(DMSO-$d_6$) δ 1.49 (s, 6, $CH_3$), 2.60 (s, 3, N-$CH_3$) and 3.23 (s, 2, $CH_2$).

*Anal.* Calcd for $C_6H_{13}N_2Cl$: C, 48.49; H, 8.82; N, 18.85. Found: C, 48.69; H, 8.90; N, 18.61.

**4-Aminobutyronitrile hydrochloride (3b)** showed the following characteristics (liquid ammonia, no solvent; ambient temperature, 40 hr): 53%; mp 144–145° (from ethanol–ether); infrared (KBr) 4.44 μ (C≡N); nmr (DMSO-$d_6$) δ 3.47 (s, 3, $-^+NH_3$).

*Anal.* Calcd for $C_4H_9N_2Cl$: C, 39.84; H, 7.52; N, 23.23. Found: C, 39.99; H, 7.49; N, 23.04.

**6-Methylaminohexanenitrile hydrochloride (3f)** showed the following characteristics (155°, 25 hr): 18%; mp 97–98° (from ethanol–ether; filtered under $N_2$ in a drybox); ir (KBr) 4.47 μ (C≡N); nmr (DMSO-$d_6$) δ 2.50 (broad singlet, 3, $CH_3$).

*Anal.* Calcd for $C_7H_{15}N_2Cl$: C, 51.69; H, 9.30; N, 17.22. Found: C, 51.55; H, 9.51; N, 17.05.

**N,N′-Dimethyl-1,4-diaminobutane (5b).**—$LiAlH_4$ (33.0 g, 0.08 mol in 125 ml of THF) reduction of 8.0 g (0.07 mol) of the free base of **4c** in 25 ml of the same solvent gave 4.0 g (50%) of **5b**, bp 71–72° (15 mm); **5b dihydrochloride** (ethanol–ether), mp 273–275° dec, lit.[15] mp 265° dec; **N,N′-dimethyl-N,N′-dibenzoyl-1,4-diaminobutane**, mp 116.5–117° (methylene chloride–hexane).

*Anal.* Calcd for $C_{20}H_{24}N_2O_2$: C, 74.05; H, 7.46; N, 8.63. Found: C, 74.26; H, 7.40; N, 8.36.

**Registry No.**—**3a**, 16011-89-5; **3b**, 16011-90-8; **3c**, 16011-91-9; **3e**, 16011-92-0; **3f**, 16011-93-1; **4a**, 7544-75-4; **4b**, 16011-95-3; **4c**, 7544-84-5; **4d**, 16012-00-3; **4e**, 7544-87-8; **4f**, 16011-96-4; **4g**, 16012-02-5; **5b**, 16011-97-5; **5b**·2HCl, 16011-98-6; N,N′-dimethyl-N,N′-dibenzoyl-1,4-diaminobutane, 16012-03-6.

[15] W. R. Boon, *J. Chem. Soc.*, 311 (1947).

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# β-Chloroalkylsulfenamides. The Addition of Dimethylaminosulfenyl Chloride to Unsaturated Hydrocarbons

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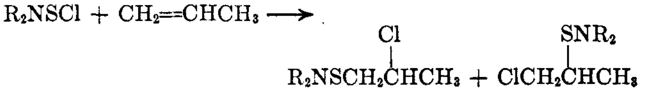
The ability of a variety of sulfenamides to act as vulcanization accelerators has been recognized for a number of years. More recently, a nematocidal activity has been ascribed to the $R_2NS$ function.[3] Therefore, the addition of dialkylaminosulfenyl chlorides to unsaturates as a synthetic route to β-chloroalkylsulfenamides is of interest. To our knowledge, the only prior work on this subject has been disclosed in the patent literature[4] and was limited to the aluminum chloride catalyzed addition of dialkyaminosulfenyl chlorides to propylene and cyclohexene. The observed exclusive Markovnikov orientation (I), *e.g.*



$$R_2NSCl + CH_2{=}CHCH_3 \longrightarrow \underset{\text{I}}{R_2NSCH_2\overset{\overset{\displaystyle Cl}{|}}{C}HCH_3} + \underset{\text{II}}{ClCH_2\overset{\overset{\displaystyle SNR_2}{|}}{C}HCH_3}$$

