Rearrangements and Fragmentations of Phenyl Styryl Sulfides

2—Labelling Studies

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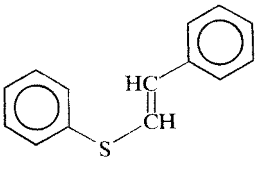
Metastable molecular ions of phenyl styryl sulfides may decompose by loss of $CH_3^{\cdot}$, $SH^{\cdot}$, $CHS^{\cdot}$, $C_6H_5^{\cdot}$, C_6H_6 or $C_7H_7^{\cdot}$. Labelling with carbon-13 and deuterium gave information about the mechanisms of these reactions. It appears that extensive rearrangements occur prior to most of these fragmentations. In the case of phenyl β-styryl sulfide both phenyl groups and both vinyl carbon atoms are found in the C_7H_7 fragment in comparable amounts. For phenyl α-styryl sulfide this fragmentation leads more specifically to the loss of the S-phenyl group and the β-vinyl carbon atom. It was concluded that rearrangements occur, partly via symmetric diphenyl ethene sulfide structures, to benzyl phenyl thione ions, from which the fragmentation occurs. For the loss of $CHS^{\cdot}$ an earlier proposed mechanism was confirmed. From both compounds the S-phenyl ring can be lost as $C_6H_5^{\cdot}$ or C_6H_6 as well as the C-phenyl ring. Fragmentation occurs from one of the initial structures as well as from benzyl phenyl thione. Loss of $CH_3^{\cdot}$ is thought to occur after ring closure with formation of dihydrobenzo[*b*]thiophenes followed by ring opening by rupture of a C—S bond. While phenyl β-styryl sulfide shows a strong tendency towards isomerization to a symmetric structure like 1,2-diphenylethene sulfide, phenyl α-styryl sulfide easily rearranges in an electrocyclic reaction with formation of benzyl phenyl thione.

INTRODUCTION

The mass spectra of phenyl vinyl sulfides show a number of fragmentations, that have to be preceded by rearrangements, as for instance loss of $C_7H_7^{\cdot}$, $CHS^{\cdot}$ and $SH^{\cdot}$.[1] Losses of $C_7H_7^{\cdot}$ and $CHS^{\cdot}$ are specific for the phenyl vinyl sulfides; loss of $SH^{\cdot}$ is found quite generally for sulfides.[2]

A study of the intensities and peak shapes observed for the decomposition of metastable molecular ions of two phenyl styryl sulfides (**1** and **2**), benzyl phenyl thione (**3**), 1,2-diphenylethene sulfide (**4**), 2,3-dihydro-2-phenylbenzo[*b*]thiophene (**5**) and the $[M-2Br]^{+\cdot}$ ions of α,α′-dibromodibenzyl sulfide (**6**) revealed that isomerizations between these ions are possible prior to fragmentation.[3] It was concluded that ions with structures $[\mathbf{3}]^{+\cdot}$–$[\mathbf{5}]^{+\cdot}$ formed upon rearrangement, could well be intermediates in the reaction sequence leading to the decomposition of $[\mathbf{1}]^{+\cdot}$ and $[\mathbf{2}]^{+\cdot}$. Although not all of the isomerization reactions are fast as compared with fragmentation, the compounds **1**–**6** all give the same fragments upon decomposition of their metastable ions.



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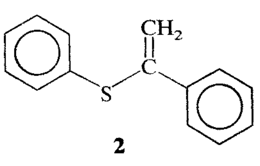

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The mechanisms of the rearrangements between the ion structures have not been elucidated yet. Therefore, labelling of **1** and **2** with carbon-13 and deuterium was used to gain insight into the isomerization and fragmentation reactions of these compounds. As in the previous study,[3] most of the work described here concerns metastable ions. Determination of the label content of fragment ions formed directly from the molecular ions gives information about these precursors.

RESULTS AND DISCUSSION

The fragmentations shown by metastable ions of **1** and **2** are loss of $CH_3^{\cdot}$, $SH^{\cdot}$, $CHS^{\cdot}$, $C_6H_5^{\cdot}$, C_6H_6 and $C_7H_7^{\cdot}$. The ratio in which these reactions occur has been given earlier.[3] In the normal 70 eV electron impact (EI) spectra these fragmentations are not always shown as being prominent. No significant differences were observed between the peak intensities in the mass spectra of the *E*- and *Z*-isomers of **1**.[3] The results given here were obtained with mixtures of *E*- and *Z*-isomers containing mainly the *E*-isomer.

Metastable ion spectra were obtained by means of a combined scan of the magnetic field (*B*) and the electrostatic analyser field (*E*), with *B*/*E* constant,[4] and with a scan of the accelerating voltage (*V* scan).[5] For the labelled compounds mixtures of fragment ions with different label content are often observed. Table 1 gives the intensity ratios observed for metastable ion decompositions of **1a**–**1e**; Table 2 gives the results for **2a** and **2b**. In these Tables the total intensity of each cluster of ions was normalized to 100. As the intensity ratios for a cluster are the same for the *B*/*E* and *V*

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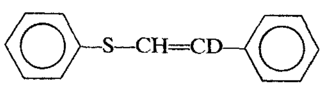
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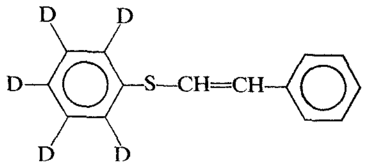
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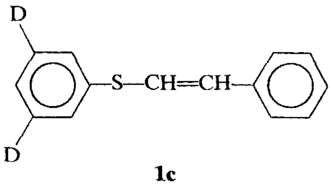
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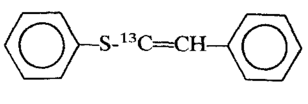
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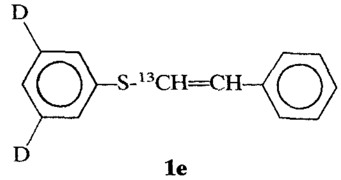
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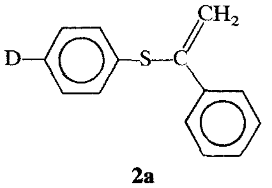
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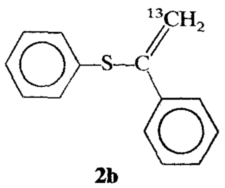

