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# Consecutive reactions of dialkyl ethynyl carbinols with acetylene in superbase KOH/DMSO suspension

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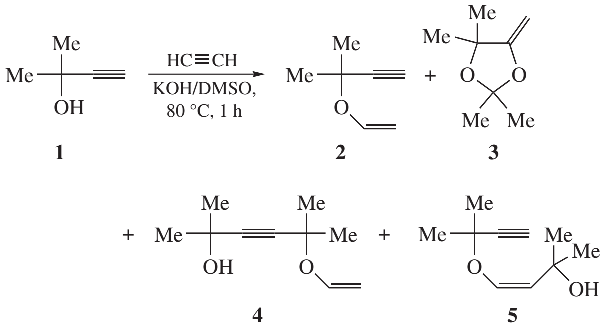
2-Methylbut-3-yn-2-ol, a tertiary propargylic alcohol, reacts with acetylene under pressure in superbase KOH/DMSO suspension (80 °C, 1 h) to afford, along with the expected vinyl ether, 2,2,4,4-tetramethyl-5-methylidene-1,3-dioxolane, 2,5-dimethyl-5-(vinyloxy)-hex-3-yn-2-ol and (*Z*)-2-methyl-4-(2-methylbut-3-yn-2-yloxy)but-3-en-2-ol.

A nucleophilic addition of alcohols to the C≡C bond (the Favorsky reaction)[1] is an industrially valuable process.[2] The systematic application of superbase catalytic systems such as MOH/DMSO (M is alkali metal) to facilitate the addition of alcohols to acetylene resulted in development of direct vinylation of propargyl alcohol itself[3] and secondary propargylic alcohols[4] that earlier represented a challenge.

In continuation of these achievements, we have found that tertiary propargylic alcohols, derived from alkyl aryl(hetaryl) ketones, when heated with acetylene in the presence of the KOH/DMSO system did not form the anticipated vinyl ethers but underwent diastereoselective cyclodimerization to afford 7-methylidene-6,8-dioxabicyclo[3.2.1]octanes in up to 80% yield.[5] However, cycloaliphatic propargylic alcohols (1-ethynylcyclohexanol and 1-ethynylcycloheptanol) under similar conditions (KOH/DMSO, 90 °C, 1 h) did form the corresponding vinyl ethers in 40 and 34% yields, respectively.[6]

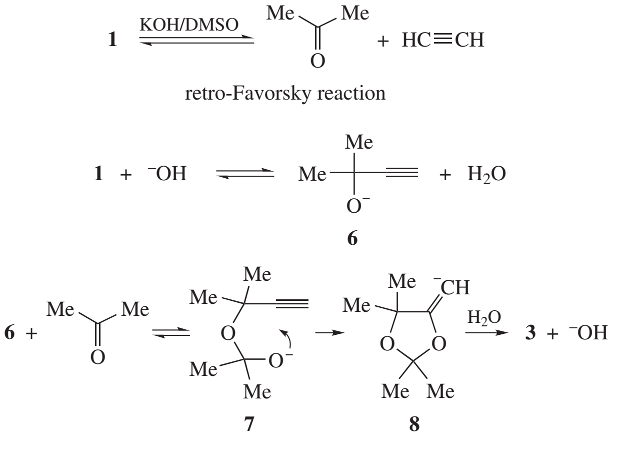
Herein, we report that open-chain tertiary propargylic alcohol such as 2-methylbut-3-yn-2-ol **1** under the same conditions reacted with acetylene in entirely different way undergoing a sequence of consecutive reactions to give, along with the expected vinyl ether **2** (6%), 2,2,4,4-tetramethyl-5-methylidene-1,3-dioxolane **3** (8%), and also vinylated acetylenic dimers **4** (26%) and **5** (26%) (Scheme 1).[†] Conversion of the starting acetylenic alcohol **1** was 75%.



**Scheme 1**

At a lower temperature (60 °C) and a longer time (6 h, other conditions remaining the same), conversion of alcohol **1** dropped to ~13%, though the products ratio did not significantly change.

Apparently, the products **3** and **4** are formed with participation of acetone *via* base-catalyzed degradation of the starting alcohol **1** (the retro-Favorsky reaction, Scheme 2). Oxygen-centered anion **6** of alcohol **1** may add to acetone to generate the intermediate anion **7** which further undergoes the ring closure to dioxolane **3** after the final protonation of carbanion **8** (Scheme 2). Similar reaction sequences have previously been observed by us in the reaction of 1-(phenylethynyl)cyclohexanol with cyclohexanone.[7]



**Scheme 2**

The monovinyl ether of acetylenic diol **4** likely resulted from the Favorsky ethynylation of acetone with compound **2** (Scheme 3).

