Chemistry of Allene Sulphoxides: Novel Transformations of Acetylenic Alcohols

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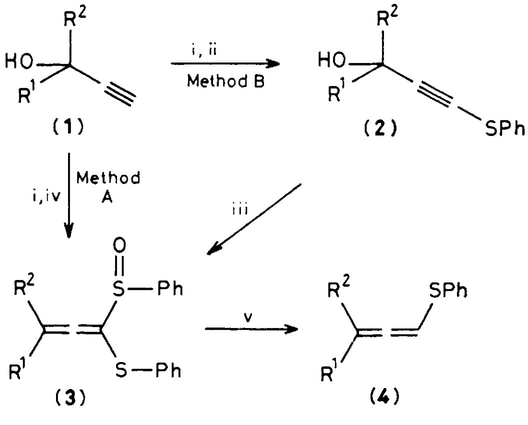
The preparation and reactions of allenes derived from 1-phenylthio substituted acetylenic alcohols are described; this chemistry offers new routes to allenyl sulphides, acyl anion equivalents, and substituted unsaturated aldehydes.

Recent interest in the chemistry of allenyl sulphides[1,2] has prompted us to report our findings in this area. We have discovered that thioacetal *S*-oxides (3)† are readily prepared from acetylenic alcohols (1) (Scheme 1, Table 1). The allenes (3) possess several types of latent functionality. Addition of nucleophiles to the central allenic carbon atom of (3) could provide acyl anion equivalents for further alkylation, or after such addition the sulphoxide moiety could undergo a 2,3-sigmatropic rearrangement[3] to provide synthetically useful 3-phenylthioallylic alcohols.[4] Removal of the sulphoxide moiety[5] in (3) would provide allenyl sulphides, which are readily metallated and converted into enones.[1]

The flexibility of Scheme 1 allows the preparation of (3) in a 'one pot' reaction (method A), or *via* the synthetically useful alcohols (2) (method B).

We have discovered that the allenes (3) react with nucleophiles in two different ways. Treatment of (3) with methyllithium in ether at −70 °C resulted in loss of the sulphoxide moiety with formation of the allenyl sulphides (4) (Scheme 1, Table 1).



Scheme 1. *Reagents:* i, Bu^nLi (2 equiv.); ii, PhSCl; iii, PhSCl, Et_3N; iv, PhSCl (2 equiv.); v, MeLi, Et_2O, −70 °C.

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† All new compounds were characterised by n.m.r. (^{13}C and ^1H) spectroscopy, together with joint application of i.r. and mass spectrometry and elemental analyses.

Table 1. Preparation of (3) and (4).

	R^1	R^2	Method	% Yield (3)	% Yield (4)[a]
a	Me	Me	A	56	56
b	$-[CH_2]_5-$		A	48	51
c	H	H	B	25	—
d	Me	$Me_2C{=}CH[CH_2]_2-$	A	40[b]	61

[a] From (3). [b] Obtained as a 1 : 1 mixture of diastereoisomers, as shown by n.m.r. spectroscopy.

Table 2. Reaction of the allenes (**3a**, **b**, **d**) with nucleophiles.

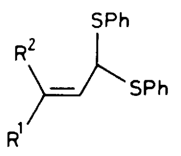
Nucleophile	Products	% Yield **a**	% Yield **b**	% Yield **d**
$LiAlH_4$	(**5a**, **b**, **d**)[a]	59	62	34
Me_2CuLi	(**6a**, **b**, **d**)	45	58	22
	(**7a**, **b**, **d**)	8	—	—
NaOEt	(**8a**, **b**, **d**)[b]	75	43	49
NaSPh, tetrahydrofuran	(**9a**, **b**, **d**)[b]	82	46	24

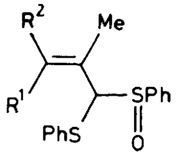
[a] See Table 1 for substituents corresponding to **a**, **b**, **d**. [b] The initially formed sulphoxides were unstable and rearrangement with loss of the phenylthio group gave the allylic alcohols (**8**) and (**9**).

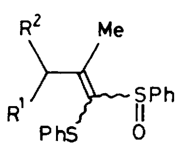
Table 3. Preparation of the unsaturated aldehydes (**10**).[a]

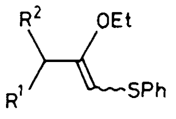
Starting material	Compound (**10**) R^1	R^2	R^3	% Yield
(**8a**)	Me	Me	OEt	53
(**8b**)			OEt	52
(**9a**)	Me	Me	SPh	48
(**9b**)			SPh	54
(**5a**)	Me	Me	H	41

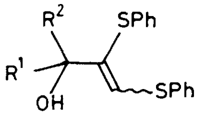
[a] *Reagents:* $HgCl_2$, H_2O, MeCN.

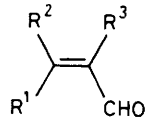

(**5**)


(**6**)


(**7**)


(**8**)


(**9**)


(**10**)

In contrast, the allenes (**3**) react with other nucleophilic reagents giving products resulting from conjugate addition (Table 2).

The chemistry described in this paper offers a new route to acyl anion equivalents (**5**) and an entry into the synthetically useful substituted unsaturated aldehydes (**10**) (Table 3) by reaction with mercury(II) chloride in aqueous acetonitrile.

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