ambient temperature with a solution of 0.3 mol of sodium sulfite in 150 ml of water for about 30 min, until the organic layer failed to give a positve test with potassium iodide–starch paper. The layers were separated and the aqueous layer extracted with methylene chloride. The organic extracts were combined, washed with water, and dried over sodium sulfate. The methylene chloride was evaporated at aspirator pressure at ambient temperature to give the reduced carbamate which was then purified by distillation or recrystallization. The following carbamates were prepared: $CH_3OCONHCH_2CH{=}CHCH_2Cl$, 89%, bp 84–88° (0.009 mm) (*Anal.* Calcd for $C_6H_{10}ClNO_2$: C, 44.38; H, 6.16; N, 8.56. Found: C, 44.05; H, 6.20; N, 8.44); $i\text{-}C_3H_7OCONHCH_2CH{=}CHCH_2Cl$, 78%, mp 61–62° (*Anal.* Calcd for $C_8H_{14}ClNO_2$: C, 50.13; H, 7.36; N, 7.31. Found: C, 49.99; H, 7.45; N, 7.45); $CH_3OCONHCH_2C(CH_3){=}CHCH_2Cl$, 76%, mp 31–32° (*Anal.* Calcd for $C_7H_{12}ClNO_2$: C, 47.33; H, 6.81; N, 7.88. Found: C, 47.29; H, 7.04; N, 7.89); $i\text{-}C_3H_7OCONHCH_2C(CH_3){=}CHCH_2Cl$, 81%, mp 51–52° (*Anal.* Calcd for $C_9H_{16}ClNO_2$: C, 52.55; H, 7.84; N, 6.81. Found: C, 52.32; H, 8.16; N, 6.81); $CH_3OCONHCH_2C(CH_3){=}C(CH_3)CH_2Cl$, 84%, mp 52–53° (*Anal.* Calcd for $C_8H_{14}ClNO_2$: C, 50.13; H, 7.36; N, 7.31. Found: C, 50.01; H, 7.30; N, 7.17); $i\text{-}C_3H_7OCONHCH_2C(CH_3){=}C(CH_3)CH_2Cl$, 86%, mp 59–61° (*Anal.* Calcd for $C_{10}H_{18}ClNO_2$: C, 54.66; H, 8.34; N, 6.38. Found: 54.43; H, 8.26; N, 6.50); $CH_3OCONHCH_2C(Cl){=}CHCH_2Cl$, 78%, mp 58–59° (*Anal.* Calcd for $C_6H_9Cl_2NO_2$: C, 36.38; H, 4.58; N, 7.07. Found: C, 36.32; H, 4.55; N, 7.18); $[CH_2OCONHCH_2C(Cl){=}CHCH_2Cl]_2$, 71%, mp 98–100° (*Anal.* Calcd for $C_{12}H_{16}Cl_4N_2O_4$: C, 36.57; H, 4.09; N, 7.11. Found: C, 36.19; H, 4.09; N, 7.20); $CH_3OCONHC_5H_8Cl$, 82%, bp 84–86° (0.004 mm) (*Anal.* Calcd for $C_7H_{12}ClNO_2$: C, 47.33; H, 6.81; N, 7.88. Found: C, 46.84; H, 6.20; N, 7.95).

Registry No.—$i\text{-}C_3H_7OCON(Cl)CH_2C(CH_3){=}C(CH_3)CH_2Cl$, 16487-91-5; $CH_3O_2CNCl_2$, 16487-46-0; $i\text{-}C_3H_6O_2CNCl_2$, 16487-47-1; $(\text{–}CH_2OCONCl_2)_2$, 16487-45-9.

Acknowledgment.—The authors wish to thank Joseph J. Clemens and Dominick S. DeCaro for their competent technical assistance. The assistance of Peter Paterson in the decoupling work is also appreciated. The elemental analyses were performed by Mr. T. J. Kielty, Jr., and his staff.

Monoadducts of Sulfenyl Chlorides and Conjugated Diolefins[1]

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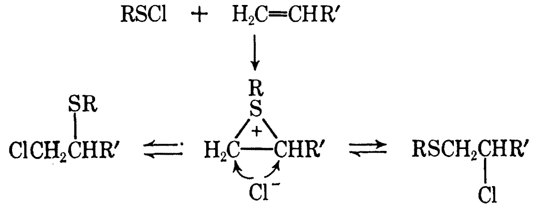
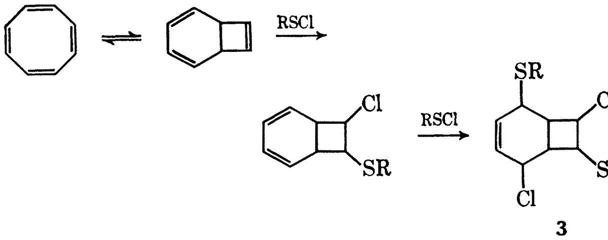
Methane- or benzenesulfenyl chloride afforded predominantly Markovnikov oriented 1,2 adducts with conjugated dienes under kinetic control. Strong preference for attack on the terminal double bond, *i.e.*, unsubstituted double bond, was found with chloroprene, piperylene, and 4-methyl-1,3-pentadiene. The reaction with isoprene, however, showed little selectivity, the substituted double bond being the slightly more favored reaction site. The kinetically controlled major adducts from methanesulfenyl chloride and piperylene, 4-methyl-1,4-pentadiene, or isoprene isomerized to their corresponding thermodynamically more stable 1,4 products. None of the benzenesulfenyl chloride adducts was found to isomerize. The mechanism of such additions and, in particular, the factors influencing the transition states most likely involved in the addition and subsequent rearrangement are discussed.

