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**Supplementary Material Available:** Spectroscopic and analytical data for compounds **4**, **8**, and **11-13** (1 page). Ordering information is given on any current masthead page.

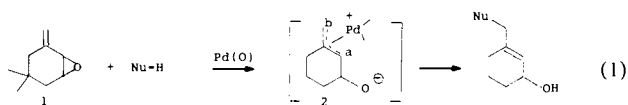
### Palladium-Mediated Vicinal Cleavage of Allyl Epoxides with Retention of Stereochemistry: A Cis Hydroxylation Equivalent

Barry M. Trost\* and Steven R. Angle

McElvain Laboratories of Organic Chemistry  
Department of Chemistry  
University of Wisconsin—Madison  
Madison, Wisconsin 53706

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The value of epoxides as synthetic intermediates in complex synthesis has increased dramatically as a result of the ability to control stereochemistry in both a relative and absolute sense.<sup>1</sup> Subsequent transformations rely on the ease of opening epoxides which, of necessity, proceeds with inversion and thus corresponds to a trans addition to the olefin. If epoxides could be opened with retention of configuration to give an equivalent of a cis addition, a practical broadening of the application of these intermediates in synthesis would result. In the case of vinyl epoxides, such as **1**, such a possibility could derive from a metal-promoted opening via **2** (eq 1). However, there is a strong bias in such systems



resulting from the presence of the oxygen substituent for a nucleophile to attack distal to that substituent (i.e., at  $\text{C}_b$  in **2**).<sup>2</sup> The net result is a clean 1,4-addition even in allyl systems of equal substitution or ones in which substitution might be thought to favor proximal attack (corresponding to  $\text{C}_a$  in **2**) even with carboxylic acids as the reacting partners. Considering oxygen nucleophiles, we are confronted with an additional problem, the product is also an excellent substrate for metal-catalyzed reactions.<sup>3</sup> In this paper we wish to report a practical solution to both of these problems involving carbon dioxide as a carboxylating agent in metal-catalyzed reactions.<sup>4,5</sup> The current great emphasis on diastereose-

**Table I.** Carbonate Synthesis from Vinyl Epoxides<sup>a</sup>

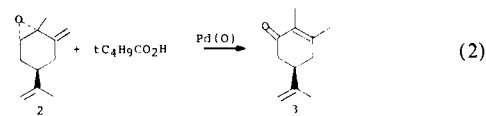
entry	vinyl epoxide	carbonate <sup>b</sup>	yield <sup>c</sup>
1			84%
2			85%
3			92%
4			95%
5			57%
6			82%
7			71%

<sup>a</sup> All reactions were performed according to the general procedure.

<sup>b</sup> All new compounds have been fully characterized spectrally and elemental composition established by high-resolution mass spectroscopy or combustion analysis. <sup>c</sup> Yields are for isolated pure products.

lective methods to form polyol systems makes such a development highly timely.

The notion to resolve the regioselectivity problem revolves around the question of anchoring a pro-nucleophile to the oxygen of **2** such that the nucleophile would be delivered in an intramolecular fashion to favor proximal attack. Such a capture of the oxygen must be faster than the known hydrogen migrations



in Pd-mediated reactions.<sup>6</sup> For example, in the case of **2**, using pivalic acid as a pro-nucleophile led only to rearrangement product **3** and no trapping.<sup>7</sup> We envisioned the possibility that a cumulative unsaturated species (carbon dioxide, carbon disulfide, isocyanate, etc.) might be a sufficiently reactive electrophile to capture the alkoxide in **2** and the resulting carboxylate or related

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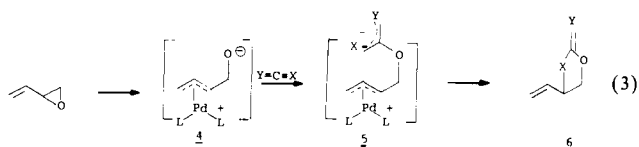
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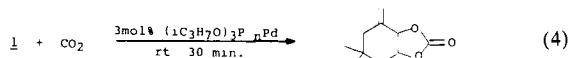
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(7) Carboxylic acids frequently act as nucleophiles in efficient and stereocontrolled 1,4-opening of vinyl epoxides in the presence of Pd(0) catalysts. Balkovec, J. M.; Angle, S. R., unpublished work in these laboratories.

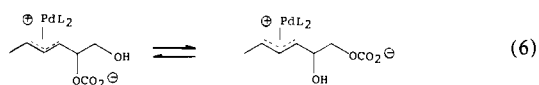
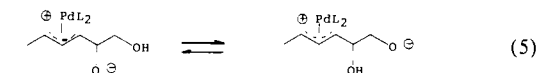
anion be a reasonable enough nucleophile to subsequently cyclize to constitute a useful approach (eq 3). The choice of the proper



catalyst proved to be critical in the realization of such a scheme. With a goal of *cis*-diol formation, pilot experiments used CO<sub>2</sub> and (Ph<sub>3</sub>P)<sub>4</sub>Pd. Reactions led to little to no reaction and fairly rapid deposition of a black solid, presumably Pd black. Anticipating that the basicity of the Ph<sub>3</sub>P leads to its being stripped from the Pd by preferential coordination to CO<sub>2</sub>, switching to a less basic phosphorus ligand may overcome destruction of the active catalyst. Indeed, generating a Pd(0) complex in situ using triisopropyl phosphite as the ligand with **1** as the substrate leads to an excellent yield of the carbonate as exemplified in eq 4 and generalized in Table I. The mildness of the reaction conditions, room temperature and 40 psi of pressure, is especially noteworthy.



