Catalytic and Stoichiometric Carbonylation of β,γ-Unsaturated Carboxylic Acids To Give Cyclic Anhydrides through Intermediate Palladium-Containing Cyclic Esters

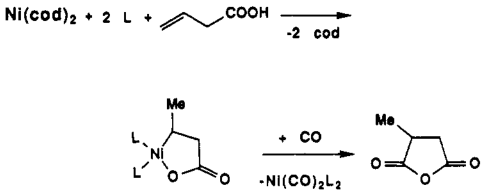
Kohtaro Osakada,* Myung-Ki Doh,[1] Fumiyuki Ozawa,[†] and Akio Yamamoto*,[‡]

Research Laboratory of Resources Utilization, Tokyo Institute of Technology,
4259 Nagatsuta, Midori-ku, Yokohama 227, Japan

Received January 23, 1990

Summary: **Palladium(0) complexes with tertiary phosphine ligands catalyze the carbonylative cyclization of 3-butenoic acid to give methylsuccinic anhydride and glutaric anhydride. Reaction of 3-butenoic acid with an equimolar amount of $Pd(CH_2{=}CHPh)(PMe_3)_2$ gives palladium-containing cyclic esters that are considered as the reaction intermediates in the above catalytic carbonylation.**

The transition-metal-promoted activation of bifunctional organic compounds followed by a carbonylative cyclization process is useful in the synthesis of various organic compounds with carbonyl functions.[2-8] Previously we observed nickel-promoted stoichiometric conversion of α,β- and β,γ-unsaturated carboxylic acids to cyclic anhydrides through formation of isolable nickel-containing cyclic esters followed by their carbonylation.[9] Accomplishment of a catalytic process with the nickel system is not feasible because the Ni^0L_2 generated in reaction 1 forms a CO-coordinated complex that is too inert to react further with the β,γ-unsaturated acid. We report here the achievement of such a catalytic transformation by employing palladium catalysts. A full characterization of a palladium-containing cyclic ester involved as the intermediate in the catalytic cycle is also included.



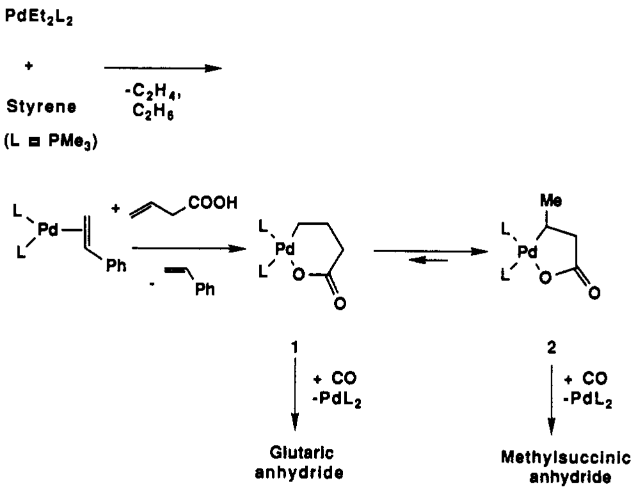
(1)

Table I. Palladium-Catalyzed Carbonylation of 3-Butenoic Acid[a]

catalyst	product yield, % crotonic acid	 glutaric anhydride	 methylsuccinic anhydride
$Pd(PPh_3)_4$	25	37	11
$Pd(PPh_3)_4$[b]	32	29	11
$Pd(PPh_3)_4$[c]	24	38	11
$Pd(CO)(PPh_3)_3$	18	38	13
$PdEt_2(PMe_3)_2$	21	13	2
$Pd(PCy_3)_2$	27	4	2

[a] Catalyst/substrate = 1/50; under 20 atm of CO for 8–10 h at 100 °C in THF unless otherwise stated. Yields were determined by GLC. [b] 70 atm of CO at 100 °C. [c] In toluene.

