

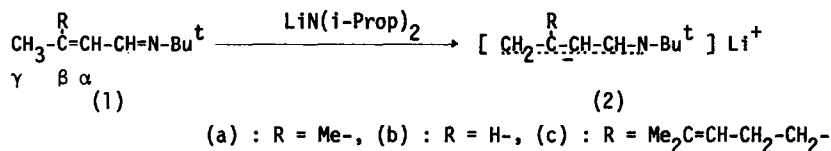
REGIOSELECTIVITY IN THE ALKYLATION OF METALATED α,β -UNSATURATED ALDIMINES

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The reactions of α -lithiated saturated aldimines with various electrophiles have been widely utilized to synthesize a variety of organic compounds.¹⁻⁴⁾ To our knowledge, the alkylation of the metalated α,β -unsaturated aldimines has not been reported. In this communication we wish to report on the regioselectivity in the alkylation and trimethylsilylation of the lithiated α,β -unsaturated aldimines and on the application to the synthesis of terpenoids. The reactions of β -methylcrotonaldimine (1a), crotonaldimine (1b) and the aldimine of citral (1c) with methyl iodide, prenyl chloride or trimethylsilyl chloride were examined.⁵⁾

We have found that the lithiated α,β -unsaturated aldimines (2a, 2b and 2c) may be readily prepared by addition of lithium diisopropylamide to α,β -unsaturated aldimine (1) in ether.



The alkylation results are presented in Table 1. The alkylation of (2a) with prenyl chloride at -15° afforded the aldimine of isolavandulal (3a) selectively in a 75% yield. This prenylation at -78° gave a mixture of (3a), (1c) and α -diprenylated aldimine (4a) in a ratio of 35 : 15 : 47 by the glc inspection. The similar results were obtained in the methylation of (2a). However, in trimethylsilylation of (2a) at -15° was identified the γ -trimethylsilylated aldimine (5a), and no products of α -silylation were isolated from this reaction. The reactions seem to proceed via the scheme as illustrated in Fig. 1.

In the methylation and prenylation, the alkyl group is mainly bonded to the α -carbon probably because of less steric requirement of those groups in comparison to trimethylsilyl group.

The similar phenomena were also observed in the alkylation and trimethylsilylation of crotonaldimine (1b) and the aldimine of citral (1c) (ref. Table 1.).

We are currently investigating the reactions of metalated α,β -unsaturated aldimines with other electrophiles.

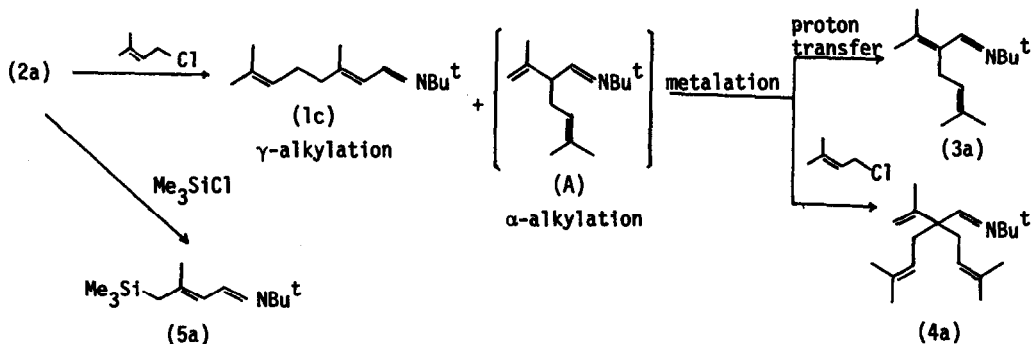


Fig. 1.

Table 1. Alkylation and silylation of metalated α,β -unsaturated aldimine

Aldimine	Reagent (eq. halide)	Temp. ($^{\circ}\text{C}$)	Alkylation products (glc %) ^{a)}			Yields (%) [] ^{b)}
			α -alkyl	α -dialkyl	γ -alkyl	
	Pre-Cl (2.0)	-15	98			75 [98]
	Pre-Cl (1.5)	-78	35	47	15	70 [74]
	MeI (1.3)	-15	63	25		68 [71]
	Me_3SiCl (1.0)	-15			100	74 [86]
	Pre-Cl (1.9)	-15		90		83 [86]
	Me_3SiCl (2.0)	-15			100	92 [95]
	Pre-Cl (2.0)	-15	100			69 [72]
	MeI (1.0)	-15	31	43		57 [62]

a) α -alkyl: (3a) type, α -dialkyl: (4a) type, γ -alkyl: (1c) or (5a) type.

b) The yields are based on the reacted aldimine.

REFERENCES AND FOOTNOTES

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- 5) The structures of all products were verified by compatible spectral data (ir, nmr and mass spectra).