Considering the high reactivity of vinyl carbonates as substrates for Pd(0),<sup>8</sup> the excellent yields demonstrate the much higher reactivity of the vinyl epoxides which we believe, in part, stems from carbon dioxide serving as a co-catalyst. Entry 7 lends some credence to this suggestion. Equilibration of either the initial alkoxide or carbonate as in eq 5 or 6 might have led to six-

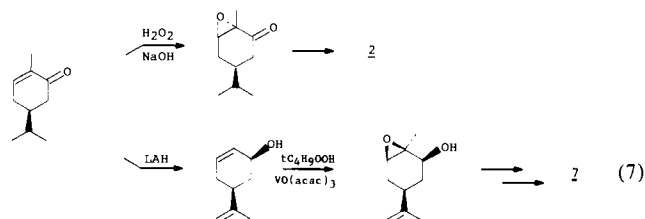


membered rings. None form. Such high chemoselectivity even in the presence of a potential neighboring group enhances the applicability of this approach. Thus, these reactions proceed rapidly at room temperature in contrast to other Pd-catalyzed reactions of vinyl epoxides. It does require a slightly elevated CO<sub>2</sub> pressure (40 psi) for satisfactory results. While formation of the carbonate is rapid (i.e., 4 → 5, eq 3), the second stage, cyclization of **5** to product **6**, is slow enough that a *cis* olefin completely isomerizes to a *trans* olefin prior to cyclization (Table I, entry 5) but fast enough that equilibration of the carbonate as in eq 6 does not occur.

The reaction exhibits high chemo-, regio-, and diastereoselectivity in both cyclic and acyclic cases. The effectiveness of this approach is illustrated by the efficiency of the *cis* carbonate formation with **2** in contrast to the failure of any trapping with a carboxylic acid (eq 2). Entry 6 is quite interesting since it contains a vinyl epoxide and a butenolide, both of which can be envisioned to be activated by Pd(0). The unfavorable geometry of the latter leaving group may account for its failure to react. Entries 3 and 4 nicely highlight the stereochemical control available in this equivalent of a *cis* hydroxylation. Vinyl epoxide **2** derives from the direct epoxidation of carvone followed by olefination, whereas the hydroxyl directed epoxidation establishes the stereochemistry of the vinyl epoxide **7** (eq 7). Having each diastereomeric epoxide translates into having either *cis*-diol.

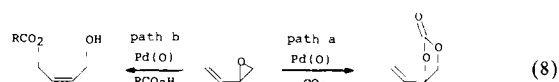
A typical experimental procedure follows. A mixture of 6.4 mg (0.029 mmol, 3 mol %) of palladium acetate and 49 μL (0.20 mmol) of triisopropyl phosphite in 1.5 mL of THF was stirred 10 min at room temperature. A solution of *n*-butyllithium (38

(8) Trost, B. M. In "New Synthetic Methodology and Biologically Active Substrates"; Yoshida, Z., Ed.; Kodansha Ltd.: Tokyo, 1981; p 78. Trost, B. M.; Runge, T. A. *J. Am. Chem. Soc.* 1981, 103, 7550. Also see: Tsuji, J.; Shimizu, I.; Minami, I.; Ohashi, Y. *Tetrahedron Lett.* 1982, 23, 4809.



μL of 1.5 M hexane solution, 0.057 mmol) was added. After 30 min, the resultant catalyst solution was added to a stirring solution of 156.5 mg (0.954 mmol) of **7** in 1.5 mL of THF in a Griffin-Worden pressure bottle (Kontes) under a CO<sub>2</sub> atmosphere and then pressurized to 40 psi with CO<sub>2</sub>. After 4 h, the solution was concentrated in vacuo and the residue chromatographed to give 188.6 mg (95%) of cyclic carbonate.

The current reaction effects a regio- and diastereoselective synthesis of *cis*-1,2-diols from vinyl epoxides (path a, eq 8); whereas, with use of carboxylic acids as partners for Pd-mediated condensation with vinyl epoxides, a *cis*-1,4-diol synthesis results (path b, eq 8). From a single substrate, palladium templates,



which enforce substitution with retention of configuration, also allow control of regioselectivity by converting an intermolecular into an intramolecular delivery of a nucleophile—a flexibility that should prove useful in the synthesis of polyoxygenated natural and unnatural products.<sup>9</sup>

**Acknowledgment.** We thank the National Science Foundation and the National Institutes of Health for their generous support of our programs.

(9) After the submission of this paper, the single reaction of butadiene monoepoxide with CO<sub>2</sub> mediated by (Ph<sub>3</sub>P)<sub>4</sub>Pd has been described: Fujinami, T.; Suzuki, T.; Kamiya, M. *Chem. Lett.* 1985, 199. We had found that the reaction of entry 6 with use of (Ph<sub>3</sub>P)<sub>4</sub>Pd as catalyst failed—depositing only Pd black. Further attempts using this catalyst for entry 1 have also failed in our hands.

## Isolation of Oxo-Centered Cobalt(III) Clusters and Their Role in the Cobalt Bromide Catalyzed Autoxidation of Aromatic Hydrocarbons

Charles E. Sumner, Jr.,\* and Guy R. Steinmetz

Research Laboratories, Eastman Chemicals Division  
Eastman Kodak Company, Kingsport, Tennessee 37662

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Oxo-centered transition-metal cluster complexes<sup>1-6</sup> of the formula [M<sub>3</sub>O(OAc)<sub>6</sub>L<sub>3</sub>]X, where M = Fe, Mn, Cr, Rh, and Ir and L = pyridine, β-picoline, H<sub>2</sub>O, and methanol, and other heteronuclear clusters<sup>2-5</sup> have recently been the subject of many spectroscopic studies. These types of complexes are of interest because they may be catalysts or catalyst intermediates in the oxidation of many organic substrates.<sup>7-9</sup> Of particular interest

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