of **4** is oxidized by selenium dioxide[28] and is iodinated at elevated temperature,[29] while that of **8** is unreactive.[30] All of these results are consistent with the pattern of kinetic acidities observed in our exchange studies.

Conclusions

Two key findings have emerged from these studies: the value of k_{OD} for exchange in 1,5-dimethyl-4-nitroimidazole is much closer to that for nitromethane than for *o*-nitrotoluene; k_{OD} is greatly depressed in **6** and **7**, the two members of the series which lack vinylogous coupling between the methyl and nitro groups. We conclude that there may be significant localization in the 4,5 double bond of N-substituted imidazoles and that canonical form **1a** may not make an important contribution to amidine stabilization in such ring systems.

Registry No. 3, 7464-68-8; **4**, 551-92-8; **5**, 57658-79-4; **6**, 13230-04-1; **7**, 5297-92-7; **8**, 5213-48-9; 4-methyl-5-nitroimidazole, 14003-66-8; 4-methyl-2-nitroimidazole, 5213-35-4.

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[31] Shimada, K.; Kuriyama, S.; Kanazawa, T.; Satoh, M. *Yakugaku Zasshi* 1971, *91*, 231; *Chem. Abstr.* 1971, *74*, 141633.

Stability and Reactivity of Thiirenium Ions. Dependence on Alkyl or Aryl Substitution at Ring Carbons

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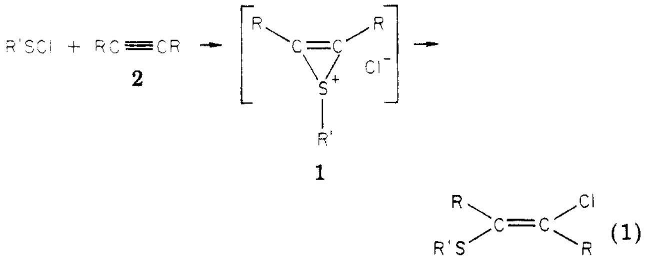
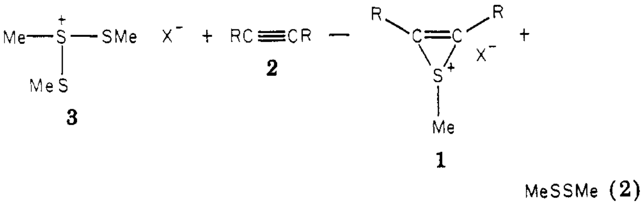
1-Methyl-2-phenyl-3-isopropylthiirenium (**1a**) hexachloroantimonate was observed at −60 °C and 1-methyl-2-phenyl-3-*tert*-butylthiirenium (**1b**) hexachloroantimonate and tetrafluoroborate were isolated as salts which were stable at room temperature. The addition of chloride ion to **1b** gives only the stereospecific anti and regiospecific Markovnikov adduct. The order of stability of ions **1a** and **1b** and the observed orientation are explained in terms of inductive and resonance properties of ring substituents.

Thiirenium ions **1** were suggested as intermediates in the addition of sulfenyl chlorides to alkynes **2** (eq 1).[1]

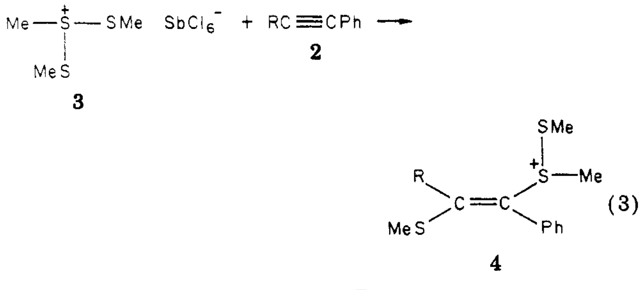


Recently we have reported the spectroscopic observation[2,3] and, in some cases,[4] the isolation of relatively stable 2,3-dialkylthiirenium ions formed by reaction of methylbis(methylthio)sulfonium (**3**) hexachloroantimonate[5] or tetrafluoroborate[6] with dialkylacetylenes **2** (eq 2).