A mechanism involving an episulfonium ion intermediate to explain the Markovnikov[4] oriented *trans* addition of 2,4-dinitrobenzenesulfenyl chloride to olefins was first postulated by Kharasch and Buess.[5] More recently episulfonium ion intermediates have been proposed to account for the *trans* stereochemistry and *anti*-Markovnikov orientation of adducts obtained from methane- or benzenesulfenyl chloride and terminal olefins.[6] It has been found that, with these sulfenyl chlorides, ring opening of the cyclic intermediate by the chloride ion is strongly dependent on the nature of R′. When R′ is an alkyl substituent, the kinetically controlled ring opening occurs predominantly at the less sterically hindered terminal carbon giving the anti-Markovnikov products (**1**). These adducts then rearrange to the thermodynamically more stable Markovnikov products (**2**). When R′ is phenyl, however, the Markovnikov adduct (**2**) is the kinetically and thermodynamically favored isomer. Thus steric factors appeared to be quite important for the ring opening of episulfonium ions from nonconjugated olefins while the results from phenyl-substituted olefins suggested strong electronic effects in the case of conjugated olefins.



1 **2**

Earlier workers had tentatively proposed 1,4 addition of sulfenyl chlorides to cyclopentadiene and cyclooctatetraene.[7] The formation of diadduct **3** from cyclooctatetraene has been postulated.



3

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[1] A preliminary account of part of this work has appeared: W. H. Mueller and P. E. Butler, *Chem. Commun.*, 646 (1966).

[2] To whom inquiries should be directed.

[3] Analytical and Information Division.

[4] Structures which have the chlorine on the most substituted carbon (the least hydrogen containing carbon) have been designated "Markovnikov" oriented while the opposite isomers, the "anti-Markovnikov" adducts, bear the chlorine on the least substituted (greatest number of hydrogens) carbon atom.

[5] N. Kharasch and C. M. Buess, *J. Amer. Chem. Soc.*, **71**, 2724 (1949).

[6] W. H. Mueller and P. E. Butler, *ibid.*, **88**, 2866 (1966); **90**, 2075 1968.

[7] H. Brintzinger and H. Ellwanger, *Chem. Ber.*, **87**, 300 (1954).

Table I.—Physical–Analytical Data for Methane- and Benzenesulfenyl Chloride–Diene Adducts

Diene	Sulfenyl chloride	Monoadduct[a] summary formula	Bp uncor, °C (mm)	Calcd, % C	Calcd, % H	Calcd, % S	Found, % C	Found, % H	Found, % S
Butadiene	CH_3SCl	C_5H_9SCl	60 (13)	43.95	6.59	23.44	43.80	6.70	23.92
	C_6H_5SCl	$C_{10}H_{11}SCl$	81–82 (0.25)	60.45	5.54	16.12	60.27	5.63	16.39
Isoprene	CH_3SCl	$C_6H_{11}SCl$	68–69 (14)	47.83	7.36	21.28	47.80	7.33	21.38
	C_6H_5SCl	$C_{11}H_{13}SCl$	77–79 (1×10^{-3})	62.10	6.16	15.07	62.31	6.37	15.32
Piperylene	CH_3SCl	$C_6H_{11}SCl$	81–82 (14)	47.83	7.36	21.28	47.62	7.44	21.52
	C_6H_5SCl	$C_{11}H_{13}SCl$	82 (1×10^{-3})	62.10	6.16	15.07	62.09	6.34	15.35
4-Methyl-1,3-pentadiene	CH_3SCl	$C_7H_{13}SCl$	71.5–73 (6)	51.04	7.96	19.47	51.31	8.03	19.79
Chloroprene	CH_3SCl	$C_5H_8SCl_2$	76–76.5 (7)	35.10	4.71	18.74	34.82	4.82	19.13
Cyclopentadiene	CH_3SCl	C_6H_9SCl	74–74.5 (8)	48.48	6.06	21.55	48.21	6.39	21.70

[a] Mixture of isomeric monoadducts.

