

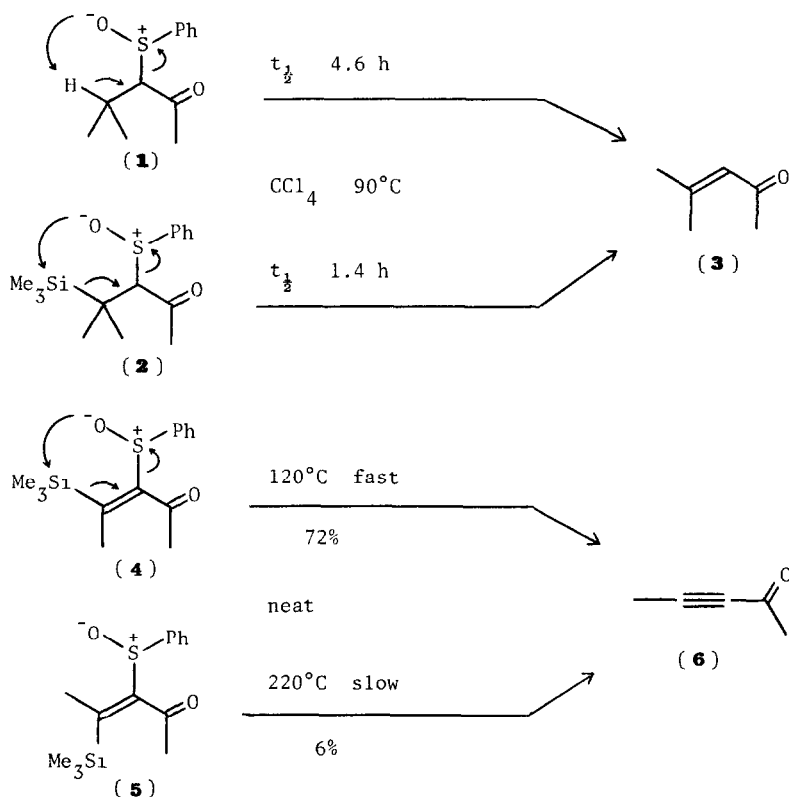
CYCLO-ELIMINATION OF SILYL AND SULPHOXIDE GROUPS
 IN COMPETITION WITH THE CONVENTIONAL CYCLO-ELIMINATION OF SULPHOXIDES¹

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Summary—The β -silylsulphoxides (**2** and **4**) undergo a fast *syn*-elimination to give the alkene (**3**) and the alkyne (**6**), respectively; however, when there is a hydrogen α to the silyl group, only hydrogen is lost, and the products are β -silylenones.

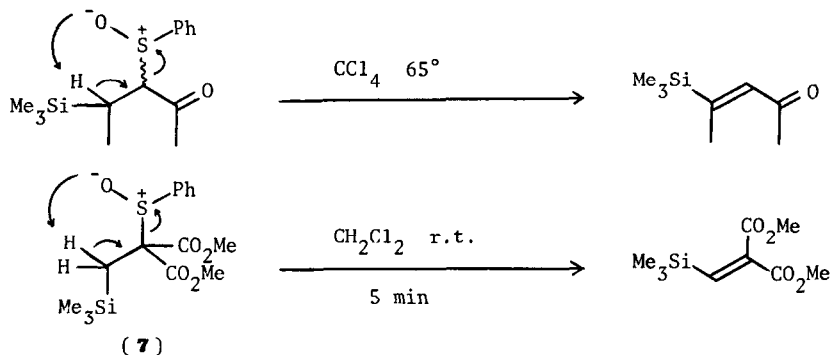
The cyclo-elimination (**1** \rightarrow **3**) of phenylsulphenic acid is a well known type of reaction.² We have now investigated the possibility of carrying out the equivalent reaction with a silyl group in place of the hydrogen atom (**2** \rightarrow **3**). We find that the latter reaction is a little faster than the conventional reaction, as befits a process in which, in a sense, an oxygen nucleophile attacks the silyl group.



The reaction also works for the formation of an alkyne (**4** \rightarrow **6**), in a process which is stereospecifically *syn*, and which has no conventional analogue in the absence of the silyl group.³

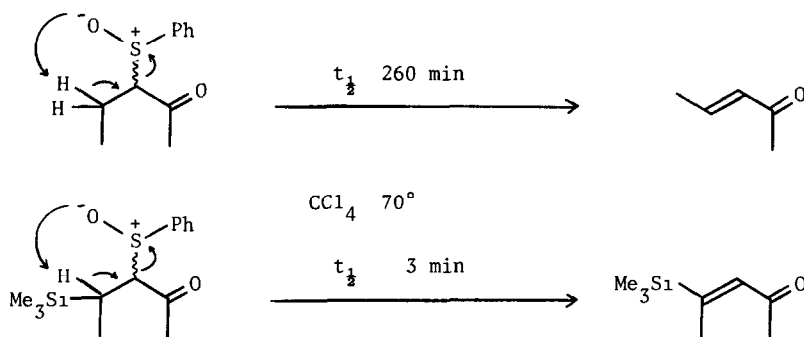
Nevertheless, when there is a choice between a silyl group and hydrogen within the same molecule, it is the hydrogen α to the silyl group which is removed, as shown by the examples in Scheme 1.⁴

SCHEME 1



The reason for this apparent anomaly is that the silyl group speeds up the loss of the hydrogen α to it, as shown by the relative rates of the two reactions in Scheme 2 and by the difference in stability between the diester (7), which starts to decompose even at -20° , and its analogue without a silyl group, which, we find, has a half-life of 20-25 min at 65° .⁴ It is known that a hydroxyl group, which is a π -donor (and σ -acceptor), slows down the loss of the hydrogen α to it.⁵ It is not, therefore, surprising that a silyl group, which is a π -acceptor (and σ -donor), should speed it up. Full details of this work will be published.

SCHEME 2



NOTES and REFERENCES

1. No reprints available.
2. B. M. Trost, T. N. Salzmann, and K. Hiroi, *J. Am. Chem. Soc.*, **98**, 4887 (1976).
3. A conventional selenoxide elimination has been shown to give acetylenes,⁶ and so has the cyclo-elimination of a dialkylboryl and a sulphoxide group.⁷ A sulphoxide elimination has been used to form the triple bond of a nitrile.⁸
4. We thank Dr. Jon Goldhill for the second reaction in Scheme 1.
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6. H. J. Reich and W. W. Willis, *J. Am. Chem. Soc.*, **102**, 5967 (1980).
7. M. Naruse, K. Utimoto, and H. Nozaki, *Tetrahedron*, **30**, 2159 (1974).
8. F. A. Davis, A. J. Friedman, and U. K. Nadir, *J. Am. Chem. Soc.*, **100**, 2844 (1978).

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