Tetrahedron Letters No.4, pp. 273-276, 1969. Pergamon Press. Printed in Great Britain.

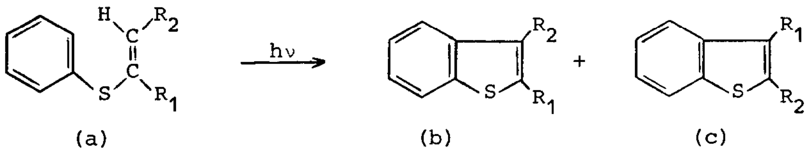
REARRANGEMENT IONS IN THE MASS SPECTRA OF PHENYL VINYL SULFIDES

W.D. Weringa

Department of Organic Chemistry, The University,
Bloemsingel 10, Groningen, The Netherlands

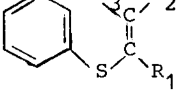
(Received in UK 4 December 1968; accepted for publication 18 December 1968)

The photocyclization reaction of phenyl vinyl sulfides to benzo[b]-thiophenes was studied in our laboratory by Groen, Kellogg, Buter and Wynberg (1).



When $R_1 = C_6H_5$, not only the normal product (b) is formed, but in addition a rearrangement product (c), in which R_1 and R_2 are interchanged. Because 1-phenyl-2-phenylthioethene (a; $R_1 = H$, $R_2 = C_6H_5$) was not formed upon irradiation of 1-phenyl-1-phenylthioethene (a; $R_1 = C_6H_5$, $R_2 = H$) and did not give cyclization products, the rearrangement does not occur in the sulfide (a). Aryl-rearrangements were found in arylthiophenes, both upon irradiation (2) and in the mass spectrometer (3).

We were interested in the behaviour of phenyl vinyl sulfides under conditions of electron impact. The mass spectra were examined of a group of sulfides with the general formula



$R_1, R_2, R_3 = H, CH_3, C_6H_5$

In addition to fragments formed by normal bond breaking, we found a number of ions which must have been formed in processes including a skeletal rearrangement. The relative abundance of these ions is given in table I.

The behaviour of aryl alkyl sulfides upon electron impact is described in the literature by Bowie and co-workers (4). They found a number of ions as $(M\text{-}SH)^+$, $(M\text{-}HCS)^+$ etc., that cannot be formed by simple bond breaking reactions. Gillis and Occolowitz (5) observed the rearrangement ions $(M\text{-}S)^+$, $(M\text{-}SH)^+$, $(M\text{-}SH_2)^+$ and $(M\text{-}SH_3)^+$ in the mass spectra of some unsaturated aliphatic sulfides.

TABLE I

Relative Abundance[†] of Rearrangement Ions in the Mass Spectra of Some Phenyl Vinyl Sulfides

	$C_6H_5\text{-}S\text{-}\underset{R_1}{C}{=}C\begin{smallmatrix}R_2\\ R_3\end{smallmatrix}$			C_6H_5CS	M-C_6H_5CS	CH_3CS	M-CH_3CS	HCS	M-HCS	C_7H_7	M-C_7H_7	M-SH	M-SH_2	M-SH_3
I	R_1=H	R_2=H	R_3=H	4.7	< 1	5.2*	12.0*	12.8	53.0	53.0	12.8	3.1	1.2	< 1
II	H	H	CH_3	6.2	1.0	7.8	19.1	22.0	25.0	19.1	7.8	19.5	9.5	13.5
III	H	H	C_6H_5	22.6	7.9	< 1	< 1	2.1	17.0	7.9	22.6	10.0	14.4	< 1
IV	H	CH_3	CH_3	12.0	2.1	4.0	4.1	13.7	9.0	19.4	1.5	8.1	4.3	4.5
V	H	CH_3	C_6H_5	15.1	2.8	1.0	4.6	3.3	2.2	18.5	3.6	2.4	2.9	2.0
VI	H	C_6H_5	C_6H_5	13.0	5.4	< 1	< 1	2.1	< 1	2.2	2.7	3.8	4.3	2.8
VII	CH_3	H	H	< 1	< 1	36.8	8.7	6.0	1.8	8.7	36.8	1.2	1.7	2.2
VIII	CH_3	H	CH_3	2.1	11.4	34.5	26.5	20.5	< 1	9.5	3.2	7.8	2.3	1.8
IX	CH_3	H	C_6H_5	3.1	1.3	4.4	25.0	2.2	< 1	15.5	5.1	5.0	1.6	< 1
X	C_6H_5	H	H	52.1	3.4	< 1	< 1	2.4	1.5	3.4	52.1	2.1	2.6	< 1
XI	C_6H_5	H	CH_3	42.5	1.8	< 1	< 1	3.0	< 1	19.0	< 1	1.2	1.0	< 1
XII	C_6H_5	H	C_6H_5	45.0	12.5	< 1	< 1	1.3	< 1	1.8	1.5	2.3	1.0	1.0

