Anal. Calcd for $C_{13}H_{17}BF_4S$: C, 53.42; H, 5.82. Found: C, 53.3; H, 5.0.

1-Chloro-1-phenyl-2-(methylthio)-3-methyl-1-butene (6a) and 1-Chloro-1-phenyl-2-(methylthio)-3,3-dimethyl-1-butene (6b). Methanesulfenyl chloride (10 mmol) in 5 mL of anhydrous dichloromethane is added dropwise to 11 mmol of 1-phenyl-3-methyltbutyne (**2a**) or 1-phenyl-3,3-dimethylbutyne (**2b**) in 5 mL of the same solvent. The reaction in kept overnight at room temperature and washed with 5% aqueous $NaHCO_3$ and water to neutrality; the solvent is dried on Na_2SO_4 and evaporated under vacuum, leaving a pale yellow oil, yields >80%.

1-Chloro-1-phenyl-2-(methylsulfonyl)-3-methyl-1-butene (7a) and 1-Chloro-1-phenyl-2-(methylsulfonyl)-3,3-dimethyl-1-butene (7b). These were prepared from the corresponding sulfides **6a** and **6b** with 3-chloroperbenzoic acid in chloroform:[10] yields >80%; mp (**7a**) 90–92 °C; mp (**7b**) 91–92 °C.

Anal. Calcd for $C_{12}H_{15}ClO_2S$ (**7a**): C, 55.71; H, 5.80; Cl, 13.73; S, 12.38. Found: C, 55.4; H, 5.9; Cl, 13.8; S, 12.5. Calcd for $C_{13}H_{17}ClO_2S$ (**7b**): C, 57.25; H, 6.24; Cl, 13.03; S, 11.74. Found: C, 56.3; H, 6.05; Cl, 13.3; S, 11.6.

Structural Analyses. For **7a**: monoclinic, space group $C2/c$, a = 21.672 (2) Å, b = 5.374 (3) Å, c = 22.971 (2) Å, β = 104.1 (.1)°, Z = 8, D_o = 1.30 g cm^{-3}, D_c = 1.32 g cm^{-3}, μ(Mo Kα) = 3.86 cm^{-1}. For **7b**: orthorhombic, space group $P2_12_12_1$, a = 21.383 (4) Å, b = 11.334 (3) Å, c = 5.716 (2) Å, Z = 4, D_o = 1.31 g cm^{-3}, D_c = 1.31 g cm^{-3}, μ(Mo Kα) = 3.63 cm^{-1}. Intensity data were obtained from single crystals on a Philips PW 1100/15 four-circle diffractometer by using Mo Kα graphite-monochromatized radiation. Totals of 2353 (for **7a**) and 1445 (for **7b**) unique reflections were collected up to θ = 25°. The structure of **7a** was solved by the tridimensional Patterson–Fourier method, while for **7b** direct methods (MULTAN program) were used. Both were refined by full-matrix least-squares methods with anisotropic thermal parameters for nonhydrogen atoms. Hydrogen atoms were found from difference Fourier maps and isotropically refined. The final R factors for 1849 (**7a**) and 1013 (**7b**) observed reflections [$I_{obsd} \geq 3\sigma(I)$] were 3.73% and 3.88%, repsectively. Full data for positional and thermal parameters of both structures, together with F_c and F_o tables are available upon request from the authors.

Registry No. **1a**, 78890-97-8; **1b** (X = $SbCl_6$), 78890-99-0; **1b** (X = BF_4), 78891-00-6; **2a**, 1612-03-9; **2b**, 4250-82-2; **3** (X = $SbCl_6$), 56648-69-2; **3** (X = BF_4), 73569-52-5; (*E*)-**6a**, 78891-01-7; (*E*)-**6b**, 78891-02-8; (*E*)-**7a**, 78891-03-9; (*E*)-**7b**, 78891-04-0.