2b

Table 1. Intensities of the metastable transitions for decomposition of the molecular ions of 1a–1e[a,b]

m/z	1a	I	1b	I	1c	I	1d	I	1e	I
121	$[M-C_7H_6D]^+$	89	$[M-C_7H_2D_5]^+$	42	$[M-C_7H_5D_2]^+$	42	$[M-C_6{}^{13}CH_7]^+$	42	$[M-C_6{}^{13}CH_5D_2]^+$	34
122	$[M-C_7H_7]^+$	11	$[M-C_7H_3D_4]^+$	6	$[M-C_7H_6D]^+$	8	$[M-C_7H_7]^+$	58	$[M-C_6{}^{13}CH_6D]^+$	4
									$[M-C_7H_5D_2]^+$	8
123					$[M-C_7H_7]^+$	50			$[M-C_6{}^{13}CH_7]^+$	3
									$[M-C_7H_6D]^+$	3
124									$[M-C_7H_7]^+$	47
125			$[M-C_7H_6D]^+$	6						
126			$[M-C_7H_7]^+$	46						
134	$[M-C_6H_5D]^{+\cdot}$	7	$[M-C_6HD_5]^{+\cdot}$	9	$[M-C_6H_4D_2]^{+\cdot}$	12				
135	$[M-C_6H_6]^{+\cdot}$	17		29	$[M-C_6H_5D]^{+\cdot}$	3	$[M-C_6H_6]^{+\cdot}$	24	$[M-C_6H_4D_2]^{+\cdot}$	11
	$[M-C_6H_4D]^+$	4			$[M-C_6H_3D_2]^+$	29				
136	$[M-C_6H_5]^+$	72		8	$[M-C_6H_6]^{+\cdot}$	9	$[M-C_6H_5]^+$	76	$[M-C_6H_5D]^{+\cdot}$	2
					$[M-C_6H_4D]^+$	8			$[M-C_6H_3D_2]$	31
137				2	$[M-C_6H_5]^+$	39			$[M-C_6H_6]^{+\cdot}$	11
									$[M-C_6H_4D]^+$	6
138				7					$[M-C_6H_5]^+$	39
139				10						
140			$[M-C_6H_5]^+$	35						
167	$[M-CDS]^+$	39					$[M-{}^{13}CHS]^+$	49		
168	$[M-CHS]^+$	61					$[M-CHS]^+$	51		
169					$[M-CHS]^+$	100			$[M-{}^{13}CHS]^+$	49
170									$[M-CHS]^+$	51
171										
172			$[M-CHS]^+$	100						
179	$[M-SD]^+$	3								
180	$[M-SH]^+$	97			$[M-SD]^+$	3	$[M-SH]^+$	100		
181					$[M-SH]^+$	97			$[M-SD]^+$	3
182									$[M-SH]^+$	97
183			$[M-SD]^+$	5						
184			$[M-SH]^+$	95						
197	$[M-CH_2D]^+$	61			$[M-CHD_2]^+$	5	$[M-{}^{13}CH_3]^+$	35	$[M-{}^{13}CHD_2]^+$	0
198	$[M-CH_3]^+$	39			$[M-CH_2D]^+$	26	$[M-CH_3]^+$	65	$[M-{}^{13}CH_2D]^+$	6
									$[M-CHD_2]^+$	5
199			$[M-CD_3]^+$	5	$[M-CH_3]^+$	69			$[M-{}^{13}CH_3]^+$	29
									$[M-CH_2D]^+$	19
200			$[M-CHD_2]^+$	15					$[M-CH_3]^+$	41
201			$[M-CH_2D]^+$	38						
202			$[M-CH_3]^+$	42						

[a] Intensities (*I*) are normalized to a total of 100 for each cluster of ions.
[b] The data for **1d** and **1e** are corrected for incomplete labelling with ^{13}C.

Table 2. Intensities of the metastable transitions for decomposition of the molecular ions of 2a and 2b[a,b]

m/z	**2a**		**2b**	
121	$[M-C_7H_6D]^+$	92	$[M-C_6{}^{13}CH_7]^+$	93
122	$[M-C_7H_7]^+$	8	$[M-C_7H_7]^+$	7
134	$[M-C_6H_5D]^{+\cdot}$	12	$[M-C_5{}^{13}CH_6]^{+\cdot}$	4
135	$[M-C_6H_6]^{+\cdot}$	17	$[M-C_6H_6]^{+\cdot}$	25
	$[M-C_6H_4D]^+$	27	$[M-C_5{}^{13}CH_5]^+$	11
136	$[M-C_6H_5]^+$	44	$[M-C_6H_5]^+$	60
167	$[M-CDS]^+$	0	$[M-{}^{13}CHS]^+$	7
168	$[M-CHS]^+$	100	$[M-CHS]^+$	93
179	$[M-SD]^+$	0		
180	$[M-SH]^+$	100	$[M-SH]^+$	100
197	$[M-CH_2D]^+$	13	$[M-{}^{13}CH_3]^+$	0
198	$[M-CH_3]^+$	87	$[M-CH_3]^+$	100

[a] Intensities (*I*) are normalized to a total of 100 for each cluster of ions.

[b] The data for **2b** are corrected for incomplete labelling with ^{13}C.

scans within experimental error, average values of the results obtained with both methods are given in Tables 1 and 2. The values for the ^{13}C labelled compounds **1d**, **1e** and **2b** are corrected for incomplete labelling.

