

BEHAVIOUR OF 1-BUTOXY-9-TETRADECYNE IN SUPERBASIC MEDA/EDA MEDIA

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Abstract. The first example of the isomerization of a non-propargylic alkoxyalkyne, 1-butoxy-9-tetradecyne, in superbasic media MEDA/EDA (M = Li, Na) is presented. The extent of the competitive elimination reaction and the influence of the type of metal in superbase on the composition of product were determined.

Key words: alkoxyalkyne, triple bond, isomerization, superbase, MEDA.

Superbases are well-known reagents in the synthesis of acetylenic compounds and in different following transformations with them [1–3]. Despite many interesting and useful reactions of acetylenes with superbases the most amazing is the “contrathermodynamic” multipositional isomerization of the internal triple bond to the terminal position under the influence of alkali metal amides of ethylenediamine or 1,3-propylenediamine. First discovered by Brown & Yamashita in 1975 [4], the reaction was extensively studied and used for the synthesis of compounds with a terminal triple bond, particularly for long chain hydrocarbons and alcohols [5, 6]. According to our best knowledge no data are available about the isomerization of the triple bond in alkoxyalkynes. On the other hand, the elimination of alcohols from propargylic alkoxy compounds with sodium amide in liquid ammonia affording the isomeric mixture of the corresponding terminal enynes has been described [7]. According to the supposed random-type mechanism of the isomerization of alkynes all positions in the carbon chain can be activated and the elimination is possible [5].

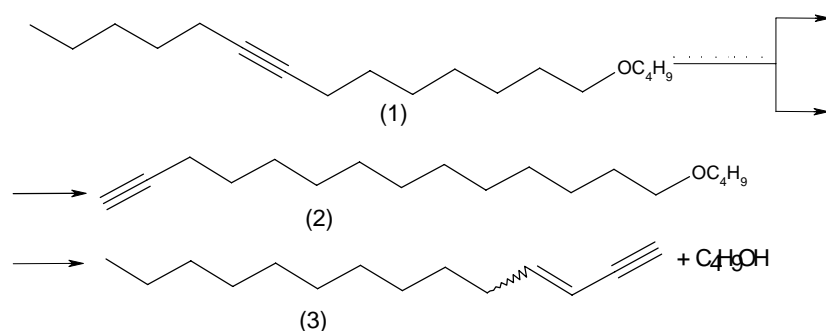
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The aim of our present work was to study the isomerization of non-propargylic alkoxyalkyne, to determine the extent of possible elimination, and to demonstrate the influence of the type of metal in MEDA/EDA superbase.

The model compound, 1-butoxy-9-tetradecyne (**1**), was effectively (reflux 8 h, 98% yield) synthesized from 9-tetradecyn-1-ol and 1-bromobutane using the solid-liquid phase transfer catalysis technique (NaOH/K₂CO₃/Bu₄NHSO₄/toluene) [8].

For the isomerization of (**1**) 7 equivalents of LiEDA or NaEDA in EDA as 1.4 M suspension and solution, respectively, were used. The reaction was relatively fast and the starting compound disappeared after 15 min reaction with NaEDA/EDA at room temperature and LiEDA/EDA at 50°C.

The proposed reaction scheme is as follows:



It was determined by GLC (fused silica capillary column with OV-101 liquid phase) that after the consumption of the starting material two groups of compounds appeared. One group corresponds to the isomeric alkoxyalkynes and the other to isomeric enynes. When NaEDA/EDA was used, after 15 min of isomerization several isomeric enynes and only 1-butoxy-13-tetradecyne (**2**) with 39% yield were detected. After stirring the reaction mixture for 1 h in the region of enynes only two peaks remained (1:1), which were separated by column chromatography on silica and identified by NMR and IR spectroscopy as Z and E isomers of 11-tetradecen-13-yne (**3**). LiEDA/EDA is a weaker base than NaEDA/EDA [6]. As a consequence, the isomerization of compound (**1**) according to the above scheme with LiEDA/EDA does not afford the pure final products (**2**) and (**3**). So, in the region of alkoxyalkynes in GLC, beside 1-butoxy-13-tetradecyne (42% yield) some small peaks (probably other positional isomers) were detected even after several hours. After 15 min of reaction ten peaks in the region of enynes were detected. Within 1 h the relative intensity of the peaks of Z and E isomers of 3-tetradecen-1-yne had substantially increased but the product was still contaminated with other compounds.

Isomerization of the triple bond consists of many equilibrium steps. One of them affords the corresponding propargylic alkoxide, which gives after elimination the corresponding enyne. The formed enyne terminates the

isomerization and is not in equilibrium with alkoxyalkynes. Therefore, all isomeric alkoxyalkynes will gradually change to enynes and longer reaction times have to be avoided to give the maximal yield of isomerization product with a terminal triple bond. From preparative point of view NaEDA/EDA should be preferred for the isomerization of alkoxyalkynes.

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1-BUTOKSÜ-9-TETRADETSÜÜNI KÄITUMINE MEDA/EDA SUPERALUSELISES KESKKONNAS

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Esmakordselt on demonstreeritud mittepropargüülse alkoksüalküüni – 1-butoksü-9-tetradetsüüni isomerisatsiooni MEDA/EDA (M = Li, Na) superaluselises keskkonnas ning määratud konkureeriva elimineerimisreaktsiooni ulatus ja produkti koostise sõltuvus kasutatud superalusest.