

METALLATION OF PROPARGYLIC AND ALLENIC ETHERS
 SYNTHESIS OF α , β -UNSATURATED CARBONYL COMPOUNDS.

Yves Leroux* and Chantal Roman

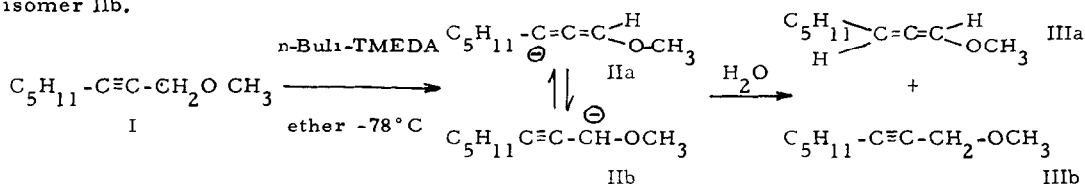
Laboratoire de Synthèse Organique, Equipe de Recherche associée au CNRS,
 Université Paris VI, Tour 44-45, 3e étage,
 4, Place Jussieu, 75230 PARIS CEDEX 05.

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Recently, metallation of propargylic ethers has been studied chiefly by Corey et. al. (1), Mercier et. al. (2) and in our Laboratory (3).

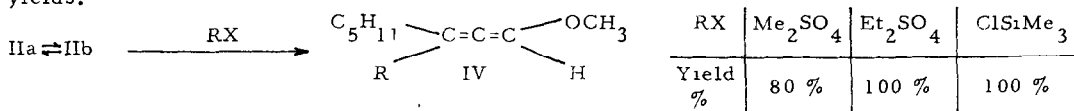
In connection with previous studies (3, 4), we wish to describe briefly, in this communication, the preparation of α , β -unsaturated ketones and aldehydes via the metallation of propargylic and allenic ethers.

Treatment of the propargylic ether I with two equivalents of the n-Buli-TMEDA reagent at -78°C gives an allenic carbanion IIa which is in equilibrium with its acetylenic isomer IIb.

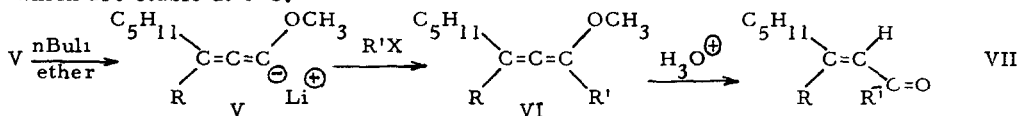


Mercier et. al., using n-Buli/THF at -70°C , obtained upon condensation of such carbanions with aldehydes a mixture of the two products derived from IIa and IIb. Corey et. al., using n-Buli/THF at -25°C , obtained after quenching with methanol-ice a mixture of the allene IIIa and the acetylene IIIb.

As a result of personal observations and in connection with the HSAB principle, we believe that the carbanion IIa has some hard character (sp_2 carbanion) in comparison with the carbanion IIb (sp_3 carbanion). Reagents which are known to be hard: Me_3SiCl , Me_2SO_4 or Et_2SO_4 for instance, react with $\text{IIa} \rightleftharpoons \text{IIb}$ to give exclusively the allenic product in very good yields.



Allenic ethers of the type IV are of course excellent precursors of α , β -ethylenic aldehydes, but they can be metallated once more and then alkylated. Thus, treatment of IV with one equivalent of *n*-butyllithium in ether, gives quite easily the allenic carbanions (V) which are stable at 0°C.



Alkylation of V then leads to the allenic ethers VI. In the following table we have summarized the data for some of these reactions. Yields are high and correspond to pure isolated products.

n°	R	Reagent	R'	Yield VI
1	Me ₃ Si	Me ₃ SiCl	Me ₃ Si	78 %
2	Me ₃ Si	Me ₂ SO ₄	Me	100 %
3	Me ₃ Si	EtI	Et	70 %
4	Me ₃ Si	EtBr	Et	61 %
5	Me	Me ₃ SiCl	Me ₃ Si	100 %
6	Me	MeI	Me	100 %

Experiments 1 and 2 can be run in one step without isolation of the allenic ether IV. With EtBr (Experiment n° 4), the alkylation reaction is accelerated by addition of 5 to 10 % of HMPT. (5).

When R'=H, Me, Et or Me₃Si, acidic hydrolysis of these allenic ethers gives α , β -ethylenic carbonyl compounds VII (6).

All of the compounds shown in the table were isolated in pure form and micro-analyses were satisfactory. IR and NMR spectra are in full agreement with the proposed structures.

References :

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