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SYNTHESIS AND REACTIONS OF LITHIUM DERIVATIVES OF MONO AND DISILYLATED T-BUTOXYALLENES.

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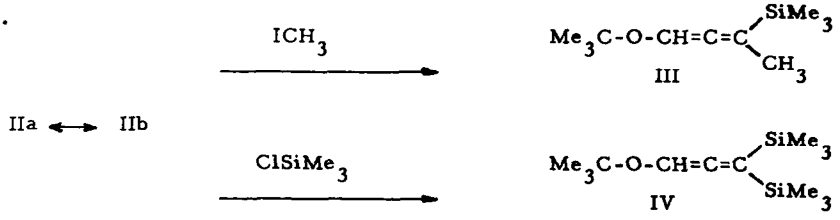
Recently, silylated allenes have been studied chiefly by Gilman et. al (1), West et. al (2) and Jaffé (3). These authors have shown that if it is rather easy to obtain a persilylated allene from different starting products (allene, propyne, perhalogenated polyenes or benzenes), it becomes very difficult to control the reaction in order to obtain selectively mono, di or tri silylated allenes and it is even more difficult to obtain functional allenes.

In this communication, we wish to describe briefly the preparation concerning the previously cited three classes of functional allenes and the use of these compounds to synthesize α ethylenic carbonyl compounds bearing silyl groups in the vinylic position.

Silylated propargylic ether I treated with one equivalent of nBu-Li at -40°C gives an allenic carbanion IIa in equilibrium with its acetylenic isomer IIb.

$$\underset{\text{I}}{Me_3C\text{-}O\text{-}CH_2\text{-}C{\equiv}CSiMe_3} \xrightarrow[\text{éther -40°C}]{\text{Bu Li}} \underset{\text{IIa}}{Me_3C\text{-}O\text{-}CH{=}C{=}\overset{\ominus}{C}SiMe_3} \longrightarrow \underset{\text{IIb}}{Me_3C\text{-}O\text{-}\overset{\ominus}{C}HC{\equiv}CSiMe_3}$$

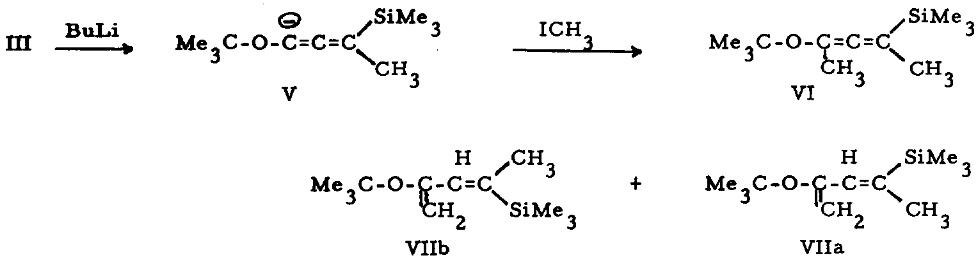
Condensation with carbonyl compounds leads to a mixture of products in which the major component is acetylenic. On the contrary, alkylation by methyl iodide or trimethyl chlorosilane gives almost exclusively the pure allenic derivatives III and IV with yields better than 60%.



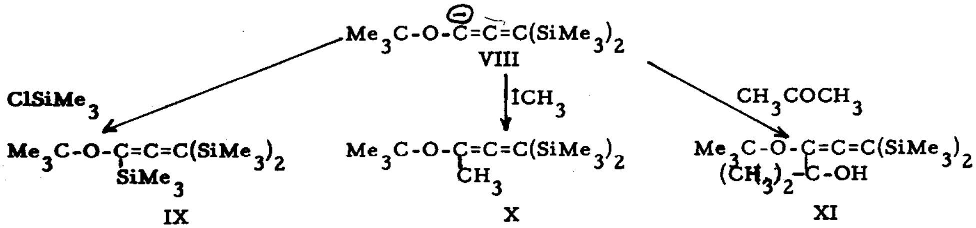
$$\text{IIa} \longleftrightarrow \text{IIb} \quad \xrightarrow{ICH_3} \quad Me_3C\text{-}O\text{-}CH{=}C{=}C\begin{matrix}\diagup SiMe_3\\ \diagdown CH_3\end{matrix} \quad \text{III}$$

$$\text{IIa} \longleftrightarrow \text{IIb} \quad \xrightarrow{ClSiMe_3} \quad Me_3C\text{-}O\text{-}CH{=}C{=}C\begin{matrix}\diagup SiMe_3\\ \diagdown SiMe_3\end{matrix} \quad \text{IV}$$

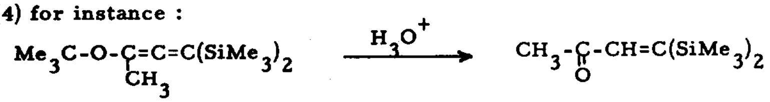
We have now a monosilylated product III or disilylated product IV, whom allenic stucture is blocked. By treatment with one equivalent of butyl lithium in ether, we obtain quite easily the allenic carbanions V and VIII whose structure is unequivocal. In the following table, we have summarized reactions done with these species. Yields are high (between 70 and 85%) and correspond to pure isolated products.



Dimethylated allenic product VI isomerizes completely to silylated alkoxydienes isomers VIIa and VIIb.



Acidic hydrolysis of these allenic ethers allowed us to obtain α ethylenic carbonyl compounds (4) for instance :



$$Me_3C\text{-}O\text{-}\underset{CH_3}{C}{=}C{=}C(SiMe_3)_2 \xrightarrow{H_3O^+} CH_3\text{-}\underset{\overset{\|}{O}}{C}\text{-}CH{=}C(SiMe_3)_2$$

All compounds shown were isolated pure. Microanalysis were satisfactory. IR and NMR spectra are in full agreement with proposed structures.

References.

(1) D. H. BALLARD, T. BRENNAN and H. GILMAN J. Organometal. Chem. 1970 22 583 and ref. quoted therein.

(2) R. WEST, A. CARNEY and I. C. MINEO J. Am. Chem. Soc. 1965 87 3788

(3) F. JAFFE J. Organometal. Chem. 1970 23 53

(4) R. MANTIONE Bull. Soc. Chim. Fr. 1969 4523