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Hydrogen Rearrangements in Alkyl-, Styryl- and Alkyl Propenyl Sulfoxides

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The McLafferty-type rearrangements, which are the most facile fragmentation for the styryl- and the alkyl propenyl sulfoxides, have been proven to involve at least a β-hydrogen by deuterium labelling studies. γ-Hydrogen also rearranges, yet a cyclopropane instead of an alkene is eliminated. Furthermore, alkyl propenyl sulfoxides undergo hydrogen migration only to the sulfinyl oxygen.

INTRODUCTION

In our previous mass spectral studies on α,β-unsaturated sulfur compounds ($R_1CH{=}CH{-}SO_nR$, R = alkyl), hydrogen rearrangements leading to alkene eliminations were found to be the most facile and interesting fragmentations for styryl alkyl thioethers (R_1 = Ph, $n = 0$),[1] styryl alkyl sulfoxides (R_1 = Ph, $n = 1$),[2] styryl alkyl sulfones (R_1 = Ph, $n = 2$),[3,4,5] propenyl alkyl sulfones ($R_1 = CH_3$, $n = 2$)[6] and sulfoxides ($R_1 = CH_3$, $n = 1$).[7] We have shown that at least a β-hydrogen is involved in this rearrangement for styryl alkyl sulfones[3,4] and have assumed similar fragmentation mechanisms for other compounds.

To conclude our study, several aspects needed to be clarified. This was done by synthesizing the appropriate deuterium-labelled compounds and studying their mass spectral fragmentations with the aid of the metastable ion (indicated by *) and high-resolution measurements. In the present paper, we have proven that at least a β-hydrogen is needed for the McLafferty-type rearrangements in the styryl- and propenyl- alkyl sulfoxides. Besides, γ-hydrogens can also undergo rearrangement, with elimination of a cyclopropane or its derivatives. In addition, qualitative migratory aptitudes of different kinds of hydrogen toward benzylic carbon vs. sulfinyl oxygen have been more precisely estimated in the styryl alkyl sulfoxides.

EXPERIMENTAL

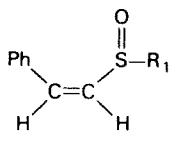
The styryl alkyl sulfoxides (**1–4**) were synthesized by the addition of sodium thiolates to phenylacetylene, followed by oxidation with sodium metaperiodate supported on acidic alumina.[8] Syntheses of the alkyl propenyl sulfoxides (**5–8**)[9,10] were carried out by the base-catalysed elimination of the corresponding β-chlorosulfoxides. The latter were obtained by oxidations of the corresponding β-chlorosulfides with sodium metaperiodate supported on acidic alumina.[6] The β-chlorosulfides were obtained by reactions of the sodium thiolates on propylene oxide; followed by chlorination of the β-hydroxysulfides with thionyl chloride.[10] These two synthetic procedures are indicated by the reaction series (1) and (2), respectively (Figure 1).

The purity of all compounds was checked by m.p. or b.p., TLC, ^{13}C- and ^1H-NMR, and IR. Mass spectral data showed that the isotopic purity of each of the deuterium-labelled compounds was better than 99%.

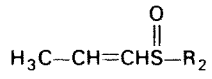
Mass spectral data were recorded on Jeol JMS-D-100 and JMS-D-300 double-focusing spectrometers with an inlet temperature of 80°C and electron energies of 70 and 12 eV, respectively. Spectra were taken at a nominal resolution of 1500. Perfluorokerosene was used for calibration of the mass scale. Metastable ion (*) measurements were made by scanning the acceleration voltage at a fixed electric sector value. Precursor ions (m) are calculated from $m_2 \times V_0/V$. Here m_2 is the daughter ion, V_0 is the initial accelerating voltage which passes m_2, and V is the accelerating voltage which passes the precursor ion m.

