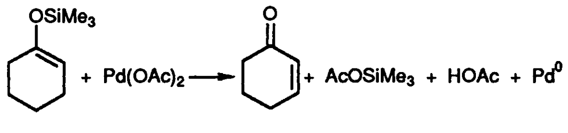
Catalytic Dehydrosilylation of 1-Trimethylsilyloxycyclopent-1-ene to Cyclopent-2-enone with Oxygen over Palladium Supported on Silica.

Toshide Baba *†
Graduate School of Science and Technology, Kobe University, Rokkodai, Nada-ku, Kobe 657, Japan
Kaichiro Nakano, Satoru Nishiyama, Shigeru Tsuruya, and Mitsuo Masai
Faculty of Engineering, Kobe University, Rokkodai, Nada-ku, Kobe 657, Japan

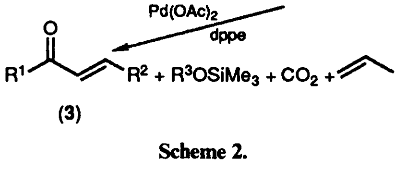
1-Trimethylsilyloxycyclopent-1-ene has been catalytically converted into cyclpent-2-enone through its reaction with oxygen in the presence of palladium(0) supported on silica. The choice of solvent is crucial, *N*-methyl-2-pyrrolidone being the most effective solvent. Thus, palladium (3.9wt%) supported on silica gave a 90.1% yield of cyclopent-2-enone and a 99.2% selectivity at 333 K for 24 h. The catalyst can be also utilized in the dehydrosilylation of 1-trimethylsilyloxycyclohex-1-ene into cyclohex-2-enone. This catalytic reaction offers a convenient and useful method for the synthesis of α,β-unsaturated ketones such as cyclopent-2-enone, since molecular oxygen can be used as a convenient oxidant. The reaction mechanism has been proposed on the basis of mass spectral measurements in the dehydrosilylation of 1-trimethylsilyloxycyclopent-1-ene with $^{18}O_2$ over palladium(0) supported on silica.

Silyl enol ethers are extensively used in organic synthesis as reactive enolate equivalents, particularly in the aldol condensation and Michael addition reactions in the presence of Lewis acids or other promoters.[1] For example, silyl enol ethers are useful intermediates in the preparation of α,β-unsaturated carbonyl compounds which are very important in the synthesis of natural products.[2–6] Ito *et al.*[7] 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 the equivalent amount of palladium acetate [Pd(OAc)$_2$] in a homogeneous system. In this method, the reaction is not catalytic and the yield is stoicheiometric with respect to Pd(OAc)$_2$, and the stoicheiometry is illustrated for the preparation of cyclohex-2-enone in Scheme 1.[8] In Scheme 1, the amount of Pd(OAc)$_2$ can be reduced by using one equivalent of *p*-benzoquinone, which is a reoxidant used to regenerate an active Pd^{II} species, although the yields of α,β-unsaturated carbonyl compounds decrease to some extent.



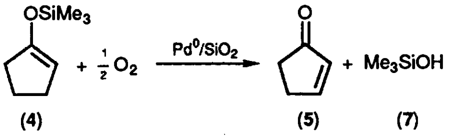
Scheme 1.

Tsuji *et al.*[9] have reported that silyl enol ethers (1) are converted catalytically into 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 homogeneous catalyst (Scheme 2).



Scheme 2.

Recently, we have reported that molecular oxygen can be used as a convenient oxidant for the oxidative esterification of butane-1,4-diol into γ-butyrolactone, when palladium (Pd^0) supported on zeolites are used as catalysts.[10,11] Since silyl enol ethers undergo interconversion to enolates by keto–enol tautomerism, we tried to apply Pd^0 catalysts for oxidative dehydrosilylation of 1-trimethylsilyloxycyclopent-1-ene as a silyl enol ether to cyclopent-2-enone. In this paper, we report that 1-trimethylsilyloxycyclopent-1-ene (4), a silyl enol ether, is catalytically converted in one step into cyclopent-2-enone (5), an α,β-unsaturated carbonyl compound, with palladium(0) supported on silica (Pd^0/SiO$_2$) as a heterogeneous catalyst in the presence of oxygen. The reaction is expressed in Scheme 3.



Scheme 3.

Experimental

Materials.—1-Trimethylsilyloxycyclohex-1-ene (9) and (4) were obtained from Petrarch System INC and were distilled under reduced pressure. Various solvents were purified just before the reaction. Amides, such as *N*-methyl-2-pyrrolidone, were shaken for 1–2 days over MgSO$_4$ (which had been dried under air at 653 K for 3 h), and then decanted. They were then distilled from CaH$_2$ under reduced pressure. Purification of acetonitrile was achieved by standing the solution with CaCl$_2$ for 1–2 days, followed by reflux with CaCl$_2$ for 3 h before distillation. Ethylene glycol dimethyl ether and *N*-butylamine were kept over CaCl$_2$ for 1–2 days and then distilled from CaCl$_2$.

Catalyst Preparation.—Silica (Davison Grade 62) obtained from Fuji Davison Industry has 296 m^2 g^{-1} BET surface area. Pd^{2+} exchanged silica was prepared using [Pd(NH$_3$)$_4$]Cl$_2$ in an aqueous NH$_3$ solution *via* an ion exchange method. The various zeolites were exchanged with [Pd(NH$_3$)$_4$]$^{2+}$ in a

---

† *Present Address:* Dept. of Chemical Engineering, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo–152, Japan.

