

Dehydration of Hex-3-ene-2,5-diol. Evidence for α -Protonation of an Aliphatic Dienol

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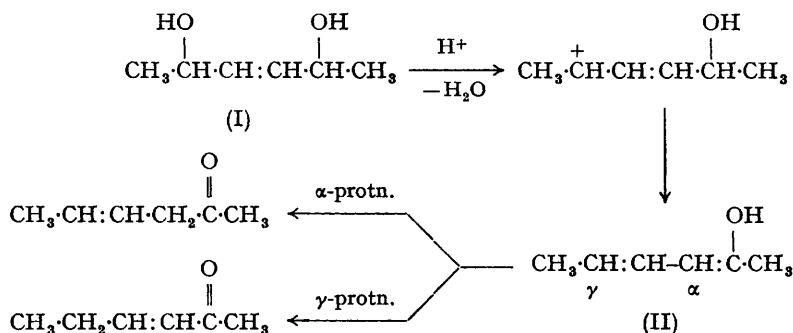
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THE considerable interest recently evident in the site of protonation of conjugated dienols,¹⁻³ prompts us to report here the results of a study on the acid-catalyzed dehydration of hex-3-en-2,5-diol (I).

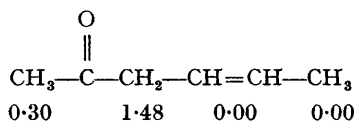
Dropwise addition of this diol to a boiling, 15% aqueous phosphoric acid solution concomitant with either steam distillation of the products or their entrainment with nitrogen, leads in moderate (*ca.* 50%) yield to a mixture of hexenones.

V.p.c. analysis of this mixture shows the non-conjugated isomer, hex-4-en-2-one, to be the predominant component, its percentage varying between 90 and 95%. The remainder is hex-3-en-2-one. This ratio is clearly not a thermodynamically determined distribution since equilibration of the ketones with toluene-*p*-sulphonic acid leads to a mixture (82%) in the conjugated isomer. Furthermore, a control experiment, in which a mixture of the two ketones was added to a boiling phosphoric acid solution, resulted in a distillate with the ratio of isomers unchanged.

A plausible mechanism for the dehydration would be:



The product is determined by the position of protonation of the intermediate dienol (II), and the predominance of the nonconjugated isomer is strong evidence for *almost exclusive* α -protonation. Confirmation for this selectivity was obtained by repeating the dehydration using D_3PO_4 in deuterium oxide. N.m.r. analysis of the v.p.c. purified hex-4-en-2-one showed the following distribution of deuterium:



The absence of deuterium at the vinyl positions confirms the formation of this isomer by exclusive α -protonation. Furthermore, the presence of more than one deuterium atom in the methylene group requires that the hex-4-en-2-one be undergoing enolization in the acid medium and again protonating at the α -position.†

Although the site of dienol protonation has been extensively studied in the alicyclic series,^{3a,b} only one other aliphatic system has been studied to date. It is reported^{3c} that 1-methoxybutadiene protonates "exclusively" at the γ -position. It is not possible to say at this time whether the contrast between that observation and the results

reported herein is due to the presence of additional methyl groups in the dienol (II), or a failure of the ether as a model system for the enol.

We gratefully acknowledge an NDEA Title IV fellowship (to S. R. K.) and the support of the National Science Foundation; and thank Professor F. McLafferty for helpful discussions.

(Received, September 18th, 1967; Com. 997.)

† An alternative rationale for the dehydration would be a 1,2-hydride shift in the initially formed cation. The dienol would thus be bypassed and the hex-4-en-2-one should form without incorporation of deuterium. Even were this to be the mechanism of the dehydration, however, the observed deuteration at the methylene group would require that the ketone enolize to (II) while in the reaction medium, and that the dienol deuteriate at the α -position.

¹ S. Malhotra and H. Ringold, *J. Amer. Chem. Soc.*, 1965, 87, 3228.

² N. Heap and G. A. Whitham, *J. Chem. Soc. (B)*, 1966, 164.

³ (a) N. A. J. Rogers and A. Sattar, *Tetrahedron Letters*, 1964, 1311; (b) N. A. J. Rogers and A. Sattar, *ibid.*, 1965, 1471; (c) T. N. Huckerby, N. A. J. Rogers, and A. Sattar, *ibid.*, 1967, 1113.