Table II.—Nuclear Magnetic Resonance Parameters of Sulfenyl Chloride–Diolefin Adducts

Olefin	RSCl	Group assignments						Chemical shift (ppm), multiplicity[a]						Coupling constant,[b] cps
	R	1	2	3	4	5	6	1	2	3	4	5	6	
Butadiene	CH_3	CH_3S	CH_2	CH(Cl)	CH	$=CH_2$		2.08 s	2.73^{c} 2.92	4.42 dt	5.75 ddd	5.25 m 5.16 m		$J_{2,3} = 7.5, 6.5; J_{2g} = 13.5; J_{3,4} = 7.5$ $J_{4,5c} = 9.5; J_{4,5tr} = 16.8$
	C_6H_5	C_6H_5S	CH_2	CH(Cl)	CH	$=CH_2$		7.38 m	3.14^{c} 3.44	4.46 dt	5.97 ddd	5.15 m		$J_{2,3} = 8.4, 6.0; J_{2g} = 14.0$ $J_{3,4} = 8.0; J_{4,5tr} = 16.8; J_{4,5c} = 10.0$
Isoprene	CH_3	CH_3S	CH_2	C(Cl)	(CH_3)	CH	$=CH_2$	2.10 s	2.91 s		1.59 s	6.00 dd	5.22 dd 5.03 dd	$J_{5,6c} = 10.0; J_{5,6tr} = 16.6$ $J_{6g} = 1.5$
		CH_3S	CH_2	CH(Cl)	$C(CH_3)$	$=CH_2$		2.04 s	2.86 d	4.47 t	1.74 m	5.00^{d} 4.87		$J_{2,3} = 7.5; J_{5g} = 1.5$
	C_6H_5	C_6H_5S	CH_2	C(Cl)	(CH_3)	CH	$=CH_2$	7.25 m	3.38 s		1.65 s	6.01 dd	5.22 dd 5.03 dd	$J_{5,6c} = 10.0; J_{5,6tr} = 16.6$ $J_{6g} = 1.5$
		C_6H_5S	CH_2	CH(Cl)	$C(CH_3)$	$=CH_2$		7.25 m	3.12^{c} 3.38	4.44 dd	1.65 s	5.08^{e} 4.88		$J_{2,3} = 8.7, 6.5; J_{2g} = 13.8$
Piperylene	CH_3	CH_3S	CH_2	CH(Cl)	CH	$=CH$	CH_3	2.10 s	2.78^{c} 2.96	4.48 ddd	....5.70 m....		1.71 d	$J_{2,3} = 8.0, 6.0; J_{2g} = 13.5; J_{3,4} = 8.0$ $J_{5,6} = 5.1$
		CH_2	$=CH$	CH(Cl)	CH	(SCH_3)	CH_3	5.25 m^{e}	5.9 m^{e}	$\sim 4.5^{e}$	3.10 dq	2.13 s	1.34 d	$J_{4,6} = 7.0$
	C_6H_5	C_6H_5S	CH_2	CH(Cl)	CH	$=CH$	CH_3	7.15 m	3.07^{c} 3.34	4.38 dt	....5.48 m....		1.54 d	$J_{2,3} = 8.5, 6.0; J_{2g} = 13.5$ $J_{3,4} = 8.5; J_{5,6} = 5.2$
		CH_2	$=CH$	CH(Cl)	CH	(SC_6H_5)	CH_3	5.17 m	5.8 m^{c}	~ 4.4	3.40 s	7.15^{e}	1.32 d	$J_{4,6} = 6.5$
Chloroprene	CH_3	CH_3S	CH_2	CH(Cl)	C(Cl)	$=CH_2$		2.13 s	2.86^{c} 3.13	4.68 dd		5.45 d 5.63 d		$J_{2,3} = 8.0, 6.8; J_{2g} = 14.0$ $J_{5g} = 2.0$
		CH_2Cl	CH	(SCH_3)	C(Cl)	$=CH_2$		....3.69^{f}....		2.09 s		5.45^{e} 5.63		
4-Methyl-1,3-pentadiene	CH_3	CH_3S	CH_2	CH(Cl)	CH	$=C(CH_3)_2$		2.09 s	2.73^{c} 3.00	4.77 ddd	5.28 dh	1.75 bs		$J_{2,3} = 8.0, 5.8; J_{2g} = 13.6; J_{3,4} = 9.9;$ $J_{4,5} = 1.3$
Cyclopentadiene	CH_3	CH_3S	CH	CH(Cl)	CH	$=CH$	CH_2	2.13 s	3.47 dt	4.92 m	....5.85 m....		2.87 m 2.38 m	$J_{2,3tr} = 3.0; J_{2,6tr} = 7.5; J_{2,6c} = 3.0$

[a] s = singlet; bs = broad singlet; d = doublet; t = triplet; q = quartet; dd = double doublet; dh = double heptet; dt = double triplet; ddd = doublet of double doublet; m = multiplet.

[b] c = *cis;* tr = *trans;* g = *gem.*

[c] Protons 2 and 3 form an ABX spin system; the chemical shifts of the AB protons are approximated by first-order analysis from the pair of overlapping quartets.

[d] The terminal methylene protons form the AB part of an ABX_3 system, and appear as a pair of double quartets.

[e] The signal for this group was partially obscured by the major isomer.

[f] Protons 1 and 2 are nearly coincident and form an A_2B multiplet.

