

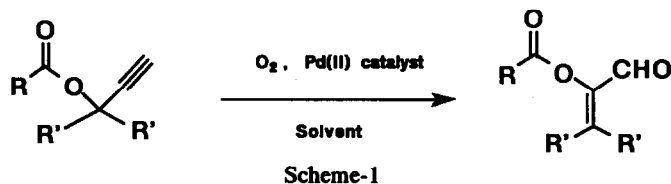
PALLADIUM(II)-CATALYZED OXIDATIVE REARRANGEMENT OF PROPARGYL ESTERS

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Abstract: Propargyl esters were converted to α -acyloxy- α,β -unsaturated aldehydes by palladium (II) catalysts under oxygen atmosphere in good to excellent yields.

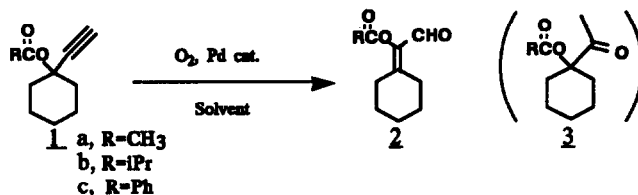
Since the discovery of the Wacker process, many oxidation reactions of olefins with homogeneous transition metal catalysts under oxygen atmosphere have been reported.¹⁾ However, similar oxidation of acetylenic compounds has scarcely been studied. In the course of our studies to develop the practical palladium-catalyzed reactions,²⁾ we found that a propargyl ester was converted to an α -acyloxy- α,β -unsaturated aldehyde by using a palladium (II) catalyst under oxygen atmosphere (Scheme 1).³⁾ In this paper, we wish to report the novel palladium (II)-catalyzed oxidative rearrangement of propargyl esters in the presence of molecular oxygen.



As shown in Table 1, the 1-ethynyl-1-cyclohexanol esters **1** were converted to the α -acyloxy- α,β -unsaturated aldehydes **2** under various conditions. Several palladium (II) compounds were effective to the reaction (Runs 1-10), and PdBr_2 was the best catalyst to give the aldehyde **2** selectively. Selection of solvents was also crucial to give the aldehydes **2** in good yields, and in THF the aldehydes **2** were afforded in >80% yields by using PdBr_2 as the catalyst. The structure of the ester moiety also influenced the yield of the aldehydes **2**, and the isobutyrate **1b** and the benzoate **1c** gave better results (92% and 89% respectively) compared to the acetate **1a** (Runs 11,12).

A typical experimental procedure for the preparation of the aldehyde **2b** is as follows: To a solution of the isobutyrate **1b** (99.0mg, 0.568mmol) in THF (2 ml) was added a catalytic amount of PdBr_2 (8mg, 0.028mmol). The reaction mixture was stirred at 65 °C under O_2 (1 atm) for 1 h. After the completion of the reaction, the solvent was removed in vacuo. The residue was chromatographed on silica gel (hexane : ether = 10:1) to give the aldehyde **2b** (98.2mg, 91% yield).⁴⁾

The reaction was completed even with 2.5 mol% of the catalyst; however it stopped after 39% conversion with 1 mol% of the catalyst (Runs 13,14). The reaction proceeded even at 25°C under air atmosphere (Runs 15,16).

Table 1. Oxidative rearrangement of the 1-ethynyl-1-cyclohexanol esters **1** ^{a)}