$[Pd(NH_3)_4]Cl_2$ solution at room temperature for 1–2 days. For example, Pd^{2+}-exchanged silica which contained 4.2 wt% palladium was prepared as follows: 10 g of silica in 500 cm^3 of a 28% NH_3 solution, in which 1.03 g of $[Pd(NH_3)_4]Cl_2$ was dissolved, was stirred under air at room temperature for 24 h. These samples were washed thoroughly with water until Cl^- was no longer detected in the filtrate. Palladium supported on activated carbon (Shirasagi C obtained from Takeda Chemical Industries), Al_2O_3 and TiO_2 (Wako Pure Chemicals), or silicalite (Toso Co. Ltd.), was prepared by incipient wetness impregnation with a solution of $[Pd(NH_3)_4]Cl_2$. The degree of palladium exchanged, or the amount of impregnated palladium, was determined by atomic absorption spectrophotometry. All catalysts were calcined statically in a flow regime under air (5 000 cm^3 h^{-1}) at various temperatures for 1 h and were then pretreated with hydrogen (5 000 cm^{-3} h^{-1}) at 623 K for 1 h. These prepared catalysts were stored in a desiccator.

Apparatus and Procedure.—(*a*) *Dehydrosilylation of silyl enol ethers over* Pd^0 *catalyst.* The dehydrosilylation of silyl enol ether was performed in a 50 cm^3 three-necked flask equipped with a condenser and a magnetic stirrer. The catalyst (0.300 g) in 4.0 cm^3 of solvent, such as *N*-methyl-2-pyrrolidone, and 1.12 mmol of (**4**) or 1.12 mmol of (**9**) was stirred under oxygen at 310–370 K for 24 h.

$^{18}O_2$ was obtained from the Commissariat a l'Energie Atomique. The purity of $^{18}O_2$ was 97.5%. Dehydrosilylation of (**4**) with $^{18}O_2$ was carried out in *N*-methyl-2-pyrrolidone over Pd^0 (4.2wt%) supported on silica at 333 K. The catalyst was calcined under air at 453 K for 1 h and was then reduced with hydrogen at 623 K for 1 h.

The products, cyclopent-2-enone and cyclohex-2-enone were identified by comparison of their ^1H NMR and IR spectra. ^1H NMR spectra were recorded on either a JEOL Model FX-90Q Fourier transform spectrometer in a $CDCl_3$ solution at 90 MHz, or on a Hitachi model R-24A in a CCl_4 solution at 60 MHz, by using tetramethylsilane as an internal standard. IR spectra were measured with a JASCO Model IRA-2 spectrometer. Cyclopent-2-enone (**5**): δ_H(90 MHz; $CDCl_3$) 2.31–2.41 (2 H, m), 2.66–2.76 (2 H, m), 6.21 (1 H, dt, *J* 5.6, 2.2 Hz), and 7.33 (1 H, dt, *J* 5.6, 2.6 Hz); ν_{max} 2 290, 1 680, 1 620, and 880 cm^{-1}. Cyclohex-2-enone (**10**): δ_H(60 MHz; CCl_4) 1.20–2.20 (6 H, m), 5.85 (1 H, dt, *J* 12, 2 Hz), and 6.68 (1 H, dt, *J* 12, 5 Hz); ν_{max} 2 920, 1 680, 1 620, and 880 cm^{-1}.

The conversion of silyl enol ethers, yields of (**5**) or (**10**) and those of by-products were determined with a gas chromatograph (1 m PEG 1500 glass column) by using 3-methylbutan-1-ol as an internal standard.

(*b*) *Gas chromatography/mass spectrometry.* Gas chromatography/mass spectrometry was performed with a gas chromatograph (25 m capillary column of PEG-20M, i.d. = 0.25 mm) interfaced to a JEOL DX303-HR mass spectrometer. The ion source was fixed at an accelerating potential of 7 kV.

(*c*) *Hydrogen adsorption on palladium supported on silica.* The adsorption of hydrogen on Pd^0 supported on silica was carried out in a conventional gas-circulating reactor. A portion of $[Pd(NH_3)_4]^{2+}$-exchanged silica (0.100 g) was evacuated at 393 K for 1 h and then calcined under air (51 kPa) at a given temperature for 1 h. It was then evacuated to 10^{-2} Pa and pretreated with 51 kPa of hydrogen at 623 K for 1 h. The sample was then evacuated to 10^{-2} Pa and cooled to 301 K before being exposed to a constant pressure of hydrogen (3.0 kPa) at 301 K. The amount of hydrogen equilibrium adsorption was then measured. Then the sample was again evacuated to 10^{-2} Pa at 301 K, and exposed to 3.0 kPa of hydrogen until the point where adsorption of the hydrogen reached equilibrium. The different amount of hydrogen adsorption in the two runs was assumed to be the amount of the irreversible hydrogen adsorption.

Results and Discussion

Catalytic Activities of Pd^0 *Supported on Various Supports.*—The catalytic activities of Pd^0 supported on various zeolites such as Na–X type zeolite (Pd^0–Na–X) and those of Pd^0 supported on activated carbon, silicalite, Al_2O_3, and TiO_2 were examined in *N*-methyl-2-pyrrolidone at 333 K for 24 h. The catalysts were calcined at 623 K for 1 h and then reduced with hydrogen at 623 K for 1 h. The loading of Pd^0 was 2.5–4.4wt%. The palladium on these supports, which was pretreated with hydrogen in a flow regime, changes into palladium metal (Pd^0), and the degree of reduction of palladium was estimated from the consumption of hydrogen when these supported palladium catalysts were pretreated with 51 kPa of hydrogen at 623 K for 1 h in a conventional gas-circulating reactor. As shown in Table 1, Pd^0 supported on silica gave the highest yield and selectivity. Namely, the yield of (**5**) was 82.4%, and the selectivity to (**5**) was 97.1%, while the conversion of (**4**) was 84.9%. Cyclopentanone (**6**) [the selectivity to (**6**) was 2.9%] was formed as a by-product. The formation of trimethylsilanol (**7**) and hexamethyldisiloxane (**8**) will be discussed later. The ratio of the amount of (**5**) to that of Pd^0 supported on silica is 8.4 (Table 1), indicating that the reaction proceeds catalytically. Silica exchanged with $[Pd(NH_3)_4]^{2+}$, which was not reduced with hydrogen, showed very little catalytic activity for the formation of (**5**) under oxygen as shown in Table 1. This result shows that the reduction of Pd^{2+} to Pd^0 with hydrogen is indispensable for the appearance of catalytic activity.

