

3-TMS-CYCLOPENTENE-1

A NEW REAGENT FOR THE SYNTHESIS OF CYCLOPENTENE DERIVATIVES

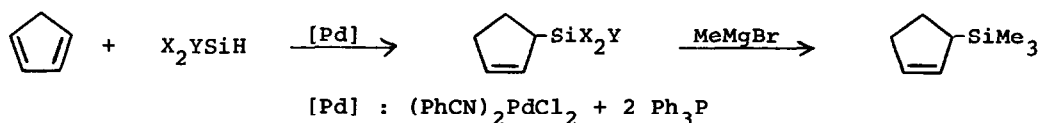
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Recently, allyltrimethylsilane has been shown to be a good reagent for allylation of acyl halides¹ or carbonyl compounds² in the presence of Lewis acid. Now we wish to report here a new and convenient route to cyclopentene derivatives using the reactions of 3-trimethylsilylcyclopentene-1, a cyclic allylsilane, with various carbonyl compounds. 3-TMS-cyclopentene-1 is a useful new reagent for the regiospecific introduction of cyclopentene skeleton in organic synthesis, which can easily be prepared by the hydrosilylation of cyclopentadiene.

We found that the hydrosilylation of cyclopentadiene was promoted effectively by the catalysis of a phosphine-palladium complex³, prepared in situ from bis(benzonitrile)palladium(II) dichloride and triphenylphosphine, to afford a 1,4-adduct exclusively: In a degassed sealed glass tube a mixture of cyclopentadiene, a chlorohydrosilane and the catalyst (0.1 mol%) was heated at 80-90°C for 6-24 hr with stirring. The reaction mixture was distilled under reduced pressure to give a 3-chlorosilylcyclopentene-1 in high yield. Then, the 3-chlorosilylcyclopentene-1 was further methylated by the action of methyl magnesium bromide to afford 3-TMS-cyclopentene-1 in moderate yield.



a: X = Cl, Y = Me; 90% b: X = Y = Cl; 83%

3-TMS-cyclopentene-1, thus obtained, displays a high reactivity towards carbonyl compounds such as aldehyde, ketone, α,β -unsaturated ketone, α -keto ester and acyl halide in the presence of Lewis acid. Results are summarized in Tables 1 and 2.

The reaction of 3-TMS-cyclopentene-1 with an aldehyde, ketone or α -keto ester proceeded readily to give a cyclopenten-2-yl alcohol or a 2-(cyclopenten-2-yl)-2-hydroxycarboxylate in moderate to high yield on using titanium tetrachloride as activating agent.

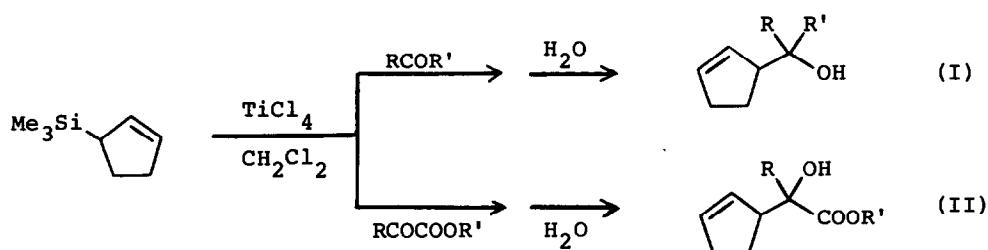


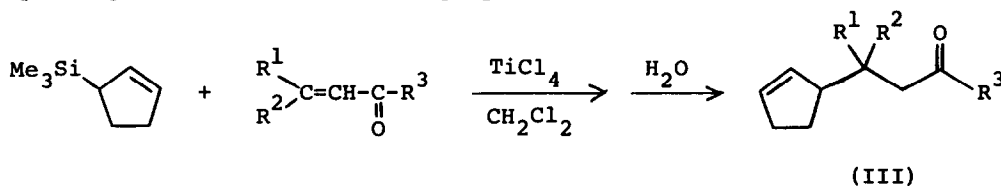
Table 1. The reactions of 3-TMS-cyclopentene-1 with aldehyde, ketone, α -keto ester and α,β -unsaturated ketone in the presence of titanium tetrachloride.

