Experimental Section[7]

Resistomycin (1).—Resistomycin was isolated from cultures of an unidentified actinomycete (Abbott M10782) and crystallized from acetone as yellow needles (mp >300°; sublimes near 210° at 50 μ of Hg): ultraviolet absorption, λ_{max} 268 mμ (ϵ 24,000), 290 (23,000), 320 (14,400), 337 (13,900), 366 (11,000), 457 (15,400).

Anal. Calcd for $C_{22}H_{16}O_6$: C, 70.21; H, 4.29; O, 25.50; mol wt 376.4. Found: C, 69.72; H, 4.37; O, 25.86.

4,11-Dichlororesistomycin (2).—Resistomycin (2.5 g, 6.8 mmoles) was suspended in 2 l. of glacial acetic acid and chlorine (1.5 g, 21 mmoles) dissolved in 50 ml of glacial acetic acid was added over a period of 15 min at room temperature. The mixture was stirred vigorously for 1 hr, then cooled and filtered. Yellow micro needles were washed with distilled water and triturated with hot acetone (yield 2.3 g, 76% of theory). Thin layer chromatography on silica gel G developed with chloroform–ethanol (9:1, v/v) showed a single spot with R_f 0.35: ultraviolet absorption, λ_{max} 220 mμ (ϵ 65,000), 273 sh, 293 (56,000), 310 sh, 370 (19,000), 523 (29,000).

Anal. Calcd for $C_{22}H_{14}Cl_2O_6$: C, 59.35; H, 3.17; Cl, 15.92; O, 21.56; mol wt, 445.2, Found: C, 59.59; H, 3.58; Cl, 15.48; O, 21.56.

4-Bromoresistomycin (3).—Finely divided resistomycin (1 g, 2.7 mmoles) was suspended in 1 l. of glacial acetic acid and bromine (1.3 g, 8.1 mmoles) dissolved in 150 ml of glacial acetic acid was added with vigorous stirring under a nitrogen atmosphere and in the dark over a period of 30 min. The temperature of the reaction mixture was raised to 80° over a period of 3 hr, residual bromine was then removed with a nitrogen sweep, and the solution slowly cooled to 20°. Bright yellow micro needles were harvested, washed with distilled water, and triturated with hot acetone (yield 0.95 g, 78% of theory). Thin layer chromatography on silica gel G developed with chloroform–ethanol (9:1, v/v) showed a single component with R_f 0.69 (resistomycin, 0.76): ultraviolet absorption, λ_{max} 218 mμ (ϵ 48,200), 270 (26,500), 291 (24,800), 326 (13,800), 338 sh (12,500), 370 (10,300), 429 (14,200).

Anal. Calcd for $C_{22}H_{15}BrO_6$: C, 58.04; H, 3.32; Br, 17.55; O, 21.09; mol wt, 455.3. Found: C, 58.17; H, 3.18; Br, 18.15; O, 21.04.

Registry No.—1, 13341-63-4; 2, 13318-35-9; 3, 13421-94-8.

Acknowledgment.—Appreciation is expressed to various members of Abbott Laboratories who contributed to this work. The interest and advice of Dr. M. Levenberg is especially acknowledged as is the excellent technical assistance of Mr. R. E. Carney.

(7) Microanalyses were performed by O. Kolsto, Scientific Services Laboratories, Abbott Laboratories, and ultraviolet absorption spectra were taken in methanol solution. Nmr spectra were taken with a Varian A-60 spectrometer at 36° in concentrated deuteriosulfuric acid using tetramethylammonium chloride as internal standard (200 cps relative to tetramethylsilane).

Orientational Effects in the Addition of Acetylthiolsulfenyl Chloride to Olefins

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Our recent work on the mechanism of sulfenyl chloride additions to unsaturates[2-4] indicated that the structures of both the olefin and the sulfenyl chloride influence the ratio of electronically *vs.* sterically controlled ring opening of the episulfonium ion intermediate. It was, therefore, of interest to study the electron-withdrawing effect of an acetyl group on the relative charge distribution in the episulfonium ion.

