Reaction of Bromo Radical 10 with Dimethyl Maleate. A mixture of 0.200 g of dibromocyclobutene **11** and 0.100 g of dimethyl maleate was degassed by several freeze–thaw cycles, and 3.0 ml of degassed, dry triglyme was distilled into the mixture. After freezing the mixture in liquid nitrogen, 10 g of mercury was poured onto the frozen organics from a side arm. The mixture was allowed to thaw, and then was heated with rapid stirring on a steam bath for 15 min. During the heating the solution turned deep green, then faded to a golden yellow. After cooling, the vacuum was released, and the solution was decanted from the mercury into water. After standing overnight, a solid precipitated and was filtered off. The solid was extracted with methylene chloride and filtered. The undissolved solid was soluble in ammonium hydroxide (presumably HgBr). The filtrate was diluted with ethanol and then concentrated until the odor of methylene chloride could no longer be detected in the vapors. Cooling the solution yielded 0.054 g (54%) of dimethyl fumarate (identified by ir). Further concentration of the mother liquor gave 0.108 g of yellow solid. Thin layer chromatography indicated this solid contained at least five components with no one predominating.

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The Influence of Substituents on the Direction of Episulfonium Ion Ring Opening

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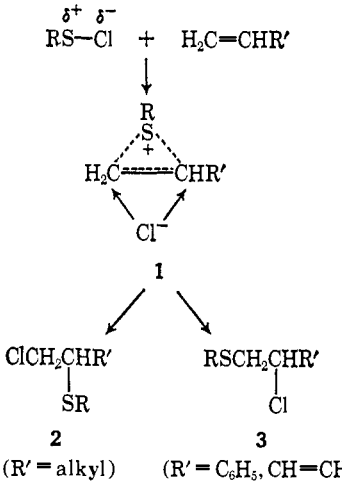
Abstract: The reactions of methanesulfenyl chloride with α,β-unsaturated carbonyl, nitrile, and sulfone systems have been investigated, and the relative distribution of isomeric adducts determined. It was also demonstrated that under the conditions used for reaction and analysis the isomer ratios were truly representative of the kinetically controlled reaction and not the result of a subsequent rearrangement to the thermodynamically preferred isomer. On this basis it was possible to obtain data concerning the influence of functional group substituents on the direction of the ring-opening attack by chloride ion on each of the episulfonium ion intermediates. The data indicate that steric factors are quite important, preferential attack occurring at the least substituted carbon unless the functional group provides strong activation for attack on the adjacent carbon. The relative ability of the functional groups to activate the α position to attack by chloride ion parallels the well-known activation of α-halocarbonyl and related compounds toward nucleophilic displacements. The extent of episulfonium ion ring opening by attack at the α carbon decreases with decreasing ability of the functional group to accommodate a nucleophile (acid chloride > ester > amide > nitrile > sulfone). The striking resemblance between α activation in nucleophilic displacement on α-halocarbonyl compounds, and activation of the α position toward chloride ion attack in the ring opening of similarly substituted episulfonium ions, suggests that similar transition-state structures in which the nucleophile is partially bonded to both the α-carbon and the functional group are important and serve to lower the energy for attack at the α position.

Kharasch and Buess[2] postulated a mechanism involving a cyclic episulfonium ion intermediate to explain the *trans* addition of 2,4-dinitrophenylsulfenyl chloride to olefins. Episulfonium ion intermediates have also been proposed to account for the unusual anti-Markovnikov orientation and *trans* stereochemistry of products from the addition of alkyl- and arylsulfenyl chlorides to olefins.[3] Both observations are consistent with a cyclic intermediate which is opened by chloride attack from a direction *trans* to the sulfur bridge.

When R′ is an alkyl substituent, the predominant ring-opening reaction occurs by attack at the terminal carbon giving the kinetically controlled anti-Markovnikov product **2**. The bonding of the chloride to the terminal position is inconsistent with an open carbonium ion and is explained more satisfactorily by invoking a cyclic intermediate **1**. The product structure would then be determined by factors influencing the



direction of the ring opening. Steric factors appear to be quite important with nonconjugated olefins since chloride ion preferentially attacks the least hindered terminal carbon giving the primary chloride.[3]

In contrast, the addition of sulfenyl chlorides to conjugated olefins[4] (R′ = C_6H_5, vinyl) gives the Mar-

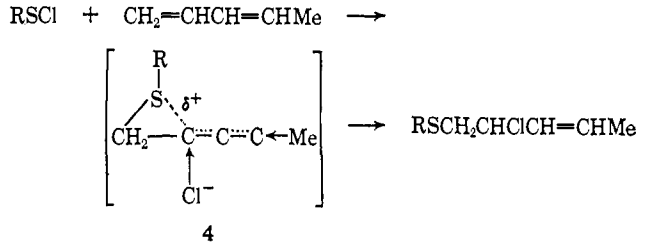
(1) To whom inquiries should be directed.
(2) N. Kharasch and C. M. Buess, *J. Am. Chem. Soc.*, 71, 2724 (1949).
(3) W. H. Mueller and P. E. Butler, *ibid.*, 88, 2866 (1966).

