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POSITIONAL SELECTIVITY IN THE METALATION OF 1,8-CYCLOTETRADECADIYNE WITH n-BUTYLLITHIUM

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Though the reactions of acetylenes with various bases have been extensively studied, little is known about the corresponding reactions of macrocyclic diynes. Hubert and Dale[1] treated such diynes with potassium tert-butoxide in tert-butanol and found no effect at low temperatures but obtained aromatisation above 160°. With dimethylsulfoxide as solvent rather than tert-butanol an extensive triple-bond migration took place and a trace of allene was observed. Finally, the diyne isomers were transformed into tricyclic olefins.[2]

The present paper reports an unusual selectivity in the course of metalation of 1,8-cyclotetradecadiyne (**1**) and an exclusive formation of products containing monocyclic nonconjugated allene-yne and diallene functionalities. Monocyclic monoallenes and diallenes, with and without functional groups, were formed by other methods.[3-5] To the best of the author's knowledge, the formation of substituted monocyclic diallene, by the metalation reaction, is reported for the first time. Compound **1** was treated with n-butyllithium under various conditions (Table) and then subsequently quenched with trimethylchlorosilane, to obtain silylated products (Scheme).

The Table indicates that no metalation occurred upon utilizing butyllithium in hexane, whereas in THF a high yield of only the disilyl product (**2**) was formed after 24 hours. Product **2** is derived from a dilithio intermediate which undergoes metalation on just one propargylic group out of the four present in **1**. This result confirms a former observation[6] in which the second proton was abstracted from the same propargylic carbon on which the first step of metalation took place. The proposed stability[6] of a sesquiacetylenic structure (**A**) with three sp-hybridized carbons and six p-orbitials containing eight electrons,

A $[\mathrm{R{-}C}\overset{\cdots}{\underset{\cdots}{\text{—}}}\mathrm{C}\overset{\cdots}{\underset{\cdots}{\text{—}}}\mathrm{C{-}R'}]^{-2}$

Table

Metalation[a] of 1 and % of silylated products.

reagent	solvent	rcn. period (hours)	composition of the rcn. mixture(%)[d]		
			2	3	4
n-BuLi	hexane	216	no reaction		
n-BuLi	THF[b]	24	99	-	-
		48	50	25	25
n-BuLi+TMEDA[c] (1:1 molar ratio)	hexane	24	60.8	21.7	17.5

a. 6:1 molar ratio of butyllithium to 1 was applied, respectively. The metalation occurs quantitatively, at room temperature.

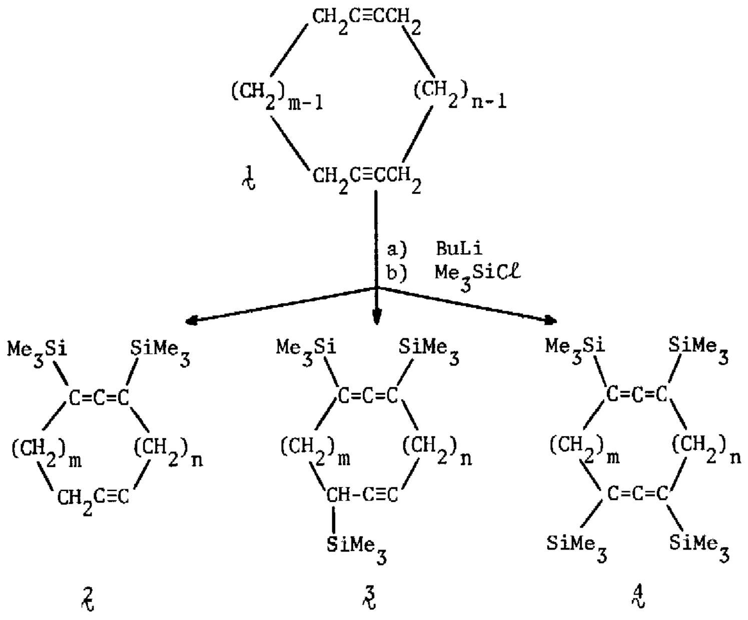
b. THF=tetrahydrofuran. In this solvent the reaction was carried out at 0°. In shorter time intervals, monometalation occurred.

c. TMEDA=N,N,N;N'-Tetramethylethylenediamine

d. The products were preparatively collected by glc, on two different columns and only one derivative of each was observed.

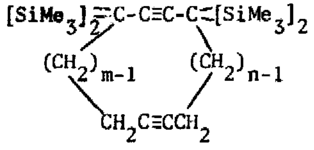
Scheme

(m=n=4)

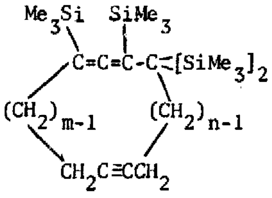


provides a rationale for this result.

Structure assignments of the silylated products are based on elemental analysis and spectroscopic data. Compound 2 has two silyl groups and no allenic hydrogens in its nmr spectrum. Furthermore, it has a strong absorption (1925cm^{-1}) in the infrared region, characteristic of an allene. It is therefore concluded that the dimetalation takes place at the same propargylic carbon atom. With regard to products 3 and 4, the general structure assigned to the skeleton in the Scheme is also supported by the spectral and analytical data. However, there is some uncertainty whether they are symmetric (m=n=4) or non-symmetric (m=5,n=3). Closer inspection of the spectra indicates that the distinction may be made. The nmr spectrum of 4 shows only one signal for all four trimethylsilyl groups which does not change upon expansion. Furthermore, all four methylene groups α to the allene are equivalent and appear as one triplet (at 1.87ppm). In its infrared spectrum there is a strong allenic absorption at 1900cm^{-1}. These data seem to support the diallenic structure of 4 in which m=n=4, though this evidence cannot be considered as conclusive. Other structural isomers of 4, such as 5 and 6 are excluded on the basis of the spectral data.



5



6

5 has no allenic group and 6 has an acetylenic functionality and two types of trimethylsilyl groups which are expected to differ in their chemical shifts (as observed for 3, see below). Thus it is unlikely that two propargylic groups, adjacent to one triple bond, will undergo tetrametalation, under these conditions, while the second triple bond remains undisturbed.

On the basis of the observation that the second step of metalation occurs at the same carbon which was previously metalated, and on the basis of the arguments presented above for the tetrasilyl derivative, it is assumed that if m=n=4 for 4, the same relation follows for 3. Product 3 is a monocyclic allene-yne and not a diallene, because no allenic hydrogens were detected in its nmr spectrum. Moreover, the infrared spectrum shows an allenic absorption ($1905cm^{1-}$) as well as an acetylenic one ($2160cm^{-1}$).

The polylithio compounds derived from **1** were also quenched with H_2O. The dilithio derivative yielded a monocyclic allene-yne whereas the tri- and tetralithio derivatives formed a monocyclic diallene. All products have an allenic absorption at $1960cm^{-1}$ in the infrared and the allenic hydrogens appear as multiplets with chemical shifts in the region 4.9-5.3ppm. By quenching the polylithio derivatives with D_2O similar products were obtained except that now deuteration took place, as was evidenced by the nmr spectra. These results strengthen the assignments made for the silylated products.

In conclusion, the metalation of **1** under the conditions described, is shown to be positionally selective. The reaction reveals a facile method of forming macrocyclic allenes or diallenes without concommitant rearrangement or trans-anular reaction of the allenic or acetylenic bonds. Studies on the generality of the reaction and the stereochemistry of the products are in progress.

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