Selective Reaction of π-Allyl(alkyloxy)palladium(II) Complexes toward β-Decarbopalladation, β-Dehydropalladation, and Reductive Elimination

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Abstract: Depending on the kind of R^1 and R^2, cyclic carbonates 1, in the presence of 10 mol% of $Pd(PPh_3)_4$ and 10 equiv of paraformaldehyde, selectively undergo three types of reaction: 1 (R^1, $R^2 \neq H$) give dienes 3 exclusively; 1 ($R^1 = R^2 = H$ and $R^1 \neq H$, $R^2 = H$) furnish 6-vinyl-1,3-dioxanes 5 exclusively, while 1 ($R^1 = H$, $R^2 \neq H$) give rise to 4-pentenyl formates 4 selectively (together with 3 as the minor products). © 1998 Elsevier Science Ltd. All rights reserved.

Owing to their synthetic and mechanistic interest, transition metal-catalyzed or -promoted cyclization reactions of ω-ene aldehydes,[1] ω-yne aldehydes,[2] ω-diene aldehydes,[3] ω-ene carboxylic esters,[4] and so on, providing cycloalkanes and heterocyclic compounds, have been studied extensively. Interestingly, however, the reverse process, ring-opening (C-C bond-breaking) reaction, has been less studied.
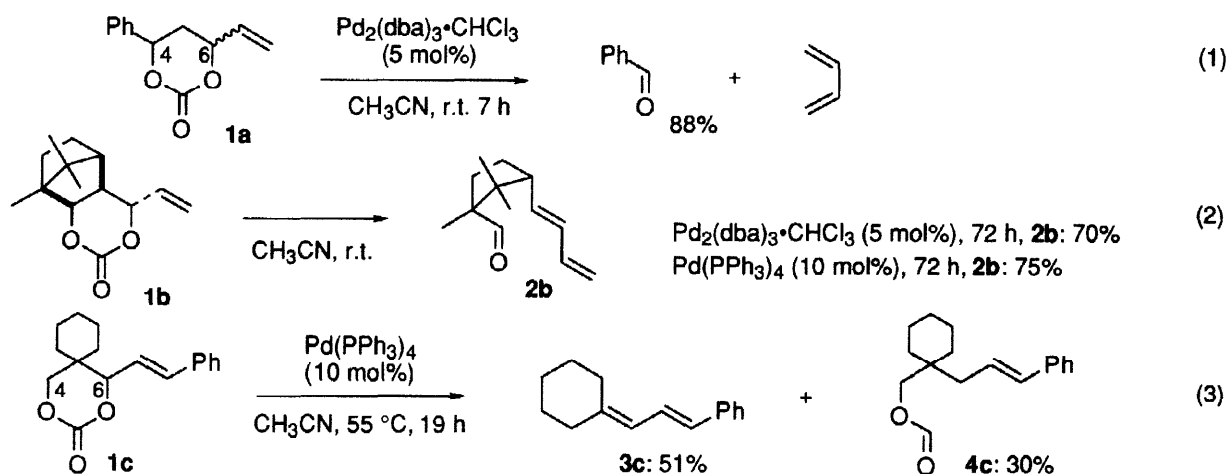

Recently, we have reported that 6-vinyl substituted mono- (e.g., eq 1), bi-, and tricyclic 1,3-dioxacyclo-hexan-2-ones 1 (cyclic carbonate, eq 2), upon stirring at room temperature in the presence of 5 mol% of $Pd_2(dba)_3\cdot CHCl_3$ (dba = dibenzylideneacetone), readily undergo extrusion of carbon dioxide and the C4-C5 bond cleavage to give either 1:1 mixtures of aldehydes and dienes (eq 1) or ω-dienyl aldehydes (eq 2) in good yields.[5] The reaction tolerates cyclic carbonates of a wide structural variety, irrespective of the length of the tether connecting C4 and C5 carbons and the substitution pattern of the olefinic moiety.