RESULTS AND DISCUSSION

In our study of (*Z*)- and (*E*)-styryl alkyl sulfoxides,[2] we found that hydrogen rearrangements with alkene elimination (Scheme 1) are equally important in the (*Z*)- and (*E*)-sulfoxides[2] with longer alkyl chains ($R \geq C_3H_7$). We thus choose the easily synthesizable (*Z*)-1-[1-(methyl-d_3)-2,2,2-d_3-ethanesulfinyl)-2-phenylethenes (**1**), (*Z*)-1-(3-methyl-3-d_1-butanesulfinyl)-2-phenylethenes (**3**), d_6-isopropyl propenyl sulfoxide (**5**) and d_1-isobutyl propenyl sulfoxide (**7**) and their corresponding hydrogen compounds (**2**), (**4**), (**6**), and (**8**) for this study. Important fragments related to this rearrangement are summarized in Tables 1 and 2, respectively.



R_1=CH(CD$_3$)$_2$ **1**, i-Pr **2**,
(CH$_2$)$_2$CD(CH$_3$)$_2$ **3**, 1-Am **4**,



R_2=CH(CD$_3$)$_2$ **5**, i-Pr **6**,
CH$_2$CD(CH$_3$)$_2$ **7**, i-Bu **8**,

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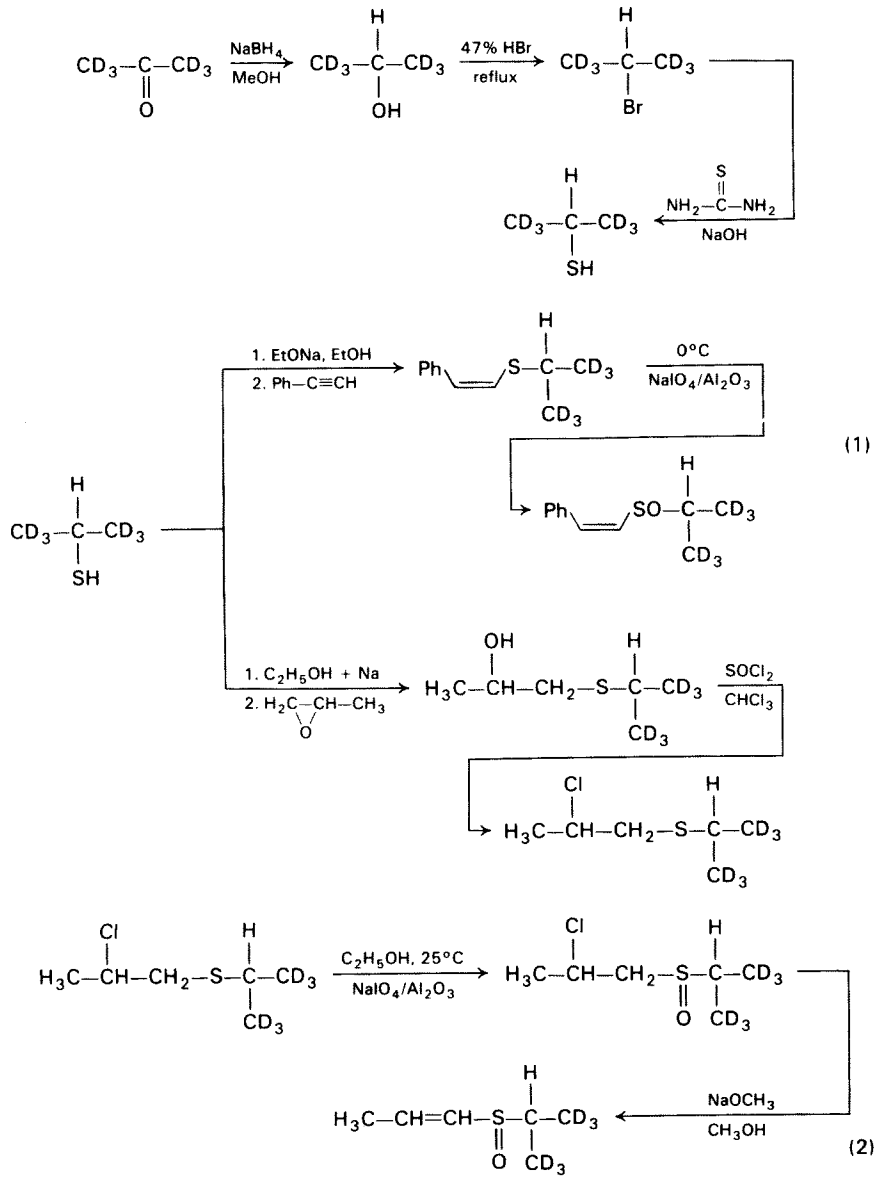
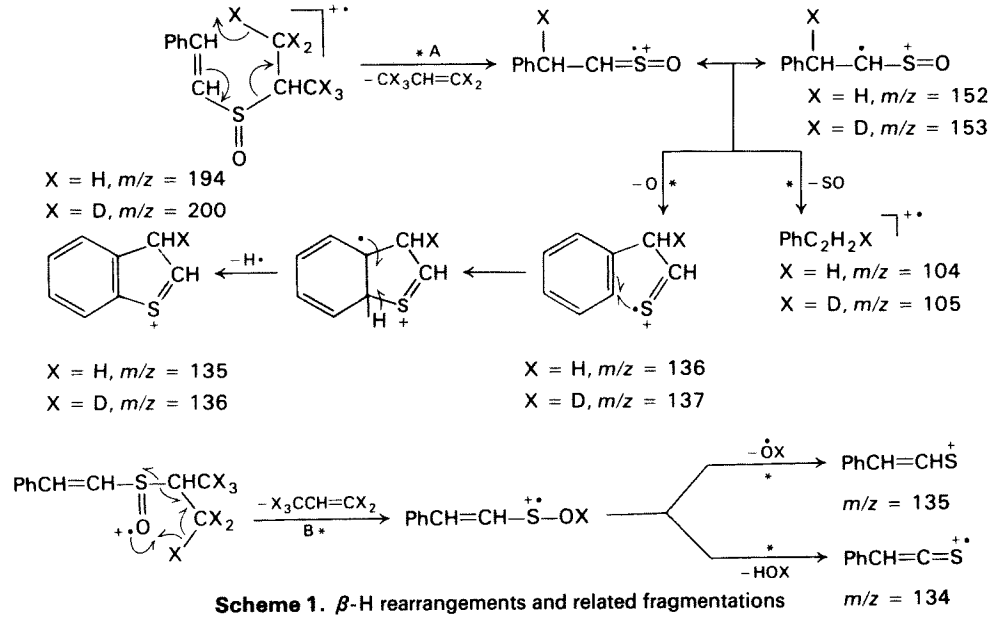


(1)

(2)

Figure 1.



Scheme 1. β-H rearrangements and related fragmentations

Table 1. Relative intensities (%) of important ions observed for PhCH=CHSOR$_1$, (a) at 70 eV and (b) at 12 eV

Compound	$M^{+\cdot}$ (m/z) (a)	(b)	m/z = 153 (a)	(b)	m/z = 152 (a)	(b)	m/z = 151 (a)	(b)	m/z = 137 (a)	(b)	m/z = 136 (a)	(b)	m/z = 135 (a)	(b)	m/z = 134 (a)	(b)	m/z = 105 (a)	(b)	m/z = 104 (a)	(b)	m/z = 103 (a)	(b)
1	4 (200)	7	100	100	11	12	0.8	0.6	11	4	64	15	27	9	8	4	65	15	10	4	–	–
2	10 (194)	11	–	–	100	100	2	–	–	–	13	3	60	16	11	–	–	–	53	16	–	–
3	14 (223)	23	49	62	93	100	7	6	14	14	22	19	53	23	18	4	33	31	47	26	61	44
4	6 (222)	7	10	9	100	100	5	3	3	2	10	5	37	14	8	1	11	14	35	16	8	5