Loss of $C_7H_7^{\cdot}$

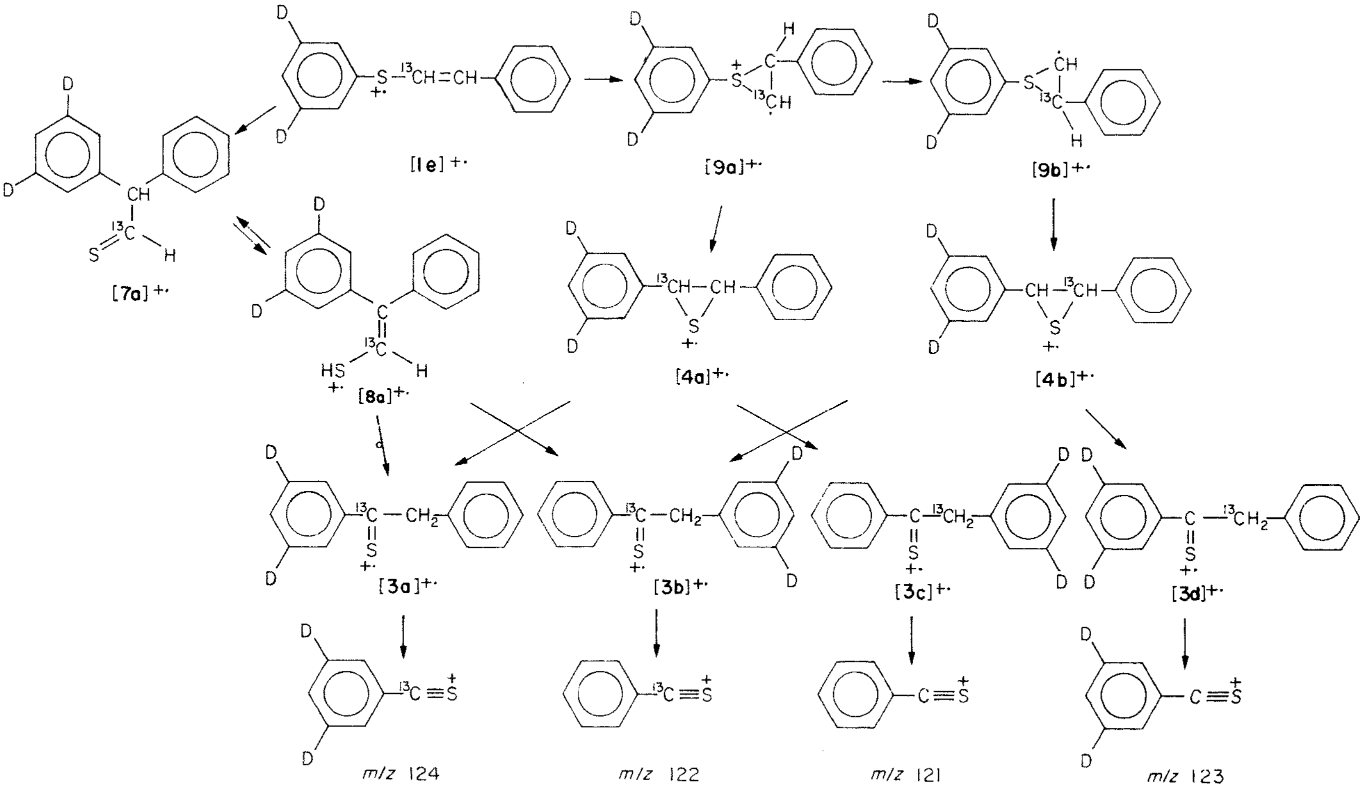
The loss of $C_7H_7^{\cdot}$ from $[\mathbf{1}]^{+\cdot}$ and $[\mathbf{2}]^{+\cdot}$ leads to the formation of ions $[C_7H_5S]^+$ (*m/z* 121). The D labelled analogues **1a**–**1c** all give mixtures of ions with different label content (Table 1). This could be due to competing reaction mechanisms, but also to a certain degree of H/D scrambling before the fragmentation. Fast H/D isomerization reactions must be expected in the C_6H_5S– group and in the $C_6H_5CH{=}CH$– moiety of the ions, while H/D transfer between these two groups will probably be somewhat slower. Nevertheless, it can be concluded that at least for the main reaction path, the two phenyl rings contribute equally to the $[C_7H_5S]^+$ ions and that the reaction proceeds via an intermediate in which the two rings have become equivalent. The results obtained for **1d** show that the two carbon atoms of the vinyl group can both become part of the $[C_7H_5S]^+$ ions, but that the α-atom predominates. This is interpreted as resulting from competition between two routes leading to the decomposing ions; in one route the two carbon atoms become equivalent due to a symmetric intermediate and in the other only the α-carbon atom can become part of the $[C_7H_5S]^+$ ion (Scheme 1). The doubly labelled compound **1e** was made with the intention of checking whether the C_6H_5 of the styryl group remains attached to the same carbon atom during the course of the reaction. If this were the case $[C_6{}^{13}CH_3D_2S]^+$ (*m/z* 124) and $[C_7H_5S]^+$ (*m/z* 121) ions would be formed as the main products. In the event of a migration of this phenyl group to the α-vinyl carbon atom, $[C_6{}^{13}CH_5S]^+$ (*m/z* 122) and $[C_7H_3D_2S]^+$ (*m/z* 123) ions could also be formed. The intensities found for *m/z* 121, 122, 123 and 124 are 34.1, 12.3, 6.5 and 47.1 respectively. The peaks at *m/z* 122 and 123 can be due to mixtures of $[C_7H_4DS]^+$ and $[C_6{}^{13}CH_5S]^+$ and of $[C_7H_3D_2S]^+$ and $[C_6{}^{13}CH_4DS]^+$ respectively, as the results for **1c** show that ions containing one D atom can be formed. If it is assumed that the ratio of ^{13}C labelled ions and ions containing no ^{13}C in **1e** is the same as in **1d**, and the ratio of dideuterated, monodeuterated and undeuterated ions is the same as in **1c**, the values given in Table 1 can be calculated. It appears that an interchange of the two phenyl groups occurs, but only for about 11% of the ions giving this fragmentation.

The results can be explained by competition between several reaction pathways leading to the decomposing ion having the structure of benzylphenyl thione (**3**) or a molecule with the same C—S skeleton. In Scheme 1 this is shown for compound **1e**. It is assumed that the loss of C_7H_7 radicals containing only one D atom (see Table 1) is caused by H/D scrambling reactions. The formation of all other ions is accounted for in the Scheme. It is thought that the majority of the ions rearrange to the episulfide $[\mathbf{4a}]^{+\cdot}$. Opening of the 3-membered ring will give equal amounts of $[\mathbf{3a}]^{+\cdot}$ and $[\mathbf{3c}]^{+\cdot}$, and upon fragmentation these will give rise to ions at *m/z* 121 and 124. A smaller part (about 6%) of the ions $[\mathbf{1e}]^{+\cdot}$ will rearrange to $[\mathbf{4b}]^{+\cdot}$. The migration of the phenyl group in the intermediate radical ion is apparently rather slow as compared with the formation of ions $[\mathbf{4}]^{+\cdot}$. Ring opening of $[\mathbf{4b}]^{+\cdot}$ will give $[\mathbf{3b}]^{+\cdot}$ and $[\mathbf{3d}]^{+\cdot}$, leading to fragment ions at *m/z* 122 and 123. In addition to ions $[\mathbf{4}]^{+\cdot}$, containing a 3-membered ring, non-cyclic ions with the structure $[PhCH{=}S{-}CHPh]^{+\cdot}$ may also be formed as intermediates. As these ions have the same metastable characteristics as ions $[\mathbf{4}]^{+\cdot}$, they cannot be distinguished.[3]

Although isotope effects will have a small influence on these reactions, they cannot explain the difference in the intensity of the ions at *m/z* 121 and 124, that can be formed from $[\mathbf{4a}]^{+\cdot}$, or of the ions at *m/z* 122 and 123, formed from $[\mathbf{4b}]^{+\cdot}$. Therefore, a third pathway via the ene thiol form $[\mathbf{8a}]^{+\cdot}$ of the thioaldehyde $[\mathbf{7a}]^{+\cdot}$ is taken into account. This reaction path shows strong resemblance to the fragmentation mechanism proposed originally, as given in Scheme 1.[1] This route, which contributes to the formation of ions at *m/z* 122 and 124, can be followed by about 10% of the ions $[\mathbf{1e}]^{+\cdot}$ giving this fragmentation. The difference in the abundance of the ions at *m/z* 121 and 124 is not fully explained in this way.

