

**CHEMICAL TRANSFORMATIONS OF DIOLS  
AND CYCLIC ETHERS. XXXV\***  
**Dehydration of Diols on Copper Catalysts**

By

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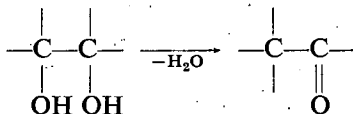
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The paper deals with the dehydration of certain di-primary and primary-secondary diols (ethylene glycol, propylene glycol, 1,3-propanediol, 1,3-butanediol, 1,4-butanediol, 1,4-pentane-1,5-diol, 1,5-pentane-1,5-diol and 1,6-hexane-1,6-diol) on the action of copper catalysts. The rates of dehydration of the 1,3-, 1,4-, 1,5- and 1,6-diols are significantly higher than those of the 1,2-diols. Under the experimental conditions used, the 1,3-diols are dehydrated to oxo compounds containing the same number of carbon atoms, and the 1,4-, 1,5- and 1,6-diols are dehydrated to cyclic ethers.

In this paper an account is given of the results obtained in a study of the transformations of diols on copper catalysts. The dehydration of certain 1,3- and 1,4-diols on the action of metal catalysts was reported earlier [1—6]. The present work deals with the dehydration of some 1,2-, 1,5- and 1,6-diols in the presence of Cu/Al and Cu/SiO<sub>2</sub> catalysts; the main aim of this work was to study the regularities of the copper-catalyzed dehydration of the diols under the same experimental conditions, as a function of the relative positions of the two hydroxy groups.

To begin with, the more important regularities established in connection with the dehydration of diols are summarized below on the basis of the literature data.

In the presence of various dehydrating agents, 1,2-diols in either liquid or gas phase are converted (with accompanying rearrangement) mainly to oxo compounds [7, 8]:

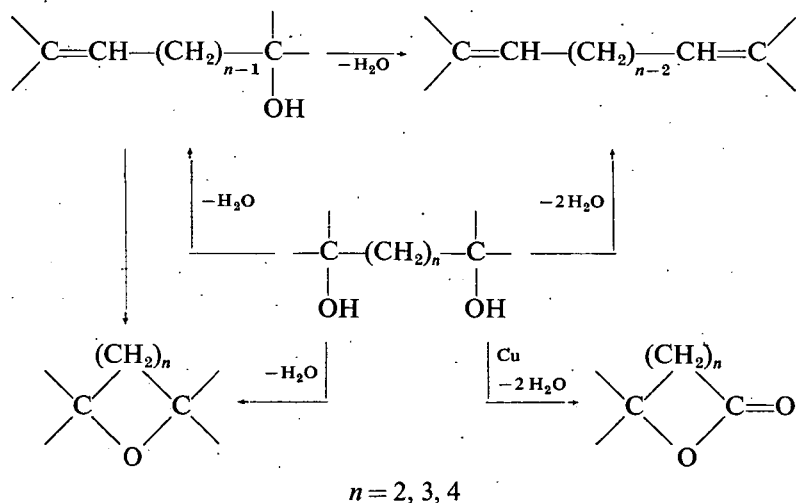


Since the discovery of the reaction [9, 10], a considerable amount of experimental work by various research groups has shown conclusively that the above process is a widespread reaction of general validity for vicinal diols, *i.e.* it is one of their characteristic reactions. This finding, which today requires certain amendments, is to be found in various textbooks, reference-books and monographs [7, 11—15,

\* Part XXXIV: F. Notheisz, M. Bartók, V. Rempert: Acta Phys. et Chem. Szeged **18**, 197 (1972).

etc.]. Our results to date show that the study of the exactness of the above regularity and its further generalization has proved to be a useful research programme. Under certain conditions 1,3-diols, too, are converted to oxo compounds with the same number of carbon atoms [1, 6]. Although similar observations were also made at the turn of the century [16, 17], no special attention was devoted to this theoretically important question.

1,4-, 1,5- and 1,6-diols are dehydrated to cyclic ethers, dienes and unsaturated alcohols [7, 18, 19], while on copper catalysts they are converted to lactones [20]:



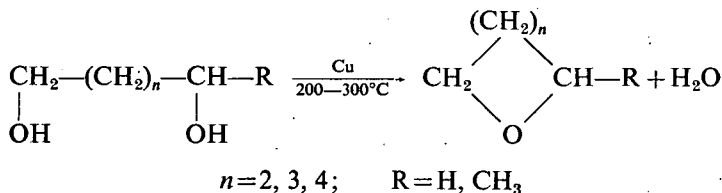
Of course, the extent of the individual reactions is significantly affected, and in some cases even determined, by the number of methylene groups  $n$ , by the order of the carbon atoms bonded to the hydroxy groups, and by the nature of the catalyst.