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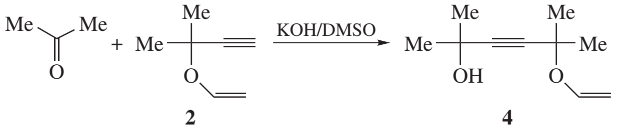
[†] *Reaction of 2-methylbut-3-yn-2-ol* **1** *with acetylene in the KOH/DMSO suspension*. A mixture of alcohol **1** (2.00 g, 23.8 mmol) and $KOH\cdot 0.5H_2O$ (1.55 g, 23.8 mmol) in DMSO (60 ml) was placed into a 0.25-$dm^3$ steel rotating autoclave. The autoclave was fed with acetylene up to 12 atm and then decompressed to atmospheric pressure to remove air. The autoclave was fed with acetylene again (initial pressure at ambient temperature was 12 atm) and heated to 80 °C for 1 h. The pressure reached its maximum of 18–20 atm as the temperature was raised to 80 °C and then dropped upon acetylene consumption in the course of the reaction. The reaction mixture, after cooling to room temperature, was diluted with cold (5–10 °C) water (50 ml). Steam distillation gave light-yellow oil (0.31 g) consisting of vinyl ether **2** and dioxolane **3** in a ratio of 1:1 ($^1$H NMR). The residue after distillation was extracted with diethyl ether (4×20 ml), the extracts were washed with water (3×15 ml) and dried ($K_2CO_3$) overnight. Removal of the solvent gave 1.86 g of a mixture which was chromatographed on the column (basic $Al_2O_3$, hexane–benzene with gradient from 1:0 to 0:1) to afford 0.50 g of alcohol **1** and 1.06 g of a mixture of ethers **4** and **5** in a ratio of 1:1. Additional column chromatography of mixture of ethers **4** and **5** gave pure ether **4** and a mixture enriched in ether **5** (~80%). Structure of dioxolane **3** was proved by comparison of its spectra with those of relative analogues.[7]



**Scheme 3**

Scheme 3 may clarify why the target vinyl ether **2** (consumed in the above Favorsky ethynylation) in fact turned to be a minor product.

In our opinion, especially interesting and unexpected product is *Z*-configured acetylenic vinylic ether **5**, which is actually the product of dimerization of the starting propargylic alcohol **1** arising from addition of alkoxide ion **6** at the triple bond of compound **1**.

Here, unusual are the three issues: (i) the easy vinylation of tertiary alcohols (which still remains a challenge),[2(*b*),8] (ii) vinylation with a mono-substituted acetylene bearing tertiary hydroxyalkyl substituents and (iii) eventually, the clear possibility to bring about olygomerization of alcohol **1**, and further, polyaddition (what is likely already happen in the reaction). The stereochemistry (100% *Z*-stereoselectivity) of the reaction is in keeping with the above pathway, *i.e.*, a classic nucleophilic concerted *trans*-addition takes place here.[9]

Similarly, another tertiary acetylenic alcohol, 3-methylpent-1-yn-3-ol, afforded the same series of the products (see Scheme 1), when allowed to react with acetylene in the KOH/DMSO system (80 °C, 1 h, initial acetylene pressure at ambient temperature was 12 atm).

Structures of all compounds were proved by complex analysis of the NMR spectra ($^1$H, $^{13}$C, 2D NOESY, HSQC, HMBC).[‡]

Although the priority character of this communication did not imply the optimization of the reactions observed, the results described here allow us to look forward to further successful development of this new facet of acetylene chemistry.

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[‡] $^1$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 MS spectrum of ether **5** was measured on a Shimadzu GCMS-QP5050A spectrometer.

*3-Methyl-3-(vinyloxy)but-1-yne* **2**: yield 6%. $^1$H NMR ($CDCl_3$) $\delta$: 6.73 (dd, 1H, OCH=, $^3J$ 13.7 Hz, $^3J$ 6.1 Hz), 4.68 (dd, 1H, $=CH_2$, $^3J$ 13.7 Hz, $^2J$ 0.7 Hz), 4.16 (dd, 1H, $=CH_2$, $^3J$ 6.1 Hz, $^2J$ 0.7 Hz), 2.04 (s, 1H, HC≡), 1.33 (s, 6H, Me). $^{13}$C NMR ($CDCl_3$) $\delta$: 147.9 (OCH=), 92.1 ($=CH_2$), 85.5 ($C^2$), 73.7 ($C^1$), 72.2 ($C^3$), 29.7 (Me).

*2,2,4,4-Tetramethyl-5-methylidene-1,3-dioxolane* **3**: yield 8%. $^1$H NMR ($CDCl_3$) $\delta$: 4.38 (d, 1H, $=CH_2$, $^2J$ 2.3 Hz), 3.72 (d, 1H, $=CH_2$, $^2J$ 2.3 Hz), 1.33, 1.30 (2s, 12H, Me). $^{13}$C NMR ($CDCl_3$) $\delta$: 166.3 ($C^5$), 110.3 ($C^2$), 81.3 ($=CH_2$), 81.2 ($C^4$), 29.7 (Me).