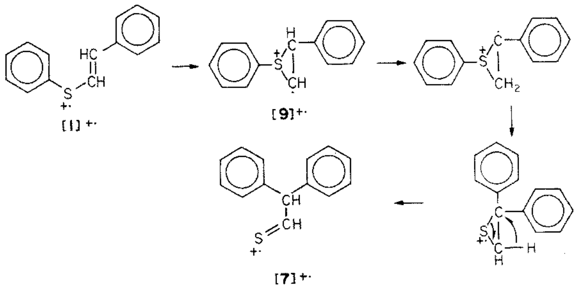
It is possible that the reaction $[\mathbf{1}]^{+\cdot} \rightarrow [\mathbf{9}]^{+\cdot} \rightarrow [\mathbf{4}]^{+\cdot}$ is an equilibrium and that some ions $[\mathbf{1}]^{+\cdot}$ in which the two phenyl groups and the two vinyl carbon atoms have equilibrated are formed from $[\mathbf{4a}]^{+\cdot}$ and $[\mathbf{4b}]^{+\cdot}$ in backward reactions. Ions $[\mathbf{3a}]^{+\cdot}$–$[\mathbf{3d}]^{+\cdot}$ could then be formed via ions $[\mathbf{7}]^{+\cdot}$. This reaction pathway can only have a minor contribution as appears from the observed intensity ratios.

An alternative for the formation of $[\mathbf{7a}]^{+\cdot}$ *from* $[\mathbf{1a}]^{+\cdot}$ according to the mechanism described earlier[1,3] is a mechanism via $[\mathbf{9a}]^{+\cdot}$, in which a hydrogen shift occurs instead of a phenyl shift (Scheme 2). Fétizon found for the fragmentation of *trans*-stilbene epoxide, that hydrogen migration was 2 to 3 times faster than a

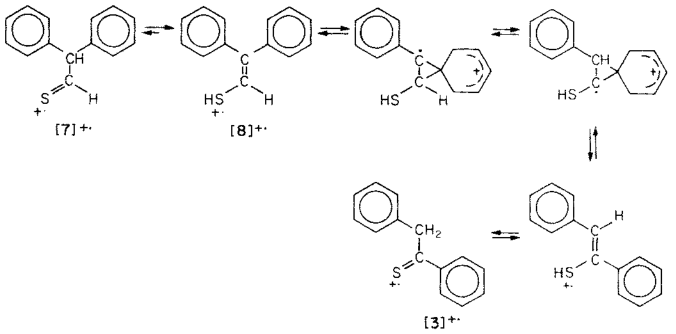


Scheme 1

phenyl shift.[6] The two mechanisms cannot be distinguished with the experiments described here.



Scheme 2



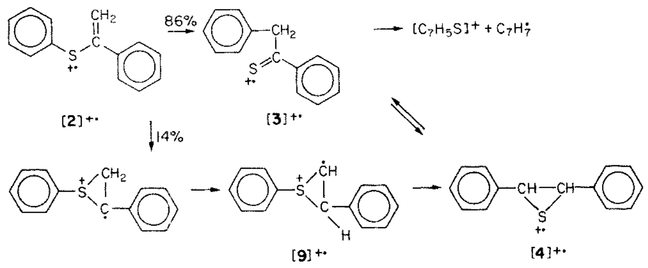
Scheme 3

Although there may be a contribution of reaction pathways leading to [C$_7$H$_5$S]$^+$ and C$_7$H$_7^{\cdot}$, in which an intermediate [**7a**]$^{+\cdot}$, formed from **1e** in a specific rearrangement, isomerizes to [**3a**]$^{+\cdot}$ and [**3b**]$^{+\cdot}$, it is striking that ions [**7**]$^{+\cdot}$, which decompose to [C$_{13}$H$_{11}$]$^+$ and CHS$^{\cdot}$, cannot be formed along this route to the extent of more than a few percent (*vide infra*).

The phenyl hydrogen interchange reaction, that was originally thought to take place in ions [**7**]$^{+\cdot}$,[1] can be understood better when it occurs in the thioenol **8**. A reasonable mechanism is given in Scheme 3.

As appears from Table 2, loss of C$_7$H$_7^{\cdot}$ from the molecular ions of compound **2** is a more specific reaction than observed for fragmentation of ions of **1**. About 93% of the [C$_7$H$_5$S]$^+$ ions formed from compound **2** contain the α-vinyl carbon atom and the phenyl group originally attached to this atom. As no double labelling experiments were carried out, it is not certain whether the same [C$_7$H$_5$S]$^+$ ions that contain the α-carbon atom also contain the C-phenyl group, as is assumed in Scheme 4, which accounts for formation of the observed ions. When it would have appeared from double labelling that the C-phenyl group is able to migrate to the β-vinyl carbon, a phenyl shift in the intermediate [**9**]$^{+\cdot}$, as given in Scheme 1, could have accounted for this. In Scheme 4 most of the ions (86%) rearrange directly to [**3**]$^{+\cdot}$ and 14% follow the route via a symmetric intermediate [**4**]$^{+\cdot}$ to [**3**]$^{+\cdot}$.

It is remarkable that the direct rearrangement of the S-phenyl group to the β-vinyl carbon atom, which is assumed for 86% of the ions [**2**]$^{+\cdot}$, is found for not more than 10% of ions [**1**]$^{+\cdot}$. Probably [**3**]$^{+\cdot}$ is a more stable ion than [**7**]$^{+\cdot}$; as in [**3**]$^{+\cdot}$ mesomeric interaction between the C=S group and the phenyl ring is possible. This, and the additional phenyl–hydrogen interchange, necessary for loss of C$_7$H$_7^{\cdot}$ from [**7**]$^{+\cdot}$, may well explain the observed difference.



Scheme 4

In the foregoing it was suggested that ions [**4**]$^{+\cdot}$, when formed as intermediates, always rearrange to ions [**3**]$^{+\cdot}$ before decomposition. Direct decomposition of a part of [**4**]$^{+\cdot}$, as tentatively proposed for ions generated with this structure,[3] would lead to the same label distribution, but the simple Gaussian peaks observed for [**1**]$^{+\cdot}$ and [**2**]$^{+\cdot}$ show that all decompositions to $[C_7H_5S]^+$ and $C_7H_7^\cdot$ must occur via one reacting intermediate.

