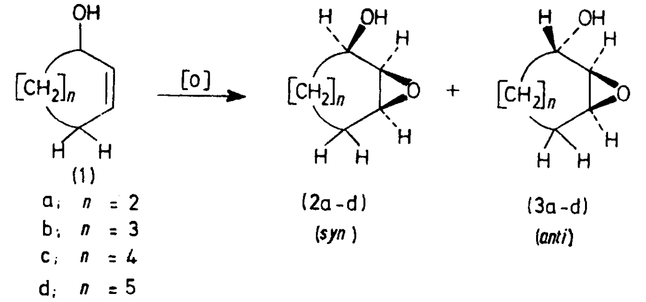
Unusual Stereochemical Course of Vanadium-catalysed Epoxidation of Medium-ring Allylic Alcohols

By TAKASHI ITOH, KIYOTOMI KANEDA, and SHIICHIRO TERANISHI*
(*Department of Chemical Engineering, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka, Japan*)

Summary The epoxidation of small to medium ring cyclic allylic alcohols with Bu^tOOH–$[VO(acac)_2]$ (acacH = pentane-2,4-dione) produces *syn*-epoxy alcohols with high stereoselectivity and in high yields.

THE transition metal-catalysed epoxidation[1] of olefinic alcohols with organic hydroperoxides has attracted considerable interest in recent years because of its higher stereoselectivity than that of the organic peroxyacid epoxidation.[2] The difference in the stereoselectivity between the metal-catalysed and peroxyacid epoxidations remains unclear.

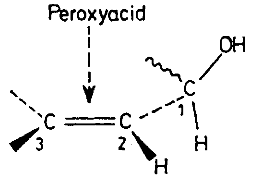


We examined the correlation between the substrate ring size and the product stereochemistry in the vanadium-catalysed epoxidation of the cyclic allylic alcohols (**1a**—**d**), and compared it with that of peroxyacid epoxidation. We now report that in the vanadium epoxidation the allylic hydroxy-group consistently functions as a *syn* director, in striking contrast to the change from *syn* to *anti* direction with increasing ring size in the peroxyacid epoxidation.

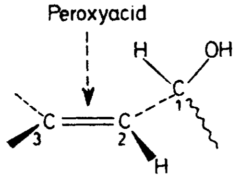
	$Bu^tOOH–[VO(acac)_2]$			*m*-CPBA		
Allylic alcohol	Total yield (%)	Epimer ratio (2) (%)	(3) (%)	Total yield (%)	Epimer ratio (2) (%)	(3) (%)
(**1a**)	86	99·7	0·3	83	95	5
(**1b**)	75	99·6	0·4	95	61	39
(**1c**)	83	97	3	81	0·2	99·8
(**1d**)	78	91	9	89	0·2	99·8

The epoxidations of (**1a**—**d**) were carried out by the following two methods: (i) using Bu^tOOH (1·5 equiv.) and $[VO(acac)_2]$ (0·005 equiv.) (acacH = $MeCOCH_2COMe$) in benzene at 20 °C for 24 h, and (ii) by treatment with *m*-chloroperoxybenzoic acid (*m*-CPBA) (1·0 equiv.) in dichloromethane at 0 °C for 24 h. The product yields and epimer distributions were analysed by g.l.c., and the results are in the Table. The direction of peroxyacid epoxidation changes from predominantly *syn* to predominantly *anti* between the small ring alcohols (**1a**) and (**1b**), and the medium ring alcohol (**1c**), compatible with previous reports.[2,3] This tendency is further confirmed by the almost exclusive formation of the *anti*-epimer (**3d**) from (**1d**)† (selectivity = 99·8%). In contrast, such a change in *syn–anti* direction was not observed in the vanadium epoxidations; the alcohols (**1a**) and (**1b**), and also (**1c**) and (**1d**), give the *syn*-epoxy alcohols selectively. Furthermore the *syn*-stereoselectivity for (**1a**) and (**1b**) is greater in the vanadium epoxidation than with peroxyacid.

The observed change from *syn* to *anti* direction as the ring size increases from $n = 3$ to $n = 4$ can be explained in terms of Whitham's model[2a] for the transition-state geometry of peroxyacid epoxidation, (**4**) and (**5**), where the partial geometry about C(1)–C(2) resembles the preferred conformation of the starting alcohols, *e.g.*, the chair conformer of the cyclohexene ring and the chair–boat conformer of the *cis*-cyclo-octene ring.[4] Such conformations cannot satisfy the requirement for the *syn*-directive and promoting effects exerted by the hydroxy-group in medium-ring allylic alcohols. The high stereoselectivity observed in the vanadium reaction is compatible with the previously proposed mechanism,[1c] which involves complex formation between the oxygen atom of the alcohol and a hydroperoxide–vanadium intermediate, followed by oxygen transfer to the double bond. Our results, furthermore, suggest that the preferred conformation of the medium-ring alcohols in such a transition state might resemble (**4**) rather than (**5**). The co-ordination of the allylic alcohol to vanadium might bring about the change in conformation. The *syn*-stereoselectivity must originate from such a modified conformation in the transition state (the Curtin–Hammett principle[5]).



(4)
Small rings



(5)
Medium rings

Finally, it should be noted that Bu^tOOH–vanadium and peroxyacid can be used for the stereoselective epoxidation of medium-ring allylic alcohols in either the *syn*- or *anti*-direction.

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† Satisfactory analytical and spectral data have been obtained for the new epoxy alcohols. All other products described here were characterized by spectroscopic and g.l.c. comparison with authentic samples.

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[2] (a) P. Chamberlain, M. L. Roberts, and G. H. Whitham, *J. Chem. Soc.* (*B*), 1970, 1374; (b) A. C. Cope, J. K. Heeren, and V. Seeman, *J. Org. Chem.*, 1963, **28**, 516; (c) H. B. Henbest and R. A. L. Wilson, *J. Chem. Soc.*, 1957, 1958.

[3] A similar change in direction from *syn* to *anti* has been reported in the Simmons–Smith methylene addition of these cyclic allylic alcohols; C. D. Poulter, E. C. Friedrich, and S. Winstein, *J. Amer. Chem. Soc.*, 1969, **91**, 6892.

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