These previous results and mechanistic considerations stimulated the present investigation of sulfenyl chloride monoadditions to conjugated diolefins. Although a double bond of a conjugated diene may formally be compared with that of styrene, it offers additional interesting possibilities such as the study of 1,2 *vs.* 1,4 addition and the influence of substituents at various positions of the diene on the adduct formation.

It was hoped that the present study would provide information to substantiate further and widen the scope of the mechanistic interpretation of sulfenyl chloride additions to double bonds. Methane- and benzenesulfenyl chloride, the simplest representatives of aliphatic and aromatic sulfenyl chlorides, were chosen as model addends. This selection also assured results comparable to those obtained from terminal olefins.[6] A variety of methyl-substituted 1,3-dienes, cyclopentadiene, and chloroprene were employed as substrates.

Results

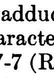
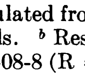
A relatively constant set of reaction conditions was maintained during the present study of the addition of sulfenyl chlorides to dienes. To a ~50% solution of 5 equiv[8] of the respective diene in dry methylene chloride, 1 equiv of methane- or benzenesulfenyl chloride was slowly added. A small amount of $CaCO_3$ was suspended in the methylene chloride solution to prevent possible postisomerization of the initial adducts.[6] The reaction temperature was maintained at −20 to −25° during the additions. Upon completion of the spontaneous and exothermic reaction, most of the methylene chloride was removed at *ca.* −10° and reduced pressure. Immediate nmr analysis of the crude products then provided both the structure(s) of the initial products and the isomer distribution. Samples suitable for elemental analysis were obtained by distillation *in vacuo* (Table I, p 2643). These samples frequently were mixtures of the isomeric adducts.

An *in situ* determination of the structure of the initial adducts was important since the tendency of certain β-halomercaptides to isomerize had been recognized in a previous study.[6] Nuclear magnetic resonance spectroscopy proved to be the most useful analytical tool for this purpose.

In general, protons α to chlorine are considerably deshielded relative to those α to sulfur.[9] The relative differences in chemical shift for the signals of such α-methylene- or methine protons have been reported for a variety of compounds to be on the order of 0.7–1.4 ppm.[6] Chemical-shift differences of similar magnitude have also been reported for benzylic or propargylic protons α to chlorine or sulfur, respectively.[10] Thus the abundance of previously compiled nmr data and in particular the earlier published nmr data gleaned from frequency sweep decoupling experiments on a 100-Mc nmr spectrum of the acetylthiosulfenyl chloride–butadiene adduct[11] simplified the structure elucidation of compounds encountered during the present study. Isomer distributions were computed from the relative intensity of nonoverlapping signals. In each case it was possible to assign ~90–95% of the total proton integral of the crude product's spectrum to proton signals of identified compounds. The only exception was the cyclopentadiene adduct where 85% of the integral was assigned. Frequently a small amount of dimethyl disulfide (singlet at 2.40 ppm) was one of the minor impurities. The nmr parameters of the major products are summarized in Table II, p 2643. Characteristic signals for minor products are discussed in the text.

Initial Adducts.—The 1,2-Markovnikov oriented adduct was the exclusive or predominant product in each case investigated (Table III). Methanesulfenyl chloride and benzenesulfenyl chloride gave essentially the same initial product distribution.

Table III.—Methane- and Benzenesulfenyl Chloride–1,3-Diene Adducts

Diene	Adducts[b]	Mole %[a] R = CH_3	Mole %[a] R = C_6H_5
$CH_2{=}CHCH{=}CH_2$	$RSCH_2CHClCH{=}CH_2$	95	98
	$ClCH_2CHSRCH{=}CH_2$	5	...
$CH_2{=}CHCH{=}CHCH_3$	$RSCH_2CHClCH{=}CHCH_3$	86	82
	$CH_2{=}CHCHClCHSRCH_3$	14	18
$CH_2{=}CHCH{=}C(CH_3)_2$	$RSCH_2CHClCH{=}C(CH_3)_2$	88	...
	$RSCH_2CH{=}CHCCl(CH_3)_2$	12	...
$CH_2{=}CCH_3CH{=}CH_2$	$RSCH_2CClCH_3CH{=}CH_2$	57	60
	$CH_2{=}CCH_3CHClCH_2SR$	43	40
$CH_2{=}CHCCl{=}CH_2$	$RSCH_2CHClCCl{=}CH_2$	85	...
	$ClCH_2CHSRCCl{=}CH_2$	15	...
		85[c]	...

[a] The adduct ratio was calculated from the relative intensity of their characteristic nmr signals. [b] Respective registry numbers: 16728-07-7 (R = CH_3), 16728-08-8 (R = C_6H_5); 16728-09-9 (R = CH_3); 16728-10-2 (R = CH_3), 16728-11-3 (R = C_6H_5); 16728-12-4 (R = CH_3), 16728-13-5 (R = C_6H_5); 16728-14-6 (R = CH_3); 16728-15-7 (R = CH_3); 16728-16-8 (R = CH_3), 16728-17-9 (R = C_6H_5); 16728-19-1 (R = CH_3), 16728-18-0 (R = C_6H_5); 16728-20-4 (R = CH_3); 16728-21-5 (R = CH_3); 16728-22-6 (R = CH_3). [c] Minimum value; minor by-products are formed which remain unidentified.

