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Palladium-Catalyzed [3 + 2] Cycloaddition Reaction of Vinylcyclopropanes with α,β-Unsaturated Esters or Ketones

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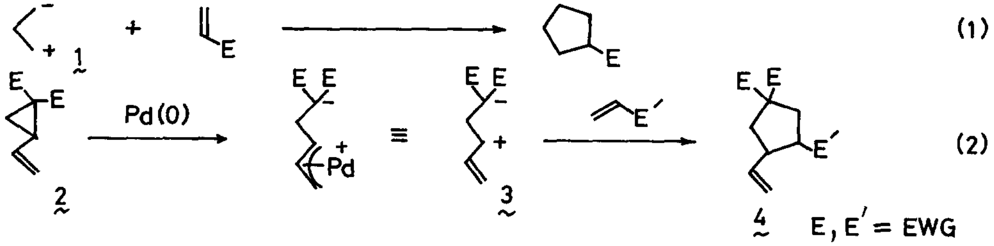
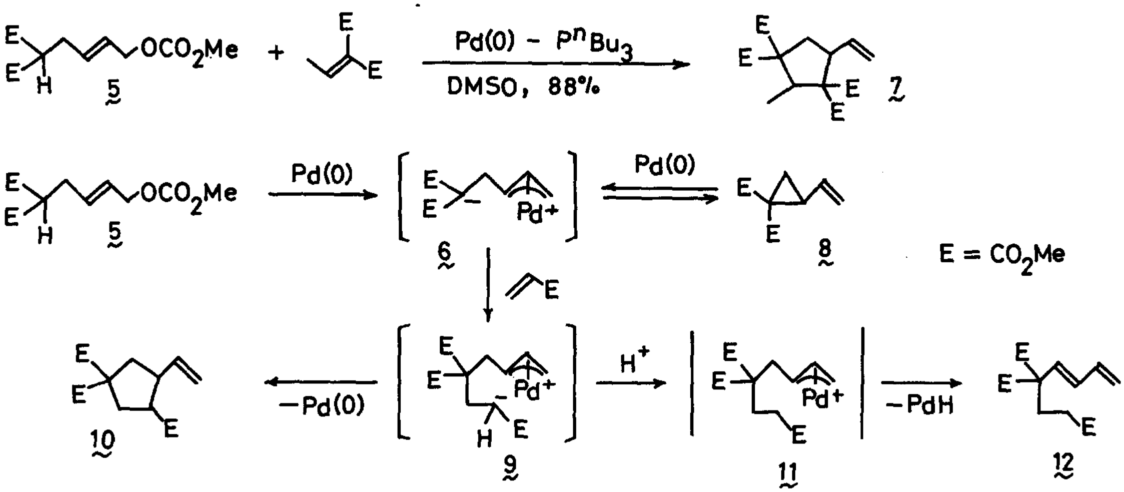
Summary: Reaction of vinylcyclopropanes having two electron-withdrawing groups with α,β-unsaturated esters or ketones in the presence of $Pd_2(dba)_3.CHCl_3$-1,2-bis(diphenylphosphino)ethane (dppe) or tributylphosphine catalyst gave vinylcyclopentanes in good yields.

Efficient synthesis of cyclopentanoids is a current interest in organic synthesis.[1] Although [3 + 2] cycloaddition reaction is useful for construction of cyclopentane systems, preparation of 1,3-dipolar moieties 1 is not easy.[2-4] (eq. 1) We wish to report here a new synthetic method for cyclopentanes **4** by palladium-catalyzed [3 + 2] cycloaddition reaction using vinylcyclopropanes **2** having two electron-withdrawing groups as a 1,3-dipolar equivalent **3**. (eq. 2)



Zwitter ionic π-allylpalladium complexes are known as useful 1,3-dipolar equivalents which react with electron deficient olefins to form methylenecyclopentanes.[3),4)] We have reported that palladium-catalyzed allylation of active methylene compounds using allylic carbonates proceeds under neutral conditions since alkoxide anion is generated in situ and behaves as a base to pick up an acidic hydrogen to give carbanions.[5] We applied this in situ formation of carbanions to the preparation of zwitter ionic π-allylpalladium complexes.[6]

As another 1,3-dipolar synthon, we have investigated the possibillity of preparing the zwitter ionic π-allylpalladium complexes **6** from the carbonate **5**. As expected, reaction of **5** (0.5 mmol) with dimethyl ethylidenemalonate (1 mmol) in the presence of $Pd_2(dba)_3.CHCl_3$ (0.0125 mmol) and tributylphosphine (0.1 mmol) in dimethylsulfoxide (DMSO, 3 mL) at 30 °C for 3 h gave the cyclopentane **7** in 88% yield. However, reaction of **5** with methyl acrylate did not give the expected cyclization product **10**, and the diene **12** produced from **9** and the vinylcyclopropane **8** from **6** were obtained as major products. This result indicates that the cycloaddition of the carbonate **5** is possible only with olefins having two electron-withdrawing groups. When methyl acrylate is used, 1,4-addition of **6** gives the carbanion **9**, which undergoes rapid proton transfer with the more acidic **5** without giving the cyclized product **10**.