Here we report that the cyclic carbonates 1 bearing no substituents at C4 (e.g., 1c)[6] display a unique and contrasting reactivity, as compared with the C-4 substituted counterparts (e.g., 1a and 1b).

Under the conditions successfully applied to 1a and 1b, the reaction of 1c was very sluggish and provided an intractable mixture of products. After many trials, we eventually found that the reaction of 1c proceeded cleanly when heated at 55 °C in the presence of 10 mol% of tetrakis(triphenylphoshine)palladium(0) in acetonitrile under N_2 (eq 3). Two types of products were obtained in a reasonable combined isolated yield, one of which being the expected diene 3c (51% isolated yield). The other product was determined to be [1-(*trans-*

Table 1. Selective Formation of Dienes **3**, 4-Pentenyl Formates **4**, and 6-Vinyl-1,3-Dioxanes **5** via Palladium(0)-Catalyzed Decarboxylative Fragmentation of 6-Vinyl-1,3-dioxacyclohexan-2-ones **1**


(4)
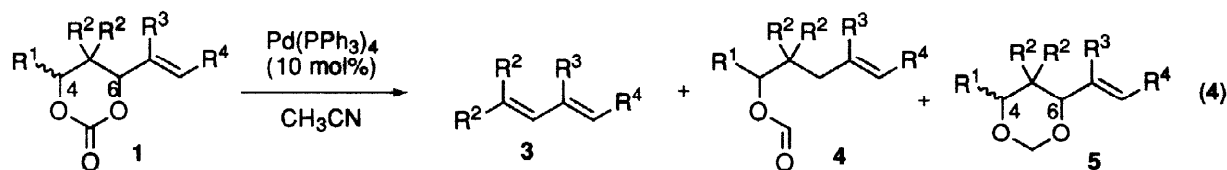
run	6-vinyl-1,3-dioxacyclohexan-2-ones 1				condi- tions[a]	time (h)	% isolated yield[b]		
	R¹	R²	R³	R⁴			3	4	5
1	1c	H	-(CH₂)₅-	H	Ph	A	19	3c: 51	4c: 30	
2	1c					B	1	3c: 18	4c: 77	
3	1c					C	4	3c: 81	4c: 0	
4	1d	H	-(CH₂)₅-	H	Et	A	4	3d: 51	4d: 36	
5	1d					B	0.3	3d: 3	4d: 80	
6	1d					C	4	3d: 76	4d: 0	
7	1e	H	Me	H	Ph	A	20	3e: 48[l]	4e: 34	
8	1e					B	1	3e: 19	4e: 66	
9	1e					C	4	3e: 87	4e: 0	
10	1f	H	H	H	Ph	B	1			5f: 80
11	1g	H	H	H	n-Pentyl	B	1			5g: 75
12	1a[c]	Ph	H	H	H	B	1			5a: 70[h]
13	1h[d]	Ph	H	Me	H	B	1			5h: 82[i]
14	1i[e]	Ph	H	H	Me	B	1			5i: 65[j]
15	1j[f]	t-Bu	H	H	H	B	1			5j: 69[k]
16	1k[g]	i-Pr	Me	H	Ph	B	1	3k: 90[l]		

