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## Chemoselective Hydrogenation of the Double Bond of Vinyl Epoxides with Homogeneous Palladium and Iridium Catalysts

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Abstract: The selective hydrogenation of the double bond of vinyl epoxides is catalyzed by either the species generated by treatment of the binuclear palladium complex,  $[(But_2PH)PdPBut_2]_2$  with oxygen, or by the cationic iridium(I) complex,  $[Ir(COD)(PPh_3)(PhCN)]BF_4$ , to produce the corresponding saturated epoxides at room temperature, and with good selectivity.

The selective hydrogenation of a particular functional group in an organic compound containing two different functional groups is a useful method in organic synthesis.<sup>1</sup> For example, transition metal complexes catalyze the hydrogenation of the double bond of  $\alpha$ , $\beta$ -unsaturated systems to give the corresponding saturated analogs.<sup>2</sup>

Specifically, the mild and selective hydrogenation of the carbon-carbon double bond of  $\alpha$ , $\beta$ unsaturated carbonyl compounds,<sup>3</sup> sulfones and phosphonates<sup>4</sup> is catalyzed by the species formed by pretreatment of the novel binuclear palladium complex, [(Bu<sup>t</sup><sub>2</sub>PH)PdPBu<sup>t</sup><sub>2</sub>]<sub>2</sub>, with oxygen.<sup>5</sup> The same catalytic system is also capable of 1,2-hydrogenation of the least substituted double bond of a conjugated diene.<sup>6</sup> On the other hand, cationic iridium(I) complexes, including [Ir(COD)(PR<sub>3</sub>)(PhCN)]<sup>+</sup> (PR<sub>3</sub> = various tertiary phosphine; COD = 1,5-cyclooctadiene) are known to be effective catalysts for the reduction of olefinic units in enamides and dehydroamino acid derivatives.<sup>7</sup>

The chemoselective hydrogenation of the double bond of monoepoxy conjugated dienes such as 2vinyloxirane can produce compounds such as 2-ethyloxirane, which are used as monomers for the synthesis of polyesters, glycols, epoxy resins, non-ionic surfactants and urethane polyols. A patent has been issued claiming the use of palladium or rhodium on carbon for the hydrogenation of butadiene monoxide (eq. 1).<sup>8</sup> However, to our knowledge, there are no publications on the selective hydrogenation of vinyl epoxides with a homogeneous catalyst. We now report the chemoselective hydrogenation of the double bond of various vinyl epoxides with homogeneous palladium and iridium catalysts at room temperature.



Catalyst = 5 % Rh/carbon or 5 % Pd/carbon

Entry	Catalyst <sup>a</sup>	Pressure (psi)		Temp	Reaction	Conv.	Products (ratio) e	Isolated
		CO	H2	( <sup>O</sup> C)	Time (hr)	(%)		Yield (%) f
1	3/O <sub>2</sub>		1 atm	rt	1.5	100	cyclooctene oxide	67
2	4	-	200	rt	1	100	cyclooctene oxide	78 g
3	4-mont <sup>b</sup>	-	300	rt	18	< 5	cyclooctanone	-
4	[Ir(COD)Cl] <sub>2</sub> c	300	<b>45</b> 0	130	15	100	cyclooctene oxide (72)	95
							cyclooctanone (26)	
							cyclooctanol (2)	
5	Ir(CO) <sub>3</sub> Cl d	-	450	100	18	100	cyclooctene oxide (68)	93
							cyclooctanone (22)	
							cyclooctanol (10)	

Table 1. Selective hydrogenation of 1,3-cyclooctadiene monoxide catalyzed by 3/O2 or 4.

a. Reaction conditions for palladium catalyst: substrate (1 mmol), 3 (0.01 mmol) and O<sub>2</sub>, THF (10 mL), 1 atm of H<sub>2</sub>; for iridium catalyst: substrate (2 mmol), catalyst (0.02 mmol), CH<sub>2</sub>Cl<sub>2</sub> (10 mL), 200 psi H<sub>2</sub>. Work-up of both catalytic systems was effected by silica gel column chromatography using hexane/ethyl acetate (5/1) as the eluant. b. **4-montmorillonite** (50 mg). c. Metallic iridium powders were formed in the absence of carbon monoxide. d. Iridium powders were detected during the reaction. e. The products were identified by comparison of spectral data, and gas chromatography retention times, with that of authentic materials. The ratio of products was determined by <sup>1</sup>H NMR. f. Isolated by silica gel column chromatography, using hexane/ethyl acetate (5/1) as the eluant. g. A small amount of cyclooctanone (*ca*. 4 %) and a trace of cyclooctanol were detected by <sup>1</sup>H NMR of crude mixture.

