Palladium-Catalyzed Reactions of Ketone α-Carbonates with Norbornenes. An Unusual Cyclopropanation

Sensuke Ogoshi, Tsumoru Morimoto, Ken-ichi Nishio, Kouichi Ohe, and Shinji Murai*

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan

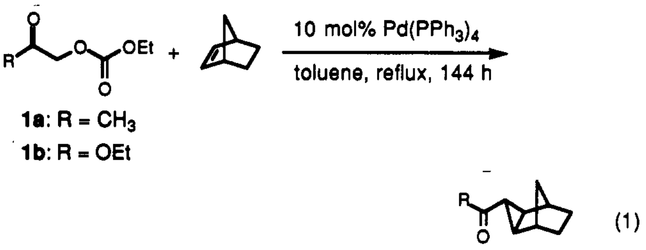
Received September 9, 1992

Summary: In the presence of a palladium(0) catalyst, ketone α-carbonates react with norbornene to give a cyclopropane derivative via an oxa-π-allylpalladium intermediate.

The chemistry of oxa-π-allylpalladium has been thoroughly investigated.[1] Most oxa-π-allylpalladium species have been generated by transmetalation of enol silyl ethers with a Pd(II) complex.[1b] However, only scattered examples of direct oxidative addition to Pd(0) species of bonds α to a carbonyl leading to the formation of oxa-π-allylpalladium complexes have been reported.[2] To the best of our knowledge, such oxidative additions are limited to a few cases: Palladium(0)-catalyzed carbonylation of α-halo ketones,[3] Pd(0)-catalyzed synthesis of pyrrolidines using an intramolecular cyclization of an α-bromo ester,[4] and conversions of α,β-epoxy ketones to 1,3-diketones[5a] and β-hydroxy ketones.[5b]

We have been interested in the formation of carbon–carbon bonds via oxa-π-allylpalladium intermediates which are obtained by oxidative addition of ketone α-carbonates to Pd(0) complexes followed by decarboxylation. We wish to report here the unusual palladium-catalyzed cyclopropanation mediated by oxa-π-allylpalladium.

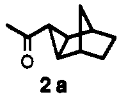
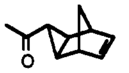
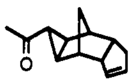
When acetonyl ethyl carbonate (**1a**)[6] reacted with norbornene in the presence of 10 mol % $Pd(PPh_3)_4$ in toluene at reflux temperature, *exo*-3-acetyltricyclo[3.2.1.0^{2,4}]octane (**2a**, 90%, GC yield) was obtained (eq 1). Similarly, the carbonate **1a** reacted with other norbornenes to give the corresponding cyclopropanation products in good yields. When the reaction was carried out in DMF, the rate of the reaction was significantly accelerated. Typical results are listed in Table I.



1a: R = CH_3
1b: R = OEt

2a 90 %
2b -

Table I. Reaction of 1a with Norbornenes[a]

norbornene	solvent	time, h	product	yield, %[c]
	toluene	144	 **2a**	90 (74)
	DMF	7		99
	toluene	111	 **3a**	81 (69)[b]
	DMF	11		52[b]
	toluene	90	 **4a**	79 (68)
	DMF	10		99

[a] Reaction conditions: carbonate **1a** (1 mmol), norbornene (10 mmol), $Pd(PPh_3)_4$ (0.1 mmol), solvent (3 mL), bath temperature 120 °C. [b] Norbornadiene (3 mmol). [c] GC yield. Isolated yields are in parentheses.

The use of excess norbornene relative to carbonate **1a** was required to obtain high yields. A carbonate of ethyl acetate, **1b**,[7] did not react with norbornene under the same reaction conditions.