Catalytic Activities of Pd^0 *Supported on Silica in Various Solvents.*—Dehydrosilylation of (**4**) over Pd^0 (3.9wt%) supported on silica [Pd^0 (3.9wt%)/SiO_2] was carried out in various solvents at 333 K for 24 h. As shown in Table 2, the choice of solvent was crucial. The formation of (**5**) proceeded satisfactorily only in *N*-methyl-2-pyrrolidone and *N,N*-dimethylformamide. *N*-Methyl-2-pyrrolidone, particularly, was the most effective solvent.

It was possible to utilize air as an oxygen source instead of pure oxygen for the formation of (**5**) in *N*-methyl-2-pyrrolidone (Table 2). When the reaction was carried out in *N*-methyl-2-pyrrolidone under nitrogen, the conversion of (**4**) and the yield of (**5**) was 98.1 and 83.6%, respectively.

Influence of Calcination Temperature.—The effect of calcination temperature under air on the catalytic activity of Pd^0 (5.4wt%) supported on silica was examined in *N*-methyl-2-pyrrolidone at 333 K. The catalyst was reduced with hydrogen at 623 K for 1 h after its calcination for 1 h at a given temperature. As shown in Figure 1, the conversion of (**4**) was not strongly influenced by the calcination temperature, and the conversion was 73–79%. The selectivity to (**5**), however, was strongly dependent upon the calcination temperature. The maximum selectivity to (**6**) lies at around 450 K and the selectivity to (**5**) was 97.8% when the conversion of (**4**) was 79.1%.

In order to investigate the properties of palladium supported on silica, the dispersion of palladium was determined by the adsorption of hydrogen. As shown in Figure 1, the maximum dispersion of palladium appeared at a calcination temperature of around 450 K and the dispersion of palladium varied in nearly the same manner as the selectivity to (**5**). This result shows that a high selectivity to (**5**) depends to a large part on the dispersion of palladium supported on silica. In the spherical particle equivalent approximation,[12] the volume–area mean diameter of catalyst (d_{va}) which showed the highest activity was 2.9 nm.

Influence of Reaction Temperature.—Figure 2 shows the reaction temperature dependence of the conversion of (**4**), and the selectivity to (**5**) over Pd^0 (5.4wt%) supported on silica. The

Table 1. Catalytic activities of Pd^0 on various supports for the dehydrosilylation of 1-trimethylsilyloxycyclopent-1-ene.

Support	Pd^0 (wt%)	Conversion of (4) (%)	Yield of (5) (%)	Selectivity to (5) (%)	(6) (%)	(5)/Pd^{0} [a]
Silica	3.9	84.9	82.4	97.1	2.9	8.4
		78.4[b]	2.2	2.9	97.1	0.2
Al_2O_3[c]	3.8	81.1	52.0	64.1	35.9	5.5
Na-Y (Si:Al = 2.8)	2.1	79.2	34.6	43.7	56.3	6.6
TiO_2 (rutile)[c]	3.9	71.0	33.8	47.7	52.3	3.5
Silicalite	3.8	71.6	27.1	37.8	62.2	2.9
K–X (Si:Al = 1.4)	4.4	41.7	27.3	65.5	34.5	2.2
Na–Mordenite (Si:Al = 5.8)	5.2	87.9	19.5	22.2	77.8	1.5
K–Y (Si:Al = 2.8)	4.0	88.0	12.7	14.4	85.6	1.3
Na–ZSM-5 (Si:Al = 52)	3.4	65.9	12.6	20.2	79.8	1.5
K–L (Si:Al = 3.2)	3.7	94.1	11.2	11.9	88.1	1.2
Na–X (Si:Al = 1.4)	3.4	68.7	6.9	10.0	90.0	0.81
Activated carbon[c]	2.5	86.2	1.7	2.0	98.0	0.27

Reaction conditions: catalyst weight, 0.300 g; reaction temperature, 333 K; reaction time 24 h; 1-trimethylsilyloxycyclopent-1-ene, 1.12 mmol, solvent was 4.00 cm^3 of *N*-methyl-2-pyrrolidone. The reaction atmosphere was oxygen (101 kPa). Catalyst was calcined under air and then reduced with hydrogen at 623 K for 1 h. [a] The ratio of the amount of (5) to that of Pd^0 supported on catalyst. [b] The catalyst was not reduced with hydrogen. [c] Catalysts were prepared with wetness impregnation.

Table 2. Dehydrosilylation of 1-trimethylsilyloxycyclopent-1-ene over Pd^0 (3.9wt%) supported on silica in various solvents.

Solvent	Conversion of (4) (%)	Yield of (5) (%)	Selectivity to (5) (%)	(6)(%)
N,N-Dimethylformamide	79.9	76.2	95.3	4.7
N,N-Dimethylacetoamide	78.9	54.7	69.3	30.7
N,N-Dimethyl-	12.0	5.6	46.7	53.3
propionamide	84.9	82.4	97.1	2.9
N-Methyl-2-pyrrolidone	90.8[a]	90.1	99.2	0.8
	98.1[a,b]	83.6	85.2	14.8
	43.1[c]	6.1	14.1	85.9
Tetrahydrofuran	89.1	60.5	73.9	26.1
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

Reaction conditions: Pd^0 (3.9wt%)/SiO_2, 0.300 g; reaction temperature, 333 K; reaction time 24 h; 1-trimethylsilyloxycyclopent-1-ene (1.12 mmol); solvent (4.0 cm^3). The reaction atmosphere was oxygen (101 kPa). Catalysts were calcined under air and then reduced with hydrogen at 623 K for 1 h. [a] Pd^0 (4.2wt%)SiO_2 was calcined under air at 453 K and then reduced with hydrogen at 623 K for 1 h. [b] The reaction was carried out under air (101 kPa). [c] The reaction was carried out under nitrogen (101 kPa).

conversion of (4) gradually increased as the reaction temperature rose and reached 98.4% at 359 K. The yield of (5) increased up to 333 K and the maximum yield was 89.1% when the conversion of (4) was 92.3% at 333 K. At higher reaction temperatures, the yield of (4) decreased. The selectivity to (5) was a constant of *ca.* 97% around 310–330 K. Above 340 K, it decreased and, mainly, the formation of (6) proceeded. Thus, the optimum reaction temperature lies around 330 K.