Butadiene and chloroprene were the only substrates which afforded a detectable amount of the corresponding anti-Markovnikov 1,2 adducts. The presence of ~5% of this minor product from the reaction of methanesulfenyl chloride and butadiene was deduced from the nmr spectrum of the product mixture. A singlet at 2.05 ppm was assigned to the protons of the methylmercapto group. The protons of the $ClCH_2$-$CH(SR)$ group appear as a multiplet at 3.2–3.9 ppm. Its multiplicity is consistent with the overlapping signals of an ABC-type spin system. The chemical shifts observed for this ABC system approximate those found for the anti-Markovnikov adduct from chloroprene (Table II) and similar systems.[10] Formation of the corresponding 1,4 adduct was ruled out by the lack of a signal for allylic CH_2Cl protons (~4.1 ppm) and additional signals at 5.6–5.9 ppm which are characteristic for internal olefinic protons (—CH=CH—).

Substituted butadienes having methyl groups on the 2 or 4 position were chosen to assess the influence of alkyl substituents on the adduct selectivity, *i.e.*, the relative reactivity of the unsubstituted *vs.* the substituted double bond of a conjugated olefin. Isoprene (2-methyl substituent) showed a slight preference for attack on the substituted double bond. With pipery-

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[8] This excess of substrate assured essentially exclusive monoaddition.

[9] J. R. Cavanange and B. P. Dailey, *J. Chem. Phys.*, **34**, 1099 (1961); B. P. Dailey and J. N. Shoolery, *J. Amer. Chem. Soc.*, **77**, 3977 (1955).

[10] P. E. Butler and W. H. Mueller, *Tetrahedron Lett.*, 3179 (1966).

[11] P. E. Butler, W. H. Mueller, and J. J. Reed, *Environ. Sci. Technol.*, **1**, 315 (1967).

lene more than 80% of the addition took place at the 1,2 double bond, and the cumulative effect of two methyl substituents in 4-methyl-1,3-pentadiene caused exclusive attack at the unsubstituted double bond. In the latter case a small amount of 1,4 adduct (Table III) was found to be a by-product. Since this was the only example during the present study where a 1,4 adduct was detected among the initial products its abundance (~8–12%) was substantiated in two consecutive experiments. The propensity for postisomerization of this major 1,2 adduct to the corresponding 1,4 adduct may be in part responsible for the occurrence of the 1,4 adduct among the "initial products" in this particular case.

Reaction with chloroprene took place exclusively at the unsubstituted double bond. In this case 15% of anti-Markovnikov adduct also derived from addition to the unsubstituted double bond was observed.

Contrary to the previously assumed 1,4 addition of sulfenyl chlorides to cyclopentadiene[7] the 1,2-Markovnikov oriented adduct was obtained in ~85% selectivity during the present investigation. The ~15% by-product(s) which were also formed with cyclopentadiene remain unidentified.

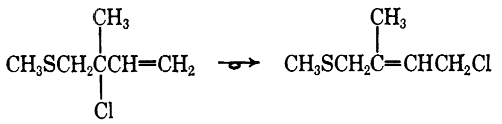
Postisomerization.—It was found that the major 1,2-Markovnikov oriented adducts initially formed from methanesulfenyl chloride and piperylene (**4**), 4-methyl-1,3-pentadiene (**6**), or isoprene (**8**) rearranged to the corresponding 1,4 products, **5**, **7**, and **9**, respectively. This isomerization took place at room temperature and could be conveniently followed by nmr analysis. The equilibrium mixtures contained >90% of the 1,4 products. The rate of rearrangement to **7** was the fastest observed, and equilibrium was reached within approximately 70 hr; the analogous isomerizations to **5** or **9** were slower by a factor of 5–10. None of the other adducts, and particularly none of the benzenesulfenyl chloride adducts, showed any tendency to isomerize under these mild conditions. More stringent conditions, however, such as elevated temperature and acid catalysis facilitated isomerization. This has been verified by the partial rearrangement of the 1,2-Markovnikov oriented adduct **10** to its corresponding 1,4 isomer **11** under acid catalyzed conditions.[12]

$$\underset{\text{Cl}}{\mathrm{CH_3SCH_2CH}}\mathrm{CH{=}CHCH_3} \rightarrow \mathrm{CH_3SCH_2CH{=}CH}\underset{\text{Cl}}{\mathrm{CH}}\mathrm{CH_3}$$

4 **5**

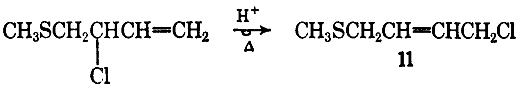
$$\underset{\text{Cl}}{\mathrm{CH_3SCH_2CH}}\mathrm{CH{=}C(CH_3)_2} \rightarrow \mathrm{CH_3SCH_2CH{=}CH}\underset{\text{Cl}}{\mathrm{C}}\mathrm{(CH_3)_2}$$