Table I. Isomer Distributions of Adducts from the Reaction of CH_3SCl with Functionally Substituted Ethylenes

Reactant	Adduct ratio, %: Initial product, Y = H	Initial product, Y = CH_3	Rearranged product[a], Y = H	Rearranged product[a], Y = CH_3
Acrylyl chloride (X = COCl)	94[b]	6	62	38
Methacrylyl chloride (X = COCl)	52[b]	48	No change[e]	
Methyl acrylate (X = $COOCH_3$)	83[b]	17	27	73
Methyl methacrylate (X = $COOCH_3$)	24[b]	76	53	47
t-Butyl acrylate (X = $COOC(CH_3)_3$)	81	19	69[c]	31
Methacrylamide (X = $CONH_2$)	8	92	76[d]	24
Acrylonitrile (X = CN)	51[b]	49	No change[e]	
Methacrylonitrile (X = CN)	...	>98[b]	No change[e]	
Methyl vinyl sulfone (X = SO_2CH_3)	...	>98	No change[e]	

[a] Heated with trace of acid unless otherwise specified. [b] No rearrangement upon distillation. [c] Rearranged upon distillation. [d] Rearranged on standing at ambient temperature. [e] No rearrangement after heating at 60° in the presence of acid.

kovnikov product orientation **3**; nevertheless, the absence of 1,4 adducts from the additions of methanesulfenyl chloride (CH_3SCl) or benzenesulfenyl chloride (C_6H_5SCl) to dienes suggests that episulfonium ion intermediates are involved since allylic carbonium ions would be expected to give at least some substitution in the 4 position. The Markovnikov orientation is attributed to electronic control of the ring opening due to the ability of the phenyl or vinyl substituents to enhance stabilization of a partial positive charge on carbon.



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The exclusive *trans* addition of methanesulfenyl chloride to acenaphthylene[3] lends further credence to an episulfonium ion mechanism for reactions with conjugated olefins while the absence of any influence of temperature on the stereospecific additions to *cis*- or *trans*-2-butene[5] provides additional support for the absence of open carbonium ion intermediates in nonconjugated systems.

Recent work in this laboratory has demonstrated that the initial products from sulfenyl chloride addition to unsaturated hydrocarbons frequently undergo facile rearrangement in which the RS and Cl groups exchange positions to give the thermodynamically more stable isomer.[3] This presented a serious problem if one wished to utilize product distribution to determine the direction of ring opening in the episulfonium ion intermediate. This problem had been circumvented by running the reactions at low temperatures in the presence of traces of base ($CaCO_3$), and utilizing nmr spectroscopy to characterize products, rather than chemical techniques which could lead to rearrangement.[3] Consequently, the direction of the ring-opening reaction of episulfonium ions derived from simple olefins and conjugated olefins can now be predicted.

Reactions of sulfenyl chlorides with various electronegatively substituted ethylenes have been reported;[6] however, the results are frequently contradictory, and the mechanism is continually being disputed in the literature.[6f] Presumably, the elucidation of the mechanism of these reactions has been hampered in part by the isomerization of the β-chloro sulfide products prior to or during analysis. In order to determine the role of electronegative substituents in sulfenyl chloride additions, a systematic investigation of such reactions has been undertaken with the goal of providing some additional insight into the features influencing the direction of episulfonium ion ring opening.

Results

The isomer distributions of initial adducts and rearrangement products derived from the reaction of methanesulfenyl chloride with acrylates, methacrylates, and their acid chloride, amide, nitrile, and sulfone analogs are summarized in Table I. In general the reactions were carried out at −65° in methylene chloride solution in the presence of a small quantity of calcium carbonate. The sulfenyl chloride was added dropwise with efficient stirring to the acrylate solution, and the reaction mixture was analyzed when the color of sulfenyl chloride was absent, or when the solution became pale yellow and did not change color any further. The gross reaction mixture was analyzed by nmr; the solvent was removed under reduced pressure while maintaining the solution at 0°. The purity (absence of solvent and unreacted starting material) was confirmed by vpc analysis and the product reanalyzed by nmr. When possible, the products were distilled and subjected to vpc, nmr, and elemental analyses. The products were reexamined at later dates,

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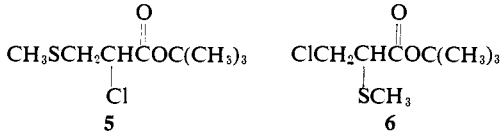
or warmed with traces of acid when possible, to determine if rearrangement was occurring.