Initial studies were conducted using 1,3-cyclooctadiene monoxide  $(1)^9$  as the reactant. The hydrogenation of the epoxide was examined with different catalytic systems, to form cyclooctene oxide (2), and the results are summarized in Table 1. The hydrogenation of 1 is readily catalyzed by the species generated from reaction of 1 mol % of the binuclear palladium complex,  $[(But_2PH)PdPBut_2]_2$  (3), with oxygen in THF, at room temperature and atmospheric hydrogen pressure, to form 2 as the only product (Table 1, entry 1). The cationic iridium(I) complex [Ir(COD)(PPh<sub>3</sub>)(PhCN)]BF<sub>4</sub> (4), catalyzes the same transformation in methylene chloride, at 200 psi hydrogen to give 2 in good yield with a small amount (ca. 4 %) of the isomerization product, cyclooctanone (Table 1, entry 2). It should be noted that the isomerization of 2 was not observed in the hydrogenation of 1 with the  $3/O_2$  system but was found with iridium complexes (see Table 1). The isomerization of epoxides to give carbonyl compounds is readily catalyzed by the palladium complexes, Pd(OAc)<sub>2</sub><sup>10</sup> and Pd(PPh<sub>3</sub>)<sub>4</sub>.<sup>11</sup> The heterogenized homogeneous catalyst, [Ir(COD)(PPh<sub>3</sub>)(PhCN)]<sup>+</sup>montmorillonite (4-mont), prepared by treatment of 4 with Na+-montmorillonite in a mixture of methanol and water, <sup>12</sup> reacts slowly with 1 to give only a trace of 2 and less than 5% of cyclooctanone (Table 1, entry 3). The iridium(I) complexes, [Ir(COD)Cl]<sub>2</sub> and Ir(CO)<sub>3</sub>Cl, are also catalytically active for the hydrogenation of 1 (Table 1, entries 4 and 5), although the selectivity for 2 is somewhat lower than that using  $3/O_2$  and 4. The results in Table 1 reveal that the mildest conditions are those utilizing the palladium complex as the catalyst,

The hydrogenation of other vinyl epoxides was examined using the catalyst derived from reaction of 3 with  $O_2$  or with the cationic iridium(I) complex, [Ir(COD)(PPh<sub>3</sub>)(PhCN)]BF<sub>4</sub> (4) as the catalyst, and the results are

Substrate	Catalyst <sup>a</sup>	Reaction	Conv.	Products (ratio) d	Isolated e
		Time (hr)	(%)		Yield (%)
(The	3/O <sub>2</sub>	3	100	cycloheptene oxide (40)	60
				2-cyclohepten-1-ol (13)	
		•		3-cyclohepten-1-ol (7)	
				cycloheptanone (40)	
	4	_ 5	100	cycloheptanone	91
=Ph	3/O2	6	100	∼Ph	88
0	4 b	20	96	ò	71 f
=Ph	3/O <sub>2</sub>	4	100	$\sqrt{Ph}$	87
Осн₃	4 <sup>c</sup>	2	100	ОСН₃	63 g
	3/O <sub>2</sub>	3	100		84
ÛŤ					
· ·					
				(25)	
$\sim \sim \sim$	3/O <sub>2</sub>	24	100		60
L NO2					
				(40)	
			ļ	ОН	ļ
				NO <sub>2</sub> (60)	
	Substrate for o = for	Substrate Catalyst a A A A A A A A A	Substrate Catalyst a Reaction Time (hr) $3/O_2$ 3 4 5 $3/O_2$ 6 4 b 20 4 b 20 4 c 2 $CH_3$ $4$ c 2 $3/O_2$ 4 4 c 2 $3/O_2$ 3 $3/O_2$ 3 $3/O_2$ 3 $3/O_2$ 3 $3/O_2$ 24	Substrate       Catalyst 4       Reaction       Conv. Time (hr) $\checkmark$ 3/O <sub>2</sub> 3       100 $\checkmark$ 5       100 $\checkmark$ 5       100 $\checkmark$ $\checkmark$ 6       100 $\checkmark$ $\bullet$ 20       96 $\checkmark$ $\uparrow$ $3/O_2$ 4       100 $\checkmark$ $\uparrow$ $20$ 96 $\checkmark$ $\uparrow$ $100$ $4^{\circ}$ $2$ 100 $\checkmark$ $\uparrow$ $3/O_2$ $4$ $100$ $\checkmark$ $\uparrow$ $100$ $100$ $100$ $\checkmark$ $\uparrow$ $100$ $100$ $100$ $\checkmark$ $\uparrow$ $100$ $100$ $100$ $100$ $\checkmark$ $\land$ $100$ $10$	Substrate Catalyst a Reaction Conv. Products (ratio) a Time (hr) (%) 3/O <sub>2</sub> 3 100 cycloheptene oxide (40) 2-cycloheptene oxide (40) 2-cyclohepten-1-ol (13) 3-cyclohepten-1-ol (13) 3-cycloheptenone (40) cycloheptanone 4 5 100 cycloheptanone $\overrightarrow{Ph}$ 3/O <sub>2</sub> 6 100 $\overrightarrow{Ph}$ 4 b 20 96 $\overrightarrow{O}$ $\overrightarrow{Ph}$ 3/O <sub>2</sub> 4 100 $\overrightarrow{O}$ $\overrightarrow{Ph}$ 3/O <sub>2</sub> 3 100 $\overrightarrow{O}$ $\overrightarrow{CH_3}$ 3/O <sub>2</sub> 3 100 $\overrightarrow{O}$

