Platinum-catalyzed Generation of Silylenes from Hydrodisilanes and Their Addition to α,β-Unsaturated Ketones

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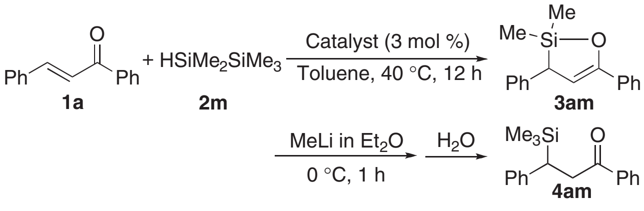
The reaction of hydrodisilanes with α,β-unsaturated ketones in the presence of a platinum catalyst gave high yields of oxasilacyclopentenes, which are probably formed by the addition of silylenes to the enones. Treatment of the oxasilacyclopentenes with methyllithium followed by hydrolysis gave the corresponding β-silyl ketones.

The reaction of silylenes (divalent silicon species, R_2Si:) with α,β-unsaturated carbonyl compounds is known to give [4 + 1] cycloaddition products.[1,2] Of several methods reported for generation of silylenes, we became most interested in transition-metal-catalyzed decomposition of hydrodisilanes leading to silylenes together with hydrosilanes,[3] because of their mild reaction conditions and the ready availability of the hydrodisilanes. Here, we wish to report that silylenes generated from hydrodisilanes under the catalysis by a platinum complex is incorporated into α,β-unsaturated ketones giving [4 + 1] cycloaddition products.[4]

In the first set of experiments, several transition-metal complexes were examined for their catalytic activity and selectivity for the reaction of 1,3-diphenyl-2-propenone (**1a**) with pentamethyldisilane (**2m**). Of the complexes examined (Table 1), $PtCl_2$(cod) (cod = 1,5-cyclooctadiene) was found to be most active for the addition of dimethylsilylene giving oxasilacyclopentene **3am**. Thus, enone **1a** was allowed to react with hydrodisilane **2m** (1.2 equiv. to **1a**) in the presence of 3 mol % of $PtCl_2$(cod) in toluene at 40 °C for 12 h. Treatment of the reaction mixture with methyllithium in ether followed by hydrolysis gave 62% yield of 1,3-diphenyl-3-trimethylsilylpropan-1-one (**4am**) (Entry 1). Formation of oxasilacyclopentene **3am** before treatment with methyllithium was confirmed by ^{1}H NMR of the reaction mixture. Two doublets with an identical coupling constant (δ 5.74 and 3.23, $J = 3.4$ Hz) and two singlets (δ 0.22 and −0.08) corresponding to the nonequivalent methyls on the silicon atom are consistent with the five-membered ring system of the silylene addition product. The yield of **4am** was much lower with a platinum complex coordinated with a phosphine ligand (Entry 2). Palladium complex, $PdCl_2$(cod), also catalyzed the present silylene reaction to some extent (Entry 3), but the reaction was not catalyzed by phosphine- or cod-complexes of nickel, gold, rhodium, and iridium under the same reaction conditions (Entries 5–8).

Table 1. Catalyst screening for silylene addition



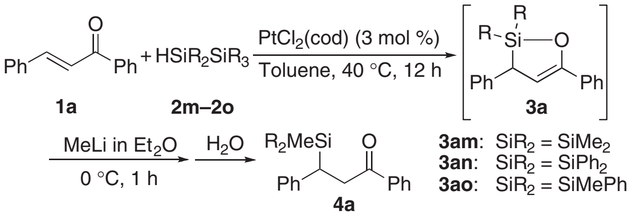
Entry	Catalyst	Yield[a]/%	Entry	Catalyst	Yield[a]/%
1	$PtCl_2$(cod)	62	5	$NiCl_2(PEt_3)_2$	0
2	$PtCl_2(PEt_3)_2$	12	6	$AuCl(PPh_3)$	0
3	$PdCl_2$(cod)	34	7	$[RhCl(cod)]_2$	<5
4	$PdCl_2(PPh_3)_2$	9	8	$[IrCl(cod)]_2$	<5

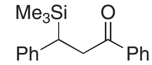
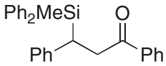
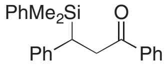
[a]The yields were determined by ^{1}H NMR of the crude products (using $MeNO_2$ as an internal standard).