*2,5-Dimethyl-5-(vinyloxy)hex-3-yn-2-ol* **4**: yield 26%. $^1$H NMR ($CDCl_3$) $\delta$: 6.59 (dd, 1H, OCH=, $^3J$ 13.8 Hz, $^3J$ 6.3 Hz), 4.44 (d, 1H, $=CH_2$, $^3J$ 13.8 Hz), 4.10 (d, 1H, $=CH_2$, $^3J$ 6.3 Hz), 2.31 (s, 1H, OH), 1.50 (s, 6H, $C^2Me_2$), 1.48 (s, 6H, $C^5Me_2$). $^{13}$C NMR ($CDCl_3$) $\delta$: 147.1 ($O\mathit{C}H=CH_2$, $^1J_{CH}$ 176.9 Hz), 91.6 ($OCH=\mathit{C}H_2$), 90.0 ($C^3$), 83.2 ($C^4$), 72.1 ($C^5$), 65.0 ($C^2$), 31.4 ($C^2\mathit{Me}$), 29.3 ($C^5\mathit{Me}$). IR (film, $\nu_{max}$/cm$^{-1}$): 3414, 3075, 2961, 2871, 2110, 1636, 1456, 1380, 1167, 1138. Found (%): C, 71.52; H, 9.30. Calc. for $C_{10}H_{16}O_2$ (%): C, 71.39; H, 9.59.

*(Z)-2-Methyl-4-(2-methylbut-3-yn-2-yloxy)but-3-en-2-ol* **5**: yield 26%. $^1$H NMR ($CDCl_3$) $\delta$: 6.33 (d, 1H, OCH=, $^2J$ 6.8 Hz), 4.71 (d, 1H, =CH, $^2J$ 6.8 Hz), 3.34 (s, 1H, OH), 2.53 (s, 1H, HC≡), 1.56, 1.35 (2s, 12H, Me). $^{13}$C NMR ($CDCl_3$) $\delta$: 138.8 ($O\mathit{C}H=CH$, $^1J_{CH}$ 157.3 Hz), 116.8 ($OCH=\mathit{C}H$, $^1J_{CH}$ 181.3 Hz), 84.3 ($\mathit{C}\equiv CH$), 73.7 ($C\equiv\mathit{C}H$), 72.8 ($O\mathit{C}Me_2$), 70.7 ($HO–\mathit{C}Me_2$), 30.5 ($HO–C\mathit{Me}_2$), 29.1 ($OC\mathit{Me}_2$). MS (EI), *m*/*z* (%): 168 (2) $[M]^{+\cdot}$, 110 (2) $[M - Me_2CO]^{+\cdot}$, 95 (96) $[M - C_4H_8O]^{+\cdot}$, 91 (13) $[C_7H_7]^+$, 79 (23), 77 (13) $[C_6H_5]^+$, 67 (47) $[C_5H_7]^+$, 59 (100) $[Me_2COH]^+$, 53 (21), 43 (65), 41 (45), 39 (36). Calc. for $C_{10}H_{16}O_2$, *m*/*z*: 168.2.

*Reaction of 3-methylpent-1-yn-3-ol with acetylene in the KOH/DMSO suspension* was carried out analogously. After the afore-described processing, from 2.00 g of 3-methylpent-1-yn-3-ol were isolated 0.11 g of a mixture of 3-methyl-3-(vinyloxy)pent-1-yne [6.62 (dd, 1H, OCH=, $^3J$ 13.8 Hz, $^3J$ 6.3 Hz), 4.55 (dd, 1H, $=CH_2$, $^3J$ 13.8 Hz, $^2J$ 0.8 Hz), 4.16 (dd, 1H, $=CH_2$, $^3J$ 6.3 Hz, $^2J$ 0.8 Hz), 2.10 (s, 1H, HC≡)] and 2,4-diethyl-2,4-dimethyl-5-methylidene-1,3-dioxolane [4.24 (d, 1H, $=CH_2$, $^2J$ 2.3 Hz), 3.68 (d, 1H, $=CH_2$, $^2J$ 2.3 Hz)] (~1:1.2) and 1.72 g of a mixture of 3,6-dimethyl-6-(vinyloxy)oct-4-yn-3-ol [6.51 (dd, 1H, OCH=, $^3J$ 13.7 Hz, $^3J$ 6.1 Hz), 4.41 (d, 1H, $=CH_2$, $^3J$ 13.7 Hz), 4.04 (d, 1H, $=CH_2$, $^3J$ 6.1 Hz)] and (*Z*)-3-methyl-1-(3-methylpent-1-yn-3-yloxy)pent-1-en-3-ol [6.31 (d, 1H, OCH=, $^2J$ 7.0 Hz), 4.55 (d, 1H, =CH, $^2J$ 7.0 Hz), 3.34 (s, 1H, OH), 2.50 (s, 1H, HC≡)] (~1:1).