Earlier workers found[5] that the addition mechanism of acetylthiosulfenyl chloride departs from the usual ring opening of the episulfonium ion intermediate. The chloride ion attacks the carbonyl rather than the ring carbon of the intermediate, forming acetyl chloride and propylene episulfide which undergoes further reaction with acetylsulfenyl chloride.

The reaction of acetylthiosulfenyl chloride (CH_3-C(=O)SSCl) with styrene, ethylene, and cyclohexene has been found by previous workers[5,6] to follow the normal addition mechanisms. No attempt was made to study adduct orientation factors, although this reagent appears to be a convenient probe to test the steric *vs.* electronic factors influencing the reaction. To determine these factors, acetylthiosulfenyl chloride was added to several selected olefins. Propylene, isobutylene, and 3,3-dimethylbutene were chosen to study the influence of alkyl substituents with increasing substituent bulkiness. Styrene, butadiene, and piperylene were selected as electronically more biased substrates. Acenaphthylene was used to determine the stereochemical course of the addition.

Acetylthiosulfenyl chloride was added under anhydrous conditions to a solution of the unsaturate in methylene chloride generally at −15 to −20°. The methylene chloride solution contained a small amount of calcium carbonate to prevent possible postisomerization of the adducts.[2] In the case of dienes, a fivefold excess of the unsaturate was used in order to ensure monoaddition. The reaction is exothermic and takes place very rapidly during the addition of the sulfenyl chloride. Conversions of >95% were obtained in each case. With the exception of the adducts of styrene and acenaphthylene, analytical samples were obtained by fractional distillation *in vacuo* as pale yellow liquids (Table I).

The relative amounts of isomeric adducts could be deduced from nmr analysis of the crude product mixtures. In general, protons α to chlorine are considerably deshielded relative to those α to sulfur.[3,7] A similar difference was observed in the chemical shift of methyl group protons β to chlorine and sulfur, respectively. The relative intensities of the two types of methyl signals were of considerable assistance in computing isomer ratios. A detailed compilation of the nmr parameters for each adduct is given in Table II.

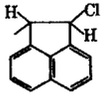
Propylene.—The addition of acetylthiosulfenyl chloride to propylene afforded 40% of the Markovnikov adduct I and 60% of the anti-Markovnikov adduct II[8] (eq 1). The product mixture was analyzed quantitatively by the intensities of the characteristic nmr signals of the methyl groups β to either chlorine or sulfur. The methyl group β to chlorine in I is a doublet

(1) Analytical Research Division.
(2) W. H. Mueller and P. E. Butler, *J. Am. Chem. Soc.*, **88**, 2866 (1966).
(3) W. H. Mueller and P. E. Butler, *Chem. Commun.*, 646 (1946).
(4) W. H. Mueller, R. M. Rubin, and P. E. Butler, *J. Org. Chem.*, **31**, 3537 (1966).
(5) H. Böhme, H. Bezzenberger, and H. D. Stachel, *Ann.*, **602**, 1 (1957).
(6) H. Böhme and M. Clement, *ibid.*, **576**, 61 (1952).
(7) P. E. Butler and W. H. Mueller, *Tetrahedron Letters*, **19**, 2179 (1966).
(8) In the present paper, Markovnikov orientation indicates adducts with the chlorine on a secondary or tertiary carbon atom while anti-Markovnikov adducts have the chlorine on the terminal carbon.

