

# Regioselective and in Some Cases Stereoselective Carbonylation of $\alpha$ -Allenic Alcohols to $\alpha$ -Vinylacrylic Acids Catalyzed by a Cationic Palladium Complex

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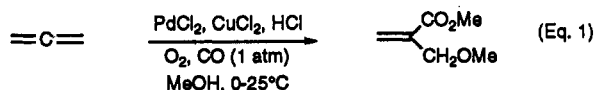
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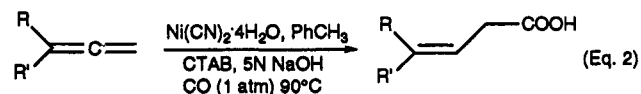
**Summary:**  $trans$ - $[(Cy_3P)_2Pd(H)(H_2O)]^+BF_4^-$ , in the presence of  $p$ -toluenesulfonic acid, catalyzes the carbonylation of  $\alpha$ -allenic alcohols to  $\alpha$ -vinylacrylic acids in 43–74% yields.

Of the few examples of the carbonylation of allenes that have been reported in the literature, all require the presence of metal compounds, in stoichiometric or catalytic amounts. During the 1960's, several reports appeared on the homogeneous carbonylation and hydroesterification of allenes catalyzed by various metal complexes. These reactions afford unsaturated carboxylic esters and acids in low to moderate yields.<sup>1,2</sup>

Allenes undergo alkoxy-alkoxycarbonylation in fine yields when treated with carbon monoxide, oxygen, palladium, and copper(II) chloride, and hydrochloric acid in methanol<sup>3</sup> (eq 1).






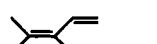

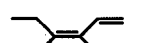

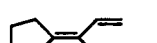
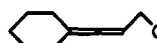
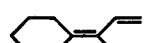

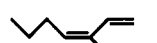






More recently, a nickel cyanide phase-transfer system was developed for the regioselective carboxylation of allenes to form unsaturated carboxylic acids<sup>4</sup> (eq 2).



In 1991, the novel hydrido-aquopalladium complex  $trans$ - $[(Cy_3P)_2Pd(H)(H_2O)]BF_4$  (1) was described in the literature.<sup>5</sup> This complex has both aquo and hydride ligands and is cationic, making it attractive as a catalyst for hydrocarbonylation reactions. Recently, this catalyst proved useful for the carbonylation of alkynols and alkynediols to give dienoic acids and esters.<sup>6</sup>

There have been no studies of the carbonylation of allenyl alcohols. We now wish to report that 1 is an effective catalyst for the selective conversion of  $\alpha$ -allenic alcohols to 2-vinylacrylic acids. Starting material was recovered when 4-methyl-2,3-hexadien-1-ol (2a) was reacted with 1 and carbon monoxide in THF (83.3/1.0 ratio of allenyl alcohol/1) at 20 atm and 100 °C. However, when the reaction was repeated in the presence of  $p$ -toluene-

Table 1. Conversion of  $\alpha$ -Allenic Alcohols to 2-Vinylacrylic Acids Catalyzed by 1

substrates <sup>a</sup>	products <sup>b</sup>	yield <sup>c</sup> (%)
2a 	2b 	64
3a 	3b 	59
4a 	4b 	55
5a 	5b 	43
6a 	6b 	58
7a 	7b 	61
8a 	8b 	74
9a 	9b 	72
10a 	10b 	64

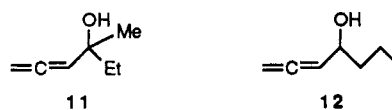
<sup>a</sup>  $\alpha$ -Allenic alcohols were synthesized using known methodology.<sup>7</sup>

<sup>b</sup> Products were identified by spectroscopic methods [IR, MS, NMR (<sup>1</sup>H, <sup>13</sup>C)]. <sup>c</sup> Isolated yield.

sulfonic acid ( $p$ -TsOH), 4-methyl-1,3-hexadiene-3-carboxylic acid (2b) was obtained in 64% yield, the  $E/Z$  ratio being 1. The ratio of 1/ $p$ -TsOH was 1/2.

A series of trisubstituted and 1,3-disubstituted  $\alpha$ -allenic alcohols were carbonylated under the conditions described for 2a, and the results are presented in Table 1. The dienoic acids were isolated in 43–62% yield in the case of trisubstituted allenic alcohols. Higher yields (61–74%) resulted using 1,3-disubstituted  $\alpha$ -allenic alcohols (7a–10a) as reactants. Furthermore, we were gratified to observe that the carbonylation of 7a–10a was stereoselective, affording exclusively the  $E$  isomer, as confirmed by NOE experiments.

