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BRIEF COMMUNICATIONS

Synthesis of Dioxolanylmethyl Methacrylates from Aldehydes, Glycerol, and Methyl Methacrylate

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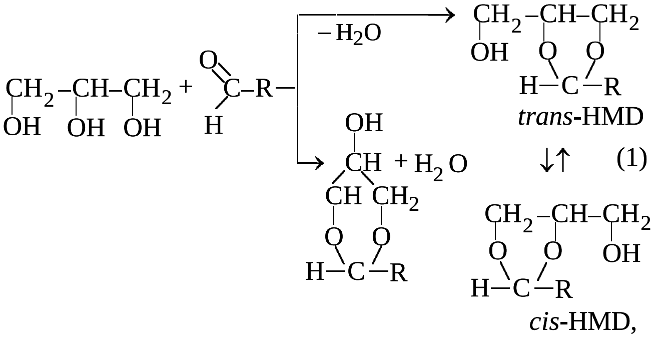
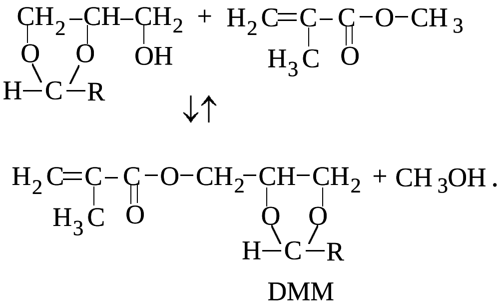
Abstract—The feasibility of preparing dioxolanylmethyl methacrylates from aldehydes in two stages (without purification of intermediate 4-hydroxymethyl-1,3-dioxane) was examined.

Proceeding with studies on synthesis of dioxolanylmethyl methacrylates (DMMs), we examined the feasibility of their synthesis from aldehydes. Previously [1, 2] we found conditions for preparing DMMs from ketones and revealed specific features of preparation of 4-hydroxymethyl-2-alkyl-1,3-dioxolanes (HMDs), intermediates in DMM synthesis. We suggested that these compounds are formed as mixtures of isomers. The goal of this study is synthesis of DMMs both from separate HMD isomers and their mixture.

The two-stage procedure for preparing dioxolanylmethyl methacrylates from aldehydes can be represented by the scheme

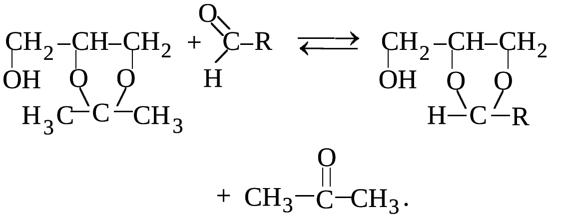


(1)



(2)

Studies were performed with acetaldehyde (in the form of paraldehyde) and propionaldehyde, following the previously described synthetic and analytical procedures [2]. First, we examined the possibility of formation of isomeric 1,3-dioxan-5-ol. For this purpose we performed an independent synthesis of HMD from 4-hydroxymethyl-2,2-dimethyl-1,3-dioxolane:



(3)

Formation of the six-membered ring in reaction (3) is impossible, and the occurrence of reaction (3) can be judged from the release of acetone. The reaction product in the chromatogram gave the same peaks with the same retention time as the HMD prepared from glycerol. This fact confirms the assumption about the isomeric composition of HMD. Furthermore, these results showed that reaction (3) can be used for preparing 1,3-dioxolane alcohols difficultly accessible by the direct route, since reaction (3) occurred under fairly mild conditions. We also prepared HMD from glycidol, i.e., by reaction also excluding formation of 1,3-dioxan-5-ol. The retention times of HMD isomers prepared by this reaction and from glycerol coincided. These facts convincingly prove that reaction of glycerol with aldehyde does not yield 1,3-dioxan-5-ol, and HMD is formed as a mixture of isomers.

To elucidate the full pattern of the two-stage synthesis, it was important to determine whether all the isomers undergo ester interchange. For this purpose, we performed thorough fractional distillation of HMD prepared from glycerol and propionaldehyde under

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reduced pressure in a nitrogen atmosphere on a 60-cm column. Separation gave two low-boiling fractions (68–70°C at 5–7 mm Hg and 72–74°C at 5–6 mm Hg) and bottoms.

Chromatographic analysis of the fractions performed on two different stationary phases showed that the first fraction was a practically individual substance (92–95% purity). The second fraction was, apparently, a mixture of *cis* and *trans* isomers (approximately 66 and 28%) with an impurity of a third isomer. Published data on isomerism of heterocyclic compounds suggest the possibility of formation of *cis* and *trans* isomers; with different substituents, the number of isomers increases to four (two isomers for each of the *cis* and *trans* forms) [3, 4]. The first fraction, practically consisting of a single isomer, was analyzed by ^{1}H NMR spectroscopy (Tesla BS-567 spectrometer, 100 MHz). The spectrum was consistent with the structure of 1,3-dioxolane containing one hydroxy group. The signal at 3.4 – 4.2 ppm (relative to HMDS) corresponds to the 1,3-dioxolane ring [5]. Thus, the ^{1}H NMR and GLC data showed that a rather complex mixture of isomers was formed. Detailed study of its composition is beyond the scope of this work.

The second stage involving reaction of HMDs with methyl methacrylate (MMA) was performed under conditions of ester interchange with HMDs based on ketones [1]. The reaction vessel was equipped with a distillation column. HMD was taken as a single isomer and as an isomeric mixture. The results were as follows. After removal of unchanged reactants by distillation under reduced pressure in a nitrogen atmosphere, DMM was obtained as a mixture of two isomers, irrespective of whether the initial HMD was an individual isomer or an isomeric mixture. It should be noted that the ratio of the HMD isomers is determined by reaction conditions, mainly by the nature of the acid catalyst. Thus, to prepare dioxolanylmethyl methacrylates from glycerol, MMA, and aldehydes, there is no need to separate the isomers formed in the first stage. The yield of DMM based on glycerol is about 60%. The physicochemical characteristics of one of DMMs, 2-methyl-1,3-dioxolan-4-ylmethyl methacrylate, are as follows: colorless transparent liquid; bp 84 – 86°C at 5 – 6 mm Hg; d_4^{20} = 1.079 g cm^{-3}; n_D^{20} = 1.4540; molecular refraction: calculated 46.35, found 46.40.

CONCLUSIONS

(1) Dioxolanylmethyl methacrylates are formed from aldehydes, glycerol, and methyl methacrylate as mixtures of two isomers, irrespective of whether the intermediate 4-hydroxymethyl-1,3-dioxolane was taken as individual isomer or isomeric mixture.

(2) 1,3-Dioxan-5-ol is not formed in reaction of aldehydes with glycerol.

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