Mechanism of Base-Induced Rearrangement of Some Quaternized 5-(Chloroalkyl)thiazoles. A Kinetic Study

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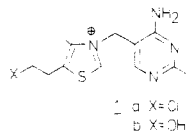
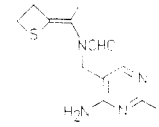
The base-induced rearrangement of quaternized 5-(chloroalkyl)thiazoles has been studied with UV kinetic spectroscopy. Rearrangement of the thiazolium compounds **5a** and **5b** proceeded in two consecutive, irreversible steps. The first of these was shown to be the nucleophilic attack of OH^- on C_2 of the thiazolium ring, affording the pseudobases **9a** and **9b** with measured second-order rate constants of 3.9 and 0.1 M^{-1} s^{-1}, respectively. The second step accessible to kinetic study was found to be the nucleophilic ring closure of the thiolates **11a** and **11b** through the displacement of Cl^- by S^- to form the thietanes **6a** and **6b**, respectively. In both cases, we obtained first-order rate constants of approximately 4×10^{-2} s^{-1}. The ring opening of the transient intermediates **9a** and **9b** was not observed, implying that this process takes place with a considerably higher rate than the other two steps. In the case of thiazolium compound **7**, only the hydrolysis step which leads to the pseudobase intermediate was observed and found to have a second-order rate constant of 3.0 M^{-1} s^{-1}. The activation parameters ΔH^* and ΔS^* for the reaction steps **5a** → **9a**, **11a** → **6a**, and **5b** → **9b** have been determined and found to support the proposed reaction mechanism.

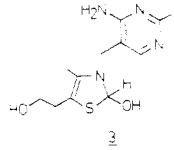
The first example of a base-induced rearrangement of 5-chloroalkylthiazolium compounds was published in 1957 by Yonemoto,[2] who found that the chloro analogue **1a** of



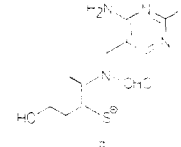
1 a X=Cl, b X=OH



2



3



thiamine rearranged to the thietane **2** on treatment with NaOH. At the same time, other workers[3] obtained this compound on treatment of thiamine (**1b**) with NaOH and benzenesulfonyl chloride. We have recently studied the rearrangement of a number of quaternized 5-(chloroalkyl)thiazoles in basic media.[1b,4] Thus, we found that the yields of the thietane products were rather sensitive to the nature of the substituents on the thiazolium ring. Furthermore, the fact that products with three- and five- to seven-membered rings could be obtained showed that the rearrangement is not restricted merely to the formation of the four-membered thietanes.

The alkaline hydrolysis of quaternized thiazoles lacking the 5-chloroalkyl group has been extensively studied. Thus, base treatment of thiamine (**1b**) has been found to involve an initial attack of OH^- on the carbon atom in position 2 of the thiazole ring, affording the pseudobase **3**.[5] This intermediate subsequently consumes a second

(1) (a) Department of Organic Chemistry. (b) Taken in part from the Ph.D. thesis of H.-J.F., Royal Institute of Technology, 1980. (c) Department of Physical Chemistry.

(2) Yonemoto, H. *Yakugaku Zasshi* **1957**, *77*, 1128; *Chem. Abstr.* **1958**, *52*, 5420*g*.

(3) (a) Kawasakai, C.; Tomita, I.; Motoyama, T. *Vitamins* **1957**, *13*, 57; *Chem. Abstr.* **1960**, *54*, 4595*d*. (b) Kawasaki, C.; Tomita, I. *Yakugaku Zasshi* **1959**, *79*, 295; *Chem. Abstr.* **1959**, *53*, 15090*f*.

(4) (a) Federsel, H.-J.; Bergman, J.; Stenhede, U. *Heterocycles* **1979**, *12*, 751. (b) Federsel, H.-J.; Bergman, J. *Heterocycles* **1980**, *14*, 33.