TABLE I

ACETYLTHIOSULFENYL CHLORIDE UNSATURATE MONOADDUCTS AND SOME PHYSICAL–ANALYTICAL DATA OF THE PRODUCTS

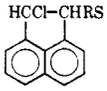
CH_3COSSR

Substrate	Mole ratio substrate/RSCl	Reaction temp, °C	Isomers, %[a] I	Isomers, %[a] II	Structure I R	Structure II R	Summary formula	Registry no.	Bp (mm), °C (uncor)	Elemental compn, % Calcd C	Calcd H	Calcd S	Found C	Found H	Found S
Propylene	1	−78	60	40	$-CH(CH_3)CH_2Cl$	$-CH_2CH(Cl)CH_3$	$C_5H_9S_2OCl$		60–61 (0.25)	32.52	4.91	34.72	32.54	5.23	35.00
Isobutylene	1	−20	32	68	$-C(CH_3)_2CH_2Cl$	$-CH_2C(Cl)(CH_3)_2$	$C_6H_{11}S_2OCl$		67 (0.25)	36.26	5.58	32.27	36.26	5.74	32.49
3,3-Dimethylbutene	1	−15	82	18	$-CH(CH_2Cl)C(CH_3)_3$	$-CH_2CH(Cl)C(CH_3)_3$	$C_8H_{15}S_2OCl$		87 (0.30)	42.37	6.67	28.28	42.93	6.69	28.42
Styrene	1	−20		100		$-CH_2CH(Cl)C_6H_5$	$C_{10}H_{11}S_2OCl$	13250-21-0	Dec	48.67	4.49	25.99	48.67	4.38	26.04
Acenaphthylene	1	−15		100 (*trans*)			$C_{14}H_{11}S_2OCl$	13250-22-1	Dec	57.03	3.76	21.75	56.88	3.89	21.51
Butadiene	5	−20		100		$-CH_2CH(Cl)CH{=}CH_2$	$C_6H_9S_2OCl$	13250-23-2	75 (0.35)	36.64	4.61	32.60	36.62	4.53	32.63
Piperylene	5	−20	82	5[b]	$-CH_2CH(Cl)CH{=}CHCH_3$	$-CH(CH_3)CH(Cl)CH{=}CH_2$	$C_7H_{11}S_2OCl$		82 (0.05)	39.89	5.26	30.43	40.32	5.37	30.19

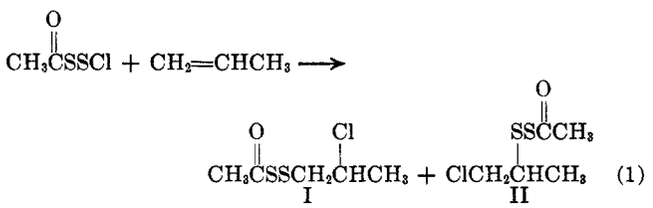
[a] Based on semiquantitative nmr analysis of the crude reaction products. [b] In addition, 13% of $CH_3COS_2CH_2CH{=}CHCH(Cl)CH_3$.

TABLE II

NMR PARAMETERS OF ACETYLTHIOSULFENYL CHLORIDE UNSATURATE ADDUCTS

Olefin	RCOSSCl R	Group assignments 1	2	3	4	5	Chemical shifts (ppm), multiplicity[a] 1	2	3	4	5	Coupling constant,[a] cps
Propylene	CH_3	CH_3	CHCl	CH_2	SR		1.65 d	3.98[b]	2.82[b]	2.49 s		$J_{1,2} = 6.5$; $J_{2,3} = 9.0, 5.3$; $J_g = 14.0$
		CH_3	CH	SR	CH_2Cl		1.39 d	2.98[b]	2.49 s	3.32[b] 3.70		$J_{1,2} = 6.5$; $J_{2,4} = 10.0, 4.0$; $J_g = 11.0$
Isobutylene	CH_3	$(CH_3)_2$	CCl	CH_2	SR		1.57 s		3.19 s	2.42 s		
		$(CH_3)_2$	CSR	CH_2Cl			1.37 s	2.45 s	3.53 s			
3,3-Dimethyl-butene	CH_3	$(CH_3)_3C$	CH	SR	CH_2Cl		1.14 s	2.83 t[b]	2.44 s	3.72[b] 3.95		$J_{2,4} = 5.6, 5.2$; $J_g = 12.0$
		$(CH_3)_3C$	CHCl	CH_2	SR		1.07 s	4.00 t[b]	3.05[b] 3.37	2.46 s		$J_{2,3} = 7.3$; $J_g = 13.7$
Styrene	CH_3	C_6H_5	CHCl	CH_2	SR		7.3 m	5.03 t	3.32 d	2.26 s		$J_{2,3} = 7.3$
Acenaphthylene	CH_3	HCCl–CHRS 					5.92 d	4.99 d ~7.5 m				$J_{1,2\,tr} = 1.6$
Butadiene	CH_3	CH_2=	CH	CHCl	CH_2	SR	5.35 m	5.97 ddd	4.49 ddd[b]	2.97[b] 3.21	2.44 s	$J_{1,2c} = 10.0$; $J_{1,2\,tr} = 17.0$; $J_{2,3} = 7.5$; $J_{3,4} = 8.0, 6.2$; $J_g = 13.7$
Piperylene	CH_3	CH_3	CH=CH	CHCl	CH_2	SR	1.74 d	5.65 m	4.49 ddd	2.93[b] 3.20[b]	2.43 s	$J_{1,2} = 1.74$; $J_{2,3} = 7.3$; $J_{3,4} = 7.2, 6.7$
		CH_3	CHCl	CH=CH	CH_2	SR	1.56 d	4.48 m	5.65 m	3.32 m	2.43 s	$J_{1,2} = 6.7$