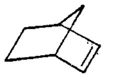
was in contrast to our recent work on the mechanism of sulfenyl chloride additions to terminal olefins.[5-7] With several sulfenyl chlorides and a variety of terminal alkenes, it had been found that sterically controlled ring opening of the episulfonium ion intermediate by the chloride ion takes place to afford predominantly the anti-Markovnikov adduct II. Postisomerization of the initial adducts led to I. Thus, it was of interest to establish a possible deviation from this mechanistic picture by aminosulfenyl chlorides, and to explore concurrently the synthetic scope of this addition reaction. For simplification of the important nmr analyses, the readily accessible dimethylaminosulfenyl chloride was chosen as a model reagent.[8]

**Addition to Olefins.**—Propylene, isobutylene, 3-methylbutene, 3,3-dimethylbutene, and norbornene were chosen as model systems. Dimethylaminosulfenyl chloride was added to a cold methylene chloride solution of the olefin. The reaction temperature employed was dependent on the reactivity of the olefin. The solution contained a small amount of calcium carbonate to prevent possible postisomerization.[5] In general, the reaction is quite sluggish in contrast to the previously experienced spontaneous reaction of methane-, benzene-, and acetylthiosulfenyl chloride with unsaturates.

The isomer distribution of the adducts obtained from the above olefins is summarized in Table I. The relative amounts of isomeric adducts could be deduced from nmr analyses of the crude product mixtures. A considerable amount of spectral data obtained during the previous studies in this area[5-7] aided the structure assignments. In general, protons α to chlorine are considerably deshielded relative to those α to sulfur.[7,9] A detailed compilation of the nmr parameters is given in Table II.

TABLE I

DIMETHYLAMINOSULFENYL CHLORIDE–OLEFIN ADDUCTS

| Olefin | Mole % adduct ratio | |
|---|---|---|
| $CH_2{=}C<$ | $\underset{Cl}{CH_2}{-}\underset{SN(CH_3)_2}{C}<$ | $\underset{SN(CH_3)_2}{CH_2}{-}\underset{Cl}{C}<$ |
| $CH_2{=}CHCH_3$ | 78[a] | 22 |
| $CH_3{=}C(CH_3)_2$ | 71 | 29 |
| $CH_2{=}CHCH(CH_3)_2$ | >90 | <10[b] |
| $CH_2{=}CHC(CH_3)_3$ | ~95 | ~5[b] |
|  | >98 (*trans*) | . . . |

[a] Registry no. in descending order are 16133-66-7, 16133-67-8, 16133-68-9, 16133-69-0, and 16133-72-5. [b] The adduct ratio was approximated due to partly overlapping nmr signals.

With the exception of the 3,3-dimethylbutene adduct, analytical samples were obtained by fractional distillation *in vacuo*.

An analysis of the data given in Table I shows that dimethylaminosulfenyl chloride additions to olefins follow the previously proposed mechanism.[5] The *trans* stereospecificity observed with norbornene supports the intervention of an episulfonium ion intermediate in the addition process.

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[1] To whom inquiries should be directed.

[2] Analytical Research Division.

[3] H. R. Williams, Canadian Patent 737,941 (1966).

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[5] W. H. Mueller and P. E. Butler, *J. Amer. Chem. Soc.*, **88**, 2866 (1966); *ibid.*, **90**, 000 (1968).

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[7] W. H. Mueller and P. E. Butler, *ibid.*, **32**, 2925 (1967).

[8] G. Weiss and G. Schulze, German Patent 1,131,222 (1962).