The structure of each isomeric product was established by detailed analysis of its nuclear magnetic resonance spectrum. For example, the structure of methanesulfenyl chloride–*t*-butyl acrylate adducts, which exhibited one of the most complex spectra (Figure 1) encountered during the course of this work, was evaluated in the following manner. The presence of the CH_3S and $CO(CH_3)_3$ groups was revealed by characteristic singlets at 2.19 and 1.49 ppm in a 1:3 ratio. The methylene–methine region of the spectrum was complex due to the overlapping ABX and ABC systems of each isomer. In regard to the Markovnikov[7] product **5** the methylene protons next to sulfur are

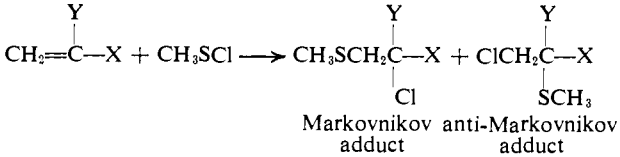


5 **6**

nonequivalent due to their proximity to the asymmetric center and appear as a pair of double doublets at 2.83 and 3.16 ppm (J_{gem} = 13.6 cps). These protons are coupled unequally to the methine proton (J_{vic} = 6.2, 8.5 cps) which is a double doublet at 4.27.

The reverse isomer **6** has the chlorine on the methylene group and the sulfur is next to the methine proton. In this case the chemical shift difference between the two groups is at a minimum resulting in a more closely coupled ABC spectrum. Using first-order approximations, the resonance pattern of the methylene–methine area was analyzed. The methylene protons are again nonequivalent due to the asymmetry of the molecule and appear as an overlapped pair of double doublets (J_{gem} = 10.3 cps) with chemical shifts of 3.65 and 3.93 ppm. They are coupled (J_{vic} = 10.3, 4.4 cps) to the highly perturbed double doublet for the methine proton at 3.44 ppm. Quantitative data were obtained by measuring the relative amounts of the methylene–methine protons on an expanded scale. Similar considerations were used to assign structures and measure the relative amounts of isomers from the other sulfenyl chloride adducts obtained during this study. The somewhat less complex spectra of these products are summarized in Table II.

Two classes of compounds were examined, monosubstituted ethylenes (Y = H and X = CO_2CH_3, $CO_2C(CH_3)_3$, C(O)Cl, $C(O)NH_2$, CN, SO_2CH_3, C(O)-CH_3) and their methyl derivatives (Y = CH_3).



Markovnikov adduct — anti-Markovnikov adduct

The presence of the methyl substituent (Y = CH_3) favored anti-Markovnikov product to a greater extent than the analogous ethylenic reactant (Y = H); however, the extent of Markovnikov orientation obtained from reactions with either of the two classes of compounds was quite sensitive to the nature of X. For example, the isomeric product distribution ranged from 94% Markovnikov orientation with acrylyl chloride to >98% anti-Markovnikov orientation with the vinyl sulfone.

(7) The structures which have chlorine on the carbon containing the least hydrogens (secondary or tertiary carbons) are considered to have a Markovnikov orientation while the opposite isomers which have the chlorine on the carbon containing the greatest number of hydrogens (primary carbon) have been designated as the anti-Markovnikov products.

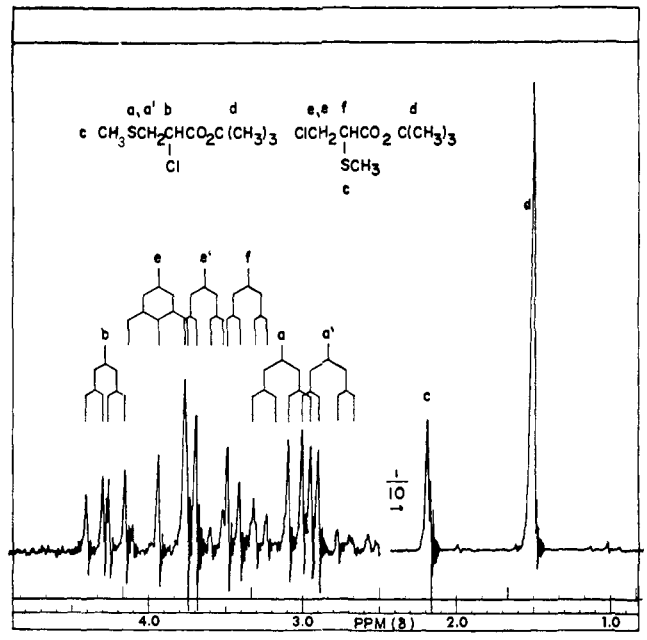
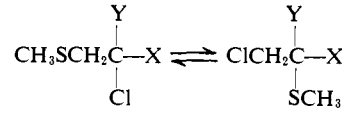


Figure 1.

