

BEHAVIOUR OF SOME ENYNOLS AND ONE DIYNOL IN SUPER BASIC SYSTEMS $\text{MNH}(\text{CH}_2)_2\text{NH}_2 / \text{H}_2\text{N}(\text{CH}_2)_2\text{NH}_2$

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Received 2 May 1996, accepted 3 June 1996

Abstract. (Z)-14-heptadecen-2-yn-1-ol, (E)-2-octadecen-13-yn-1-ol, and 2,13-octadecadiyn-1-ol were synthesized and their behaviour in super basic systems $\text{MNH}(\text{CH}_2)_2\text{NH}_2/\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}_2$ ($\text{M} = \text{Li}, \text{Na}, \text{K}$) was studied. Instead of the expected products—alcohols with a terminal triple bond—corresponding alkynes as products of the retro-Favorskii type defragmentation reaction was detected. Using the most effective superbase $\text{KNH}(\text{CH}_2)_2\text{NH}_2/\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}_2$ the $-\text{CH}_2\text{OH}$ fragment was removed and the corresponding terminal alkynes with a yield of 83–95% were prepared. (E)-2-octadecen-13-yn-1-ol gave under the same conditions a very complicated mixture of compounds.

Key words: isomerization of enynols, super base, retro-Favorskii reaction.

INTRODUCTION

The isomerization of the carbon–carbon triple bond along the carbon chain in alkynes and alkynols is well known. In 1975 Brown introduced the system $\text{KNH}(\text{CH}_2)_3\text{NH}_2/\text{H}_2\text{N}(\text{CH}_2)_3\text{NH}_2$ for the isomerization (acetylenic zipper) as a synthetic method for the preparation of 1-alkynes and ω -alkynols [1, 2]. This method was modified later by Abrams, who successfully used $\text{MNH}(\text{CH}_2)_n\text{NH}_2/\text{H}_2\text{N}(\text{CH}_2)_n\text{NH}_2$ ($\text{M} = \text{Li}, \text{Na}, \text{K}; n = 2, 3$) [3, 4]. The method gives terminal alkynes or alkynols from good to excellent yield. By the isomerization of acetylenic carboxylic acids 3,5-dienic

acids were obtained [5]. Isomerization of conjugated alkadiynes and hydroxydiynes gives the corresponding terminal diyne derivatives with good and poor yield respectively [6, 7]. Abrams demonstrated a selective isomerization of 2,13-tetradecadiyn-1-ol to the 3,13-tetradecadiyn in $\text{LiNH}(\text{CH}_2)_2\text{NH}_2/\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}_2$ with 50% yield [5]. The moving of the triple bond from the internal to the terminal position is believed to be a concerted multiple alkyn-allene isomerization process [1, 2, 8].

No data are available on the isomerization of any type of enynols and nonconjugated diynols with a nonterminal triple bond. It was very attractive to investigate the isomerization of these relatively easily available compounds. The expected products – conjugated enynols and diynols – could be very useful building blocks for the synthesis of wide spectra of biologically active compounds or materials for nonlinear optics.

EXPERIMENTAL

Infrared spectra of compounds in the form of neat liquids were recorded on a Specord M82 (Carl Zeiss, Jena) spectrometer. The ^1H and ^{13}C NMR spectra were measured with a Bruker AC200P spectrometer at 200 MHz and 50 MHz, respectively. Chemical shifts are reported relative to TMS in CDCl_3 . GC-MS analyses were done on a Saturn 3 (Varian) instrument with 50–70 eV ionization energy using a DB-5 fused silica capillary column 30 m \times 0.32 mm. GLC analyses were performed on a Fractovap 4160 series (Carlo Erba Strumentazione) capillary gas chromatograph and Chrom 5 (Laboratori Przistroje, Praha) equipped with FID, using fused silica capillary columns OV-101 25 m \times 0.2 mm, Nordibond NB 20M 25 m \times 0.32 mm, and a glass column 2.5 m \times 3 mm packed with 5% Carbowax 20M on a Chromosorb W AW-DMCS 80–100 mesh.

All experiments were carried out under an atmosphere of dry, CO_2 and O_2 free argon. The starting compounds were synthesized as described in literature.

(Z)-14-heptadecen-2-yn-1-ol (1) was synthesized from (Z)-11-tetradecen-1-ol by bromination and alkylation of the dilithium derivative of 2-propyn-1-ol [9]. Total yield 21%.

