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ONE-POT SYNTHESIS OF DIVINYLOXY PROPENES BY REACTION OF GLYCEROL WITH ACETYLENE

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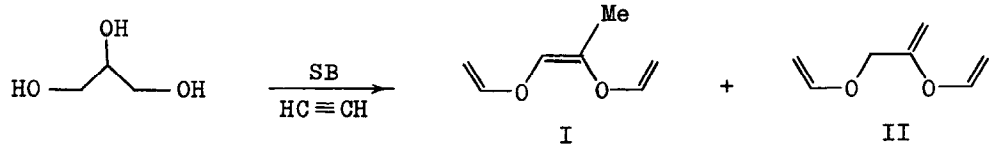
Summary: The synthesis of 1,2-divinyloxy-1-propene (I) and 1,2-divinyloxy-2-propene (II), via the reaction of glycerol with acetylene in the potassium hydroxide-hexamethylphosphoramide (HMPA) system is reported.

Glycerol is known to undergo the conventional base-catalysed vinylation by acetylene to produce expected vinyl ethers and 1,3-dioxolanes,the yields and ratio of which being dependent on the reaction conditions[1,2]. Recently new families of superbase-catalysed acetylene reactions have been discovered and now are being rapidly developed[3-5].

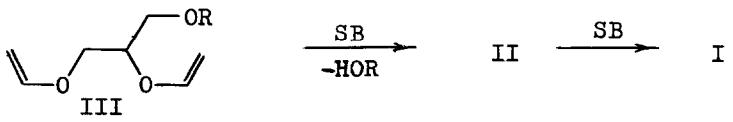
In this letter we report an unusual transformation of glycerol when it reacts with acetylene in the superbasic catalytic system KOH-HMPA. In this case, 1,2-divinyloxy-1-propene (I) and 1,2-divinyloxy-2-propene (II) are formed in about 12% yield together with the conventional products,4-hydroxy-2-methyl-1,3-dioxolane and 2-methyl-4-vinyloxy-1,3-dioxolane (IV); 2-vinyloxy-1,3-butadiene (V), a known hydratotrimer of acetylene[3,4], is also present in the reaction mixture.



I II

SB = superbase = KOH/HMPA cis:trans 5:6

The rationalization of this result is shown in the scheme below



III

R = H, $OCH{=}CH_2$

Under the action of superbase (SB) the intermediate vinyl ethers (III) seem to be capable of dehydration or elimination of vinyl alcohol (R = $OCH=CH_2$), to give II which subsequently undergoes prototropic isomerization into I.

The experimental details are as follows. Glycerol (10 g), KOH (5 g), HMPA (100 ml) were loaded into rotating a 1-l autoclave, saturated with acetylene under the pressure 10 atm, and heated (150-160°C) with rotation of the autoclave for 2 h. After flash distillation, 3.4 g of the fraction with b.p.51-59° (10 mm Hg) was collected. According to GLC, the fraction contains I (24% trans and 20% cis) and II (4%), IV (30%) and V (20%); trans-I (isolated by PGLC): n_D^{20} 1.4470, d_4^{20} 0.8930.

The structures of I and II were assigned basing on NMR (^1H, ^{13}C), IR, and mass-spectroscopic data. In the ^1H NMR spectrum of trans-I the following signals are observed (ppm): 1-$OCH=CH_2$ - 6.37 q (H_α), 4.49 q (H_β-trans), 4.16 q (H_β-cis); 2-$OCH=CH_2$ - 6.29 q (H_α), 4.35 q (H_β-trans), 4.07 q (H_β-cis); 6.12 q - H_1; 1.81 d - Me ($^4J_{CH_3C=CH}$ = 1.2 Hz). The vinyloxy group signals were assigned[6] the following constant for $^2J_{gem}$: 2.5 Hz for 1-$OCH=CH_2$ and 1.5 Hz for 2-$OCH=CH_2$. The ^1H NMR spectrum of cis-I is very similar to trans-I: 1-$OCH=CH_2$ - 6.37 q (H_α), 4.37 q (H_β-trans), 4.09 q (H_β-cis); 2-$OCH=CH_2$ - 6.35 q (H_α), 4.37 q (H_β-trans), 4.09 q (H_β-cis); 5.75 q - H_1; 1.75 d - Me ($^4J_{CH_3-C=CH}$ = 1.2 Hz). The assignment of vinyloxy group signals is the same as in trans-I: $^2J_{gem}$ = 2.2 Hz (1-$OCH=CH_2$) and 1.8 Hz (2-$OCH=CH_2$). ^1H NMR spectrum of II: 2-$OCH=CH_2$ - 6.40 q (H_α), 4.69 q (H_β-trans), 4.35 q (H_β-cis), $^2J_{gem}$ = 1.6 Hz; 1-$OCH=CH_2$ - 6.37 q (H_α), 4.17 q (H_β-trans), 4.35 q (H_β-cis), $^2J_{gem}$ = 2.2 Hz; 4.39 d and 4.31 d - CH_2, $^2J_{gem}$ = 2.6 Hz, 4.09 s - 3-CH_2.

^{13}C NMR spectral data in ppm are as follows; trans-I: 150.22 and 148.71 - C_α^2 and C_α^3; 143.30 - C_2; 129.00 - C_3, 93.15 - C_β^3; 89.99 - C_β^2; 13.00 - C_1. cis-I: 149.90 and 148.98 - C_α^2 and C_α^3; 136.68 - C_2; 126.33 - C_3; 91.00 - C_β^3; 91.41 - C_β^2; 15.16 - C_1. II: 156.83 - C_2; 151.36 and 146.43 - C_α^1 and C_α^2; 96.36 - C_β^2; 89.60 - C_3; 87.87 - C_β^3; 67.71 - C_1.

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