Kinetic control of the product composition was substantiated by demonstrating that the thermodynamically preferred isomer had an orientation which was the reverse of the initial product (Table I). Although a few of the products rearranged spontaneously on standing at room temperature or during distillation, rearrangements were generally accomplished by warming the initial products in the presence of traces of acid. In a few instances the products could not be induced to rearrange under conditions short of decomposition.



During preliminary experiments we observed that contrary to earlier reports of equal quantities of Markovnikov and anti-Markovnikov adducts from the addition of alkanesulfenyl chlorides to methyl acrylate,[6c,d,f] the isomer with the Markovnikov orientation was the major reaction product when precautions were taken to keep the reaction free from traces of acid. Repeat experiments during which low-temperature nmr's were obtained immediately after addition of the reagent indicated the same 83% Markovnikov orientation. Reactions using pentane or dimethylformamide as solvents in place of methylene chloride continued to exhibit the same isomer composition despite the large difference in reaction rate (increasing with solvent polarity). Treatment of the distilled products with excess trimethylamine rapidly precipitated trimethylamine hydrochloride corresponding to 12% conversion of the reaction product. Prolonged heating was unsuccessful at bringing about further reaction. The minor adduct rapidly eliminates hydrogen chloride

Table II. Nmr Parameters of Sulfenyl Chloride Adducts[a]

Olefin reactants	Anti-Markovnikov adducts: Group assignments 1	2	3	4	Chemical shift, ppm 1	2	3	4	Coupling constant, J, cps J_{gem}	$J_{1,2}$	Markovnikov adducts: Group assignments 1	2	3	4	Chemical shift, ppm 1	2	3	4	Coupling constant, J, cps J_{gem}	$J_{2,3}$
CH_2=CHCOCl	$ClCH_2$	CH	(SCH_3)	COCl	—3.85 m—		2.23 s				CH_3	SCH_2	CH(Cl)	COCl	2.23 s	2.98 dd 3.25 dd	4.72 dd		14.5	6.5 8.0
CH_2=$C(CH_3)$COCl	$ClCH_2$	$C(CH_3)$	(SCH_3)	COCl	3.60 d 4.08 d	1.69 s	2.25 s		11.0		CH_3	SCH_2	$C(CH_3)Cl$	COCl	2.12 s	3.07 d 3.27 d	1.92 s		14.1	
CH_2=$C(CH_3)CONH_2$	$ClCH_2$	$C(CH_3)$	(SCH_3)	$CONH_2$	3.57 d 4.07 d	1.58 s	2.12 s	~7.2 b	11.3		CH_3	SCH_2	$C(CH_3)Cl$	$CONH_2$	2.21 s	2.99 d 3.27 d	1.82 s	~7.2 b	14.1	
CH_2=$CHCO_2CH_3$	$ClCH_2$	CH	(SCH_3)	CO_2CH_3	3.35 m	4.12 m	2.17 s	3.76 s			CH_3	SCH_2	CH(Cl)	CO_2CH_3	2.17 s	2.86 dd 3.16 dd	4.41 dd	3.79 s	14.0	6.4 8.4
CH_2=$C(CH_3)CO_2CH_3$	$ClCH_2$	$C(CH_3)$	(SCH_3)	CO_2CH_3	3.54 d 4.11 d	1.55 s	2.12 s	3.76 s	10.8		CH_3	SCH_2	$C(CH_3)Cl$	CO_2CH_3	2.12 s	2.97 dd 3.32 dd	1.82 s	3.79 s	14.0	
CH_2=$CHCO_2(CH_3)_3$	$ClCH_2$	CH	(SCH_3)	$CO_2C(CH_3)_3$	3.65 dd 3.93 dd	3.34 dd	2.19 s	1.66 s	10.3	4.4 10.3	CH_3	SCH_2	CH(Cl)	$CO_2C(CH_3)_3$	2.19 s	2.83 d 3.16 d	4.27 dd	1.66 s	13.6	6.2 8.5
CH_2=CHCN	$ClCH_2$	CH	(SCH_3)	CN	—3.88 m—		2.33 s				CH_3	SCH_2	CH(Cl)	CN	2.25 s	3.11 d	4.76 t		7.1	
CH_2=$C(CH_3)CN$	$ClCH_2$	$C(CH_3)$	(SCH_3)	CN	3.56 d 3.93 d	1.71 s	2.35 s		11.3											
CH_2=$CHSO_2CH_3$	$ClCH_2$	CH	(SCH_3)	SO_2CH_3	—4.10 m—		2.40 s	3.14 s												