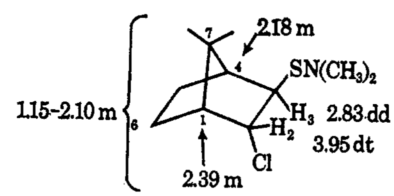
[9] P. E. Butler and W. H. Mueller, *Tetrahedron Lett.*, **19**, 2179 (1966).

TABLE II

NMR PARAMETERS OF DIMETHYLAMINOSULFENYL CHLORIDE–UNSATURATE ADDUCTS

| Olefin | Structures and group assignments[f] 1 | 2 | 3 | 4 | 5 | Chemical shifts,[a] ppm 1 | 2 | 3 | 4 | 5 | Coupling constant,[a] cps |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Propylene | $CH_3$ | $CHCl$ | $CH_2$ | $SNR_2$ | | 1.57 d | 4.18[b] | ~3.15[b,c] | 2.72 s | | $J_{1,2} = 6.4$; $J_{2,3} = 9.0, 5.3$ |
| | $CH_3$ | $CH$ | $(SNR_2)$ | $CH_2Cl$ | | 1.19 d | ~3.15[b,c] | 2.72 s | 3.46[b] dd<br>3.90 dd | | $J_{1,2} = 6.5$; $J_{2,4} = 3.3$;<br>$J_{2,4'} = J_{4g} = 9.4$ |
| 3-Methylbutene | $(CH_3)_2$ | $CH$ | $CH$ | $(SNR_2)$ | $CH_2Cl$ | 1.11 d<br>0.82 d | 2.21 dh | 3.00[b] ddd | 2.68 s | 3.88 [b]dd<br>3.95 dd | $J_{1,2} = 6.6$; $J_{2,3} = 4.0$; $J_{5g} = 10.8$<br>$J_{3,5} = 8.8, 5.8$ |
| 3,3-Dimethylbutene | $(CH_3)_3$ | $C$ | $CH$ | $(SNR_2)$ | $CH_2Cl$ | 1.03 s | | 2.80[b] t | 2.70 s | 3.71 [b]dd<br>3.93 dd | $J_{3,5} = 5.7, 5.3$; $J_{5g} = 11.3$ |
| Isobutylene | $(CH_3)_2$ | $C(SNR_2)$ | $CH_2Cl$ | | | 1.21 s | 2.73 s | | 3.68 s | | |
| | $(CH_3)_2$ | $C(Cl)$ | $CH_2$ | $SNR_2$ | | 1.51 s | | 3.12 s | 2.66 s | | |
| Methylacetylene | $CH_3$ | $C(SNR_2)=$ | $CHCl$[d] | | | 1.94 d | 2.73 s | 6.10 q | | | $J_{1,3} = 1.4$ |
| | $CH_3$ | $C(SNR_2)=$ | $CHCl$[e] | | | 2.17 d | 2.73 s | 6.44 q | | | $J_{1,3} = 0.7$ |
| | $CH_3$ | $C(Cl)=$ | $CH$ | $SNR_2$[d] | | 2.14 d | | 6.59 q | 2.66 s | | $J_{1,3} = 1.0$ |
| *t*-Butylacetylene | $(CH_3)_3$ | $C$ | $C(SNR_2)=$ | $CHCl$[d] | | 1.26 s | | 2.68 s | 5.90 s | | |
| | $(CH_3)_3$ | $C$ | $C(SNR_2)=$ | $CHCl$[e] | | 1.34 s | | 2.68 s | 6.03 s | | |

[a] Notation: s = singlet, d = doublet, t = triplet, q = quartet, h = heptet, m = multiplet, g = geminal. [b] These protons form an ABX-type spin system, the parameters are derived from first-order approximations. In general the methylene protons are a pair of double doublets overlapped and the methine proton a four-line double doublet pattern (in several cases the methine proton is further split by coupling with ddjacent protons). [c] The chemical shifts are approximate due to overlapping of peaks. [d] The dimethylaminosulfenyl and the chloro groups are *trans*. [e] The dimethylaminosulfenyl and the chloro groups are *cis*. [f] R = $CH_3$.