Table 2. Relative intensities (%) of important ions observed for CH_3—CH=CHSOR$_2$, (a) at 70 eV and (b) at 12 eV

Compound	$M^{+\cdot}$ (m/z) (a)	(b)	m/z = 93 (a)	(b)	m/z = 92 (a)	(b)	m/z = 91 (a)	(b)	m/z = 90 (a)	(b)	m/z = 75 (a)	(b)	m/z = 74 (a)	(b)	m/z = 73 (a)	(b)	m/z = 41 (a)	(b)
5	5 (138)	7	5	6	9	4	100	100	9	10	30	18	9	4	31	10	68	5
6	5 (132)	10	<1	<1	8	7	8	7	100	100	3	4	14	21	25	12	91	18
7	9 (147)	11	<1	<1	5	6	30	49	100	100	8	17	6	9	31	20	93	28
8	5 (146)	7	<1	<1	6	6	6	6	100	100	<1	<1	11	30	28	13	95	51

Substitution of β-hydrogens with deuterium atoms in isopropyl styryl sulfoxides causes a shift of one unit in the mass/charge ratio to m/z 153 (X = D) in compound **1** compared to the m/z 152 ion (X = H) of the unlabelled compound **2**. This fact proved that the hydrogen rearranged in sulfoxides arises from the β-hydrogen instead of an α- or a phenyl-hydrogen.

These data can also be used to calculate the extent of the rearrangement of β-deuteriums. Correction of natural isotopic contributions derived from the m/z 152 ions (PhC_2H_3SO), and the m/z 151 ions (PhC_2H_2SO), from relative intensities of the m/z 153 (X = D) ion at 70 eV and 12 eV are given below

70 eV:

$$\left(100 - 11\left[\frac{8 \times 1.1}{100} + \frac{0.78}{100}\right] - 0.8\left[\frac{4.4}{100} + \frac{0.2}{100}\right]\right)\% = 98.8\%$$

12 eV:

$$\left(100 - 12\left[\frac{8 \times 1.1}{100} + \frac{0.78}{100}\right] - 0.6\left[\frac{4.4}{100} + \frac{0.2}{100}\right]\right)\% = 98.7\%$$

These values represent contributions of β-deuterium in compound **1** for rearrangement. Since they are close to 99% either at high (70 eV) or low (12 eV) ionizing energies, these results prove that β-hydrogens are the only rearrangement source for compounds with no γ-hydrogen.