Effect of Amount of Pd^0 *Supported on Silica.*—The dependence of the catalytic activities on the amount of Pd^0 supported on silica at 333 K is shown in Figure 3. Silica does not have catalytic activity towards the formation of (5), though the conversion of (4) was 72.1%. The conversion of (4) showed the minimum value (*ca.* 58%) around 0.5wt% Pd^0 and gradually increased up to *ca.* 3wt% Pd^0, at which point it reached a constant value of about 90%. The yield of (5) increased linearly to *ca.* 3wt% Pd^0. The maximum yield (*ca.* 90%) was obtained at *ca.* 3–5wt% Pd^0. With more than *ca.* 5wt% Pd^0, the yield of (5) gradually decreased. The selectivity to (5) changed in the same manner as the yield of (5). The maximum selectivity to (5) reached *ca.* 99% at 3–5 wt% Pd^0. Remarkably, the yield of (5) was 90.1% and selectivity to (5) was 99.2% when the amount of Pd^0 supported on silica was 4.2wt%.

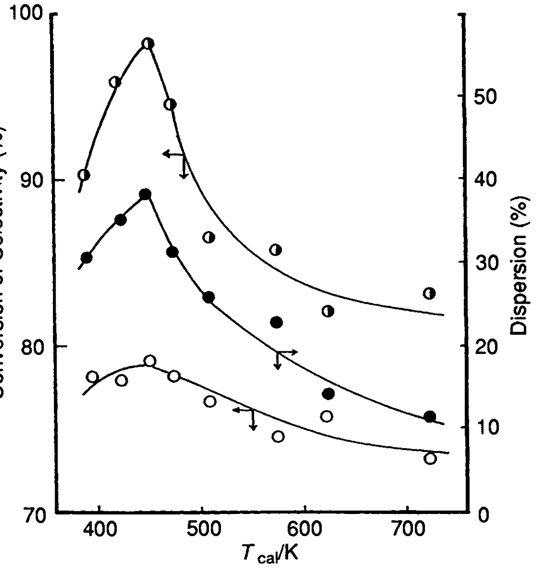


Figure 1. Influence of calcination temperature on the catalytic activity of Pd^0 (5.4wt%) supported on silica for dehydrosilylation of 1-trimethylsilyloxycyclopent-1-ene at 333 K under oxygen and dispersion of Pd^0 supported on silica: ○, conversion of 1-trimethylsilyloxycyclopent-1-ene; ◑, selectivity to cyclopent-2-enone. The catalyst was calcined under air at each temperature and was then reduced with hydrogen at 623 K for 1 h. 1-Trimethylsilyloxycyclopent-1-ene (1.12 mmol), catalyst (0.30 g), solvent, *N*-methyl-2-pyrrolidone (4.0 cm^3); reaction time, 24 h. ●, dispersion of Pd^0 supported on silica determined by hydrogen adsorption at 301 K.

Synthesis of Cyclohex-2-enone.—It was also possible to utilize Pd^0 supported on silica for the dehydrosilylation of (9) into cyclohex-2-enone (10). Table 3 shows the catalytic activities of Pd^0 (3.9wt%) supported on silica in various solvents at 333 K for 24 h. The catalyst was calcined at 453 K under air for 1 h,

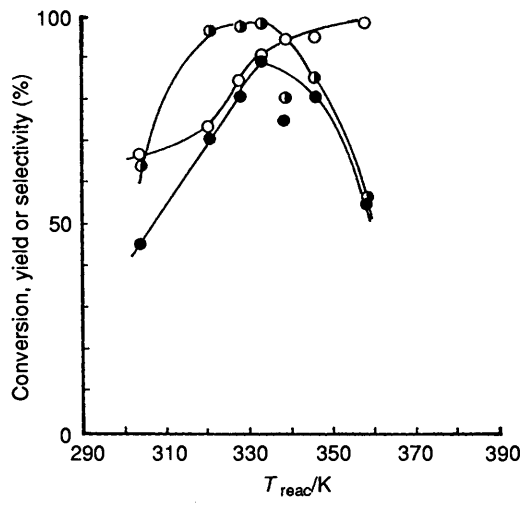


Figure 2. Influence of reaction temperature on the catalytic activity of Pd^0 (5.4wt%) supported on silica for the dehydrosilylation of 1-trimethylsilyloxycyclopent-1-ene under oxygen at 333 K: ○, conversion of 1-trimethylsilyloxycyclopent-1-ene; ●, yield of cyclopent-2-enone; ◑, selectivity to cyclopent-2-enone. The catalyst was calcined under air at 453 K and then reduced with hydrogen at 623 K for 1 h. Other reaction conditions, see Figure 1.

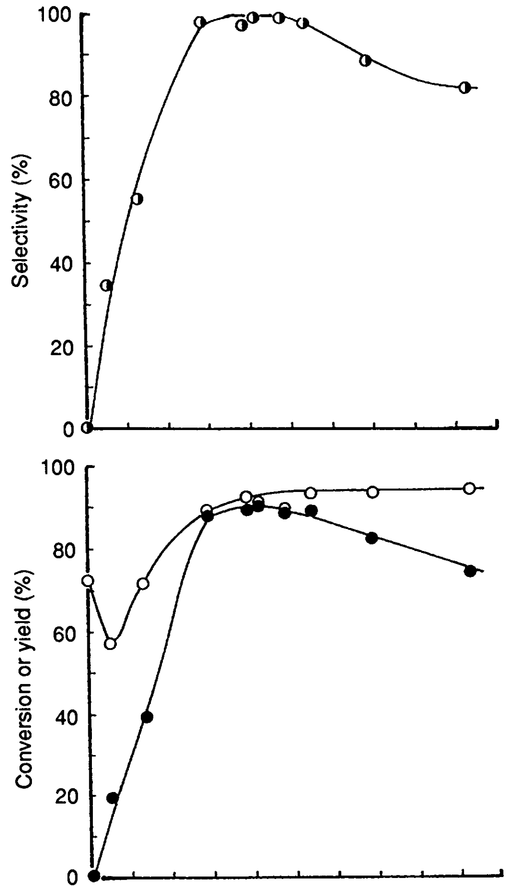


Figure 3. Dependence of the amount of Pd^0 supported on silica on: ○, the conversion of 1-trimethylsilyloxycyclopent-1-ene; ●, the yield of cyclopent-2-enone; ◑, the selectivity to cyclopent-2-enone in *N*-methyl-2-pyrrolidone at 333 K under oxygen. The catalyst was calcined under air at 453 K and then reduced with hydrogen for 1 h. Other reaction conditions, see Figure 1.