R = alkyl; X = $SbCl_6$, BF_4

The stability of ions **1** depends so much on the nature of substituents on the ring carbons that we have been able to detect dialkyl-substituted species only. Attempts to detect thiirenium ions from the reaction of sulfonium ion **3** with 1-phenylpropyne or 1-phenyl-1-butyne failed as only the addition products **4** could be observed (eq 3).[6]



R = Me,Et

We report two cases where the nature of the alkyl residue in phenylacetylenes makes 2-phenyl-substituted

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[1] For pertinent reviews see: (a) Kharasch, N. In "Organic Sulfur Compounds"; Kharasch, N., Ed.; Pergamon Press: New York, 1961; Vol. 1, p 375. (b) Modena, G.; Scorrano, G. *Mech. React. Sulfur Compd.* **1968**, *3*, 115. (c) Schmid, G. H. *Top. Sulfur Chem.* **1977**, *3*, 101.

[2] Capozzi, G.; De Lucchi, O.; Lucchini, V.; Modena, G. *J. Chem. Soc., Chem. Commun.* **1975**, 248.

[3] Capozzi, G.; Lucchini, V.; Modena, G. *Rev. Chem. Intermed.* **1979**, *2*, 347.

[4] Capozzi, G.; Lucchini, V.; Modena, G.; Scrimin, P. *Tetrahedron Lett.* **1977**, 911.

[5] Capozzi, G.; Lucchini, V.; Modena, G.; Rivetti, F. *J. Chem. Soc., Perkin Trans. 2* **1975**, 900.

[6] Capozzi, G.; Da Col. L.; Lucchini, V.; Modena, G.; Valle, G. *J. Chem. Soc., Perkin Trans. 2* **1980**, 68.

0022-3263/81/1946-4720$01.25/0

Table I. ^{1}H NMR Parameters for Compounds Described in the Text

	solvent (temp, °C)	chemical shift, δ (J, Hz) SMe or SO_2Me	t-Bu	i-Pr H	i-Pr Me (^3J)	Ph
1-methyl-2-phenyl-3-isopropylthiirenium ion (**1a**)	SO_2 (−60)	2.69		*a*	1.66, 1.64 (6.8)	8.13–7.57
1-methyl-2-phenyl-3-*tert*-butylthiirenium ion (**1b**)	SO_2 (−60)	2.74	1.70			8.07–7.69
(*E*)-1-chloro-1-phenyl-2-(methylthio)-3-methyl-1-butene (**6a**)	$CDCl_3$	1.74		3.45	1.14 (7.0)	7.52–7.10
(*E*)-1-chloro-1-phenyl-2-(methylthio)-3,3-dimethyl-1-butene (**6b**)	$CDCl_3$	1.88	1.47			7.45–7.21
(*E*)-1-chloro-1-phenyl-2-(methylsulfonyl)-3-methyl-1-butene (**7a**)	$CDCl_3$	2.58		3.61	1.49 (7.0)	7.41
(*E*)-1-chloro-1-phenyl-2-(methylsulfonyl)-3,3-dimethyl-1-butene (**7b**)	$CDCl_3$	2.52	1.67			7.42

[a] Hidden under decomposition peaks.

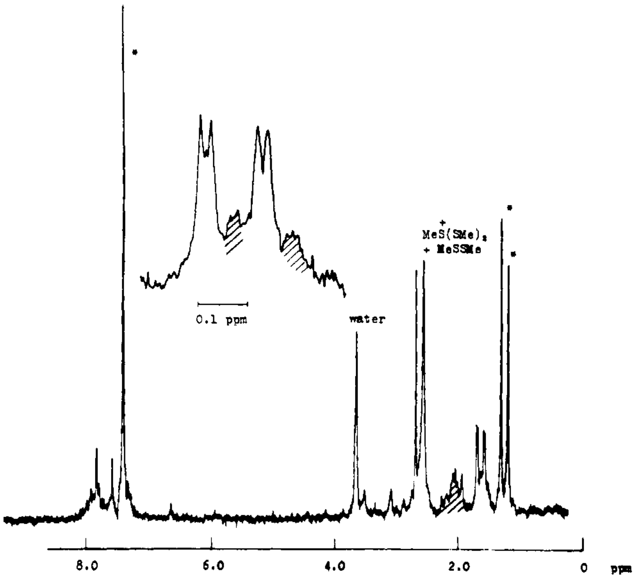
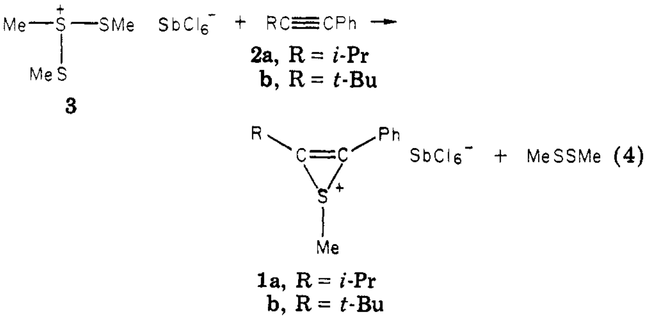


