JOURNAL OF THE CHEMICAL SOCIETY

Chemical Communications

Number 22
1989

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

**T. Baba,[a]* K. Nakano,[b] S. Nishiyama,[b] S. Tsuruya,[b] and M. Masai[b]**

[a] *Graduate School of Science and Technology, Kobe University, Rokkodai, Nada-ku, Kobe 657, Japan*
[b] *Faculty of Engineering, Kobe University, Rokkodai, Nada-ku, Kobe 657, Japan*

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.

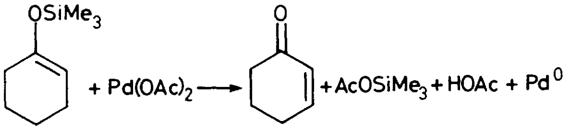
Silyl enol ethers[1] are known as useful intermediates for organic syntheses such as the preparation of α,β-unsaturated carbonyl compounds which are very important in the synthesis of natural products.[2–4] Ito *et al.* have reported that α,β-unsaturated carbonyl compounds, such as cyclohex-2-enone, 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 stoicheiometric 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 stoicheiometric 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 ($Pd^0/SiO_2$) as a heterogeneous catalyst by using oxygen. The reaction can be expressed by equation (3).

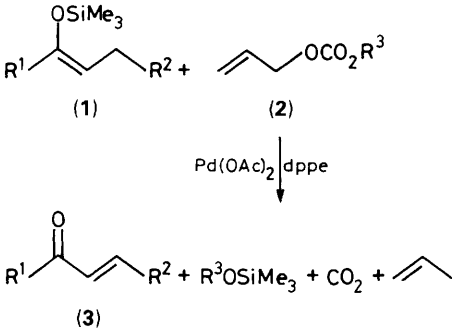
1-Trimethylsilyloxycyclopent-1-ene (**4**) and trimethylsilyloxycyclohex-1-ene (**7**) obtained from Petrarch System Inc. were distilled under reduced pressure. Various solvents were purified just before the reaction.

Silica exchanged with $Pd^{2+}$ was prepared using $[Pd(NH_3)_4]Cl_2$ dissolved in $NH_3$ solution *via* an ion exchange method. The degree of exchanged palladium (wt%) was determined by atomic absorption analysis. Catalysts supported on $Pd^0$ were prepared as follows: $Pd^{2+}$-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.

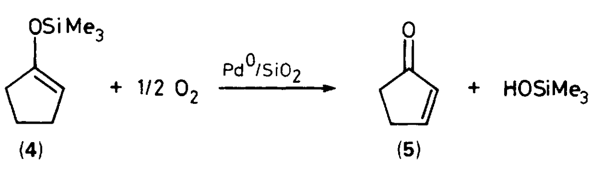
The dehydrosilylation of silyl enol ether was performed in a 50 ml three-neck flask equipped with a condenser and a magnetic stirrer. The catalyst (0.300 g) in a solvent (4 ml) such as *N*-methyl-2-pyrrolidone and (**4**) (1.12 mmol) or (**7**) (1.12 mmol) were stirred under oxygen at 333 K for 24 h.



(1)



(2)



(3)

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 varioius solvents was carried out over $Pd^0$ (3.9 wt%) supported on silica [$Pd^0$ (3.9 wt%)/$SiO_2$].

**Table 1.** Dehydrosilylation of 1-trimethylsilyloxycyclopent-1-ene over $Pd^0$ (3.9 wt%) supported on silica in various solvents at 333 K.

| Solvent | Conversion of (**4**)/% | Yield of (**5**)/% | Selectivity to (**5**)/% | (**6**)/% |
|---|---|---|---|---|
| *N,N*-Dimethylformamide | 79.9 | 76.2 | 95.3 | 4.7 |
| *N,N*-Dimethylacetamide | 78.9 | 54.7 | 69.3 | 30.7 |
| *N,N*-Dimethylpropionamide | 12.0 | 5.6 | 46.7 | 53.3 |
| *N*-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 |
| *N*-Butylamine | 67.6 | 0 | 0 | 0 |

[a] $Pd^0$ (4.2 wt%)/$SiO_2$ was calcined under air at 453 K and then was reduced with hydrogen at 623 K for 1 h.