Carbonyl Compound	Conditions	Product	Yield(%) ^a	bp. (°C/mmHg)
$n\text{-C}_3\text{H}_7\text{CHO}$	-15° , 1 hr	I	78	98/18
$n\text{-C}_6\text{H}_{13}\text{COCH}_3$	-15° , 1 hr	I	40	90/0.2
$\text{CH}_3\text{COCOOEt}$	-15° , 2 hr	II	86	80/2.0
PhCOCOOEt	-15° , 2 hr	II	90	115/0.25
$(\text{CH}_3)_2\text{C}=\text{CHCOCH}_3$	-15° , 2 hr	III	78	120/35
$\text{PhCH}=\text{CHCOCH}_3$	-15° , 2 hr	III	77	109/0.2
$\text{PhCH}=\text{CHCOPh}$	-15° , 2 hr	III	84	144/0.3

^a Isolated yield after distillation.

The following procedure is typical. To a mixture of carbonyl compound (15 mmol) and 3-TMS-cyclopentene-1 (20 mmol) in dichloromethane (20 ml) was added dropwise 15 ml of 1M dichloromethane solution of titanium tetrachloride at -15°C with stirring. The reaction mixture was stirred at -15°C for 1-2 hr. The completion of the reaction was checked by GLC analysis. Then, the reaction mixture was poured into ice-water for hydrolysis, and the mixture was extracted with chloroform. After the extract was concentrated the residue was distilled under reduced pressure to give the corresponding cyclopenten-2-yl alcohol.

Similarly, 3-TMS-cyclopentene-1 was allowed to react with α,β -unsaturated ketones in the presence of titanium tetrachloride at -15°C to afford the corresponding Michael adducts in high yields.



The reaction of 3-TMS-cyclopentene-1 with acyl chloride was carried out in the presence of aluminum trichloride to give cyclopenten-2-yl ketone in good yield. Typically, an acyl chloride (15 mmol) was added to the suspension of aluminum trichloride (15 mmol) in dichloromethane (30 ml) at -15°C with stirring. The mixture turned into a homogeneous solution within half an hour. Then, 3-TMS-cyclopentene-1 (20 mmol) was added to the solution and the reaction mixture was stirred at -15°C for 2 hr. After hydrolysis by pouring the reaction mixture into ice-water, a usual work-up afforded the corresponding cyclopenten-2-yl ketone (IV). Titanium tetrachloride was also found to promote the reaction although aluminum trichloride seemed to be a better activating agent. Results are summarized in Table 2. Cyclopenten-2-yl ketone (IV), thus obtained, was easily isomerized to cyclopenten-1-yl ketone (V) during a column chromatography on silica gel.

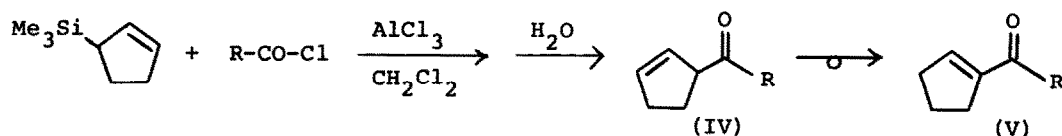


Table 2. The reaction of 3-TMS-cyclopentene-1 with acyl chlorides

Acyl Chloride	Lewis Acid	Conditions	Yield(%) ^a	bp. (°C/mmHg)
(CH ₃) ₂ CHCOCl	AlCl ₃	-15°, 2 hr	57	75/23
	TiCl ₄	-15°, 2 hr	27	
PhCOCl	AlCl ₃	-15°, 2 hr	72	86/0.2
	AlCl ₃	-15°, 2 hr	68 ^{b,c}	94/0.4
	TiCl ₄	-15°, 2 hr	57 ^b	
(CH ₃) ₂ C=CHCOCl	AlCl ₃	-15°, 2 hr	62	44 ^d
	TiCl ₄	-15°, 2 hr	60 ^b	98/18

^a Isolated yield of V after chromatography on silica gel unless otherwise noted. ^b Yield of IV containing small amount (<10%) of V. ^c Isolated yield after distillation of the reaction mixture. ^d Melting point(°C)

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