† Abundances are given as % of the base peak. The parent peak is the base peak for compounds I-IX, for X and XI the base peak is M-C_6H_5, for XII it is M-C_6H_5SH.

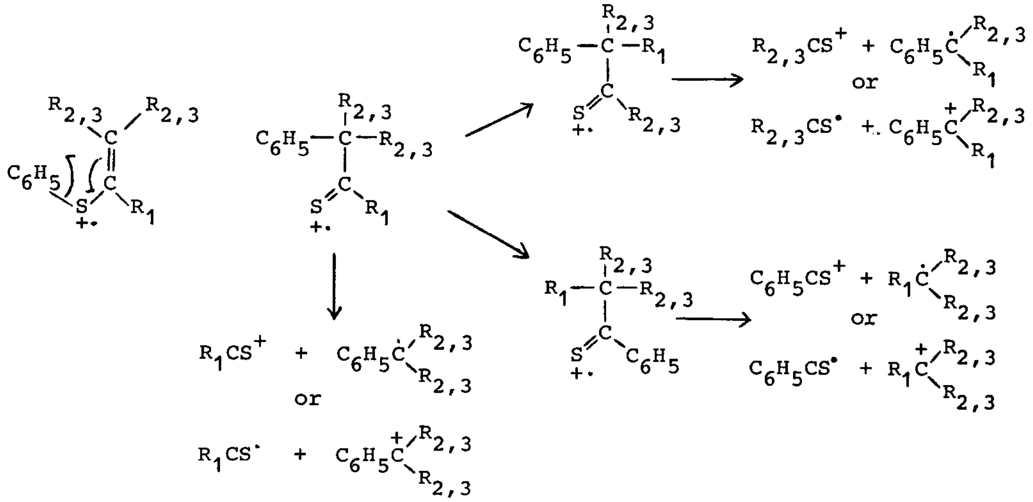
* Clearly, the eliminated group of atoms in this case is not CH_3CS but the isomeric $CH_2{=}CH\text{-}S$-group, formed by normal bond breaking.

In the spectra of the phenyl vinyl sulfides, a most interesting feature is the occurrence of ions $C_6H_5CS^+$, $(M\text{-}C_6H_5CS)^+$, CH_3CS^+, $(M\text{-}CH_3CS)^+$, HCS^+ and $(M\text{-}HCS)^+$. The high abundance of $C_6H_5CS^+$, CH_3CS^+ and (in most cases) HCS^+ ions when $R_1 = C_6H_5$, CH_3 or H, respectively, makes it most probable that the group of atoms R_1CS can be eliminated from the molecules.

The occurrence of ions R_2CS^+, $(M-R_2CS)^+$, R_3CS^+ and $(M-R_3CS)^+$ mostly with somewhat lower intensity may be explained by assuming a rearrangement of the substituents of the vinyl group preceding this elimination (6). For some compounds in which R_1 = H and R_3 = C_6H_5 (III, V, VI) C_6H_5CS is even more abundant than HCS. The reason for this may be that the $C_6H_5CS^+$ (or $C_7H_5S^+$) ion seems to have enhanced stability, as already was mentioned by Bowie et al (4), who found this fragment in the spectra of compounds containing a $CH_3C_6H_4S$- or $C_6H_5CH_2S$- unit. The data of table I show that $C_6H_5CS^+$ and $(M-C_6H_5CS)^+$ ions are also found in the spectra of compounds without phenyl substituents at the vinyl group (I, II, IV, VII and VIII). This makes it probable that a shift of the phenyl group to one of the carbon atoms of the vinyl group is possible.