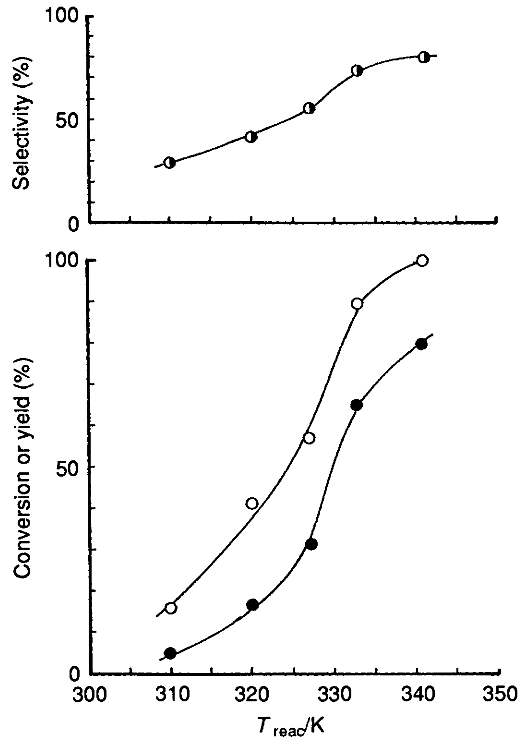


Figure 4. Influence of reaction temperature on the catalytic activity of Pd^0 (4.8wt%) supported on silica for dehydrosilylation of 1-trimethylsilyloxycyclohex-1-ene at 333 K under oxygen: ○, conversion of 1-trimethylsilyloxycyclohex-1-ene; ●, yield of cyclohex-2-enone; ◑, selectivity to cyclohex-2-enone. Catalyst, Pd^0 (4.8wt%)/SiO$_2$, 0.30 g; solvent, *N*,*N*-dimethylformamide, 4.0 cm^3; 1-trimethylsilyloxycyclohex-1-ene, 1.12 mmol. The catalyst was calcined under air at 453 K and then reduced with hydrogen for 1 h.

Table 3. Dehydrosilylation of 1-trimethylsilyloxycyclohex-1-ene over Pd^0 (3.1wt%) supported on silica in various solvents.

			Selectivity to	
Solvent	Conversion of (**9**) (%)	Yield of (**10**) (%)	(**10**) (%)	(**11**) (%)
N,*N*-Dimethylformamide	94.3	68.6	72.7	27.3
N,*N*-Dimethylacetoamide	94.5	69.2	72.3	27.7
N,*N*-Dimethylpropionamide	6.9	3.6	52.9	47.1
N-Methyl-2-pyrrolidone	99.3	50.1	50.5	49.5
Ethylene glycol dimethyl ether	14.4	8.8	61.2	38.8
Acetonitrile	18.0	6.0	33.5	66.5

Reaction conditions: Pd^0 (3.1wt%)/SiO$_2$ (0.300 g); reaction temperature, 333 K; reaction time 24 h; 1-trimethylsilyloxycyclohex-1-ene, 1.12 mmol; solvent (4.0 cm^3). The reaction atmosphere was oxygen (101 kPa). The catalyst was calcined under air at 453 K and then reduced with hydrogen at 623 K for 1 h.

and then reduced with hydrogen at 623 K for 1 h. Compound (**10**) was the main product in *N*,*N*-dimethylformamide, *N*,*N*-dimethylacetamide, and *N*-methyl-2-pyrrolidone. The yields of (**10**) were 68.6% and 69.2% in *N*,*N*-dimethylformamide and *N*,*N*-dimethylacetamide, respectively. Other reaction products were cyclohexanone, (**11**), (**7**), and (**8**).

The influence of the reaction temperature on the catalytic activity of Pd^0 (4.8wt%) supported on silica was examined at 623 K for 24 h. As shown in Figure 4, the conversion of (**9**) gradually increased as the reaction temperature rose, and reached 100% at 341 K. The yield of (**10**) and selectivity to (**10**) were greater at higher reaction temperatures, and were 80.1 and 80.3%, respectively at 341 K.

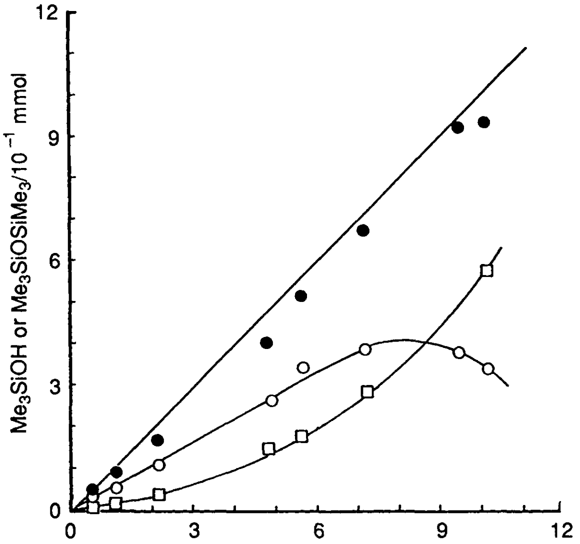


Figure 5. The amount of trimethylsilanol (○) and twice that of hexamethyldisiloxane (□) and the sum of them (●) are plotted against the amount of formation of cyclopent-2-enone. The straight solid line shows the theoretical line when the formation of cyclopent-2-enone, trimethylsilanol, and hexamethyldisiloxane is assumed to proceed as in Schemes 3 and 4. The dehydrosilylation of 1-trimethylsilyloxycyclopent-1-ene was carried out over Pd^0 (4.2wt%) supported on silica at 333 K for the various reaction times. Catalyst, Pd^0 (4.2wt%)/SiO$_2$ (0.30 g); solvent, *N*-methyl-2-pyrrolidone (4.0 cm^3), 1-trimethylsilyloxycyclopent-1-ene (1.12 mmol).