Table 2. Selective hydrogenation of vinyl epoxides catalyzed by 3/O2 or 4.

a. Reaction conditions for palladium catalyst: substrate (1.0 mmol), 3 (0.01 mmol) preactivated with  $O_2$ , THF (10 mL), room temperature, 1 atm of H<sub>2</sub>; for iridium catalyst: substrate (1.0 mmol), catalyst (0.01 mmol), CH<sub>2</sub>Cl<sub>2</sub> (5 mL), room temperature, 200 psi H<sub>2</sub>. Work-up of both catalytic systems was effected by silica gel column chromatography using hexane/ethyl acetate (5/1) as the eluant. b. substrate (1.0 mmol), 4 (0.02 mmol), 500 psi H<sub>2</sub>. c. substrate (1.0 mmol), 4 (0.03 mmol), 1,000 psi H<sub>2</sub>. d. The products were identified by comparison of spectral data, and gas chromatography retention times with that of authentic materials, and the ratio of products was determined by <sup>1</sup>H NMR. e. Isolated by silica gel column chromatography, using hexane/ethyl acetate (5/1) as the eluant. f. A small amount (*ca.* 4 %) of 1-phenyl-2-butanone was observed by <sup>1</sup>H NMR of the crude mixture. g. An appreciable quantity (*ca.* 17 %) of 2-methyl-2-phenyl butanal was detected by <sup>1</sup>H NMR of the crude mixture.

presented in Table 2. The hydrogenation of 1,3-cycloheptadiene monoxide, catalyzed by 3 and oxygen, did not show high selectivity, and gave a mixture of four hydrogenation products, cycloheptene oxide (40 %), 2cyclohepten-1-ol (13 %), 3-cyclohepten-1-ol (7 %) and cycloheptanone (40 %), whereas cycloheptanone was obtained almost quantitatively, with a trace amount of cycloheptene oxide, when the iridium complex, 4, was employed as the catalyst. These observations may be explained by the rapid isomerization of the produced cycloheptene oxide during the catalysis (Table 2, entry 1). The acyclic terminal olefinic epoxides,  $^{13}$  2-phenyl3-vinyl-oxirane and 2-methyl-2-phenyl-3-vinyloxirane, are easily hydrogenated by the catalyst generated from 3 and O<sub>2</sub> to give the corresponding saturated epoxides in high yields. The unsaturated epoxides also react with 4 under a high pressure of hydrogen, at room temperature, to produce the saturated aldehydes, accompanied by a small amount of isomerization products: 4 % of the hydrogen shift product, 1-phenyl-2-butanone, was formed from 2-phenyl-3-vinyloxirane while 2-methyl-2-phenyl-3-vinyloxirane afforded an appreciable amount (*ca.* 17 %) of 2-methyl-2-phenylbutanal, which may arise by ethyl migration (Table 2, entries 2 and 3). It has been reported that [Rh(CO)<sub>2</sub>Cl]<sub>2</sub> and Mo(CO)<sub>6</sub> catalyze the alkyl or aryl group migration of epoxides.<sup>14</sup>

The reactions of acyclic internal olefinic epoxides<sup>15</sup> with  $3/O_2$  affords the corresponding saturated epoxides which can experience further reaction to give saturated alcohols (Table 2, entries 4 and 5).

In conclusion, various saturated epoxides can be obtained selectively from the hydrogenation of vinyl epoxides with homogeneous palladium or iridium catalysts under mild conditions. The catalyst generated from the binuclear palladium complex, 3 with oxygen is more effective than the iridium compound, 4, for the chemoselective reduction of the double bond of vinyl epoxides.

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