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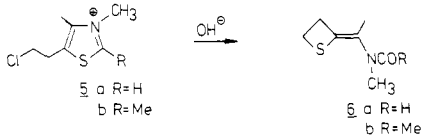
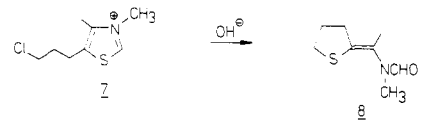
Scheme I



Scheme II



mole of OH^- and undergoes a ring opening to the thiolate **4**. For elucidation of the mechanistic action of thiamine (vitamin B_1) in biological systems, great efforts have been made to investigate the kinetics for the hydrolytic ring opening of various thiazolium compounds.[6]

The present kinetic investigation has been performed in order to examine the mechanism of the rearrangement of quaternized 5-(chloroalkyl)thiazoles. This process has previously[4] been proposed to consist of a base-induced ring opening followed by a ring closure through an internal displacement of Cl^- by S^-. We now report conclusive evidence for such a two-step procedure via a transient thiolate intermediate.

Results

UV spectroscopic measurements confirmed that the reactions shown in Schemes I and II are quantitative in dilute (10^{-3}–10^{-4} M) aqueous alkaline solutions (pH >10).

Reactions in Scheme I. The UV absorbance at the isosbestic points was found to be time dependent at pH >11.5, indicating the presence of a transient intermediate in each of the reaction sequences. UV spectra of these intermediates were obtained by kinetic measurements at different wavelengths at pH 14. In Figure 1, the UV spectra of starting material **5a**, the intermediate (i.e., **11a**), and product **6a** are shown.

The kinetics of each reaction was always independent of the wavelength throughout the pH interval 10–14. At pH <11.5, the measured pseudo-first-order rate constants were strictly proportional to $[OH^-]$ and afforded second-order rate constants of 3.9 ± 0.2 M^{-1} s^{-1} (**5a** → **6a**) and 0.1 ± 0.005 M^{-1} s^{-1} (**5b** → **6b**). The measured rate of product formation is independent of $[OH^-]$ at pH >13, and first-order rate constants of $(4.0 \pm 0.2) \times 10^{-2}$ and $(3.7 \pm 0.2) \times 10^{-2}$ s^{-1} were obtained, respectively.

Activation parameters have been determined for the two steps in the rearrangement of **5a** → **6a** and for the first step in the reaction sequence **5b** → **6b**. Thus, the following values were obtained: **5a** → **6a**, step 1, $\Delta H^{\ddagger} = 17.8$ kcal mol^{-1}, $\Delta S^{\ddagger} = 4.1$ eu; step 2, $\Delta H^{\ddagger} = 21.0$ kcal mol^{-1}, $\Delta S^{\ddagger} = 6.4$ eu; **5b** → **6b**, step 1, $\Delta H^{\ddagger} = 20.0$ kcal mol^{-1}, $\Delta S^{\ddagger} = 5.4$ eu.

Reaction in Scheme II. The UV absorbance was found to be time independent at the isosbestic point. Reactant consumption and product formation were found to be pseudo first order at all pH values (10–14), and a second-order rate constant of 3.0 ± 0.1 M^{-1} s^{-1} was obtained.

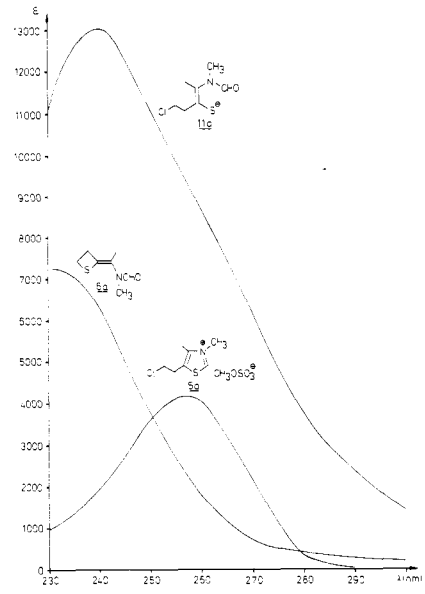


Figure 1. UV spectra of **5a** and **6a** recorded in water and of transient reaction intermediate **11a**.

