Russian Journal of Organic Chemistry, Vol. 39, No. 9, 2003, pp. 1356–1357. Translated from Zhurnal Organicheskoi Khimii, Vol. 39, No. 9, 2003, pp. 1428–1429.

SHORT COMMUNICATIONS

Synthesis of 1,2-Divinyloxypropenes from Glycerol and Acetylene in the Superbasic System CsF–NaOH–DMSO

B. A. Trofimov[1], S. F. Malysheva[1], N. K. Gusarova[1], A. A. Tatarinova[1], and J. Henkelmann[2]

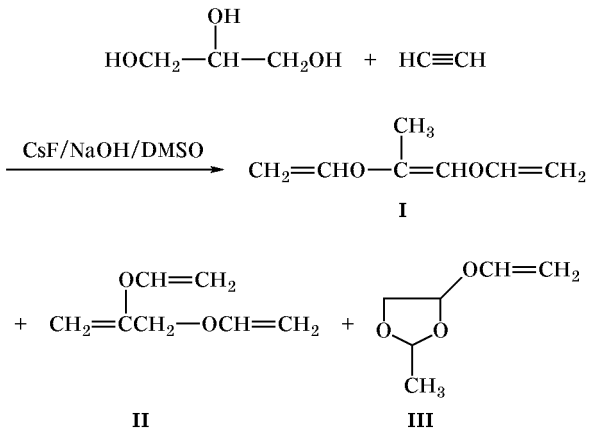
[1] *Favorskii Irkutsk Institute of Chemistry, Siberian Division, Russian Academy of Sciences, ul. Favorskogo 1, Irkutsk, 664033 Russia*

[2] *BASF Actiengesellschaft, Ammonia Laboratory, Ludwigshafen, Germany*

Received March 27, 2003

1,2-Divinyloxypropene (**I**) and 2,3-divinyloxypropene (**II**) were obtained for the first time [1] in an overall yield of 68% by heating at 100–110°C of a mixture of glycerol and acetylene in the superbasic system KOH–DMSO which turned out to be efficient in the vinylation reactions [2]. Propenes **I** and **II** were synthesized in a high-pressure reactor using a considerable excess of KOH (90–130 mol %) relative to glycerol. Under these conditions, 2-methyl-4-vinyloxymethyl-1,3-dioxolane (**III**) was also formed in up to 9% yield [1].

We have found that the superbasic system CsF–NaOH–DMSO is more advantageous in the synthesis of propenes **I** and **II**. By heating at 100°C of a mixture of glycerol with CsF (30 mol %) and NaOH (30 mol %) in DMSO under acetylene pressure we obtained propenes **I** and **II** in an overall yield of 73%, and the yield of dioxolane **III** was 7%.



When potassium hydroxide (30 mol %) was used instead of the catalytic couple CsF–NaOH, almost no propenes **I** and **II** were formed. In the reaction mixture we identified dioxolane **III** and 1,2,3-trivinyloxypropane (**IV**, exhaustive glycerol vinylation product); their yields were 11 and 9%, respectively.

Divinyloxypropenes **I** and **II** are formed via elimination of vinyl alcohol from trivinyl ether **IV** and prototropic isomerization of 2,3-divinyloxypropene by the action of superbase, as was experimentally shown by us previously [1, 3].

Thus our results indicate that the catalytic superbasic system CsF–NaOH–DMSO is superior to KOH–DMSO in the vinylation of glycerol.

1,2-Divinyloxypropene (I) and 2,3-divinyloxypropene (II). A mixture of 10 g (108.7 mmol) of glycerol, 1.48 g (37 mmol) of NaOH, and 5.62 g (37 mmol) of CsF in 100 ml of DMSO was stirred for 30 min at 100–110°C and was then transferred into a rotating high-pressure reactor. The mixture was heated for 5 h at 100°C under acetylene pressure (initial pressure at room temperature 14 atm, maximal pressure 30 atm, residual pressure 5 atm), diluted with 100 ml of water, and extracted with ether. The extract was washed with water, dried over K_2CO_3, and evaporated, and the residue was subjected to fractional distillation under reduced pressure to isolate 11.1 g of a product, bp 55–62°C (10 mm) containing (according to the GLC data), 10 g (73%) of propenes **I** and **II** (ratio of the *Z* and *E* isomers of propene **I** and propene **II** 40:53:7, respectively) and 1.1 g (7%) of dioxolane **III**. In the reaction performed with 30 mol % of KOH instead of CsF–NaOH, other conditions being

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equal, we isolated 11% of dioxolane **III** and 9% of trivinyl ether **IV**. The physical constants of compounds **I**–**IV** and their spectral parameters (IR, ^{1}H and ^{13}C NMR) were consistent with those reported in [1].

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