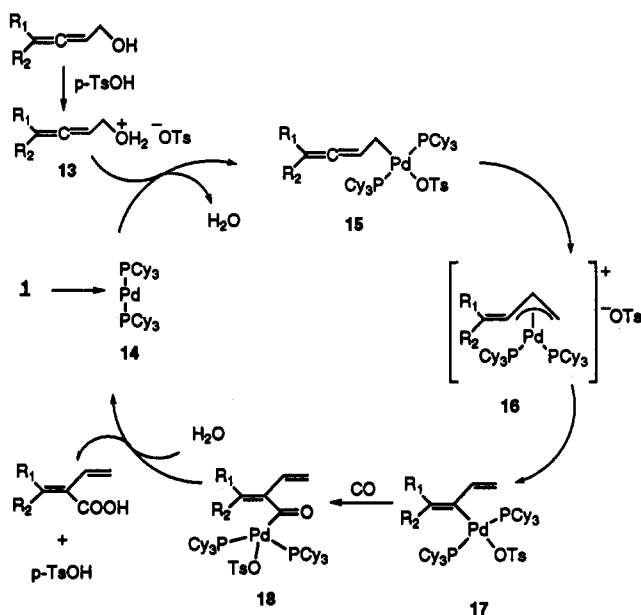
No unsaturated carboxylic acid was obtained from the reaction of the monosubstituted allenic alcohols 11 and 12 under the same conditions. Instead, some uncharacterized



polymeric material was found. The presence of carbonyl groups (<sup>13</sup>C NMR: 172.5, 177.2, 182.2 ppm for product of

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 (1) Pino, P.; Piacenti, F.; Bianchi, M. In *Organic Synthesis via Metal Carbonyls*; Wender, I., Pino, P., Eds.; Wiley Interscience: New York, 1977; Vol. 2, pp 256–259.  
 (2) Jacobs, T. L. In *The Chemistry of the Allenes*; Landor, S. R., Ed.; Academic Press: New York, 1982; Vol. 2, pp 277–347.  
 (3) Alper, H.; Hartstock, F. W.; Despeyroux, B. *J. Chem. Soc., Chem. Commun.* 1984, 905.  
 (4) Satyanarayana, N.; Amer, I.; Alper, H. *Organometallics* 1990, 9, 284.  
 (5) Leoni, P.; Sommovigo, M.; Pasquali, M.; Midollini, S.; Braga, D.; Sabatino, P. *Organometallics* 1991, 10, 1038.  
 (6) Huh, K. T.; Orita, A.; Alper, H. *J. Org. Chem.* 1993, 58, 6956.  
 (7) Cowie, J. S.; Landor, P. D.; Landor, S. R. *J. Chem. Soc., Perkin Trans. I* 1973, 720.

Scheme 1



11) in the polymers indicates that the reaction occurs in the same way as the di- and trisubstituted allenyl alcohols, but the lack of alkyl substituents at the terminus of the  $\alpha,\beta$ -unsaturated acid results in facile polymerization. In support of this possibility, acrylic acid was subjected to the same reaction conditions affording polymeric material.

A possible mechanism for the reaction is outlined in Scheme 1. *p*-Toluenesulfonic acid can protonate the allenic alcohol to give 13. Reaction of the latter with the Pd(0) complex 14 generated from 1 would form the allylpalladium intermediate 16 via 15. The same type of intermediate, where the  $\pi$ -allyl group is directly attached to the double bond, has been suggested for the reaction of allenyl esters and carbonates using Pd(0) catalysts.<sup>8</sup> On the other hand, oxidative addition of Pd(0) complexes to allylic alcohols to form allylpalladium complexes has been proposed by Trost and Verhoeven.<sup>9</sup> The formation of the

conjugated diene would be the driving force for the conversion of the  $\pi$ - to the  $\sigma$ -bonded complex 17. Carbonyl migration may then occur forming the acyl complex 18, and acylpalladium hydrolysis will give the product and regenerate the Pd(0) species.

To support the participation of 13 in this mechanism, some reactions were carried using bis(tricyclohexylphosphine)palladium(0) as the catalyst, and the same products and yields were obtained. It is not clear whether 14 is formed during the reaction, although an equilibrium between 1 and 14 can exist in solution.<sup>5</sup>

The following general procedure was used: a mixture of allenic alcohol (1 mmol), 1 (10 mg, 0.012 mmol), *p*-TsOH (4.6 mg, 0.024 mmol), and THF (5 mL) was reacted in an autoclave at 20 atm of carbon monoxide for 24 h at 100 °C. The reaction mixture was cooled to room temperature and filtered through Celite. The filtrate was diluted with ether (20 mL) and extracted with 0.5 N NaOH (3 × 10 mL). The combined aqueous phase was acidified with 1 N HCl and then extracted with ether (3 × 20 mL). The combined organic phase was dried (MgSO<sub>4</sub>), filtered, and concentrated under low pressure to give the product.

In conclusion, 1 is a good catalyst for the carbonylation of allenic alcohols to 2-vinylacrylic acids. The reaction is stereoselective in cases where the allene is 1,3-disubstituted. In addition, it is shown that 1, an air-stable complex, can be used as a precursor of the very reactive bis(tricyclohexylphosphine)palladium(0) complex. Finally, this reaction is remarkable since it involves formal activation of the C–O bond of alcohols, a rather uncommon process.

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**Supplementary Material Available:** <sup>1</sup>H and <sup>13</sup>C NMR spectra of all products (21 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(8) Nokami, J.; Maihara, A.; Tsuji, J. *Tetrahedron Lett.* 1990, 31, 5629.

(9) Trost, B. M.; Verhoeven, T. R. *J. Am. Chem. Soc.* 1980, 102, 4730 and references cited therein.