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Hydridotetrakis(triphenylphosphine)rhodium(I) as an Effective Catalyst for the Regiospecific Hydrosilation of α,β-Unsaturated Carbonyl Compounds

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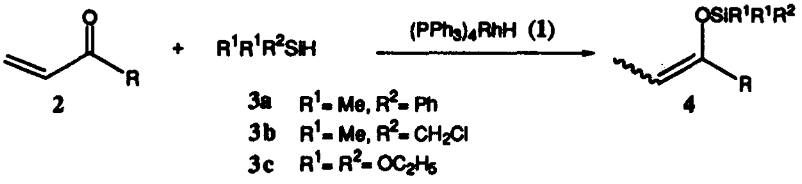
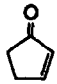
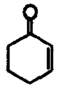
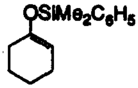
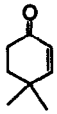
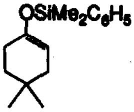
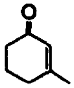
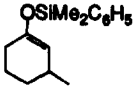
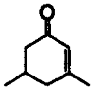
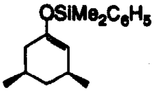
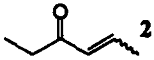
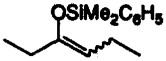
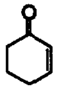
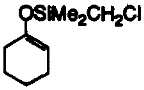
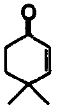
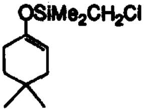
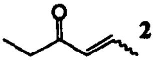
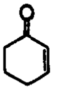
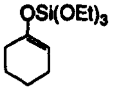
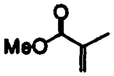
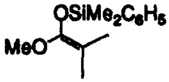
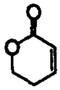
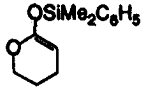
Summary: Hydridotetrakis(triphenylphosphine)rhodium(I) acts as an effective catalyst for the reactions of α,β-unsaturated carbonyl compounds with silanes to give regioselectively the enol silyl ethers in a 1,4-hydrosilation.

Enol silyl ethers have assumed increasing importance as useful synthons in organic synthesis.[1,2,3] Regiospecific synthesis of enol silyl ethers can be achieved from α,β-unsaturated carbonyl compounds by metal reduction followed by silylation.[4] Alternatively, hydrosilation of α,β-unsaturated carbonyl compounds provides a reliable route to enol silyl ethers. In this connection, a number of catalysts, including tris(triphenylphosphine)rhodium(I) chloride,[5] rhodium(III) chloride,[6] and chloroplatinic acid,[7] have been developed for that purpose. In choosing the proper catalyst, in addition to the mildness of the reaction conditions, high regioselectivity between 1,2- and 1,4-hydrosilation is clearly required.[8] We wish to report that hydridotetrakis(triphenylphosphine)rhodium(I) (1) has been found to be extremely effective as a catalyst for the regiospecific 1,4-reduction of α,β-unsaturated carbonyl compounds. Previously, 1 was reported as catalyst for transfer hydrogenation[9], isomerization[10] and hydrosilation of alkenes[11], but not for carbonyl compounds.



The hydrosilation of 2-cyclopenten-1-one (2a) by dimethyl-phenylsilane (3a) can serve as a typical example. In a 5 ml round-bottomed flask equipped with a magnetic stirring bar and sealed with a rubber septum, the catalyst 1 (3 mg, 0.3% M/M) was placed under argon. 2-Cyclopenten-1-one (2a, 82 mg, 1.0 mmol) and then

Table 1: Hydrosilation of α,β-unsaturated carbonyl compounds:

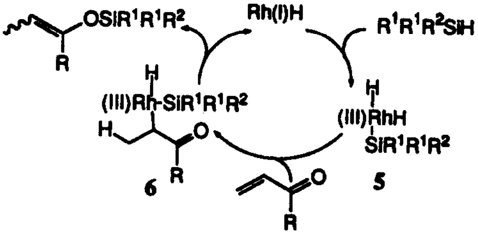
Entry	Reactant		Rh(I), Conditions	Silane[a]	Product		Yield[b]
1		**2a**	0.3% M/M, r.t. 12h	**3a**		**4a**	83%
2		**2b**	0.3% M/M, r.t.12h	**3a**		**4b**	84%
3		**2c**	0.4% M/M, r.t. 12h	**3a**		**4c**	96%
4		**2d**	0.5% M/M, 50°C, 24h	**3a**		**4d**	89%
5		**2e**	0.5% M/M, 50°C, 24h	**3a**		**4e**	87% *cis:trans*=92:8
6		**2f**	0.2% M/M, r.t. 6h	**3a**		**4f**	73% *E/Z*=33:67
7		**2g**	0.2% M/M, r.t. 6h	**3a**		**4g**	82% *E/Z*=77:23
8		**2b**	0.1% M/M, r.t. 0.5h	**3b**		**4h**	83%
9		**2c**	0.3% M/M, r.t. 4h	**3b**		**4i**	80%
10		**2f**	0.2% M/M, r.t. 1.5h	**3b**		**4j**	85% *E/Z*=2:1
11		**2g**	0.3% M/M, r.t. 10h	**3b**		**4k**	83% *E/Z*=1:4
12		**2b**	0.3% M/M, r.t. 12h	**3c**		**4l**	93%
13		**2f**	0.3% M/M, r.t. 20h	**3c**		**4m**	75% *E/Z*=44:56
14		**2h**	0.3% M/M, r.t. 1.5h	**3a**		**4n**	91%
15		**2i**	0.3% M/M, r.t. 12h	**3a**		**4o**	85%