Scheme I shows plausible paths for the formation of the cyclopropane. First, oxidative addition of **1a** followed by decarboxylation affords oxa-π-allylpalladium A. In path a, an ethoxy group abstracts a proton α to palladium to generate α-ketocarbene palladium B, which can be expected to react with various olefins.[8] However, carbonate **1a** reacted only with norbornene derivatives to give cyclopropanated products.[9] Thus path a does not seem likely. In path c, proton abstraction from a methyl group leads to formation of oxatrimethylenemethanepalladium D (oxatrimethylenemethane = OTMM), which reacts with norbornene to give a cyclopropane through an intermediate E. The intermediacy of E has been postulated in the reaction of OTMMpalladium species with norbornene

---

(1) (a) Tsuji, J. *J. Organomet. Chem.* **1986**, *300*, 281. (b) Ito, Y.; Aoyama, H.; Hirao, T.; Mochizuki, A.; Saegusa, T. *J. Am. Chem. Soc.* **1979**, *101*, 494. Ito, Y.; Aoyama, H.; Saegusa, T. *J. Am. Chem. Soc.* **1980**, *102*, 4519. Kende, A. S.; Roth, B.; Sanfilippo, P. J. *J. Am. Chem. Soc.* **1982**, *104*, 1784.

(2) It has been reported that oxidative addition of allyl enol carbonates to Pd(0) followed by decarboxylation had led to the formation of π-allylpalladium enolate (oxa-π-allyl). See ref 1a.

(3) Stille, J. K.; Wong, P. K. *J. Org. Chem.* **1975**, *40*, 532.

(4) Mori, M.; Kubo, Y.; Ban, Y. *Tetrahedron Lett.* **1985**, *26*, 1519. Mori, M.; Kubo, Y.; Ban, Y. *Tetrahedron* **1988**, *40*, 4321.

(5) (a) Suzuki, M.; Watanabe, A.; Noyori, R. *J. Am. Chem. Soc.* **1980**, *102*, 2096. (b) Trii, S.; Okumoto, H.; Nakayasu, S.; Kotani, T. *Chem. Lett.* **1989**, 1975.

(6) Hosokawa, T.; Aoki, S.; Takano, M.; Nakahira, T.; Yoshida, Y.; Murahashi, S. *J. Chem. Soc., Chem. Commun.* **1991**, 1559. Sasaki, Y. *Tetrahedron Lett.* **1986**, *27*, 1573.

(7) Kissei Pharmaceutical Co., Ltd. Jpn. Patent 59216885, 1984; *Chem. Abstr.* **1985**, *103*, 104836p. Fujisawa Pharmaceutical Co., Ltd. Ger. Patent DE 2239511, 1973; *Chem. Abstr.* **1973**, *79*, 41506u.

(8) α-Ketocarbenepalladium species can form cyclopropanes with olefins. Mende, U.; Radüchel, B.; Skuballa, W.; Vorbrüggen, H. *Tetrahedron Lett.* **1975**, *16*, 629. Suda, M. *Synthesis* **1981**, 714. Anciaux, A. J.; Hubert, A. J.; Noels, A. F.; Petiniot, N.; Teyssie, P. *J. Org. Chem.* **1980**, *45*, 695.

(9) The carbonate **1a** did not react with other olefins (ethyl acrylate, styrene, acrylonitrile, vinyl ethyl ether) under the palladium-catalyzed conditions.

0022-3263/93/1958-0009$04.00/0

Scheme I

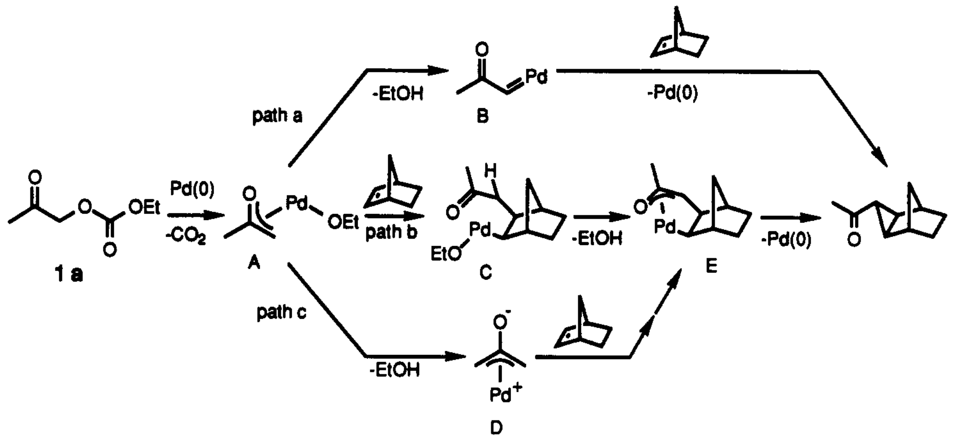
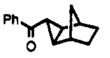
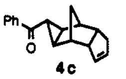


