mueller and P. E. Butler, *J. Org. Chem.*, **32**, 2925 (1967).



Facile isomerization was observed with R being methyl. Benzenesulfenyl chloride adducts, however, rearrange much more slowly, whereas little or no tendency for post-isomerization had been found with acetylthiosulfenyl chloride or O,O-dimethylphosphorylsulfenyl chloride adducts, respectively. The relative electronegativity of R decreases the availability of the unshared electrons on the sulfur atoms and impairs or prevents participation in S_N2 displacement of the chlorine.

Finally, strong support for the intermediacy of a bridged ion, particularly during the rearrangement, is derived from displacement reaction with various nucleophiles, *e.g.*, acetate ion, on either adduct isomer XV or XVI.³³ Displacement on the anti-Markovnikov adduct XV, as well as displacement on the Markovnikov adduct XVI, affords products of identical isomer distribution. The product mixtures contain isomer XVII in high selectivity and in a similar distribution as was obtained from sulfenyl chloride addition to propylene, provided that the nature of nucleophile Z does not allow post-isomerization of product XVII.

In conclusion it has been shown that sulfenyl chloride additions to monoolefins can involve a wide range of subtly different reaction mechanisms. These may range from an episulfonium ion with little charge on the carbon atoms to an intermediate approaching an open carbonium ion in extreme cases. Variables neglected in this study, such as solvent effects, reaction temperature, etc., are also expected to be of major importance for the reaction course.

Experimental Section

Nmr Analyses. Neat samples containing tetramethylsilane as an internal standard were run on a Varian A-60 spectrometer at ambient temperature unless stated otherwise.

Starting Materials. Dimethyl disulfide, diphenyl disulfide, and 1,1-diphenylethylene were obtained from Eastman Organic Chemicals Company. Propylene (99.7% purity), ethylene (99.5% purity), isobutylene (>99% purity), and vinyl chloride (99.9% purity) were Matheson products. The 3-methyl-1-butene (99%) was from Phillips Chemical Company. All these materials were used as such. Styrene was freshly distilled and norbornene freshly sublimed prior to their use. Acenaphthylene from Columbia Organic Company was recrystallized three times from hexane, mp 92–93°.

Methanesulfenyl Chloride. The previously reported preparation³⁴ from dimethyl disulfide and sulfur chloride was slightly modified by omitting tetrachloroethane as a solvent. The distilled methanesulfenyl chloride was obtained in *ca.* 90% yield and >98% purity as indicated by its nmr spectrum which shows a singlet at 2.91 ppm (dimethyl disulfide shows a singlet at 2.41 ppm).

Benzenesulfenyl Chloride. Freshly distilled sulfur chloride (20.3 g; 0.15 mol) was slowly added at ambient temperature to a solution of 32.7 g (0.15 mol) of diphenyl disulfide in 100 ml of CH₂Cl₂ (dry) containing 3 ml of pyridine. After completion of the addition, the solution was stirred for an additional hour, and

(33) W. A. Thaler and W. H. Mueller, data to be published.

(34) H. Brintzinger, K. Pfau, H. Koddebusch, and K. Kling, *Ber.*, **83**, 87 (1950).

then the solvent was removed at ambient temperature (12 mm). Subsequent distillation of the residue afforded 33 g (76% yield) of the dark red benzenesulfonyl chloride, bp 49° (4 mm), n_D^{20} 1.613 (lit.³⁵ n_D^{20} 1.610).

General Procedure for the Addition of Methane- or Benzenesulfonyl Chloride to Olefins. An equimolar amount of methane- or benzenesulfonyl chloride was slowly added to a ca. 30% solution of the olefin in dry methylene chloride. The solution had a small amount of calcium carbonate (ca. 50 mg in a 0.1 M reaction) suspended in it. The reaction was carried out under a nitrogen atmosphere, and reaction temperatures were in general maintained at -20 to -25° during the addition. The low boiling point of propylene and ethylene made slightly different reaction conditions necessary. Additions to propylene were carried out at -78°, and in the case of ethylene the gaseous unsaturate was slowly introduced into a methylene chloride solution of methanesulfonyl chloride at -30°. All reactions were strongly exothermic and took place spontaneously. Decolorization of the orange sulfonyl chloride indicated completion of the reaction. This is particularly helpful if the olefin is introduced into the sulfonyl chloride. Immediately after completion of the addition the solvent was removed under reduced pressure at -5 to -10° and the adducts' isomer ratio (Table III) determined by nmr spectroscopy. All products were pale yellow oils which were formed in essentially quantitative yield. In general, analytical samples of mixtures of the two isomers were obtained by distillation *in vacuo* (Table I).