Run	R	Catalyst (mol%)	Time(h)	Additive(eq.)	Solvent	Product yield(%) ^{b,c)}
1	CH ₃	Na ₂ PdCl ₄ (10)	6	none	THF	48
2	"	"	1	H ₂ O(5)	"	26 (30) ^{d)}
3	"	"	5	none	CH ₃ CN	18
4	"	"	2	H ₂ O(5)	"	33 (10)
5	"	"	4	none	DMF	15
6	"	PdCl ₂ (10)	6	"	THF	50
7	"	PdSO ₄ (10)	7	"	"	42
8	"	PdBr ₂ (10)	1	"	"	81
9	"	"	1	H ₂ O(5)	CH ₃ CN	65 (0)
10	"	K ₂ PdBr ₄ (10)	1	none	THF	71
11	iPr	PdBr ₂ (10)	1	"	"	92
12	Ph	"	1.5	"	"	89 ^{e)}
13	iPr	PdBr ₂ (2.5)	8	"	"	87
14	"	PdBr ₂ (1)	8 ^{f)}	"	"	30
15 ^{g)}	"	PdBr ₂ (7)	9	"	"	97
16 ^{h)}	"	PdBr ₂ (7)	11	"	"	95
17	"	PdBr ₂ (5)	8 ⁱ⁾	2,6-Lutidine(0.1)	"	21
18	"	PdBr ₂ (1)	3	35% <i>HBr</i> (0.5)	"	56
19	"	"	3	36% <i>HCl</i> (0.5)	"	57
20 ^{j)}	"	PdBr ₂ (5)	1	<i>t</i> -BuOOH(10)	"	62

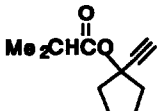
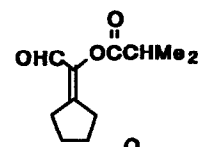
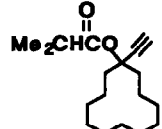
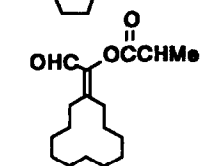
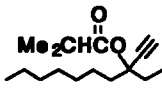
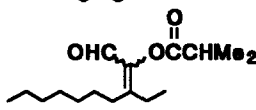
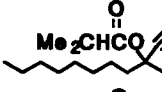
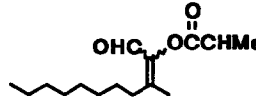
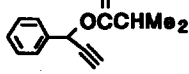
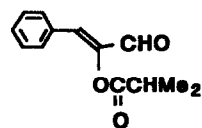
a). All reactions were carried out at 65 °C under oxygen atmosphere using 0.5mmol of the propargyl ester **1** and 2ml of the solvents unless otherwise noted. b). Determined by G.C. using *n*-hexadecane as an internal standard. c). All the products gave satisfactory NMR, IR, and mass spectra. d). Yield of the methyl ketone **3** is indicated in parenthesis. e). Isolated yield. f). Conversion 39%. g). The reaction was carried out at 25 °C. h). The reaction was carried out at 25 °C under air. i). Conversion 64%. j). The reaction was carried out under N₂.

Addition of water resulted in the increase of the rate of the reaction; however the methyl ketones **3** were also produced with Na₂PdCl₄ catalyst (Runs 2,4). In the presence of *HCl* or *HBr*, the reaction was completed for 1 h even with 1 mol % of the catalyst (Runs 18,19). On the other hand, addition of base deactivated the catalyst (Run

17). The reaction also proceeded with *t*-BuOOH under nitrogen atmosphere (Run 20). When the absorption of O₂ during the reaction was measured, one molecular of O₂ was found to be consumed for the production of two molecules of the aldehyde (Run 15).

Several examples of the oxidative rearrangement are demonstrated in Table 2. All reactions proceeded smoothly to afford the corresponding α -isobutyryloxy- α,β -unsaturated aldehydes in good to excellent yields.

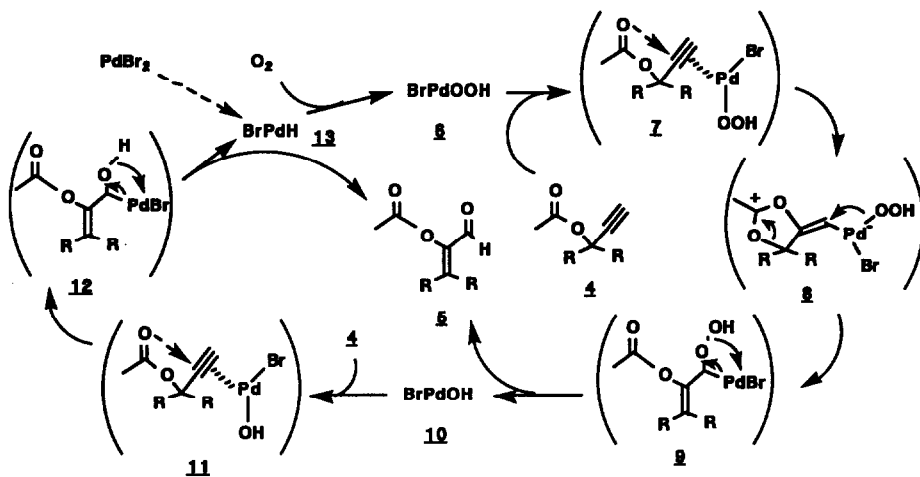
Table 2. Oxidative rearrangement of propargyl esters catalyzed by PdBr₂ in THF under oxygen atmosphere ^{a)}