6 **7**



$$\mathrm{CH_3SCH_2}\overset{\mathrm{CH_3}}{\underset{\text{Cl}}{\mathrm{C}}}\mathrm{CH{=}CH_2} \rightarrow \mathrm{CH_3SCH_2}\overset{\mathrm{CH_3}}{\mathrm{C}}\mathrm{{=}CHCH_2Cl}$$

8 **9**



$$\underset{\text{Cl}}{\mathrm{CH_3SCH_2CH}}\mathrm{CH{=}CH_2} \xrightarrow[\Delta]{H^+} \mathrm{CH_3SCH_2CH{=}CHCH_2Cl}$$

11

10

The following nmr parameters served to identify the rearranged products. Compound **5** showed a singlet for its methylmercapto group at 2.06 ppm. The methyl, methylene, methine, and olefin protons of the carbon backbone form a complex virtual coupling system.[13] The vinylic methyl group appears as a doublet at 1.58 ppm, the allylic S-methylene group is a multiplet at 3.08 ppm, the allylic methine proton next to chlorine is a multiplet at 4.60 ppm, and the nearly equivalent olefin protons are a multiplet centered near 5.74 ppm.

The structure of compound **7** is characterized by a six-proton singlet at 1.57 ppm for the *gem*-dimethyl group protons β to chlorine. The unsplit (singlet) nature of the peak is good evidence for the —$C(CH_3)_2Cl$ group. The olefin and S-methylene protons form an ABXY virtual coupling system which is not amenable to first-order approximation. The two-proton multiplet for the olefinic protons is centered at about 5.72 ppm, while that of the S-methylene group is at 3.05 ppm (double irradiation of either multiplet collapses the other multiplet to a singlet). In support of the nmr assignment pertinent infrared bands were found at 1670 cm^{-1} (*trans* —CH=CH— stretching), 3040 cm^{-1} (—CH= stretching), and 963 cm^{-1} (—CH= out of plane deformation) which verified the *trans* nature of the double bond.

Compound **9** has characteristic peaks in the proper area ratio for the allylic S-methylene group (3.06 ppm, broad singlet), the vinylic methyl group (1.78 ppm broad singlet), the olefinic methine proton (5.55 ppm, triplet), and the allylic chloromethylene protons (4.10 ppm, doublet) which supports the assigned structure.

Discussion

The most obvious characteristic of the reactions of sulfenyl chlorides with conjugated dienic substrates is the highly selective formation of 1,2-Markovnikov oriented initial adducts and the preference of the addend for the terminally unsubstituted double bond of the diene. This addition reaction is in some cases followed by postisomerization of the 1,2-Markovnikov adduct to its corresponding 1,4 product. These basic observations and their mechanistic interpretation will be discussed in the order of their occurrence.

The first event is the selection of the reaction site on the dienic substrate by the approaching reagent. When methyl substituents are in the 4 position, *e.g.*, piperylene and 4-methyl-1,3-pentadiene, the terminal double bond becomes the strongly preferred point of attack. A methyl substituent in the 2 position (isoprene), however, does not hinder the attack on the substituted double bond. In fact, this position becomes the slightly favored reaction site. It appears, therefore, that steric as well as electronic factors can govern the approach of the two reactants. Strong steric requirements are introduced when methyl groups are in the 4 position of the diene. This steric effect is not observed when this substituent is located in the 2 position. Enhanced nucleophilicity of the double bond from electron release of the methyl substituent may be responsible for the preferred attack on the substituted site of isoprene. The low selectivity encountered in this case, however, indicates the relatively small over-

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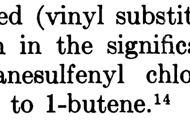
(12) W. A. Thaler, private communication; partial isomerization had been obtained at 60° in the presence of a catalytic amount of concentrated H_2SO_4.

(13) J. I. Musher and E. J. Corey, *Tetrahedron*, **17**, 791 (1962).

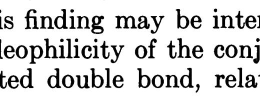
all significance of the electronic influence of a methyl substituent on the substrate. Strong electronic factors were recognized with chloroprene. Here the exclusive site of the reaction is the more nucleophilic unsubstituted double bond.

The above discussion of conjugated dienes in terms of isolated (vinyl substituted) double bonds finds justification in the significantly slower rate of addition of methanesulfenyl chloride to butadiene when compared to 1-butene.[14] This finding may be interpreted on the basis of lower nucleophilicity of the conjugated diene, *i.e.*, vinyl-substituted double bond, relative to that of an alkyl-substituted double bond toward the sulfenyl chloride. In that case the vinyl substituent appears to have a significant electron-withdrawing inductive effect.

The kinetically controlled formation of the 1,2-Markovnikov oriented products may involve, without closer inspection of the data on hand, transition state **12** or **13**. Product analysis, *i.e.*, high selectivity toward the 1,2-Markovnikov adduct, does not allow differentiation between **12** and **13**. Existing data on the polar addition of hydrogen bromide[15] and hydrogen chloride[16] to butadiene show mainly 1,2 addition while the ionic chlorination[17] and the (assumed ionic) bromination[18] of butadiene gave approximately equal amounts of 1,2 and 1,4 products.



