


Communication

Formation of an Isomeric Mixture of Dienynes Instead of a Diallene

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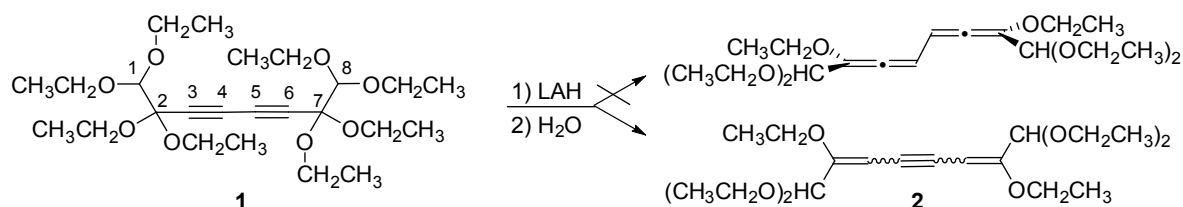
Abstract: Attempts to convert 1,1,2,2,7,7,8,8-octaethoxyocta-3,5-diyne to a symmetric allene by reduction with lithium aluminum hydride failed. Instead reduction accompanied by isomerization occurred and afforded 1,1,2,7,8,8-hexaethoxyocta-2,6-dien-4-yne as a mixture of three isomers in 63% total isolated yield.

Keywords: conjugated diyne; LAH reduction; diacetal; pent-1,2,3,4-tetraene intermediate

1. Introduction

Since the synthesis of 3,3,4,4-tetraethoxybutyne (TEB) was reported some 15 years ago [1–3], many of its chemical properties have been uncovered and used to prepare a range of chemical compounds with rich structural diversity [4–15]. Among the most densely functionalized molecules made is 1,1,2,2,7,7,8,8-octaethoxyocta-3,5-diyne (**1**), which has one ketal moiety in propargylic position to each of the triple bonds [16]. The compound therefore belongs to a group of compounds that can undergo S_N2' reactions by nucleophilic attack of the triple bond, which is accompanied by C–C bond migration that leads to the release of a leaving group from the propargylic carbon and formation of an allene moiety. The most common leaving groups are alkanoates [17–19], bromide [20,21], and chloride [22,23], but examples involving alkoxides have also been published [24–27]. As for the nucleophiles, both carbanions and hydride have been applied [17–27].

On this basis, we envisaged that **1** might be used as a substrate to make a functionalized diallene by two S_N2' reactions, one at each of the propargylic moieties, using hydride as a nucleophile (Scheme 1). Lithium aluminum hydride (LAH) was deemed to be a suitable reagent [23] but, as reported here, when the reaction was performed, the expected product was not obtained; instead, an isomeric mixture of 1,1,2,7,8,8-hexaethoxyocta-2,6-dien-4-yne (**2**) was the only product formed.



Scheme 1. Expected and obtained products from lithium aluminum hydride (LAH) reduction of **1**.

2. Results and Discussion

The reaction was carried out under anhydrous conditions in refluxing diethyl ether using six equivalents of hydride with respect to diallene formation. The reaction was monitored by TLC and when quenched and worked up after 1 h, three products were detected and subsequently isolated by

flash chromatography. All the products had the same molecular weight as the expected product, but their IR spectra did not show any absorption in the allene region ($1955\text{--}1925\text{ cm}^{-1}$) [28], which rules out that diallene formation had occurred. However, absorptions in the $1680\text{--}1620\text{ cm}^{-1}$ and $840\text{--}790\text{ cm}^{-1}$ regions indicate the presence of trisubstituted alkenes [28], and this requires the presence of a C–C triple bond to be compatible with the determined molecular weight. Considering the symmetry of the starting material, the triple bond would be expected to be symmetrically substituted, and this would explain the absence of an absorption in the $2270\text{--}2120\text{ cm}^{-1}$ region [28]. In order to determine whether this was a reasonable assumption, the Raman spectrum of **2** was recorded. To our satisfaction, a strong absorption appeared at 2186 cm^{-1} . This observation made the structure elucidation fairly straightforward when ^1H - and ^{13}C -NMR data were considered, and the three compounds, isolated in 26%, 34% and 3% yield, were proved to be the (Z,Z), (E,Z) and (E,E) isomers of 1,1,2,7,8,8-hexaethoxyocta-2,6-dien-4-yne, **2a**, **2b** and **2c**, respectively.

