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REDOX TRANSFORMATIONS OF CYCLIC ACETALS

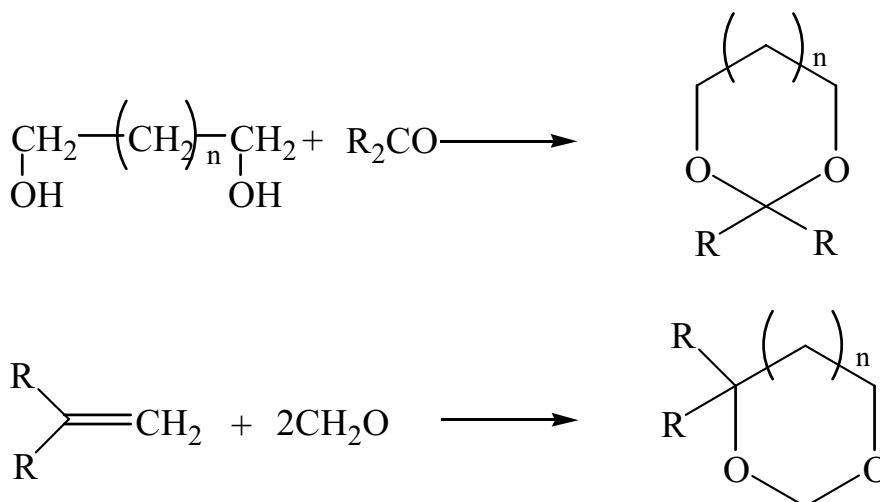
INTRODUCTION

Oxygen-containing compounds, exactly formaldehyde, acetone, methylethylketon, ethylene oxide, ethylenglycol, propylene oxide and 1,3-propylenglycol, pentaerythrite and others - are the most important large-scale products of the modern petrochemical synthesis [1].

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PREVIOUS DATA RETRIEVAL TECHNIQUES

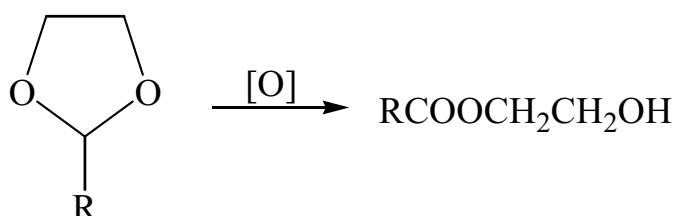
Last years the production of a number of cyclic acetyals based on the above products is rapidly developing [2]. Besides that the various 4,4-disubstituted-1,3-dioxanes are obtained according to Prins reaction: by olefins condensation with formaldehyde [3].



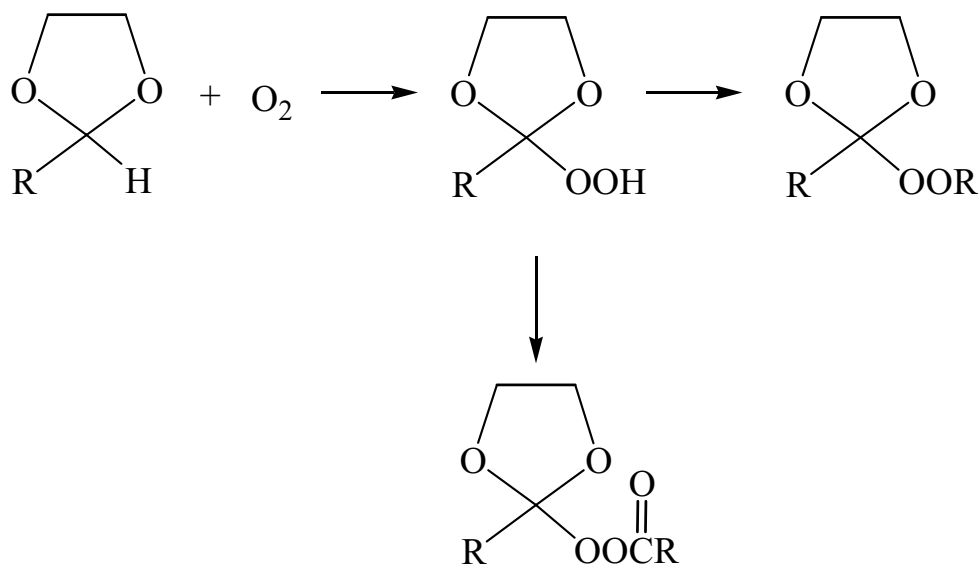
That is why now cyclic acetals are becoming cheap and available products and development of the methods for synthesis of polyfunctional compounds based on them is an important and interesting task.