Pentaphenyldisilane (**2n**) was found to be a better silylene source for the present platinum-catalyzed reaction with enone **1a**, giving a higher yield of the corresponding oxasilacyclopentene **3an**,[5] which is incorporated with diphenylsilylene. Treatment of the reaction mixture containing **3an** with methyllithium followed by hydrolysis gave β-diphenyl(methyl)silyl ketone **4an** in 89% yield (Table 2, Entry 2). The reaction of 1,2-diphenyl(trimethyl)disilane (**2o**), which is expected to generate methyl(phenyl)silylene by the platinum catalysis, gave, after methylation and hydrolysis, 46% of β-dimethyl(phenyl)silyl ketone **4ao** together with a minor amount (24%) of β-trimethylsilyl ketone **4am** (Entry 3). The formation of **4am** indicates that the alkyl scrambling took place on the platinum catalyst between dialkylsilylene and trialkylsilyl group.[6]

Table 3 summarizes the results obtained for the platinum-catalyzed reaction of pentaphenyldisilane (**2n**) with several types of α,β-unsaturated ketones. β-Phenyl ketones **1b**–**1d** are good substrates for the silylene addition giving high yields of the β-silyl ketones (Entries 2–4).[7] Cyclic enones **1e** and **1f** also underwent the silylene addition to give the corresponding β-silyl ketones where silyl and acetyl groups are cis (Entries 5 and 6).

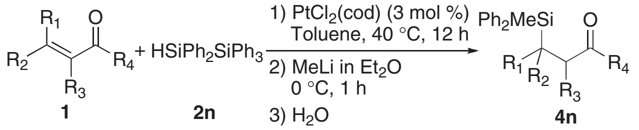
Table 2. Hydrodisilanes for platinum-catalyzed silylene addition

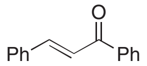
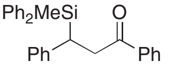
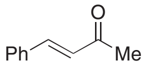
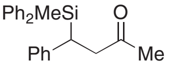
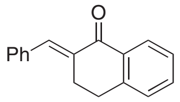
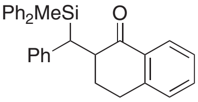
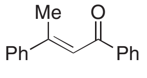
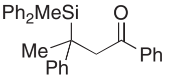
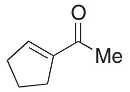
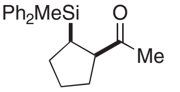
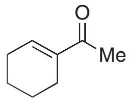
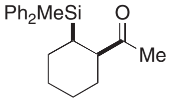
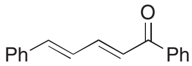
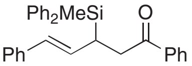
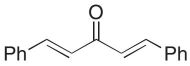
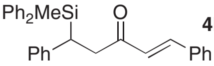


Entry	Hydrodisilane	Product	Yield[a] /%
1	$HSiMe_2SiMe_3$ **2m**	 **4am**	62
2	$HSiPh_2SiPh_3$ **2n**	 **4an**	89
3	$HSiMePhSiMe_2Ph$ **2o**	 **4ao**	46[b]

[a]Isolated yield. [b]Product **4am** (24%) was also obtained.