[a] Notation: s = singlet, d = doublet, t = triplet, m = multiplet, c = *cis*, tr = *trans*, g = geminal. [b] These protons form an ABX-type system; the parameters are derived from first-order approximations. In general, the methylene protons are a pair of overlapping quartets and the methine proton a double doublet (in several cases the methine proton is further split by coupling with adjacent protons.



$$CH_3\overset{O}{\overset{\|}{C}}SSCl + CH_2{=}CHCH_3 \longrightarrow \underset{\text{I}}{CH_3\overset{O}{\overset{\|}{C}}SSCH_2\overset{Cl}{\overset{|}{C}}HCH_3} + \underset{\text{II}}{ClCH_2\overset{|}{C}HCH_3}\overset{O}{\overset{\|}{S}}SCH_3 \quad (1)$$

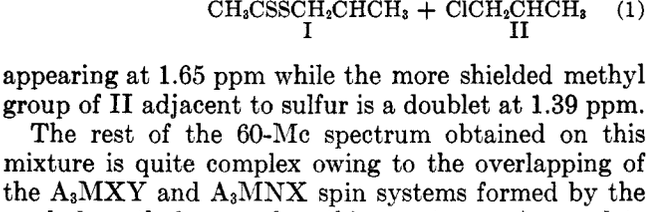
appearing at 1.65 ppm while the more shielded methyl group of II adjacent to sulfur is a doublet at 1.39 ppm.

The rest of the 60-Mc spectrum obtained on this mixture is quite complex owing to the overlapping of the A_3MXY and A_3MNX spin systems formed by the methyl, methylene, and methine protons. A complete analysis of the parameters for each spin system was achieved, however, on a 100-Mc spectrum and served as a model for the elucidation of the spectra of the other products.

The methylene protons α to sulfur in the secondary chloride I are nonequivalent and appear as double doublets at 2.82 and 3.08 ppm. Their multiplicity is due to the large geminal coupling of 14.0 cps and unequal coupling with the adjacent methine proton ($J_{2,3} = 9.0$; $J_{2,3'} = 5.3$). The methine proton is a 16-line pattern at 3.98 ppm. This is caused by splitting of each line of the double doublet, owing to coupling with the nonequivalent methylene protons, into 1:3:3:1 quartets by the protons of the methyl group. This methyl–methine coupling was confirmed by frequency sweep decoupling of the methyl group at 1.65 ppm.

For the primary chloride II, an approximately first-order spectrum results even though the chemical shift between the methine proton α to sulfur and one of the nonequivalent methylene protons α to chlorine is only 34 cps. The methylene protons appear as a pair of double doublets at 3.32 and 3.70 ppm. The upfield double doublet appears as a "triplet" owing to the coincidence of the internal lines caused by the nearly equal geminal and vicinal coupling constants. The methine proton at 2.98 ppm is again a 16-line pattern. Only 11 of the 16 lines are visible owing to overlapping with peaks of the methylene protons of the reverse isomer.

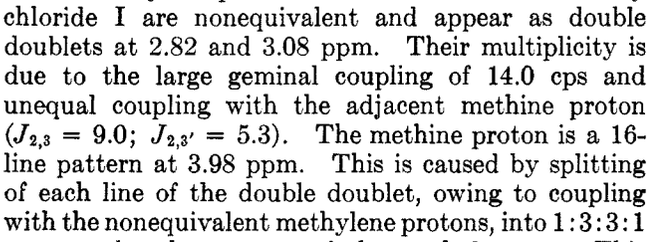
Isobutylene.—From isobutylene and acetylthiosulfenyl chloride, isomers III and IV were obtained in 68 and 32% yields, respectively (eq 2). The adduct



$$CH_3\overset{O}{\overset{\|}{C}}SSCl + CH_2{=}C(CH_3)_2 \longrightarrow \underset{\text{III}}{CH_3\overset{O}{\overset{\|}{C}}SSCH_2\overset{Cl}{\overset{|}{C}}(CH_3)_2} + \underset{\text{IV}}{ClCH_2\overset{|}{C}(CH_3)_2}\overset{O}{\overset{\|}{S}}SCH_3 \quad (2)$$

ratio was deduced from the nmr spectrum of the mixture (Table II).