Loss of CHS$^\cdot$

Loss of CHS$^\cdot$ leads to the formation of ions $[C_{13}H_{11}]^+$ (*m/z* 167). For metastable molecular ions of **1** this is the predominant fragmentation. Of the labelled analogues of **1**, the ^{13}C containing compound **1d** gives a mixture of almost equal amounts of $[C_{13}H_{11}]^+$ and $[C_{12}{}^{13}CH_{11}]^+$. This again points to the existence of an intermediate, in which both vinyl carbon atoms have become equivalent. Compounds **1b** and **1c**, both labelled with D in the -SPh- moiety, only show loss of CHS$^\cdot$, so the hydrogen atom of this radical does not originate from this phenyl ring and no H/D scrambling occurs between the H/D atoms of this ring and the H atoms that contribute to the formation of the CHS radical. As expected now, the doubly labelled compound **1e** shows the same ratio for CHS$^\cdot$ and ^{13}CHS$^\cdot$ as **1d**. The monodeuterated compound **1a** gives more loss of CHS$^\cdot$ than of CDS$^\cdot$. This is best explained by a mechanism in which the two vinyl H/D atoms contribute equally to the formation of the radical, while some H/D scrambling occurs in the $C_6H_5CD{=}CH{-}$ part of the molecular ion of **1a** prior to fragmentation.

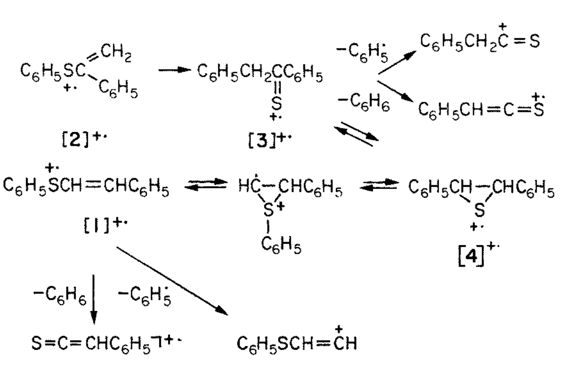
For compound **2**, Table 2 shows that the carbon atom of the CHS radical most probably originates mainly from the α-vinyl position and the hydrogen atom does not come from the S-phenyl ring. So the main part of ions [**2**]$^{+\cdot}$ do not rearrange to a symmetric intermediate like [**4**]$^{+\cdot}$, as observed for ions [**1**]$^{+\cdot}$. Most probably, the C_α—S bond remains intact and no C_β—S bond is formed in the reaction sequence leading to loss of CHS$^\cdot$.

A reaction scheme in agreement with these results has been given earlier (Ref. 3, Scheme 3). It is thought that ions [**1**]$^{+\cdot}$ decompose after a rearrangement to [**4**]$^{+\cdot}$, in which both vinyl carbon atoms and both hydrogen atoms have become equivalent. After that, fragmentation occurs along two pathways. Ions [**2**]$^{+\cdot}$ first rearrange to [**3**]$^{+\cdot}$ and then follow the same fragmentation pathways for the main part without going through a symmetric intermediate like [**4**]$^{+\cdot}$. A smaller part (about 14%) could well follow a route via [**4**]$^{+\cdot}$ or decompose by a mechanism in which the β-vinyl C atom is lost specifically (not shown in the Scheme).

Loss of $C_6H_5^\cdot$ and C_6H_6

These two fragmentations, that in principle could occur without preceding rearrangements, lead to the formation of ions $[C_8H_7S]^+$ (*m/z* 135) and $[C_8H_6S]^{+\cdot}$ (*m/z* 134) respectively. Both reactions are found with rather low abundance, but loss of $C_6H_5^\cdot$ is approximately three times as intense as loss of C_6H_6. Labelling with ^{13}C (compounds **1d**, **1e**, and **2b**) does not give much information. It only shows that no carbon scrambling occurs between the phenyl rings and the vinyl moiety prior to fragmentation. Upon D labelling, the two fragmentations together with the H/D scrambling process may lead to complicated multiplets and overlapping peaks of ions with different label content. For compounds **1** some approximations have to be made to unravel the results. When isotope effects are neglected, the measured intensities for **1a** easily lead to the values given in Table 1. (Intensities are normalized to a total of 100% for all labelled and unlabelled $[M-C_6H_5]^+$ and $[M-C_6H_6]^{+\cdot}$ ions together.) For **1c** and **1e** the additional assumption was made that the amount of H/D scrambling is the same for the two fragmentations. For compound **1b** H/D scrambling is still more extensive and no attempt was made to separate the contributions of the two reactions to the observed intensities. Although there are some uncertainties, it can be concluded that the C_6H_5 radicals as well as the C_6H_6 molecules originate from both phenyl rings of **1**. The contribution of the S-phenyl to the C_6H_5 molecule is somewhat higher than that of the C-phenyl. A small excess of the C_6H_5 radicals originate from the C-phenyl group.

For compound **2** similar results are obtained. Both phenyl groups contribute to the $C_6H_5^\cdot$ and C_6H_6 fragments, but the C-phenyl about 1.5 times as much as the S-phenyl. A reaction sequence via structures like [**4**]$^{+\cdot}$, [**7**]$^{+\cdot}$ and [**8**]$^{+\cdot}$ would lead to loss of equal amounts of the C-phenyl and the S-phenyl rings. From the metastable peak shapes it was concluded that losses of $C_6H_5^\cdot$ and C_6H_6 from [**1**]$^{+\cdot}$ and [**2**]$^{+\cdot}$ both occur, at least mainly, from the same reacting configuration and the same pathway is followed by ions generated with structure [**3**]$^{+\cdot}$. Scheme 5 gives a possible explanation for the results. Again it is assumed that the main part of the ions [**1**]$^{+\cdot}$ rearrange to [**4**]$^{+\cdot}$ while ions [**2**]$^{+\cdot}$ first rearrange to [**3**]$^{+\cdot}$ by means of the electrocyclic reaction discussed earlier.[3] A reaction pathway via an equilibrium between [**3**]$^{+\cdot}$ and [**4**]$^{+\cdot}$, followed by most of the ions [**2**]$^{+\cdot}$, explains the loss of both phenyl groups. It is thought that [**3**]$^{+\cdot}$ is the decomposing structure for most of the ions as it leads to the formation of stable fragment ions. When some ions [**3**]$^{+\cdot}$ decompose before reaction to [**4**]$^{+\cdot}$ can take place, this causes the loss of excess C-phenyl as observed for $C_6H_5^\cdot$ as well as for C_6H_6. For ions [**1**]$^{+\cdot}$ a second pathway must be available for loss of C_6H_6, as



