

## Silicon-directed Elimination from $\beta$ -Trimethylsilyl Sulphoxides and the Regiospecific Synthesis of Olefins

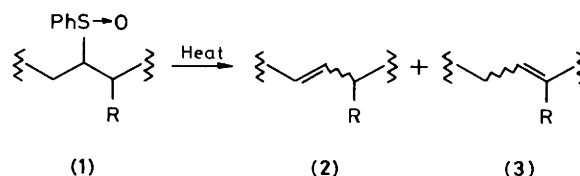
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The regiospecific formation of olefins by the thermal elimination of sulphenic acid from  $\beta$ -trimethylsilyl sulphoxides followed by protodesilylation is reported and the effect of the trimethylsilyl group on the thermal elimination is discussed.

Elimination from a sulphoxide plays an important role in synthetic organic chemistry because it provides a means for the facile introduction of a double bond.<sup>1</sup> If there are two possible directions for such an elimination, it is necessary to have a means of controlling the regiospecificity of the double bond formation. The factors controlling regiochemistry (steric interactions, proton acidity, dipole-dipole interactions, and reaction temperature) have already been documented.<sup>1,2</sup> We report here a new method to achieve the regiospecific introduction of a double bond.

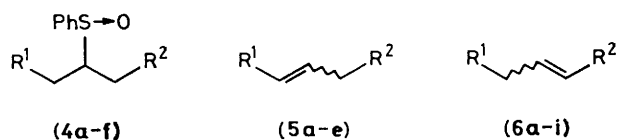
The following order for the ease of proton abstractions has been reported:<sup>2b</sup>  $C=CCH_2 \sim C \equiv CCH_2 > ArCH_2 \sim CH_3 > CH_2 \gg CH$ . The thermolysis of the sulphoxide (1) ( $R = H$ ) usually results in the formation of a mixture of olefin regioisomers, (2) and (3) ( $R = H$ ). However the introduction of a trimethylsilyl group at the carbon atom  $\beta$  to the sulphoxide function resolves this regiochemical ambiguity, because both the allylsilane (2) ( $R = Me_3Si$ ) and the vinylsilane (3) ( $R = Me_3Si$ ), the possible products from thermolysis of the sulphoxide (1) ( $R = Me_3Si$ ), on protodesilylation produce the olefin (3) ( $R = H$ ) in a completely regiospecific manner.<sup>3</sup> As an example of a similar reaction Kocienski has reported the synthesis of terminal olefins through the fluoride-induced elimination of  $\beta$ -trimethylsilyl sulphones.<sup>4</sup>



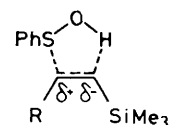
On thermolysis of 1-benzylethyl phenyl sulphoxide (4a) in refluxing carbon tetrachloride for 35 h, a preference for the abstraction of the benzylic proton was observed, and an olefin mixture consisting of *E*- $\beta$ -methylstyrene, its *Z*-isomer (5a), and prop-2-enylbenzene (6a) was obtained in 61, 5, and 13% yields, respectively.<sup>†</sup> In contrast with (4a), the thermal elimination from the  $\beta$ -trimethylsilyl sulphoxide (4b)<sup>‡</sup> proceeded much more smoothly and the direction of the proton

<sup>†</sup> 21% of the sulphoxide (4a) was recovered.

<sup>‡</sup> Methyl phenyl sulphoxide was treated with  $Bu^{\text{n}}Li$  and  $Me_3SiCH_2I$  in tetrahydrofuran (THF) in the presence of hexamethylphosphoramide (HMPA) to afford  $Me_3SiCH_2CH_2S(O)Ph$  in 58% yield, which on benzylation using MeLi and benzyl bromide in THF gave (4b) in 62% yield. Sulphoxides (4c)—(4f) were prepared by a similar method.



