

A NEW ALLENIC DIANION : SELECTIVE MONO AND BIALKYLATION.

Yves Leroux and Richard Mantine

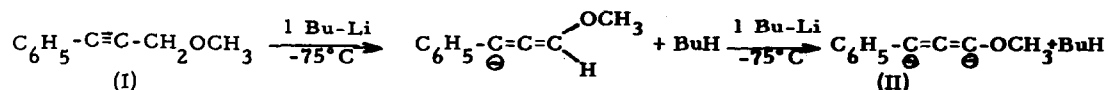
Laboratoire de Synthèse Organique, Equipe de Recherche associée au CNRS

Faculté des Sciences, 1 rue Victor Cousin Paris 5<sup>e</sup>

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In our recent paper, we showed that we were able to obtain allenic (1) or cumulen-ic (2) carbanions by treatment of the  $\alpha$  acetylenic ethers or  $\alpha, \alpha'$  acetylenic bis ethers with n-butyllithium in ether. The use in organic synthesis of allenic carbanions allowed us to synthesize some complex furans and dihydrofurans (3). Experiments concerning polymetalation of 1 butyne have been reported by Eberly and Adams (4) and of 1 propyne by West et. al (5) using an excess of alkyl lithium solution. These authors used only one reagent ; trimethylchloro-silane with the poly lithium derivatives.

In this communication, we wish to report the existence of a new allenic dianion and we define its reactivity. At  $-75^{\circ}\text{C}$ , treatment of one equivalent of the acetylenic ether (I) with two equivalents of Bu-Li in ether leads to the formation of an allenic dianion (II), the existence of which is proved in the following manner :



The solution is maintained at  $-50^{\circ}\text{C}$  (upper limit temperature of the dianion-stability). The butane formed with the exchange reaction H-Li is recovered in vacuo in a trap cooled by liquid nitrogen. The use of a gazometer shows us that the stoichiometric quantity of butane is evolved. This gas is identified by its IR and NMR spectra.

In order to avoid any decomposition of the dianion, our alkylation experiments were done at  $-75^{\circ}\text{C}$ , this temperature giving us a safety margin when alkylation reaction is very exothermic (with trimethylchlorosilane for instance). The different possibilities offered by this dianion are :

- a) bialkylation reaction.
- b) selective monoalkylation followed by hydrolysis.
- c) selective monoalkylation followed by a second monoalkylation.

We can accelerate alkylation reactions if the reagent is not powerful (ethyl bromide for instance)