Reaction Process in the Heterogeneous System.—In order to verify that the reaction is heterogeneous, the following experiment was carried out. Pd^0 (4.2wt%) supported on silica (0.600 g) was stirred in *N*-methyl-2-pyrrolidone (8.0 cm^3) under oxygen for 24 h at 338 K. Then the mixture was carefully filtered to separate the catalyst from the solvent through two filter papers under nitrogen. The catalyst was washed with a large amount of diethyl ether, and then dried out under air at 373 K for 3 h. The reaction was then carried out under identical reaction conditions by using the catalyst (0.300 g) which had been separated and washed. 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 (4.2wt%)/SiO$_2$ with no treatment with the solvent (Table 2). This result shows that the reaction [the formation of (**5**)] is mainly heterogeneous, and that the role of dissolved palladium is insignificant in the formation of (**5**).

The reaction was also carried out by using 4.0 cm^3 of the filtrate and 1.12 mmol of (**4**) under oxygen at 333 K for 24 h. The amount of palladium in 4.0 cm^3 of the filtrate was determined as 5.4×10^{-4} mmol (*i.e.* 14.4 ppm) 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 also shows that the contribution of dissolved palladium to the catalysis may be regarded as insignificant.

Formation of Trimethylsilanol and Hexamethyldisiloxane.—When the dehydrosilylation of (**4**) was carried out over palladium supported on silica, (**7**) and (**8**) were formed. In Figure 5, the amount of (**7**), twice that of (**8**), and the sum of the two were plotted against the amount of (**5**), when the dehydrosilylation of (**4**) was carried out over Pd^0 (4.2wt%)/SiO$_2$ at 333 K. The dashed line in Figure 5, shows the theoretical line when the formation of (**5**), (**7**), and (**8**) is assumed to proceed as in Schemes 3 and 4.

$$\underset{(7)}{2Me_3SiOH} \longrightarrow \underset{(8)}{Me_3Si\text{-}O\text{-}SiMe_3} + H_2O$$

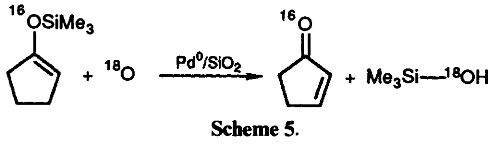
Scheme 4.

The amount of (**7**) increased nearly linearly and reached the maximum as the amount of (**5**) increased. On the other hand, the amount of (**8**) gradually increased and exceeded the level of (**7**), as shown in Figure 5. This result shows that (**8**) is formed successively by condensation of the two molecules of (**7**) as in Scheme 4. Figure 5 also shows that the sum of the amount of (**7**) and two times that of (**8**) is almost equal to the yield of (**5**), indicating that the formation of (**5**) proceeds as in Scheme 3. It should be noted that the selectivities to (**5**) were more than 98% under these reaction conditions.

Dehydrosilylation of 1-*Trimethylsiloxycyclopent*-1-*ene with* ^{18}O$_2$ *over* Pd^0/SiO$_2$.—(*a*) *Mass spectra of compounds containing* ^{18}O. In order to investigate the role of oxygen and the mechanism of the formation of (**5**) and (**6**), gas chromatography/mass spectrometry was used to analyse the compounds containing ^{18}O, when the dehydrosilylation of (**4**) with ^{18}O$_2$ was carried out over Pd^0 (4.2wt%)/SiO$_2$ in *N*-methyl-2-pyrrolidone at 333 K. Table 4(*a*–*d*) shows the mass spectral data of (**5**)–(**8**), respectively, when the conversions of (**4**) were 3 and 98%. The mass spectral data of the corresponding samples containing ^{16}O are also shown in Table 4(*a*–*d*) (column 1). The natural abundances of ^{28}Si, ^{29}Si, and ^{30}Si are 92.2, 4.7, and 3.1%, respectively.

The oxygen atom in *N*-methyl-2-pyrrolidone, which was used as a solvent in the dehydrosilylation of (**4**) with ^{18}O$_2$ over Pd^0 (4.2wt%)/SiO$_2$ at 333 K for 24 h, did not exchange with the oxygen atom of ^{18}O$_2$ at all. Moreover, the oxygen in SiO$_2$ could not be exchanged with ^{18}O$_2$, when ^{18}O$_2$ at 5.2 kPa was placed in contact with 0.5 g of Pd^0 (4.2wt%)/SiO$_2$ at 333 K for 24 h.

(*b*) *Formation of cyclopent-2-enone, trimethylsilanol, and hexamethyldisiloxane.* Both at the beginning of the reaction, where the conversion of (**4**) was 3% and at the end of reaction, where it was 98%, ^{18}O was hardly observed in (**5**) as shown in Table 4(*a*) (columns 2 and 3), respectively. When the conversion of (**4**) was 3%, ^{18}O was observed in (**7**) as shown in Table 4(*b*) (column 2). The relative intensities of the peaks for Me$_2$Si–^{16}OH ($m/z = 75$) and Me$_2$Si$^+$–^{18}OH ($m/z = 77$) are 100:28. These results, in which ^{18}O is not contained in (**5**), but contained in (**7**), show that the oxygen atom dissociated over palladium(0) takes part in the dehydrosilylation of (**4**) and that dehydrosilylation of (**4**) with ^{18}O$_2$ proceeds as in Scheme 5. This reaction mechanism may explain that non-reduced catalyst (silica exchanged with [Pd(NH$_3$)$_4$]$^{2+}$), as shown in Table 1, showed very little catalytic activity for the formation of (**5**), since molecular oxygen cannot be dissociated over palladium cation.