The stereoisomers could be differentiated by a detailed study of the 3.4–5.5 ppm region of their proton NMR spectra, shown in Figure 1. The (Z,Z) and (E,E) isomers both exhibit C₂ symmetry, and the methine protons at C-1 and C-8 consequently have the same chemical shift, as do the olefinic protons at C-3 and C-6, and the methylene groups in the ethoxy groups attached to C-2 and C-7. These isomers will therefore show the same number of signals in the 3.4–5.5 ppm region. The asymmetry of the corresponding (E,Z) isomer results in twice the number of signals in this region, giving rise to the middle spectrum in Figure 1, which interestingly is almost identical to that obtained when the top and the bottom spectra are combined.

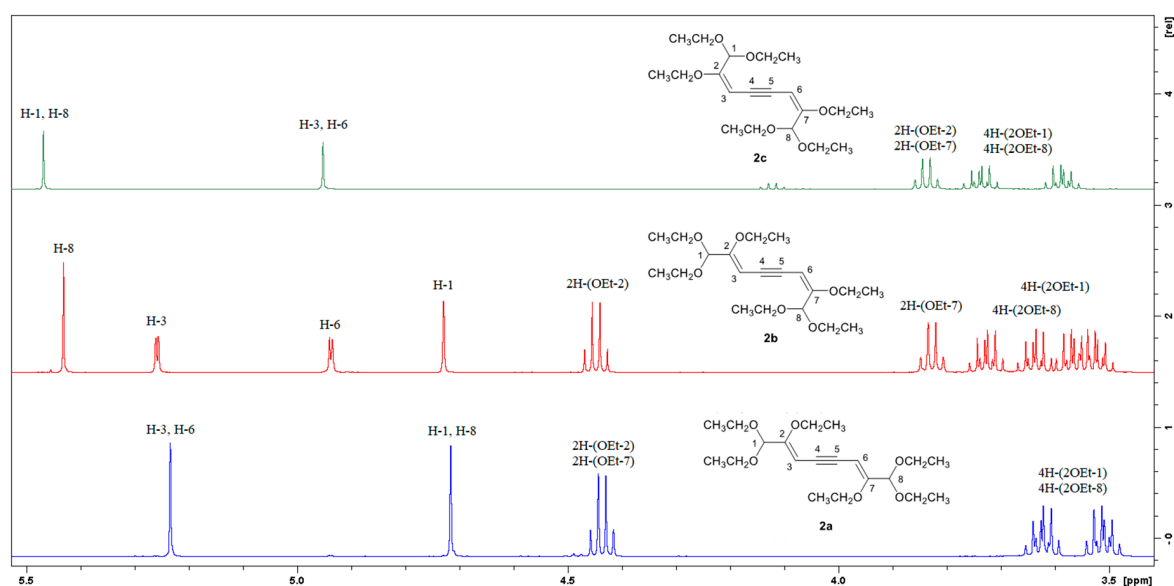


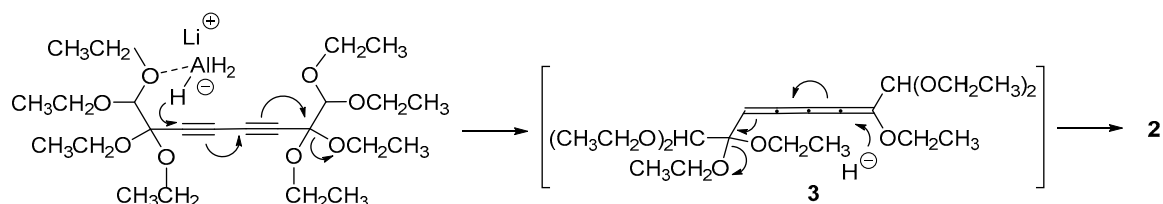
Figure 1. The 5.5–3.4 ppm region of the ^1H -NMR spectra of the three isomers of **2**. The signals in the 4.6–3.4 ppm region are due to the methylene moieties in the ethoxy groups attached to C-1, C-2, C-7, and C-8. To denote the two hydrogen atoms in the methylene group in EtO attached to C-*n*, the following notation is used: 2H-(OEt-*n*).

