

UDC 547.32

HALOALKOXYLATION OF 3-ORGANYLOXY-1-PROPENES IN DIMETHYLACETYLENECARBINOL MEDIUM

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Received 08.11.2019

Abstract: Reaction of alkoxyhalogenation 3-organyloxy-1-propenes with *N*-bromosuccinimide (or iodine) in dimethylacetylenecarbinol medium proceeds regioselectively according to NMR spectra. It proceeds at a low temperature cooling the reaction mixture with ordinary ice. The main reaction products, diethers – 3-bromo (iodine) -1,2-propanediol, are formed in high yields. It founded that the alkoxyhalogenation of allyl ethers with propinol proceeds regioselectively with fixation of the halogen atom to the peripheral carbon atom of C=C bond. The yields of bromine-containing products are higher than those for iodine analogues. Iodine-containing products boil at a higher temperature than bromine analogues. In the reaction products, substances with the replacement of the halogen atom with unsaturated alcohol are not observed. The reaction was monitored by means of thin layer chromatography. Similar synthesized compounds are used as biologically active compounds.

Keywords: alkoxyhalogenation, C₃-unsaturated alcohols, β-halogenethers, FT-IR spectra, ¹H NMR spectra

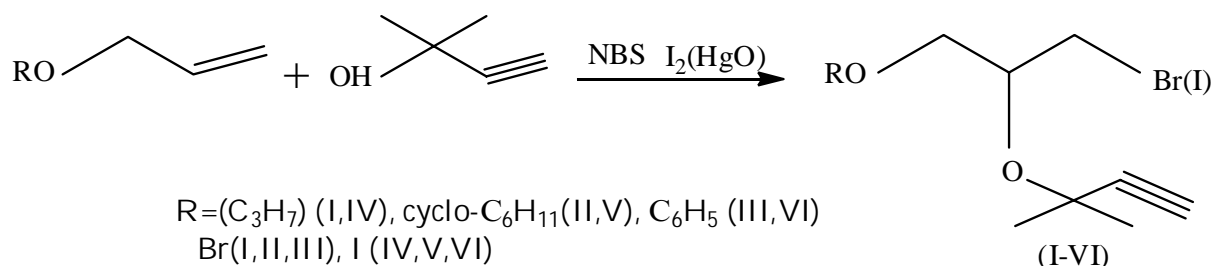
DOI: 10.32737/2221-8688-2020-1-102-105

Introduction

Alkoxyhalogenation of alkenes [1,2] with C₃-unsaturated alcohols is a common method for the synthesis of unsaturated β-halogenethers which are used in the synthesis of heterocyclic compounds [4-6] and biologically active preparations [3-9].

Experimental

The reaction was carried out at low temperature (-5±0 °C) in order to prevent tarring process. Upon implementation the same process in the temperature range (-5 ÷ 10 °C) was observed yield reduction (I-VI) by about half.



We found that the alkoxyhalogenation of allyl ethers with propinol proceeds regioselectively with fixation of the halogen atom to the peripheral carbon atom of C=C bond. Regioselectivity of reactions (according

to the Markovnikov rule) is confirmed by ¹H NMR spectral data of compounds (I-VI) which says that the presence of doublet signals of protons in methylene groups bonded to a halogen atom due to spin-spin interaction with

methine protons in the region of 3.28 dd (1H, J = 10.3, 5.8 Hz CH₂I), 3.41 dd. (1H, J = 10.3, 5.8 Hz CH₂I) for CH₂I and 3.38 dd (1H, J=10.5, 5.7 Hz CH₂Br) and 3.42 dd. (1H, J=10.5, 5.7 Hz CH₂I), for CH₂Br respectively.

In the FT-IR spectra of synthesized compounds (I-VI), absorption bands are observed in the region of 1150–1085 cm⁻¹ due to asymmetric stretching vibrations of the C-O-C bond. The bands in the regions of 3333–3267 cm⁻¹ and 2140–2100 cm⁻¹ are

characteristic for stretching vibrations of monosubstituted acetylenes.

The synthesized compounds are readily soluble in organic solvents and stable when stored under normal conditions.

This method allows to synthesize 3-halo-1,2-propanediol diethers in 60-70% yield.

The composition and structure of the obtained compounds are established on the basis of FT-IR and ¹H NMR spectral data.

Results and discussion

FT-IR spectra of compounds were measured on Specord-75 instruments in the microlayer and using KBr disks. ¹H NMR spectra of substances in the solution CDCl₃ recorded on «Bruker SF-400" (300.134 MHz) device, an internal standard HMDS.