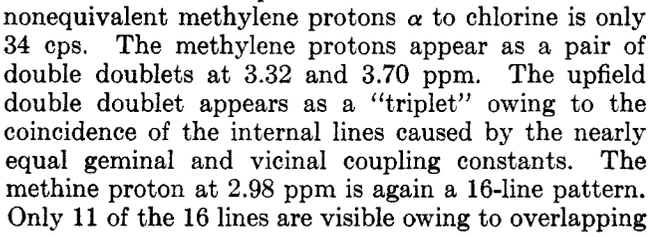
3,3-Dimethyl Butene.—Adducts V (18%) and VI (82%) were obtained from acetylthiosulfenyl chloride and 3,3-dimethylbutene (eq 3). The difference in chem-



$$CH_3\overset{O}{\overset{\|}{C}}SSCl + CH_2{=}CHC(CH_3)_3 \longrightarrow \underset{\text{V}}{CH_3\overset{O}{\overset{\|}{C}}SSCH_2\overset{Cl}{\overset{|}{C}}HC(CH_3)_3} + \underset{\text{VI}}{ClCH_2\overset{|}{C}HC(CH_3)_3}\overset{O}{\overset{\|}{S}}SCH_3 \quad (3)$$

ical shifts of the *t*-butyl protons of the two isomers (Table II) allowed a simple determination of the adduct ratio in the product mixture. The multiplicity and relative chemical shifts of the methine and methylene protons are in accord with earlier published data on similar compounds.[7]

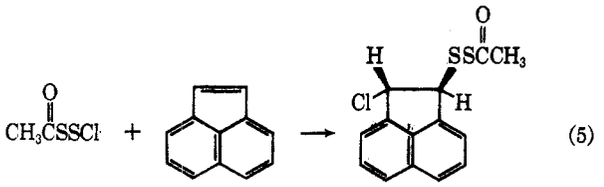
Styrene.—From styrene and acetylthiosulfenyl chloride only the Markovnikov oriented adduct was obtained (eq 4). This finding contrasts with the pre-



$$CH_3\overset{O}{\overset{\|}{C}}SSCl + CH_2{=}CH\text{–}C_6H_5 \longrightarrow CH_3\overset{O}{\overset{\|}{C}}SSCH_2\overset{Cl}{\overset{|}{C}}H\text{–}C_6H_5 \quad (4)$$

viously reported adduct mixture containing predominantly the anti-Markovnikov adduct.[5] The adduct's structure was readily deduced from its nmr spectrum. The observed nmr parameters (Table II) are again in agreement with previously published data.[7]

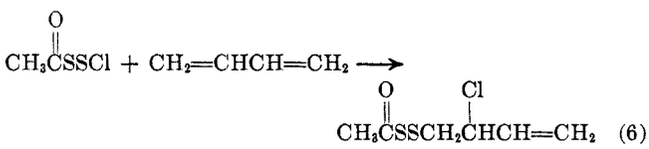
Acenaphthylene.—The reaction of acetylthiosulfenyl chloride with acenaphthylene afforded only the *trans* adduct (eq 5). The exclusive *trans* addition was



(5)

verified by nmr analysis. The protons α to sulfur and chlorine appear as two doublets. The observed coupling constant of 1.6 cps for these vicinal protons is diagnostic for their *trans* stereochemical relationship.[2] A *cis* spacial arrangement is reported to produce a coupling constant of ~8 cps.[9]