[a] Abbreviations used: s, singlet; d, doublet; t, triplet; dd, double doublet; m, multiplet; b, broad.

$$CH_3SCH_2CHCOOCH_3 + ClCH_2CHCOOCH_3 \xrightarrow{(CH_3)_3N}$$
$$\underset{88\%}{\underset{|}{Cl}} \qquad \underset{12\%}{\underset{|}{SCH_3}}$$
$$CH_3SCH_2CHCOOCH_3 + CH_2{=}CCOOCH_3$$
$$\underset{88\%}{\underset{|}{Cl}} \qquad \underset{12\%}{\underset{|}{SCH_3}}$$

while the major product is unaffected. The removal of anti-Markovnikov adduct by the amine was indicated by nmr analysis while the 2-thiomethyl methyl acrylate structure was confirmed by nmr and vpc time-of-flight mass spectrometry.

These observations suggested that the initial kinetically controlled product was predominately the Markovnikov adduct, a fact which was established unequivocally by demonstrating that the anti-Markovnikov orientation was preferred thermodynamically.

$$\underset{83\%}{CH_3SCH_2CHClCOOCH_3} + \underset{17\%}{ClCH_2CH(SCH_3)COOCH_3} \xrightarrow[[H^+]]{60^\circ}$$
$$\underset{27\%}{CH_3SCH_2CHClCOOCH_3} + \underset{73\%}{ClCH_2CH(SCH_3)COOCH_3}$$

Similar procedures were used throughout this study to establish the course of the addition of CH_3SCl to acrylate and methacrylate analogs. Fortunately, whenever it was possible to examine rearrangements, the minor initial isomer turned out to be the thermodynamically more stable isomer. On this basis one can be confident that these product distributions are indeed kinetically controlled. Admittedly, in the few instances where isomerization could not be achieved one cannot be as confident that isomerization has not occurred prior to analysis; however, it should be pointed out that this would require exceedingly rapid isomerization at low temperatures and under basic conditions. Such behavior would in our experience be rather unique. Furthermore, such facile equilibrations of these products are not observed when the system is "robbed" of the anti-Markovnikov isomer by reaction with trimethylamine (see Experimental Section for details of the dehydrohalogenations).

The derivatives of acrylic acid and methacrylic acid as well as methacrylonitrile and methyl vinyl sulfone all reacted cleanly with methanesulfenyl chloride. Acrylonitrile gave some unidentified side products whose structure was not determined. Acrolein and methyl vinyl ketone gave rather unstable adducts which decomposed under our general reaction conditions.

Discussion

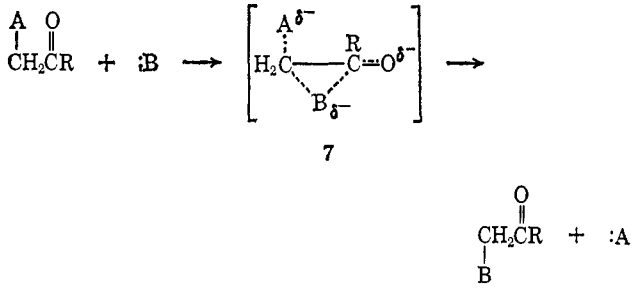
It was postulated previously that the preferential introduction of chloride onto the least hindered carbon during sulfenyl chloride additions to simple olefins is the result of SN2 displacement on an episulfonium ion intermediate.[3] The rather striking change in the ratio of products from functionally substituted olefins when Y in CH_2=CYX is changed from H to Me must be a steric effect, and may be used as an additional argument supporting SN2-type attack by chloride ion on the episulfonium intermediate when relatively little positive charge resides on carbon.

The most important consideration arising from this study is the marked difference in the ability of functional groups on the ring to direct the attack of chloride ion. The preferential formation of adducts with the Mar-

kovnikov orientation from conjugated olefins and methanesulfenyl chloride stems from the ability of the vinyl or phenyl substituents to delocalize a positive charge, thereby lowering the transition-state energy for nucleophilic attack by chloride at the more highly substituted position. Electronegative substituents such as acid chloride or ester groups certainly do not favor positive charge formation on the α-carbon, and although reactants such as methyl acrylate and acrylyl chloride contain conjugated double bonds, analogy to styrene or butadiene to explain the preferential Markovnikov orientation cannot be justified. The very fact that other conjugated olefins such as the sulfone and to a lesser degree the nitrile react to give the anti-Markovnikov orientation preferentially belies this consideration.

