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

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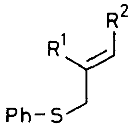
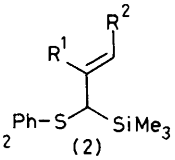
Summary Acylation of the α-trimethylsilylallyl sulphides (**2**) by reaction with the acid halides (**3**) (1·2 equiv.) in the presence of aluminium chloride (1·2 equiv.) in methylene dichloride at −78 °C gave compounds (**4a**—**i**) in good yields with extremely high regioselectivity.

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 allylsilanes[2] 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.

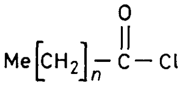


(1)



(2)

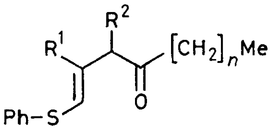
	R^1	R^2
a;	Me	H
b;	H	Me
c;	H	H



$$\mathrm{Me[CH_2]_n{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}Cl}$$

(3)

a; $n = 0$ d; $n = 5$
b; $n = 2$ e; $n = 6$
c; $n = 3$



(4)

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.* $TiCl_4$, $SnCl_4$, BF_3–OEt_2, and CF_3CO_2H), 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.

[1] D. A. Evans and G. C. Andrews, *Acc. Chem. Res.*, 1974, **7**, 147; P. M. Atlani, J. F. Biellmann, S. Dube, and J. J. Vicens, *Tetrahedron Lett.*, 1974, 2665; Y. Yamamoto, H. Yatagi, and K. Maruyama, *Chem. Lett.*, 1979, 385; *J. Org. Chem.*, 1980, **45**, 195, and references cited therein.

[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.