^{13}C NMR δ = 14.3 (C-17); 18.7 (C-4); 20.5 (C-16); 27.1 (C-13); 28.6–29.7 (C-5 to C-12); 51.3 (C-1); 78.3 (C-3); 86.6 (C-2); 129.3 (C-14); 131.5 (C-15).

IR (cm^{-1}): 3340 (—OH); 3003 (=CH—); 2287, 2225 ($\text{C}\equiv\text{C}$); 1653 (Z $\text{C}=\text{C}$); 1015 (—C—O); 721 (— CH_2 —*rock* + Z $\text{C}=\text{C}$).

2.13-Octadecadiyn-1-ol (2) was synthesized from 1-bromo-9-pentadecyn by alkylation of the dilithium derivative of 2-propyn-1-ol [9]. Total yield 27%.

^{13}C NMR δ = 13.6 (C-18); 18.6 (C-15, C-12, and C-4); 22.0 (C-17); 28.7–29.7 (C-5 to C-11); 31.4 (C-16); 51.4 (C-1); 78.6 (C-3); 80.2 (C-13 and C-14); 86.6 (C-2).

IR (cm^{-1}): 3370 (—OH); 2293, 2230 ($\text{C}\equiv\text{C}$); 1015 (—C—O); 724 (— CH_2 -*rock*).

(E)-2-octadecen-13-yn-1-ol (3) was synthesized by the reduction of (2) with LiAlH_4 in THF [10]. Yield 63%.

^{13}C NMR δ = 13.6 (C-18); 18.4–18.7 (C-12 and C-15); 21.9 (C-17); 28.8–29.4 (C-5 to C-11); 31.3 (C-4); 32.2 (C-16); 63.8 (C-1); 80.2 (C-13 and C-14); 128.8 (C-2); 133.5 (C-3).

IR (cm^{-1}): 3337 (—OH); 3010 ($=\text{CH}$ —); 1669, 969 (E $\text{C}=\text{C}$); 1006 (—C—O); 723 (— CH_2 -*rock*).

Typical isomerization procedure

All reactions were carried out in dry ethylenediamine distilled several times from sodium under the atmosphere of pure argon on magnetic stirrer, using 1.2 M solutions of super base in 7 equivalents per alcohol. Lithium ethylenediamide (LiEDA) was prepared from lithium grains in EDA by heating at 50°C for 0.5 h. NaEDA was formed by the reaction of NaNH_2 with EDA at room temperature for 1.5 h. KEDA was prepared by adding a stoichiometric amount of K-*t*-BuO to LiEDA. All experiments were done in the mmolar scale.

For the work-up the reaction mixture was poured to ice, water was added, extracted with diethyl ether (3 times), ether extracts were acidified, washed to neutral with brine, dried (MgSO_4), evaporated to dryness, and purified by column chromatography on silica using hexane-diethyl ether (2:1) as eluent.

The experiment of compound (1) with NaEDA for 30 h gave (Z)-13-hexadecen-1-yn with 83% yield.

^{13}C NMR δ = 14.4 (C-16); 18.4 (C-3); 20.5 (C-15); 27.1 (C-12); 29.5 (C-4 to C-11); 68.0 (C-1); 84.8 (C-2); 129.3 (C-13); 131.5 (C-14).

IR (cm^{-1}): 3313 ($\equiv\text{CH}$); 3006 ($=\text{CH}$ —); 2123 ($\equiv\text{C}$ —); 1654 ($=\text{CH}_{\text{cis}}$ —); 724 (— CH_2 -*rock*); 631 ($\equiv\text{CH}$).

MS:

M/Z	Intensity, %	Fragment
39	45	$\text{CH}_2-\text{C}\equiv\text{CH}$
41	100	$^+\text{CH}-\text{CH}_2\text{CH}_2$
55	65	$^+\text{CH}-\text{CH}_2\text{CH}_2\text{CH}_3$
67	56	$\text{HC}\equiv\text{C}-\text{CH}_2\text{CH}_2\text{CH}_2$

Under the same conditions compound (2) gave 1,12-heptadecadiyn with 85–95% yield.

^{13}C NMR δ = 13.5 (C-17); 18.4 (C-11); 18.7 (C-3); 22.6 (C-14); 24.7 (C-16); 28.2–29.7 (C-4 to C-10); 31.3 (C-15); 68.0 (C-1); 80.1 (C-12 and C-13); 84.7 (C-2).

