Catalytic Allylation of 1-Trimethylsilyloxycyclopent-1-ene into 2-Allylcyclopentanone over Palladium supported on Silica

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1-Trimethylsilyloxycyclopent-1-ene can be catalytically converted into 2-allylcyclopentanone by its reaction with diallyl carbonate over palladium supported on silica.

The palladium-catalysed allylation reaction of active methylene compounds is a well established reaction.[1] In a homogeneous system, the palladium catalysed allylation of silyl enol ethers with allyl acetate,[2] allyl ammonium salts,[3] and allyl carbonates[4] have been reported. For example, Tsuji *et al.*[4—5] have reported that silyl enol ethers (**1**) can be converted into α-allyl ketones (**3**) and aldehydes in tetrahydrofuran (THF) by reaction with allyl carbonates (**2**) in the presence of tris(dibenzylideneacetone)dipalladium-(chloroform) [$Pd_2(dba)_3CHCl_3$] by using 1,2-bis-(diphenylphosphino)ethane (dppe) as the most suitable ligand (equation 1).

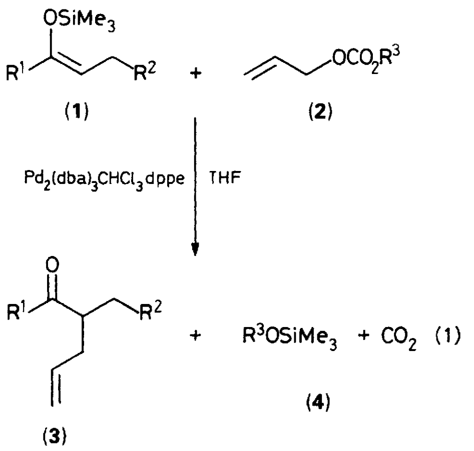
Recently, we have reported that in a heterogeneous system, silyl enol ethers (**1**) can be selectively converted into α,β-unsaturated ketones over palladium(0) supported on silica (Pd^0/SiO_2) in the presence of oxygen.[6] Here, we report that 1-trimethylsilyloxycyclopent-1-ene (**5**), as a silyl enol ether, can be catalytically converted in one step into 2-allylcyclopentanone (**7**) over palladium(0) supported on silica as a heterogeneous catalyst by its reaction with diallyl carbonate (**6**). The reaction can be expressed by equation (2). 1-Trimethylsilyloxycyclopent-1-ene (**5**) from Petrarch System INC was distilled under reduced pressure. Solvents were purified just before the reaction.

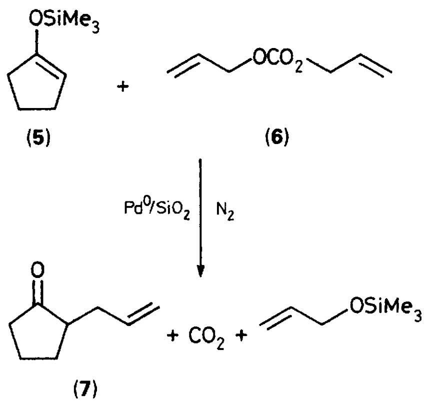
Pd^{2+}-exchanged silica which contained 4.1 wt% palladium was prepared using $[Pd(NH_3)_4]Cl_2$ dissolved in an NH_3 solution *via* an ion exchange method as follows. Silica (10 g)

Table 1. Allylation of 1-trimethylsilyloxycyclopent-1-ene (**7**) with diallyl carbonate into 2-allylcyclopentanone (**8**) over Pd^0 (4.1 wt%) supported on silica in various solvents.[a]

Solvent	Conversion of (**5**) /%	Yield of (**7**) /%	Selectivity (%) to (**7**)	(**8**)	(**9**)
Ethylene glycol dimethyl ether	78.1	74.9	95.9	4.0	0.1
	10.1[b]	—	—	31.2	68.8
	62.4[c]	29.7	47.7	14.3	38.0
Diethylene glycol dimethyl ether	75.8	71.8	94.7	4.9	0.4
Diethylene glycol diethyl ether	72.0	68.9	95.7	3.8	0.5
Isopropyl ether	69.9	60.5	86.6	4.4	9.0
n-Butyl ether	83.5	52.8	69.7	6.0	24.3
N,N-Dimethylformamide	61.3	40.8	60.6	7.5	25.9
N-Methyl-2-pyrrolidone	47.3	36.7	77.6	1.2	21.2
	97.1[c]	19.7	20.3	39.4	40.3
THF	25.6	24.2	94.7	5.2	0.1
Benzonitrile	41.6	14.7	35.3	2.4	62.3

[a] *Reaction conditions*; Pd^0 (4.1 wt%)/SiO_2 0.30 g, 333 K, 24 h, 1-trimethylsilyloxycyclopent-1-ene (1.12 mmol), diallyl carbonate (2.66 mmol), solvent (4.0 ml). The reaction was carried out under nitrogen (101.3 kPa). Catalyst was calcined under air at 453 K for 1 h and was then reduced with hydrogen at 623 K for 1 h. [b] Catalyst was not pretreated with hydrogen. [c] The reaction was carried out under oxygen (101.3 kPa).





