Electrocatalytic Oxidation of Cyclic Ketones


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The oxidation of ketones is a way for preparing carboxylic acids and their derivatives, bifunctional compounds such as α-hydroxyketones, diketones and other useful intermediates in organic synthesis. The formation of adipic acid from cyclohexanone is an important industrial process.

The advance of electrooxidation procedures has provided organic chemists with a synthetic device of great promise. But in the case of the electrooxidation of ketones only some reactions which could provide product-selectivity are known.

The first attempts of the electrochemical oxidation of ketones resulted in the formation of a mixture of acids, saturated and unsaturated hydrocarbons, carbon monoxide and dioxide. The anodic oxidation of cycloalkanones in aqueous alcohols gave mixtures of lactones of different types.

In some oxidative transformations of ketones such as halof ormation and Favorskii rearrangement, the preliminary α-halogenation of ketones is necessary. So for certain cases selective indirect electrooxidation of ketones with the electrochemically generated halides is also known.

Continuing our studies on the electrooxidation of ketones we have accomplished indirect electrochemical oxidation of cyclic ketones in the presence of sodium halides.

It has been found that the result of the electrooxidation of cyclic ketones in methanol in the presence of sodium halides in an undivided cell depends mainly on the ring size of cyclic ketone.

Cyclopentanone affords 2,2-dimethoxycyclopentanone. While cyclohexanone gives rise 2,2-dimethoxy-cycloalkenecarboxylates containing in the ring on the electrochemically induced Favorskii rearrangement with the formation of methyl halides in an undivided cell depends mainly on the ring size of cyclic ketone.

It should be mentioned that the substituent R in all possible isomers of anion A presumably exists in the equatorial position. It has been established earlier that the isomer with both an axial halogen and a hydroxy anion substitutent undergoes faster cyclization into the cis-epoxide 4. cis-Epoxide 4 exists in the form of a distorted chair with axial and equatorial epoxide C=O bonds. Thus, in the resulting cis-epoxide 4 both R and MeO substituents are equatorial, the O=C(OMe) bond is axial and the O=C(H) bond is equatorial.

The following attack on cis-epoxide 4 by the second methoxide anion resulted in the formation of ketal 2 with both the R and OH substituents equatorially oriented, i.e., leads to cis-5-substituted-2,2-dimethoxy-cyclohexanols 2. Thus, kinetic and thermodynamic products coincide in the reaction studied.

Under the similar conditions 1-substituted-4-piperidinones were transformed into 1-substituted-4,4-dimethoxy-3-piperidinones in which hydroxy group exists in axial position most probably because of hydrogen bond between hydroxy group and nitrogen atom of the cycle.

Electrolysis of 2,2,6,6-tetramethyl-4-piperidone led to the mixture of methyl 2,2,5,5-tetramethyl-3-pyrrolidinone-carboxylate and methyl 2,2,5,5-tetramethyl-2,5-dihydro-1H-pyrrolcarboxylate as a result of the electrochemically induced Favorskii rearrangement.

REFERENCES