

**CHEMISTRY OF DIOLS AND CYCLIC ETHERS,
 XLV*. STERICALLY-HINDERED HYDROGEN-TRANSFER REACTIONS
 IN THE TRANSFORMATIONS OF 2-SUBSTITUTED
 1,3-PROPANEDIOLS ON A COPPER CATALYST**

By

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During the transformations of 2-*n*-butyl-, 2-isopropyl-, 2-*tert*-butyl-, 2-cyclohexyl- and 2-phenyl-1,3-propanediol (I–V) on a copper catalyst, unsaturated aldehyde (and unsaturated alcohol) is also formed besides the saturated compounds. In the case of V, the formation of the unsaturated compounds is the characteristic reaction. The product distribution can be interpreted in terms of the steric and electronic properties of the substituents.

In the course of our earlier investigations in connection with the mechanisms of the metal-catalyzed reactions of 1,3-diols, it was established that in the presence of copper catalysts the 1,3-diols are transformed to oxo compounds containing the same number of carbon atoms, or are cleaved to give two molecules of oxo compound (Fig. 1) [1, 2].

The final step of the dehydration process occurs *via* a hydrogen-transfer reaction between the α , β -unsaturated oxo compounds formed and the starting diol. Our results relating to diols containing a cyclohexane skeleton [3] showed that

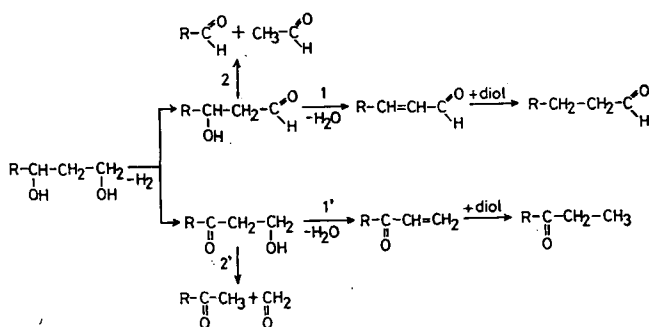
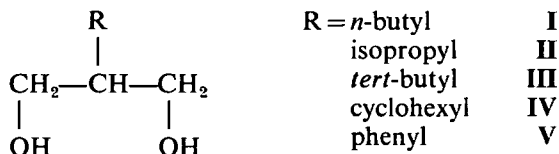


Fig. 1. Reaction pathways of 1,3-diols on copper catalysts.
 Pathway 1 and 1': dehydration Pathway 2 and 2': dealdolization

* Part XLIV: M. Bartók, Á. Molnár: Acta Chim. (Buda pest) 100, 203 (1979).

with certain compounds [2-(1-hydroxyethyl)-1-cyclohexanol and 2-(1-hydroxybutyl)-1-cyclohexanol] this step is hindered, and thus the intermediate unsaturated oxo compounds also appear among the products.

In our recent investigations, some new examples of this hindered hydrogen-transfer have been found. The present paper describes results obtained during the transformations of some 2-substituted 1,3-propanediols (I—V).



Our preliminary studies with 2-isopropyl-1,3-propanediol (II) on three different copper catalysts (Cu/Al, Cu/SiO₂, and Cu) demonstrated the otherwise expected fact that the ratio of the saturated and unsaturated compounds depends on the nature of the catalyst (Table I). Accordingly, since our aim was to study how

Table I
Product distribution of 2-isopropyl-1,3-propanediol (II) on copper catalysts
(conversion 100%)

Catalyst Temperature (C°)	Cu/Al 200	Cu/SiO ₂ 225	Cu 210
3-methylbutanal	8	15	19
2-isopropylpropenal	27	5	30
2,3-dimethylbutanal	37	50	21
3-methyl-1-butanol	6	13	13
2,3-dimethyl-1-butanol	12	14	6
2-isopropyl-2-propen-1-ol	5	—	8
unidentified	5	3	3

the properties of the substituent in position 2 (steric and electronic effects) influence the occurrence of the hydrogen-transfer, we carried out examinations on only a single catalyst. For this purpose the Cu catalyst prepared by reduction from CuO was selected, for, as indicated by the data in Table 1, this displayed the lowest activity in the hydrogen-transfer.

Experimental

Diols I, II and IV were prepared in a known way, by malonic ester synthesis and subsequent reduction with Li[AlH₄]. (I: b.p. 102—107 °C/5 torr; b.p. [4]: 105—108 °C/5 torr. II: b.p. 110—115 °C/5 torr; b.p. [5]: 114—116 °C/6 torr. IV: m.p. 93.5 °C; m.p. [5]: 94 °C.) In the preparation of III, the procedure described in [6] was followed, and the diol was then obtained by reduction (m.p. 59—61 °C; m.p. [5]: 61 °C). V was prepared by Li[AlH₄] reduction of diethylphenylmalonate, obtained by the method described in [7] (m.p. 44—48 °C; m.p. [8]: 48.5—49 °C).