Scheme 5

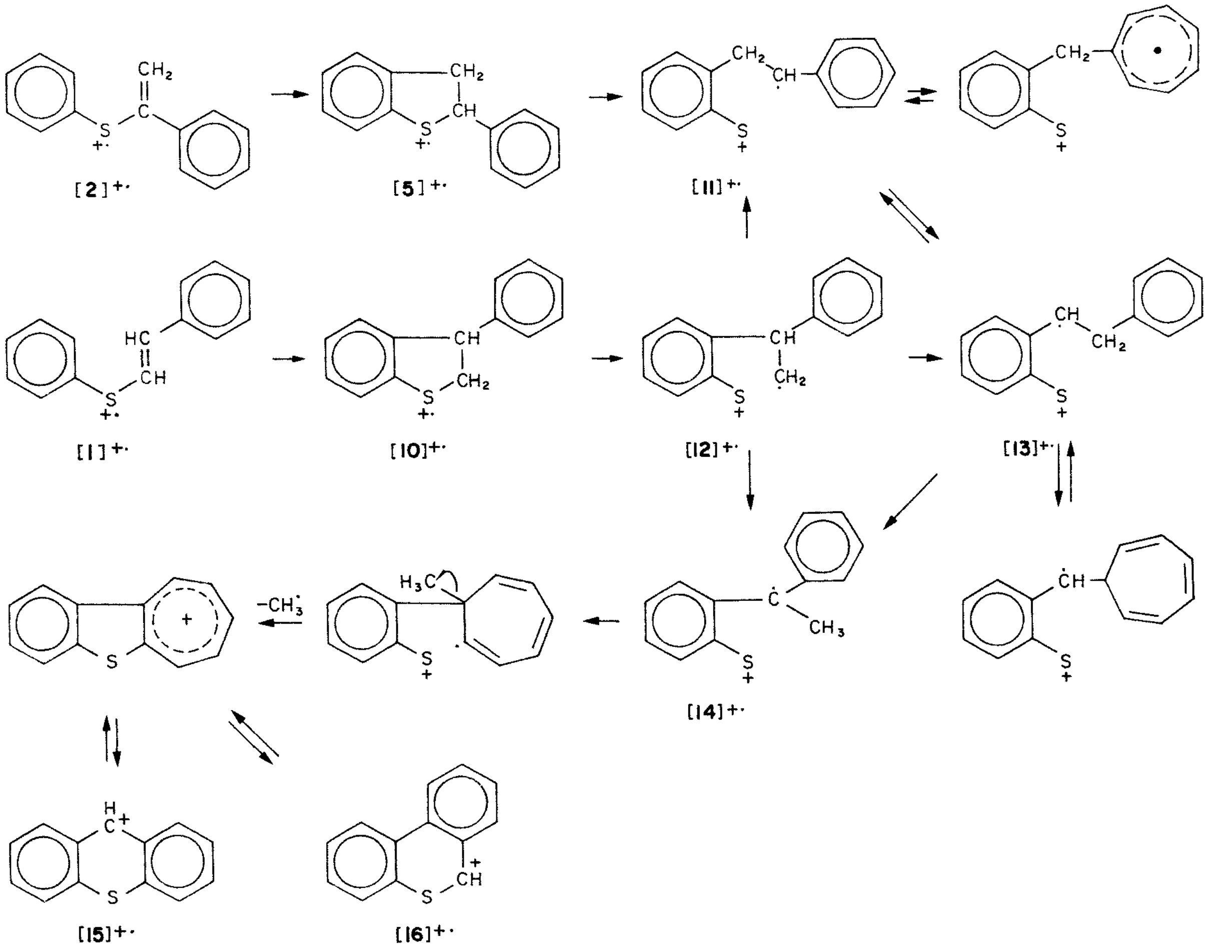
a definite complex peak is observed for this fragmentation. In the Scheme it is suggested that some fragmentation occurs from the initial structure $[\mathbf{1}]^{+\cdot}$. A 1,1-elimination could explain the excess of S-phenyl lost as C_6H_6. From the peak shape it is not certain whether loss of $C_6H_5^\cdot$ from $[\mathbf{1}]^{+\cdot}$ follows only one pathway or more. Some fragmentation directly from $[\mathbf{1}]^{+\cdot}$ would explain the loss of excess C-phenyl (Scheme 5).

Loss of $SH^\cdot$

This intense fragmentation leads to formation of ions $[C_{14}H_{11}]^+$ (*m/z* 179). Loss of $SH^\cdot$ is found in the mass spectra of many sulfides. It is a reaction that has to be preceded by a rearrangement. D labelling does not give much information about the mechanism. The results for **1b** and **1c** show that some H/D scrambling occurs. Remarkably, **1a**, **1b** and **1c** all lose less $SD^\cdot$ than expected for a statistical H/D distribution. This means that the hydrogen atom of the SH radical originates from the C-phenyl ring or the α-vinyl position, or that an isotope effect influences the SH/SD ratio. The latter seems to be most probable.

Loss of $CH_3^\cdot$

This fragmentation gives rise to the formation of ions $[C_{13}H_9S]^+$ (*m/z* 197). Labelling of **1** with ^{13}C (compound **1d**) shows that 35% of the CH_3 carbon atoms originate from the β-vinyl position. Surprisingly, compound **2b** labelled with ^{13}C in the β-vinyl position, does not lose any $^{13}CH_3^\cdot$ but only unlabelled methyl radicals. Upon D labelling, fragmentation competes with H/D scrambling. Compound **1a** loses 61% $CH_2D^\cdot$; this shows that the β-vinyl hydrogen atom of $[\mathbf{1}]^{+\cdot}$ contributes to the formation of the CH_3 radical. Compounds **1b** and **1c**, labelled with deuterium in the S-phenyl ring, both lose more $CH_3^\cdot$ than expected for a statistical distribution of H and D atoms. This means that either the hydrogen atoms of this ring do not become part of the CH_3 radical or that an isotope effect influences the label distribution. In Scheme 6



Scheme 6

giving a mechanism for the loss of CH_3 from $[\mathbf{1}]^{+\cdot}$ and $[\mathbf{2}]^{+\cdot}$, the latter is assumed. Compound **2a**, containing one D atom in the S-phenyl ring, loses 13% $CH_2D^{\cdot}$. This indicates that the hydrogen atoms of the S-phenyl ring contribute to the formation of the CH_3 radical.