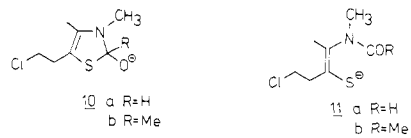
Discussion

Hydrolysis Step. A comparison of the second-order rate constants for the reactions **5a** → **6a** and **5b** → **6b** suggests that the point of OH^- attack is the 2-position of the thiazolium ring. The decreased rate constant in the case of compound **5b** is consistent with the observed increase of $\Delta H^{\ddagger}$. This observation is rationalized by the steric influence of the 2-methyl substituent on the OH^- attack as well as by the decreased electrophilic character of the carbon atom in this position, due to the electron-donating ability of the methyl group.[6b]

For both hydrolysis reactions in Scheme I, we find small positive values for $\Delta S^{\ddagger}$. It may seem surprising that a reaction involving association of two species should have a positive value for the entropy of activation. However, it has been pointed out that such a situation is not uncommon in cases where oppositely charged reactants form a neutral transition state.[7] The observed positive $\Delta S^{\ddagger}$ is therefore consistent with the formation of an uncharged pseudobase.

As expected, the chain length of the 5-chloroalkyl group has essentially no influence on the rate of OH^- attack, which is seen from a comparison of the second-order rate constants for **5a** and **7**.

Ring Closing Step. The UV spectra of the transient intermediate formed in each of the reaction sequences **5a** → **6a** and **5b** → **6b** were recorded. Since each intermediate decomposes in a pH-independent manner, their structure could be that of either a deprotonated pseudobase, **10**, or a ring-opened thiolate, **11**.



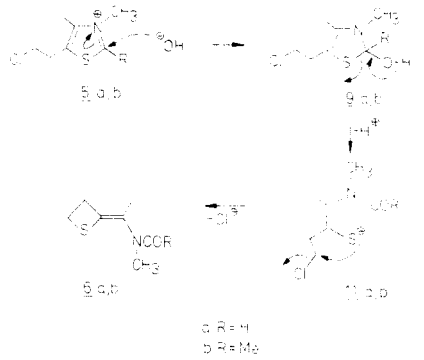
Depending on the structure assigned to the intermediate, we can attribute the measured first-order rate constant either to the ring opening of the deprotonated pseudobase

(5) (a) Maier, G. D.; Metzler, D. E. *J. Am. Chem. Soc.* **1957**, *79*, 4386, 6583 and references cited therein. (b) Breslow, R. *J. Am. Chem. Soc.* **1958**, *80*, 3719. (c) Yatco-Manzo, E.; Roddy, F.; Yount, R. G.; Metzler, D. E. *J. Biol. Chem.* **1959**, *234*, 733.

(6) (a) Vorsanger, H. *Bull. Soc. Chim. Fr.* **1967**, 551, 2124. (b) Haake, P.; Duclos, J. M. *Tetrahedron Lett.* **1970**, 461. (c) Vera, J.; Vidal-Abarca, J. B.; Serna, A. *An. Quim.* **1971**, *67*, 125. (d) Duclos, J. M.; Haake, P. *Biochemistry* **1974**, *13*, 5358. (e) Jordan, F.; Mariam, Y. H. *J. Am. Chem. Soc.* **1978**, *100*, 2534; **1980**, *102*, 7618. (f) Zoltewicz, J. A.; Uray, G. *J. Org. Chem.* **1980**, *45*, 2104. (g) Kluger, R.; Chin, J.; Smyth, T. *J. Am. Chem. Soc.* **1981**, *103*, 884.

(7) Willi, A. V. In "*Comprehensive* Chemical Kinetics"; Bamford, C. H., Tipper, C. F. H., Eds.; Elsevier: Amsterdam, 1977; Vol 8, pp 16–19.