[a] Method A: **1** (1 mmol), Pd(PPh₃)₄ (0.1 mmol) in dry MeCN (5 ml) at 55 °C under N₂. Method B: **1** (1 mmol), Pd(PPh₃)₄ (0.1 mmol), paraformaldehyde (10 mmol) in dry MeCN (5 ml) at reflux under N₂. Method C: **1** (1 mmol), Pd(PPh₃)₄ (0.1 mmol), t-octylamine (1.1 mmol) in dry MeCN (5 ml) at 55 °C under N₂. [b] All products **3**-**5** are isolated by column chromatography over silica gel and characterized properly by ¹H NMR (400 MHz), IR, and HRMS, or elemental analyses. cis- and trans-Isomers are not separated and analyzed as the mixtures. [c] cis-**1a**:trans-**1a** = 2:1. [d] cis-**1h**:trans-**1h** = 3:1. [e] cis-**1i**:trans-**1i** = 1.5:1. [f] cis-**1j**:trans-**1j** = 1.6:1. [g] cis-**1k**:trans-**1k** = 5.2:1. [h] cis-**5a**:trans-**5a** = 4.2:1. [i] cis-**5h**:trans-**5h** = >25:1. [j] cis-**5i**:trans-**5i** = 3.9:1. [k] cis-**5j**:trans-**5j** = 2.4:1. [l] **3e** = **3k**

cinnamyl)cyclohexyl]methyl formate (**4c**)[7] on the basis of the spectral and analytical data (HRMS and elemental analyses). The diagnostic spectral data that indicate the presence of the formic acid ester and trans-cinnamyl moieties are as follows: IR (neat) 1720 (s) and 970 (m) cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 6.18 (dt, J = 15.4, 7.7 Hz, 1 H), 6.39 (d, J = 15.4 Hz, 1 H), 8.13 (s, 1 H); HRMS m/z (relative intensity) 258.1609 (M⁺, 45), 212 (M⁺ - HCO₂H, 19). Other derivatives **1d** and **1e** showed similar reactivity, providing the mixtures of dienes **3** (~ 50% yield) and formic acid esters **4** (~ 35% yield) (runs 4 and 7, Table 1).

A reasonable reaction sequence accounting for the formation of **3** and **4** is outlined in Scheme 1. As proposed in our previous communication,[5] cyclic carbonates **1** fragment into aldehydes and dienes **3** via β-decarbopalladation of 5-vinyl-2-oxa-1-palladacyclopentane intermediates **I** (path A); however, the cyclic carbon-

ates 1c-e are distinct from 1a and 1b in providing formaldehyde as the product. Formaldehyde is exceedingly susceptible to addition reactions over aromatic and aliphatic aldehydes, the products produced from 1a and 1b. Accordingly, the thus-formed formaldehyde may spontaneously insert into the Pd-O bond of the intermediates I[8] to generate 7-vinyl-2,4-dioxa-1-palladacycloheptanes II. Apparently, these intermediates II are structurally more flexible than I and may be allowed to take a conformation appropriate for β-dehydropalladation.[9] The β-H elimination, followed by C7,H-reductive elimination may finally furnish 4 (path B).
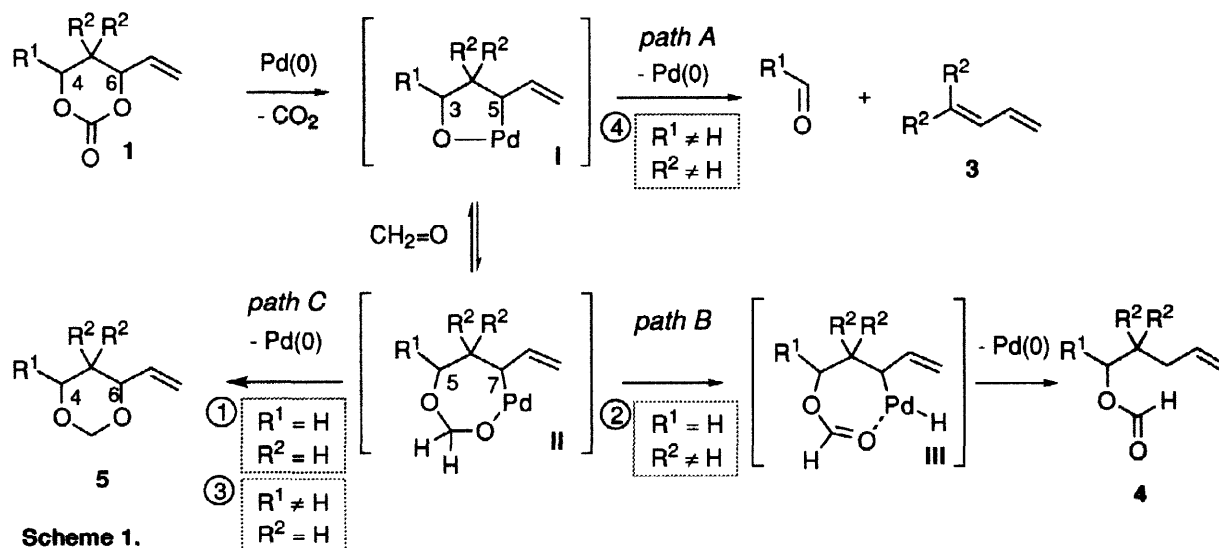
Scheme 1.

