

Nucleophilic Addition to Acetylenes in Superbasic Catalytic Systems: XVI*. Vinylation of Alcohols of the Furan Series under Atmospheric Pressure

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Abstract—2-Hydroxymethylfuran and 2-hydroxymethyltetrahydrofuran reacted with acetylene in the superbasic catalytic system KOH–DMSO at 75–85°C under atmospheric pressure to give in 1.5–3 h the corresponding 2-vinyloxymethyl derivatives in 88 and 91% yield, respectively.

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In the recent years continuously increasing attention is given worldwide to the preparation of practically important products from renewable raw materials. In particular, this is the reason that in the past decades furfural derivatives have found wide application as universal solvents and precursors of biopolymers and other biodegradable chemical substances.

At present, furfural (hydrolysis product of pentosan materials) is used mainly to produce furfuryl alcohol (**Ia**) and tetrahydrofurfuryl alcohol (**Ib**). The first of these is a starting material for the manufacture of furan resins, adhesives, and paints, and the second is generally recognized as “green” solvent for large-scale preparation of acrylates and epoxy resins and is a component of ecologically benign diesel fuel [2] and technical purifiers [3]. Due to low toxicity [4], biodegradability [5], and high solubility in organic and aqueous media 2-hydroxymethyltetrahydrofuran and its derivatives are successfully used in pharmaceutical industry and cosmetics, in particular as synthetic aromatizers.

Selective modification of alcohols **Ia** and **Ib** could considerably extend their synthetic and practical potentials. From this viewpoint, quite promising is their vinylation with acetylene as a convenient atom-economic and ecologically friendly method of synthesis of new important monomers and intermediate products, namely reactive but still difficultly accessible vinyl ethers having a furan fragment. The known methods

for the preparation of furfuryl vinyl ether (**IIa**, 2-vinyloxymethylfuran) and tetrahydrofurfuryl vinyl ether (**IIb**, 2-vinyloxymethyltetrahydrofuran) from alcohols **Ia** and **Ib** and acetylene suffer from such disadvantages as high acetylene pressure (initial pressure 16 atm at room temperature, which rises to 30–50 atm at the required temperature) and elevated temperature (up to 180°C) [6–9]. Patent [10] is the only publication where the synthesis of 2-vinyloxymethyltetrahydrofuran by vinylation of alcohol **Ib** under atmospheric pressure at 170–190°C in the system potassium alkoxide–secondary or tertiary aromatic amine was reported; however, the yield and purity of the product were not given.

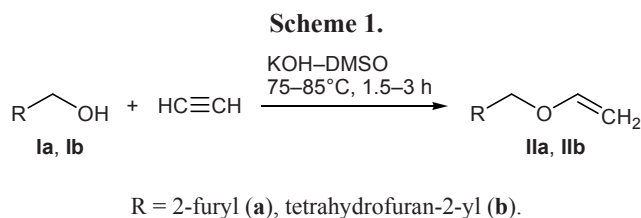
We previously reported [11–15] on the effective use of superbasic systems for addition of various nucleophiles to compounds containing a triple carbon–carbon bond, in particular for addition of oxygen-centered nucleophiles for chemoselective preparation of vinyl ethers. In continuation of these studies, in the present work we examined vinylation of 2-hydroxymethylfuran (**Ia**) and 2-hydroxymethyltetrahydrofuran (**Ib**) with acetylene according to the developed methodology [11–15].

In the preceding communication [1] we described an efficient procedure for the synthesis of 2-vinyloxymethylfuran (**IIa**) from alcohol **Ia** and acetylene under increased pressure in the system MOH–DMSO (M = Na, K). By lowering the reaction temperature to 75–

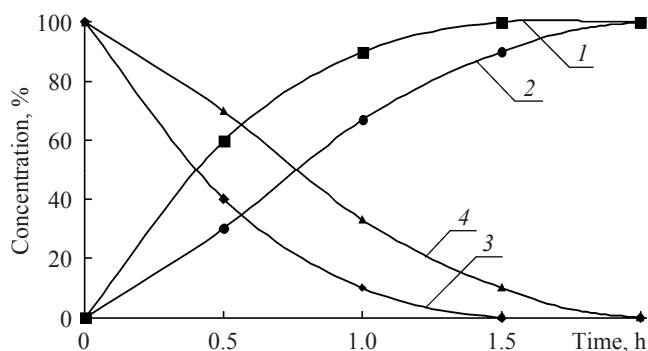
* For communication XV, see [1].

85°C we succeeded in minimizing side processes leading to tar formation and improving the yield of vinyl ether **IIa** to 80% (previously, its yield did not exceed 68% [7]). We now made an attempt to develop even simpler and more practical method for the vinylation of furan alcohols **Ia** and **Ib** with acetylene under atmospheric pressure.