12

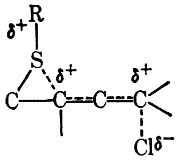


13

In our view a transition state as depicted in **12** satisfactorily accommodates all data available for the kinetically controlled product formation. Markovnikov orientation is the result of stabilization of this transition state due to π-bond overlap of the p orbital of the electron-deficient α carbon with the vinyl substituent's π cloud. This parallels the previously observed Markovnikov orientation of sulfenyl chloride additions to styrene.[6,19] The kinetically favored attack of the chloride on the 2 position rather than on the 4 position of the episulfonium ion intermediate is derived from the relative degree of electron deficiency of the two carbons in question. The partial positive charge residing on the carbon in the 2 position receives its additional stabilization from overlap of the electron-deficient orbital on carbon with the sulfur orbitals. The lower reactivity of dienes *vs.* simple olefins[14] is also in accord with a transition state where relatively little positive charge is developed on carbon (**12**). Higher reactivity of dienes would be expected from the intervention of a resonance-stabilized allylic carbonium ion **13**. Further support for a bridged unsymmetrical episulfonium ion stems from the observed *trans* stereospecific addition of sulfenyl chlorides to acenaphthylene.[6,20] If resonance stabilization of a potential carbonium ion could lead to a deviation from our previous conclusion[4] of a bridged episulfonium ion, it would be expected to become evident here as nonstereospecific addition to acenaphthylene.

The tendency for postisomerization of some of the 1,2-Markovnikov adducts to their corresponding 1,4 products, observed under the mild conditions described in this paper, depends on two factors which could be recognized with the models presently investigated. First, none of the initial benzenesulfenyl chloride adducts rearranged. Second, methyl substituents in the 4 or 2 position of the initial adduct facilitate the rearrangement.

This differing propensity for rearrangement of methane- and benzenesulfenyl chloride adducts finds its explanation in the relative electronegativity of R on sulfur. Increasing electronegativity of R (*i.e.*, C_6H_5– > CH_3–) decreases the availability of the unshared electrons on the sulfur atom and diminishes neighboring-group participation, *i.e.*, displacement of the chlorine. The relative propensity for postisomerization previously found with terminal olefin–sulfenyl chloride adducts also parallels this present finding.[6] This is strong evidence that the rearrangement involves the same episulfonium ion intermediate as the initial addition reaction. It also follows that formation of this intermediate is reached through transition state **12**. Isomerization then proceeds through a higher energy transition state **14** to form the thermodynamically favored 1,4 products *via* S_N2' displacement by the chloride. This step is essentially irreversible, since it would require an unfavorable S_N2' displacement of the chloride in the 4 position by the methylmercapto group.



14

The role of methyl substituents on the rearrangement can be attributed to the additional stabilization of transition state **12** by electron release of the substituents in the 2 or 4 position. The minor adduct isomers from piperylene, 4-methyl-1,3-pentadiene, and isoprene (Table III) bear methyl substituents in the 1 and 3 position, respectively. No contribution to lowering the transition-state energy would be expected in these positions which is consistent with the failure of such adducts to rearrange. Furthermore, methyl substituents in the 4 position can also contribute to lowering the energy of transition state **14** by stabilizing a partial positive charge on carbon 4. This explains the greater ease of rearrangement observed with the 1,2 adduct **6** from 4-methyl-1,3-pentadiene to its corresponding 1,4 compound **7**.

It is expected that the results obtained in the present study are to some degree subject to reaction conditions, solvent polarity, and the nature of the sulfenyl chloride.

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[14] Addition of methanesulfenyl chloride (0.1 mol) to an equimolar mixture of 1-butene (0.4) and butadiene (0.4) resulted in a 7:3 adduct ratio in favor of the butylene adduct.

[15] M. S. Kharasch, E. T. Margolis, and F. R. Mayo, *J. Org. Chem.*, **1**, 393 (1936).

[16] M. S. Kharasch, J. Kritchevsky, and F. R. Mayo, *ibid.*, **2**, 489 (1937).

[17] M. L. Poutsma, *ibid.*, **31**, 4167 (1966).

[18] L. F. Hatch, P. D. Gardner, and R. E. Gilbert, *J. Amer. Chem. Soc.*, **81**, 5943 (1959).

[19] W. L. Orr and N. Kharasch, *ibid.*, **75**, 6030 (1953).

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

Experimental Section

Nmr Analyses.—Neat samples containing tetramethylsilane as an internal standard were run on a Varian A-60 spectrometer at ambient temperature. Infrared spectra were recorded on a Beckman Model IR-10 infrared spectrophotometer.