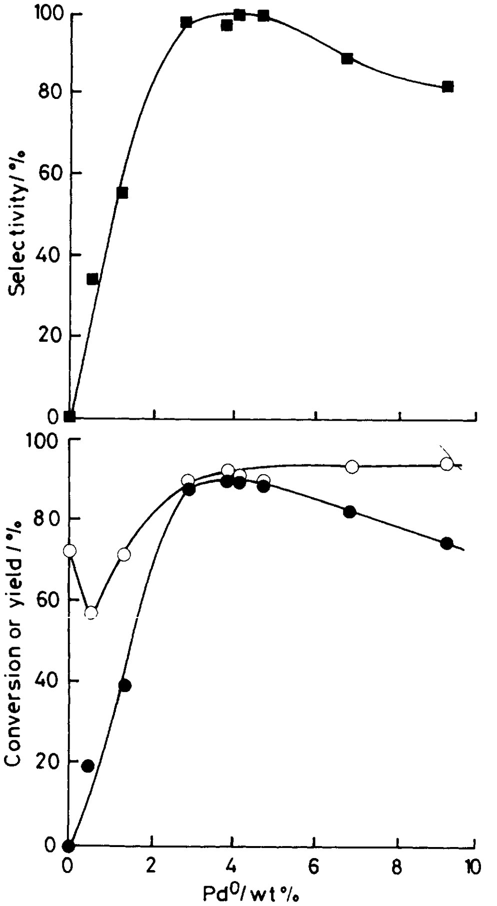


**Figure 1.** The dependence of the amount of $Pd^0$ supported on silica on the conversion of 1-trimethylsilyloxycyclopent-1-ene (○), the yield of cyclopent-2-enone (●) and the selectivity to cyclopent-2-enone (■) in n-methyl-2-pyrrolidone at 333 K. *Reagents and conditions;* $Pd^0$ (3.9 wt%)/$SiO_2$ (0.300 g), 1-trimethylsilyloxycyclopent-1-ene (1.12 mmol), *N*-methyl-2-pyrolidone (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 $[Pd(NH_3)_4]^{2+}$, 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 $Pd^0/SiO_2$ for the formation of (**5**) could be achieved by changing the amount of $Pd^0$ supported on silica and the temperatures of the air treatment. The dependence of the amount of $Pd^0$ 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 $Pd^0$ 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% $Pd^0$ and gradually increased up to 3 wt% $Pd^0$. In addition, it reached a constant value at about 90%. The yield of (**5**) linearly increased up to 3 wt% $Pd^0$, the maximum yield around 3—5 wt% $Pd^0$ being around 90%. The yield of (**5**) gradually decreased by more than 5 wt% $Pd^0$. The selectivity to (**5**) changed in the same manner as the yield of (**5**). The maximum selectivity to (**5**) was around 3—5 wt% $Pd^0$ and reached about 99%. In particular, the yield of (**5**) was 90.1% and selectivity to (**5**) was 99.2% when the amount of $Pd^0$ supported on silica was 4.2 wt%.

In order to verify that the reaction is heterogeneous, the following experiment was carried out. $Pd^0$ (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 $Pd^0$ (4.2 wt%)/$SiO_2$ 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 $Pd^0$ 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 $5.4 \times 10^{-4}$ (*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.

*Received, 12th April 1989; Com. 9/01502G*

## References

1 P. Brownbridge, *Synthesis*, 1983, 1 and 85.
2 R. E. Ireland, J. D. Godfrey, and S. Thaisrivongs, *J. Am. Chem. Soc.*, 1981, **103**, 2446.
3 B. M. Trost, Y. Nishimura, and K. Yamamoto, *J. Am. Chem. Soc.*, 1979, **101**, 1328..
4 P. A. Wender and J. C. Lechleiter, *J. Am. Chem. Soc.*, 1980, **102**, 6340.
5 Y. Ito, T. Hirao, and T. Saegusa, *J. Org. Chem.*, 1978, **43**, 1011.
6 R. F. Heck, 'Palladium Reagents in Organic Synthesis,' Academic Press, 1985, p. 107.
7 J. Tsuji, I. Minami, and I. Shimizu, *Tetrahedron Lett.*, 1983, **24**, 5635.