a) **3a**: dimethyphenylsilane; **3b**: (chloromethyl)dimethylsilane; **3c**: triethoxysilane.
b) Purified yields (Kugelrohr distillation apparatus).

dimethylphenylsilane (**3a**, 150 mg, 1.1 mmol) were introduced to the flask via syringe. The mixture was stirred at room temperature for 12 h. Hexane (1 ml) was added and the mixture was filtered. The filtrate was concentrated and distilled (Kugelrohr) to give the product **4a** (182 mg, 83%), b. p. 95°/5 mm Hg. Other examples of hydrosilation of α,β-unsaturated ketones are summarised in Table 1. Higher reaction temperature (50°) was required when the β-position was di-substituted (entries 4 and 5). In cases where geometrical isomers for the enol silyl ethers were possible, both isomers were formed. Interestingly, in the case of 3,5-dimethylcyclohex-2-en-1-one (**2e**), hydrosilation with **3a** gave one major enol silyl ether, **4e**, with the two methyl groups assigned the cis-stereochemistry (cis:trans=92:8).[12] Care should be taken in handling the catalyst **1** due to its sensitivities to air and moisture. Exposure of the catalyst to air or moisture would retard the reaction. While larger amount of the catalyst accelerated the reaction, unwanted side products also increased. The catalyst appeared to favour specifically the conjugated addition. ^{1}H nmr of the crude reaction mixture, after reaction completion, showed no signal due to vinyl protons of the starting materials or that of 1,2-addition products. This was further confirmed in the case of hydrosilation of cyclohexenone (**2b**) by hydrolysis of the reaction products. The hydrolyzed mixture was then analyzed by capillary gas chromatography. No detectable amount of 2-cyclohexen-1-ol was found in the hydrolyzed products.

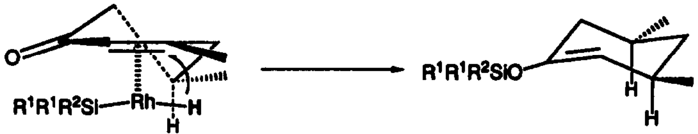
Other functionalised silanes, such as triethoxysilane (**3b**) and dimethylchloromethylsilane (**3c**), could be used in the hydrosilation of α,β-unsaturated carbonyl compounds with **1** as the catalyst (entries 8 to 13, Table 1). Furthermore, α,β-unsaturated esters can also be hydrosilated under similar reaction conditions to give the ketene silyl acetals (entries 14 and 15). It is interesting to note that in these two cases, no C-silyl esters were observed. The reaction was clearly 1,4-conjugated addition and not hydrosilation of the olefinic double bond.

A tentative mechanism which accounts for the catalytic activity of **1** is presented in scheme 1. Insertion of the Rh(I) catalyst into silane[10] gives the intermediate **5**. Hydrometallation of the carbonyl substrate by **3** gives the intermediate **6**. Reductive elimination of **6** gives the enol silyl ether, and regenerates the Rh(I) species. The stereoselectivity observed in the reaction of **2e** can then be explained by the transition state **7** in which the hydrometallation step delivers the hydrogen to a chair conformer of **2e** giving the cis-product.



Scheme 1

In comparison with the familiar Wilkinson catalyst[5], 1 offers the following advantages. The regioselection for 1,4-hydrosilation is somewhat better with 1. The ratio of 1,4-/1,2-hydrosilation using the Wilkinson catalyst varies between 100/0 to 64/36 depending on the substrate.[5] Compound 1 is also a more active catalyst. For example, the substrate 2e did not undergo 1,2- nor 1,4-hydrosilation by using Wilkinson's catalyst with various silanes.[13] Finally, 1,4-hydrosilation of α,β-unsaturated esters has not been reported with the Wilkinson catalyst.[5]



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