In order to avoid the rapid proton transfer, we selected dimethyl 2-vinylcyclopropane-1,1-dicarboxylate **8**, as a precursor of zwitter ionic complexes **6**.[7] The diester **8** was prepared from the dicarbonate **13** and dimethyl malonate in 67% yield using of $Pd_2(dba)_3.CHCl_3$-dppe (0.5 mol%) catalyst in dry THF at room temperature for 20 h. As expected, vinylcyclopropanedicarboxylate **8** (0.5 mmol) underwent smooth [3 + 2] cycloaddition reaction with methyl acrylate (1 mmol) in the presence of $Pd_2(dba)_3.CHCl_3$ (0.0125 mmol) and dppe (0.05 mmol) in DMSO (3 mL) at 80 °C for 2 h to give the vinylcyclopentane **10** in 84% yield as a mixture of diastereomers after chromatographic purification on SiO_2 with hexane-ether.[8]

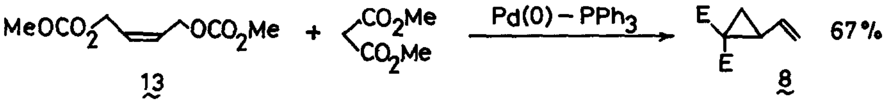
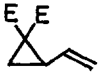
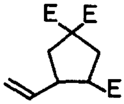
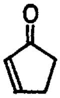
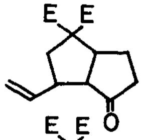
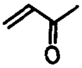
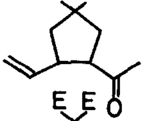
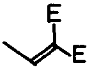
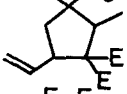
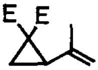
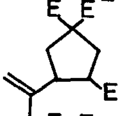
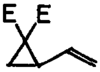
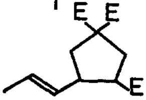
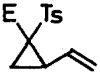
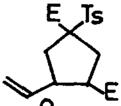
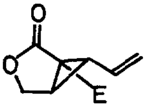
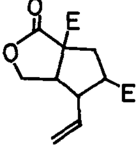


Table. Palladium-catalyzed Reaction of Vinylcyclopropanes and α,β-Unsaturated Esters and Ketones

	Vinylcyclopropane		Olefin	Ligand	Temp (°C)	Time (h)	Product[a)]		Yield[b)] (%)
1		(**8**)		dppe	80	2		(**10**)	84
2	**8**			P^nBu_3	30	1		(**14**)	87
3[c)]	**8**			P^nBu_3	30	1			66
4	**8**			P^nBu_3	30	3		(**7**)	89
5				dppe	80	3			78
6				dppe	80	3			77
7				P^nBu_3	30	3			77
8				dppe	80	2			23

$E = CO_2Me$

a) All products were identified by ^1H-NMR, ^{13}C-NMR, and IR analyses.

b) Isolated yield after column chromatography.

c) 2.5 mmol of methyl vinyl ketone was used.

Formation of cyclopentanes using various vinylcyclopropanes and α,β-unsaturated ketones or esters are summarized in Table 1. As the ligand of palladium, both dppe and P^nBu_3 are efficient. Reaction of **8** with cyclopentenone gave the bicyclo[3.3.0]octane **14**. This reaction is useful for cyclopentanoid synthesis. Further application is in progress.

References and Notes:

1. For a review, see; L. A. Paquette, "Recent Synthetic developments of Polyquinane Chemistry" Top. Curr. Chem., **119** (1984).
2. For recent works, see;
   (a) J. P. Marino, E. Laborde, J. Am. Chem. Soc., **107**, 734 (1985).
   (b) R. L. Boger, C. E. Brotherton, J. Am. Chem. Soc., **106**, 805 (1984).
   (c) R. L. Danheiser, D. J. Carini, D. M. Fink, A. Basak, Tetrahedron, **37**, 935 (1983).
   (d) R. D. Little, G. W. Muller, M. G. Venegas, G. L. Carrol, A. Bukhari, L. Patton, K. Stone, Tetrahedron, **37**, 4371 (1981).
3. P. Binger, U. Schunchardt, Chem. Ber., **114**, 3313 (1981).
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5. J. Tsuji, I. Shimizu, I. Minami, Y. Ohashi, Tetrahedron Lett., **23**, 4809 (1982).
6. I. Shimizu, Y. Ohashi, J. Tsuji, Tetrahedron Lett., **25**, 5183 (1984).
7. Preparation of similar zwitterionic intermediates from 2-dienylcyclopropane-1,1-dicarboxylates with Pd(0) and subsequent cyclization to vinyl cyclopentanes have been reported. Y. Morizawa, K. Oshima, H. Nozaki, Israel J. Chem., **24**, 149 (1984). However, the presence of the dienyl group is essential for this palladium-catalyzed rearrangement to vinylcyclopentanes, and no rearrangement takes place with vinylcyclopropanedicarboxylates. On the other hand, we found that vinylcyclopropane-1,1-dicarboxylates react with electron-deficient olefins to give vinyl cyclopentanes, as shown in the present paper.
8. Spectral and analytical data for a mixture of **11** are as follows; ^{1}H-NMR ($CDCl_3$): δ 1.82-2.86 (m, 5H), 2.86-3.17 (m, 1H), 3.63 and 3.68 (s, 3H), 3.74 (s, 6H), 4.97-5.16 (m, 2H), 5.93-5.95 (m, 1H). ^{13}C-NMR ($CDCl_3$) δ 36.0 (t), 37.4 (t), 38.6 (t), 39.9 (t), 45.9 (d), 47.5 (d), 47.5 (d), 48.0 (d), 49.5 (d), 51.4 (q), 51.7 (q), 52.8 (q), 58.7 (s), 59.3 (s), 115.7 (t), 116.4 (t), 136.7 (d), 138.4 (d), 171.7 (s), 171.9 (s), 172.2 (s), 172.8 (s), 173.5 (s), 173.9 (s). IR (neat): 2950, 1730, 990, 920 cm^{-1}. Anal. calcd for $C_{13}H_{18}O_6$: C, 57.77; H, 6.71. Found: C, 57.59; H, 6.70.

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