Scheme III



or to the nucleophilic ring closure of the thiolate. The following four reasons strongly favor a ring-opened thiolate structure for the transient intermediate. (1) Earlier kinetic studies[6] on the hydrolysis of quaternized thiazoles indicate that the ring opening of a pseudobase is a considerably faster process than is indicated by the rate constants obtained for the reactions in Scheme I (e.g., $k \approx 4 \times 10^{-2}$ s^{-1}). (2) The UV curves for intermediate and end product of each reaction sequence show a similarity in shape, especially in the case of **6b**, which speaks in favor of the intermediate having the closest structural resemblance to the product (i.e., the thiolate). (3) The first-order rate constants obtained for the reactions in Scheme I are practically identical. However, if the structure of the intermediate would be the deprotonated pseudobase, one would expect to observe an influence on the rate of ring opening depending on the nature of the substituent at thiazole position 2. (4) The rate constants for hydrolysis of **5a** and **7** are practically identical. In the reaction sequence shown in Scheme II (i.e., **7** → **8**), no intermediate was detected, indicating that the rate of its consumption must be orders of magnitude higher than that for the corresponding reaction of Scheme I (i.e., intermediate → **6a**). It would be unreasonable to expect such a drastically increased rate for the opening of the deprotonated pseudobase **10a** on extending the chain length at thiazole position 5 with one methylene group. However, if we assume that the intermediate is the ring-opened thiolate **11a**, the kinetic results can be neatly rationalized by a decrease in ring strain on going from a four-membered (e.g., thietane **6a**) to a five-membered ring (e.g., thiolane 8).

Reaction Mechanism. On the basis of the kinetic results mentioned above, we propose the mechanism shown in Scheme III for the rearrangement reaction.

Stereochemistry. Results from NMR spectroscopy and GC indicate that only one of the two possible geometrical isomers of the products is formed. Good agreement was found between the experimentally determined dipole moment for the compound obtained from **5a** (μ = 5.27 ± 0.07 D) and the theoretically calculated value[8] for the *Z* isomer **6a** (μ_{max} = 5.50 D). Furthermore, X-ray crystallography[9] has shown that the product (i.e., **2**) obtained from base treatment of **1a** has the originally proposed[2,3] *Z* configuration. Finally, it has been shown that the ring opening of thiophenes in the presence of alkyl halides affords the *Z* isomers of the S-alkylated products.[10] Thus, there are several results indicating that the rearrangement products have the *Z* configuration.

It has been reported that treatment of the (*Z*)-thiolate **4** with sulfur leads to an equilibrium with the (*E*)-thiolate by an isomerization process involving a thiocarbonyl intermediate.[11] Thus, it was possible to isolate the *E* isomer of **2** after treatment of this equilibrium mixture with cyanogen bromide and to make a definite determination of its structure with X-ray crystallography.[12]

Conclusions

Depending on the pH value and the length of the 5-chloroalkyl side-chain, the rate-determining step for the formation of rearranged product is either the OH^- attack on the carbon atom in position 2 of the thiazolium ring or the nucleophilic ring closure of the thiolate intermediate. A 2-methyl substituent reduces the rate of OH^- attack, whereas the rate of ring closure is practically unaffected. The rearrangement products have the *Z* configuration.

Experimental Section

General Methods. Ultraviolet spectra were recorded with water as the solvent on a Shimadzu MPS-50L UV/vis spectrophotometer. Infrared spectra were obtained on a Perkin-Elmer 257 spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker WP-200 instrument. Chemical shifts are reported as δ values in parts per million relative to tetramethylsilane (δ 0.00). Mass spectra were obtained on a LKB 9000 spectrometer (IP 70 eV). Melting points (Leitz hot-stage microscope) and boiling points are uncorrected. The pH was measured on a Metrohm E520 pH meter.

Dipole Moment Determination. The dielectric measurements were performed on a Wissenschaftlich-Technischen Werkstätten Dipolmeter DM 01 (measuring frequency 2 MHz) equipped with a DFL 2 measuring cell. The cell and a Hilger–Abbe-type refractometer were thermostated at 25 ± 0.2 °C. Cyclohexane (Merck, analytical grade) was used as the solvent to prepare solutions in the 0–0.1 M range. The measuring scale of the dipolmeter was linear in ϵ and was calibrated with solvents of known ϵ. For this purpose cyclohexane and di-*n*-butyl ether (Merck, Uvasol) were used. The values used for their dielectric constants ϵ at 25.0 °C were 2.0148 and 3.048, respectively.[13]

The dipole moment was calculated using the Guggenheim[14] method.