PROPOSED METHOD

The systematic investigations [4-6] proved that under influence of oxygen, ozone and a number of other organic and inorganic oxidants cyclic acetals can selectively form the corresponding glycol monoethers.



As a rule, acetal hydroperoxides are the intermediate products, which can be used for obtaining of polymerization initiators.

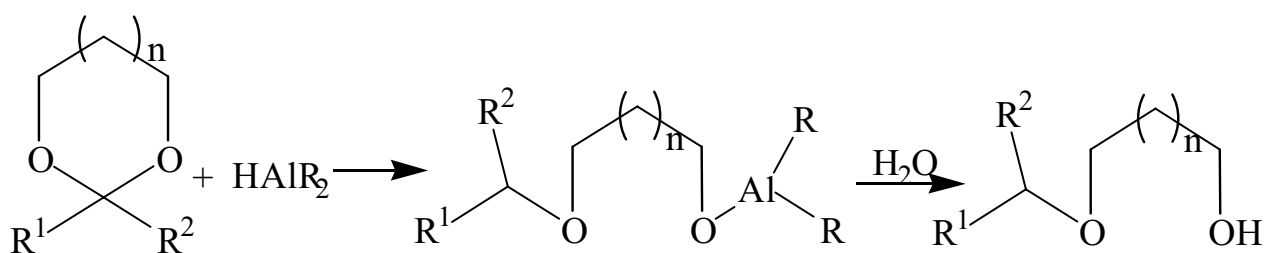


In some cases the final products – glycol monoethers - are hardly obtained by other methods, so oxidation of the cyclic acetals is a convenient and promising method for synthesis of such structures.

The processes of cyclic acetals reduction in liquid phase proceed under influence of organometallic compounds [7]. Interaction of cyclic acetals with organoaluminum compounds is studied in details.

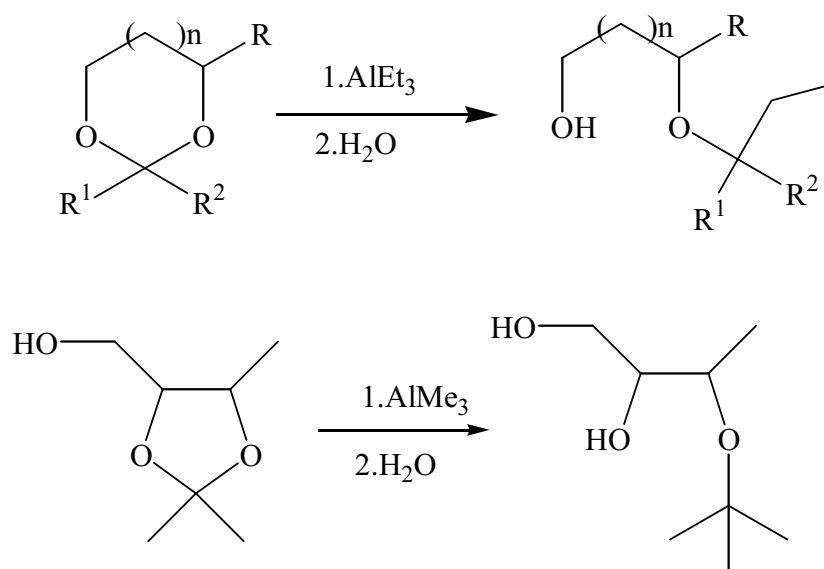
Organoaluminum compounds are known to be efficient, specific and highly selective reductants which are able to reduce ethyleneglycol acetals and ketals to the corresponding monoethers [8-10]. Now glycol monoethers are widely used in perfume production, in paint and varnish industry and for synthesis of important biologically active substances, sugars, antibiotics.