Our experiments showed that alcohols **Ia** and **Ib** selectively react with acetylene (flow rate ~1–1.5 l/h) in the superbasic catalytic system KOH–DMSO on heating to 75–85°C (1.5–3 h); the products were vinyl ethers **IIa** and **IIb** which were isolated in high yield (88 and 91%; Scheme 1). The ¹³C NMR spectra of the reaction mixtures contained only signals assignable to the final products, indicating high selectivity of the process.



We estimated the relative reactivity of alcohols **Ia** and **Ib** toward acetylene by the competing reaction technique. For this purpose acetylene was bubbled through an equimolar mixture of alcohols **Ia** and **Ib** in a suspension of KOH in DMSO, heated to 80–82°C, and samples were withdrawn from the mixture every 30 min. The concentrations of alcohols **Ia** and **Ib** and vinyl ethers **IIa** and **IIb** in the reaction mixtures were determined by ¹H NMR spectroscopy, following the intensity of signals from the exocyclic CH₂O methyl-

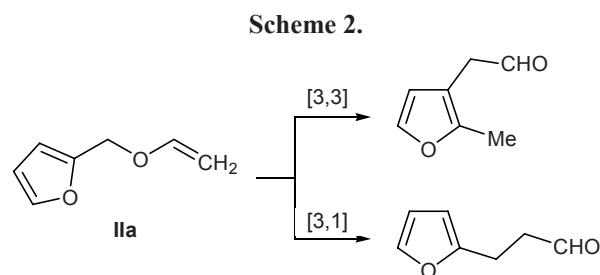


Plots of the concentrations of (1) 2-vinyloxymethylfuran (**IIa**), (2) 2-vinyloxymethyltetrahydrofuran (**IIb**), (3) 2-hydroxymethylfuran (**Ia**), and (4) 2-hydroxymethyltetrahydrofuran (**Ib**) versus time in the vinylation of an equimolar mixture of compounds **Ia** and **Ib** with acetylene in the superbasic system KOH–DMSO at 80–82°C (atmospheric pressure).

ene protons, δ 4.72 (**IIa**), 3.62 (**IIb**), 4.36 (**Ia**), 3.21 and 3.28 ppm (**Ib**). The results showed that 2-hydroxymethylfuran (**Ia**) reacts with acetylene at a higher rate than does 2-hydroxymethyltetrahydrofuran (**Ib**) (see figure). As followed from the intensities of signals from the *trans*-protons in the vinyloxy groups (δ 4.32 and 4.16 ppm for **IIa** and **IIb**, respectively), the concentration of vinyl ether **IIa** was twice as large as the concentration of **IIb** in 0.5 h. After 1 h, the ratio **IIa/IIb** fell down to 1.4, and after 2 h, the reaction mixture contained no initial alcohol, while the ratio **IIa/IIb** became 1:1.

The lower reactivity of 2-hydroxymethyltetrahydrofuran compared to 2-hydroxymethylfuran in nucleophilic addition to acetylene seems to be surprising, taking into account that 2-furyl group is a stronger electron acceptor than tetrahydrofuryl fragment. This follows from appreciable downfield shift of the CH₂O and vinyl proton signals of vinyl ether **IIa** relative to the corresponding signals in the ¹H NMR spectrum of 2-vinyloxymethyltetrahydrofuran (see Experimental). Presumably, the observed pattern originates from steric factor: unlike furan ring, tetrahydrofuran ring is non-planar; therefore, the hydroxy group in some conformers of tetrahydrofurfuryl alcohols is turned toward the ring and is shielded by the neighboring CH protons.

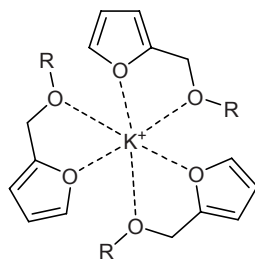
With a view to obtain additional information on the reaction of 2-hydroxymethylfuran (**Ia**) with acetylene and elucidate main factors determining the selectivity of this reaction, we examined the possibility for vinyl ether **IIa** to undergo intramolecular rearrangements typical of allyl vinyl ether is capable of undergoing [1,3]- and [3,3]-sigmatropic (Claisen) rearrangements leading to 3-(2-furyl)propanal and 2-(2-methyl-3-furyl)ethanal, respectively [16, 17] (Scheme 2). Aldolization of the latter in the presence of alkali metal hydroxides could give polymeric products, and just strong tarring was



the main factor responsible for the low yield of 2-vinyloxymethylfuran under classical vinylation conditions [6, 7].

We found that heating (80–82°C, 5 h) of an equimolar mixture of vinyl ethers **IIa** and **IIb** (the latter was taken for comparison) in the system KOH–DMSO resulted in insignificant reduction of the concentration of compound **IIa** (¹H NMR data). After appropriate treatment, we isolated a mixture of vinyl ethers **IIa** and **IIb** at a ratio of 1:1.07 (GLC). These findings provide an additional support to the assumption that the contribution of Claisen rearrangement in vinyl ether **IIa** is insignificant under the given conditions.