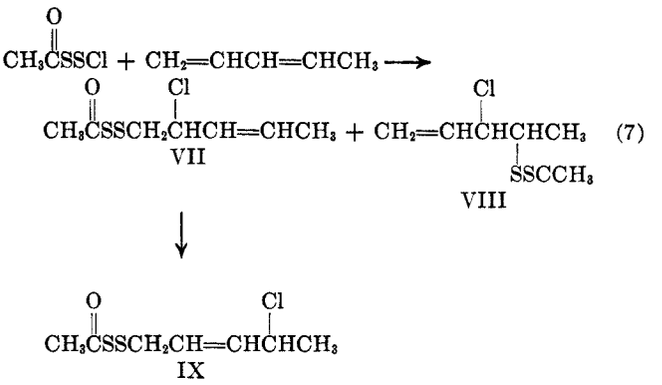
Butadiene.—The monoaddition of acetylthiosulfenyl chloride to butadiene yielded a single product derived from Markovnikov 1,2-addition (eq 6). Strong support for the assignment of the 1,2-adduct was received from characteristic infrared bands for the terminal vinyl group at 1645 cm^{-1} (C=C stretching), 3100 cm^{-1} (=CH_2 stretching), 3015 cm^{-1} (=CH stretching), 985 cm^{-1} (out-of-plane hydrogen deformation), and 925 cm^{-1} (=CH_2 out-of-plane deformation). The 60-Mc nmr spectrum confirmed this assignment. The nonequivalent terminal methylene protons show up as a multiplet centered near 5.35 ppm. These protons are coupled unequally with the internal vinyl proton which is a doublet of a double doublet at 5.97 ppm owing to further coupling with the methine proton α to chlorine. The methylene protons are nonequivalent owing to the asymmetry of the molecule and form a strongly coupled ABX-type system with the methine proton. The chemical shifts of the methylene protons are 2.97 and 3.21 ppm while the methine proton is a doublet of a doublet at 4.49 ppm.



(6)

Piperylene.—The reaction of piperylene with acetylthiosulfenyl chloride resulted in three monoadducts (eq 7). Predominant addition occurs at the terminal double bond[10] with the formation of 82% of the Markovnikov oriented 1,2-adduct VII. In addition, 5% of compound VIII, derived from addition to methyl substituted double bond, and 13% of the 1,4-adduct IX were obtained.

Mixtures of VII, VIII, and IX were quantitatively determined using nmr by measuring the characteristic methyl group doublets of each isomer (CH_3CH= 1.74 ppm, $CH_3C(S)H$– 1.38 ppm,[11] $CH_3C(Cl)H$– 1.56 ppm).

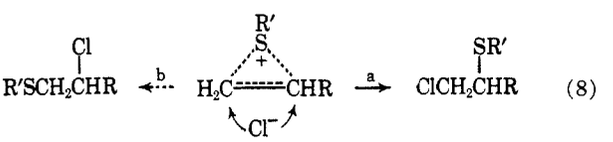


(7)

Compound IX is most likely the result of post-isomerization of adduct VII. Further allylic rearrangement of VII to the thermodynamically more stable compound IX was observed even in the presence of base on standing at ambient temperatures. This is in agreement with observations on similar terminally methyl substituted compounds.[3]

The infrared spectrum of IX suggests a *trans* nature of the double bond. It has characteristic bands at 3040 cm^{-1} (=CH stretching), 1673 cm^{-1} (C=C stretching), and 960 cm^{-1} (=CH– out-of-plane deformation) as expected for structure IX. Nmr parameters of compounds VII and IX are summarized in Table II.

Previous work on the addition of methane–sulfenyl chloride to alkyl-substituted terminal olefins has demonstrated that little or no partial charge is developed on the carbon atoms involved in the episulfonium ion intermediate.[2] Steric factors were found to control the ring opening and product formation proceeded predominantly *via* path a of eq 8. Path b, however,



(8)

becomes preferred if R represents an electronically more biased substituent such as vinyl or phenyl capable of stabilizing a partial positive charge at the site of chloride ion attack.[3]

In the present study it could be shown that the withdrawing effect of the acetyl group in R′ ($CH_3C(=O)$-S–) tends to destabilize a positive charge on the sulfur atom in the episulfonium ion, thus contributing to the development of a partial positive charge on the alkyl substituted carbon atoms. The result is more of a competition between a sterically and electronically controlled ring opening and subsequently lower adduct selectivity. As expected, a sterically controlled ring opening becomes increasingly important with the bulkiness of the substituent R (methyl or *t*-butyl).

