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PALLADIUM(0)-CATALYZED CYCLIZATION OF 2-BUTENYLENE DICARBAMATES FORMING 4-VINYL-2-OXAZOLIDONES

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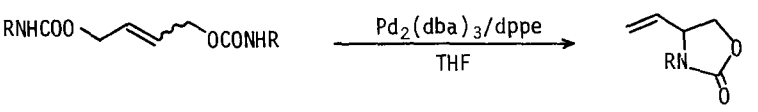
Summary: 2-Butenylene dicarbamates prepared from but-2-en-1,4-diol and isocyanates readily undergo the cyclization in the presence of a phosphine-palladium(0) catalyst to produce 4-vinyl-2-oxazolidones in high yields.

There have been reported a number of palladium-catalyzed reactions which proceed by way of π-allylpalladium intermediates.[1] Tsuji and coworkers have developed the allylation of carbonucleophiles by use of allyl carbonates[2] and carbamates[3] as effective allylating agents. Here we report a new type of palladium-catalyzed cyclization where 2-butenylene dicarbamates give 4-vinyl-2-oxazolidones in high yields.

Dicarbamates **1** were readily obtained by treatment of but-2-en-1,4-diol with a slight excess of isocyanates in pyridine and THF.[4] In the first set of experiments, catalytic activities of several palladium complexes were examined for the reaction of (E)-2-butenylene N,N'-diphenyldicarbamate (**1a**) (Scheme 1). Phosphine complexes prepared in situ by mixing (Pd/P = 1.0/2.2) $Pd_2(dba)_3$[5] with bisphosphine ligands, dppe,[6] dppb,[6] and dppf,[6] were all effective giving rise to over 90% yield of the cyclization product, 4-vinyl-3-phenyl-2-oxazolidone (2a), at reflux in THF for 1 h. A quantitative formation of aniline was found to accompany the cyclization. A little lower activity (81% yield) was observed with tetrakis(triphenylphosphine)palladium(0). On the other hand, palladium complexes lacking phosphine ligands, such as $Pd(OAc)_2$, $PdCl_2$, and $Pd_2(dba)_3$, did not catalyze the cyclization at all.

Scheme 1



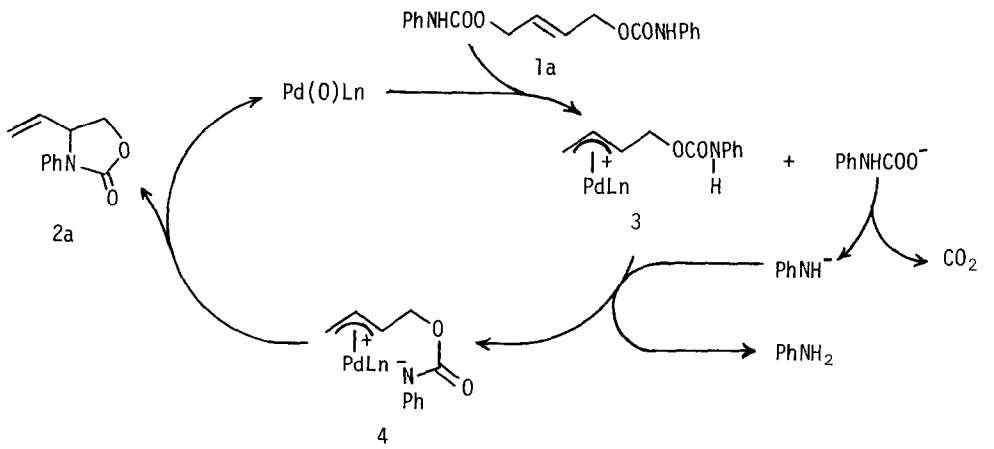
1a-h 2a-h

1a: R = Ph (*E*) 1e: R = $PhCH_2$ (*E*)
1b: R = Ph (*Z*) 1f: R = i-Pr (*E*)
1c: R = p-$MeOC_6H_4$ (*E*) 1g: R = Me (*E*)
1d: R = p-ClC_6H_4 (*Z*) 1h: R = PhCO (*E*)

The cyclization giving the vinyloxazolidone can be well understood by the catalytic cycle shown in Scheme 2. Oxidative addition of the dicarbamate **1a** to a palladium(0) forms the cationic π-allylpalladium(II) complex **3** bearing 1-(N-phenylcarbamoyloxymethyl)-π-allyl group to leave phenylcarbamate anion. Proton abstraction from the phenylcarbamoyloxy group on **3**, probably by phenylamide generated on decarboxylation of the carbamate anion, followed by

intramolecular attack of the nitrogen nucleophile[7] on **4** produces the vinyloxazolidone **2a** to regenerate palladium(0). It has been proposed in the allylation of carbonucleophiles with allyl carbamates that amide anions formed by decarboxylation of carbamates abstract a proton from carbonucleophiles.[3] The formation of vinyloxazolidones in the palladium-catalyzed reaction of diene monoxides with isocyanates, reported by Fujinami and coworkers,[8] is thought to take place via the same intermediate **4**.