The assignments of the proton spectra of **2a**, **2b** and **2c** shown in Figure 1 were arrived at by using information harvested from the DEPT-90, DEPT-135, HSQC, and HMBC spectra of each of the isomers. The DEPT and HSQC spectra confirmed the presence of the methyl, methylene, and methine protons, the olefinic CH groups, and the quaternary carbon atoms, whereas the HMBC spectrum showed the correlation between hydrogen and carbon atoms two and three bonds apart. The HMBC spectra can therefore be used to assign the H-1, H-8 and H-3, H-6 singlets, which is clearly illustrated by the spectrum for **2c** (Figure S13). In this spectrum, the proton singlet at 5.47 ppm correlates through three bonds with the methylene carbon atoms at 63.1 ppm due to the ethoxy groups at C-1 and C-8 and

through two bonds with the quaternary carbon atoms at 161.9 ppm (C-2 and C-7); thus, this proton singlet is due to H-1 and H-8. This assignment is further supported by correlations between the proton singlet at 4.95 ppm and the olefinic quaternary carbons at 161.9 ppm (C-2 and C-7) and the acetal carbon atoms at 98.4 ppm (C-1 and C-8).

In order to differentiate between the (*Z,Z*) and (*E,E*) isomers, the chemical shifts of the methine hydrogen at C-1 (and C-8) and the methylene protons in the ethoxy group attached to C-2 (and C-7) in the two isomers were compared. Due to the anisotropy of the triple bond attached to C-3 (and C-6), protons *cis* to the acetylenic moiety will be deshielded, whereas those in *trans* position will be shielded [29]. Thus, since the methylene quartet in the bottom spectrum appears at a lower field than in the top spectrum, 4.44 ppm compared to 3.84 ppm, and the methine singlet in the bottom spectrum appears at a higher field than in the top spectrum, 4.72 ppm compared to 5.47 ppm, the bottom spectrum belongs to (*Z,Z*)-**2** (**2a**) and the top spectrum to (*E,E*)-**2** (**2c**).

The complete absence in the reaction mixture of the expected diallene and any of the by-products this cumulene conceivably could have given under the reaction and work-up conditions [30–33] indicates that **1** is not attacked initially at C-4 (and C-5). A likely explanation for this is that the 1,1,2,2-tetraethoxyethyl groups attached to the ends of the buta-1,3-diyne moiety render its termini relatively electropositive and make initial attack of C-3 (and C-6) more favorable. It is also conceivable that coordination of one or several oxygen atoms to species derived from LAH at some stage will facilitate the same sort of attack (see Scheme 2). This leads to formation of a pent-1,2,3,4-tetraene derivative (**3**), which is unstable in the presence of a hydride source and reacts quickly to give dienyne 1,1,2,7,8,8-hexaethoxyocta-2,6-dien-4-yne (**2**) (Scheme 2). Thus, the two hydrogens replacing the two ethoxy groups in the conversion of **1** to **2** are attached by hydride attack in a S_N2' fashion, not by reaction with water during the quenching of the reaction. In accordance with this, quenching using D_2O did not lead to deuterium incorporation in **2**. Traces of any intermediate were not detected, neither spectroscopically nor by TLC.



Scheme 2. Possible mechanism for formation of dienyne **2** from diyne **1** by two subsequent S_N2' reactions with hydride as a nucleophile.