According to Scheme 1, it is expected that when *path A* proceeds much faster than *path B*, 3 (and aldehyde) may be formed selectively, while, when *path B* proceeds much faster than *path A*, a mixture of 3 and 4 may be produced in an equal amount (i.e., in 50% yield, each). The product distribution observed for the reactions of 1c-e (~ 50% of 3c-e and 30 ~ 36% of 4c-e; runs 1, 4, and 7) clearly indicates that *path B* participates overwhelmingly over *path A* in these reactions.

The following two sets of experiments support further the reaction sequence. The first set of experiments was undertaken in the presence of 10 equiv of paraformaldehyde (only a part of which being dissolved in the reaction medium) in acetonitrile at reflux (conditions B, runs 2, 5, and 8). As expected, in these reactions, the formic acid esters 4c-e were obtained selectively at the expense of 3c-e, respectively. The second set of experiments was performed in the presence of 1.1 equiv of *tert*-octylamine [(CH$_3$)$_3$CCH$_2$C(CH$_3$)$_2$NH$_2$] in acetonitrile at 55 °C (conditions C, runs 3, 6, 9) in expectation that this primary amine would promptly react with formaldehyde to form a Shiff base and interrupt the formation of II, and hence, guide the reaction to give 3 selectively. Indeed, dienes 3c-e were obtained exclusively and no formic acid esters 4c-e were detected at all.

Here, a question emerges; why do the intermediates II only take the course of β-H elimination (*path B*), ignoring completely an alternative O,C7-reductive elimination process, providing 6-vinyl-1,3-dioxanes 5 (*path C*) ? This question led us to examine extensively, under conditions B, the reaction behavior of carbonates 1 bearing R^1 and R^2 of all possible combinations: ① R^1 = R^2 = H; ② R^1 = H, R^2 ≠ H; ③ R^1 ≠ H, R^2 = H; ④ R^1, R^2 ≠ H. The results for the cases of ① and ③ are listed in runs 10-11 and 12-15, respectively. Surprisingly, all the carbonates 1a, 1f-j, belonging to the cases ① and ③, were subject to the O,C7-reductive elimination (*path C*) and furnished 5a, 5f-j as single products. On the other hand, the carbonate 1k (case ④) gave rise to the diene 3k, exclusively (run 16).

All these observations under conditions B may be rationalized as follows: When R^1, R^2 ≠ H (case ④),

steric repulsion between R^1 and R^2 is such that I would readily undergo β-C elimination to provide dienes **3** (and aldehydes, *path A*). When both R^1 and R^2 are H (case ①) or either one of R^1 and R^2 is H (cases ② and ③), the insertion of formaldehyde into the Pd-O bond of **I** proceeds much faster than the β-C elimination of **I**. The thus-formed intermediates **II** (R^2 = H), irrespective of the kind of R^1, selectively undergo O,C7-reductive elimination to give **5** (*path C*), while the intermediates **II** ($R^2 \neq$ H), probably owing to steric repulsion between R^2 and vinyl groups, are unable to undergo the O,C7-reductive elimination, and alternatively undergo β-H elimination to give **4** (*path B*). The cyclic carbonate **1b** ($R^1 \neq$ H, one of two R^2 is H and the other is not H) is an intermediate case between ③ and ④; hence, a mixture of **2b** (*path A*) and **5b** (*path C*) results (eq 5).

