

Catalytic Dehydrosilylation of 1-Trimethylsilyloxycyclopent-1-ene into Cyclopent-2-enone with Oxygen over Palladium supported on Silica

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1-Trimethylsilyloxycyclopent-1-ene can be catalytically converted to cyclopent-2-enone by its reaction with oxygen in the presence of palladium supported on silica, which gave the 90.1% yield of cyclopent-2-one and the 99.2% selectivity at 333 K for 24 h.

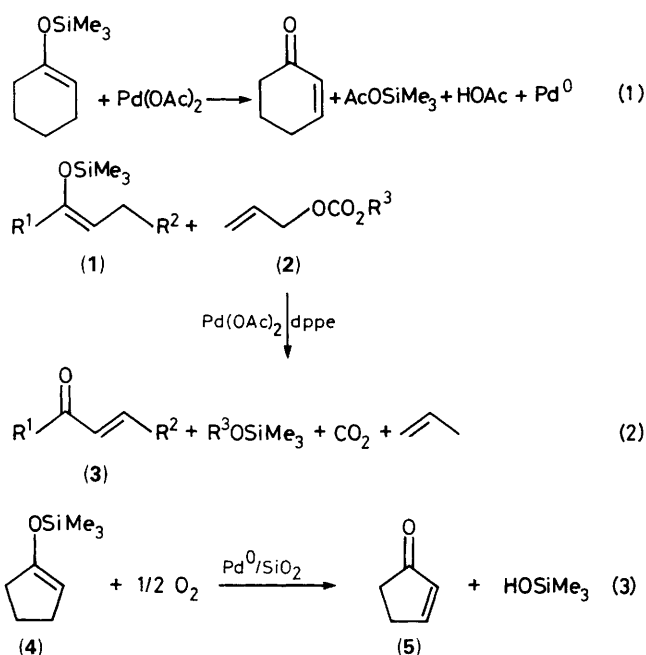
Silyl enol ethers¹ are known as useful intermediates for organic syntheses such as the preparation of α,β -unsaturated carbonyl compounds which are very important in the synthesis of natural products.^{2–4} Ito *et al.* have reported that α,β -unsaturated carbonyl compounds, such as cyclohex-2-enone, are synthesized by the reaction of the corresponding silyl enol ethers with palladium acetate [Pd(OAc)₂] in acetonitrile.⁵ In this method, the reaction is not catalytic and the yield is stoichiometric with respect to Pd(OAc)₂. The procedure is illustrated for the preparation of cyclohex-2-enone in equation (1).⁶ Though the catalytic cycle can be attained when *p*-benzoquinone is added, the rates and yields decrease under the catalytic conditions. Recently, Tsuji *et al.*⁷ have reported that silyl enol ethers (1) are converted catalytically to α,β -unsaturated carbonyl compounds (3) by the reaction with allyl carbonate (2) in acetonitrile using Pd(OAc)₂ and 1,2-bis(diphenylphosphino)ethane (dppe) as a catalyst [equation (2)]. In this method, more than the stoichiometric amount of (2) is required.

We found that 1-trimethylsilyloxycyclopent-1-ene (4), as a silyl enol ether, could be catalytically converted in one step to cyclopent-2-enone (5), an α,β -unsaturated carbonyl compound, over palladium(0) supported on silica (Pd⁰/SiO₂) as a heterogeneous catalyst by using oxygen. The reaction can be expressed by equation (3).

1-Trimethylsilyloxycyclopent-1-ene (4) and trimethylsilyloxycyclohex-1-ene (7) obtained from Petrarch System Inc. were distilled under reduced pressure. Various solvents were purified just before the reaction.

Silica exchanged with Pd²⁺ was prepared using [Pd(NH₃)₄]Cl₂ dissolved in NH₃ solution *via* an ion exchange method. The degree of exchanged palladium (wt%) was determined by atomic absorption analysis. Catalysts supported on Pd⁰ were prepared as follows: Pd²⁺-exchanged silica was calcined in air at 453 or 632 K for 1 h, and was then reduced with hydrogen at 623 K for 1 h.