Kinetic Measurements. The experiments were performed at ambient temperature, and the course of the reactions was followed in the wavelength interval 230–290 nm. Reactions were initiated by injecting 250 μL of a stock solution ($\approx 10^{-3}$ M) of the thiazolium compound in water with a syringe into a UV cuvette containing 2.5 mL of buffer solution, followed by manual shaking of the cuvette for ≈5 s. All kinetic plots were first-order up to at least 4 half-lives. Observed first-order rate constants were obtained by plotting ln $(A_\infty - A_t)$ vs. time, where A_t is the absorbance at time t and A_∞ is the final absorbance, and from the equation $k_{obsd} = 0.693/t_{0.5}$.

Temperature kinetic studies were performed in the interval 0–40 °C at points separated by 5 °C. The temperature was maintained with an accuracy of ±0.1 °C by circulating thermostated ethanol through the jacket of the sample holder. Measurements of temperature were performed in the cuvette. The activation parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$ were obtained from plots of ln k/T vs. $1/T$.[15]

5-(β-Chloroethyl)-3,4-dimethylthiazolium Methyl Sulfate (5a). Dimethyl sulfate (2.5 g, 0.02 mol) was added (1–2 min) to

(8) Federsel, H.-J.; Norne, J. E., unpublished results. The theoretical value for the *E* isomer of **6a** was found to be μ_{max} = 4.80 D.

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(10) (a) Jakobsen, H. J. *Acta Chem. Scand.* **1970**, *24*, 2263. (b) Gronowitz, S.; Frejd, T. *Int. J. Sulfur Chem., Part A*, **1972**, *2*, 165.

(11) Murakami, M.; Takahashi, K.; Iwanami, M.; Iwamoto, H. *Yakugaku Zasshi* **1965**, *85*, 752; *Chem. Abstr.* **1965**, *63*, 13249e.

(12) Kazuhide, K.; Wada, Y.; Nishikawa, M.; Asakawa, H.; Hirano, H. *Takeda Kenkyushoho* **1970**, *29*, 394; *Chem. Abstr.* **1971**, *74*, 104236.

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(14) Guggenheim, E. A. *Trans. Faraday Soc.* **1949**, *45*, 714.

(15) Frost, A. A.; Pearson, R. G. "Kinetics and Mechanism", 2nd ed.; Wiley: New York, 1961; Chapter 5, p 98.

a solution of freshly distilled 5-(β-chloroethyl)-4-methylthiazole[16] (3.2 g, 0.02 mol) in acetone (analytical grade, 10 mL) at room temperature. The reaction mixture was subsequently kept at ≈20 °C for 24 h. After storage of the reaction mixture in the refrigerator for 1–2 h, a white precipitate was formed. This was collected and washed with acetone (25 mL) to afford the white crystalline product: yield 4.9 g (85%); mp 92 °C; ^{1}H NMR (200 MHz, D_2O) δ 2.57 (s, 3, C_4-CH_3), 3.48 (t, 2, J = 7 Hz, C_5-CH_2), 3.72 (s, 3, CH_3O), 3.93 (t, 2, J = 7 Hz, CH_2Cl), 4.17 (s, 3, NCH_3), 9.78 (s, 1, C_2-H). Anal. Calcd for $C_8H_{14}ClNO_4S_2$: C, 33.39; H, 4.90; N, 4.87; S, 22.28. Found: C, 33.31; H, 5.03; N, 4.84; S, 22.40.

