Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2012, **22**, 62–63
Mendeleev Communications

Base-catalyzed O-vinylation of tertiary propargylic alcohols with acetylene: first examples

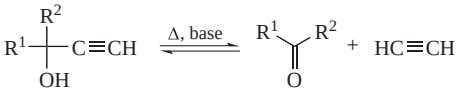
Boris A. Trofimov,* Elena Yu. Schmidt, Elena V. Skital'tseva, Ivan A. Bidusenko, Nadezhda V. Zorina and Al'bina I. Mikhaleva

A. E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences, 664033 Irkutsk, Russian Federation. Fax: +7 3952 419 346; e-mail: boris_trofimov@irioch.irk.ru

DOI: 10.1016/j.mencom.2012.03.002

1-Ethynylcyclohexanol and 1-ethynylcycloheptanol are O-vinylated with acetylene in KOH/DMSO superbase system (90 °C, autoclave, initial acetylene pressure of 14 atm, 1 h) to afford the corresponding vinyl ethers in 40 and 34% yields, respectively.

It is a common knowledge that tertiary propargylic alcohols in the presence of bases readily undergo defragmentation to ketones and acetylene (a classic reverse Favorsky reaction, Scheme 1).[1]



Scheme 1

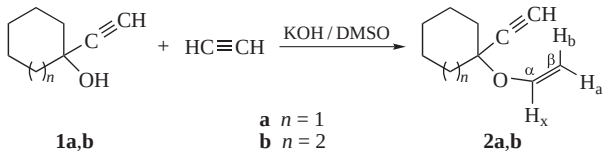
No wonder that O-vinylation of such alcohols with acetylene under basic conditions (another classic Favorsky reaction)[2] was not so far reported. Theoretically, such a vinylation is not impossible provided its rate being significantly greater than that of the defragmentation.

In past few decades, the classic O-vinylation of alcohols with acetylene was principally improved (with respect to its rate) due to the application of superbasic catalytic systems like KOH/DMSO.[3] In particular, these catalysts allowed propargyl alcohol itself[4] and secondary propargyl alcohols[5] to be successfully vinylated, though the initially formed vinyl ethers were further prototropically isomerized to vinyloxyallenes and/or vinyloxy-1,3-dienes. Therefore, one may expect that a superbase catalytic system will accelerate the vinylation better than the reverse Favorsky reaction. Moreover, the latter usually does not require too strong base for its implementation (often, for this even traces of potassium carbonate are enough[6]).

In view of these achievements, we have undertaken systematic efforts towards O-vinylation of tertiary propargylic alcohols. Here we report on preparatively meaningful procedure for the synthesis of vinyl ether of such alcohols using 1-ethynylcyclohexanol **1a** as a standard compound.

When alcohol **1a** was allowed to contact with acetylene in the KOH/DMSO system (**1**:KOH molar ratio was 1:1) at 90 °C for 1 h under pressure, the earlier unknown vinyl ether **2a** was formed in 40% isolated yield (Scheme 2).†

Initial acetylene pressure at room temperature was 14 atm which reached its highest value (23–25 atm) and then rapidly dropped, thus indicating the vinylation progress.



1a,**b** **a** $n = 1$ **b** $n = 2$ **2a**,**b**

Scheme 2

The crude products contained mainly the target vinyl ether **2a** and starting alcohol **1a** in various ratios depending on the reaction conditions (Table 1).

The same conditions (90 °C, 1 h) were proved to be valid for vinylation of 1-ethynylcycloheptanol **1b**, the non-optimized yield of the expected vinyl ether **2b** being 34% (Scheme 2).†

† ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE 400 instrument (400.13 and 101.61 MHz respectively) equipped with inverse gradient 5 mm probe in $CDCl_3$ with HMDS as internal standard. All 2D NMR spectra were recorded using a standard gradient Bruker pulse programs. IR spectra were obtained on a Bruker Vertex 70 spectrometer.