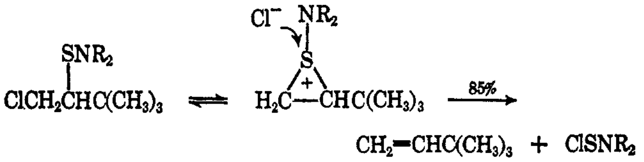
$J_{1,2} = 4.1$ cps
$J_{2,6_{exo}} = 1.2$ cps
$J_{2,3} = 4.3$ cps
$J_{3,4} = 0$ cps
$J_{3,7_{anti}} = 2.5$ cps

m = multiplet, dd = double doublet, dt = double triplet

The importance of steric factors in the kinetically controlled ring opening is reflected in the observed increase in adduct selectivity (attack by chloride at the primary carbon) with increasing bulkiness of the alkyl substituent on the olefin.

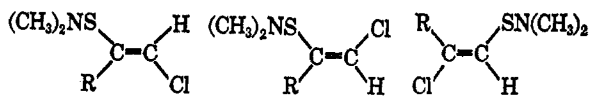
In contrast to the corresponding methane- or benzenesulfenyl chloride adducts, little tendency for postisomerization to the Markovnikov adducts was noted during the present study.

Attempts to distil the 3,3-dimethylbutene adduct revealed a strong tendency of this compound to revert to the starting materials. Steric crowding seems to facilitate the formation of the episulfonium ion. Subsequent attack of the chloride on the sulfur atom rather than on the substituted carbon atom explains the observed reversal. The preservation of the *t*-butyl group indicates a highly concerted cleavage mechanism. To our knowledge, this is the first reversible sulfenyl chloride addition to an olefin.



During this work, certain limitations of the synthetic value of this addition reaction have been found. Adducts from electronically more biased olefins, such as styrene or butadiene, decompose and polymerize rapidly at room temperature or in the latter case even as low as −20°.

**Additions to Acetylenes.**—Methylacetylene and *t*-butylacetylene were chosen as model substrates. The reactivity of the aminosulfenyl chloride toward the triple bond was found to be significantly less than that observed with terminal olefins. Semiquantitative nmr analysis (Table II) of the crude adduct mixtures permitted the determination of the isomer distribution. Methylacetylene adducts III, IV, and V were obtained in a selectivity of 84, 5, and 10%, respectively. The *t*-butylacetylene afforded only the adducts III and IV in a 9:1 molar ratio.



III IV V

Infrared bands at 3050 (CH stretching[10a]), 1592 (C=C stretching[10b]), and in the 790-cm$^{-1}$ region (=CH-out-of-plane deformation[10c]) for the methylacetylene adducts and similar bands at 3050 and 803 cm$^{-1}$ for the *t*-butylacetylene adducts support the assigned trisubstituted olefinic structures.

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(10) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1959, (a) p 44, (b) p 36, (c) p 51.

The structures of the major *trans*-adduct, III, and the *cis*-adduct, IV, both formed by anti-Markovnikov addition to the acetylenic bond, are assigned by analogy to the similar addition with dimethylphosphorylsulfenyl chloride.[6] In general, *trans* addition of sulfenyl chlorides to acetylenes has been assumed.[11,12] The dependence of product orientation on solvent has recently been reported.[12] A small increase of the *cis*-adduct, IV, due to postisomerization on standing at ambient temperature was noted during the present study.

## Experimental Section

**Starting Unsaturates.**—Propylene (99.7% purity), isobutylene (+99% purity), and methylacetylene (+98% purity) were obtained from Matheson Co. The 3,3-dimethylbutene and *t*-butylacetylene were products of the Columbia Organic Chemicals Co. and were distilled before use. The 3-methylbutene (99% purity) was obtained from Phillips Chemical Co. Norbornene from the Matheson Co. was sublimed prior to its use.

