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Synthesis of 2-Vinyl-γ-butyrolactones by the Palladium-Catalyzed Decarboxylative Carbonylation of 3-Vinyl-1-oxo-2,6-dioxacyclohexanes

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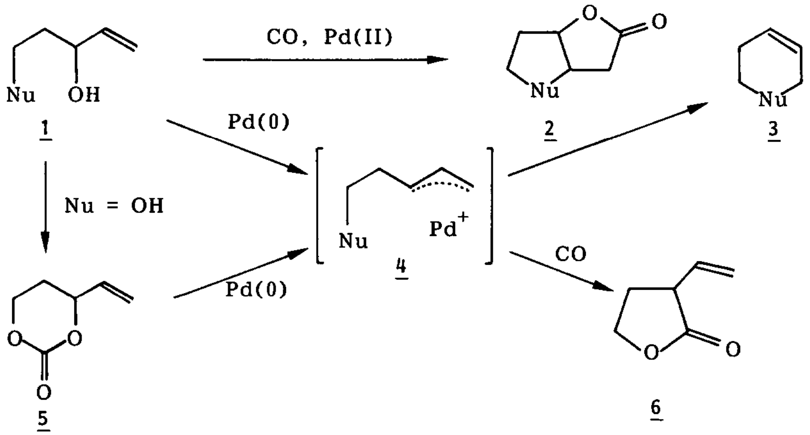
Summary: 3-Vinyl-1-oxo-2,6-dioxacyclohexanes undergo a decarboxylative carbonylation by a catalysis of Pd(0) to give 2-vinyl-γ-butyrolactones in high yield (typically in the presence of 3 mol% of $Pd(PPh_3)_4$ in dioxane at room temperature under 1 atm of CO).

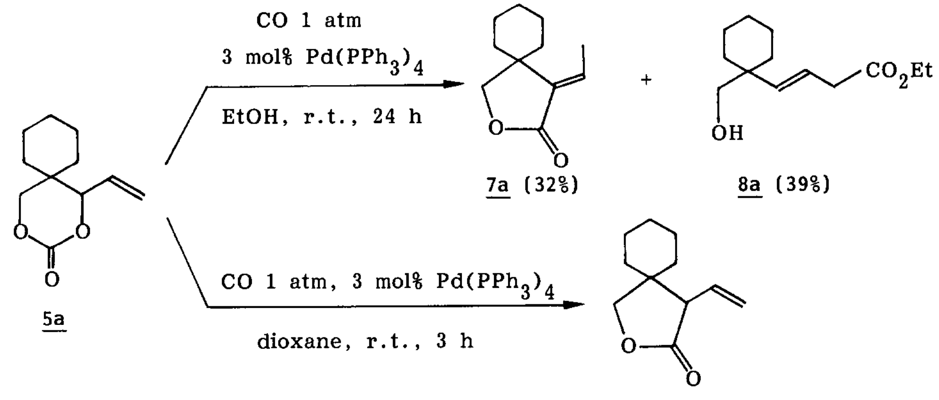
Recently we have shown that 3-hydroxy-4-pentenes 1 possessing an oxygen or nitrogen nucleophile at the C-1 position undergo a Pd(II)-catalyzed double cyclization to provide bicyclic lactones 2 (1 atm of CO, 0.01 - 0.1 equiv. of $PdCl_2$, 3 equiv. of $CuCl_2$ in AcOH-AcONa or in EtOH).[1] In some cases, tetrahydropyridines 3 (Nu = N) or dihydropyranes 3 (Nu = O) were produced in considerable amounts together with 2 (Scheme I).

Scheme I



In persuit of a possible intermediacy of π-allylpalladium 4 for the formation of 3 (1 → 4 → 3), we examined Tsuji's carbonate method (5 → 4 → 3).[2] However, 4, generated from carbonate 5a, did not undergo a cyclization to give 3 under conditions ever examined: Under argon in the presence of 3 mol% of $Pd(PPh_3)_4$, in dioxane no reaction took place and 5a was recovered unchanged (room temperature for 17 h), while in ethanol 5a was consumed only to give an intractable mixture of products (room temperature for 20 h).[3] All these results suggest that 4 is not an intermediate responsible for the formation of 3.[4] In fact, in an atmosphere of 1 atm of carbon monoxide just like the conditions for the transformation of 1 to 2 and 3,[1] the reaction took a complete different course and gave 2-vinyl-γ-butyrolactone 6 in high yield.