3. Materials and Methods

3.1. General

The chemicals were obtained from commercial suppliers and used without further purification. Thin-layer chromatography (TLC) was performed using pre-coated aluminum TLC plates (Alugram, 0.20 mm Silica Gel 60 F₂₅₄) and eluting with a 95:5 mixture of hexanes and ethyl acetate. The R_f values were determined after the liquid front had migrated 4–5 cm. Visualization of the chromatograms was done with phosphomolybdic acid ($(NH_4)_4MoO_4 \cdot 4H_2O$) in ethanol followed by heating. Flash-column chromatography (FC) was performed manually using Silica Gel from Fluka Analytical (230–400 mesh) and eluting with a 80:20 mixture of hexanes and ethyl acetate. NMR spectra were recorded on a Bruker Biospin AV500 instrument (500 MHz for 1H , 125 MHz for ^{13}C) in $CDCl_3$ as solvent, using the solvent peaks as references in both 1H - and ^{13}C -NMR spectra (7.26 and 77.16 ppm, respectively). The chemical shifts are reported in ppm, the coupling constants (J) in Hz, and the multiplicity is given as s (singlet), d (doublet), t (triplet), and m (multiplet). Infrared (IR) spectra were recorded on a Nicolet Protege 460 FT-IR spectrophotometer with an attenuated total reflectance (ATR) unit attached. Samples were analyzed neat on a ZnSe crystal, and absorption peaks are reported in wavenumbers (cm^{-1}) and

characterized as strong (s), medium (m), weak (w) and broad (br). Raman spectra were recorded on a Kaiser RamanRxn1TM instrument operated under standard conditions. High-resolution mass spectra (HRMS) were obtained on a Jeol AccuTOFTM mass spectrometer operated in the ESI mode under standard conditions.

3.2. Reduction of 1,1,2,2,7,7,8,8-Octaethoxyocta-3,5-diyne (**1**)

A two-necked, round-bottom flask, equipped with a magnetic stirring bar, a condenser with a CaCl₂ tube, and a septum, was charged with dry diethyl ether (6 mL) and LAH (0.099 g, 2.6 mmol). The suspension was cooled (ice/water) and a solution of **1** (0.399 g, 0.87 mmol) in dry diethyl ether (3.0 mL) was added dropwise with a syringe. The bath was removed, and the resulting mixture was stirred under reflux for 1 h. The mixture was then added to some ice and when the ice had melted, a saturated solution of Rochelle salt was added. The hydrolysate was extracted with diethyl ether (4 × 10 mL); the combined organic phases were dried (Na₂SO₄), filtered, and concentrated under vacuum on a rotary evaporator. The residue contained three products (TLC), which were isolated by flash chromatography and proved to be isomers of 1,1,2,7,8,8-hexaethoxyocta-2,6-dien-4-yne (**2**) based on the following spectroscopic and spectrometric data.

(*Z,Z*)-1,1,2,7,8,8-Hexaethoxyocta-2,6-dien-4-yne (**2a**): Yellowish liquid (0.090 g, 26%); *R*_f 0.48; FT-IR (film): ν_{\max} 2976 (s), 2930 (m), 2883 (m), 2171 (w), 1649 (m), 1621 (m), 1180 (s), 1110 (s), 1049 (s), 913 (s), 841 (m), 793 (m) cm⁻¹; ¹H-NMR (CDCl₃, 500 MHz): δ 5.23 (s, 2H, 2 CH(OEt)₂), 4.72 (s, 2H, 2 -CH=), 4.44 (q, 4H, *J* = 7.0 Hz, 2 OCH₂CH₃), 3.65–3.48 (m, 8H, 4 OCH₂CH₃), 1.30 (t, 6H, *J* = 7.0 Hz, 2 OCH₂CH₃), 1.21 (t, 12H, *J* = 7.0 Hz, 4 OCH₂CH₃) ppm; ¹³C NMR (CDCl₃, 125 MHz): δ 158.6 (2C), 100.1 (2C), 88.4 (2C), 85.7 (2C), 66.6 (2C), 62.0 (4C), 15.6 (2C), 15.3 (4C) ppm; HRMS Calcd for C₂₀H₃₄O₆Na⁺ [M + Na]⁺ *m/z* 393.22531, found *m/z* 393.22555.