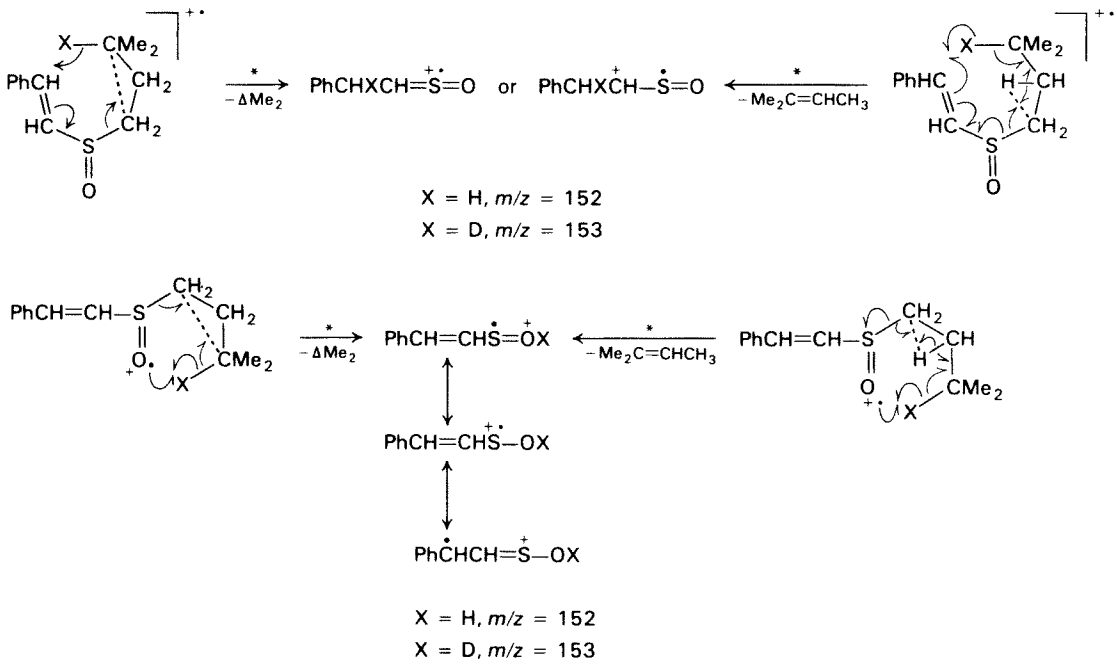
To prove that the rearranged hydrogen may also come from γ-hydrogens, the mass spectra of the γ-deuterium compound **3** and its corresponding hydrogen compound **4** are compared. Examination of molecular models reveals that elimination of an alkene in these cases requires rearrangement of two hydrogens, while elimination of a cyclopropane derivatives requires one γ-deuterium instead. Since alkene and cycloalkane have the same general formula of C_nH_{2n}, it is obvious that rearrangement of a single hydrogen occurs more easily than a double hydrogen rearrangement. This fragmentation pathway is illustrated in Scheme 2. Since the relative abundance of the m/z 153 ion in compound **4** is negligible after correction for the isotopic contributions of its m/z 152 ions, we can conclude that double hydrogen rearrangements are unlikely. Formation of the m/z 153 ion (relative abundance = 49%) in the deuterium compound **3** thus mainly arose from a γ-deuterium rearrangement with elimination of 1,1-dimethylcyclopropane. Furthermore, we can use the data obtained from compounds **3** and **4** to calculate the rearrangement ratio of γ-deuterium *vs.* β-hydrogen. Since we have shown that at least a β-hydrogen is needed for rearrangement, we can assume that the relative abundances of the m/z 152 ion in compound **3** (93% at 70 eV, 100% at 12 eV) are derived mainly from the β-hydrogen rearrangement. After correction for the $(P + 1)$ natural isotope contributions of the m/z 151 ion (PhC_2H_2SO, 7% at 70 eV and 6% at 12 eV), the relative abundances of the m/z 152 ions at high and low ionizing energies can be expressed as follows:

70 eV:

$$\left(93 - 7\left[\frac{8 \times 1.1}{100} + \frac{0.78}{100}\right]\right)\% = 92.3\%$$

12 eV:

$$\left(100 - 6\left[\frac{8 \times 1.1}{100} + \frac{0.78}{100}\right]\right)\% = 99.4\%$$



Scheme 2. γ-H rearrangements in styryl alkyl sulfoxides

Similarly, the relative intensity of the m/z 153 ions in compound **3** are mainly derived from rearrangement of γ-deuterium, and can be corrected as follows:

70 eV:

$$\left(49 - 93\left[\frac{8 \times 1.1}{100} + \frac{0.78}{100}\right] - 7\left[\frac{4.4}{100} + \frac{0.2}{100}\right]\right)\% = 39.8\%$$

12 eV:

$$\left(62 - 100\left[\frac{8 \times 1.1}{100} + \frac{0.78}{100}\right] - 6\left[\frac{4.4}{100} + \frac{0.2}{100}\right]\right)\% = 52.1\%$$