Figure 1. ^{1}H NMR spectrum of thiirenium ion **1a** in SO_2 at −60 °C; an asterisk denotes signals of alkyne **2a**; decomposition bands and signals from acetone-d_6 capillary (lock) are shaded.

thiirenium ions stable enough for detection and, in one case, isolation.

Results

We investigated the reaction of sulfonium **3** hexachloroantimonate with 1-phenyl-3-methylbutyne (**2a**) and 1-phenyl-3,3-dimethylbutyne (**2b**) in sulfur dioxide at −60 °C (eq 4). The reaction, as monitored by ^{1}H NMR spectroscopy, is slow in both cases and can be brought to completion only in the case of acetylene **2b**: the hexachloroantimonate salt of 1-methyl-2-phenyl-3-*tert*-butylthiirenium ion (**1b**) shows remarkable stability and can be isolated at room temperature. Under the same conditions, 1-methyl-2-phenyl-3-isopropylthiirenium (**1a**) hexachloroantimonate is not equally stable, and extensive decomposition occurs before the completion of the reaction.



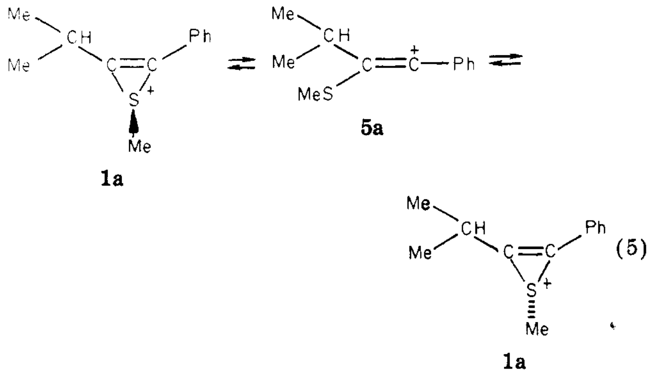
3

2a, R = *i*-Pr
b, R = *t*-Bu

1a, R = *i*-Pr
b, R = *t*-Bu

The ^{1}H NMR parameters of thiirenium ions **1a** and **1b** are reported in Table I. In Figure 1 the spectrum of **1a** is also shown: it should be noticed that the frequency difference of the geminal methyls in the isopropyl moiety of **1a**, which arises from the chirality of sulfonium sulfur, is a consequence of its rigid pyramidal arrangement. This arrangement has already been demonstrated theoretically[7] and experimentally[3,8] on other thiirenium ions.

The magnetic nonequivalence of the geminal methyls may be lost either through pyramidal inversion at sulfonium sulfur (a very unlikely possibility[7]) or through a process of ring opening–ring closure with the intermediacy of the achiral vinyl cation **5a** (eq 5). β-Thiovinyl cations **5** have also been proposed, together with or alternatively to thiirenium ions **1**, as intermediates for the addition reaction (eq 1).[1]



1a **5a** **1a**

At −40 °C, when thiirenium ion **1a** can still be detected for a sufficiently long time, the peaks of geminal methyls show no tendency to coalescence. For a chemical shift difference between geminal methyl resonances of 1.3 Hz at 60 MHz, the rate constant for the process at the temperature T_c of coalescence is 2.9 s^{-1}. On the assumption of $T_c = -40$ °C, a free energy of activation of $\Delta G^{\ddagger} = 13$ kcal mol^{-1} can be deduced[9] from the Eyring equation. This value must be considered a lower limit for the actual free energy of activation for the process of ring opening in thiirenium ion **1a** as well as in other thiirenium ions.