Another rearrangement ion that appears in the spectra of all of the phenyl vinyl sulfides is $C_7H_7^+$. This ion is also found in the spectra of alkyl phenyl sulfides but the intensity is greater than 5% for methyl phenyl sulfide only (4). In the case when there are no substituents at the vinyl group, $C_7H_7^+$ is identical with $(M-HCS)^+$, when there is only one C_6H_5 or CH_3 substituent (II, III, VII and X), $C_7H_7^+$ is identical with $(M-C_6H_5CS)^+$ or $(M-CH_3CS)^+$ respectively. When R_1, R_2 or R_3 is C_6H_5, it is probable that at least part of the $C_7H_7^+$ ions are formed out of the $-SCR_1 = CR_2R_3$ group (7). The fact, however, that there is a large 91 peak present in the spectra of compounds without C_6H_5 substituents at the vinyl group indicates that rearrangements including a shift of the C_6H_5 group bonded to the sulfur atom must be possible.

A scheme that can account for all of the rearrangements mentioned so far is



The preponderence of fragments R_1CS over R_2CS and R_3CS is then explained by the fact that for these fragments only one rearrangement is necessary, whereas the other fragments (and also C_6H_5CS) need two shifts. When $C_7H_7^+$ ions are not formed directly in this way, they may originate from further degradation of the rearrangement ions $C_6H_5\overset{+}{C}R_{2,3}R_{2,3}$, $C_6H_5\overset{+}{C}R_1R_{2,3}$ or $R_1\overset{+}{C}R_{2,3}R_{2,3}$.

Another group of ions that is present in the spectra of phenyl vinyl sulfides are $(M-SH)^+$, $(M-SH_2)^+$ and $(M-SH_3)^+$. In the spectra of alkyl phenyl sulfides only a M-SH peak is found, the abundance of which is very low when the alkyl group is other than methyl (4). In the spectra of unsaturated aliphatic sulfides (5) peaks of M-SH, $M-SH_2$ and $M-SH_3$ are present, so most probably these ions are characteristic for alkenyl sulfides.

Ions with mass M-2, that possibly would have been formed in a reaction analogous to the photochemical cyclization, were only found in the spectra of I (7.5%) and III (2.6%); it is not clear, however, if these ions really have a benzo[b]thiophene structure.

To get more information about the $(M-H_2)^+$ ions and also for a better understanding of the processes that lead to the rearrangement ions described in this paper, labelling experiments would be very useful. These experiments are in progress.

The phenyl vinyl sulfides were prepared in our laboratory by Groen, Kellogg, Buter and Wynberg (1). The mass spectra were determined on an AEI MS9 mass spectrometer operating at 70 eV. An all glass heated inlet system at 120-160° or a direct inlet system was used. The identity of all rearrangement ions was proved by exact mass measurement.

Acknowledgment: The author is indebted to Professor M.J. Janssen for stimulating discussions. We thank the Netherlands Organization for Pure Research (Z.W.O.) for a grant for the mass spectrometer.

REFERENCES

1. S.H. Groen, R.M. Kellogg, J. Buter and H. Wynberg, *J. Org. Chem.*, **33**, 2218 (1968).
2. H. Wynberg, R.M. Kellogg, H. van Driel and G.E. Beekhuis, *J. Am. Chem. Soc.*, **89**, 3501 (1967).
3. S. Meyerson and E.K. Fields, *Organic Mass Spectrometry* **1**, 263 (1968).
4. J.H. Bowie, S.-O. Lawesson, J.Ø. Madson, G. Schroll and D.H. Williams, *J. Chem. Soc.*, (B), 951 (1966).
5. R.G. Gillis and J.L. Occolowitz, *Tetrahedron Letters*, 1997 (1966).
6. F.W. McLafferty, *Anal. Chem.*, **31**, 2072 (1959).
7. The spectrum of $n-C_3H_7S-C(C_6H_5)=CHCH_3$ also shows a large 91 peak (28%).