Examination of Table I reveals that the tendency for a functional group to favor formation of the Markovnikov isomer follows the same order as the reactivity of the functional group toward solvolysis. Thus the decreasing reactivity of the functional groups toward nucleophiles ($C(O)Cl > C(O)OR > C(O)NH_2 > CN > SO_2R$) is paralleled by the decrease in the relative amount of Markovnikov isomer from sulfenyl chloride addition to the corresponding substituted ethylene. This order of reactivity for chloride ion attack at the α-carbon to open the episulfonium ion is also reminiscent of nucleophilic displacement reactions of α-halocarbonyls and related compounds.[8-10] Dramatic activation of the α position to nucleophilic attack, in which the activating ability of the functional groups follows the above sequence, is well established. The nature of the activation in displacements at the α-carbon has been postulated by Dewar[11] and by Winstein[12] and is supported by the classical experiment of Bartlett and Trachtenberg.[8]

The reactivity of such functional groups toward solvolysis as well as the degree to which these groups activate an α-halide substituent toward nucleophilic displacement are both related to the ability of the substituent to accommodate a pair of electrons from the attacking nucleophile. For example, the order of reactivity for α-halide displacement is acid chlorides > esters > amides > nitriles, the reactivity paralleling the polarization of the functional group. The enhanced rate of nucleophilic substitution on α-halocarbonyl compounds has been attributed to the important contribution of transition-state structures in which the incoming nucleophile is bonded to both the carbonyl carbon and the α-carbon simultaneously.[10-12]



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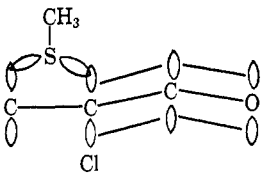
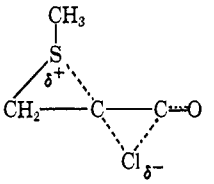
The striking resemblance between α-activation in nucleophilic displacement on α-halocarbonyl compounds and α-activation in the direction of episulfonium ion ring opening suggests that similar transition-state structures **8** wherein the carbonyl group is at right angles to the entering and leaving groups are important and serve to lower the energy for α attack



8A (delocalized orbitals)



8B (localized orbitals)

(Markovnikov product formation). As the ability of the functional group to accommodate a nucleophile decreases, contribution of such resonance structures to the transition state also diminishes and a progressively greater amount of β attack (anti-Markovnikov product) occurs. The tendency, as we have pointed out earlier, is to favor sterically controlled β attack by chloride ion; therefore, only those electrophilic substituents which can most effectively participate in a transition state such as **8** are capable of extensively diverting the attack by chloride ion to the α position. Functional groups such as sulfones which do not effectively participate in such structures exhibit strong steric effects which deactivate the α position.[13]

Experimental Section

Methylacrylate–Methanesulfenyl Chloride Adducts. Methanesulfenyl chloride, 41.3 g (0.5 mol), was added dropwise to a stirred solution of 43 g (0.5 mol) of freshly distilled methyl acrylate in 100 ml of methylene chloride and 0.5 g of suspended calcium carbonate. The solution was maintained at $-65°$ until the sulfenyl chloride color was essentially absent. The methylene chloride and most of the unreacted starting material was removed (according to vpc analysis) by placing the reaction flask in ice water and evacuating with a vacuum pump (0.25 mm) connected to a Dry Ice trap. The crude reaction product weighed 80.0 g, 95% yield. Nmr analysis revealed that this product consisted of 83% $CH_3SCH_2CHClCOOCH_3$ and 17% $ClCH_2CH(SCH_3)COOCH_3$.

After distillation, the product (bp 49–51° (0.05 mm)) contained 86–88% of the former isomer and 12–14% of the latter. *Anal.* Calcd for $C_5H_9O_2SCl$: C, 35.61; H, 5.38; S, 19.02. Found: C, 35.68; H, 5.32; S, 19.12.

A 40% solution of the distilled product in $CDCl_3$ together with a microdrop of H_2SO_4 was warmed at 60° and nmr analysis performed at intervals. The analysis revealed a decrease in the Markovnikov adduct and an increase in the anti-Markovnikov product.

Partial elimination of HCl from the adduct mixture (88% Markovnikov–12% anti-Markovnikov) was accomplished by heating 3.37 g (0.02 mol) of the adduct with 6.21 g (0.105 mol) of anhydrous trimethylamine. A white precipitate which was identified as trimethylamine hydrochloride precipitated immediately upon mixing at Dry Ice temperature. Vapor phase chromatographic analysis indicated that only 12% of the product mixture was converted to a more volatile product. Subsequent analyses, after the reaction was kept at room temperature for several hours, indicated no further reaction was occurring. Even prolonged heating did not cause further conversion. Analysis of the reaction mixture by nmr and vpc coupled to a time-of-flight mass spectrometer indicated that 12% of the adduct was converted to 2-thiomethyl methylacrylate