The addition to isobutylene demonstrated that the accumulative electron-releasing effect of dialkyl substitution also becomes sufficient to favor path b. No evidence, however, for a true carbonium ion intermediate was detected. Otherwise, one would expect 1,4-adducts from butadiene and methyl migration during the addition to 3,3-dimethylbutene. The observed *trans* stereospecific addition to acenaphthylene also supports the postulated episulfonium ion intermediate.

(9) M. J. S. Dewar and R. C. Fahey, *J. Am. Chem. Soc.*, **85**, 2245, 2705 (1963).

(10) Predominant attack of the terminal double bond of piperylene and 4-methyl-1,3-pentadiene has also been observed with benzene- and methanesulfenyl chloride.[3]

(11) All other signals are partly overlapped by those of the major adducts.

Experimental Section

Method of Analyses.—Nmr spectra were recorded on either a Varian Model A-60 or HA-100 resonance spectrometer. The infrared spectra were obtained on a Beckman Model IR-10 infrared spectrophotometer.

Starting Materials. Starting Olefins.—The 3,3-dimethyl butene, *trans*-piperylene, and acenaphthylene were obtained from Columbia Organic Chemicals Co. Styrene, butadiene, and isobutylene are Matheson Co. products. The acenaphthylene was recrystallized three times from hexane, mp 92–93°. Butadiene of +95% purity and isobutylene of 99% purity were used as such. All other starting materials were distilled prior to their use.

Acetylthiosulfenyl Chloride.—To a stirred solution of 37.5 g (0.25 mole) of diacetyl disulfide[12] in 50 ml of dry methylene chloride 33.75 g (0.25 mole) of freshly distilled sulfuryl chloride was slowly added. The reaction was carried out under a nitrogen atmosphere and the reaction temperature kept at 10–15°. After the addition was completed, the mixture was stirred for 1.5 hr at ambient temperature. The progress of the reaction can be conveniently followed by nmr analysis. The following singlets were observed: diacetyldisulfide (2.50 ppm), acetylthiosulfenyl chloride (2.67 ppm), acetyl chloride (2.63 ppm). The acetyl chloride and solvent were removed on a rotary evaporator at ambient temperature (15 mm), thus affording 35 g (*ca.* 98% yield) of acetylthiosulfenyl chloride. Nmr analysis of the product indicated *ca.* 1% of the starting disulfide and no other impurities.

General Procedures for the Addition of Acetylthiosulfenyl Chloride to Unsaturates.—Acetylthiosulfenyl chloride was slowly added to a stirred 50% solution of the unsaturate in methylene chloride containing about 0.5% of suspended $CaCO_3$. Anhydrous reaction conditions were employed. Mole ratios of the reactants and reaction temperatures are tabulated in Table I.

The addition reaction is exothermic and very rapid. After the addition was completed, the reaction mixture was stirred at the reaction temperature for an additional 15–30 min, then the solvent and possible excess of the unsaturate were removed at 0° (2 mm). Nmr analysis of the crude product provided the isomer distribution (Table I) and conversion data to the adducts of >95%. The conversion was also confirmed by the weight of the crude product. Part of the product was purified by fractional distillation *in vacuo* which afforded samples for elemental analysis.

Registry No.—I, 13250-14-1; II, 13250-15-2; III, 13250-16-3; IV, 13250-17-4; V, 13250-18-5; VI, 13270-33-2; VII, 13270-34-3; VIII, 13250-19-6; IX, 13250-20-9; acetylthiosulfenyl chloride, 13250-24-3.

Acknowledgment.—The authors wish to thank W. C. Whitlock for excellent technical assistance and Dr. J. R. J. Reed for obtaining the 100-Mc nmr data.

(12) Diacetyl disulfide was prepared *via* oxidation of thiolacetic acid with dimethyl sulfoxide.

