LETTERS TO THE EDITOR

CYCLIZATION OF 3-METHYL-3-BUTEN-1-OL

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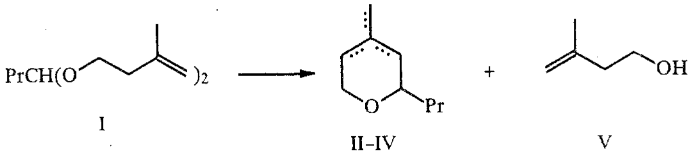
It is known that acetals of homopropargyl alcohol undergo cyclization to 4-X-5,6-dihydro-2H-pyrans under the influence of an equimolar amount of TiX_4(X = Cl, Br) [1]. Only 4-X-tetrahydropyrans are formed from derivatives of homoallyl alcohols under similar conditions [1, 2].

In the case of 3-methyl-3-buten-1-ol butyral we observed that unsaturated cyclic ethers can also be obtained from such starting compounds under the most diverse conditions: by heating in the presence of catalytic amounts of p-toluenesulfonic acid (65°C), without a catalyst (180-200°C), and on the surface of anhydrous aluminum sulfate.



The last variation is the most efficient — the reaction takes place at 20°C and is complete in 1 h. A mixture of isomers, among which 2-propyl-4-methylenetetrahydropyran (45-80%) and 3-methyl-3-buten-1-ol predominate, is formed in all cases.

This sort of cyclization is evidently characteristic precisely for acetals of homoallyl alcohols, since the allyl derivatives remain virtually unchanged under the examined conditions.

Acetal I was synthesized from alcohol V and butanol (2:1) in the presence of $CaCl_2$ by the method previously used to obtain acetals of aromatic aldehydes [3]. It was obtained in 55% yield and had bp 160-162°C (60 hPa), n_D^{20} 1.4911, and $C_{14}H_{26}O_2$. PMR spectrum (CCl_4): 0.88 (3H, s, CH_3), 1.41 (4H, m, $2CH_2$), 1.66 (6H, s, $2CH_3$), 2.16 (4H, t, $2CH_2$), 3.46 (4H, t, $2CH_2O$), 4.36 (1H, t, CH), 4.64 (4H, s, $2CH_2$).

The reaction products were identified from their retention times by comparison with the values for samples obtained by a known method [4]. Analysis by GLC was accomplished with a Khrom-5 chromatograph [flame-ionization detector, 200 by 0.3 cm column, 7% XE-60 on Chromosorb W-HP (80-100 mesh) as the sorbent, column temperature 120-160°C].

A 0.1-g sample of I was applied to 1 g of calcined (at 300°C for 6 h) powdered aluminum sulfate, and the mixture was shaken and allowed to stand for 1 h at 20°C. Acetone (3 ml) was then added, and the mixture was filtered. The solid material on the filter was washed twice with 3-ml portions of acetone and analyzed by GLC.

A mixture of 1.1 g of acetal I, 6 ml of hexane, and 3 mass % p-toluenesulfonic acid was refluxed for 12 h, after which 5 ml of water was added, and the organic layer was separated, dried with $MgSO_4$, and analyzed by GLC.

A 2-g sample of acetal I was heated at 200°C for 3 h and then analyzed by GLC. In all cases acetal I underwent 100% conversion to a mixture of II-IV and V.

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