Tetrahedron Letters No. 32, pp 2737 - 2738, 1974. Pergamon Press. Printed in Great Britain.

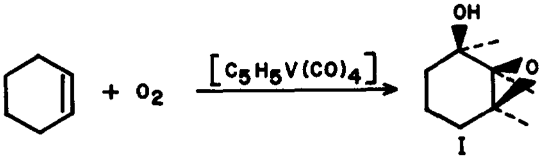
THE STEREOSELECTIVE OXIDATION OF CYCLOHEXENE TO cis-1,2-EPOXYCYCLOHEXANE-3-OL IN THE PRESENCE OF $[C_5H_5V(CO)_4]$

James E. Lyons
Corporate Research and Development Department
Sun Oil Company, P. O. Box 1135, Marcus Hook, Pennsylvania 19061

(Received in USA 30 May 1974; received in UK for publication 24 June 1974)

The oxidation of cyclohexene in the presence of transition metal complexes has been the subject of a number of recent studies.[1-7] The usual products of this reaction are mixtures of cyclohexenyl hydroperoxide, 2-cyclohexene-1-ol, 2-cyclohexene-1-one, cyclohexene oxide, dimers and polymers.[1-7] Allison et al.,[8] have reported that 1,2-epoxycyclohexane-3-ol was formed in 24% yield at 15% conversion of cyclohexene during oxidation in the presence of vanadium naphthenate; however, the geometrical configuration of the product was not reported in this case.

We wish to report that the complex, $[C_5H_5V(CO)_4]$, (C_5H_5 = cyclopentadienyl), is an efficient catalyst for the stereoselective oxidation of cyclohexene to cis-1,2-epoxycyclohexane-3-ol, I, in good yield. The cis-epoxy alcohol, I, accounts for 65% of the products of reaction after 10% of the cyclohexene has reacted and 55% after 30% of the cyclohexene has been oxidized (see Table). The stereoselectivity of this reaction is ~99%.



Reactions were run in the neat olefin or in 1:1 mixtures of cyclohexene and 1,2-dichloroethane. Solutions became pale amber and remained clear during reaction. After vacuum transfer from the catalyst and a viscous residue, spinning band distillation yielded I, bp 96°/10 mm, in 99.5% glpc purity which was identified by comparison of its ir and nmr spectra with literature data.[9] A small amount of trans-1,2-epoxycyclohexane-3-ol was separated from the cis-isomer by preparative glpc and identified by its ir and nmr spectra.[9]

The formation of I as the predominant product of cyclohexene oxidation contrasts sharply with the more conventional results obtained using molybdenum and iron complexes having a similar ligand system. These complexes formed the usual products[1-7] when used as catalysts for cyclohexene oxidation. The low-valent vanadium complex, $[C_5H_5V(CO)_4]$, also gives superior

cis-1,2-Epoxycyclohexane-3-ol Via Oxidation of
Cyclohexene[a] in the Presence of Cyclopentadienylmetalcarbonyl Complexes, $[C_5H_5M(CO)_x]_y$

Metal Complex	Solvent	Reaction Time, hrs.	Conversion of Cyclohexene, %	Yield[b] of I, %
$[C_5H_5V(CO)_4]$	CH_2ClCH_2Cl[c]	3	10	65
		5	30	55
$[C_5H_5V(CO)_4]$	--	3	11	51
		5	20	47
		9	48	42
$[C_5H_5Fe(CO)_2]_2$	--	5	20	--
$[C_5H_5Mo(CO)_3]_2$	--	5	24	1

[a] Oxygen was bubbled, 2.0 l/hr., through 80 ml of cyclohexene containing 0.25 gram of the catalyst with stirring at 65°C. Products were vacuum transferred at 65°C and 0.01 mm from the catalyst and residue and analyzed by glpc. [b] Yield based on cyclohexene which has reacted. [c] Oxygen was bubbled, 0.5 l/hr., through 6 ml of 1,2-dichloroethane and 6 ml cyclohexene containing 0.05 gram of the catalyst at 65°C. Analytical procedure identical to (a).

yields of I compared with $VO(acac)_2$, $V(acac)_3$ and vanadium naphthenate.[8] Furthermore, cyclohexene oxidations run in the presence of $[C_5H_5V(CO)_4]$ do not exhibit the long induction periods which occur when vanadium (III) and vanadium (IV) complexes are used in the absence of radical initiators. Complete product analyses in these systems as well as the mechanistic implications of the stereochemistry of epoxy alcohol formation during oxidation of cyclic systems will be published elsewhere.

Acknowledgement: The author thanks Miss Caroline Link for technical assistance and Mr. Ronald Bingeman and Mr. Robert Warren for technical assistance and for helpful discussions regarding the isolation and identification of products.

References

1. H. Arzoumanian, A. Blanc, U. Hartig, and J. Metzger, *Tetrahedron Lett.*, 1011 (1974).
2. K. Kaneda, T. Itoh, Y. Fujiwara, and S. Teranishi, *Bull. Chem. Soc. Japan*, 46, 3810 (1973).
3. A. Fusi, R. Ugo, F. Fox, A. Pasini, and S. Cenini, *J. Organometal. Chem.*, 26, 417 (1971).
4. E. Gould and M. Rado, *J. Catal.*, 13, 238 (1969).
5. A. Fusi, R. Ugo, and G. Sanderighi, private communication.
6. V. Kurkov, J. Pasky, and J. Lavigne, *J. Amer. Chem. Soc.*, 90, 4744 (1968).
7. J. P. Collman, M. Kubota, and J. Hosking, *J. Amer. Chem. Soc.*, 89, 4811 (1967).
8. K. Allison, P. Johnson, G. Foster, and M. Sparke, *Ind. Eng. Chem. Prod. Res. Develop.*, 5, 166 (1966).
9. P. Chamberlain, M. Roberts, and G. Whitham, *J. Chem. Soc. (B)*, 1970, 1374.