THERMAL DECOMPOSITION OF SULFENYL CHLORIDES

Thomas J. Barton and Rodney G. Zika
Department of Chemistry, Iowa State University, Ames, Iowa 50010

The considerable degree of current interest in the mechanism of sulfenyl halide additions to olefins (1) prompts us to report some results from our laboratory concerning the thermolysis of stilbene-sulfur dichloride adducts.

Addition of sulfur dichloride (SCl_2) to a solution of trans-stilbene in methylene chloride affords a 2:1 adduct (1).   Structure 1 is supported by elemental analysis, mass spectrum and the 100 MHz nmr spectrum [δ ($CDCl_3$): 2 doublets 3.38 and 3.61 (2 methine SC-H) (J=10 cps.), doublet 4.86 (2 methine Cl-C-H), complex multiplet 7.16 (20 Ar-H)] (2); the stereochemistry is assumed from the well documented trans-additions of SCl_2 (3) and sulfenyl halides (4). Thermolysis of 1 at ca. 200° in vacuo produces a complex mixture of products. Separation of all but the very minor products was accomplished by laborious preparative layer chromatography.   Composing about 70% of the product mixture was trans-stilbene with the next largest product being meso-1,2-dichloro-1,2-diphenylethane (2) (5).   Very minor amounts (<3% each) of d,ℓ-1,2-dichloro-1,2-diphenylethane (3) (5), chlorostilbene (4) and 3-chloro-2-phenylbenzo[b]thiophene (5) (6).


(Eqn. 1)

1

major
2

minor
3
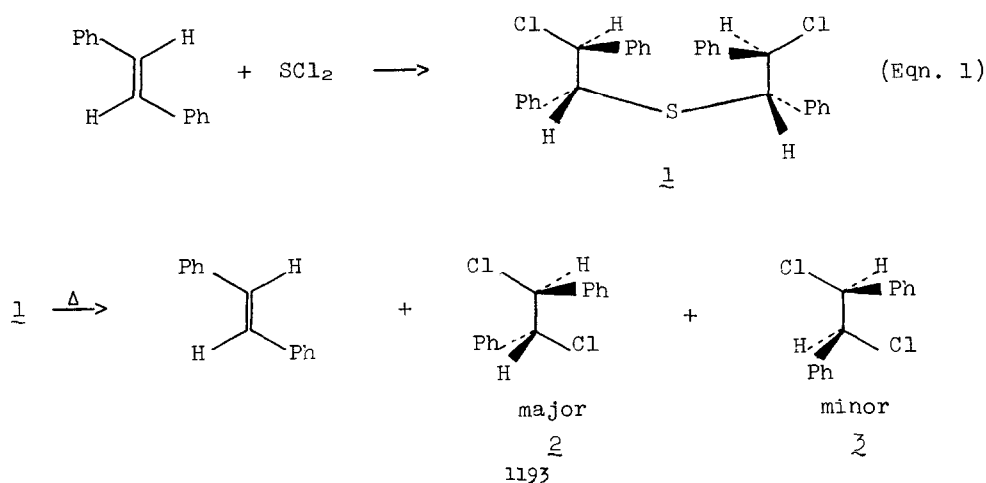
The results of this thermal decomposition came as a surprise, as a simple expulsion of two molecules of HCl was expected. Much of the _trans_-stilbene product may be explained by a reversal of the final addition process. The other products would therefore have to result from decomposition of the β-chlorosulfenyl chloride (6). To test this supposition, 6 [δ(CDCl$_3$): doublet 4.75 (1 methine ClS-C-H$_a$); doublet 5.42 (1 methine Cl-C-H$_b$), singlet 7.29 (10 Ar-H); $J_{a,b}$ = 8 cps.] was prepared from the reaction of excess SCl$_2$ and _trans_-stilbene and proved to be a rather stable molecule. Thermal decomposition of 6 (200°) provided the same products as before, with considerably less _trans_-stilbene. The most difficult result to explain is the predominance of the meso form of α,α'-dichlorobibenzyl (2). Formation of 6 corresponds to a substitution of chlorine for SCl with retention of configuration. Clearly, this does not arise from normal intermolecular addition of a chloride anion to an unassociated carbonium ion or a chloride atom to an unassociated free radical center. Conceivably, 2 could arise from complete decomposition to _trans_-stilbene, sulfur and chlorine followed by addition of chlorine to _trans_-stilbene. However, it is known (5) (at least in solution) that the reaction of Cl$_2$ and _trans_-stilbene leads largely to the d,ℓ-form,3. An intriguing possibility is the concerted, intramolecular double-displacement involving six electrons illustrated in Equation 4. The explanation which we currently favor involves an internal, frontside displacement of sulfur by chlorine (Equation 5). This could either be formulated as concerted or involving a tight ion-pair.