Here we report a very convenient and high yield synthesis of 6, an important intermediate for the syntheses of many physiologically interesting compounds, via a Pd(0)-catalyzed decarboxylative carbonylation of 3-vinyl-1-oxo-2,6-dioxacyclohexanes 5. The carbonates 5 were prepared by treatment of 1 (Nu = OH) with 6 equiv. of methyl chloroformate and 8 equiv. of triethylamine in dichloromethane at 0°C - room temperature. The reaction shows a high solvent dependence. In ethanol, 7a and 8a were obtained as a 1:1 mixture (eq. 1). The latter is a type of compounds obtained by Tsuji by the carbonylation of allyl carbonates.[5] In an aprotic solvent (e.g., dioxane, THF, benzene), 6 was selectively obtained (eq. 2).



5a

7a (32%)

8a (39%)

(eq.1)

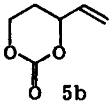
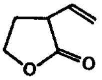
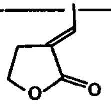
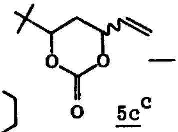
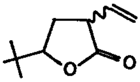
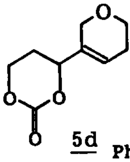
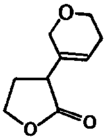
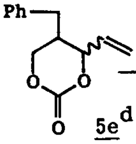
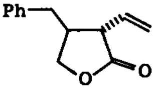
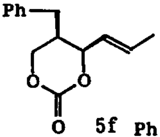
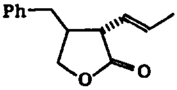
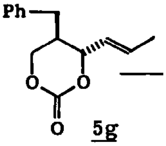
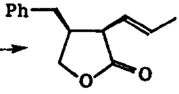
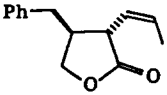
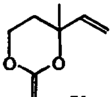
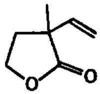
6a (89%)

(eq 2)

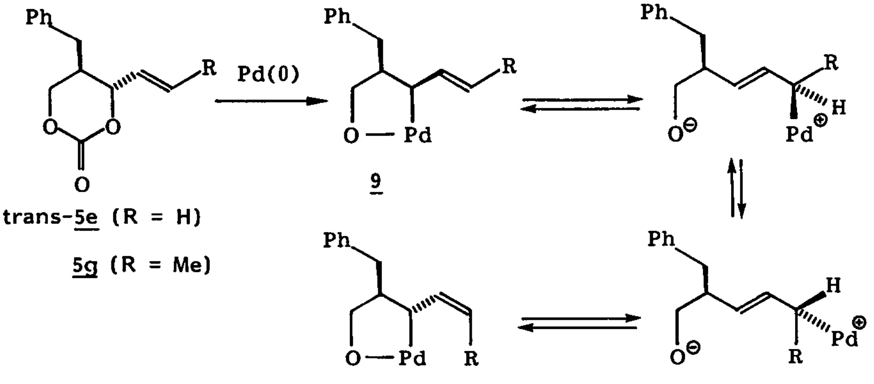
Results of the reaction in an aprotic solvent are summarized in Table I, which covers carbonates with characteristic structural features and reveals a wide scope of the reaction.[6] Generally the reaction proceeds at room temperature or below under 1 atm of CO in the presence of 3 mol% of $Pd(PPh_3)_4$. The reaction tolerates substitution on both the ring carbons and the olefinic carbons. However we met difficulties in the less substituted substrates (runs 1 and 2). In these cases the lower temperatures and the higher pressures of CO were required. Under the usual conditions (1 atm of CO, room temperature, 4 h), 5b provided a mixture of 6b (25%), 7b (14%), and a minor product (9%), whose structure was tentatively assigned as 2-vinyl-2-(5'-hydroxy-2'-pentenyl)-γ-butyrolactone.