Scheme I



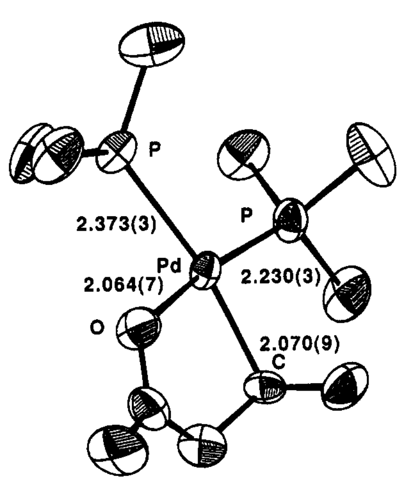


Figure 1. Molecular structure of $(Me_3P)_2\overline{Pd(OCOCH_2CHCH_3)}$ (2).

As shown in Table I, triphenylphosphine-coordinated palladium(0) complexes convert 3-butenoic acid into me-

---

[†] Present address: Catalysis Research Center, Hokkaido University, Sapporo 060, Japan.

[‡] Present address: Department of Applied Chemistry, School of Science and Engineering, Waseda University, Okubo, Shinjuku-ku, Tokyo 169, Japan.

(1) On leave from the Department of Chemistry, Yeungnam University, 713-749 Korea.

(2) (a) Falbe, J.; Korte, F. *Chem. Ber.* **1962**, *95*, 2680. (b) Mullen, A. In *New Syntheses with Carbon Monoxide*; Falbe, J., Ed.; Springer-Verlag: Berlin, Heidelberg, New York, 1980. (c) Falbe, J. *Carbon Monoxide in Organic Synthesis*; Springer-Verlag: Berlin, Heidelberg, New York, 1970; Chapter 4.

(3) McMurry, J. E.; Andrus, A.; Ksander, G. M.; Musser, J. H.; Johnson, M. A. *J. Am. Chem. Soc.* **1979**, *101*, 1330.

(4) (a) Murray, T. F.; Norton, J. R. *J. Am. Chem. Soc.* **1979**, *101*, 4107. (b) Murray, T. F.; Samsel, E. G.; Varma, V.; Norton, J. R. *J. Am. Chem. Soc.* **1981**, *103*, 7520.

(5) (a) Ishikura, M.; Mori, M.; Terashima, M.; Ban, Y. *J. Chem. Soc., Chem. Commun.* **1982**, 741. (b) Uozumi, Y.; Kawasaki, N.; Mori, E.; Mori, M.; Shibazaki, M. *J. Am. Chem. Soc.* **1989**, *111*, 3725.

(6) Villemin, D. *Tetrahedron Lett.* **1983**, *24*, 2855.

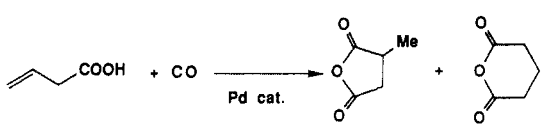
(7) Ozawa, F.; Yanagihara, H.; Yamamoto, A. *J. Org. Chem.* **1986**, *51*, 415.

(8) Negishi, E.; Zhang, Y.; Shimoyama, I.; Wu, G. *J. Am. Chem. Soc.* **1989**, *111*, 8018.

(9) (a) Yamamoto, T.; Igarashi, K.; Komiya, S.; Yamamoto, A. *J. Am. Chem. Soc.* **1980**, *102*, 7448. (b) Yamamoto, T.; Sano, K.; Yamamoto, A. *Ibid.* **1987**, *109*, 1092.

0276-7333/90/2309-2197$02.50/0

thylsuccinic anhydride and glutaric anhydride at 100 °C under moderate CO pressure:[10]



(2)

The reaction is accompanied by isomerization of the 3-butenoic acid to crotonic acid. Employment of basic tertiary phosphines such as trimethyl- and tricyclohexylphosphine gave less active catalysts, but PMe_3 served as a suitable ligand to allow the isolation and characterization of reaction intermediates.