(Eqn. 4)

2 + S

(Eqn. 5)

-S → 2

-HSCl → 4
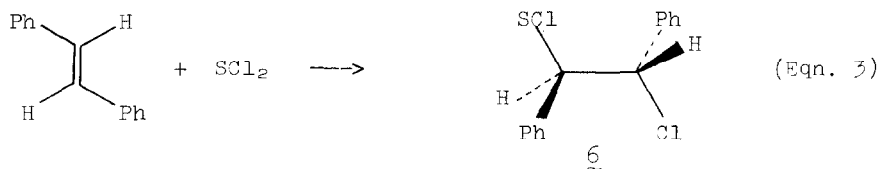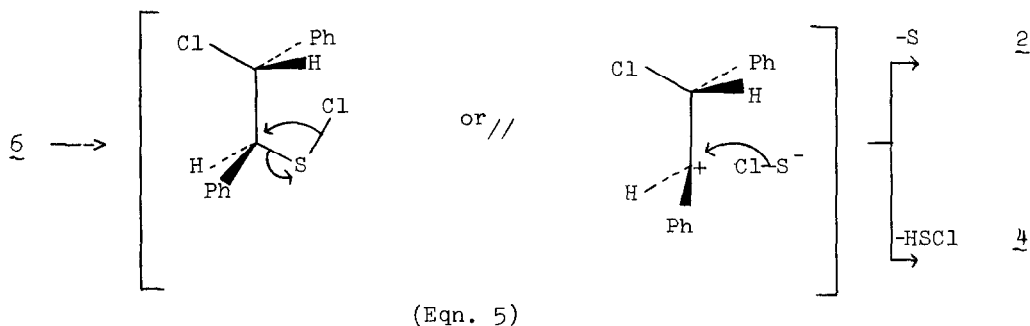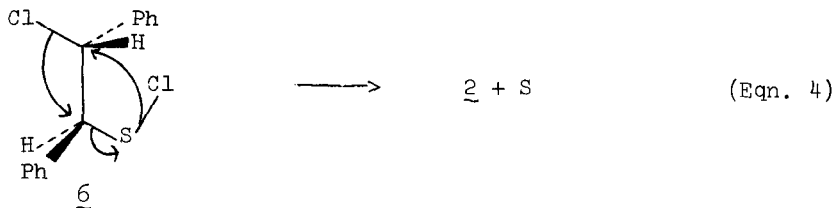
The isolation of 5 is somewhat disturbing as 2-phenylbenzo[b]thiophene would appear to be a more likely product. It is possible that 5 arises from decomposition to diphenylacetylene followed by SCl_2 addition, for 5 is indeed the product of this reaction. However, we have been unable to observe any diphenylacetylene among the various products of these decompositions.

To check the generality of the retention of configuration involved in the chlorine-sulfur substitution, the sulfenyl chloride, (7), resulting from addition of SCl_2 to cis-stilbene, was prepared. This adduct (7) [δ ($CSCl_3$): doublet 4.91 (1 methine ClS-C-H_a), doublet 5.42 (1 methine Cl-C-H_b), multiplet 7.05 (10 Ar-H); $J_{a,b}$ = 7 cps.] proved to be considerably less stable than 6 and decomposed over a period of two weeks at room temperature to a mixture largely composed of 6 and 3. By far the major product was 3 (Equation 6). Thermolysis (200°) of 7 yielded the same products as did thermolysis of 6 however now 3 was the major product and only a minor amount of 2 could be detected by nmr.

$\xrightarrow{\Delta}$ 3   (Eqn. 6)
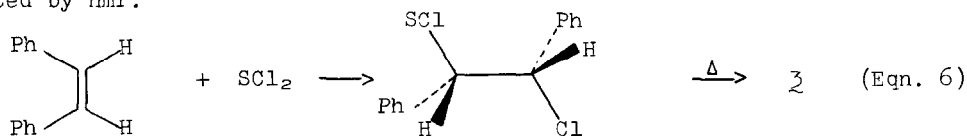
Although the decomposition of methanesulfenyl chloride has been reported (7) to afford a small amount of methyl chloride, no conclusions have been reached as to the correct mechanism for this process. Key experiments now in progress in our laboratory involve the decomposition of optically active sulfenyl halides where sulfur is directly bonded to the assymetric carbon atom.

References

1. W. H. Mueller and P. E. Butler, J. Amer. Chem. Soc., 90, 2075 (1968), and references therein.
2. There are two possible orientations which trans-stilbene may take toward the two enantiomeric forms of 1. Trans-addition can occur in four ways, two of which lead to the same meso product and two result in a d,ℓ-pair. Under our conditions these two stereoisomeric systems are formed in roughly equal amounts and we have been unable to achieve total separation. The nmr spectrum is therefore of a mixture of meso- and d,ℓ-forms and hence the two sets of methine (SC-H) doublets. The stereoisomers of 1 formed from SCl_2 and cis-stilbene result in an analogous mixture which we have succeeded in separating, however assignment has thus far been impossible. The existence of 1 as a meso/d,ℓ-mixture has no effect on our thermolysis results as each member results presumably from trans-addition.
3. E. J. Corey and E. Block, J. Org. Chem., 31, 1663 (1966); E. D. Weil, K. J. Smith and R. J. Gruber, ibid., 31, 1669 (1966); F. Lautenschlaeger, ibid., 31, 1679 (1966); F. Lautenschlaeger, Can. J. Chem., 44, 2813 (1966); F. Lautenschlaeger, J. Org. Chem., 33, 2620; ibid., 2627 (1968).
4. N. Kharasch and C. M. Buess, J. Am. Chem. Soc., 71, 2724 (1949); D. J. Cram, ibid., 71, 3383 (1949); N. Kharasch and A. J. Havlik, ibid., 75, 3734 (1953); A. J. Havlik and N. Kharasch, ibid., 78, 1207 (1956); W. H. Mueller and P. E. Butler, ibid., 88, 2866 (1966); W. H. Mueller and P. E. Butler, ibid., 90, 2075 (1968).
5. R. E. Buckles and D. F. Knaack, J. Org. Chem., 25, 20 (1960); R. E. Buckles, W. E. Steinmetz, and N. G. Wheeler, J. Amer. Chem. Soc., 72, 2496 (1950).
6. E. J. Geering, U. S. Patent 3278552 (1966).
7. I. B. Douglass, et. al., J. Org. Chem., 6, 1803 (1969).