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(CH_2=$C(SCH_3)COOCH_3$) at the expense of the anti-Markovnikov adduct, and only the Markovnikov product $CH_3SCH_2CHClCOOCH_3$ remained unchanged.

t-Butyl Acrylate–Methanesulfenyl Chloride Adducts. The reaction of *t*-butyl acrylate and methanesulfenyl chloride was carried out in the same fashion as the previous experiment. A 95% yield of product remained after removal of solvent. Analysis by nmr indicated that the product was 92% pure and consisted of a mixture of 81% Markovnikov ($CH_3SCH_2CHClCOOC(CH_3)_3$) and 19% anti-Markovnikov ($ClCH_2CH(SCH_3)COOC(CH_3)_3$) oriented adducts. Distillation gave a product (bp 78–83° (0.6 mm)) which contained 69 and 31% of the respective isomers with a purity of 96%. *Anal.* Calcd for $C_8H_{15}O_2ClS$: C, 45.60; H, 7.17; Cl, 16.83; S, 15.22. Found: C, 45.89; H, 7.26; Cl, 16.76; S, 15.17.

Methyl Methacrylate–Methanesulfenyl Chloride Adducts. Addition of methanesulfenyl chloride to freshly distilled methyl methacrylate, in the manner of the first experiment, gave the adduct with 91% purity which consisted of 24% Markovnikov ($CH_3SCH_2CCl(CH_3)COOCH_3$) and 76% anti-Markovnikov product ($ClCH_2C(CH_3)(SCH_3)COOCH_3$). The ratio of the two isomers was unchanged after distillation (bp 54–58° (0.25 mm)). *Anal.* Calcd for $C_6H_{11}O_2SCl$: C, 39.45; H, 6.07; Cl, 19.41. Found: C, 39.97; H, 6.10; Cl, 19.68. Heating a solution of the distilled product in $CDCl_3$ solution for 3 days at 60° in the presence of a trace of sulfuric acid rearranges the adducts to a mixture of 53% Markovnikov and 47% anti-Markovnikov product.

Acrylyl Chloride–Methanesulfenyl Chloride Adduct. Methanesulfenyl chloride was added to acrylyl chloride in the same fashion as the previous experiments. A 97% crude yield remained after stripping, which contained 91% of the adduct along with about 8% unreacted acrylyl chloride. The adduct had 94% Markovnikov orientation ($CH_3SCH_2CHClCOCl$) and 6% of the reverse isomer ($ClCH_2CH(SCH_3)COCl$). The isomer distribution remained essentially unchanged (96:4) by distillation (bp 58–62° (0.25 mm)). *Anal.* Calcd for $C_4H_6OSCl_2$: C, 27.76; H, 3.49; Cl, 40.97; S, 18.54. Found: C, 28.21; H, 3.57; Cl, 40.22; S, 18.60.

Upon warming at 60° overnight in the presence of a trace of acetic acid the distilled product rearranged from 96% Markovnikov isomer to a mixture of 62% Markovnikov and 38% anti-Markovnikov orientations.

Methacrylyl Chloride–Methanesulfenyl Chloride Adducts. Reaction of equimolar quantities of methanesulfenyl chloride and methacrylyl chloride in the same manner as the previous experiments gave a 95.8% yield of product which contained ~80% adduct. The impurities consisted of 9% methyl disulfide and 11% unreacted acid chloride. The initial product contained 52% Markovnikov and 48% anti-Markovnikov orientation. The isomer distribution remained essentially unchanged (55:45) upon distillation (bp 67–69° (0.3 mm)). *Anal.* Calcd for $C_5H_8OSCl_2$: C, 32.10; H, 4.31; Cl, 37.90; S, 17.14. Found: C, 32.16; H, 4.28; Cl, 38.03; S, 17.22. Heating this material at 60° in the presence of a trace of acid caused no isomerization.

Methacrylamide–Methanesulfenyl Chloride Adducts. The reaction of methanesulfenyl chloride with methacrylamide in CH_2Cl_2 at −65° in the presence of $CaCO_3$ gave an 89% yield of crude product after stripping. Analysis by nmr indicated that impure adduct was a mixture of 8% Markovnikov ($CH_3SCH_2CCl(CH_3)CONH_2$) and 92% anti-Markovnikov isomers ($ClCH_2C(SCH_3)(CH_3)CONH_2$). The reaction mixture was a heavy oil which contained traces of solid in suspension which could be removed by centrifugation. The adduct underwent rapid isomerization at room temperature to give a mixture containing 76% Markovnikov and 24% anti-Markovnikov products. The oil did not crystallize and was not distillable.