Of the diols, the dehydrations of mainly 1,4-butanediol, 1,3-butanediol and 3-methyl-1,3-butanediol have been dealt with, and the results are collected in some monographs [7, 18, 21]. The aim of the investigations was the preparation of 1,3-butadiene and isoprene. The most suitable catalysts for these purposes proved to be phosphoric acid and various inorganic phosphates. The dehydration of diols on metal catalysts has been dealt with in only one or two publications. Of these, mention should be made of the paper by PINES and STEINGASZNER [22] describing the dehydration of 1,4-butanediol and 1,5-pentanediol accompanied by the formation of cyclic ethers.

In our study of the dehydration of 1,3- and 1,4-diols on Cu/Al and Cu/SiO<sub>2</sub> catalysts, it was found that in the case of 1,3-diols three main reactions take place, depending on the structures of the 1,3-diols [3]: the formation of oxo compounds containing the same number of carbon atoms as the diols, 1,2-elimination and fragmentation processes. Under similar experimental conditions 1,4-diols are dehydrated with the formation of tetrahydrofuran homologues [2].

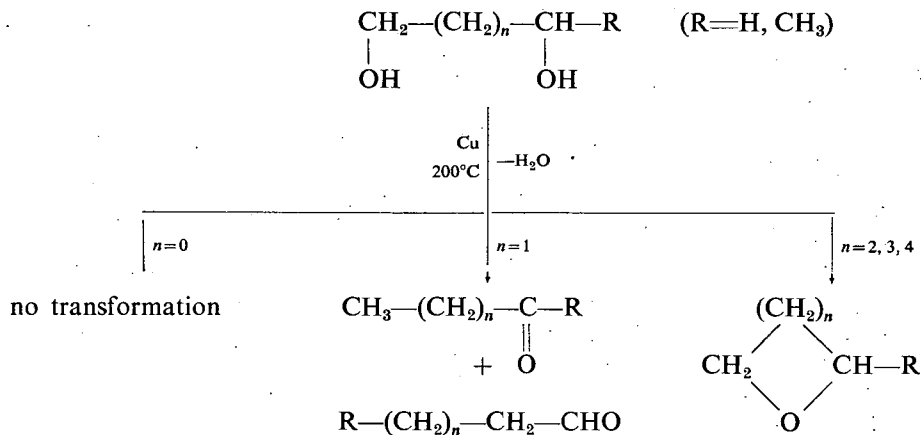


addition to oxa-cycloheptane as main product (ca. 40%) from hexamethylene glycol the formation of other so far unidentified compounds is also observed:



In the low-conversion transformation of 1,4-diols, oxy-oxo compounds and other so far unidentified products are also formed; the further study of these may provide useful information for elucidating the mechanism of dehydration of diols on metal catalysts.

Our experimental results therefore indicate that the studied diols are dehydrated on Cu/Al and Cu/SiO<sub>2</sub> catalysts in accordance with the following scheme:



The mechanisms of the observed processes will be dealt with in a later paper.

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ХИМИЧЕСКИЕ ПРЕВРАЩЕНИЯ ДИОЛОВ  
И ЦИКЛИЧЕСКИХ ЭФИРОВ. XXXV.  
ДЕГИДРАТАЦИЯ ДИОЛОВ НА МЕДНЫХ КАТАЛИЗАТОРАХ

*М. Барто́к, А. Молнар и Ф. Ноте́йс*

Исследована дегидратация некоторых ди-первичных и первично-вторичных диолов (этиленгликоль, пропиленгликоль, 1,3-пропандиол, 1,3-бутандиол, 1,4-бутандиол, 1,4-пентандиол, 1,5-пентандиол, 1,6-гександиол) на медных катализаторах. Скорость дегидратации 1,3-, 1,4-, 1,5- и 1,6-дио́лов значительно больше скорости дегидратации 1,2-дио́лов. При исследованных нами экспериментальных условиях 1,3-дио́лы превращаются в оксосоединения с одинаковым числом углеродных атомов, а 1,4-, 1,5- и 1,6-дио́лы дегидратируются в соответствующие органические окиси.