As related mechanisms for the loss of $CH_3^{\cdot}$ from $[\mathbf{1}]^{+\cdot}$ and $[\mathbf{2}]^{+\cdot}$ are probable, it is assumed that in both cases the reaction sequence starts with a ring closure, leading to the formation of the benzo[*b*]thiophenes $[\mathbf{10}]^{+\cdot}$ and $[\mathbf{5}]^{+\cdot}$ (Scheme 6). Ring opening by fission of a C—S bond leads to the formation of a primary radical $[\mathbf{12}]^{+\cdot}$ for $[\mathbf{10}]^{+\cdot}$, that is stabilized by a shift of a hydrogen atom, a C_6H_5 or a C_6H_4S group, leading to $[\mathbf{14}]^{+\cdot}$, $[\mathbf{13}]^{+\cdot}$ and $[\mathbf{11}]^{+\cdot}$ respectively. Ring opening of $[\mathbf{5}]^{+\cdot}$ leads to a secondary radical $[\mathbf{11}]^{+\cdot}$, that is probably in equilibrium with the more stable $[\mathbf{13}]^{+\cdot}$. A one-step rearrangement leads to $[\mathbf{14}]^{+\cdot}$ from where several routes are possible that all give loss of the CH_3 radical and formation of stable ions like $[\mathbf{15}]^{+\cdot}$ or $[\mathbf{16}]^{+\cdot}$. An example is given in the Scheme. Ring expansion and contraction is possible in several stages of the reaction sequence. This may contribute to the loss of positional identity of the hydrogen atoms, which is reflected in the formation of mixtures of fragment ions upon D labelling. Examples are shown in the Scheme.

Table 3. EI mass spectra at 70 eV [*m/z* (rel. int. %)][a,b]

1a	39 (12.0), 50 (12.7), 51 (28.1), 63 (5.4), 65 (11.3), 66 (7.5), 69 (7.8), 74 (6.0), 77 (42), 78 (14.3), 91 (9.6), 92 (17.7), 103 (9.0), 104 (11.1), 109 (12.5), 110 (13.1), 121 (26.0), 135 (22.1), 136 (20.9), 166 (5.8), 167 (10.0), 168 (14.8), 178 (5.1), 179 (19.0), 180 (14.4), 211 (5.8), 212 (32.1), 213 (100), 214 (18.9), 215 (6.2).
1b	42 (5.5), 50 (5.7), 51 (15.8), 52 (6.4), 54 (15.3), 70 (10.1), 71 (6.3), 77 (27.5), 82 (11.5), 91 (15.8), 102 (7.8), 103 (9.3), 105 (7.4), 114 (5.5), 115 (11.4), 121 (11.2), 126 (14.4), 134 (9.6), 135 (9.3), 140 (5.5), 172 (17.9), 182 (8.9), 183 (8.9), 184 (8.0), 215 (10.8), 216 (20.0), 217 (100.0), 218 (16.7), 219 (5.5).
1c	39 (7.0), 40 (5.5), 45 (5.4), 50 (14.7), 51 (28.8), 52 (15.8), 53 (6.3), 63 (10.8), 65 (7.3), 67 (15.4), 68 (12.8), 69 (5.3), 73 (6.7), 74 (11.8), 75 (10.7), 76 (16.4), 77 (46.7), 78 (7.7), 79 (14.3), 89 (5.6), 91 (26.6), 102 (52.5), 103 (28.5), 104 (5.3), 105 (13.7), 111 (15.6), 112 (14.8), 121 (13.6), 123 (15.2), 134 (14.1), 135 (12.5), 136 (8.3), 137 (6.6), 167 (8.1), 168 (5.0), 169 (20.7), 179 (8.7), 180 (19.3), 181 (13.0), 182 (6.5), 184 (7.4), 212 (7.9), 213 (34.7), 214 (100.0), 215 (18.2), 216 (6.4).
1d	39 (11.4), 50 (9.7), 51 (28.6), 52 (6.4), 63 (5.1), 65 (12.0), 66 (9.7), 69 (5.4), 76 (7.2), 77 (40.9), 7.8 (19.0), 91 (17.5), 92 (5.6), 102 (5.4), 103 (11.2), 104 (13.6), 109 (17.4), 110 (29.6), 121 (11.2), 122 (13.0), 135 (13.0), 136 (11.5), 167 (10.6), 168 (6.8), 179 (14.4), 180 (9.1), 211 (5.9), 212 (33.7), 213 (100.0), 214 (15.2), 216 (8.1).
1e	39 (5.6), 40 (5.0), 50 (5.5), 51 (18.2), 52 (15.0), 53 (6.3), 65 (5.3), 67 (8.0), 77 (17.5), 78 (14.7), 79 (13.4), 91 (22.1), 92 (6.0), 103 (10.3), 104 (9.8), 111 (7.7), 112 (9.5), 121 (12.8), 124 (14.8), 135 (18.0), 136 (16.4), 137 (9.4), 138 (8.0), 167 (5.4), 168 (5.2), 169 (15.9), 170 (9.9), 180 (10.3), 181 (21.4), 182 (14.2), 214 (44.3), 215 (100.0), 216 (20.5), 217 (8.9).

[a] All peaks with a relative intensity >5% are given.
[b] The intensities are not corrected for incomplete labelling.

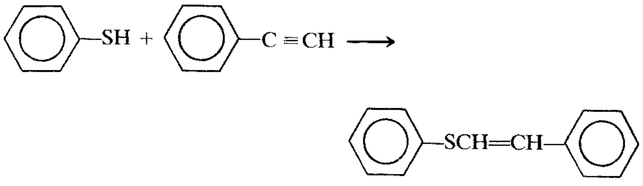
70 eV EI spectra

Table 3 gives the relative abundance of the most intense peaks (>5%) in the 70 eV EI spectra of **1a**–**1e**. No spectra of **2a** and **2b** are given, as these compounds contained some impurity (~3% diphenyl disulfide). The fragmentation mechanisms concluded for decomposition of metastable ions could well be valid for higher energy ions too in the case of some fragmentations, as appears from the label distribution. For most of the fragmentations the same fragment ions are observed, but the intensity ratios are sometimes very different from those observed for metastable decompositions (Table 1). This can as well be due to differences in internal energy, leading to a different use of the pathways also available to metastable ions, as to the existence of decomposition routes that are only attainable for high energy ions.

In the loss of $C_7H_7^{\cdot}$ both phenyl groups and both vinyl carbon atoms are involved; the CHS fragment may contain each of the two vinyl carbon and hydrogen atoms.