Scheme 5.

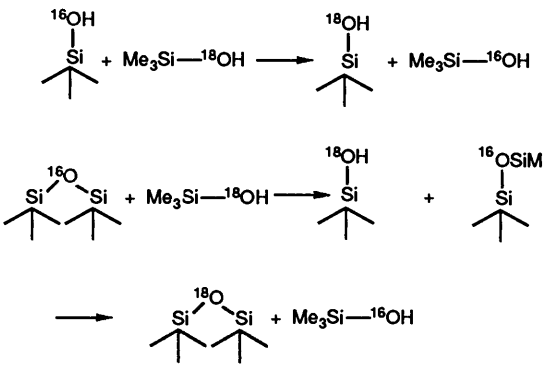
A part of the oxygen atoms dissociated over Pd^0 oxidizes a part of Pd^0 supported on silica into Pd^{2+}, which accelerates the adsorption of (**4**) onto the catalytic surface, since it is well known that palladium cations interact with alkenes in the formation of complexes such as π-allylic complex.[13] The adsorbed species are then converted into (**5**) by the reaction with the oxygen atoms dissociated over Pd^0 supported on silica.

Table 4. Mass spectrum data of compounds containing ^{18}O.

	m/z		Relative abundance			
			1[a]	2[b]	3[c]	4[a]
(*a*) Cyclopent-2-enone (**5**)	82		100	100	100	100
	83		6	7	7	6
	84		0	3	8	19
(*b*) Trimethylsilanol (**7**)	75	(Me_2Si^+OH)	100	100	100	100
	76		5	6	17	19
	77		3	28	69	31
	78		0	4	11	5
	79		0	3	8	3
(*c*) Hexamethyldisoloxane (**8**)	147	($Me_3SiOSi^+Me_2$)	100	100	100	100
	148		18	18	17	19
	149		4	16	69	31
	150		0	4	11	5
	151		0	1	8	3
(*d*) Cyclopentanone (**6**)	84		100	100	100	100
	85		4	5	5	5
	86		0	1	64	16

The dehydrosilylation of 1-trimethylsilyloxycyclopent-1-ene (**4**) was carried out in *N*-methyl-2-pyrrolidone at 333 K in the presence of $^{18}O_2$ at 101 kPa. Catalyst Pd^0 (4.2wt%)/SiO_2, 0.30 g; solvent, *N*-methyl-2-pyrrolidone (4.0 cm^2); 1-trimethylsilyloxycyclopent-1-ene, 1.12 mmol. (1): The corresponding samples containing ^{16}O. (2): The conversion of (**4**) was 3%. (3): The conversion of (**4**) was 98%. (4): The samples whose conversion of (**4**) was 98% were stored in the presence of Pd^0 (4.2wt%)/SiO_2 under nitrogen at room temperature for 30 days. [a] The corresponding samples containing ^{16}O. [b] The conversion of (**4**) was 3%. [c] The conversion of (**4**) was 98%. [d] The samples which showed 98% of (**4**) were stored in the presence of Pd^0 (4.2wt%)/SiO_2 under nitrogen at room temperature for 30 days.

As described above, the main product in Scheme 7 is the compound containing ^{16}O when the dehydrosilylation of (**4**) was carried out over Pd^0/SiO_2 in the presence of $^{18}O_2$. This result can be explained by an oxygen exchange of OH groups, or a bridged oxygen in SiO_2, on the silica surface with the oxygen of (**7**) as in Scheme 6. It has been reported that an oxygen exchange between $H_2{}^{18}O$ and Al_2O_3 occurs.[14] The reason why the relative intensity of the peak of $Me_3Si^+{-}^{16}OH$ is higher than that of $Me_3Si^+{-}^{18}OH$ at low conversion of (**4**) is that the rate of reaction in Scheme 6 is fast.



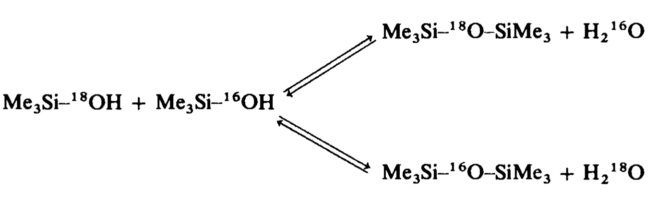
Scheme 6.

It has been reported that the formation of (**8**) proceeds as in Scheme 4. When the conversion of (**4**) was 3%, ^{16}O and ^{18}O were observed in (**8**) as shown in Table 4(*c*) (column 2). The relative intensities of the peaks for $Me_3Si{-}^{16}O{-}Si^+Me_2$ (m/z = 147) and $Me_3Si{-}^{18}O{-}Si^+Me_2$ (m/z = 149) are 100:16. This result explains that (**8**) containing ^{18}O or ^{16}O is formed by the condensation of $Me_3Si^{18}OH$ and $Me_3Si^{16}OH$ which is formed as shown in Scheme 4.

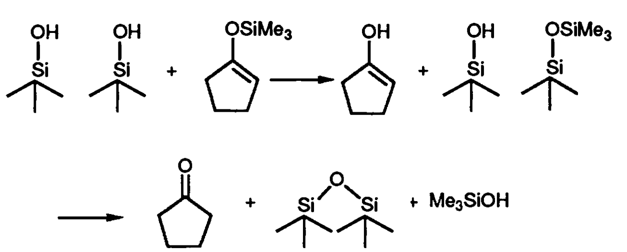
When the conversion of (**4**) was 98%, the relative abundance of (**7**) and (**8**) containing ^{18}O increased. That is to say, the relative intensities of peaks for m/z = 75 and m/z = 77 are 100:46 [Table 4(*b*) (column 3)] and those for m/z = 147 and m/z = 149 are 100:68 [Table 4(*c*) (column 3)]. This result might explain that the amount of ^{18}OH groups on the silica surface increased by the mechanism in Scheme 6 as the conversion of (**4**) increased.