Thiirenium ion **1b** was also isolated as the tetrafluoroborate salt from the reaction in sulfur dioxide at −60 °C

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(7) Csizmadia, I. G.; Bernardi, F.; Lucchini, V.; Modena, G.; *J. Chem. Soc., Perkin Trans. 2* **1977**, 542.

(8) Destro, R.; Pilati, T.; Simonetta, M. *Nouv. J. Chim.* **1979**, *3*, 533.

(9) Martin, M. L.; Delpuech, J. J.; Martin, G. J. "Practical NMR Spectroscopy"; Heyden: London, 1980; pp 300, 340.

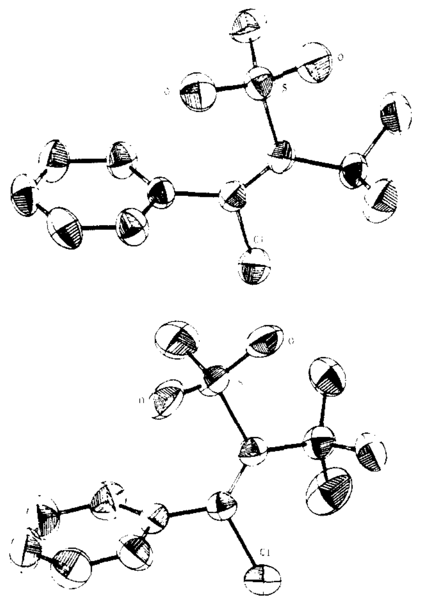
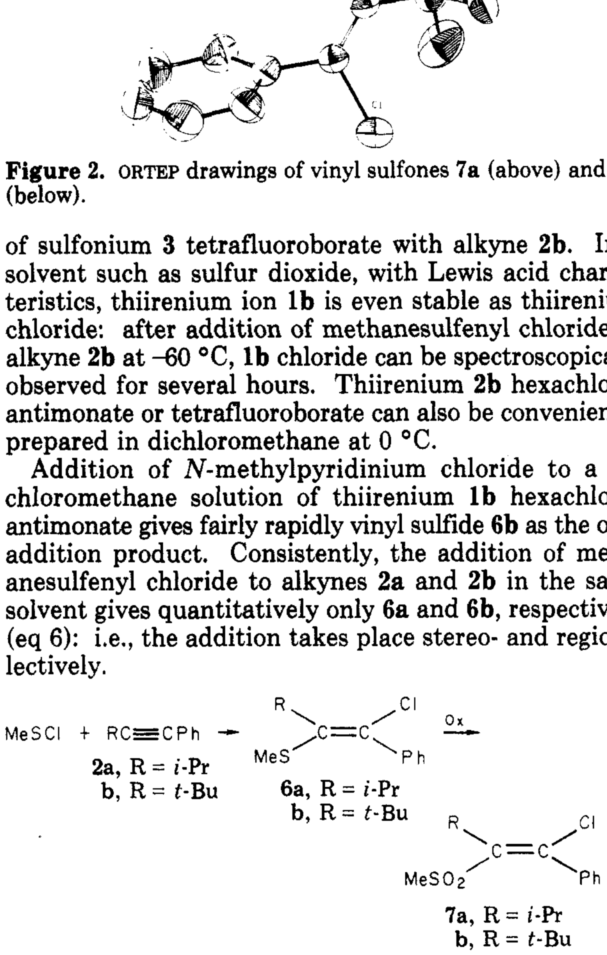


Figure 2. ORTEP drawings of vinyl sulfones **7a** (above) and **7b** (below).

of sulfonium **3** tetrafluoroborate with alkyne **2b**. In a solvent such as sulfur dioxide, with Lewis acid characteristics, thiirenium ion **1b** is even stable as thiirenium chloride: after addition of methanesulfenyl chloride to alkyne **2b** at −60 °C, **1b** chloride can be spectroscopically observed for several hours. Thiirenium **2b** hexachloroantimonate or tetrafluoroborate can also be conveniently prepared in dichloromethane at 0 °C.

Addition of *N*-methylpyridinium chloride to a dichloromethane solution of thiirenium **1b** hexachloroantimonate gives fairly rapidly vinyl sulfide **6b** as the only addition product. Consistently, the addition of methanesulfenyl chloride to alkynes **2a** and **2b** in the same solvent gives quantitatively only **6a** and **6b**, respectively (eq 6): i.e., the addition takes place stereo- and regioselectively.