**Method of Analyses.**—Nmr spectra were recorded neat on a Varian Model A-60 resonance spectrometer using tetramethylsilane as an internal standard. The infrared spectra were obtained on a Beckman Model IR-10 infrared spectrophotometer.

**Dimethylaminosulfenyl Chloride.**—Dimethylamine (2 mol) was treated in an ethereal solution with 1 mol of freshly distilled sulfur dichloride according to a procedure described in a German patent.[8] The pure sulfenyl chloride, bp 55° (45 mm), was obtained in 55% yield. Its nmr spectrum showed a singlet at 3.12 ppm.

**General Procedure for the Addition of Dimethylaminosulfenyl Chloride to Unsaturated Hydrocarbons.**—An equimolar amount of the sulfenyl chloride was slowly added to a solution of the olefin in methylene chloride containing a small amount of suspended $CaCO_3$. In the case of acetylenes, a two- to fourfold excess of the unsaturate was used to avoid diadduct formation. The reactions were carried out under anhydrous conditions (nitrogen blanket) and at various reaction temperatures depending on the reactivity of the olefin, its boiling point being the limiting factor. Magnetic stirring was applied during all reactions. The progress of the addition was followed by nmr spectroscopy. Upon near completion of the reaction, the excess unsaturate and solvent were removed at 0° *in vacuo* (*ca.* 5 mm). The products were then again sampled for semiquantitative nmr analysis. In general, the crude products were found to be ~90% pure. For purposes of elemental analysis part of each product was further purified by fractional distillation *in vacuo*.

**To Propylene.**—To 9.7 g (0.23 mol) of propylene condensed into 50 ml of $CH_2Cl_2$ at −70°, 22.3 g (0.2 mol) of dimethylaminosulfenyl chloride was slowly added. The reaction mixture was kept at −70° for 2 hr and then for 1 additional hr at −50°. The solution was then slowly warmed to 0°. Removal of the solvent afforded 29.5 g (96%) of a pale yellow oil. An analytical sample, bp 77° (30 mm), was obtained on fractional distillation.

*Anal.* Calcd for $C_5H_{12}NSCl$: C, 39.06; H, 7.87; S, 20.85. Found: C, 39.08 H, 7.98; S, 20.85.

**To Isobutylene.**—The addition of 8 g (0.072 mol) of sulfenyl chloride to a solution of 4.1 g (0.073 mol) of isobutylene in 30 ml of $CH_2Cl_2$ proceeded slightly exothermically at −20°. The solvent was removed after 10 min at −20° and afforded 11.4 g (94%) of a pale yellow liquid which distilled at 73° (19 mm).

*Anal.* Calcd for $C_6H_{14}NSCl$: C, 42.97; H, 8.41; S, 19.12. Found: C, 42.87; H, 8.72; S, 19.03.

**To 3-Methylbutene.**—The sulfenyl chloride (8 g, 0.072 mol) was added to 5.1 g (0.073 mol) of 3-methylbutene in 30 ml of $CH_2Cl_2$ at −20°. After completion of addition the solution was slowly warmed to 0° and kept at this temperature for 30 min. Removal of the solvent afforded 12 g (92%) of crude product. The adduct distilled at 73–74° (9 mm).

*Anal.* Calcd for $C_7H_{16}NSCl$: C, 46.26; H, 8.87; S, 17.64. Found: C, 46.18; H, 9.03; S, 17.59.

**To 3,3-Dimethylbutene.**—The sulfenyl chloride (8 g, 0.072 mol) was added to 6.1 g (0.073 mol) of 3,3-dimethylbutene in 30 ml of $CH_2Cl_2$ at −20°. The solution was then allowed to warm to 0° and then kept at this temperature for 30 min. After an additional 30 min at ambient temperature, the solvent was removed at this temperature and 3 mm. A tan liquid, 11.8 g (84%), was obtained.

*Anal.* Calcd for $C_8H_{18}NSCl$: C, 49.08; H, 9.27; S, 16.38. Found: C, 48.99; H, 9.27; S, 16.70.