Table 3. Platinum-catalyzed addition of diphenylsilylene to α,β-unsaturated ketones



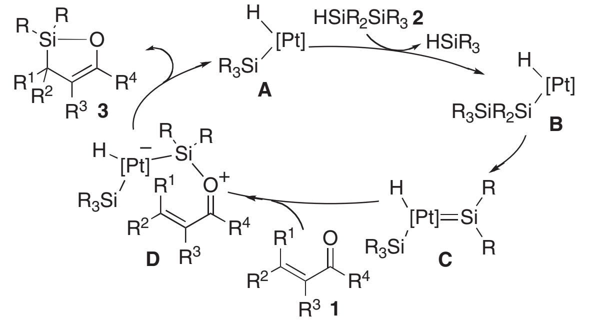
Entry	Enone		Product		Yield[a] /%
1		**1a**		**4an**	89
2		**1b**		**4bn**	73
3[b]		**1c**		**4cn**	71[c]
4		**1d**		**4dn**	67
5		**1e**		**4en**	55[d]
6		**1f**		**4fn**	55[d]
7		**1g**		**4gn**	65[e]
8		**1h**		**4hn**	56

[a]Isolated yield. [b]The reaction was carried at 100 °C. [c]Ratio of the diastereoisomers is 6:1. [d]Cis isomer with >99% selectivity. [e]MeMgBr in Et_2O/THF was used instead of MeLi in Et_2O.

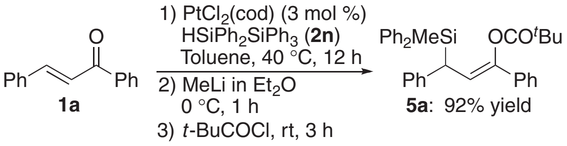
The cis-geometry is accounted for by protonation of the lithium enolates from the other side of silyl group. In the reaction of 2,4-dienone **1g**, the silylation took place on the β-carbon with perfect regioselectivity (Entry 7). The reaction of 1,4-dien-3-one **1h** resulted in the exclusive formation of mono-silylated ketone **4hn** (Entry 8) because the silylene addition intermediate, which is an alkenyl-substituted oxasilacyclopentene, does not undergo the second silylation.

A catalytic cycle proposed for the present silylation giving oxasilacyclopentene **3** is shown in Scheme 1. Generation of dialkylsilylenes from hydrodisilanes has been reported to take place on transition-metal complexes including platinum.[8] It is most probable that the reaction proceeds through nucleophilic attack of the carbonyl oxygen of enone **1** onto a dialkylsilylene **C** stabilized by coordination to platinum, which is generated from hydrodisilane **2** and a platinum complex **A** by way of **B**. Cyclization on zwitterionic species **D**[9] produces oxasilacyclopentene **3** leaving **A**.

Because the oxasilacyclopentenes **3** formed by the present silylation have a cyclic structure, the lithium enolates generated by treatment with methyllithium should have exclusive Z geometry.[10] The (Z)-lithium enolates can be trapped as (Z)-enol esters by O-acylation. Thus, successive treatment of the oxasilacyclopentenes **3** with methyllithium and then pivaloyl chloride gave enol pivalates **5** with perfect Z geometry from both linear and cyclic enones (eqs 1 and 2).



Scheme 1. A proposed catalytic cycle.

 (1)

 (2)

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References and Notes

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2 For examples of the reactions of conjugate enones or enoates with silylenes, see: a) M. Ishikawa, K. Nakagawa, M. Kumada, *J. Organomet. Chem.* **1977**, *135*, C45. b) J. Heinicke, B. Gehrhus, *J. Organomet. Chem.* **1992**, *423*, 13. c) J. Heinicke, S. Meinel, *J. Organomet. Chem.* **1998**, *561*, 121. d) S. A. Calad, K. A. Woerpel, *J. Am. Chem. Soc.* **2005**, *127*, 2046.
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4 We have reported another type of silylene reaction giving oxasilacyclohexenes; K. Okamoto, T. Hayashi, *Org. Lett.* **2007**, *9*, 5067.
5 A considerable amount (>90% yield) of triphenylsilane was also formed.
6 For example of the alkyl-scrambling on a iridium(III) complex, see: M. Okazaki, H. Tobita, H. Ogino, *Chem. Lett.* **1997**, 437.
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11 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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