Starting Materials.—Isoprene, piperylene, and chloroprene (50% solution in xylene) were obtained from Columbia Organic Chemicals Co. and distilled prior to their use. Butadiene from Matheson Co. and 4-methyl-1,3-pentadiene from Chemical Samples Co. were of ~99% purity and used as such. The cyclopentadiene was freshly prepared by destructive distillation of dicyclopentadiene from Enjay Chemical Co. Methane- and benzenesulfenyl chloride were synthesized *via* chlorination of the corresponding disulfides according to previously described procedures.[6]

General Procedure for the Addition of Methane- or Benzenesulfenyl Chloride to Conjugated Dienes.—To a 50% solution of 5 equiv of the respective diene in dry methylene chloride, 1 equiv of methane- or benzenesulfenyl chloride was slowly added. The solution had a small amount of calcium carbonate (~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. All reactions were strongly exothermic and took place spontaneously. Decolorization of the orange sulfenyl chloride indicated completion of the reaction. Immediately after completion of the addition the solvent and excess unsaturate were removed under reduced pressure at −5 to −10° and the adducts' isomer ratio (Table III) was 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).

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Selenium Dioxide Oxidations. III. The Oxidation of Olefins

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Details of the oxidation of 1,3-diphenylpropene with selenium dioxide were studied. In acetic acid at 115° an isotope effect (k_H/k_D) of 3.2 was observed for oxidation at the benzylic position; this indicates that an allylic carbon–hydrogen bond is being broken in the rate-determining step. Oxidation is most rapid for electron-rich olefins and is hindered if the double bond is shielded. A mechanism is proposed that involves the formation of an allylic selenium(II) ester (RCH=CHCHROSeOH) that decomposes to products through a solvolysis reaction. Evidence for a second pathway for oxidation is presented. This proceeds through the addition of selenium dioxide and acetic acid to the double bond, followed by pyrolysis of the selenoxide that is produced to the allylic acetate. The intermediate in this reaction was isolated and characterized. Oxidation of the optically active 3- and 4-methylcyclohexenes in acetic acid and in *n*-butanol was investigated, and products that arise from the introduction of oxygen into the 2, 3, and 4 positions were isolated. For the oxidation of the olefins in *n*-butanol, it was found that the product that is formed is in each case the thermodynamically unstable ether. An analysis of the data suggests that oxidation occurs through addition of selenium dioxide and solvent to the double bond, followed by pyrolytic elimination of selenium in a lower oxidation state to produce allylically oxidized product.

Selenium dioxide is often an attractive reagent for oxidizing olefins since it provides a direct entry into the allylic position. Although the reaction frequently proceeds in moderate to poor yields, its simplicity will usually outweigh this disadvantage. Despite the numerous examples of oxidation that are recorded in the literature,[3] few systematic studies concerned with evaluating the stereochemistry of the reaction, the nature of the intermediates, the effect of asymmetry, and electronic influences on the course of reaction have been reported. In an effort to define the characteristics of the reaction more precisely and to correlate the data that are currently available, we have studied certain details of the oxidation of several olefins and have obtained data that clarify some mechanistic aspects of the reaction.

From an examination of the literature, it is apparent that in many cases the oxidation product that is isolated must result from an allylic rearrangement. For example, oxidation of 1-hexene yields hex-2-en-1-yl acetate as the major product.[4] Although in many instances, rearrangement of the double bond may be an artifact arising from subsequent conversion of a kinetically favored product into one that has a greater thermodynamic stability, we felt that it was critical to obtain data on this point since the results would have important implications relating to the reaction intermediates. Accordingly, our initial studies were focused upon the oxidation of 1,3-diphenylpropene (**1**) and its derivatives.

Oxidation of **1** with selenium dioxide in 99% acetic acid at 115° was rapid and produced 1,3-diphenyl-2-propen-1-yl acetate (**2**) in high yields; no significant quantities of other organic products could be characterized. To elaborate the role of the allylic methylene group in the oxidation process, 1,3-diphenylpropene-3-*d* (**1**-*d*) was prepared. The experimental route to this product is shown in Scheme I. Benzoin was deuterated either by a base-catalyzed exchange with deuterium oxide or by neutralization of its disodium salt (from sodium hydride) with deuterium oxide. The product of these reactions was oxidized to benzaldehyde-1-*d* (**3**-*d*) with lead tetraacetate. Condensation of **3**-*d* with acetophenone yielded the deuterated chalcone (**4**-*d*), which subsequently was reduced to 1,3-diphenylpropan-1-ol-3-*d* (**5**-*d*) by lithium aluminum hydride. Dehydration of **5**-*d* by distillation from potassium acid sulfate yielded **1**-*d* containing 0.87 atom of deuterium per molecule. The nmr spectrum indicated the presence of two vinyl protons and therefore precludes any significant hydride shifts during the dehydration process.

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[1] For paper II in this series, see J. P. Schaefer, *J. Amer. Chem. Soc.*, **84**, 717 (1962).

[2] The results of this work are taken in part from the Ph.D. theses of B. Horvath and H. P. Klein as submitted to the Graduate College of the University of Arizona.

[3] N. Rabjohn, *Org. Reactions*, **5**, 331 (1949).

[4] A. Guillemonat, *Ann. Chim.* (Paris), **11**, 143 (1939).