- a; R<sup>1</sup> = Ph, R<sup>2</sup> = H  
 b; R<sup>1</sup> = Ph, R<sup>2</sup> = Me<sub>3</sub>Si  
 c; R<sup>1</sup> = *p*-MeOC<sub>6</sub>H<sub>4</sub>, R<sup>2</sup> = Me<sub>3</sub>Si  
 d; R<sup>1</sup> = *p*-ClC<sub>6</sub>H<sub>4</sub>, R<sup>2</sup> = Me<sub>3</sub>Si  
 e; R<sup>1</sup> = *p*-MeOC<sub>6</sub>H<sub>4</sub>, R<sup>2</sup> = H  
 f; R<sup>1</sup> = Pr<sup>n</sup>, R<sup>2</sup> = Me<sub>3</sub>Si  
 g; R<sup>1</sup> = *p*-ClC<sub>6</sub>H<sub>4</sub>, R<sup>2</sup> = H  
 h; R<sup>1</sup> = *p*-MeOC<sub>6</sub>H<sub>4</sub>, R<sup>2</sup> = H  
 i; R<sup>1</sup> = *p*-ClC<sub>6</sub>H<sub>4</sub>, R<sup>2</sup> = H



Thermolysis of the sulfoxide (**4f**) was shown to be regio-specific to give a 99% yield of a mixture of *E*- and *Z*-vinylsilane (**6f**) in a ratio of 57:1. Protodesilylation of the mixture afforded hex-1-ene in good yield.

The elimination of sulphenic acid on thermolysis of the sulfoxides is generally regarded to occur *via* a concerted process. Its transition state is believed to have a planar structure,<sup>6</sup> and some charge separation has been proposed.<sup>1a,7</sup> For the thermolysis of  $\beta$ -trimethylsilyl sulfoxides, the large rate increase and highly regiospecific abstraction of hydrogen from the carbon atom bearing the trimethylsilyl group can be rationalized by assuming a charge separation in the transition state (**7**). The transient partial positive charge  $\beta$  to the silicon atom and the negative charge next to the silicon atom in the transition state (**7**) will be stabilized considerably by the trimethylsilyl group. Steric interactions may account in part for the rate enhancement for the thermolysis.

**Table 1.** A summary of the thermolysis of a number of  $\beta$ -trimethylsilyl sulfoxides and of the subsequent olefin synthesis by protodesilylation.

Sulfoxide	Thermolysis <sup>a</sup> products	% Yield <sup>b</sup>	Proto-desilylation <sup>a</sup> product	% Yield <sup>c</sup>
<b>(4b)</b>	<b>(5b)</b> + <b>(6b)</b>	100	<b>(6a)</b>	79
<b>(4c)</b>	<b>(5c)</b> + <b>(6c)</b> <sup>d</sup>	100	<b>(6g)</b>	68
<b>(4d)</b>	<b>(5d)</b> + <b>(6d)</b> <sup>d</sup>	94	<b>(6h)</b>	93
<b>(4e)</b>	<b>(5e)</b> + <b>(6e)</b> <sup>d</sup>	93	<b>(6i)</b>	86

<sup>a</sup> Reactions were performed as described in the text. <sup>b</sup> Isolated yield. <sup>c</sup> G.l.c. yield. <sup>d</sup> More than 80% of the products was the *E*-vinylsilane.

abstraction was noticeably changed: on refluxing (**4b**) in carbon tetrachloride, the elimination reaction was complete within 30 min to give a quantitative yield of a mixture of *E*-allylsilane (**5b**), *E*-vinylsilane, and its *Z*-isomer (**6b**) in the ratio 12:83:5. The structures of the products were confirmed by comparison with authentic samples. Successive protodesilylation of the mixture of (**5b**) and (**6b**) using hydroiodic acid in benzene at room temperature afforded (**6a**) regio-specifically in 79% yield.<sup>5</sup> Formation of the regioisomer (**5a**) was not observed. The results of the regiospecific synthesis of olefins using this procedure are summarized in Table 1.

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