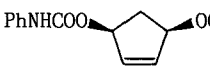
Scheme 2



The results obtained for the reaction of several 2-butenylene dicarbamates **1a-h** bearing substituents on the nitrogens are summarized in Table 1. The reaction of (Z) dicarbamate **1b** proceeded as well as that of **1a**, and gave **2a** in a quantitative yield (entries 1 and 2). Substituents on the phenyl group did not strongly affect the cyclization, the oxazolidones being obtained in high yields from both **1c** and **1d** which have 4-methoxyphenyl and 4-chlorophenyl groups, respectively (entries 3 and 4). On the other hand, dicarbamates derived from alkyl isocyanates, **1e**, **1f**, and **1g**, were reluctant to undergo the cyclization (entries 5-7). It seems that the anion of more basic amide in the intermediate **4** is less reactive with π-allylpalladium. The cyclization of N,N'-dibenzoyldicarbamate **1h** also proceeded successfully to give 3-benzoyloxazolidone **2h** which can be readily converted into unsubstituted vinylglycinol (entry 8).

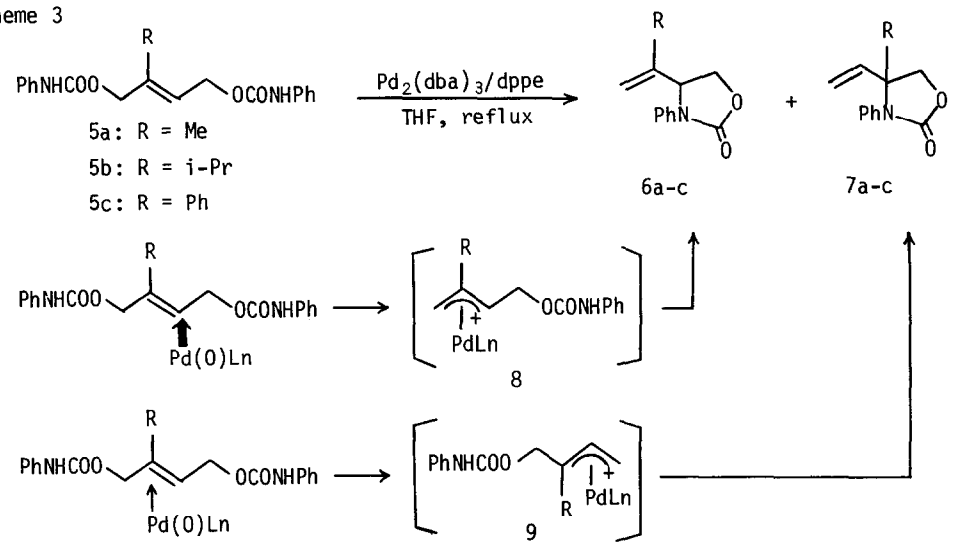
The regiochemistry was studied with dicarbamates substituted with methyl (**5a**), i-propyl (**5b**), and phenyl (**5c**) at 2-position of 2-butenylene (Scheme 3). The oxazolidone **6** which has the substituent on the vinyl group was formed preferentially over the regioisomer **7**, the ratio of **6**/**7** being 89/11 (89%), 96/4 (89%), and >99/<1 (93%) for **5a**, **5b**, and **5c**, respectively (entries 9-11 in Table 1). The major isomer **6** should be formed from the π-allylpalladium intermediate **8** bearing the substituent at 2-position of the π-allyl, and the minor isomer **7** should be formed from **9**. The preferential formation of the π-allylpalladium **8** led us to propose that the oxidative addition of the dicarbamates to palladium(0) forming π-allylpalladium occurs by S_N'-type attack of palladium(0) on the allylic substrate.[9] Nucleophilic attack of palladium(0) on the sterically less hindered carbon of the double bond in S_N' manner will form the π-allylpalladium **8**.

