KINETICS OF THE ACID-CATALYZED INTERCONVERSION OF 3-HYDROXYCYCLOHEXANONE AND 2-CYCLOHEXENONE: REINTERPRETATION OF THE DECOMPOSITION OF 3-ALKOXYALLYLIC ALCOHOLS

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(Received 20 May 1961)

A very useful synthesis of α,β-unsaturated aldehydes and ketones involves reduction of the enol ether of a β-dicarbonyl compound and treatment of the resulting hydroxy enol ether with aqueous acid (equation 1). In the course of studying the mechanisms of several reactions which center about

7 O.P. Vig, T.P. Sharma and S.M. Mukherji, Chem. & Ind. 381 (1956).
9 R.F. Church, R.E. Ireland and J.A. Marshall, Tetrahedron Letters No. 1, 34 (1961); the authors are grateful to Professor Ireland for communicating his results to us prior to publication and for many stimulating discussions of this problem.
11 J.F. Arens and D.A. Van Dorp, Rec.Traz.Chim. 67, 973 (1948) prepared the intermediates by a different method.
β-hydroxy ketones, we have obtained kinetic information which clarifies the mechanism of reaction (1) and contradicts most previous interpretations.²⁻⁵,⁸,¹⁰

Treatment of 3-ethoxy-2-cyclohexenone¹² with lithium aluminum hydride furnished the alcohol (I, R=H), b.p. 69⁰/0.7 mm, nD¹⁰ 1.4843 (Found: C, 67.33; H, 9.84) which was stable toward alkali and in the absence of moisture. The compound was converted quantitatively to cyclohexenone (II, R=H) by 10⁻³ M hydrochloric acid at 0⁰ or by solution in water at room temperature; in neither case could any hydroxy ketone (III) be found. The alcohol (I, R=CH₃) b.p. 99.0-100.5⁰/5 mm (Found: C, 70.68; H, 10.60) prepared by reduction of 5,5-dimethyl-3-ethoxy-2-cyclohexenone¹¹ was equally sensitive to "hydrolysis".

The rate of formation of cyclohexenone from I (R=H) was followed spectrophotometrically at 25.2⁰ C in both phosphate and ammonia buffers between pH 7 and 9. The reaction is clearly acid-catalyzed, with first-order rate constants k₁ (min⁻¹) described by the equation: log k₁ = -0.945 pH + 5.52.

Reaction of dihydroresorcinol with β-mercaptoethanol and p-toluene-sulfonic acid in benzene furnished both the mono-hemithioketal, b.p. 90⁰/0.05 mm (Found: C, 55.61; H, 7.0), and the bis-hemithioketal, m.p. 61⁰

(Found: C, 51.72; H, 7.09). Reduction of the former with lithium aluminum hydride yielded the corresponding alcohol, b.p. 110-111°/0.5 mm (Found: C, 54.96; H, 8.11; S, 18.36) which was converted by refluxing in acetone with Raney nickel to 3-hydroxycyclohexanone (III, R=H) b.p. 75.0-75.5°/0.25 mm, nD 1.4831 (Found: C, 63.17; H, 8.89). The hydroxy ketone was not measurably affected by 10⁻³ M hydrochloric acid. In 0.10-5.0 M hydrochloric acid, either the hydroxy ketone (III) or cyclohexenone (II) is converted to an equilibrium mixture in which (II)/(III) = 2.36 ± 0.09 (average of 10 experiments).

Measurement of the rate of dehydration of III in 0.10-5.0 M hydrochloric acid gave values for the first-order rate constant k₂ which were accurately proportional to neither acid concentration nor the Hammett acidity

![Graph](image)

**FIG. 1.**
First-order rate constants (min⁻¹) for the formation of cyclohexenone from 3-ethoxy-2-cyclohexen-1-ol (left) and from 3-hydroxycyclohexanone (right) at 25.2°.
function \( \mathcal{h}_2 \), although both conditions were approximated at the lower acidities. \(^{13}\) Comparison of the rates of formation of cyclohexenone from I and from III (Fig. 1) shows that the hydroxy ketone dehydrates too slowly by a factor of ca. \( 10^8 \) to be an intermediate, as has been assumed, \(^{2-5,8,10}\) in the "hydrolysis" of the hydroxy enol ethers. Thus some especially favored path from I to II takes precedence over the normal hydrolysis of the enol ether function. Consideration of the kinetic information and the well-known rearrangement of allylic alcohols \(^{14}\) leads us to suggest the mechanism of equation (2). A more detailed discussion will follow.

We are indebted to Gwyn V. Hudson for some exploratory experiments, and to the National Institutes of Health for partial support (RG 5780).

\(^{13}\) Similar kinetic behavior in the acid-catalyzed dehydration of certain acyclic \( \beta \)-hydroxy ketones has been reported: D.S. Noyce and W.L. Reed, \textit{J.Amer.Chem.Soc.} \textbf{80}, 5539 (1958).

\(^{14}\) E.A. Braude, \textit{Quart.Rev.} \textbf{4}, 407 (1950) clearly anticipated this mechanism for the reaction under discussion.