The methanesulfonyl chloride adduct of acenaphthylene and vinyl chloride decomposed on attempted distillation. Satisfactory elemental analyses were obtained from the "crude" products. Attempts to crystallize the acenaphthylene adduct were unsuccessful.

endo-2-Chloro-exo-3-phenylthio-7,7-dimethylnorbornane (IX). A solution of 1.83 g (0.015 mol) of 7,7-dimethylnorbornane in 10 ml of dry methylene chloride was allowed to react with 2.17 g (0.015 mol) of benzenesulfonyl chloride at -25° according to the general procedure. After the addition was complete, the solvent was removed at -5° (1 mm). Semiquantitative nmr analyses of the crude product (3.9 g) indicated the formation of adduct IX in ca. 85% selectivity. Pertinent nmr data of this compound are summarized in Table IV. Gas-liquid partition chromatography on a 3-ft column packed with 3% Dowfax 9N40 on 60-80 mesh Gas Chromosorb P revealed several minor compounds (a total of ca. 15 area %) with similar retention time to that of the major product.

(35) I. B. Douglass, K. R. Brower, and P. I. Murrin, *J. Am. Chem. Soc.*, **74**, 5570 (1952).

Distillation *in vacuo* afforded a +95% pure sample of IX, bp 106-107° (5×10^{-5} mm), which solidified to give a colorless wax, mp 35-38°.

Anal. Calcd for $C_{15}H_{19}SCl$: C, 67.52; H, 7.18; S, 12.02. Found: C, 67.31; H, 7.25; S, 12.16.

endo-2-Chloro-exo-3-phenylsulfonyl-7,7-dimethylnorbornane (X). A sample of 1.066 g (0.004 mol) of adduct IX was dissolved in 2 ml of dry benzene containing a catalytic amount of vanadium pentoxide. The solution was heated to 55° and 0.792 g (0.0088 mol) of *t*-butyl hydroperoxide slowly added. The strongly exothermic reaction was controlled by removing the heating bath and utilizing a slow rate of *t*-butyl hydroperoxide addition. After completion of the addition the reaction mixture was heated for 1 hr at 60°, then 10 ml of benzene added, the vanadium pentoxide removed by filtration and the solvent removed on a rotary evaporator. The crude product, 1.1 g of a tan solid, mp 108-112°, was treated with charcoal and recrystallized from ether. The pure sulfone X (0.98 g; 88% yield) was obtained as colorless crystals, mp 112-114°. Pertinent nmr parameters of X are recorded in Table IV.

Anal. Calcd for $C_{15}H_{19}SO_2Cl$: C, 59.98; H, 6.88; S, 10.68. Found: C, 59.62; H, 6.95; S, 11.18.

Addition of Methanesulfonyl Chloride to 1,1-Diphenylethylene. To a solution of 3.15 g (0.0175 mol) of 1,1-diphenylethylene in 5 ml of dry methylene chloride (high concentration suitable for direct nmr analysis) containing 10 mg of $CaCO_3$, 1.445 g (0.0175 mol) of methanesulfonyl chloride was slowly added at -50°. The obtained isomer distribution (Table III) was then determined by low-temperature nmr (Table II). Violent HCl evolution and darkening of the product took place at ambient temperature. This decomposition occurred also with a more moderate rate (ca. 80 hr) at -20°. The black solution was dissolved in 50 ml of ether, washed with 5% aqueous $NaHCO_3$ solution followed by water, and dried over $MgSO_4$, and then the solvent removed on a rotary evaporator. The crude product, a dark solid, was treated with charcoal and recrystallized from ether-pentane. A colorless crystalline compound (2.7 g) melting at 70-71.5° was obtained. Its nmr spectrum (50% solution in CCl_4) characterized by singlets at 2.25, 6.50, 7.17, and 7.28 ppm and elemental analysis were consistent with 1,1-diphenyl-2-methylthioethylene.

Anal. Calcd for $C_{15}H_{14}S$: C, 79.60; H, 6.23; S, 14.26. Found: C, 79.99; H, 6.30; S, 14.02.

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