$$\text{(5)}$$

2b: 68%   **5b**: 14%
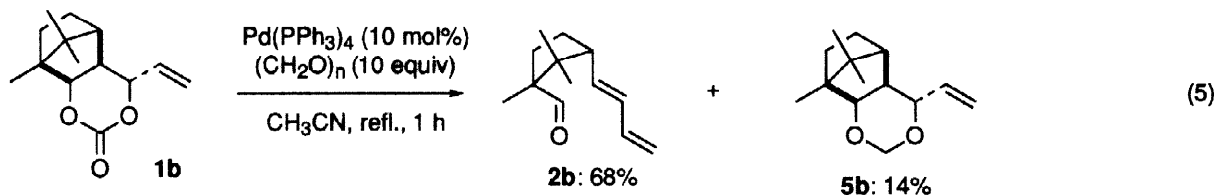
In conclusion, 6-vinyl substituted cyclic carbonates **1**, in the presence of a catalytic amount of Pd(PPh₃)₄ and an excess amount of paraformaldehyde, display three contrasting fragmentation patterns depending on the kind of R^1 and R^2: **1** (R^1, $R^2 \neq$ H) give dienes **3** exclusively; **1** ($R^1 = R^2 =$ H and $R^1 \neq$ H, $R^2 =$ H) furnish 6-vinyl-1,3-dioxanes **5** exclusively, while **1** ($R^1 =$ H, $R^2 \neq$ H) give rise to 4-pentenyl formates **4** selectively (together with **3** as the minor products). Besides being interesting from a mechanistic point of view, these reactions, particularly, the reactions providing 1,1-disubstituted 1,3-dienes in good yields [**3c-e**, in the presence of *tert*-octylamine (runs 2, 5, 8); **3k**, even in the absence of the amine (runs 16)] are important from a synthetic point of view, since such dienes, according to our experiences, are available albeit in low yields by the Wittig reaction.[10]

References and Notes

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(5) Harayama, H.; Kuroki, T.; Kimura, M.; Tanaka, S.; Tamaru, Y. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2352-2354.

(6) Although not being correct for some derivatives, for simplicity, the 1,3-dioxacyclohexan-2-one and 1,3-dioxane systems are numbered uniformly as indicated in equation 4.

(7) The selective hydrogen delivery at C3 (not at the allylically related C5, providing 3-pentenyl formates) suggests an intermediacy of σ-allyl(hydrido)palladium(II) species **III**, stabilized by an intramolecular formyl group coordination to the palladium(II) metal.

(8) Insertion of formaldehyde into Ni-O bonds: Han, R.; Hillhouse, G. L. *J. Am. Chem. Soc.* **1997**, *119*, 8135-8136.

(9) (a) Murahashi, S.-I.; Naota, T.; Ito, K.; Maeda, Y.; Taki, H. *J. Org. Chem.* **1987**, *52*, 4319-4327. (b) Tamaru, Y.; Yamada, Y.; Inoue, K.; Yamamoto, Y.; Yoshida, Z. *ibid.* **1983**, *48*, 1286-1292.

(10) For example, 4,8-dimethyl-1,3,7-nonatriene was obtained in less than 3% isolated yield by the reaction of 6-methyl-5-hepten-2-one and allyltriphenylphosphonium bromide (*tert*-BuOK, THF or *n*-BuLi, ether). The triene was prepared in 61% yield according to Yamamoto's modification: Ikeda, Y.; Ukai, J.; Ikeda, N.; Yamamoto, H. *Tetrahedron* **1987**, *43*, 723-730.