The treatment of $PdEt_2(PMe_3)_2$ with styrene gives a coordinatively unsaturated styrene complex, $Pd(CH_2{=}CHPh)(PMe_3)_2$,[11] that serves as an appropriate precursor for the reaction with 3-butenoic acid. NMR (^{31}P and ^{13}C) spectra of the reaction mixture of $Pd(CH_2{=}CHPh)(PMe_3)_2$ with an equimolar amount of 3-butenoic acid at room temperature reveals the following reaction course. Initially the intermediate six-membered palladium-containing cyclic ester $(Me_3P)_2\overline{Pd(OCOCH_2CH_2CH_2})$ (1) is formed predominantly and it undergoes skeletal isomerization to give an equilibrated mixture of 1 and the five-membered palladium-containing cyclic ester $(Me_3P)_2\overline{Pd(OCOCH_2CH}CH_3)$ (2) in a ratio of 5:95. Complex 2 was fully characterized by single-crystal X-ray analysis,[12] spectroscopic means, and elemental analysis, whereas 1 was characterized by means of NMR spectroscopy in situ.[13] Figure 1 shows the molecular structure of 2 determined by X-ray crystallography. Complex 2 has a somewhat disordered square-planar coordination around the palladium center. The two Pd–P bond distances showed a significant difference from each other due to the different trans influences of the coordinating carbon atom and the coordinating oxygen atom. The reaction of 2 with CO at 20 atm and 100 °C preferentially gives methylsuccinic anhydride, presumably by CO insertion into the Pd–C bond followed by reductive elimination.[14] The formation of glutaric anhydride in the catalytic process can be accounted for analogously as the conversion of 1 and CO into the six-membered cyclic anhydride and a Pd(0) complex.[15]

Conversion of the six-membered nickel-containing cyclic ester into the methyl-substituted five-membered nickel-containing cyclic ester, proceeding through β-hydrogen elimination and an olefin insertion process, has been found to be controlled by chiral phosphine ligands.[9b] The realization of the catalytic process as reported herein now suggests the feasibility of catalytic asymmetric conversion of β,γ-unsaturated acids to chiral succinic anhydride derivatives.

Acknowledgment. We are grateful for support of this work by a Grant-in-Aid for Scientific Research by the Ministry of Education, Science, and Culture of Japan.

Registry No. 1, 127973-37-9; 2, 127973-38-0; *trans*-$PdEt_2(PMe_3)_2$, 124717-55-1; $Pd(PPh_3)_4$, 14221-01-3; $Pd(CO)(PPh_3)_3$, 24670-32-4; $Pd(PCy_3)_2$, 33309-88-5; styrene, 100-42-5; 3-butenoic acid, 625-38-7; methylsuccinic anhydride, 4100-80-5; glutaric anhydride, 108-55-4; crotonic acid, 3724-65-0.

Supplementary Material Available: An ORTEP drawing and tables of positional and anisotropic thermal parameters and bond distances and angles for complex 2, a listing of all NMR data for complexes 1 and 2, and a description of the experimental procedure for the preparation of the complexes (10 pages); a listing of observed and calculated structure factors for complex 2 (11 pages). Ordering information is given on any current masthead page.

---

[10] Similar catalytic carbonylations of other unsaturated carboxylic acids were also examined. γ,δ-Unsaturated carboxylic acids such as 4-pentenoic acid and 3-phenyl-3-butenoic acids react with CO under similar conditions to give a small amount (<10%) of 2-methyl- and 2-phenylglutaric anhydride, respectively. Carbonylation of methacrylic acid gives polymeric products rather than the desired cyclic anhydride.

[11] The complex $Pd(CH_2{=}CHPh)(PMe_3)_2$ was not isolated in crystalline form due to its high solubility in most common organic solvents and was characterized in situ by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. See: Ozawa, F.; Ito, T.; Nakamura, Y.; Yamamoto, A. *J. Organomet. Chem.* **1979**, *168*, 375.

