

SHORT
COMMUNICATIONS

Unusual Dimerization of Acetylene γ -Hydroxyaldehydes

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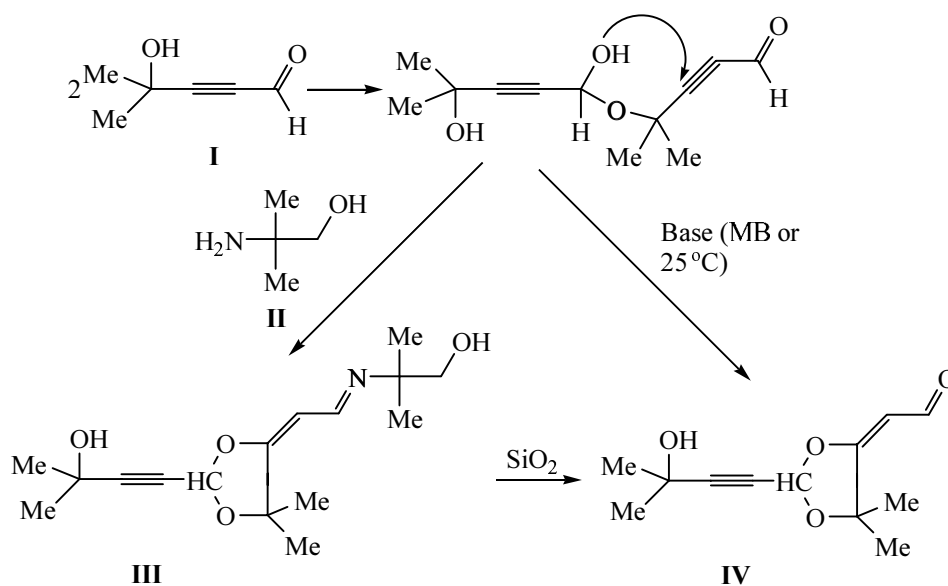
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Acetylene γ -hydroxyaldehydes add primary amines at the carbonyl group affording acetylene azomethines [1]. We unexpectedly found that reaction between 4-hydroxy-4-methyl-2-pentynal (**I**) with 2-amino-2-methyl-1-propanol (**II**) in CHCl_3 (25°C) instead of expected azomethine $\text{Me}_2\text{C}(\text{OH})\text{C}\equiv\text{CCH}=\text{NC}(\text{Me}_2)\text{CH}_2\text{OH}$ or the product of its intramolecular cyclization, the corresponding 1,3-oxazolidine, afforded azomethine of 1,3-dioxolan **III** in 70% yield (^1H NMR data). The chromatographic treatment on a column charged with SiO_2 provided dioxolan **IV**, product of γ -hydroxyaldehyde **I** dimerization formed in keeping with assumed scheme. The structure of dioxolan **IV** was proved by IR and NMR spectroscopy (HMBC, HSAQ).

The reaction readily occurred also in the presence of catalytic amounts (5 mol%) of 2-amino-2-methyl-1-propanol, 2-aminopyridine, or triethylamine. The most efficient was 2-aminopyridine that ensured a quantitative yield of the product. At the use of microwave irradiation the dimerization is strongly accelerated (2 h at 25°C or 2 min at microwave irradiation in an unmodified microwave oven of 700 W power). 2-(1-Propynyl)-1,3-dioxolan described in the literature was obtained in 22% yield by addition of ethylene glycol to 1-methoxybut-1-en-3-yne catalyzed by sodium glycolate [2].

[2-(3-Hydroxy-3-methylbut-1-ynyl)-5,5-dimethyl[1,3]dioxolan-4-ylidene]acetaldehyde (**IV**). A



solution of 0.57 g (5 mmol) of aldehyde (I) and 0.45 g (5 mmol) of 2-amino-2-methyl-1-propanol in 5 ml of CHCl_3 was kept at room temperature for 2 h. On removing the solvent the residue (0.97 g) was subjected to column chromatography (SiO_2 , CHCl_3 - CH_3OH , 30:1). We obtained 0.51 g (52%) of dioxolan IV as oily liquid. IR spectrum, ν , cm^{-1} : 1650 (CH=O, C=CH), 2245 (C \equiv C), 3400 (OH). ^1H NMR spectrum of *Z*-isomer, δ , ppm: 1.45 s and 1.59 s [6H, (CH $_3$) $_2$], 1.55 s [6H, (CH $_3$) $_2$ COH], 2.65 br.s (1H, OH), 5.08 d (1H, =CH, 3J 8.0 Hz), 6.11 s (1H, H 2), 9.92 d (1H, CH=O). ^{13}C NMR spectrum, δ , ppm: 25.32 and 26.43 [(CH $_3$) $_2$], 30.83 [(CH $_3$) $_2$ COH], 64.84 (C 3), 75.22 (C 1), 83.82 (C 5), 93.56 (C 2), 95.44 (C 2), 98.53 (=CH), 175.13 (C 4), 189.41 (CH=O). ^1H NMR spectrum of *E*-isomer, δ , ppm: 1.37 s and 1.48 s [6H, (CH $_3$) $_2$], 1.67 s

[6H, (CH $_3$) $_2$ COH], 5.59 d (1H, =CH, 3J 8.0 Hz), 6.08 s (1H, H 2), 9.76 d (1H, CH=O). Found, %: C 64.40; H 7.50. $\text{C}_{12}\text{H}_{16}\text{O}_4$. Calculated, %: C 64.27; H 7.19.

IR spectrum was recorded on spectrophotometer Specord 75IR. ^1H and ^{13}C NMR spectra were registered on spectrometer Bruker DPX-400, internal reference HMDS, solvent CDCl_3 . As sorbent for column chromatography was applied silica gel Merck 60 (70–230 mesh).

REFERENCES

1. Medvedeva, A.S., Safronova, L.P., Chichkareva, G.G., and Voronkov, M.G., *Izv. Akad. Nauk, SSSR, Ser. Khim.*, 1976, p. 121.
2. Volkov, A.N. and Khudyakova, A.N., *Zh. Org. Khim.*, 1975, vol. 11, p. 43.