Cyclic acetals and ketals at 70-80 °C are easily reduced by diisobutylaluminumhydride and diethylaluminumhydride to the corresponding aluminates, which in the process of hydrolysis give oxiethers [11]. Transformation of a five-members cycle into a six-members heterocycle of acetals and ketals doesn't result in a notable change of their reaction ability.

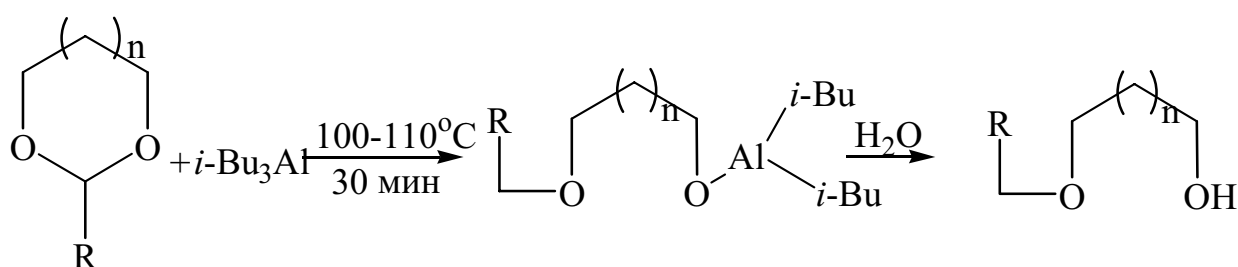


Triethylaluminum and trimethylaluminum react with cyclic acetals and ketals when boiling in hexane, and highly regioselectively form the products of reductive alkylation [12, 13]. In the conditions described the cyclic formals (1,3-dioxan and 1,3-dioxolane) don't react with triethylaluminum. If in the heterocycle of 1,3-dioxacyclane there is an alkyl substituent in the fourth position triethylaluminum alkylates the second atom of carbon [11, 14]. In 1,3-dioxacyclane molecule sterical screening of the neighbour oxygen atom by alkyl group doesn't allow aluminum atoms to fulfil coordination from the side of $C^2-O^3-C^4$ bonds, and

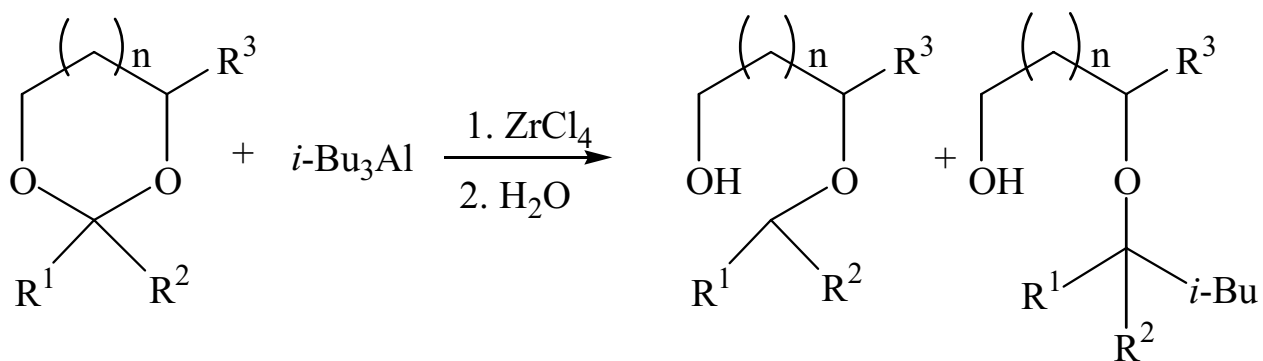
as a result the cycle is splitted at O¹-C² bond only and the ethers with the primary alcohol group are formed.