The dehydrosilylation of silyl enol ether 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 (4 ml) such as *N*-methyl-2-pyrrolidone and (4) (1.12 mmol) or (7) (1.12 mmol) were stirred under oxygen at 333 K for 24 h.

Cyclopent-2-enone (5) and cyclohex-2-enone (8) were identified by comparison of their ¹H NMR and IR data with those of synthetic samples. The conversion of silyl enol ethers, yield of cyclopent-2-enone (5) or cyclohex-2-enone (8) and those of by-products were determined with a gas chromatograph (1 m PEG 1500 glass column) by using 3-methylbutan-1-ol as a standard.

Dehydrosilylation of (4) in various solvents was carried out over Pd⁰ (3.9 wt%) supported on silica [Pd⁰ (3.9 wt%)/SiO₂].

Table 1. Dehydrosilylation of 1-trimethylsilyloxycyclopent-1-ene over Pd⁰ (3.9 wt%) supported on silica in various solvents at 333 K.

Solvent	Conversion of (4)/%	Yield of (5)/%	Selectivity to (5)/% (5)/(6)/%	
<i>N,N</i> -Dimethylformamide	79.9	76.2	95.3	4.7
<i>N,N</i> -Dimethylacetamide	78.9	54.7	69.3	30.7
<i>N,N</i> -Dimethylpropionamide	12.0	5.6	46.7	53.3
<i>N</i> -Methyl-2-pyrrolidone	84.9	82.4	97.1	2.9
	90.8 ^a	90.1	99.2	0.8
Tetrahydrofuran	70.9	59.6	84.0	16.0
Ethylene glycol dimethyl ether	75.0	51.4	68.5	31.5
Acetonitrile	96.5	10.2	10.6	89.4
<i>N</i> -Butylamine	67.6	0	0	0

^a Pd⁰ (4.2 wt%)/SiO₂ was calcined under air at 453 K and then was reduced with hydrogen at 623 K for 1 h.

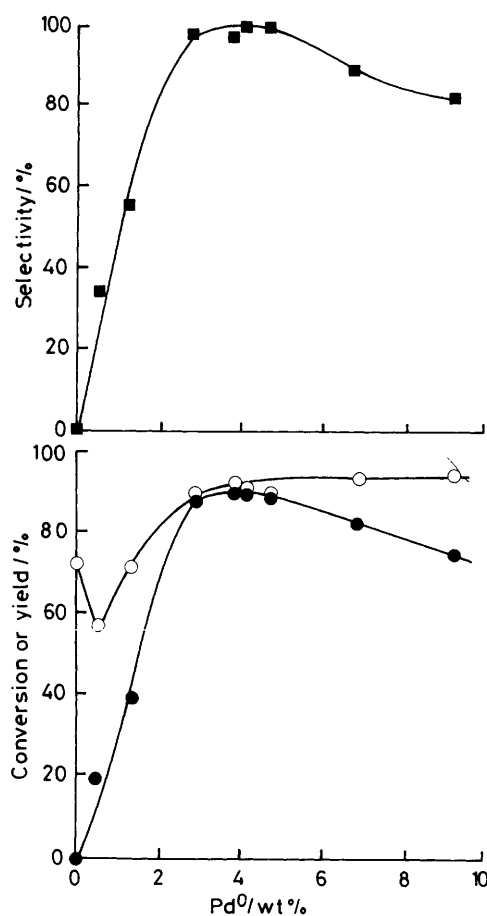


Figure 1. The dependence of the amount of Pd⁰ supported on silica on the conversion of 1-trimethylsilyloxycyclopent-1-ene (○), the yield of cyclopent-2-enone (●) and the selectivity to cyclopent-2-enone (■) in *N*-methyl-2-pyrrolidone at 333 K. *Reagents and conditions*; Pd⁰ (3.9 wt%)/SiO₂ (0.300 g), 1-trimethylsilyloxycyclopent-1-ene (1.12 mmol), *N*-methyl-2-pyrrolidone (4.0 ml), 333 K, 24 h. Each catalyst was calcined in air at 453 K for 1 h and then reduced with hydrogen at 623 K for 1 h.