(*E,Z*)-1,1,2,7,8,8-Hexaethoxyocta-2,6-dien-4-yne (**2b**): Yellowish liquid (0.110 g, 34%); *R*_f 0.36; FT-IR (film): ν_{\max} 2976 (s), 2930 (m), 2882 (m), 2187 (w), 1641 (m), 1612 (m), 1252 (s), 1110 (s), 1049 (s), 839 (m), 793 (m) cm⁻¹; ¹H-NMR (CDCl₃, 500 MHz): δ 5.43 (s, 1H, CH(OEt)₂), 5.26 (d, 1H, *J* = 2.6 Hz, -CH=), 4.94 (d, 1H, *J* = 2.6 Hz, -CH=), 4.72 (s, 1H, CH(OEt)₂), 4.45 (q, 2H, *J* = 7.0 Hz, OCH₂CH₃), 3.83 (q, 2H, *J* = 7.0 Hz, OCH₂CH₃), 3.76–3.49 (m, 8H, 4 OCH₂CH₃), 1.36 (t, 3H, *J* = 7.0 Hz, OCH₂CH₃), 1.31 (t, 3H, *J* = 7.0 Hz, OCH₂CH₃), 1.24 (t, 6H, *J* = 7.0 Hz, 2 OCH₂CH₃), 1.22 (t, 6H, *J* = 7.0 Hz, 2 OCH₂CH₃) ppm; ¹³C NMR (CDCl₃, 125 MHz): δ 162.2 (1C), 158.4 (1C), 100.1 (1C), 98.4 (1C), 88.1 (1C), 87.7 (1C), 85.9 (1C), 84.5 (1C), 66.5 (1C), 64.1 (1C), 63.2 (2C), 62.1 (2C), 15.6 (1C), 15.32 (2C), 15.27 (2C), 14.3 (1C) ppm; HRMS Calcd for C₂₀H₃₄O₆Na⁺ [M + Na]⁺ *m/z* 393.22531, found *m/z* 393.22566.

(*E,E*)-1,1,2,7,8,8-Hexaethoxyocta-2,6-dien-4-yne (**2c**): Yellowish liquid (0.009 g, 3%); *R*_f = 0.20; FT-IR (film): ν_{\max} 2976 (s), 2930 (m), 2881 (m), 2172 (w), 1626 (s), 1254 (s), 1198 (s), 1110 (s), 1048 (s), 956 (s), 794 (s) cm⁻¹; ¹H-NMR (CDCl₃, 500 MHz): δ 5.47 (s, 2H, 2 CH(OEt)₂), 4.95 (s, 2H, 2 -CH=), 3.84 (q, 4H, *J* = 7.0 Hz, 2 OCH₂CH₃), 3.77–3.55 (m, 8H, 4 OCH₂CH₃), 1.37 (t, 6H, *J* = 7.0 Hz, 2 OCH₂CH₃), 1.25 (t, 12H, *J* = 7.1 Hz, 4 OCH₂CH₃) ppm; ¹³C NMR (CDCl₃, 125 MHz): δ 161.9 (2C), 98.4 (2C), 87.3 (2C), 84.4 (2C), 64.1 (2C), 63.1 (4C), 15.3 (4C), 14.4 (2C) ppm. HRMS Calcd for C₂₀H₃₄O₆Na⁺ [M + Na]⁺ *m/z* 393.22531, found *m/z* 393.22567.

Supplementary Materials: The following are available online, Figures S1–S9: IR, ¹H-NMR, and ¹³C-NMR spectra of compounds **2a**, **2b**, and **2c**; Figures S10–S13: DEPT-90, DEPT-135, HSQC, and HMBC spectra of **2c**; Figure S14: Raman spectrum of a mixture of compounds **2a**, **2b**, and **2c**.

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