The reaction of 1-ethynylcyclohexanol **1a** *with acetylene in the KOH/DMSO suspension*. A mixture of alcohol **1a** (2.00 g, 16.1 mmol) and $KOH \cdot 0.5 H_2O$ (1.05 g, 16.1 mmol) in DMSO (50 ml) was placed into a 0.25 dm^3 steel rotating autoclave. The latter was fed with acetylene under pressure of 14 atm and then decompressed to atmospheric pressure to remove air. The autoclave was fed with acetylene again (initial pressure at ambient temperature was 14 atm and heated to 90 °C). The pressure value reached maximum of 23–25 atm at the reaction temperature and then dropped upon acetylene consumption during the reaction. The reaction was processed at 90 °C within 1 h. The reaction mixture, after cooling to room temperature, was diluted with cold (5–10 °C) water (50 ml), neutralized with NH_4Cl and extracted with diethyl ether (4 × 20 ml). The combined organic extract was washed with water (3 × 15 ml) and dried (K_2CO_3) overnight. After removal of the solvent, 2.30 g of a crude residue was obtained, which was distilled *in vacuo* to collect a fraction (1.15 g), bp 50–70 °C (2 Torr) containing (^{1}H NMR) starting alcohol **1a** and vinyl ether **2a** in 1:5 ratio. The fraction was diluted with Et_2O (30 ml) and alcohol **1a** was extracted with water (6 × 5 ml). After removal of Et_2O pure vinyl ether **2a** (0.96 g, 40% yield) was obtained.

1-Ethynyl-1-(vinyloxy)cyclohexane **2a**: colourless viscous liquid with smell of pine needles, n_D^{21} 1.5184. ^{1}H NMR, δ: 6.65 (dd, 1H, H_x, $^3J_{H_xH_b}$ 13.7 Hz, $^3J_{H_xH_a}$ 6.1 Hz), 4.48 (dd, 1H, H_b, $^3J_{H_bH_x}$ 13.7 Hz, $^2J_{H_bH_a}$ 1.0 Hz), 4.11 (dd, 1H, H_a, $^3J_{H_aH_x}$ 6.1 Hz, $^2J_{H_aH_b}$ 1.0 Hz), 2.56 (s, 1H, ≡CH), 1.91–1.88, 1.70 –1.66, 1.57–1.55 (m, 10 H, CH_2). ^{13}C NMR, δ: 146.7 (C-α), 91.7 (C-β), 84.3 (*C*≡CH), 75.1 (C-1) 74.7 (C≡*C*H), 37.4 (2 C-2), 25.0 (C-4), 22.4 (2 C-3). IR (film, ν_{max}/cm^{-1}): 3307, 2934, 2859, 2108, 1752, 1673, 1629, 1448, 1180, 1147, 1065, 974, 906. Found (%): C, 80.05; H, 9.47. Calc. for $C_{10}H_{14}O$ (%): C, 79.96; H, 9.39.

1-Ethynyl-1-(vinyloxy)cycloheptane **2b** was prepared from alcohol **1b** analogously. Colourless viscous liquid, n_D^{20} 1.4928. ^{1}H NMR, δ: 6.58 (dd, 1H, H_x, $^3J_{H_xH_b}$ 13.8 Hz, $^3J_{H_xH_a}$ 6.3 Hz), 4.43 (dd, 1H, H_b, $^3J_{H_bH_x}$ 13.7 Hz, $^2J_{H_bH_a}$ 1.0 Hz), 4.09 (dd, 1H, H_a, $^3J_{H_aH_x}$ 6.1 Hz, $^2J_{H_aH_b}$ 1.0 Hz), 2.45 (s, 1H, ≡CH), 2.02–1.98, 1.84–1.78, 1.65–1.53 (m, 12 H, CH_2). ^{13}C NMR, δ: 147.1 (C-α), 91.4 (C-β), 82.9 (*C*≡CH), 74.9 (C-1) 74.2 (C≡*C*H), 40.6, 29.2, 27.8, 22.2 (2 C-2, 2 C-3, 2 C-4). IR (film, ν_{max}/cm^{-1}): 3308, 2925, 2855, 2108, 1700, 1654, 1448, 1380, 1138, 1031, 955, 916, 645, 627. Found (%): C, 80.48; H, 9.50. Calc. for $C_{11}H_{16}O$ (%): C, 80.44; H, 9.82.