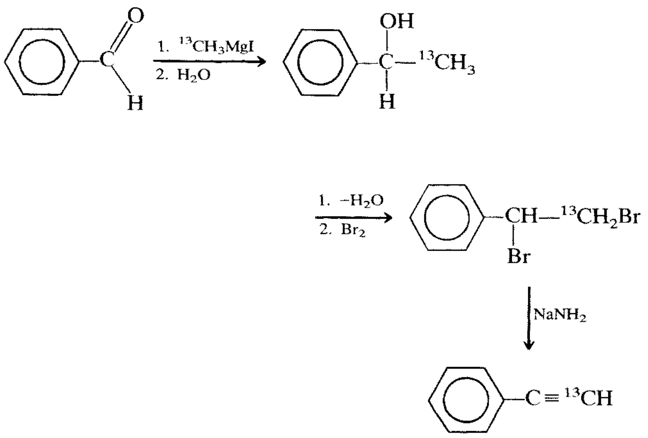
Synthesis of the labelled compounds

The simplest synthesis of **1** is by addition of thiophenol to phenylacetylene:[7]

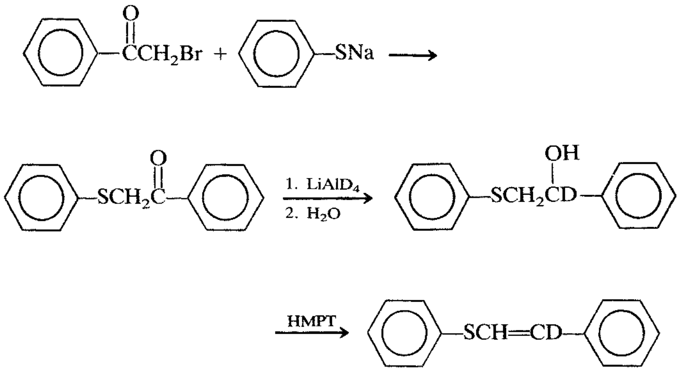


1

This reaction was used for the preparation of **1**, **1b**, **1c**, **1d** and **1e**. Pentadeuterothiophenol and 3,5-dideuterothiophenol for the synthesis of **1b**, **1c** and **1e** were made from pentadeuterobromobenzene and 3,5-dideuterobromobenzene[8] respectively via the corresponding lithium compounds.[9] ^{13}C labelled phenylacetylene for the synthesis of **1d** and **1e** was made according to the following reaction scheme:[10]

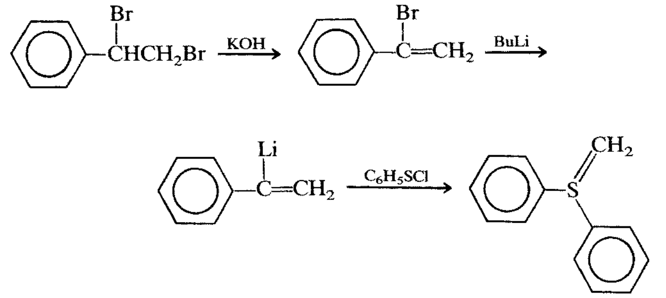


Compounds **1** labelled specifically with deuterium on one of the vinyl positions cannot be made by the method described above, as this leads to products with the deuterium label scrambled over the two vinyl positions. The method used for the synthesis of **1a** is:[11]



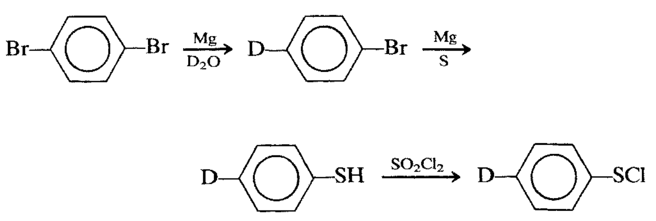
1a

Although compound **2** has already been described in the literature,[12] a new synthesis was developed, which allowed an efficient preparation of **2a** and **2b**.[13]



2

4-Deuterophenylsulfenylchloride for the synthesis of **2a** was made from 1,4-dibromobenzene:[8,13a]



α-Bromostyrene-β-^{13}C for the preparation of **2b** was obtained by elimination of HBr from the labelled 1,2-dibromo-1-phenylethane described above.[13]

EXPERIMENTAL

All measurements were performed on an AEI MS 902 double focusing mass spectrometer, updated with a VG Micromass electronics console. Ions were produced by electron impact with 70 eV electrons; the electron trap current was 200 μA. The source temperature was 130 °C. Samples were introduced via an all glass heated inlet system with a temperature of 140 °C. Fragmentation reactions of metastable ions in the first field free region were recorded by means of a combined scan of the magnetic field B and the electric sector voltage E with B/E constant,[4] or by a scan of the accelerating voltage.[5] The instrument was equipped with a variable β-slit. The width of the main beam was 2.5 V.

The purity of all compounds was checked by gas chromatography and nuclear magnetic resonance spectroscopy, and was better than 99% for compounds **1** and better than 97% for **2a** and **2b**. The impurities did not interfere in the measurements of metastable intensities. The isotopic purity of the ^{13}C labelled compounds was ~90%, of the D-labelled compounds better than 99%.

1-Phenyl-1-deutero-2-phenylthioethene (1a)

1-Phenyl-1-deutero-2-phenylthioethanol (5.3 g), 23 mmol) was refluxed for 1 h in 25 cm^3 hexamethylphosphortriamide (HMPT). After cooling the mixture was diluted with 50 cm^3 ether and extracted with 250 cm^3 water and 2×100 cm^3 2 M sulfuric acid respectively. The brown oil, obtained after drying ($MgSO_4$) and evaporation of the solvent was purified by chromatography over a column of alumina (Merck Neutral, Akt. I) using hexane–dichloromethane (1:1) as the solvent. A small pure fraction (500 mg, 2 mmol) was used for the mass spectrometric measurements.

1-Phenyl-1-(4-deuterophenylthio)ethene (2a)

Sulfurylchloride (1.3 g, 9.0 mmol) was added in 5 min to a solution of 4-deuterothiophenol (0.7 g, 6.4 mmol) in 10 cm^3 carbon tetrachloride at 0 °C. After refluxing for 1 h the solvent was evaporated and the residue was added to a solution of styryllithium, made by addition of 2.5 cm^3 of a 15% solution of n-butyllithium in hexane to 1.0 g (5.5 mmol) α-bromostyrene in 15 cm^3 ether (distilled from lithium aluminium hydride) in a nitrogen atmosphere at −35 °C. After 10 min, the temperature was raised to 20 °C and a white precipitate was formed. After addition of 30 cm^3 0.7 N sulfuric acid, the mixture was extracted with 2×20 cm^3 ether. After drying ($MgSO_4$) and distillation 350 mg (1.65 mmol) of the product was obtained (97% pure, some diphenyldisulfide was present).

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