

The Stereospecific Oxidation of Saturated Secondary Alcohol
with Dichlorodicyanoquinone

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It is well-known that allyl alcohols are readily oxidized to α,β -unsaturated ketones and aldehydes with the potential quinones such as 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)¹⁾. The saturated alcohols have been generally believed to be almost inactive for the reagent in the absence of light²⁾, though a few examples are recorded where saturated steroid alcohols are dehydrogenated with excess DDQ³⁾. No systematic study on the oxidation of saturated alcohols with DDQ has yet appeared in literature. We present here the new results on the oxidation of saturated secondary alcohols with DDQ and discuss the reaction stereochemically.

The oxidation of saturated alcohols to the corresponding saturated ketones were carried out by refluxing alcohol with DDQ in toluene. The results are summarized in Table, which shows that the cyclic secondary alcohols with more hindered hydroxyl group are more readily oxidized to the ketones, compared with the less hindered alcohols. Thus, isoborneol (I) having an exo-hydroxyl group hindered strongly by the bridge gem-dimethyl groups was more readily oxidized than its epimer, borneol (II), whose hydroxyl group is less hindered than I

α -Norborneol (IV) possessing an endo-hydroxyl group affected by the non-bonded interaction due to axial hydrogen, was also oxidized at the slower rate than that of above compounds, while β -norborneol (III) involving the less or unhindered hydroxyl group was completely recovered on the reaction as well as in the case of cyclohexanol (V) and cyclopentanol (VI).

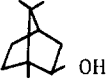
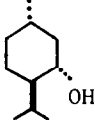
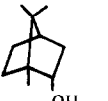
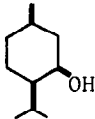
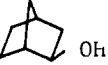
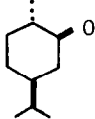
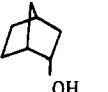
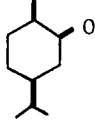
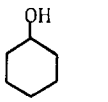
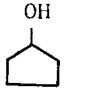
The above results suggest that there is a considerable similarity between DDQ and chromic acid in their steric requirement for the oxidation of saturated alcohols, but it appeared that the DDQ oxidation is more strongly dependent on the steric factor than the chromic acid oxidation⁴⁾

The steric effect due to the non-bonded interaction was also observed on the oxidation of menthol series. The reasonable explanation for reactivities in this series is based on the strain relief of sterically crowded hydroxyl group due to 1,3-diaxial interaction between alkyl and hydroxyl group. This idea was supported by the fact that neo-isomenthol (VIII) involving an axial hydroxyl group in its favorable conformation was readily subjected to the oxidation with DDQ but menthol (VII) and carvomenthol (IX) having an equatorial hydroxyl group in their predominant conformations were almost unreactive. Neo-isocarvomenthol (X) was also oxidized at the slower rate than VIII but more active than VII and IX. Model consideration for X shows that the equatorial alcohol is favorable in its conformational equilibration, while the axial isomer resulting from the contribution of the less favorable conformation may be more favorably permitted to exist than VII and IX, which have all substituents on the axial positions in the corresponding conformations. The reaction of X, accordingly, may be also accelerated by the 1,3-diaxial repulsion between isopropyl and hydroxyl group

On the other hand, Braude et al²⁾ reported that the measurable dehydrogenation was not observed on the oxidation of saturated alcohol with DDQ in the absence of light. However, our results were independent on its presence. The oxidation of saturated alcohols observed in steroid³⁾ is also well explainable from the above consideration concerning the steric repulsion of alcohol

Consequently, it is concluded that DDQ is an elegant and useful reagent for the stereospecific oxidation of saturated secondary alcohol with steric compression. The mechanistic study on the reaction is in progress

Table Yield (%) of Saturated Ketones on Oxidation with DDQ*

Starting Alcohol	Refluxing Hour				Starting Alcohol	Refluxing Hour			
	1.0	2.0	3.0	8.0		1.0	2.0	3.0	8.0
 (I)	18.2 (17.4)	23.6 (26.0)	29.8 (28.8)	95.8	 (VII)	-	-	-	1.2
 (II)	7.8 (13.0)	17.6 (16.2)	21.0 (22.2)	95.3	 (VIII)	35.1	37.9	39.7	48.0
 (III)	-	-	-	none	 (IX)	-	-	-	trace
 (IV)	7.4	13.4	20.4	68.8	 (X)	18.9	25.2	28.8	39.6
 (V)	-	-	-	none	 (VI)	-	-	-	none

* The mixture, 1:1 molar ratio of alcohol to DDQ, was refluxed in toluene. Resulting ketone was determined gas chromatographically (), in the absence of light.

Acknowledgement

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