5-(β-Chloroethyl)-2,3,4-trimethylthiazolium Methyl Sulfate (5b). The same procedure as for **5a** was used by starting from 5-(β-chloroethyl)-2,4-dimethylthiazole[17] (0.88 g, 0.005 mol) and dimethyl sulfate (0.63 g, 0.005 mol) in acetone (3 mL). After evaporation of the solvent, the product was obtained as an oil which was used without purification: ^{1}H NMR (200 MHz, D_2O) δ 2.49 (s, 3, C_4-CH_3), 2.92 (s, 3, C_2-CH_3), 3.38 (t, 2, J = 6 Hz, C_5-CH_2), 3.71 (s, 3, CH_3O), 3.86 (t, 2, J = 6 Hz, CH_2Cl), 3.92 (s, 3, NCH_3).

5-(γ-Chloropropyl)-3,4-dimethylthiazolium Methyl Sulfate (7). The same procedure as for **5a** was used by starting from 5-(γ-chloropropyl)-4-methylthiazole[18] (3.4 g, 0.019 mol) and dimethyl sulfate (2.4 g, 0.019 mol) in acetone (10 mL). After evaporation of the solvent, the product was obtained as an oil which was used without purification: ^{1}H NMR (200 MHz, D_2O) δ 2.17 (m, 2, J = 7 Hz, CCH_2C), 2.51 (s, 3, C_4-CH_3), 3.13 (t, 2, J = 7–8 Hz, C_5-CH_2), 3.66 (t, 2, J = 6 Hz, CH_2Cl), 3.73 (s, 3, CH_3O), 4.11 (s, 3, NCH_3), 9.68 (s, 1, C_2-H). Anal. Calcd for $C_9H_{16}ClNO_4S_2$: C, 35.82; H, 5.34; N, 4.64; S, 21.25. Found: C, 35.34; H, 5.57; N, 4.56; S, 20.71.

***N*-Methyl-*N*-[(*Z*)-1-(2-thietanylidene)ethyl]formamide (6a).** Compound **5a** (2.9 g, 0.01 mol) was dissolved in water (10 mL) at room temperature, and trichloroethylene (10 mL) was added. The water phase was separated after extraction and a new portion of trichloroethylene (10 mL) was added followed by 1 M sodium hydroxide (22 mL, ≈0.022 mol) in one portion. After the two-phase system was stirred for 5–10 min at ambient temperature, the phases were separated, and the water phase was extracted with trichloroethylene (10 mL). The combined organic phases were dried (Na_2SO_4) and evaporated. Distillation afforded the product as a colorless oil: yield 1.2 g (78%); bp 71–73.5 °C (0.05 mmHg); n^{25}_D 1.5514; IR (neat) 1670 cm^{-1} (amide C=O); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.72 (t, 3, J = 1.5 Hz, =CCH_3), 2.91 (d, 3, NCH_3), 3.15–3.22 (2 t, 2 H, J = 6–7 Hz, SCH_2), 3.47–3.55 (m, 2, C=CH_2), 8.02 (s, 1, CHO); ^{13}C NMR ($CDCl_3$) δ 15.0, 20.6, 28.7, 34.2, 124.3, 129.3, 162.4[19]; mass spectrum, m/z (relative intensity) 157 (42, M^+), 124 (66), 116 (43), 111 (84), 68 (37), 56 (100). Anal. Calcd for $C_7H_{11}NOS$: C, 53.47; H, 7.05; S, 20.39. Found: C, 53.18; H, 6.93; S, 20.10.

***N*-Methyl-*N*-[(*Z*)-1-(2-thietanylidene)ethyl]acetamide (6b).** The same procedure as for **6a** was used by starting from **5b** (0.91 g, 0.003 mol) dissolved in water (5 mL), trichloroethylene (5 mL), and 1 M NaOH (7 mL, ≈0.007 mol). Distillation afforded the product as a colorless oil: yield 0.29 g (56%); bp 65–67 °C (0.05 mmHg); IR (neat) 1655 cm^{-1} (amide C=O); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.70 (s, 3, =CCH_3), 2.04 (s, 3, CH_3CO), 2.91 (s, 3, NCH_3), 3.17 (t, 2, J = 6–7 Hz, SCH_2), 3.48 (t, 2, J = 6 Hz, =CCH_2); ^{13}C NMR ($CDCl_3$) δ 14.6, 20.3, 20.8, 31.5, 34.0, 126.6, 132.4, 170.4; mass spectrum, m/z (relative intensity) 171 (23, M^+), 138 (54), 125 (78), 124 (14), 110 (12), 100 (22), 95 (24), 94 (11), 82 (28), 56 (100). Anal. Calcd for $C_8H_{13}NOS$: C, 56.11; H, 7.65; S, 18.72. Found: C, 55.57; H, 7.74; S, 18.60.

