

Regioselective Acylation of Allyl Sulphides *via* α -Silyl Intermediates

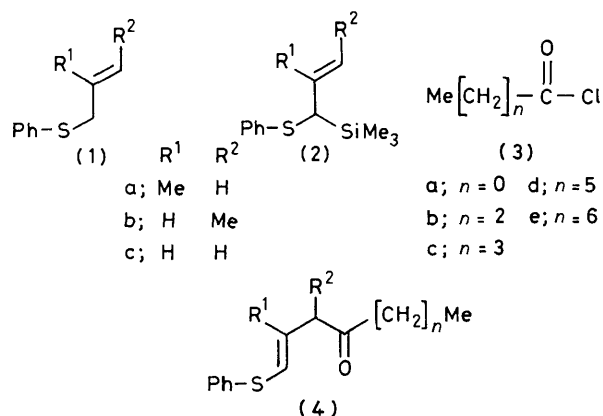
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Summary Acylation of the α -trimethylsilylallyl sulphides (**2**) by reaction with the acid halides (**3**) (1.2 equiv.) in the presence of aluminium chloride (1.2 equiv.) in methylene

dichloride at -78 °C gave compounds (**4a—i**) in good yields with extremely high regioselectivity.

ALLYL SULPHIDES have been used as intermediates for the preparation of complex molecules, usually with base-catalysed regioselective alkylation.¹ More recently the acid-catalysed alkylation of allylsilanes² has been shown to be a potentially valuable method for the regioselective introduction of alkyl groups, the π -bond nucleophilicity of allylsilanes being enhanced by σ (Si-C)- π -conjugation. We now report the highly regioselective γ -acylation of allyl sulphides *via* α -silyl intermediates.



The α -trimethylsilylallyl sulphides (**2a–c**) were prepared quantitatively by the normal base-catalysed silylation of the allyl sulphides (**1a–c**) (lithium di-isopropylamide, -78°C , tetrahydrofuran, Me_3SiCl) with complete regioselectivity.

The α -silylallyl sulphides (**2**) failed to undergo acid-catalysed intermolecular alkylation with alkyl halides, aldehydes, and ketones using various acidic catalysts (*e.g.* TiCl_4 , SnCl_4 , $\text{BF}_3\text{-OEt}_2$, and $\text{CF}_3\text{CO}_2\text{H}$), although intramolecular alkylation was observed previously.³ However, the acid-catalysed acylation of (**2**) with various acid

halides proceeded successfully in the presence of aluminium chloride under mild conditions with extremely high regioselectivity.

TABLE. Regioselective acylation of α -trimethylsilylallyl sulphides (**2a–c**).^a

(4)	R ¹	R ²	n	Reaction time/h	% Yield of (4) ^{b,c}
a	Me	H	0	7	63
b	"	"	2	"	84
c	"	"	3	"	92
d	"	"	5	"	84
e	"	"	6	"	86
f	H	Me	2	8	75 (91)
g	"	"	3	"	67 (90)
h	"	"	5	"	63 (75)
i	"	H	3	5	57 ^d (75)

^a The α -trimethylallyl sulphides (**2a–c**) were treated with (**3a–e**) (1.2 equiv.) in the presence of AlCl_3 (1.2 equiv.) in CH_2Cl_2 at -78°C . ^b Yields corrected for recovered starting materials are in parentheses. ^c The structures of compounds (**4**) were confirmed by n.m.r., i.r., and mass spectral analyses and by microanalyses. ^d Includes 10% of the $\alpha\beta$ -unsaturated ketone formed by migration of the double bond in (**4i**).

Reactions of (**2a**) with 1.2 equiv. of the acid halides (**3a–e**) were carried out in methylene dichloride in the presence of 1.2 equiv. of aluminium chloride at -78°C for 7 h to give compounds (**4a–e**),[†] without any formation of α -acylated allyl sulphides, in the high yields reported in the Table. Regioselective acylation of (**2b,c**) under the same conditions afforded (**4f–i**) in the yields shown in the Table with some recovery of starting material.

Attempted direct acylation of the allyl sulphides (**1**) under the normal basic conditions was not successful.

This novel method for the highly regioselective γ -acylation of allyl sulphides *via* α -silyl derivatives thus provides a simple method for preparing synthetically valuable intermediates for 1,4-diketone synthesis.

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[†] All new compounds gave satisfactory analytical data, which were in full agreement with the proposed structures.

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² I. Fleming, *Chem. Ind. (London)*, 1975, 449; T. H. Chan and I. Fleming, *Synthesis*, 1979, 761; E. W. Colvin, *Chem. Soc. Rev.*, 1978, **7**, 15; S. S. Washburne, 'Organometallic Chemistry Review; Annual Surveys; Silicon-Tin-Lead,' Vol. 4, eds. D. Seyferth and R. B. King, Elsevier, Amsterdam, 1977, p. 263.

³ A. Itoh, K. Oshima, and H. Nozaki, *Tetrahedron Lett.*, 1979, 1783.