FLECTROPHILIC REACTIONS OF 1-PHENVITHIO-1-TRIMETHYISILYLETHENE

By David J. Ager

(Department of Organic Chemistry, Robert Robinson Laboratories, P.O. Box 147, Liverbool, 169 3BX).

Summary: The reaction of 1-phenylthio-1-trimethylsilylethene (1) with various electrophiles, in particular acid chlorides, has been investigated.

In connection with some other work, we have been using 1-phenylthio-l-trimethylsilylethene¹(1) to prepare aldehydes² and ketones³ by nucleophilic addition; this paper presents our results for the reaction of the olefin(1) with electrophiles, as this has not been investigated in depth4.

The olefin(1) is of interest because it has two possible modes of reaction with an electrophile :-



Pathway (a) is controlled by the sulphur atom and gives a carbonium ion stabilised by this group, while pathway (b) gives a carbonium ion stabilised by the silicon group. The results show that pathway (a) is the reaction course normally followed².

When bromine was added to the olefin(1) in carbon tetrachloride at $\cap^{o}C$, the dibromide(2) was formed quantitatively. Reaction with sodium methoxide in methanol gave the vinylbromide(3) in high yield (89%). These reactions parallel those of a vinylsilane⁶. Treatment of (1) with hydrogen



bromide gave the bromide(4) exclusively; possible products from addition via pathway (b) were not observed and the sulphur group controls the mode of addition.

† No reprints will be available.



The vinylsulphide(1) failed to undergo a reaction with alkyl halides, ketones or aldehydes with titanium(IV) chloride or aluminium(III) chloride as Lewis acid catalyst in dichloromethane but reacted with acid chlorides to give, after basic work-up, the enones(5)⁷ in high yield. Again the reaction follows pathway (a) and is controlled by the sulphur group.



Finally, the alkene(1) was acylated with acetic anhydride in the presence of aluminium(JII) chloride to give (5;R=Me) in 51% yield.

l-Phenylthio-l-trimethylsilylethene(1), therefore, reacted with the electrophiles investigated via pathway (a); that is to give the carbonium ion stabilised by the sulphur group.

References and Notes:

1)Prepared as previously described - see reference 2.

2)D.J. Ager, Tetrahedron Lett., 1981, 22, 587.

3)D.J. Ager, Unpublished results.

- 4) Magnus has reported the reaction of (1) with ∝,β-unsaturated acid chlorides to give 3-phenylthiocyclopent-2-en-1-ones; P. Magnus, <u>Aldrichimica Acta</u>, 1980, <u>13</u>, 43 and F. Cooke, R. Moerck, J. Schwindeman and P. Magnus, <u>J. Org. Chem</u>., 1980, <u>45</u>, 1046.
- 5) Mase has reported the Friedal-Crafts acylation of a 1-thio-2-silylalkene (MeS(CH₂)₃SCH=CHSiMe₃) to give the 3-thio-2-en-1-one (MeS(CH₂)₃SCH=CHCOMe) in 46% yield (T.A. Hase and L. Lahtinen, <u>Tetrahedron Lett.</u>, 1981, 22, 3285). Although in this case, the silicom and sulphur atoms are working together to stabilise the resultant carbonium ion, the yield is lower than those reported in this paper because of competing acylation of sulphur (T.A. Hase, Private communication). Hiroi and Chen have found that 1-phenylthio-1trimethylsily1-2-alkenes react cleanly with acid chlorides in the presence of aluminium(III) chloride in high yield (K. Hiroi and L.-M. Chen, <u>J. Chem. Soc., Chem. Commun.</u>, 1981, 377); here the sulphur takes no part in the reaction and the alkenes react, as expected, as allylsilanes.

6)T.H. Chan and I. Fleming, Synthesis, 1979, 761.

7)The chemistry of these interesting products is being investigated at present.

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