[12] Crystal data: $C_{10}H_{24}O_2P_2Pd$, triclininc, space group $P\bar{1}$, $a = 9.854$ (2) Å, $b = 10.445$ (1) Å, $c = 9.332$ (2) Å, $\alpha = 103.73$ (1)°, $\beta = 120.74$ (1)°, $\gamma = 94.35$ (1)°, $V = 778.4$ (3) Å^3, $Z = 2$, $d_{calcd} = 1.471$ g cm^{-3}, $d_{obsd} = 1.47$ g cm^{-3}, $3° < 2\theta < 45°$, 2072 unique data, 1960 observed data ($F_o > 3\sigma(F_o)$). The structure was solved by direct methods (SAPI85) and Fourier techniques and refined by full-matrix least-squares calculations. $R = 0.039$; $R_w = 0.037$.

[13] NMR data for 1: $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2, −40 °C, ppm referenced from the solvent signal (53.2 ppm)) 179.2 ($C{=}O$), 39.1 (CH_2CO, $J(CH) = 124$ Hz), 28.0 (CH_2Pd, d, $J(CP) = 93$ Hz, $J(CH) = 125$ Hz), 25.1 ($CH_2CH_2CH_2$, $J(CH) = 127$ Hz), 15.7 ($P(CH_3)_3$, d, $J(CP) = 16$ Hz), 13.9 ($P(CH_3)_3$, d, $J(CP) = 17$ Hz); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −40 °C, ppm referenced from external PPh_3) 4.9 (d, $J(PP) = 42$ Hz), 14.2 (d). NMR data for 2: $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −40 °C, ppm referenced from the solvent signal (53.2 ppm)) 187.4 ($C{=}O$), 48.3 (CH_2, d, $J(CP) = 6$ Hz, $J(CH) = 125$ Hz), 33.2 (CH, d, $J(CP) = 91$ Hz, $J(CH) = 127$ Hz), 17.0 ($P(CH_3)_3$, dd, $J(CP) = 32$ and 4 Hz), 15.4 ($P(CH_3)_3$, d, $J(CP) = 18$ Hz); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −40 °C, ppm referenced from external PPh_3) −0.2 (d, $J(PP) = 39$ Hz), −15.7 (d). The $^{31}P\{^1H\}$ NMR signal of PPh_3 appears ca. 6.0 ppm downfield from that of 85% H_3PO_4 in CD_2Cl_2.

[14] In the stoichiometric carbonylation of PdMe(OR)(dppe) (R = $CH(CF_3)_2$; dppe = 1,2-bis(diphenylphosphino)ethane) we observed CO insertion into the Pd–O bond rather than into the Pd–C bond, whereas CO insertion into the Pd–C bond rather than into the Pd–O bond was observed in *trans*-$PdMe(OPh)(PEt_3)_2$ and PdMe(OPh)(dppe). See: Komiya, S.; Akai, Y.; Tanaka, K.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1985**, *4*, 1130. Kim, Y.-J.; Osakada, K.; Sugita, K.; Yamamoto, T.; Yamamoto, A. *Ibid.* **1988**, *7*, 2182. Kim, Y.-J.; Osakada, K.; Sugita, K.; Yamamoto, T.; Yamamoto, A. *J. Am. Chem. Soc.* **1990**, *112*, 1096. This fact suggests that the ease of CO insertion depends on the stability of the Pd–O bond. In the present case CO insertion into the Pd–C bond is a probable reaction pathway.

[15] Since methylsuccinic anhydride does not undergo isomerization into glutaric anhydride under the conditions of the catalytic carbonylation, the ratio of the yields of the two products depends on the relative stability of the five- and six-membered palladium-containing cyclic esters or the relative reactivity toward CO between them. The preponderance of glutaric anhydride in the catalytic reaction products seems to indicate a significant influence of their relative reactivity toward CO in the present case.