We already noted general character of vinylation of both alcohols **Ia** and **Ib** with acetylene under atmospheric pressure. The reaction occurs at unusually low temperature (75–85°C) and ensures high yields of the corresponding vinyl ethers. The optimal temperature matches the conditions for vinylation of oligoethylene glycols [18] and is lower than the temperature required for the vinylation of methyl [19] or allyl alcohol [20]. The most probable reason is intrinsic superbasicity of the reaction mixture, i.e., binding of alkali metal cation by either alcohol molecules **Ia** or **Ib** or vinyl ether molecules **IIa** or **IIb** according to the chelation pattern typical of polyethers [13, 14, 21].



Thus we have found conditions for almost quantitative vinylation of large-scale furfural derivatives, 2-hydroxymethylfuran and 2-hydroxymethyltetrahydrofuran. The reaction is performed in the superbasic system KOH–DMSO under atmospheric pressure at 75–85°C. The products, 2-vinyloxymethylfuran and 2-vinyloxymethyltetrahydrofuran are promising monomers and key starting materials for the synthesis of new furan derivatives.

EXPERIMENTAL

The IR spectra (400–4000 cm⁻¹) were recorded from samples prepared as thin films on a Bruker JFS-25 spectrometer. The ¹H and ¹³C NMR spectra

were measured at room temperature on a Bruker DPX-400 instrument at 400.13 and 100.62 MHz, respectively, using DMSO-*d*₆ as solvent and reference. GLC analysis was performed on an Agilent 6890N chromatograph.

Vinylation of furan alcohols Ia and Ib with acetylene under atmospheric pressure (general procedure). A mixture of 100 ml of DMSO, 100 mmol of alcohol **Ia** or **Ib**, and 2.8 g (50 mmol) of potassium hydroxide was heated to 75–85°C, and acetylene was passed through the mixture at a flow rate of ~1–1.5 l/h over a period of 1.5–3 h under stirring (until signals of the initial alcohol disappeared from the ¹³C NMR spectrum of the reaction mixture). When the reaction was complete, the mixture was diluted with 100 ml of water and extracted with diethyl ether (6×30 ml), the extracts were combined, washed with water (3×20 ml), and dried over potassium carbonate, the solvent was removed on a rotary evaporator, and the residue was distilled under reduced pressure.

2-Vinyloxymethylfuran (IIa). Yield 10.90 g (88%), colorless liquid which turned yellow on storage, bp 45°C (12 mm), *n*_D²⁰ = 1.4741. IR spectrum, *v*, cm⁻¹: 1503 (furan ring); 1618, 1638 (C=C). ¹H NMR spectrum, *δ*, ppm: 4.05 d.d (1H, *cis*-H, ³*J* = 6.7, ²*J* = 1.8 Hz), 4.32 d.d (1H, *trans*-H, ³*J* = 14.2, ²*J* = 1.8 Hz), 4.72 s (2H, CH₂O), 6.45 d.d (1H, 4-H, ³*J* = 3.2, ³*J* = 1.7 Hz), 6.53 m (2H, 3-H, =CHO), 7.66 br.s (1H, 5-H). ¹³C NMR spectrum, *δ*_C, ppm: 62.5 (OCH₂), 88.4 (CH₂=), 110.7 (C⁴), 111.1 (C³), 144.0 (C⁵), 150.7 (C²), 151.8 (OCH=). Found, %: C 67.67; H 6.47. C₇H₈O₂. Calculated, %: C 67.73; H 6.50.

2-Vinyloxymethyltetrahydrofuran (IIb). Yield 11.65 g (91%), colorless liquid, bp 62°C (15 mm), *n*_D²⁰ = 1.4492; published data: bp 163°C (750 mm), *n*_D²⁰ = 1.4500 [8]; bp 55.5°C (14 mm), *n*_D²⁰ = 1.4489 [9]. IR spectrum, *v*, cm⁻¹: 1618, 1638, 1653 (C=C). ¹H NMR spectrum, *δ*, ppm: 1.56 m (1H, 3-H), 1.80 m (2H, 4-H), 1.91 m (1H, 3-H), 3.62 m (3H, 5-H, OCH₂), 3.72 m (1H, 5-H), 3.95 d.d (1H, *cis*-H, ³*J* = 6.7, ²*J* = 1.4 Hz), 3.99 m (1H, 2-H), 4.16 d.d (1H, *trans*-H, ³*J* = 14.2, ²*J* = 1.4 Hz). ¹³C NMR spectrum, *δ*_C, ppm: 25.5 (C⁴), 27.9 (C³), 68.2 (C⁵), 70.2 (OCH₂), 76.8 (C²), 86.3 (CH₂=), 151.8 (OCH=). Found, %: C 65.56; H 9.47. C₇H₁₂O₂. Calculated, %: C 65.60; H 9.44.

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