3-Hydroxydamsin, a New Pseudoguaianolide from *Ambrosia Psilostachya* DC (Compositae)

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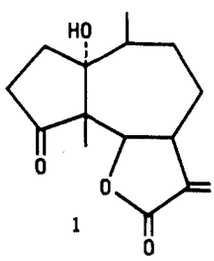
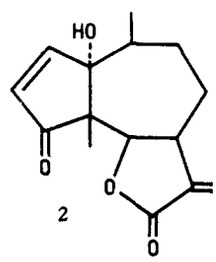
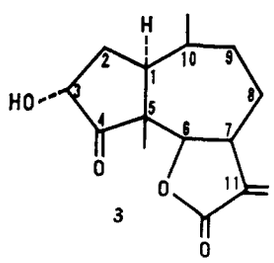
An investigation[2] of the infraspecific variation of sesquiterpene lactones in the Compositae species *Ambrosia psilostachya* DC has led to the isolation and structure determination of a new pseudoguaianolide, which we named 3-hydroxydamsin. Chloroform extraction of plant material from central Texas yielded two pseudoguaianolides of known structures, coronopilin (**1**) and parthenin (**2**), in addition to the new substance, 3-hydroxydamsin (**3**), $C_{15}H_{20}O_4$.



1



2



3

The spectral data suggested that the new sesquiterpene lactone contained several functional groups typically found in pseudoguaianolides: an α,β'-unsaturated γ-lactone [λ_{max} 212 mμ (ϵ 9400); infrared bands at 1750 (carbonyl) and 1660 cm^{-1} (double bond); and nmr signals at δ 4.74[3] (doublet, J = 9 cps, for the C-6 lactonic proton), 3.4 (multiplet for the C-7 proton), 5.59 and 6.30 (two doublets, J = 3 cps, for the C-11 methylene group protons)]; a 5-ring keto group [λ_{max} 308 mμ (ϵ 38) and the strong infrared band at 1750 cm^{-1} which was in accord with the presence of two carbonyl functions]; a C-5 tertiary methyl group [nmr singlet at δ 1.12]; a C-10 secondary methyl group [nmr doublet at δ 1.10, J = 6 cps]; and a secondary hydroxyl group [infrared band at 3500 cm^{-1}; nmr in deuteriochloroform, a double doublet at δ 4.37 (J = 7 and 2.5 cps, for the C-3 proton; in deuterated dimethyl sulfoxide, a doublet at δ 5.54 (J = 5 cps, for the hydroxyl proton)].

The new pseudoguaianolide (**3**) was transformed on silica gel into an isomeric $C_{15}H_{20}O_4$ substance to which we assigned structure **4**, in part, on the basis of the spectral data [λ_{max} 211 mμ (ϵ 9600) and 290 (45); infrared bands at 3530, 1750, and 1660 cm^{-1}; nmr in deuteriochloroform, the spectrum was similar to the one obtained for **3** with the exception that the δ 4.37 double doublet was replaced by a singlet at 4.13, which can be ascribed to the C-4 proton; in deuterated dimethyl sulfoxide, the δ 4.13 singlet disappeared and two new doublets (J = 5.5 cps) were observed at 3.98 (C-4 proton) and 5.05 (C-4 hydroxyl proton)]. Compound **4** was synthesized from damsin (**5**)[4] by bromination with trimethylaniline perbromide,[5] followed by an alkaline treatment. Based on the obvious relationship between

(1) National Institutes of Health Pre-doctoral Trainee, 1964–1967, Grant 511 GM-789.

(2) For recent investigations on the sesquiterpene lactones in this species, see (a) T. J. Mabry, H. E. Miller, H. B. Kagan, and W. Renold, *Tetrahedron*, **22**, 1139 (1966); (b) T. J. Mabry, W. Renold, H. E. Miller, and H. B. Kagan, *J. Org. Chem.*, **31**, 681 (1966); (c) H. B. Kagan, H. E. Miller, W. Renold, M. V. Lakshmikantham, L. R. Tether, W. Herz, and T. J. Mabry, *ibid.*, **31**, 1639 (1966).

(3) All chemical shift values are reported in parts per million (δ scale).

(4) For a discussion of the stereochemical features shown in **5** for damsin, see T. J. Mabry, H. B. Kagan, and H. E. Miller, *Tetrahedron*, **22**, 1943 (1966).

(5) A. Marquet and J. Jacques, *Bull. Soc. Chim. France*, 90 (1963).