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# Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information: <u>http://www.tandfonline.com/loi/lsyc20</u>

# ON THE STEREOSELECTIVITY IN BISDIHYDROXYLATION OF 1,5-CYCLOOCTADIENE WITH OSMIUM TETROXIDE

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To cite this article: Kentaro Kawazoe, Yoshio Furusho, Saburo Nakanishi & Toshikazu Takata (2001) ON THE STEREOSELECTIVITY IN BISDIHYDROXYLATION OF 1,5-CYCLOOCTADIENE WITH OSMIUM TETROXIDE, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 31:14, 2107-2112, DOI: <u>10.1081/SCC-100104460</u>

To link to this article: http://dx.doi.org/10.1081/SCC-100104460

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#### SYNTHETIC COMMUNICATIONS, 31(14), 2107–2112 (2001)

## ON THE STEREOSELECTIVITY IN BISDIHYDROXYLATION OF 1,5-CYCLOOCTADIENE WITH OSMIUM TETROXIDE

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#### ABSTRACT

In the bisdihydroxylation of 1,5-cyclooctadiene with  $OsO_4$ , use of a stoichiometric amount of  $OsO_4$  yielded a 1:1 mixture of *syn*- and *anti*-isomers, while use of a catalytic amount of  $OsO_4$  gave only *syn*-(1 $R^*$ ,2 $S^*$ ,5 $R^*$ ,6 $S^*$ )-cyclooctane-1,2,5,6-tetrol. This *syn*-selectivity was attributed to the favorable formation of an intramolecular osmium(VI) bisglycolate ester in the catalytic reaction.

For years, chemists have made efforts to develop osmium-catalyzed dihydroxylation which is utilized as a powerful tool to build 1,2-diols.<sup>1</sup> At the same time, the reaction mechanism leading to the first stable product, a cyclic osmate(VI) complex, is still under discussion.<sup>2</sup> Development

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of an enantioselective catalytic version of the reaction based on cinchona alkaloids facilitated preparation of highly oxygenated molecules.<sup>3</sup> However, the osmium-catalyzed polydihydroxylation of polyenes has been hardly explored due to various reasons.<sup>1</sup> We have investigated the osmium-catalyzed bisdihydroxylation of 1,5-cyclooctadiene **1** as part of our program to utilize  $(1R^*, 2S^*, 5R^*, 6S^*)$ -cyclooctane-1,2,5,6-tetrol *syn*-**2** as a scaffold for supramolecules.<sup>4</sup> Recently, Sharpless has reported<sup>5</sup> the bisdihydroxylation of several dienes, including **1**, by use of Narasaka's method.<sup>6</sup> Herein we report the stereoselective bisdihydroxylation of **1** and the origin of the stereoselectivity.



The bisdihydroxylation of **1** was carried out with a catalytic amount of osmium tetroxide (1 mol%) and an equivalent of *N*-methylmorpholine *N*-oxide (NMO) as cooxidant in aqueous media, acetone-water (1/2 (v/v), r.t., 12 h).<sup>7</sup> The bisdihydroxylated product was obtained in 99% yield after chromatography and identified as *syn*-isomer (1 $R^*$ ,2 $S^*$ ,5 $R^*$ ,6 $S^*$ )-**2** from the spectroscopic results.

No *anti*-isomer  $(1R^*, 2S^*, 5S^*, 6R^*)$ -**2** was detected. The results of this bisdihydroxylation were similar to those of Sharpless.<sup>5</sup> The issue of *syn/anti*-stereochemistry for the tetrol had remained unresolved<sup>8</sup> until it was determined by us<sup>4</sup> and Sharpless.<sup>5</sup> We established the *syn*-stereochemistry of the product by X-ray crystallography (Figure 1).<sup>9</sup>

On the other hand, bisdihydroxylation of **1** under stoichiometric conditions gave a 1:1 mixture of *syn*- and *anti*-**2** in 89% yield. To investigate the origin of the *syn*-selectivity of the catalytic system, dihydroxylation of **1** with one mole of NMO was carried out. The reaction selectively afforded *syn*-**2** in 49% yield and neither *anti*-**2** nor a monodihydroxylated product was detected at all. These results indicate that the diol moiety formed first enhances the rate of the second dihydroxylation and controls the stereoselectivity in the bisdihydroxylation.

To confirm such possibility, dihydroxylation of three other olefins  $3\sim5$  was conducted under the catalytic conditions. The results are shown in Table 2. Dihydroxylation of *cis*-5-cyclooctene-1,2-diol  $3^8$  gave *syn*-2 in 99% yield, whereas 1,2-*O*-isopropylidene-5-cyclooctene-1,2-diol  $4^{10}$  afforded a 1:1 mixture of *syn*- and *anti*-diol 6 in 94% yield.<sup>11</sup> On the other hand,

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Figure 1. The ORTEP drawing of syn-2.