Thus, the rearrangement ratio of β-hydrogen *vs.* γ-deuterium at 70 eV and 12 eV is 2.3 and 1.9, respectively

$$70 \text{ eV } \beta : \gamma = 92.3\% : 39.8\% = 2.3 : 1$$

$$12 \text{ eV } \beta : \gamma = 99.4\% : 52.1\% = 1.9 : 1$$

Thus migration of β-hydrogen, which involves an elimination of alkene (Scheme 1), is more favored than rearrangement of a γ-hydrogen at both high and low ionizing energies. Elimination of alkene with γ-hydrogen migration required a double hydrogen rearrangement (Scheme 2), and is less favorable as compared with a single hydrogen rearrangement involving elimination of 1,1-dimethylcyclopropane. We therefore conclude that in compounds where both β- and γ-hydrogens can rearrange, migration of β-hydrogens is more favored than γ-hydrogens by a factor of ~ 2. Because there are two β-hydrogens and only one γ-deuterium in compound **3**, this correction leads to an equal migratory probability for β- and γ-hydrogens.

Owing to the large difference between ionization energies of styrene and propene, only hydrogen rearrangement to sulfinyl oxygen was observed in alkyl propenyl sulfoxides.[6] This hydrogen rearrangement was also accompanied by alkene elimination with formation of a protonated propenyl sulfinyl ion (X = H, m/z 90; X = D, m/z 91). Mechanisms for its formation and its subsequent fragmentation are postulated in Scheme 3. A similar mechanism had been proposed by Aplin and Bailey for dialkyl sulfoxides.[7] Mass spectra were recorded at both high (70 eV) and low (12 eV) ionizing energies. Only fragments derived from the hydrogen rearrangement and subsequent fragmentations were summarized in Table 2, and are discussed below.

In order to prove that a similar mechanism is involved in the hydrogen rearrangement in these alkyl propenyl sulfoxides we used the d_6-isopropyl propenyl sulfoxide **5** and isopropyl propenyl sulfoxide **6** for our mass spectral study. Replacement of β-hydrogens with deuterium causes the increment of one unit in the mass/charge ratio for fragments derived from the hydrogen rearrangement (X = H, m/z 90, 100%; X = D, m/z 91, 100%, Table 2) and subsequent fragmentations (Scheme 3). This proves that the hydrogen rearrangement in alkyl propenyl sulfoxides (RCH=CHSOR', R=CH_3) also required at least a β-hydrogen; as with their styryl analogues (RCH=CHSOR', R=Ph). This conclusion can also be obtained by similar calculations to those indicated below.

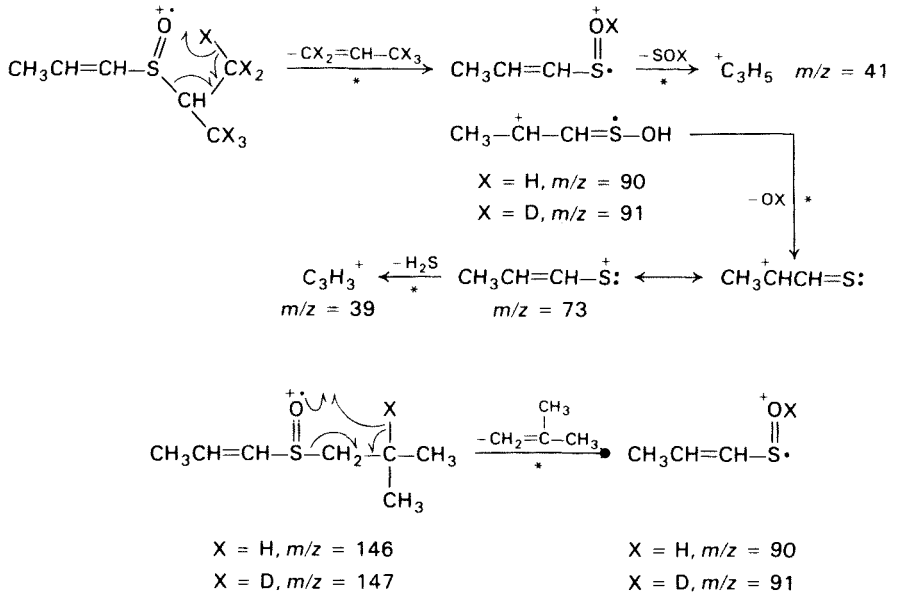
The relative abundances of the m/z 91 ion in compound **5**, after correction for the isotopic contributions of their corresponding m/z 90 and 89 ions, are:

