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NEW TRANSFORMATIONS OF SUBSTITUTED ALLENE SULPHOXIDES

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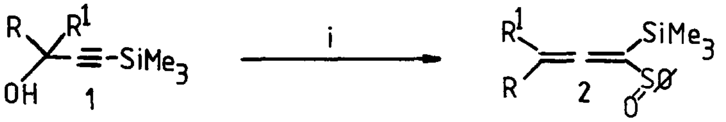
The preparation and reactions of trimethylsilyl substituted allene sulphoxides are described. Allenes (2) rearrange on warming to give α,β-unsaturated thiol esters.

Since the original work of Horner and Binder[1] on the preparation and reactions of allenyl sulphoxides, other groups have used this chemistry to solve synthetic problems.[2,3,4] Our work in this area led us to consider the synthesis of new carbonyl equivalents from allenyl sulphoxides. We have recently shown that α,β-unsaturated aldehydes are easily made from 3-trimethylsilyl substituted allylic alcohols, and now report a similar 2,3-sigmatropic rearrangement of acetylenic alcohols (1) giving allenes (2) (Scheme 1).



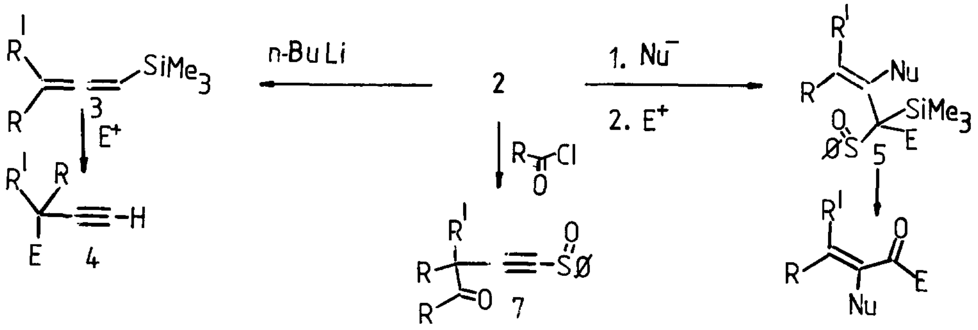
Reagents: i) ØSCl Et_3N/Ether -20°C

SCHEME 1

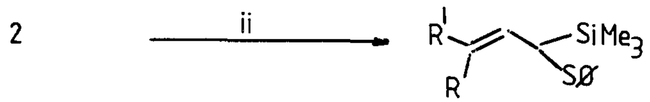
	2	Yield (%)
a	$R=R^1=Me$	56
b	$R,R^1=(CH_2)_5$	66
c	$R=Me\ R^1=Me_2C=CH(CH_2)_2-$	81
d	$R=R^1=H$	45
e	$R=H\ R^1=CH_3(CH_2)_4-$	70

The allenes (2) possess all the requirements for multifunctional ketone synthesis (Scheme 2). Thus on treatment with nBuLi (2) should give allenyl silanes (3) which have been used in acetylenic synthesis,[5] similarly acetylenic sulphoxides (7) could be made. Nucleophilic reagents could also add to (2) giving acyl anion equivalents (5).

In this letter we report that allenes (2) react with $LiAlH_4$ to give useful acyl anion equivalents (8)[6] or allyl silanes (Scheme 3).



SCHEME 2

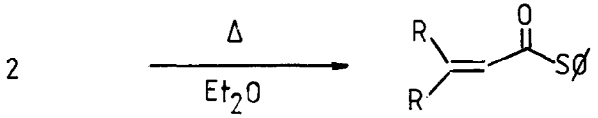


Reagents: ii LiAlH$_4$/Et$_2$O −50^{o}C

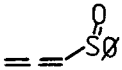
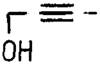
8	Yield (%)
a	65
b	68
c	35
d	59
e	21

SCHEME 3

When investigating the chemical properties of (2) we found that a facile rearrangement occurred on heating (2) giving unsaturated esters (9) (Scheme 4).



9	Yield (%)
a	40
b	56
c	69
d	- *

*Only  and  −SiMe$_3$ were isolated in this example.

SCHEME 4

This reaction presumably proceeds through a silicon mediated Pummerer rearrangement.[6] This offers a new route to activated esters (9), important intermediates for lactone synthesis.

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