## A NEW ALLENIC DIANION : SELECTIVE MONO AND BIALKYLATION. Yves Leroux and Richard Mantione

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In our recent paper, we showed that we were able to obtain allenic (1) or cumulenic (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 alkyllithium solution. These authors used only one reagent ; trimethylchlorosilane with the polylithium derivatives.

In this communication, we wish to report the existence of a new allenic dianion and we define its reactivity. At  $-75^{\circ}$ 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 :

$$C_{6}H_{5}-C \equiv C-CH_{2}OCH_{3} \xrightarrow{1 \text{ Bu-Li}} C_{6}H_{5}-C \equiv C \equiv C = C \xrightarrow{OCH_{3}} + BuH \xrightarrow{1 \text{ Bu-Li}} C_{6}H_{5}-C \equiv C \equiv C = C \xrightarrow{OCH_{3}} + BuH \xrightarrow{1 \text{ Bu-Li}} C_{6}H_{5}-C \equiv C \equiv C = C \xrightarrow{OCH_{3}} + BuH \xrightarrow{1 \text{ Bu-Li}} C_{6}H_{5}-C \equiv C \equiv C \xrightarrow{OCH_{3}} + BuH \xrightarrow{1 \text{ Bu-Li}} C_{6}H_{5}-C \equiv C = C \xrightarrow{OCH_{3}} + BuH \xrightarrow{1 \text{ Bu-Li}} C_{6}H_{5}-C \equiv C \xrightarrow{OCH_{3}} + BuH \xrightarrow{1 \text{ Bu-Li}} C_{6}H_{5}-C \equiv C \xrightarrow{OCH_{3}} + BuH \xrightarrow{1 \text{ Bu-Li}} C_{6}H_{5}-C \equiv C \xrightarrow{OCH_{3}} + BuH \xrightarrow{1 \text{ Bu-Li}} C_{6}H_{5}-C \equiv C \xrightarrow{OCH_{3}} + BuH \xrightarrow{1 \text{ Bu-Li}} C_{6}H_{5}-C \equiv C \xrightarrow{OCH_{3}} + BuH \xrightarrow{1 \text{ Bu-Li}} C_{6}H_{5}-C \equiv C \xrightarrow{OCH_{3}} + BuH \xrightarrow{1 \text{ Bu-Li}} C_{6}H_{5}-C = C \xrightarrow{OCH_{3}} + BuH \xrightarrow{1 \text{ Bu-Li}} C_{6}H_{5}-C = C \xrightarrow{OCH_{3}} + BuH \xrightarrow{1 \text{ Bu-Li}} C_{6}H_{5}-C \xrightarrow{OCH_{3}} + BuH \xrightarrow{1 \text{ Bu-Li}} + BuH \xrightarrow{1$$

The solution is maintained at  $-50^{\circ}$ 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 stoechiometric 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°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 :

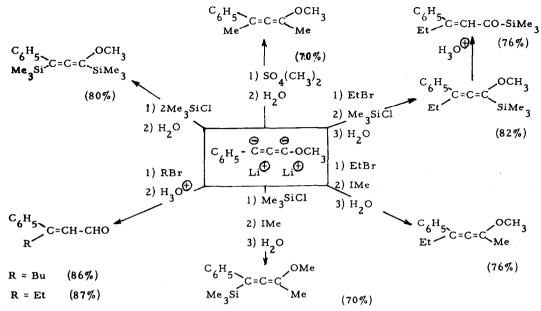
a) bialkylation reaction.

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)

while operating at  $-75^{\circ}$  C, by addition of 5 to 10% of HMPT (6). Table I summarizes these results :



Notes : 1) All compounds shown are isolated pure. Microanalysis are satisfactory. IR and NMR spectra are in full agreement with proposed structures.

2) Allenic products are obtained in very good yields. No amounts of by-products are detected by NMR. All these compounds present an enol-ether function and lead by acidic hydrolysis to a  $\alpha$  ethylenic carbonyl compound.

3) This dianion presents also a peculiar relationship between its selectivity and reactivity. In reality, if we alkylate with a very strong reagent like trimethylchlorosilane or a poor reagent like butyl bromide or ethyl bromide, the first alkylation takes place always on the  $\alpha$  carbon atom near the phenyl group.

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