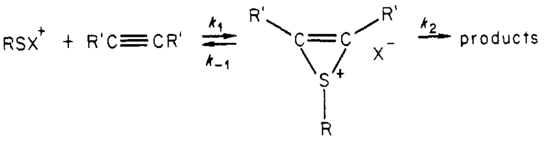
(6)

The absolute configuration of vinyl sulfides **6** was established through oxidation with 3-chloroperbenzoic acid to the corresponding sulfones **7** and diffractometric analysis of the latter. The results are shown in Figure 2. Because it is safe to assume that molecular rearrangements do not occur during the oxidation process,[10] it is clear from Figure 2 that the addition to phenylacetylenes is stereospecifically anti and regiospecifically Markovnikov. The magnetic parameters of vinyl sulfides **6** and vinyl sulfones **7** are given in Table I.

Discussion

The results above reported show that the introduction of a bulky isopropyl or *tert*-butyl group at the other ring carbon of 2-phenylthiirenium ions makes these species stable enough for detection or even isolation. Lower homologues (3-methyl and 3-ethyl) have never been detected: when they are formed, they react immediately even with such a poor nucleophile as dimethyl disulfide.[6]

It must be pointed out that a relevant contribution to the possibility of observation or isolation of thiirenium ions is given by their stability toward nucleophiles. Thiirenium ions may be in equilibrium with precursors (as it is clear from many pieces of evidence[3,11]) and destroyed by nucleophiles[2-4] (eq 7); i.e., the electrophilicities of the sulfur



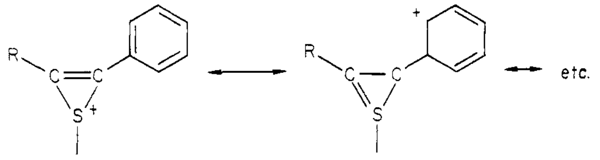
(7)

X = Cl⁻ or RSSR

atom and the ring carbon atoms may determine the order of stability experimentally found. Since the reactions that lead to products are generally irreversible, the order of stability is dependent on the ratio $k_1/(k_{-1} + k_2)$. It follows that differences in carbon electrophilicities (which act on k_2 only) are more relevant than differences in sulfur electrophilicities (which cause a variation of the same sign in k_1 and k_{-1}). Consistent with these considerations, we could observe 1-(4-chlorophenyl)thiirenium ions (2,3-dimethyl or 2,3-diethyl substituted), which are only slightly less stable than the corresponding 1-methylthiirenium ions.[3]

On the contrary, the lifetime of thiirenium ions is dramatically altered depending on the type of substitution on the ring carbons. All ions so far detected are characterized by the presence of one or two alkyl groups, and when only one alkyl group is present, it must exhibit some degree of bulkiness. Steric and inductive properties of alkyl groups may partially explain the order of stability found for these ions.

On the other hand, in phenyl-substituted thiirenium ions, a resonance interaction between the double bond π system and the phenyl group is possible when the rings are coplanar (structures **8**).[12,13] Our results seem to indicate that this interaction does not sensibly stabilize the system.



8

As for the stereo- and regioselectivity observed, it may in principle be explained with the intermediacy of the α-phenyl-β-thiovinyl cations **5**, stabilized through delocalization of the charge into the phenyl ring. Indeed, the relative stability of the two isomeric vinyl cations will determine the regioselectivity (Markovnikov), whereas, as already suggested,[14] the stereoselectivity may be rationalized by assuming that the vacant p orbital on the α-carbon and the lone pair on sulfur interact, making the anti addition preferred or exclusive.

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[10] Maioli, L.; Modena, G.; Taddei, F. *Boll. Sci. Fac. Chim. Ind. Bologna* **1960**, *18*, 58.

[11] (a) Modena, G.; Tonellato, U. *J. Chem. Soc. B* **1971**, 374. (b) Modena, G.; Scorrano, G.; Tonellato, U. *J. Chem. Soc., Perkin Trans. 2* **1973**, 493.

