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Palladium(0)-catalyzed Cycloaddition of Activated Vinylcyclopropanes with Aryl Isocyanates

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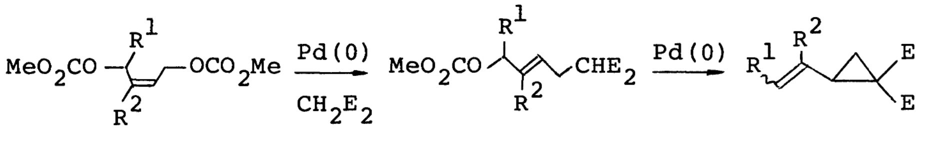
Zwitterionic π-allylpalladium complexes formed by a reaction of activated vinylcyclopropanes with Pd(0) complexes as a catalyst react with aryl isocyanates (or diphenylketene) to give five-membered cycloaddition products in good yields.

The 1,3-dipolar cycloaddition reaction plays a crucial role in five-membered ring formation.[1)] We report here a palladium-catalyzed cycloaddition of activated vinylcyclopropanes with certain heterocumulenes, which relies on a facile access of the zwitterionic π-allylpalladium intermediates.

Recently, we[2)] and another group[3)] have found that the reaction of activated vinylcyclopropanes with palladium(0) complexes forms zwitterionic π-allylpalladium complexes as useful 1,3-dipolar equivalents which react with electron-deficient olefins. This type of palladium-catalyzed cycloaddition has a few precedents.[4)]

Although requisite dimethyl 2-vinylcyclopropane-1,1-dicarboxylate and methyl substituted derivatives **3** may be prepared from bis-allylic halides and malonates, it should be mentioned that Pd(0)-catalyzed cyclization of appropriate carbonates **2**[5)] is also a very convenient preparative route (Eq. 1).[2)]

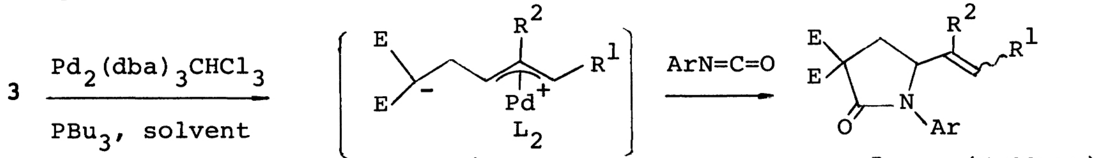


a: $R^1=R^2=H$
b: $R^1=H$, $R^2=Me$
c: $R^1=Me$, $R^2=H$
(E:Z=60:40)

(1)

1 **2** **3** ($E=CO_2Me$)

The diester **3**, as a precursor of the zwitterionic intermediate **4**,[2)] was found to undergo smooth cycloaddition with some aryl isocyanates (Eq. 2). The results are given in Table 1.



4 **5a-c** ($E=CO_2Me$)

(2)

Ease of the cycloaddition depends markedly on both ligands of Pd(0) and solvents used. Thus, tributylphosphine ligand and aprotic dipolar solvents likely assist facile oxidative addition of the substrate **3** to Pd(0) complex to give the zwitterion **4** which in turn undergoes addition to the central carbonyl carbon of aryl isocyanates to form the five-membered ring compounds **5**. Attempted reactions with alkyl isocyanates did not afford any cyclization product.

Table 1. Pd(0)-Catalyzed Cycloaddition of Vinylcyclopropanes with Isocyanates[a]

Entry	Substrate	Isocyanate	Ligand	Solvent	Temp	Time	**5**,	Yield[b]
					°C	h		%
1	**3a**	PhN=C=O	dppe	DMF	80	12	**5a**	40
2	"	"	"	DMSO	"	1.5	"	65
3	"	"	Bu_3P	"	25	"	"	63
4	"	"	"	HMPA	"	1.3	"	87
5	"	"	"	THF-HMPA	"	1.5	"	84
6	**3b**	"	"	HMPA	"	15	**5b**	90
7	**3c**	"	"	"	"	9	**5c**	77
8	**3a**	p-$MeOC_6H_4NCO$	"	"	"	1	**5d**[c]	86
9	"	p-$NO_2C_6H_4NCO$	"	"	"	24	**5e**[d]	69

a) $Pd_2(dba)_3 \cdot CHCl_3$ (2.5 mol%) (dba: dibenzylideneacetone). b) Isolated yield.
c) **5d**: N-(p-Methoxyphenyl) derivative of **5a**. d) **5e**: N-(p-Nitrophenyl) of **5a**.

The zwitterion **4** also reacted with diphenylketene to give 2,2-diphenyl-5,5-bis(methoxycarbonyl)-3-vinylcyclopentanone in 85% yield. (Trimethylsilyl)ketene, however, was found to be inert in the reaction.

A typical procedure is as follows: A mixture of $Pd_2(dba)_3 \cdot CHCl_3$ (0.025 mmol) and Bu_3P (0.15 mmol, 3 equiv.) in HMPA (2 mL) was stirred for 10 min at room temperature. To a solution of **3a** (1.0 mmol) and phenyl isocyanate (2.0 mmol) in HMPA (2 mL) was added the catalyst solution at room temperature and the whole mixture was stirred for 1.3 h. The reaction mixture was poured into water and organic materials were extracted with ether. After the usual workup, the residue was purified by column chromatography to give N-phenyl-2,2-bis(methoxycarbonyl)-4-vinylbutyrolactam (**5a**) (87%); ^1H NMR: δ2.60(dd, J=6.0, 13.4 Hz, 1H), 3.06(dd, J=7.4, 13.4 Hz, 1H), 3.82(s, 3H), 3.83(s, 3H), 4.68(br q, J=6.1 Hz, 1H), 5.18(d, J=9.4 Hz, 1H), 5.22(d, J=18.0 Hz, 1H), 5.62(ddd, J=18.0, 8.9, 7.1 Hz, 1H), and 7.1-7.6(m, 5H). $^{13}C\{^1H\}$ NMR: δ35.2, 53.3, 53.4, 59.9, 77.3, 118.6, 123.7, 126.1, 128.7, 134.0, 136.6, 165.7, 167.5, and 167.8. IR(neat): 1700, 1730 cm^{-1}.

References

1) R. Huisgen, "1,3-Dipolar Cycloaddition Chemistry," ed by A. Padwa, John-Wiley & Sons, New York (1984), Chap. 1.

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5) The carbonate **2** must be used for easy cyclization to give **3**. An acetate analog of **2** reacted in the presence of a Pd(0) catalyst (5 mol%) with added base (NaH, 1 equiv.), but the resulting malonate anion species underwent intermolecular allylation without giving **3**; K. Yamamoto, T. Ishida, and J. Tsuji, 52nd National Meeting of the Chemical Society of Japan, Kyoto, April 1986, Abstr. No.4W31.

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