Run	Propargyl ester	Time (h)	Product ^{b)}	Yield (%) ^{c)}
1		1.5		65
2		1		80
3		1		80 ^{d)}
4		1		82 ^{d)}
5		2		43 ^{e)}

a) All reactions were carried out at 65 °C in THF under oxygen atmosphere using 0.5mmol of the starting material and 5mol% of PdBr₂. b). All the products gave satisfactory NMR, IR, and mass spectra. c). Isolated yield. d). These products were about 1:1 mixture of the olefinic isomers. e). Only *Z* isomer was detected.

A possible mechanism for the oxidative rearrangement is proposed in Scheme 2. An active catalytic species is considered to be a hydroperoxopalladium (II) 9 ^{a,c,d,g} which coordinates to the acetylenic bond to lead the migration of the acyloxy group, followed by the internal addition of hydroperoxy moiety to give the intermediate 9. Then 9 decomposes to the aldehyde 5 and a hydroxy palladium 10, which also works as an active catalyst and catalyze the reaction to produce the second aldehyde 5 and a palladium hydride 13 via the intermediate 12. Finally a hydroperoxopalladium 6 is regenerated by the oxidation of 13 with O₂. At the initial stage of the reaction, the

catalytic species **13** would be produced from PdBr₂; however the mechanism for the production of **13** from PdBr₂ is unclear.



Scheme 2.

Further mechanistic studies and application of the present oxidative rearrangement for organic synthesis are now in progress.

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References and Notes

- (1) Recent works on transition-metal-catalyzed oxidation of olefins under O₂; (a) M.Roussel, H.Mimoun, *J.Org.Chem.*, **45**, 5387, (1980). (b) J.Tsuji, H.Nagashima, K.Hori, *Tetrahedron Lett.*, **23**, 2679 (1982). (c) T.Hosokawa, T.Uno, S.Inui, S.Murahashi, *J.Am.Chem.Soc.*, **103**, 2318 (1981). (d) K.Takehira, H.Orita, I.H.Ho, C.R.Leobardo, G.C.Martinez, M.Shimazu, T.Hayakawa, T.Ishikawa, *J.Mol.Catal.*, **42**, 247 (1987). (e) D.E.Hamilton, R.S.Drago, A.Zombeck, *J.Am.Chem.Soc.*, **109**, 374 (1987). (f) S.Inoki, T.Mukaiyama, *Chem.Lett.*, 67 (1990). (g) T.Hosokawa, S.Murahashi, *Acc.Chem.Res.*, **23**, 49 (1990), and references cited therein.
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- (3) The same type of compound was detected in a related reaction. V.Rautenstrauch, *Tetrahedron Lett.*, **25**, 3845 (1984).
- (4) Analytical data for the aldehyde **2b**: ¹H NMR (500MHz,CDCl₃) : δ 9.87 (s,1H,CHO), 2.70-2.82 (m,3H,allylic CH₂ and CH), 2.25-2.32 (m,2H,allylic CH₂), 1.60-1.80 (m,6H,CH₂), 1.29 (dJ=6.7Hz,6H,CH₃); IR (neat) 1770, 1695, 1655, 1300, 1020, 950, 865, 820 cm⁻¹; MS calcd for C₁₂H₁₈O₃ 210.1256, found 210.1248.

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