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THE EFFECT OF ENVIRONMENT ON THE REACTIONS OF THIIRANIUM IONS[1]

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ABSTRACT: *The thiiranium ion formed by the reaction of Z-1-phenylpropene and $(4\text{-}ClC_6H_4S)_2SC_6H_4ClSbCl_6$ in CH_2Cl_2 at -70°C reacts with Cl^- to form both erythro- and threo-Markownikoff B-chlorosulfides.*

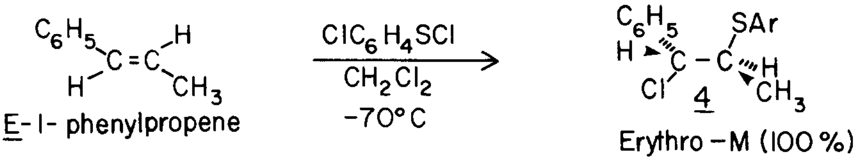
Thiiranium ions have been postulated as intermediates in the reactions of RSCl[2] and $(CH_3)_2SSCH_3^+\ BF_4^-$ with alkenes[3]. Doubt has been cast on this postulate by the report that the products of reaction of stable thiiranium ions with nucleophiles are formed with predominant Markownikoff (M) orientation[4]. In contrast the products of kinetic control of RSCl addition to alkenes have predominant anti-Markownikoff (aM) orientation[2]. While the regiochemistry of the products is different in these two reactions, nothing is known about the stereochemistry of the M product formed in the reaction of stable thiiranium ions with nucleophiles. We report a comparison of the stereo- and regiochemistry of the products of the reaction of Cl⁻ with the same thiiranium ion formed under comparable conditions in the two ways shown in equations 1 and 2.

$$\begin{array}{c} \underline{E}\text{- or } \underline{Z}\text{-}C_6H_5CH{=}CHCH_3 \\ + \\ (ArS)_2SAr^+SbCl_6^- \end{array} \xrightarrow[-70^\circ C]{CH_2Cl_2} \left[\begin{array}{c}\text{Stable Thiiranium}\\ \text{Ion}\end{array}\right] \xrightarrow{(C_2H_5)_4N^+\ Cl^-} \text{product} \qquad (1)$$

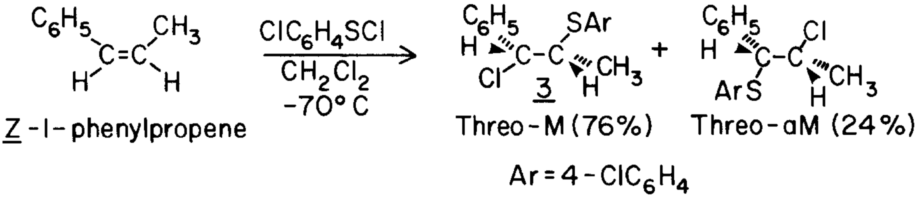
$$\begin{array}{c} ArSCl \\ + \\ \underline{E}\text{- or } \underline{Z}\text{-}C_6H_5CH{=}CHCH_3 \end{array} \xrightarrow[-70^\circ C]{CH_2Cl_2} \left[\begin{array}{c}\text{Thiiranium Ion}\\ \text{Intermediate}\end{array}\right] \xrightarrow{Cl^-} \text{product} \qquad (2)$$

$Ar{=}4\text{-}ClC_6H_4$

The stereo- and regiochemistry of the products of addition of ClC_6H_4SCl to E- and Z-1-phenylpropene in CH_2Cl_2 at -70°C are shown in equations 3 and 4[5].



(3)

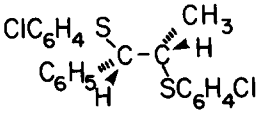
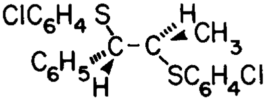


(4)

The stereo- and regiochemistry of these products is readily established by pmr[6].

The stable thiiranium ion 1 was prepared by the addition of $[(ClC_6H_4S)_2SC_6H_4Cl]^+SbCl_6^-$ to Z-1-phenylpropene in CH_2Cl_2 at -70°C under argon[7]. The isomeric ion 2 was prepared by the analogous addition reaction to E-1-phenylpropene. The thiiranium ions were allowed to remain at -70°C for varying times before addition of a precooled solution of $(C_2H_5)_4N^+Cl^-$ in CH_2Cl_2. The product compositions are given in the Table.