Attempted distillation at 80° (bath temperature) and 55 mm resulted in strong foaming and reversal of the adduct to its starting materials. Approximately 85% of the sulfenyl chloride and 3,3-dimethylbutene were collected in separate traps.

**To Norbornene.**—A slightly exothermic reaction at −20° was observed upon addition of 11.15 g (0.1 mol) of the sulfenyl chloride to 9.4 g (0.1 mol) of norbornene in 15 ml of $CH_2Cl_2$. After 15 min at −20° the reaction mixture was allowed to warm to −10°. Removal of the solvent at this temperature left 19.2 g (93%) of an orange oil. Distillation *in vacuo* afforded a tan liquid, bp 52–53.5° (0.001 mm).

*Anal.* Calcd for $C_9H_{16}NSCl$: C, 52.54; H, 7.84; S, 15.58. Found: C, 52.15; H, 8.05; S, 15.39.

**To Methylacetylene.**—The sulfenyl chloride (11.15 g, 0.1 mol) was slowly added to 20 g (0.5 mol) of methylacetylene condensed into 30 ml of $CH_2Cl_2$ at −30°. After 3 hr at this temperature, nmr analysis indicated only 20% conversion of the sulfenyl chloride. Therefore, 140 mg of $AlCl_3$ was added. Within 20 hr at −30° the reaction mixture had gradually darkened and the conversion had reached 85%. The excess methylacetylene was then removed at −30° and under slight vacuum. The solution was then cooled to −80°, 100 ml of precooled $CH_2Cl_2$ added, and the cold solution washed with 20 ml of 5% aqueous $NaHCO_3$ solution followed by 20 ml of water. After drying with $MgSO_4$ and removal of the solvent at ambient temperature (60 mm), 9.5 g (67%) of a dark liquid was obtained. Distillation afforded a tan, malodorous liquid, bp 88–89° (48 mm).

*Anal.* Calcd for $C_5H_{10}NSCl$: C, 39.60; H, 6.65; S, 21.14. Found: C, 40.07; H, 6.90; S, 21.18.

**To *t*-Butylacetylene.**—The sulfenyl chloride (2.78 g, 0.025 mol) was added to a solution of 6.3 g (0.077 mol) of *t*-butylacetylene in 5 ml of $CH_2Cl_2$ at 0°. After 15 min, at this temperature, the reaction mixture was allowed to reach room temperature and was then kept at ambient temperature for 5 hr. Removal of the solvent and excess unsaturate afforded 3.9 g (81%) of a light brown liquid. Distillation resulted in a yellow, malodorous liquid of bp 29–33° (0.003 mm).

*Anal.* Calcd for $C_8H_{16}NSCl$: C, 49.59; H, 8.32; S, 16.55. Found: C, 49.29; H, 8.13; S, 16.48.

**Registry No.**—III (R = $CH_3$), 16133-70-3; III (R = *t*-Bu), 16133-71-4.

**Acknowledgment.**—The authors wish to thank Mr. W. C. Whitlock for excellent technical assistance.

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[12] V. Calò, G. Melloni, G. Modena, and G. Scorrano, *Tetrahedron Lett.*, **49**, 4399 (1965), and references therein.

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# The Chemistry of Sulfoacetic Acid Derivatives.
# I. Reactions of Chlorosulfonylacetyl Chloride with Nucleophiles

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Vieillesfosse,[1] Bodendorf and Senger,[2] and Hinman and Locatell[3] have all investigated the course of the

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[3] (a) R. L. Hinman and L. Locatell, Jr., *J. Amer. Chem. Soc.*, **81**, 5655 (1959); (b) B. E. Hoogenboom, R. Abbott, L. Locatell, Jr., and R. L. Hinman, *J. Org. Chem.*, **24**, 1983 (1959); (c) R. L. Hinman and B. E. Hoogenboom, *ibid.*, **26**, 3461 (1961).