Acrylonitrile–Methanesulfenyl Chloride Adducts. The reaction of methanesulfenyl chloride with a CH_2Cl_2 solution of acrylonitrile in the presence of a small quantity of $CaCO_3$ was sluggish at −20° but reacted smoothly when the temperature was raised to 0°. Removal of the solvent at 0° gave an 85% yield of a pale yellow oil. In addition to the two isomeric adducts (51:49), nmr revealed two unidentified singlets at 2.58 and 4.17 ppm of *ca.* 2:1 intensity, respectively. This impurity accounted for *ca.* 15% of the total integral and was always present in subsequent experiments. Distillation *in vacuo* (bp 57–58° (3 mm)) did not free the product from the unidentified impurity (51:49 before → 47:53 after).

A trace of concentrated H_2SO_4 was added to the reaction product. No change in isomer ratio could be detected after 10 hr at ambient temperature. Some decomposition took place at 60° and 5 hr.

An ethereal solution of an approximately 1:1 mixture of the two isomeric adducts derived from acrylonitrile and methanesulfenyl chloride was treated with 0.5 equiv of trimethylamine at −20°. The reaction was exothermic and trimethylamine hydrochloride precipitated immediately. Additional quantities of trimethylamine were added at room temperature but no further reaction took place. Nmr analysis of the product remaining after filtration and removal of ether indicated that all of the anti-Markovnikov adduct ($ClCH_2CH_2(SCH_3)CN$) had been converted to 1-methylthio-1-cyanoethylene (H_2C=$C(SCH_3)CN$). None of the other isomer had been dehydrohalogenated. The following assignments were made for the nmr absorptions of the dehydrohalogenation product.

J = 1.5 cps: 5.81 ppm (d) H, SCH_3 2.41 ppm (s); 6.04 ppm (d) H, CN; C=C

Methacrylonitrile–Methanesulfenyl Chloride Adducts. Methanesulfenyl chloride was added to 1 equiv of freshly distilled methacrylonitrile in the same fashion as the previous experiments. Little if any reaction took place at −65° but a slow reaction (~8 hr) took place at −20°. After removal of solvent an 89% yield of crude product remained. Nmr analysis indicated that the product was about 90% pure and contained about 8% unreacted methacrylonitrile. The product had the anti-Markovnikov orientation ($ClCH_2C(CH_3)(SCH_3)CN$) with no evidence for any of the opposite isomer. Since 98% of the product had been accounted for, the Markovnikov isomer must be less than 2%. Distillation of this product (bp 77–78° (0.50)) gave pure anti-Markovnikov product. *Anal.* Calcd for C_5H_8NSCl: C, 40.13; H, 5.39; Cl, 23.69; S, 21.43. Found: C, 40.45; H, 5.79; Cl, 23.51; S, 21.76. Heating this product overnight at 60° in the presence of acid produced no change in structure.

Methyl Vinyl Sulfone–Methanesulfenyl Chloride Adducts. Methanesulfenyl chloride was added to 1 equiv of 97% pure methyl vinyl sulfone in CH_2Cl_2 solution ($CaCO_3$ present) at −20°. The reaction was strongly exothermic. After addition, the solvent was removed under vacuum giving a 97% crude yield of a white solid, Recrystallization from ether afforded a white solid, mp 58.5–60°, in 80% over-all yield. Nmr analysis of the recrystallized product and mother liquor indicated that only anti-Markovnikov product ($ClCH_2CH(SCH_3)SO_2CH_3$) had been formed. About 10% impurity in the initial reaction mixture appears to be the result of a side reaction of CH_3SCl with the active hydrogens of CH_3SO_2–. *Anal.* Calcd for $C_4H_7S_2O_2Cl$: C, 25.46; H, 4.81; S, 33.98. Found: C, 25.82; H, 4.79; S, 34.07.

A $CHCl_3$ solution of the adduct was warmed at 60° for 15 hr in the presence of a trace of H_2SO_4. No rearrangement could be detected at the end of this period.

An ether solution of the adduct was treated at −10° with a slight excess of trimethylamine. A precipitate of trimethylamine hydrochloride formed immediately. Filtration and removal of ether *in vacuo* afforded an 82% yield of about 90% pure H_2C=$C(SCH_3)SO_2CH_3$. The sample was purified by distillation (bp 70° (0.1 mm)). *Anal.* Calcd for $C_4H_8O_2S_2$: C, 31.56; H, 5.30; S, 42.12. Found: C, 31.20; H, 5.30; S, 42.87. The following designations were assigned to the nmr absorptions of the dehydrohalogenation product.

J = 2.5 cps: 6.35 ppm (d) H, SCH_3 2.42 ppm (s); 5.80 ppm (d) H, SO_2CH_3 3.05 ppm (s); C=C

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