***N*-[(*Z*)-1-(Dihydro-2(3*H*)-thienylidene)ethyl]-*N*-methylformamide (8).** The same procedure as for **6a** was used by starting from **7** (3.0 g, 0.01 mol) dissolved in water (10 mL), trichloroethylene (10 mL), and 1 M NaOH (22 mL, ≈0.022 mol). Recrystallization from hexane–methanol afforded the product as white crystals: yield 1.6 g (92%); mp 50–52 °C; IR ($CHCl_3$) 1665 cm^{-1} (amide C=O); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.89 (s, 3, =CCH_3), 2.15 (m, 2, J = 6–7 Hz, CCH_2C), 2.61 (t, 2, J = 6–7 Hz, SCH_2), 2.94 (s, 3, NCH_3), 3.01 (t, 2, J = 6 Hz, =CCH_2), 8.01 (s, 1, CHO); ^{13}C NMR ($CDCl_3$) δ 18.7, 28.3, 30.6, 33.4, 33.7, 122.5, 141.3, 163.1; mass spectrum, m/z (relative intensity) 171 (78, M^+), 143 (10), 142 (16), 130 (45), 124 (65), 115 (10), 114 (16), 112 (26), 111 (18), 110 (10), 109 (10), 87 (10), 82 (19), 71 (10), 59 (10), 58 (12), 56 (100). Anal. Calcd for $C_8H_{13}NOS$: C, 56.11; H, 7.65; S, 18.72. Found: C, 56.12; H, 7.72; S, 18.72.

Registry No. 5a methyl sulfate, 78919-46-7; **5b** methylsulfate, 78891-19-7; **6a**, 71114-46-0; **6b**, 78891-20-0; **7** methylsulfate, 78891-22-2; **8**, 78891-23-3; dimethyl sulfate, 77-78-1; 5-(β-chloroethyl)-4-methylthiazole, 533-45-9; 5-(β-chhloroethyl)-2,4-dimethylthiazole, 31299-90-8; 5-(γ-chloropropyl)-4-methylthiazole, 6469-36-9.

(16) This compound was obtained from A. B. Astra, 15185 Södertälje, Sweden.
(17) This compound was prepared according to the method of: Lindberg, U. H.; Bexell, G.; Ulff, B. *Acta Pharm. Suec.* **1971**, *8*, 49.
(18) This compound was obtained as the ethanedisulfonate salt from de Laire Chimie SA, 62104 Calais, France.
(19) For assignment of ^{13}C NMR signals of compound **6a**, see ref 4a.

Amidoselenation of Olefins and Its Utilization for Synthesis of Allylic Amides

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The reaction of phenylselenyl chloride with olefins in acetonitrile containing trifluoromethanesulfonic acid and water affords β-acetamidoalkyl phenyl selenides in good to excellent yields. This represents the first example of one-pot amidoselenation of mono- and disubstituted olefins. The reaction can be carried out in benzonitrile, propionitrile, butyronitrile, or ethyl cyanoacetate. It was confirmed that the amidoselenation reaction proceeds with trans stereospecificity. Oxidative elimination of the produced β-amidoalkyl phenyl selenides gives allylic amides selectively in good to excellent yields. These two reactions constitute a good method for conversion of olefins to allylic amides.

The chemistry of organoselenium compounds is of current interest owing to their fertile and easily manipulated nature.[1] For utilization in organic syntheses, one of the key reactions is the introduction of selenium into

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