Stereoselective γ-*cis*-Vinylic Metallation of Tertiary Allylic Alcohols

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Tertiary allylic alcohols are converted by Bu^{n}Li–tetramethylethylenediamine into the γ-*cis*-vinyl-lithium derivatives which can be alkylated in moderate yields.

Olefins can be metallated in an allylic position and heteroatoms have been shown to have a profound influence on the ease and direction of metallation[1] mainly of aromatic substrates.[2]

Linalo-ol (**1**) was treated with Bu^{n}Li–tetramethylethylenediamine (TMEDA) in hexane and the reaction mixture quenched with D_2O (Scheme 1). ^{1}H N.m.r. spectroscopy showed that the product was quantitatively and stereoselectively ($J_{1,2}$ = 11 Hz), deuteriated in the γ-*cis*-vinylic position (**3**; X = D).

There are, to our knowledge, few examples of the substitution by a metal of a vinylic hydrogen in non-activated olefins.[3] Stabilisation of the metallation product by intramolecular co-ordination seems reasonable.

The reaction of the intermediate (**2**) with a variety of electrophiles was investigated: methyl bromide leads to 4,8-dimethylnona-2,7-dien-4-ol (**3**; X = Me) (55% yield; 98% *Z*, 2% *E*). The yields with other electrophiles are moderate to fair but stereochemistry is clearly *Z* (Table 1). The reaction with higher alkyl halides had to be catalysed with transition metal complexes.

The vinyl-lithium intermediate (**2**) thus appears less reactive than normal vinyl-lithium derivatives. A similar observation has been made with the *Z* addition product of Grignard reagents to prop-2-ynylic alcohols,[4] the *E* products being much more reactive.[5]

Table 1. Metallation and alkylation of linalo-ol (**1**).

E	X^j	% Yield	$J_{1,2}$/Hz
D_2O	D	$72^{a,b}$	11
MeBr	Me	$55^{c,d}$	12
$Me_2CH[CH_2]_2Br$	$Me_2CH[CH_2]_2$	5^c	g
		$28^{a,e}$	
		$35^{a,f}$	
Me_3SiCl	Me_3Si	52^a	15.5^h
$Me_2C{=}O$	Me_2COH	51^a	13
CO_2	$-C(O)-O-^i$	48^a	7

[a] Isolated yield. [b] Deuteriation is quantitative by ^{1}H n.m.r. or mass spectrometry. [c] G.l.c. yield. [d] 98% *Z*, 2% *E* by capillary g.l.c. [e] Catalyst: $CoCl_2(PPh_3)_2$, 5%. [f] Catalyst: $Fe(PhCOCHCOPh)_3$, 2%. [g] Could not be determined by ^{1}H n.m.r. at 250 MHz. [h] In agreement with literature value for silylated compounds (ref. 6). [i] Lactone. [j] All new compounds gave analytical results (^{1}H, ^{13}C n.m.r., m.s.) in agreement with their structure.

A similar stereoselective metallation could be observed with dihydrolinalo-ol and *trans*-nerolidol.

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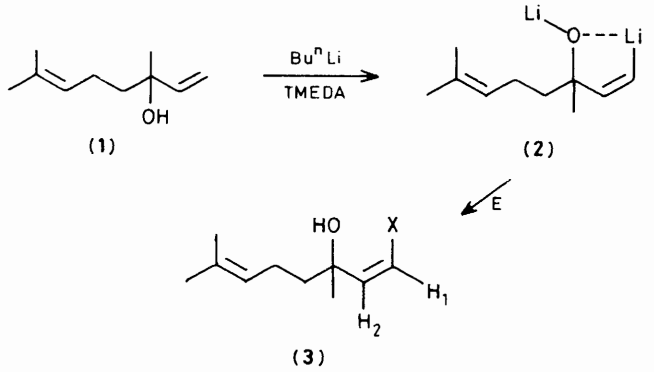

Scheme 1

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