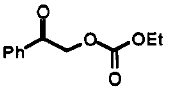
Table II. Reaction of 1c and 1d with Norbornenes[a]

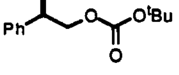
carbonate	norbornene	solvent	time, h	product	yield, %[c]
1c		toluene	48	 2c	58 (56)
		DMF	1		82 (82)
		toluene	24	 3c	33[b] (29)
		DMF	3		43[b]
		toluene	16	 4c	31 (29)
		DMF	1		35
1d		toluene	48	2c	52 (40)
		DMF	5		(55)

[a] Reaction conditions: carbonate 1a (1 mmol), norbornene (10 mmol), Pd(PPh$_3$)$_4$ (0.1 mmol), solvent (3 mL), bath temperature 120 °C. [b] Norbornadiene (3 mmol). [c] GC yield. Isolated yields are in parentheses.

giving the same product.[10] In path b, the intermediate A adds to norbornene to give an intermediate C, in which proton abstraction at the γ-position leads to the formation of E, releasing ethanol.

The reactions of phenacyl ethyl carbonate (1c) with norbornenes were examined (Table II).[11] This carbonate


1c


1d

also underwent cyclopropanation with norbornenes to give 2c, 3c, and 4c. This observation ruled out path c, since the reaction of 1c with the Pd(0) complex cannot give OTMMpalladium. As a consequence, path b is the most likely course of this cyclopropanation reaction. The formation of a byproduct, acetophenone, might have decreased the yield of the cyclopropanated product.[12]

We have described here an unusual cyclopropanation in the palladium-catalyzed reaction of ketone α-carbonates with norbornene. This reaction proceeds via the oxa-π-allylpalladium intermediate. More detailed studies on the scope and usefulness of this oxa-π-allylpalladium species are in progress.

Acknowledgment. Partial support of this work by Grants-in-Aid from the Ministry of Education, Science, and Culture and Fellowships of the Japan Society for Promotion of Science for Japanese Junior Scientists (4-2234) is acknowledged. Thanks are also due to the Analytical Center, Faculty of Engineering, Osaka University, for the use of JEOL JNM-GSX 400 and Bruker AM600 spectrometers.

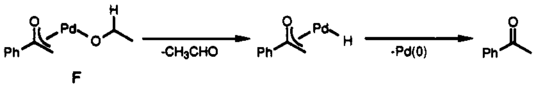
Supplementary Material Available: Typical experimental procedures and data for all prepared compounds (3 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

---

[10] Trost, B. M.; Schneider, S. *J. Am. Chem. Soc.* **1989**, *111*, 4430. Trost, B. M.; Urabe, H. *Tetrahedron Lett.* **1990**, *31*, 615. It has been also reported that azatrimethylenemethanepalladium reacted with norbornene to bring about a similar cyclopropanation. Ohe, K.; Ishihara, T.; Chatani, N.; Murai, S. *J. Am. Chem. Soc.* **1990**, *112*, 9646.

[11] Typical procedure for reaction of 1c with norbornene: Under a nitrogen atmosphere, 206 mg (0.989 mmol) of carbonate 1c, 942 mg (9.89 mmol) of norbornene, and 116 mg (0.1 mmol) of Pd(PPh$_3$)$_4$ were dissolved in 3 mL of dry DMF. The solution was stirred at 120 °C (bath temperature) for 1 h and concentrated in vacuo. The residue was purified by column chromatography (silica gel, 100–200 mesh, hexane/Et$_2$O = 5/1) to give 2c (82%) and acetophenone (16%).

[12] A considerable amount (18–67% yields) of acetophenone has also been obtained, probably consuming the common intermediate F which otherwise leads to the cyclopropanation product (see also ref 13). To suppress the formation of acetophenone, the reaction of 1d, which has no β-hydrogen, with norbornene was attempted, but acetophenone (16%) was generated. We cannot propose a suitable reaction path to account for the formation of acetophenone. Thus, further studies are required.



F

[13] The β-elimination from the intermediate F may lead to the formation of an oxa-π-allylpalladium hydride. See for a related reaction: Tsuji, J.; Minami, I.; Shimizu, I. *Tetrahedron Lett.* **1984**, *25*, 279.