The selection of solvent was crucial. The formation of (5) proceeded satisfactorily only in *N,N*-dimethylformamide and particularly in *N*-methyl-2-pyrrolidone. Thus, the yield of (5) was 82.4% and the selectivity to (5) was 97.1%. A small amount of cyclopentanone (6) was formed as a by-product. When the reaction was carried out in *N*-methyl-2-pyrrolidone

under nitrogen, the conversion of (4) and the yield of (5) were 43.1 and 6.3%, respectively. The main product was cyclopentanone (6). Silica exchanged with [Pd(NH₃)₄]²⁺, which was not pretreated with hydrogen, showed very little catalytic activity for the formation of (5) under oxygen. Thus, the yield of (5) was 2.2% and that of (6) was 72.6% when the conversion of (4) was 74.8%.

The higher catalytic activity of Pd⁰/SiO₂ for the formation of (5) could be achieved by changing the amount of Pd⁰ supported on silica and the temperatures of the air treatment. The dependence of the amount of Pd⁰ supported on silica on the catalytic activities at 333 K are shown in Figure 1, the catalysts being calcined under air at 453 K, and were then reduced with hydrogen at 623 K for 1 h. Silica on which Pd⁰ was not supported, did not reveal catalytic activity for the formation of (5). Thus, the conversion of (4) was 72.1% and the formation of (5) was not observed under this reaction condition.

The conversion of (4) showed the minimum value (58%) around 0.5 wt% Pd⁰ and gradually increased up to 3 wt% Pd⁰. In addition, it reached a constant value at about 90%. The yield of (5) linearly increased up to 3 wt% Pd⁰, the maximum yield around 3–5 wt% Pd⁰ being around 90%. The yield of (5) gradually decreased by more than 5 wt% Pd⁰. The selectivity to (5) changed in the same manner as the yield of (5). The maximum selectivity to (5) was around 3–5 wt% Pd⁰ and reached about 99%. In particular, the yield of (5) was 90.1% and selectivity to (5) was 99.2% when the amount of Pd⁰ supported on silica was 4.2 wt%.

In order to verify that the reaction is heterogeneous, the following experiment was carried out. Pd⁰ (4.2 wt%) supported on silica (0.60 g), which gave the highest activity for the formation of (5) (see Figure 1), was stirred in *N*-methyl-2-pyrrolidone (8.0 ml) under oxygen for 24 h at 338 K. This mixture was carefully filtered to separate the catalyst from the solvent through a couple of filter papers under nitrogen. 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 (4), the yield of (5), and the selectivity to (5) were 91.7, 86.3, and 94.1%, respectively. This catalytic activity is essentially the same as that of Pd⁰ (4.2 wt%)/SiO₂ which was not treated with solvent under oxygen beforehand (Table 1). This result shows that the reaction [the formation of (5)] is mainly heterogeneous, and Pd⁰ supported on silica is responsible for the selective reaction. The reaction was also carried out by using 4.0 ml of the filtrate and 1.12 mmol of (4) under oxygen at 333 K for 24 h. The amount of palladium in 4.0 ml of the filtrate was determined as 5.4×10^{-4} (i.e. 14.4

p.p.m.) by using atomic absorption analysis. This amount corresponds to the elution of 0.46% of total palladium to the solvent. The conversion of (4), and the yield of (5) were 7.1 and 6.4%, respectively. This shows that the contribution of dissolved palladium to the catalysis is small.

It was also possible to apply Pd^0/SiO_2 to the dehydrosilylation of 1-trimethylsilyloxycyclohex-1-ene (7) into cyclohex-2-enone (8). Thus, 0.300 g of Pd^0 (3.9 wt%)/ SiO_2 gave a 87.4% yield of (8) and 82.3% selectivity to (8) in n-methyl-2-pyrrolidone at 333 K for 24 h, when the catalyst was calcinated at 453 K under air for 1 h and then was reduced with hydrogen at 623 K for 1 h.

The features of Pd^0 supported on silica may be summarized as follows: firstly, Pd^0 supported on silica as a heterogeneous catalyst has a high catalytic activity and a high selectivity for this reaction; secondly, this reaction catalytically proceeds under oxygen; thirdly, molecular oxygen can be used as a

convenient oxidant, and fourthly, the catalyst can be easily separated from the product.

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