A couple of results in runs 5 and 6 deserves comments concerning the stereochemical course of the reaction. cis-Carbonate 5f was specifically converted to trans-lactone 6f. trans-Carbonate 5g, on the other hand, gave a mixture of cis-lactone 6g and trans-lactone with cis double bond 6g'. These results, indicating an involvement of either an inversion of configuration at

Table I. Pd(0)-Catalyzed Decarboxylative Carbonylation of Vinyl Carbonate 5

run	substrate 5	conditions[a]	product 6 (isolated yield)	
1	 5b	0°C, 7 h[b] then rt, 10 h 45 atm of CO	 6b (53%)	 7b (4%)
2	 5c[c]	0°C, 2 h[b] then rt, 4 h 45 atm of CO	 6c (62%)[c]	
3	 5d	rt, 7 h 1 atm of CO	 6d (77%)	
4	 5e[d]	rt, 17 h[e] 1 atm of CO	 6e (88%)	
5	 5f	rt, 8 h 1 atm of CO	 6f (86%)	
6	 5g	rt, 5 h 1 atm of CO	 6g (40%)	 6g' (36%)
7	 5h	rt, 2.5 h 1 atm of CO	 6h (66%)	

a) Usual Conditions: carbonate (1 mmol), $Pd(PPh_3)_4$ (0.03 mmol) in 5 mL of dioxane under carbon monoxide. b) In dioxane:THF = 5:1 c) cis:trans = 1.0:1.0 d) cis:trans = 1.0:1.3 e) $Pd(OAc)_2(PPh_3)_2$



Scheme II

the C-3 of 5 or an isomerization of the double bond, might be rationalized by invoking an equilibrium between 9 and 10 (Scheme II). For instance, the intermediate 9 (R = H), formed from trans-5e by an addition of Pd(0) to the allylic C-O bond with an inversion of configuration,[2] might isomerize to the relatively stable isomer 10 (R = H) and undergo carbonylation via 10 with a retention of configuration[7] to specifically provide 6e. For the case of 5g, the difference of stability between 9 and 10 (R = Me) is so small that both intermediates are responsible for carbonylation and give a mixture of 6g and 6g', respectively.

Experiment was typically undertaken as follows (run 6): Into a flask containing $Pd(PPh_3)_4$ (34.7 mg, 0.03 mmol), equipped with a CO baloon, was introduced a solution of 5g (232 mg, 1 mmol) in 5 mL of dry dioxane via a syringe. The mixture was stirred at an ambient temperature for 5 h. After evaporation of the solvent, the residue was directly subjected to a silica gel column (benzene - ethyl acetate gradient) to give 6g (Rf = 0.61) and 6g' (Rf = 0.59 in benzene - ethyl acetate 8:1)

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(2) J. Tsuji, Tetrahedron, 42, 5361 (1986).

(3) For Pd(0)-catalyzed isomerization of vinylethylene carbonate to 3-butenal, see T. Fujinami, T. Suzuki, M. Kamiya, S. Fukuzawa, and S. Sakai, Chem. Lett., 199 (1985).

(4) Some Lewis acid, which may be formed from $PdCl_2$, $CuCl_2$, and CO, seems to be a catalyst for the cyclization (1 → 3). For instance, treatment of trans 2-benzyl-4-hexene-1,3-diol with $PdCl_2$ (0.1 equiv.), $CuCl_2$ (3 equiv.), and 1 atm of CO in acetonitrile at room temperature for 3 days provides 1-oxa-2-methyl-5-benzylcyclohexene-3 (11) in 51% yield as a single stereoisomer. Omission of CO or of both CO and $CuCl_2$ results in a formation of 11 in 24% (a mixture of stereoisomers) or in less than 5% yields, respectively.

(5) J. Tsuji, K. Sato, and H. Okumoto, J. Org. Chem., 49, 1341 (1984).

(6) All the products reported here were properly characterized by spectral means (IR, ^{1}H NMR, ^{13}C NMR, and high-resolution MS) and in some cases by elemental analyses.

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