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On The Mechanism of Asymmetric Dihydroxylation(AD) of Alkenes**

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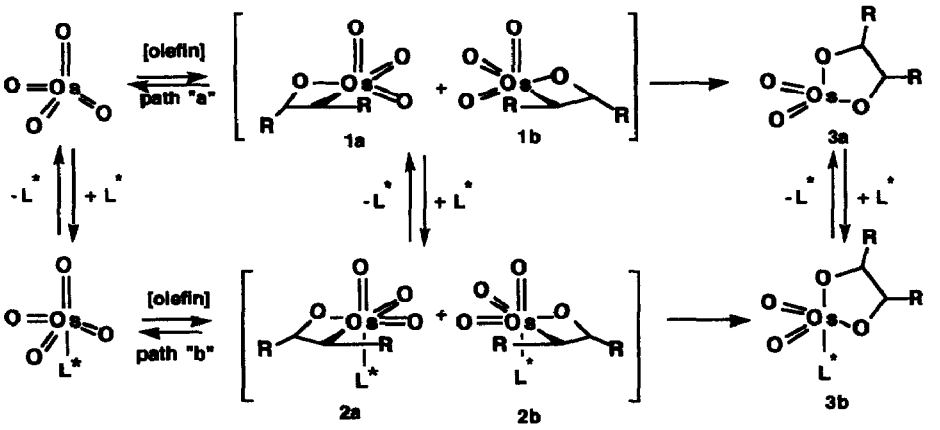
Abstract: ^{1}H NMR studies on bis(9-*O*-dihydroquinidinyl)terephthalate(DHQD$_2$-TP) with various concentrations of osmium tetroxide and *trans*-3-hexene reveal that OsO_4 is bound to both the quinuclidine moieties of DHQD$_2$-TP but only one of the bound OsO_4 reacts with alkenes in the AD process.

Göbel and Sharpless[1] have recently reported the effect of temperature on the enantiomeric excesses of the diols and suggested the existence of an *inversion temperature* and hence proposed two alterative routes, both proceeding *via* [2+2] cycloaddition pathways as shown in Scheme 1.



Scheme 1. Proposed [2+2] mechanism for the dihydroxylation of alkenes L* symbolizes the chiral alkaloid ligands

However, these authors do not distinguish which pathway might be operating in the AD reaction. In this letter, we wish to report our ^{1}H NMR studies which suggest that pathway "b" is a more likely route than pathway "a". In an NMR experiment, DHQD$_2$-TP was dissolved in $CDCl_3$ and subsequently one and two equivalents of OsO_4 were added. The NMR spectra showed a slight shift of H-9 proton to the down field region. Further addition of OsO_4 did not show any change in the ^{1}H NMR spectra. In separate experiments when DHQD$_2$-TP was treated with one and two equivalents of OsO_4 followed by *trans*-3-hexene, within 0.5 h, 42 % of *trans*-3-hexene was found to be bound (Figure 1a). Even after 6-8 h, 50 % of the olefin was found to be free. Despite the presence of two equivalents of OsO_4, *trans*-3-hexene is not able to react with it

Dedicated to Dr. S. Rajappa on the occassion of his 60th birthday

suggesting that all the OsO_4 is bound to the alkaloid but only one of the complexed OsO_4 molecules can react efficiently.[2] When the ^1H NMR spectrum was recorded after 16 h (Figure 1b) and 40 h (Figure 1c), the amount of bound olefin was found to increase slowly and an equilibrium (3:1) was attained perhaps between the monoglycolate and bisglycolate species respectively[3] which did not change even after 5 days. These experiments clearly suggest that in the presence of ligand, free OsO_4 is negligibly small to react with free olefin[4,5] and hence path "a" is not a feasible pathway to AD reaction.

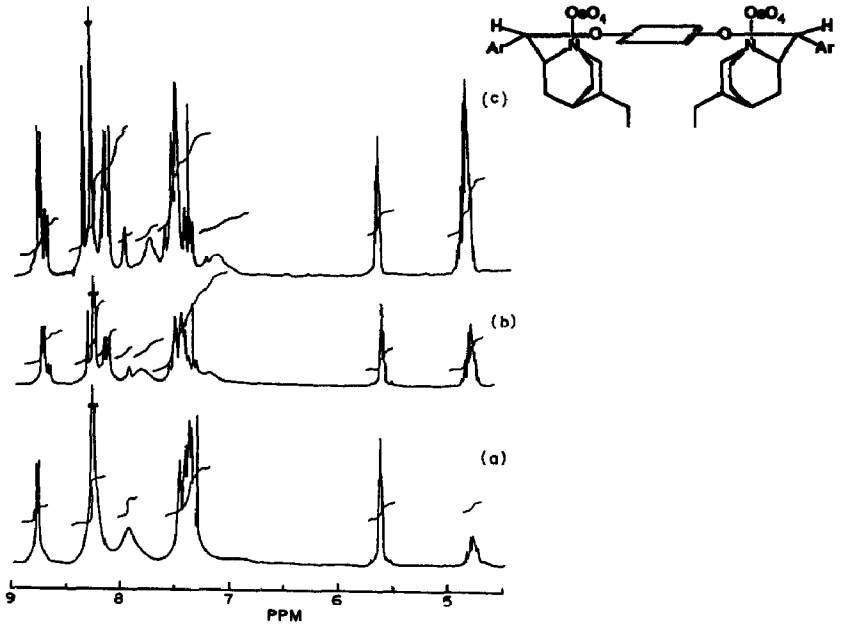


Figure 1: ^1H NMR (200 MHz) spectrum of $DHQD_2$-TP-$[OsO_4]_2$-[*trans*-3-hexene]$_2$ in $CDCl_3$ after (a) 0.5 h (b) 16 h (c) 40 h

In summary, we have ruled out the possibility of OsO_4 reacting with olefin before binding to the ligand followed by diastereoselective ligand accelerated rearrangement of metalloxetane to five membered adduct **3a** specially in the presence of DHQD-derivatives.

Acknowledgement: We are thankful to DST, New Delhi for financial assistance. EN thanks CSIR, New Delhi for a fellowship.** N.C.L. Commun. No. 4954.

References:

1. Göbel, T.; Sharpless, K. B. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1329.
2. (a) Lohray, B. B.; Bhushan, V. *Tetrahedron Lett.* **1992**, *33*, 5113; (b) Lohray, B. B. *Tetrahedron Asymmetry* **1992**, *3*, 1317.
3. In monoglycolate one molecule of alkene is bound to $DHQD_2$-TP-$[OsO_4]_2$ complex whereas in bisglycolate two molecules of olefin are bound to the same complex at different osmium sites.
4. When *trans*-stilbene was treated with two equivalents of OsO_4 and one equivalent of $DHQD_2$-TP, hydrobenzoin was isolated in 66 % yield and > 98 % ee suggesting that the olefin has not reacted with free OsO_4 and hence free OsO_4 does not exist.
5. Sharpless *et al.* (*J. Am. Chem. Soc.* **1993**, *115*, 12226) report the presence of free OsO_4 along with [(OsO_4)L] based on IR data. However, ^1H NMR obervations under the above experimental conditions support the formation of [$(OsO_4)_2$ L] as the major reacting species.

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