The experimental technique and the preparation of the Cu catalyst were reported earlier [2]. Products were identified with the aid of a GC technique and IR and NMR spectroscopy. The aldehydes were also identified via precipitation of (2,4-dinitrophenyl)-hydrazones.

The experimental results are summarized in Tables I—V.

Table II

*Transformation of 2-n-butyl-1,3-propanediol (I)
on Cu catalyst at 250 °C (conversion 100%)*

Products	mol %
hexanal	22
2-methylhexanal	38
1-hexanol	16
2-methyl-1-hexanol	22
unidentified	2

Table III

*Transformation of 2-tert-butyl-1,3-propanediol (III)
on Cu catalyst at 250 °C (conversion 100%)*

Products	mol %
3,3-dimethylbutanal	32
2-tert-butylpropenal	13
2,2,3-trimethylbutanal	14
3,3-dimethyl-1-butanol	34
2,3,3-trimethyl-1-butanol	2
2-tert-butyl-2-propen-1-ol	2
unidentified	3

Table IV

*Transformation of 2-cyclohexyl-1,3-propanediol (IV)
on Cu catalyst at 270 °C (conversion 100%)*

Products	mol %
cyclohexylacetaldehyde	24
2-cyclohexylpropenal	26
2-cyclohexylpropanal	24
2-cyclohexylethanol	20
2-cyclohexyl-1-propanol	3
2-cyclohexyl-2-propen-1-ol	2
unidentified	1

Table V
Transformation of 2-phenyl-1,3-propanediol (V)
on Cu catalyst at 280 °C (conversion 100%)

Products	mol %
phenylacetaldehyde	9
2-phenylpropenal	34
2-phenylpropanal	5
2-phenylethanol	21
2-phenyl-1-propanol	3
2-phenyl-2-propen-1-ol	22
unidentified	6

Discussion

The experimental results in Tables I—V, and the comprehensive data in Table VI, lead to the following findings:

Table VI
Product distributions of the transformations of compounds I—V according
to the reaction pathways

Compound	Percentage amounts of products with the same number of carbon atoms as the diol			Percentage amounts of products obtained by dealdolization
	unsaturated	saturated	total	
I	—	60	60	38
II	38	27	65	32
III	15	16	31	66
IV	28	27	55	44
V	56	8	64	30

1. The straight-chain substituent (the *n*-butyl group in compound I) does not exert an inhibitory effect on hydrogen-transfer (Table II).

2. The branched-chain substituents (isopropyl and *tert*-butyl groups, II and III) impede hydrogen-transfer, and hence unsaturated aldehyde and (by reduction of this) unsaturated alcohol are also obtained in both cases (Tables I and III). In the case of III, the large bulk of the *tert*-butyl group not only affects this reaction, but at the same time increases the probability that the intermediate hydroxy-oxo compound will undergo further conversion by the other reaction pathway, *i.e.* dealdolization (Fig. 1, pathway 2 and 2'). The large extent of this side-reaction means that the effect of the *tert*-butyl group on hydrogen-transfer can not be examined, and accordingly can not be compared with that of the isopropyl group.

3. The cyclohexyl group influences hydrogen-transfer to a similar extent as do the branched-chain substituents (Table IV).

4. In the transformation of the diol (V) containing the phenyl group, strikingly large amounts of unsaturated compounds are formed (Table V). In our view, such

a marked increase in the inhibition can be ascribed to electronic factors. The conjugation effect between the phenyl group and the double-bond leads to such an electron-shift (e.g. the structure A in Fig. 2) that as a consequence the C—C double-bond becomes depleted in electrons. A similar situation results from the mesomerism between the C=C and C=O bonds (Fig. 2, B). The mechanism of the

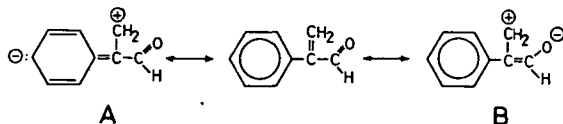


Fig. 2. Electron-shift effects occurring in 2-phenylpropenal

hydrogen-transfer was elucidated by EADON and SHIEKH [9]. In the first step, hydrogen is bound on the β -carbon atom of the α, β -unsaturated oxo compound, and therefore the above effects probably induce this significant phenomenon by decreasing the rate of this reaction step.

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ХИМИЯ ДИОЛОВ И ЦИКЛИЧЕСКИХ ЭФИРОВ, XLV.

Пространственно затрудненный переход водорода при превращении 2-замещённых 1,3-пропандиолов на медном катализаторе.

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При превращении 2-н-бутил-, 2-изопропил-, 2-трет-бутил-, 2-циклогексил-, 2-фенил-1,3-пропандиола (I—V) на медном катализаторе образуются ненасыщенный альдегид (и ненасыщенный спирт), кроме насыщенных соединений. В случае диола V, образование ненасыщенных соединений является характерным. Результаты объясняются пространственными и электронными факторами заместителей.