70 eV:

$$\left(100 - 9\left[\frac{3 \times 1.1}{100} + \frac{0.78}{100}\right] - 9\left[\frac{4.4}{100} + \frac{0.2}{100}\right]\right)\% = 99.2\%$$

12 eV:

$$\left(100 - 10\left[\frac{3 \times 1.1}{100} + \frac{0.78}{100}\right]\right)\% = 99.6\%$$



Scheme 3. Single hydrogen rearrangement and subsequent fragmentations in propenyl alkyl sulfoxides

Thus for compounds without a γ-hydrogen, β-hydrogens are the sole source for rearrangement.

It is known from Table 2, that the extent of rearrangement of the γ-hydrogen in compounds **7** and **8** is the same (relative abundance 100% before correction) both at high and low ionizing energies. While rearrangement of β-deuterium in compound **7** (X = D, Scheme 3) is calculated as 25.6% (relative abundance) and 44.6% (relative abundance) at 70 eV and 12 eV, respectively. Thus the rearrangement ratio of β-deuterium *vs.* γ-hydrogen in propenyl isobutyl sulfoxide is $\sim$2/7 (25.6/91) and $\sim$1/2 (44.6/90) at high and low ionizing energies, respectively.

CONCLUSIONS

In conclusion, our present study proved that the alkene elimination *via* hydrogen rearrangements required at least a β-hydrogen in both the styryl- and the propenyl-alkyl sulfoxides. Rearrangement of a γ-hydrogen is also feasible, but a cyclopropane derivative is eliminated instead. This is true for both the styryl alkyl sulfoxides and for the propenyl alkyl sulfoxides. However, the migratory aptitude is different for these two types of sulfoxides. The β-hydrogen has a higher tendency to rearrange than the γ-hydrogen in the styryl alkyl sulfoxides (**1–4**), whereas in alkyl propenyl sulfoxides, the γ-hydrogen rearrangement is more preferable. This discrepancy arises from the facts that different sites of ionization and migration terminals are involved in the styryl and the propenyl sulfoxides.[6]

Acknowledgements

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REFERENCE

1. L. K. Liu and F.-T. Luo, *Proc. Natl. Sci. Council, Republic of China*, **5**, 350 (1981).
2. L. K. Liu and F.-T. Luo, *Org. Mass Spectrom.* **18**, 22 (1983).
3. L. K. Liu and C. T. Hong, *Org. Mass Spectrom.* **13**, 675 (1978).
4. L. K. Liu, F.-T. Luo and T.-P. Hsieh, *Bull. Inst. Chem. Academic Sinica*, **33**, 29 (1986).
5. S. Y. Shia, Master Thesis, National Tsing Hua University, Hsin-Chu, Taiwan, June (1979).
6. L. K. Liu and W. S. Huang, *J. Chin. Chem. Soc.* **31**, 357 (1984).
7. R. T. Aplin and K. Bailey, *J. Chem. Soc.* (*B*), 513 (1967).
8. L. K. Liu, F.-T. Luo and S. Y. Shia, *J. Chin. Chem. Soc.* **29**, 21 (1982).
9. W. S. Hwang, Master Thesis, National Tsing Hua University, Hsin-Chu, Taiwan, June (1982).
10. L. K. Liu and C. T. Hong, *J. Chin. Chem. Soc.* **25**, 87 (1978).
11. R. Smakman and Th. J. de Boer, *Org. Mass Spectrom.* **3**, 1561 (1970).