Table 1. Cyclization of 2-Butenylene Dicarbamates in the Presence of Palladium Catalyst, $Pd_2(dba)_3$/dppe.[a]

entry	dicarbamate	reaction time (h)	yield[b] (%)	product
	$RNHCOOCH_2CH=CHCH_2OCONHR$			
1	R = Ph (E) (1a)	1	91	2a
2	R = Ph (Z) (1b)	2	95	2a
3	R = 4-MeO-C_6H_4 (E) (1c)	2	90	2c
4	R = 4-Cl-C_6H_4 (Z) (1d)	2	98	2d
5	R = $PhCH_2$ (E) (1e)	15	59	2e
6[c]	R = i-Pr (E) (1f)	14	58	2f
7	R = Me (E) (1g)	15	24	2g
8	R = PhCO (E) (1h)	2	88	2h
	$PhNHCOOCH_2CR=CHCH_2OCONHPh$			
9	R = Me (5a)	1	89	6a/7a (89/11)
10	R = i-Pr (E) (5b)	4	89	6b/7b (96/4)
11	R = Ph (E) (5c)	7	93	6c/7c (>99/<1)
12	$PhNHCOOCMe_2CH=CHCH_2OCONHPh$ (E)-(10)	63	81	11/12 (84/16)
13	 (14)	1	87	15

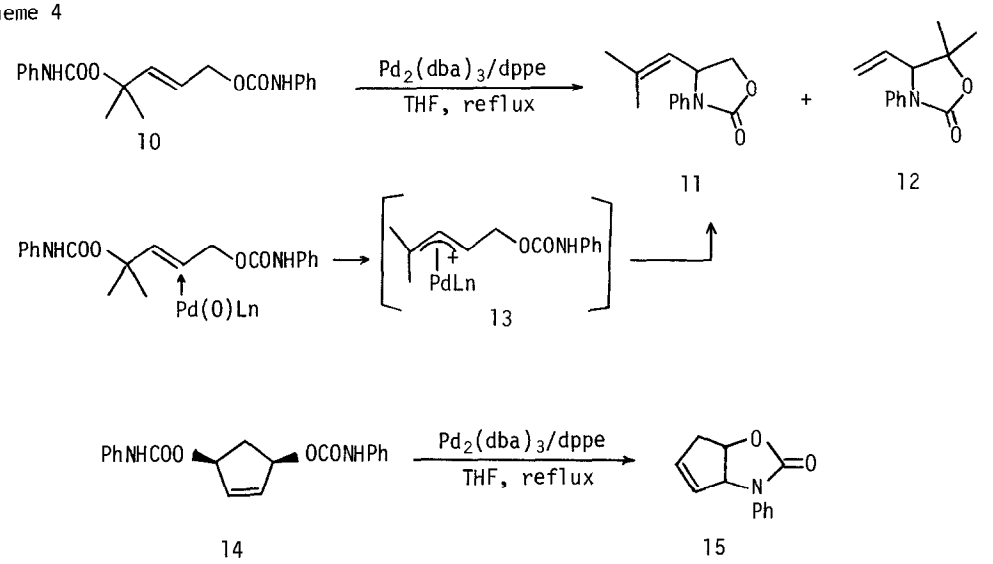
[a] A mixture of $Pd_2(dba)_3 \cdot CHCl_3$ (0.009 mmol), 1,2-bis(diphenylphosphino)ethane (dppe) (0.020 mmol), and 3 ml of THF was stirred at room temperature for 30 min. A dicarbamate (0.60 mmol) was added, and the mixture was heated to reflux for the given period of time. Evaporation of the solvent followed by preparative TLC on silica gel (hexane/ethyl acetate = 3/1 - 2/1) gave the vinyloxazolidone. [b] Isolated yield. [c] Reaction at 40°C in the presence of $Pd_2(dba)_3$/dppf (dppf = 1,1'-bis(diphenylphosphino)ferrocene).

Scheme 3



The similar regioselectivity was observed in the reaction of 1,1-dimethyl-2-butenylene dicarbamate **10**, which gave the vinyloxazolidones **11** and **12** in a ratio of 84/16 (entry 12). Palladium(0) attacks selectively the olefin carbon more distant from the dimethyl to form the π-allylpalladium **13**, which produces on cyclization the major regioisomer **11**. The dicarbamate of cyclic diol **14** was also subject to the palladium-catalyzed cyclization to give bicyclic product **15** (entry 13).

Scheme 4



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6 The abbreviations, dppe, dppb, and dppf, stand for 1,2-bis(diphenylphosphino)ethane, 1,4-bis(diphenylphosphino)butane, and 1,1'-bis(diphenylphosphino)ferrocene, respectively.

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