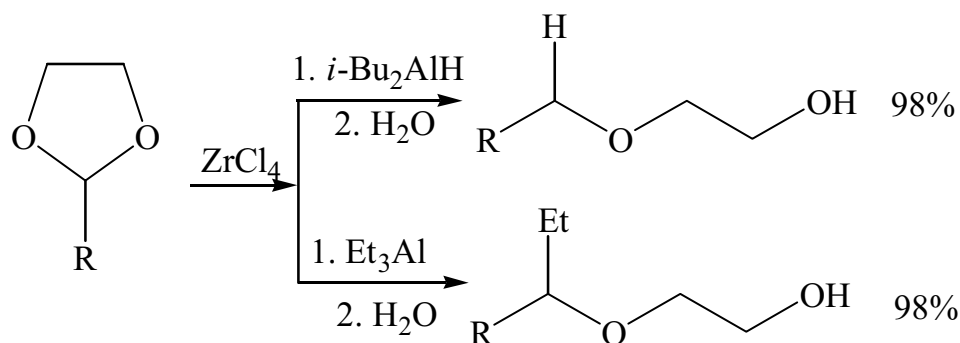
Differently from the above trialkylaluminums, trimethylaluminum and triethylaluminum, triisobutylaluminum reacts with cyclic acetals only when boiled in toluene and as a result only the products of reductive splitting are formed. The reaction is accompanied by isobutylene separation. Probably in the conditions of this reaction triisobutylaluminum is transformed into diisobutylaluminumhydride which further reacts according to the usual scheme [15].



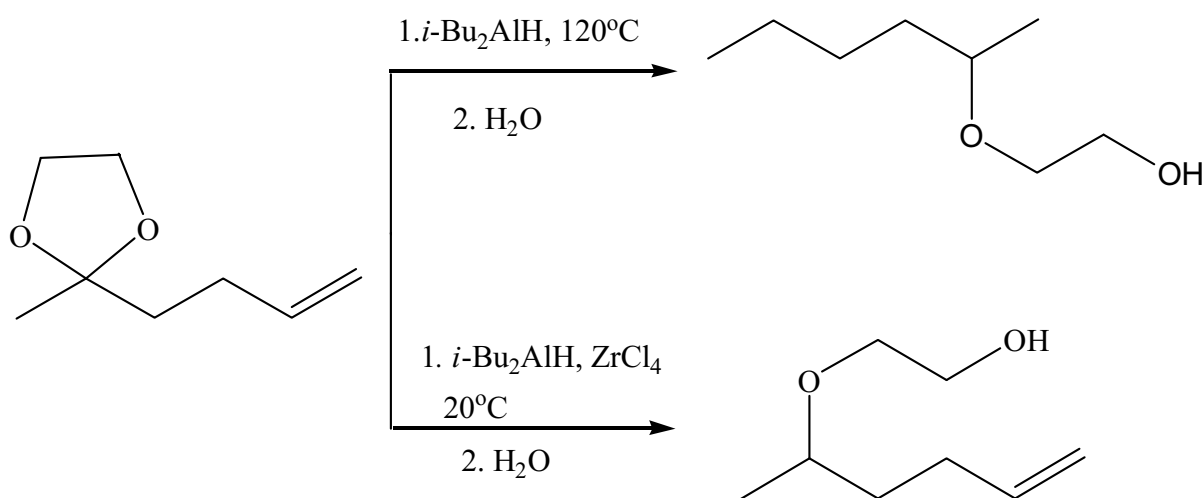
In presence of catalytic amounts of $ZrCl_4$ or $Ni(acac)_2$ triisobutylaluminum reacts with cyclic acetals at room temperature in hexane and besides the products of reductive splitting the products of reductive alkylation are formed with total yield not less than 70% [16].



Though diisobutylaluminumhydride can easily split cyclic acetals at 60–70°C, presence of catalytic amounts of ZrCl₄ allows to decrease the reaction temperature to 20–25°C and to reach quantitative yields of monoethers.



Hydroalumination of diisobutylaluminumhydride cyclic acetals with terminal double bond proceeds at 120°C with simultaneous opening of the acetal ring. In presence of catalytic amounts of ZrCl₄ the selective reductive splitting of diisobutylaluminumhydride dioxolan cycle takes place at room temperature, but the terminal bond is not affected.



As a whole on the base of cyclic acetals a wide range of organic reagents can be obtained, which can be efficiently used to intensify the processes of oil delivery, transportation and refining.

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