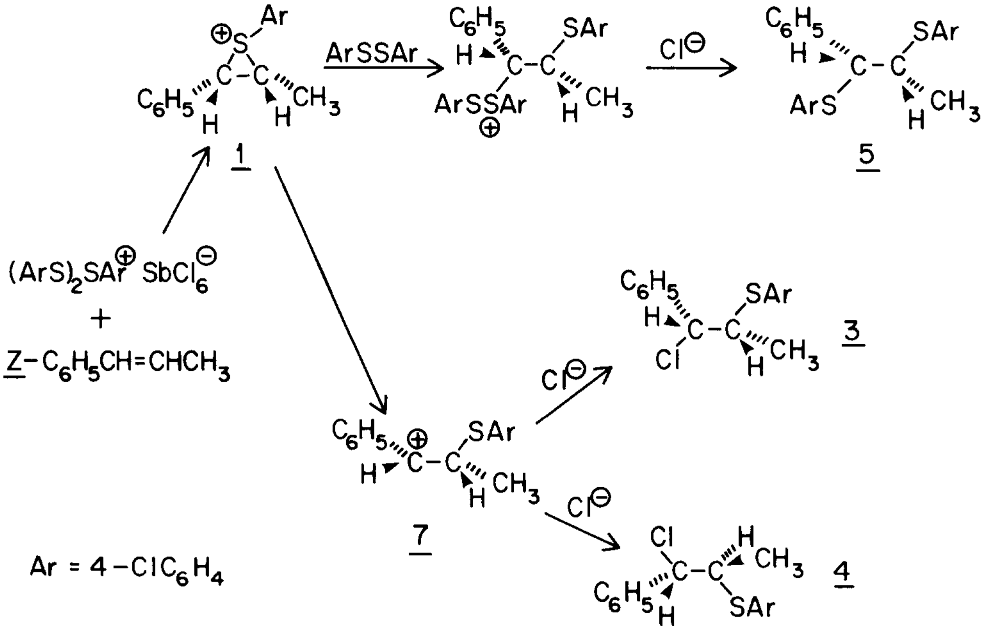
TABLE Effect of Time on the Products of the Reaction of Chloride Ion and the Thiiranium Ions 1 and 2 in CH_2Cl_2 at -70°C.

		β-chlorosulfides		Bis-sulfides	
Thiiranium Ion	t^a (min)	threo M (3)	erythro M (4)	 Threo (5)	 Erythro (6)
1	4	75[b]	7	15	0
1	8	74	11	15	0
1	23	63[b]	25	9	0
1	145	50	50	0	0
1	290	50	50	0	0
2	11	0	85	0	15
2	105	0	90	0	10
2	250	0	89	0	11

a. Time between adding $(ClC_6H_4S)_2SC_6H_4Cl^+SbCl_6^-$ to alkene and adding $(C_2H_5)_4N^+Cl^-$ to reaction mixture. *b*. A small amount (~2%) of threo-aM isomer was detected which is believed to be formed by slow M-aM isomerization.

The reaction of Cl$^-$ with 2 forms β-chlorosulfides with the same stereo- and regiochemistry as the kinetically controlled product formed in the addition of 4-ClC$_6$H$_4$SCl to E-1-phenylpropene. This product of M orientation is in accord with previous work[8]. However the β-chlorosulfide products formed in the reaction of 1 with Cl$^-$ are a mixture of threo-M(3) and erythro-M(4) isomers. The regio- and stereochemistry of these products differ markedly from the kinetically controlled product formed by addition of 4-ClC$_6$H$_4$SCl to Z-C$_6$H$_5$CH=CHCH$_3$. Furthermore the percent of erythro M product increases with the time between formation of the ion and its reaction with Cl$^-$. It is formed to a maximum of 50% at the expense of 3 and the threo bis-sulfide product 5.

The formation of both 3 and 4 in the reaction of 1 with Cl$^-$ requires the presence of an open benzylic ion in the reaction mechanism prior to the product forming step. Thus either the first formed ion is an open one or if a thiiranium ion is involved, it slowly forms the open ion 7 as shown in the following mechanistic scheme.



The stereospecific formation of bis-sulfide 5 suggests that a thiiranium ion is indeed involved in this reaction. This implies that at least two intermediates are involved in the mechanism of this reaction: 1 and 7. Furthermore since only products of reaction of Cl$^-$ with 7 are formed at longer times, the ion 7 is thermodynamically more stable than thiiranium ion 1.

The *bis*-sulfides 5 and 6 were prepared independently by reaction of the appropriate β-chlorosulfide with 4-ClC_6H_4SNa in CH_3OH. Thus 6 was prepared from 4 and 5 from a mixture of 3 and its aM regioisomer.

Clearly the reactions of a particular thiiranium ion are different depending upon its method of preparation. Even though the two reactions used to prepare thiiranium ions 1 or 2 were carried out in the same solvent and same temperature, the environment of the ions is completely different. Therefore it is not surprising that their chemistry may also differ. The kinetic stability[9] of a particular thiiranium ion is changed by transferring it from one environment to another. In our case, the thiiranium ion prepared by equation 1 has the greater kinetic stability. As a result, this allows it access to other reaction pathways that are not available to the structurally similar thiiranium ion formed as an intermediate in the addition of 4-ClC_6H_4SCl to *Z*-1-phenylpropene (reaction 2).

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