(*c*) *Formation of cyclopentanone.* In the first reaction stage, ^{18}O was not observed in (**6**) as shown in Table 4(*d*) (column 3). As described above, only (**6**) formed when the dehydrosilylation of (**4**) was carried out over SiO_2 (Figure 3). When the dehydrosilylation of (**4**) was carried out under SiO_2 under nitrogen, only (**6**) was formed, and the yield was 73.3%. This yield of (**6**) remains the same as that under oxygen (Figure 3), indicating that while oxygen does not take part in the formation of (**6**), silica plays a major role in the formation of (**6**). Judging from these results, (**6**) is formed by the reaction of (**4**) and OH groups on the surface of silica as shown in Scheme 8. It is well known that silyl compounds easily react with OH groups on the silica surface.[15]

The formation of (**6**) proceeded mainly over Pd^0 supported on zeolites and activated carbon as shown in Table 1. The higher selectivity to (**6**) over Pd^0 supported on zeolites rather than over Pd^0/SiO_2 can be explained by Scheme 8 which



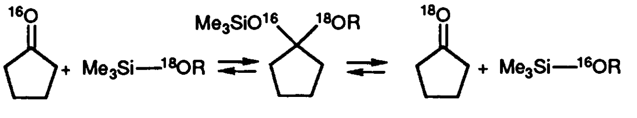
Scheme 7.



Scheme 8.

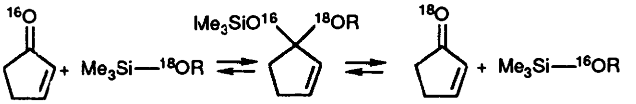
proceeds easily over the zeolite surface, since the acidity of the OH groups on zeolites is higher than on silica. It has been reported that activated carbon has acidic properties on its surface and shows activity as a solid acid catalyst for the dehydration of propan-2-ol.[16]

When the conversion of (4) increased to 98%, the relative abundance of (6) which contained ^{18}O increased, and the relative intensities of peaks for $m/z = 84$ and $m/z = 86$ are 100:63. This result may be explained by the reaction of (6) and $Me_3Si{-}^{18}OR$ in the presence of Pd^0/SiO_2 in Scheme 9, where R is H or $SiMe_3$.



Scheme 9.

(*d*) *After* 30 *days*. The samples which showed 98% conversion of (4) were stored in the presence of Pd^0/SiO_2 under nitrogen at room temperature for 30 days and the mass spectra of the samples were measured again. The relative intensities of the peaks for (7), (8), and (6) containing ^{18}O, dramatically decreased [Table 4(*b–d*) (column 4) respectively], while those for (5) containing ^{18}O, increased slightly [Table 4(*a*) (column 4)]. This result can be explained by the reaction shown in Scheme 10. The decrease in the relative intensities of the peaks for (7), (8), and (6) which contain ^{18}O can be explained by the reactions shown in Schemes 6 and 9.



Scheme 10.

Utility of Pd^0 *supported catalyst*. It should be noted that our method does not require the use of *p*-benzoquinone as a reoxidant to regenerate the active palladium species and make the reaction catalytic. Thus, the truly catalytic reaction reported here offers a more convenient and useful method.

The benefits of Pd^0 supported on silica may be summarized as follows. (*i*) Pd^0 supported on silica as a heterogeneous catalyst has a high catalytic activity and a high selectivity towards the formation of α,β-unsaturated ketones from silyl enol ethers in the presence of oxygen. (*ii*) Molecular oxygen can be used as a convenient oxidant. (*iii*) The catalyst can be easily separated from the product.

Acknowledgements

The authors are deeply grateful to Dr. Shyohhei Hashiguchi (Takeda Chemical Co. Ltd.) for his much-appreciated advice as well as for his continuous encouragement throughout the present work. The authors are deeply grateful to Professor Takashi Takahashi and Dr. Haruo Yamada (Tokyo Institute of Technology) for their helpful advice as well as the NMR measurements. The authors are deeply grateful to Dr. Kuniaki Goto and Dr. Toshiro Yamada (Nippon Zeon Co. Ltd.) for their useful advice as well as the GC–MS measurements.

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 P. A. Mender and J. C. Lechleiter, *J. Am. Chem. Soc.*, 1980, **102**, 6430.
6 R. E. Ireland, J. D. Godfrey, and S. Thaisrivongs, *J. Am. Chem. Soc.*, 1981, **103**, 2446.
7 Y. Ito, T. Hirao, and T. Saegusa, *J. Org. Chem.*, 1978, **43**, 1011.
8 R. F. Heck, 'Palladium Reagents in Organic Synthesis,' Academic Press, 1985, p. 107.
9 J. Tsuji, I. Minami, and I. Shimizu, *Tetrahedron Lett.*, 1983, **24**, 5635.
10 T. Baba, K. Kameta, S. Nishiyama, S. Tsuruya, and M. Masai, *J. Chem. Soc., Chem. Commun.*, 1989, 1072.
11 T. Baba, K. Kameta, S. Nishiyama, S. Tsuruya, and M. Masai, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 255.
12 J. R. Anderson, 'Structure of Metallic Catalyst,' Academic Press, New York, 1975, ch. 6.
13 R. F. Heck, 'Palladium Reagents in Organic Synthesis,' Academic Press, 1985, ch. 1.
14 V. Solbakken, A. Solbakken, and P. H. Emmett, *J. Catal.*, 1969, **15**, 90.
15 H. P. Boehm and H. Knözinger, 'Catalysis; Science and Technology,' eds. J. R. Anderson and M. Boudart, Springer-Verlag, Berlin, Heidelberg, New York, 1983, ch. 2.
16 I. Furuoya, T. Yanagihara, and T. Shirasaki, *Kogyo Kagaku Zasshi*, 1969, **72**, 1436.

Paper 0/00306I
Received 6th *November* 1989
Accepted 5th *February* 1990