3-[(1-Bromo-3-propyloxypropan-2-yl)oxy]-3-methylbut-1-in (I). It was gradually added with 44 g of N-bromosuccinimide (NBS) to a cooled equimolar mixture of 25 g allylpropyl ether and 14 g propargyl alcohol with stirring, so that a temperature of the reaction mixture could not exceed 0 °C. The stirring was carried out for a period 5 hours at a room temperature. The succinimide formed was filtered off, and the mixture was alkalinized by solution of 15 g of sodium hydroxide in 100 ml of water, then extracted with ether and dried with CaCl₂. Following ether removal, the residuo was distilled by means of vacuum distillation method. Allocated 41.15 g (70 %) of compound (I) T. boil. 65-66 °C (2 mmHg art.) d_4^{20} 1.2728, η_{20}^D 1.4924. MR_D 53.63, calcd. 52,95. FT-IR spectra (v/sm⁻¹): 620 (C-Br), 1100 (C-O-C), 2100 and 3300 (C≡CH). ¹H NMR (δ, ppm.,CDCl₃): 0.75 t (3H, CH₃, J=7.5 Hz), 1.08 s (6H, 2CH₃) 1.21 k (2H, CH₂, J=7.5 Hz), 2.48 s (¹H, CH), 3.21 m (4H, CH₂OCH₂), 3.38 dd (¹H, CH₂Br, J=10.5, 5.7 Hz), 3.42 dd (¹H, CH₂Br, J=10.5, 5.7 Hz), 3.85 m (¹H, CH). Found %: C 50.22, H 7.30, Br 30.38. C₁₁H₁₉BrO₂. Calculated,%: C 50.20, H 7.28, Br 30.36.

Similarly based on:

-allylcyclohexyl ether, propargyl alcohol and NBS was obtained **3-Bromo-2-[(2-methylbut-3-in-2-yl)oxy]propyl)cyclohexane (II)** by yield of 65%, T.boil.80-82°C (2 mm

Hg art.), d_4^{20} 1.2763, η_{20}^D 1.5060. MR_D 64.06, calcd. 64.68. FT-IR spectra (v/sm⁻¹): 628 (C-Br), 1140 (C-O-C), 2100 and 3300 (C≡CH). ¹H NMR (δ, ppm.,CDCl₃): 0.782-1.24 m, (11H, 1.09 s, (6H, 2CH₃) protons of the cycle), 2.48 s (1H≡CH), 3.39 dd (1H, CH₂Br, J=10.5, 5.7 Hz), 3.42 dd (1H, CH₂Br, J=10.5, 5.7 Hz), 3.83 m (1H, CH). Found %: C 55.47, H 7.67, Br 26.37. C₁₄H₂₃BrO₂. HMDS. calculated,%: C 55.45, H 7.65, Br 26.35.

- allylphenyl ether, propargyl alcohol and NBS **3-Bromo-2-[(2-methylbut-3-yn-2-yl)oxy]propyl]benzene (III)** obtained by yield of 68.5 %, T.boil. 99-100 °C d_4^{20} 1.2894, η_{20}^D 1.5256. MR_D 64.04,. calculated,%: 63.52. Found %: C 56.60, H 5.79, Br 26.91. C₁₄H₁₇BrO₂. HMDS. calculated,%: C 56.58, H 5.77, Br 26.89.

3 - [(1-Iodo-3-propoxypropan-2-yl) oxy] - 3-methylbut-1-in (IV). It was added 26 g (0.12 mol) of HgO to a cooled (-5 ÷ 0 °C) and intensively stirred mixture of 14 g (0.25 mol) of propargyl alcohol and 25 g (0.25 mol) of allyl propyl ether ,then 63.45 g (0.25 mol) of finely crushed crystal of iodine (1 g each). The stirring was carried out for a period 3-4 hours at a room temperature, the mixture was filtered, the filtrate washed by Na₂S₂O₃ solution and extracted with ether. The extract is dried using CaCl₂. Ether was removed in a rotary evaporator, and the residue was recrystallized. Received 47.9 g (68%) of substance (IV), melt.point 52-53 ° C (from heptane). FT-IR spectra (v/sm⁻¹): 550 (C-I), 1100 (C-O-C) 2100 and 3300 (C≡CH). ¹H NMR (δ, ppm.,CDCl₃): 0.75 t. (3H, CH₃), 1.11s (6H, 2CH₃), 1.24 m. (2H, CH₂), 2.43 s. (1H, ≡CH), 3.21-3.43 m. (4H, CH₂OCH₂),

3.28 dd. (1 H, CH₂I, J=10.5, 5.7 Hz), 3.41 dd. (1H, CH₂I, J=10.5 5.7 Hz), 3.85 m. (1H, CH), Found %: C 42.62, H 6.19, I 40.93. C₁₁H₁₉IO₂. HMDS. calculated, %: C 42.60, H 6.17, I 40.91.

