



Short Note

8,13-Dimethylicosa-9,11-diyne-8,13-diol

Sarvinoz I. Tirkasheva 1,+, Odiljon E. Ziyadullaev 1,+, Vasiliy M. Muzalevskiy 2 and Askar B. Parmanov 3,*

- ¹ Department of Chemistry, Chirchik State Pedagogical University, A.Temur, 104, Chirchik 111700, Uzbekistan
- ² Department of Organic Chemistry, Moscow State University, Leninskiye Gory, 1, Moscow 119991, Russia
- ³ Department of General and Oil-Gas Chemistry, National University of Uzbekistan, University Street, 4,
 - Almazar District, Tashkent 100174, Uzbekistan
- Correspondence: asqar.parmanov@mail.ru; Tel.: +998-97-422-72-98
- + These authors contributed equally to this work.

Supporting information

- I. General Experimental Methods
- II. Spectral data of 3-Methyldec-1-yn-3-ol and 8,13-Dimethylicosa-9,11-diyne-8,13-diol
- III. Characterization Spectrum.

I. General Experimental Methods

Materials

The raw materials such as copper (I) chloride, copper (I) iodide, copper (I) bromide, TMEDA (*N*,*N*,*N*'*N*'-tetramethylethylenediamine), cyclohexanone, tetrachloromethane, tetrahydrofuran, acetonitrile, ethylene glycol, ethanol, methanol were purchased from Qingdao Sigma Chemical Co., Ltd. 3-methyldec-1-yn-3-ol [19] was synthesized according to the literature procedures and its structure was proved by the ¹H and ¹³C_NMR spectra. All reagents were used at reagent grade or used after distillation.

Preparation of 3-methyldec-1-yn-3-ol (1a)

In a 12 mL vial (or a one –necked 50 mL round bottom flask) 1 mmol (142 mg) of nonanone-2 (methylheptylketone), 2.7 mmol (173 mg) of calcium carbide and 3 mL of DMSO (dimethylsulfoxide) as a solvent were added. Then 0.174 g (0.5 mmol) TBAF·3H₂O (tetrabutylammonium fluoride trihydrate) (75%) as a catalyst and 3.0 mmol H₂O (0.054 g) were added and rotated in a magnetic stirrer at room temperature for 48 hours. Then 2 mL of H₂O was added to neutralize the unreacted calcium carbide and stirred for 15 minutes. The reaction mixture was extracted with dichloromethane and water. The product was separated into fractions using silica gel 60 column chromatography with different system eluents (CH₂Cl₂, CH₂Cl₂:MeOH 100:1, 30:1) and the product was purified by TLC. The reaction scheme is given below (Scheme S1).



Scheme S1. Synthesis of 3-methyldec-1-yn-3-ol.

Synthesis of 8,13-dimethylicosa-9,11-diyne-8,13-diol

A one –necked 50 mL round bottom flask (or 12 mL vial) was charged with 3methyldec-1-yn-3-ol (1.0 mmol, 0.168g), TMEDA (2 mmol, 0.255g), CuCl (1.0 mmol) in MeOH (2 mL) in atmospheric air condition. The reaction mixture was kept at 20-30 $^{\circ}$ C under stirring for 30 minutes using ultrasonic irradiation bath. CCl₄ 0.2 mL was added slowly and mixed for 12 hours on the magnetic stirrer. Volatiles were evaporated in vacuo, and the residue was purified by column chromatography using appropriate mixtures of hexane and CH₂Cl₂ (3:1 followed by 1:1 and 0:1) as eluents. The reaction scheme is given in Scheme 1.

Determination of favorable conditions for this dimerization process

The dimerization process was studied at of 20-30 °C with CuCl, CuJ and CuBr (1.0 mmol) catalysts in TMEDA (N,N,N'N'-tetramethylethylenediamine) (2.0 mmol), CCl₄ in various solvents - MeCN, THF, CH₂OHCH₂OH, PrOH, ethanol and methanol (Table 1).

II. Spectral data of 3-Methyldec-1-yn-3-ol and 8,13-Dimethylicosa-9,11-diyne-8,13-diol



3-Methyldec-1-yn-3-ol¹a: – yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ 2.41 (s. 1H, C=CH), 2.11 (s. 1H, OH), 1.69-1.59 (m, 2H, CH₂), 1.52-1.42 (m, 5H, CH₂, CH₃), 1.31-1.25 (m, 8H, 4CH₂), 0.88 (t, 3H, CH₃, *J*=7.2 Hz). ¹³C NMR (101 MHz, CDCl₃) δ 87.8, 71.1, 68.1, 43.5, 31.8, 29.64, 29.61, 29.2, 24.5, 22.6, 14.1.



8,13-Dimethylicosa-9,11-diyne-8,13-diol^{2a}: – slightly brown oil, yield 0.274 g (82%). ¹H NMR (400.1 MHz, CDCl₃): 2.02 (s, 2H, 2OH), 1.71-1.59 (m, 4H, 2CH₂), 1.52-1.40 (m, 10H, 2CH₂, 2CH₃), 1.34-1.21 (m, 16H, 8CH₂), 0.87 (t, 6H, 2CH₃, *J*=6.9 Hz); ¹³C NMR (100.6 MHz, CDCl₃): δ 83.2, 68.7, 67.4, 43.5, 31.8, 29.6, 29.5, 29.2, 24.6, 22.6, 14.1. IR: 3367 sm⁻¹ (–OH), 2954-2855 sm⁻¹ (–CH₂), 2216 sm⁻¹ and 2046 sm⁻¹ (–C=C–), 1458-1370 sm⁻¹ (–CH₂), 1307-1253 sm⁻¹ (–CH₂), 1220-1098 sm⁻¹ (C-O-H), 1016-733 sm⁻¹ (–CH₂). HRMS (ESI-TOF): m/z [M-H]⁺ Calcd for C₂₂H₃₇O⁺: 317.2839; found: 317.2848.



III. Characterization Spectrum.

Figure S1. ¹H NMR spectrum of 3-methyldec-1-yn-3-ol.



Figure S2. ¹³C NMR spectrum of 3-methyldec-1-yn-3-ol.



Figure S3. ¹H NMR spectrum of 8,13-dimethylicosa-9,11-diyne-8,13-diol.



Figure S4. ¹³C NMR spectrum of 8,13-dimethylicosa-9,11-diyne-8,13-diol.



Figure S5. IR spectrum of 8,13-dimethylicosa-9,11-diyne-8,13-diol.

Reference

 Hosseini, A.; Seidel, D.; Miska, A.; Schreiner, P.R. Fluoride-Assisted Activation of Calcium Carbide: A Simple Method for the Ethynylation of Aldehydes and Ketones. Org. Lett. 2015, 17, 2808–2811. https://doi.org/10.1021/acs.orglett.5b01219.