1 → 2 acetone-water (1/2) r.t., 12h			
Entry	$OsO_4/mol\%$	NMO/mol%	Yield/% <sup>a</sup>
1	1	200	97 ( <i>svn</i> : <i>anti</i> = 100:0)
$2^b$	200	0	89 ( <i>svn:anti</i> = 50:50)
3	1	100	49 (syn:anti = 100:0)

Table 1.	Bisdihydroxylation of 1,5-Cyclooctadiene (1)
	OsO4, NMO

<sup>a</sup>Isolated yield. <sup>b</sup>CH<sub>2</sub>Cl<sub>2</sub> was used as solvent instead of acetone-water.

bisdihydroxylation of 1,4-cyclohexadiene 5 gave a 1:2 mixture of *syn*- and *anti*-tetrol 7.<sup>12</sup>

Based on the results described above, we propose the reaction mechanism of the catalytic bisdihydroxylation of 1,5-cyclooctadiene as illustrated in Scheme 1.<sup>13</sup> The key intermediate is an intramolecular osmium(VI) bisglycolate ester  $C^{14}$ , which is crucial for elucidating the *syn*-selectivity of the bisdihydroxylation of 1. First of all, 1 reacts with OsO<sub>4</sub> to form a primary osmate **A**. **A** is oxidized with NMO to give osmium(VIII) trioxoglycolate **B**, which is quickly converted to bisglycolate ester **C** through intramolecular cyclization. *cis*-5-Cyclooctene-1,2-diol **3**, which might be formed *via* hydrolysis of **A**, smoothly reacts with OsO<sub>4</sub> to give **B**. Neither **A** nor **B** is converted to bisosmate **D** or **E**, since the concentration of OsO<sub>4</sub> is very low under



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Scheme 1. Proposed mechanism of OsO<sub>4</sub>-catalyzed bisdihydroxylation of 1,5cyclo-octadiene.

×	/		
	OsO <sub>4</sub>	(1 mol%), NMO	hial
olefin polyol acetone-water (1/2) r.t., 12 h			
Entry	Substrate	Product (isomer ratio)	Yield/a
H 1 H		но он он	99
	3	<b>2</b> ( <i>syn:anti</i> = 100:0)	
$_{2}$ >		Хон	94
	4	<b>6</b> ( <i>syn:anti</i> = 52:48)	
3	$\bigcirc$	HO OH	34
-	5	<b>7</b> (syn:anti = 33:67)	54
at 1 . 1			

Table 2.	Osmium-catalyzed	Dihydroxylation	of
Olefins (3-	-5)		

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#### 1,5-CYCLOOCTADIENE WITH OSMIUM TETROXIDE

the catalytic conditions. If **D** or **E** were formed, the *syn*-selectivity should be lowered. This is understandable from the results of the experiment using a stoichiometric amount of  $OsO_4$ . The *syn/anti* product distribution of the dihydroxylation of **4** and **5** well supports our proposed mechanism, in which the formation of the intramolecular bisglycolate ester is unambiguously indispensable to attain the *syn*-selectivity: (1) because **4** does not have a diol moiety, intramolecular bisglycolate ester cannot be formed, resulting in the reaction without *syn*-selectivity; (2) since the distance between the two olefin moieties in the 6-membered ring of **5** is too short to form the corresponding intramolecular bisglycolate ester, the second dihydroxylation either takes place sluggishly or occurs after hydrolysis of the primary osmate. The primary osmate or the diol moiety formed first acts as steric hindrance, thus to increase *anti*-selectivity.

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- To a mixture of OsO<sub>4</sub> (7 mg, 0.03 mmol), NMO (6.2 mmol), water (2.4 mL), and acetone (1.2 mL) was added 1 (324 mg, 3.0 mmol). The mixture was stirred at room temperature for 12 h. After addition of sat.Na<sub>2</sub>SO<sub>3</sub>aq, the mixture was evaporated and the residue was chromatographed over silica gel (eluent: water-ethanol-ethyl acetate (1:2:5)) to afford *syn*-2 as white crystals; mp 176–178°C (lit.<sup>5</sup> 171–173°C); IR (KBr): v<sub>O-H</sub> 3384 cm<sup>-1</sup>; <sup>1</sup>H NMR (270 MHz, DMSO-*d*<sub>6</sub>, 295 K): δ 4.19



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(4H, br s, O*H*), 3.57 (4H, m, C*H*), 1.86 (4H, m, C*H*<sub>2</sub>), 1.36 (86 (4H, m, C*H*<sub>2</sub>)); <sup>13</sup>C NMR (270 MHz, DMSO-*d*<sub>6</sub>, 295 K): δ 71.9, 26.8.

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- 10. 4 was prepared from 3 and acetone by use of  $FeCl_3$  as catalyst.
- The *syn/anti* isomer ratio of 6 was determined by the <sup>1</sup>H NMR spectra. The <sup>1</sup>H NMR assignment was achieved by comparing with that of *syn*-6 prepared independently by monoacetalization of *syn*-2.
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