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STEREOSELECTIVE BORON PROMOTED EPOXIDATION OF 1,5,9-CYCLODODECATRIENES

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While boric acid promoted oxidation of paraffins and cycloparaffins[1)] has received considerable attention. the application of this oxidation to olefins has been the subject of sporadic study[2)]. In the course of the investigation of air oxidation of stereoisomeric 1,5,9-cyclododecatrienes(CDTs)in the presence of boric acids or their esters, the author found that a major product was the corresponding 1,2-epoxycyclododeca-5,9-diene accompanied with 2,6,10-cyclododecatrienols. Moreover, in the case of cis, trans, trans-CDT, only trans double bond was stereoselectively epoxidized with air in the presence of boric acids of their esters to afford 1,2-trans-epoxy, cis-5,trans-9-cyclododecadiene(I). Similarly, trans,trans, trans-CDT gave 1,2-trans-epoxy, trans-5,trans-9-cyclododecadiene(II). In a typical example, air was bubbled into a mixture of cis, trans, trans-CDT(50.0g) and tri-sec-butyl borate(11.6g) at a rate of 270ml/min. at 112-113 °C for 3hrs. To the mixture, then, was added 20ml of water and the whole was refluxed for 2hrs., and extracted with ether. Amounts of I and three isomeric(cis, trans, trans)-2,6,10-cyclododecatrienols were determined by means of gas chromatography.

Table I shows some examples of the air oxidation of CDTs in the presence of various boric acids and their esters.

The product I(b.p.80.3-81.7°C/0.36mmHg) was identified by elemental analysis (Calcd.for $C_{12}H_{18}O$:C,80.85;H,10.18;Found C,80.43; H,10.38), mass (M^+,178),i.r.(975cm^{-1} for trans double bond, 690cm^{-1} for cis double bond and 958,873 and 765cm^{-1} for epoxide) and n.m.r.(τ4.5-5.0 for olefinic protons, m, 4H).

TABLE I. Air oxidation of CDTs in the presence of boric acids and their esters[a]

CDT	BORON COMPOUNDS	CONVERSION (%)	SELECTIVITY (%)	
			EPOXYCYCLODODECA-TRIENE	CYCLODODECATRIENOL
cis,trans,trans	H_3BO_3	13.2	53.2	21.9
	HBO_2	10.5	51.0	18.8
	B_2O_3	10.4	50.7	15.4
	$(n\text{-PrO})_3B$	11.0	71.7	24.8
	$(n\text{-BuO})_3B$	35.0	61.3	16.8
	$(iso\text{-BuO})_3B$	29.7	57.9	13.4
	$(sec\text{-BuO})_3B$	16.3	73.0	24.9
	$(n\text{-AmylO})_3B$	27.5	52.0	15.0
	$(iso\text{-AmylO})_3B$	34.4	44.6	16.5
	$(sec\text{-AmylO})_3B$	16.5	58.8	23.9
	$(tert\text{-AmylO})_3B$	9.0	54.7	24.6
	$(\text{CyclohexylO})_3B$	48.0	36.6	12.6
trans,trans,trans	H_3BO_3	16.0	45.1	18.5
	$(sec\text{-BuO})_3B$	25.9	63.9	24.9

a) Reaction Conditions; molar ratio of boron to CDT:0.163, temperature: 112-120°C, time: 3hrs.

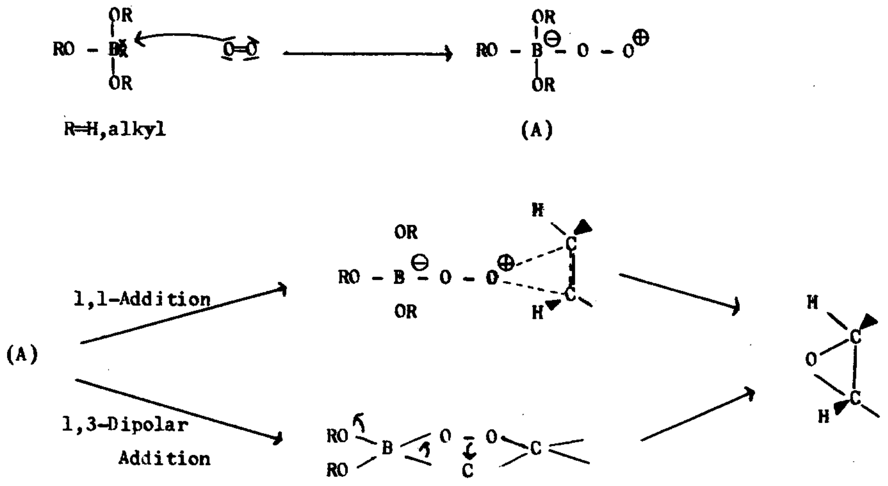
Configuration of the epoxide in I was assigned to be trans by (a) coupling constant of vicinal protons of the epoxide in n.m.r.spectra obtained in the presence of $Eu(DPM)_4$ and by the application of double resonance,($J_{H_1,H_2} \approx 2Hz$)[3], (b) hydrogenation of I by Pd/C to 1,2-trans-epoxycyclododecane(III), which was entirely different from an authentic 1,2-cis-epoxycyclododecane prepared by epoxidation of cis-cyclododecene[4] with peracetic acid and (c) quantitative hydrolysis of III by aq.perchloric acid (60%) to known cyclododecane-cis-1,2-

diol[5],m.p.164°C. The minor products (b.p.96.3°C/0.38mmHg) were identified as three stereoisomeric (cis,trans,trans)-2,6,10-cyclododecatrienols by elemental analysis,i.r.,mass and quantitative conversion into cyclododecanol by catalytic hydrogenation.

Similarly, the oxidation products of trans, trans, trans-CDT were found to be II (b.p. 82°C/2mmHg)whose coupling constant of vicinal protons was $J_{H_1,H_2} \simeq 1$ Hz, indicating trans configuration of the epoxide, and trans, trans, trans-2,6, 10-cyclododecatrienol (b.p.90°C/ 2mmHg).

Mechanisms proposed by early workers[6] to explain epoxide formations in liquid phase oxidation can be classified as follows:(a) formation of cyclic peroxide which decomposes to epoxide and presumably oxygen atom,(b) reaction of a double bond with hydroperoxide and (c) reaction of a double bond with peroxy radical. The present stereoselective epoxidation with molecular oxygen can be explained by none of the above mechanisms. Moreover, according to the more probable mechanisms (b) and (c), the yield of epoxides cannot exceed that of alcohols.

Consequently, the following reaction mechanism may be proposed for the main path of the present reaction.



In this mechanism, electron attraction by boron might arise by overlap of the occupied 2p-orbitals of oxygen atom with the vacant 2p-orbitals of boron atom. By the resultant boron peroxide (A) (the existence of which was estimated by reduction of iodide in a blank test), one of the trans double bonds in CDTs can be stereoselectively epoxidised via the electrophilic 1,1-addition as suggested by Bartlett7)or the 1,3-dipolar addition proposed by Kwart et al8). Wolf and Barnes9)proposed a similar boron peroxide as an intermediate in epoxidation of olefins by alkylperoxide and cyclohexyl metaborate. As to the high preference of the intermediate (A) for trans double bond over cis double bond, reasonable explanation for the selective oxidation with OsO_4 and $KMnO_4$ of trans double bond of cis, trans, trans-CDT proposed by Ohno et al10). might be adopted if the reaction proceeds through 1,3-dipolar addition mechanism.

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