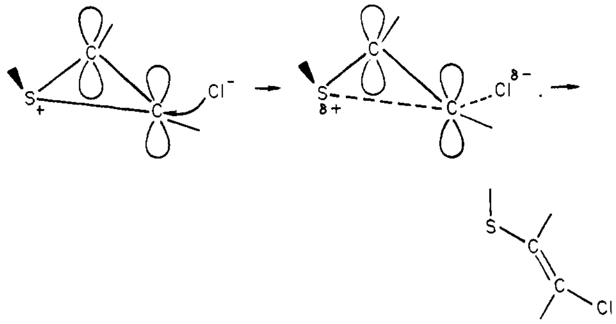
[12] Okuyama, T.; Izawa, K.; Fueno, T. *J. Org. Chem.* **1973**, *39*, 351.

[13] Schmid, G.; Modro, A.; Garratt, D. G.; Yates, K. *Can. J. Chem.* **1976**, *54*, 3045.

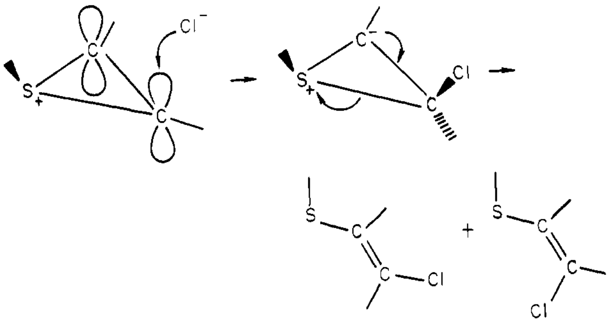
[14] Modena, G.; Tonellato, U. *J. Chem. Soc. B* **1971**, 381.

However, since vinyl cations **5** have never been detected even as transient species and since ab initio molecular orbital calculations[7,15] suggest that thiirenium ions are relatively more stable than the corresponding vinyl cation valence tautomers, we shall try herein to offer a rationale for the stereo- and regiospecificity observed on the basis of the exclusive intermediacy of thiirenium ions **1**. This, of course, does not rule out the possibility that under some circumstances β-thiovinyl cations **5** may exist and play a role as reaction intermediates.

Nucleophiles add stereospecifically anti to a cyclic intermediate such as thiirenium ion, provided that the attack occurs in the plane containing the ring and from the backside with respect to the sulfur atom[3,16] (eq 8). This mechanism, reminiscent of the S_N2 mechanism, is not the generally accepted one for nucleophilic substitution at an ethylenic carbon, where an attack perpendicular to the molecular plane is more often proposed, with the possible formation of a tetrahedral intermediate. However, this mechanism requires that anti and syn adducts are formed with almost equal ease (eq 9). Because of the absolute anti stereospecificity observed in these additions, the S_N2-type mechanism with in-plane attack of the nucleophile is to be preferred.



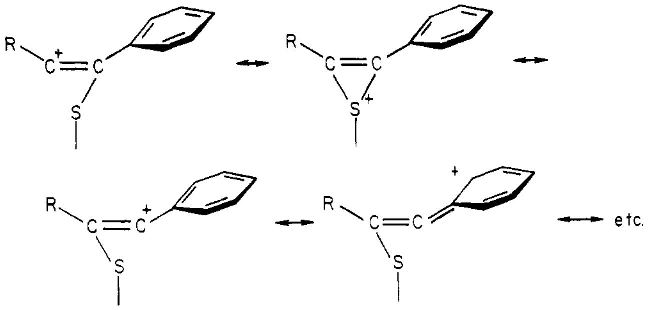
(8)



(9)

On the other hand, the in-plane attack of chloride ion on a phenyl-substituted carbon atom (Markovnikov-type addition) is possible only when thiirenium ring and phenyl ring are perpendicular: when the rings are coplanar, the approach of chloride ion is sterically hindered by ortho protons.[13]

Thiirenium ion **1** may be represented by a number of resonance structures, **9**, some of them presenting characteristics of a vinyl cation structure, with the positive charge located on unsaturated carbon atoms. The charge on phenyl-substituted carbon may be delocalized, in the perpendicular rotamer, into the phenyl ring (structures **9**). On the other hand, inductive effects associated with alkyl and aryl groups give rise to a charge distribution which can approximately be described as in **10**.