Table 1 The product compositions for reaction of **1a** with acetylene.

Reaction temperature/°C	Reaction time/h	**1a**:**2a** molar ratio
90	1	1:5
80	1	1:2
80	2	1:4

Pure vinyl ethers **2a**,**b** were isolated from the corresponding alcohol **1a**,**b**–ether **2a**,**b** mixtures on diluting with Et_2O and extraction of unreacted alcohols **1a**,**b** with water.

Note that application of acetylene under pressure for vinylation of tertiary propargylic alcohols is crucial since this does not only significantly increases the reaction rate but, what is of not a lesser importance, the high concentration of acetylene in the reaction mixture shifts the equilibrium of the reverse Favorsky reaction toward tertiary propargylic alcohols thus maintaining their concentration sufficient for the vinylation.

In conclusion, the results obtained have shown for the first time that against the common knowledge, the direct base-catalyzed vinylation of tertiary propargylic alcohols is not impossible. Consequently, from now on vinyl ethers of tertiary propargylic alcohols, synthetically promising building blocks, synthons and monomers, are becoming accessible.

The work was supported by the Russian Foundation for Basic Research (grant no. 11-03-00270-a).

References

1 (*a*) A. V. Shchelkunov, R. L. Vasil'eva and T. A. Favorskaya, *Zh. Org. Khim.*, 1969, **5**, 1148 (in Russian); (*b*) A. V. Shchelkunov, Z. M. Muldakhmedov, N. A. Rakhimzhanova and T. A. Favorskaya, *Zh. Org. Khim.*, 1970, **6**, 930 (in Russian); (*c*) G. T. Crisp and Y.-L. Jiang, *Synth. Commun.*, 1998, **28**, 2571.

2 (*a*) A. E. Favorsky, *Zh. Ross. Khim. Ob-va*, 1888, **20**, 445 (in Russian); (*b*) B. A. Trofimov, in *Modern Problems of Organic Chemistry*, eds. R. R. Kostikov, M. A. Kuznetsov and M. S. Baird, St. Petersburg University Press, St. Petersburg, 2010, Issue 15, pp. 23–48.

3 (*a*) B. A. Trofimov, *Curr. Org. Chem.*, 2002, **6**, 1121; (*b*) B. A. Trofimov, in *Modern Problems of Organic Chemistry*, eds. A. A. Potekhin, R. R. Kostikov and M. S. Baird, St. Petersburg University Press, St. Petersburg, 2004, Issue 14, pp. 121–163; (*c*) B. A. Trofimov and N. K. Gusarova, *Usp. Khim.*, 2007, **76**, 550 (*Russ. Chem. Rev.*, 2007, **76**, 507).

4 B. A. Trofimov, O. A. Tarasova, S. V. Amosova, M. V. Sigalov and L. M. Sinegovskaya, *Zh. Org. Khim.*, 1986, **22**, 2007 (in Russian).

5 (*a*) O. A. Tarasova, B. A. Trofimov, A. V. Afonin, L. M. Sinegovskaya, N. A. Kalinina and S. V. Amosova, *Zh. Org. Khim.*, 1991, **27**, 1172 (in Russian); (*b*) O. A. Tarasova, B. A. Trofimov, V. V. Keiko and S. V. Amosova, *Zh. Org. Khim.*, 1991, **27**, 1180 (in Russian).

6 S. V. Klyatskaya, E. V. Tretyakov and S. F. Vasilevsky, *ARKIVOC*, 2003, **xiii**, 21.

Received: 6th October 2011; Com. 11/3812