Similarly based on:

- allyl ether of cyclohexanol, propargyl alcohol and crystalline iodine was obtained {**3-Iodo-2-[(2-methylbut-3-yn-2-yl)oxy]propyl}cyclohexane (V)** by yeald of 57.6%, melt.point 60-61 °C (from heptane). FT-IR spectra (v/sm⁻¹): 560 (C-I), 1100 (C-O-C), 2100 and 3330 (C≡CH). ¹H NMR (δ, m.d.,CDCl₃): 1.08 (6H, 2CH₃) m. (10H, C₆H₁₀), 2.45 t.(1H, ≡CH), 3.28 dd. (1H, CH₂I, J=10.5 5.7 Hz), 3.45 d (2H, 2CHO), 3.65 m. (2H 2CHO), Found %: C 48.03, H 6.64, I

36.25, C₁₄H₂₃IO₂. HMDS. calculated,%: C 48.01, H 6.62, I 36.23.

- allyl ether of phenol, propargyl alcohol and crystalline iodine was obtained **3-Iodo-2 - [(2-methylbut-3-yn-2-yl) oxy] propyl} benzene (VI)** by yeald of 67.2%, t. boil. 115 °C (2 mmHg art.), d_4^{20} 1.4502, η_{20}^D 1.5450., MR_D 68.93, calculated 68.93 FT-IR spectra (v/sm⁻¹): 560 (C-I), 1100 (C-O-C), 2100 and 3330 (C≡CH), 1515, 1620, 3060, 3080 (C₆H₅). ¹H NMR (δ, ppm, CDCl₃): (δ, m.d.,CDCl₃): 2.5 t.(1H, ≡CH, J=2.4Hz), 3.41 d. (2H, 2 CH₂O), 3.28 dd. (1H, CH₂I, J=10.5 5.7 Hz), 7.15 m. (5H, C₆H₅). Found %: C 48.87, H 5.02, I 36.89, C₁₄H₁₇IO₂. HMDS. calculated,%: C 48.85, H 4.98, I 36.87.

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3-ORQANİLOKSİ-1-PROPENLƏRİN DİMETİLASETİLENKARBİNOL MÜHİTİNDƏ HALOGENALKOKSİDLƏŞDİRİLMƏSİ

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NMR spektrlərin nəticələrinə görə dimetilasetilenkarbinolda *N*-bromsuksinimid (və ya kristal yod) ilə 3-*orqaniloksi-1-propen*lərin alkoksihalogenləşməsi ikiqat rabitə üzrə regiosektiv gədir. Reaksiya aşağı temperaturda adi buzla soyudularaq aparılır. Əsas reaksiya məhsulları 3-brom(yod)-1,2-propandioldiefirləri yüksək çıxımla alınır. Müəyyən edilib ki, allil efirlərinin propinolla alkoksihalogenləşmə reaksiyası halogen atomunun C=C rabitəsinə regiosektiv birləşməsi ilə həyata keçir. Bromsaxlayan birləşmələrin məhsuldarlığı yodsaxlayan analoqlarından daha yüksəkdir. Yod tərkibli məhsullar bromlu analoqlarından daha yüksək temperaturda qaynayır. Reaksiya məhsullarında halogen atomu doymamış spirtlə əvəz olunmur. Reaksiya nazik laylı xromatoqrafiya vasitəsilə müşahidə edilir. Bu tip birləşmələr üzvi kimyada və bioloji aktiv birləşmələr kimi istifadə olunur.

Açar sözlər: alkoksihalogenləşmə, allil efirləri, propinol, regiosektivlik, dimetilasetilenkarbinol

ГАЛОГЕНАЛКОКСИЛИРОВАНИЕ 3-ОРГАНИЛОКСИ-1-ПРОПЕНОВ В СРЕДЕ ДИМЕТИЛАЦЕТИЛЕНКАРБИНОЛА

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Алкоксигалогенирование 3-органилкси-1-пропенов *N*-бромсукцинимидом (или кристаллическим иодом) в среде диметилацетиленкарбинола по данным ЯМР спектров протекает региоселективно по двойной связи. Реакцию проводят при низкой температуре, охлаждая реакционную смесь обычным льдом. Основные продукты реакции – диэфиры-3-бром(иод)-1,2-пропандиола образуются с высокими выходами. Установлено, что алкоксигалогенирование аллиловых эфиров пропинолом протекает региоселективно с фиксацией атома галогена у периферийного атома углерода связи C=C. Выходы бромсодержащих продуктов выше их иоданалогов. Иодсодержащие продукты кипят более высокой температуре, чем их броманалоги. В продуктах реакции не наблюдаются вещества с заменой атома галогена непредельным спиртом. За ходом реакции следили с помощью тонкослойной хроматографии. Синтезированные соединения используются в качестве биологически активных соединений.

Ключевые слова: алкоксигалогенирование, пропинол, диэфиры 3-бром(иод)-1,2-пропандиола, диметилацетиленкарбинол