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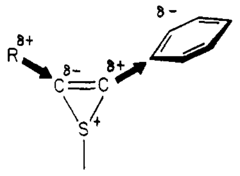

10

From a comprehensive consideration of the effects described above, it emerges that some electrophilic character is to be attributed to unsaturated ring carbons and that this character is enhanced by phenyl substitution; as a consequence, a nucleophile adds to ring carbons with preferential or exclusive Markovnikov orientation. Furthermore, Markovnikov addition brings about the cleavage of that carbon–sulfur bond which, as can be inferred from resonance structures **9**, is longer and weaker.

As a final point, the greater electrophilic character of phenyl-substituted ring carbons may explain why a poor nucleophile as dimethyl disulfide can attack 2-phenylthiirenium ions (eq 3). The greater electrophilicity of phenyl-substituted thiirenium ions, together with the presence, at least in one rotamer, of inherently weaker carbon–sulfur bonds, may partially justify the lower stability of these compounds, as compared with that of alkyl substituted analogues.

Experimental Section

^{1}H NMR spectra were recorded with a Bruker WP-60 spectrometer equipped with a variable-temperature unit. For low-temperature experiments a reagent is added to the frozen solution of the other reagent and mixed with a glass rod until melting occurs.

Materials. Methanesulfenyl chloride,[17] 1-phenyl-3-methylbutyne (**2a**),[18] 1-phenyl-3,3-dimethylbutyne (**2b**),[19] and methylbis(methylthio)sulfonium (**3**) hexachloroantimonate[5] and tetrafluoroborate[6] were prepared by published methods. High-purity solvents were used without further purification.

1-Methyl-2-phenyl-3-*tert*-butylthiirenium (1b) Hexachloroantimonate. Methylbis(methylthio)sulfonium (**3**) hexachloroantimonate (1.1 mmol) in 15 mL of dichloromethane is added in 15 min at 0 °C to 1.3 mmol of 1-phenyl-3,3-dimethylbutyne (**2b**) in 15 mL of the same solvent. The product is precipitated with anhydrous ethyl ether, filtered, and crystallized from dichloromethane/ethyl ether: white crystals; 50% yield; mp 80 °C dec.

Anal. Calcd for $C_{13}H_{17}Cl_6SSb$: C, 28.90; H, 3.17; Cl, 39.39. Found: C, 28.9; H, 3.2; Cl, 39.55.

1-Methyl-2-phenyl-3-*tert*-butylthiirenium (1b) Tetrafluoroborate. By use of the same procedure, 1.6 mmol of methylbis(methylthio)sulfonium (**3**) tetrafluoroborate is added in 15 min at −15 °C to 1.7 mmol of acetylene **2b**: yield 65%; mp 67 °C dec.

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[15] Csizmadia, I. G.; Lucchini, V.; Modena, G. *Gazz. Chim. Ital.* **1978**, *108*, 543.

[16] Rappoport, Z. *Tetrahedron Lett.* **1978**, 1073, and references cited therein.

[17] Britzinger, H.; Koddesbuch, H.; Kling, K. H.; Jung, G. *Chem. Ber.* **1952**, *85*, 455.

[18] Schluback, H. H.; Repenning, K. *Justus Liebigs Ann. Chem.* **1958**, *614*, 37.

[19] Mortreux, A.; Blanchard, M. *Bull. Soc. Chim. Fr.* **1970**, 4035.

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, $\beta = 104.1$ (.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 $\theta = 25°$. 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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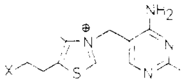
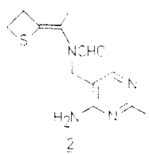
The base-induced rearrangement of quaternized 5-(chloroalkyl)thiazoles has been studied with UV kinetic spectroscopy. Rearrangement of the thiazolium compounds **5a** and **5b** proceeded in two consecutive, irreversible steps. The first of these was shown to be the nucleophilic attack of OH^- on C_2 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.

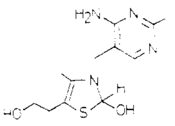
The first example of a base-induced rearrangement of 5-chloroalkylthiazolium compounds was published in 1957 by Yonemoto,[2] who found that the chloro analogue **1a** of thiamine rearranged to the thietane **2** on treatment with NaOH. At the same time, other workers[3] obtained this compound on treatment 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.



1 a X=Cl
b X=OH



2



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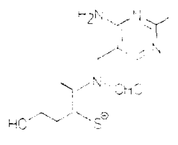

4

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

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[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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