(Davison Grade 62) in an NH_3 28% solution (500 ml), in which $[Pd(NH_3)_4]Cl_2$ (1.03 g) was dissolved, was stirred under air at room temperature for 24 h. The sample was washed throughly with water until Cl^- could not be detected in the filtrate. The loading of the palladium supported on silica (wt%) was determined by atomic absorption analysis. The Pd^0 supported catalysts were prepared by heating Pd^{2+}-exchanged silica under air at 453 K for 1 h, followed by reduction with hydrogen at 623 K for 1 h.

The allylation of silyl enol ether (**5**) was performed in a 50 ml three-neck flask equipped with a condenser and a magnetic stirrer. The catalyst (0.300 g) in a solvent such as ethylene glycol dimethyl ether (4.0 ml) (**5**) (1.12 mmol), and diallyl carbonate (**6**) (2.66 mmol) was stirred under nitrogen at 333 K for 24 h. 2-Allylcyclopentanone (**7**) was identified with ^1H NMR and IR spectroscopy. The conversion of (**5**), yield of (**7**), and those of the by-products were determined with a gas chromatograph (1 m PEG 1500 glass column) using 3-methylbutan-1-ol as an internal standard.

The allylation of (**5**) with (**6**) in various solvents was carried out under nitrogen over Pd^0 (4.1 wt%) supported on silica [Pd^0 (4.1 wt%)/SiO_2]. The selection of solvent was crucial as shown in Table 1. The formation of (**7**) proceeded satisfactorily in some ethers. Ethylene glycol dimethyl ether was the most effective solvent, giving 74.9% yield of (**7**) and 95.9% selectivity to (**7**). Here, the molar ratio of the formed (**7**) to the amount of Pd^0 supported on silica was 7.3, indicating that the reaction is catalytic. Small amounts of cyclopent-2-enone (**8**) and cyclopentanone (**9**) were formed as by-products.

As shown in Table 1, the allylation of (**5**) with (**6**) did not proceed over the silica exchanged with $[Pd(NH_3)]^{2+}$ which had not been pretreated with hydrogen. It is clear that the reduction of Pd^{2+} to Pd^0 with hydrogen is indispensable for the appearance of catalytic activity. When the reaction of (**5**) with (**6**) was carried out under oxygen in ethylene glycol dimethyl ether, the yield of (**7**) dramatically decreased, and the selectivity to (**7**) was very low (Table 1).

In order to verify that the allylation of (**5**) with diallyl carbonate by using Pd^0/SiO_2 as a catalyst proceeds in a heterogeneous system, the following experiment was carried out. Pd^0 (4.1 wt%) supported on silica (0.60 g) was stirred in ethylene glycol dimethyl ether (8.0 ml) under nitrogen at 333 K for 30 h. This mixture was filtered to separate the catalyst from the solvent through filter paper. Then, the reaction was carried out under the same reaction conditions as given in Table 1 by using 0.30 g of the catalyst which was separated, washed with a large amount of diethyl ether, and then dried under air at 373 K for 3 h. The conversion of (**5**), the yield of (**7**), and the selectivity to (**7**) were 76.1, 71.8, and 94.3%, respectively. This catalytic activity is essentially the same as that of a fresh Pd^0 (4.1 wt%)/SiO_2 catalyst. This result shows that the allylation of (**5**) with (**6**) under nitrogen is truly heterogeneous, and Pd^0 supported on silica is responsible for the selective allylation.

The reaction was also carried out by using the filtrate (4.0 ml), (**5**) (1.12 mmol), and (**6**) (2.66 mmol) under nitrogen at 333 K for 24 h. The amount of palladium in 4.0 ml of the filtrate was determined as 3.2×10^{-4} mmol (*i.e.*, 8.5 p.p.m.) by using atomic adsorption analysis. The formation of (**7**) was not observed at all, and the conversion of (**5**) was 3.1%. The yields of (**8**) and (**9**) were 1.3% and 1.8%, respectively. This result shows that the palladium dissolved into the solvent does not contribute to the formation of (**7**).

The utility of Pd^0/SiO_2 may be summarized as follows: (i) Pd^0 supported on silica as heterogeneous catalyst has a high catalytic activity for the formation of 2-allyl ketones. (ii) The third compound such as dppe for a suitable ligand in a homogeneous system is not needed. (iii) The catalyst can be easily separated from the product.

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References

1 J. Tsuji, 'Organic Synthesis with Palladium Compounds,' Springer-Verlag, Heidelberg, 1980.
2 M. B. Trost and E. Keian, *Tetrahedron Lett.*, 1980, **21**, 2591.
3 T. Hirao, N. Yamada, O. Ohshiro, and T. Agawa, *J. Organomet. Chem.*, 1982, **236**, 409.
4 J. Tsuji, I. Minami, and I. Shimizu, *Chem. Lett.*, 1983, 1325.
5 J. Tsuji, K. Takahashi, I. Minami, and I. Shimizu, *Tetrahedron Lett.*, 1984, **25**, 4783.
6 T. Baba, K. Nakano, S. Nishiyama, S. Tsuruya, and M. Masai, *J. Chem. Soc., Chem. Commun.*, 1989, 1697.