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The Chromium(VI) Oxide Oxidation of Epimeric 1,2,3,4-Tetrahydro-1-naphthols

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Synopsis. The rates of the chromium(VI) oxide oxidation of 2- and 3-substituted 1-tetralols(1,2,3,4-tetrahydro-1-naphthols) have been determined. In the 3-substituted compounds, the rates of *cis*-isomers(eq'-OH) are markedly larger than those of *trans*-isomers(ax'-OH). On the other hand, in the case of 2-substituted compounds, the rates of the *cis*-isomers(ax'-OH) and *trans*-isomers (eq'-OH) are almost equal.

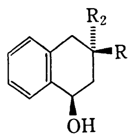
It is well known[1)] that the epimeric axial cyclohexanols are oxidized more rapidly by chromium(VI) oxide than the equatorial ones. However, turning to the allylic alcohols, it has been demonstrated that the quasi-equatorial alcohols are oxidized more rapidly than the quasi-axial ones.[2)] Although isolated studies of the oxidation rates of allyl alcohols are on record, few systematic studies have been made.

Recently, Yamaguchi *et al.*[3)] have studied the chromium(VI) oxide oxidation of 4-chromanols and discussed the effect of conformational and strain factors.

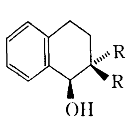
1-Tetralols are considered to have conformations similar to those of the corresponding 4-chromanols. In order to learn more about the stereochemistry of the chromium(VI) oxide oxidation of the cyclic benzyl alcohols, we have examined the chromium(VI) oxide oxidation of 2- and 3-substituted 1-tetralols. The results are summarized in Table 1.

TABLE 1. OXIDATION RATE OF EPIMERIC 1-TETRALOLS

Compound	Preferred conformation of OH	k(l/mol·s)	k_{cis}/k_{trans}
Ia	eq'	0.296	1.60
Ib	ax'	0.185	
IIa	eq'	0.428	1.80
IIb	ax'	0.238	
IIIa	eq'	0.208	1.03
IIIb	ax'	0.215	
IVa	eq'	0.292	0.91
IVb	ax'	0.267	



Ia $R_1=C_6H_5$, $R_2=H$
Ib $R_1=H$, $R_2=C_6H_5$
IIa $R_1=CH_3$, $R_2=H$
IIb $R_1=H$, $R_2=CH_3$



IIIa $R_2=C_6H_5$, $R_1=H$
IIIb $R_2=H$, $R_1=C_6H_5$
IVa $R_2=CH_3$, $R_1=H$
IVb $R_2=H$, $R_1=CH_3$

These results show the rates of *cis*-3-substituted 1-tetralols (eq'-OH) to be markedly larger than those of *trans*-isomers(ax'-OH). In the case of 2-substituted 1-tetralols, on the other hand, the rates of the *cis*-isomers (ax'-OH) and *trans*-isomers(eq'-OH) are almost equal.

In the 3-substituted compounds, it is considered that the greater reactivity of the *cis*-isomer over the *trans*-isomer should be attributed to the relief of strain from the *peri*-interaction—the $A^{1,2)}$ strain between the hydroxyl group and the aromatic methin group at Position 8 —when the above 1-tetralols are converted to the ketones. The *peri*-interaction in the *cis*-isomer involving a quasi-equatorial hydroxyl group may be larger than that is the *trans*-isomer; therefore, the former epimer will undergo oxidation more rapidly than the latter.

In the oxidation of *cis*-2-substituted 1-tetralols, the steric effect due to the *gauche* interaction between the hydroxyl group and the adjacent substituent should also be considered. In this case, the steric effect of the *peri*-interaction in the *trans*-isomer and the *gauche* interaction in the *cis*-isomer appear to be almost equal.

Experimental

Materials. 1-Tetralols were prepared by the reduction of the corresponding α-tetralones according to the literature.[4)] The conformations of 1-tetralols were examined by means of their NMR[5)] and IR[6)] spectra.

Kinetic Determinations. The chromium(VI) oxide oxidations were carried out at 25±0.1 °C and were followed spectrophotometrically by measuring the decrease in the optical density of the Cr^{VI} maximum at 380 nm, as has been described in the literature.[3)] The medium was 85% acetic acid; the concentrations of alcohol and CrO_3 were 1.75×10^{-3} M and 2.00×10^{-3} M respectively. A Hitachi ESP-3T spectrophotometer and standard 1.00-cm quartz cells were used.

References

1) E. L. Eliel, S. H. Shroeter, T. J. Brett, F. J. Biros, and J. Richer, *J. Am. Chem. Soc.*, **88**, 3327 (1966).
2) S. H. Burstein and H. J. Ringold, *J. Am. Chem. Soc.*, **89**, 4722 (1967).
3) S. Yamaguchi, K. Kabuto, Y. Kikuchi, and N. Inoue, *Bull. Chem. Soc. Jpn.*, **44**, 3487 (1971).
4) K. Hanaya, *Nippon Kagagku Zasshi*, **87**, 745, 991, 995 (1966).
5) S. Mitsui, A. Kasahara, and K. Hanaya, *Bull. Chem. Soc. Jpn.*, **41**, 2526 (1968).
6) H. Iwamura and K. Hanaya, *Bull. Chem. Soc. Jpn.*, **43**, 3901 (1970); K. Hanaya, S. Onodera, and H. Kudo, *ibid.*, **47**, 2607 (1974).