IR (cm^{-1}): 3313 ($\equiv\text{CH}$); 2123 ($-\text{C}\equiv\text{CH}$); 1333 ($\equiv\text{CH}$); 725 ($-\text{CH}_2\text{-rock}$); 630 ($-\text{C}\equiv\text{CH}$).

MS:

M/Z	Intensity, %	Fragment
39	63	$\text{CH}_2-\text{C}\equiv\text{CH}$
41	79	$^+\text{CH}-\text{CH}_2\text{CH}_2$
67	99	$\text{CH}\equiv\text{C}-\text{CH}_2\text{CH}_2\text{CH}_2$
81	100	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{C}\equiv\text{C}$
95	66	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{C}\equiv\text{CCH}_2$

DISCUSSION

It is well known that the reactivity of MEDA is decreasing from K to Li [4]. However, LiEDA is quite active for the isomerization of alkynols. Isomerization of (1) with LiEDA was relatively slow probably due to the presence of a double bond in the molecule. After 5.5 h at 50°C the reaction stopped and ca 50% of the starting compound was isomerized to impure (Z)-14-heptadecen-3-yn-1-ol contaminated with other isomeric (Z)-14-heptadecenyn-1-ols. As the ^{13}C NMR spectral data indicated, no enynols with conjugated double bond were detected and only two signals of isolated double bond at 129.3 and 131.5 ppm were present. Using NaEDA the total amount of isomerized (Z)-14-heptadecenyn-1-ols reached 10–20%. From the very beginning of the reaction a new unexpected product – (Z)-12-hexadecen-1-yn (4) – appeared. After 30 h compound (4) with the yield of 83% was obtained. This defragmentation of $-\text{CH}_2\text{OH}$ seems to be a retro-Favorskii type reaction, which is not correctly described for primary propargyl alcohols. The isomerization of the triple bond seems to be faster than the formation of a compound with a terminal triple bond. Therefore, isomerization with KEDA was carried out to avoid the formation of side product (4). After 3 h (1) was completely isomerized to a mixture of isomeric (Z)-14-heptadecen-yn-1-ols separated by GLC. According to the data of ^{13}C NMR spectroscopy of this mixture the triple bond was not present and some new signals appeared in the double bond region (119; 124; 130; 132). Later the defragmentation was started even at room temperature.

The isomerization process of compound (2) with NaEDA was similar to the previous compound. After 3 h 14% of isomerized octadecadiynols

and 36% of 1,12-heptadiyn (5) were formed, but after 21 h (5) with an excellent yield of 85–95% was obtained. In the presence of KEDA at 70°C after 0.5 h only a mixture of isomeric alcohols was detected. Longer reaction gave only compound (5).

The treatment of (E)-2-octadecen-13-yn-1-ol with LiEDA, NaEDA, and KEDA yielded unexpectedly a very complicated mixture consisting of 15 hydrocarbons. The mechanism of the formation of these compounds remains yet unsolved.

For the verification of our idea of a retro-Favorskii reaction 2-decyn-1-ol was treated with one equivalent of NaEDA at 50°C for 30 h. Under these conditions the isomerization of the triple bond is practically excluded and only 1-nonyne was formed.

We can conclude that by the isomerization of 2-alkyn-1-ols in MEDA/EDA super bases a parallel retro-Favorskii reaction is taking place and the composition of the product depends on the relative rates of these reactions. The reaction with NaEDA is already of preparative value. However, KEDA gave selectively the isomerization of the triple bond, the products obtained contained a mixture of several isomeric alkenynols or alkadiynols.

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MÕNEDE ENÜNOOLIDE JA ÜHE DIÜNOOLI KÄITUMINE SUPERALUSELISTES SÜSTEEMIDES $MNH(CH_2)_2NH_2/H_2N(CH_2)_2NH_2$

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On sünteesitud (Z)-14-heptadetseen-2-üün-1-ool, (E)-2-oktadetseen-13-üün-1-ool ja 2,13-oktadekadiüün-1-ool ning uuritud nende käitumist erinevates superalustes $MNH(CH_2)_2NH_2/H_2N(CH_2)_2NH_2$ ($M = Li, Na, K$). On avastatud 2-alküün-1-oolide retro-Favorski tüüpi defragmenteerumine. On uuritud erinevate superaluste ja reaktsioonijaaja mõju produkti koostisele.