NOTES *Bull. Chem. Soc. Jpn.*, **54**, 1279—1280 (1981)

Reduction of Ketones and Aldehydes *via* Catalytic Hydrosilylation Using Triethoxysilane and Trimethoxysilane

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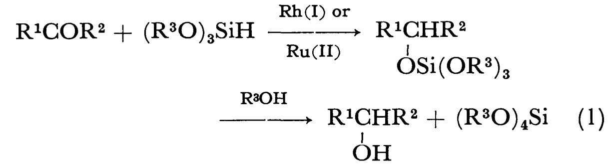
(Received October 30, 1980)

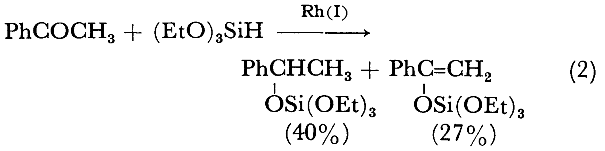
Synopsis. It was found that ketones and aldehydes can be effectively reduced *via* catalytic hydrosilylation using triethoxysilane and trimethoxysilane in the presence of $RhCl(PPh_3)_3$ or $RuCl_2(PPh_3)_3$, followed by ethanolysis or methanolysis.

Reduction of carbonyl compounds *via* hydrosilylation catalyzed by group VIII metal complexes has been extensively investigated.[1,2] In most of the previous work alkyl- and arylsilanes were employed (*e.g.*, Et_3SiH, Et_2SiH_2, $PhMe_2SiH$, and Ph_2SiH_2, *etc.*), and only few examples of the corresponding hydrosilylation by alkoxysilanes have been reported to date.[3] Recently, it has been reported that trialkoxysilanes such as $(EtO)_3SiH$ and $(MeO)_3SiH$ can be readily prepared in large quantities by the direct reaction of silicon with the corresponding alcohols.[4] With such situation in view, we felt it pertinent to explore the reduction of carbonyl compounds by these trialkoxysilanes in some detail. We report herein our finding that various ketones and aldehydes can be smoothly hydrosilylated by $(EtO)_3SiH$ and $(MeO)_3SiH$ in the presence of $[RhCl(PPh_3)_3]$ or $[RuCl_2(PPh_3)_3]$ as catalyst and that alcoholysis of the resultant adducts with the respective alcohol gave desired reduction products in good yields.



$$R^1COR^2 + (R^3O)_3SiH \xrightarrow[\text{Ru(II)}]{\text{Rh(I) or}} \underset{\displaystyle OSi(OR^3)_3}{R^1CHR^2} \xrightarrow{R^3OH} \underset{\displaystyle OH}{R^1CHR^2} + (R^3O)_4Si \quad (1)$$

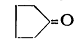
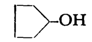
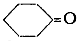
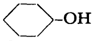
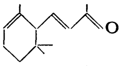
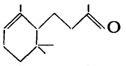
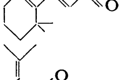
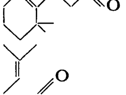
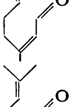
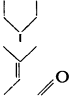
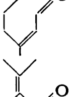
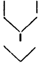
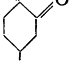
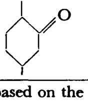
Results for the reduction of ketones and aldehydes studied in the present work are summarized in Table 1. The addition of $(EtO)_3SiH$ and $(MeO)_3SiH$ to diethyl ketone, cyclopentanone, cyclohexanone, acetophenone, and benzaldehyde was conducted using the ruthenium complex $[RuCl_2(PPh_3)_3]$ as a catalyst. The reaction in the presence of 0.5 mol% of the catalyst at temperatures of 60—120 °C reached completion after 3—10 h to give the corresponding adducts in high yields. It has been reported that the ruthenium(II) complex catalyzes the reaction of Et_3SiH and $Ph(1-C_{10}H_7)SiH_2$ with ketones (*e.g.*, acetophenone) and aldehydes (*e.g.*, benzaldehyde), but that it is not as effective a catalyst as $[RhCl(PPh_3)_3]$.[5] We found that this particular ruthenium complex is much more selective than the rhodium(I) complex in the present addition reactions. For instance, the ruthenium(II)-catalyzed reaction of $(EtO)_3SiH$ with acetophenone produced the adduct in 85% yield whereas the rhodium(I)-catalysis was accompanied by the concurrent formation of a considerable amount of the silyl enol ether.



$$PhCOCH_3 + (EtO)_3SiH \xrightarrow{\text{Rh(I)}} \underset{\displaystyle (40\%)}{\underset{\displaystyle OSi(OEt)_3}{PhCHCH_3}} + \underset{\displaystyle (27\%)}{\underset{\displaystyle OSi(OEt)_3}{PhC{=}CH_2}} \quad (2)$$

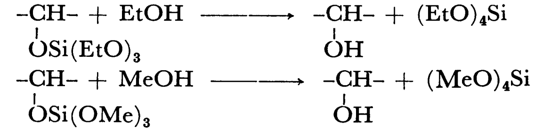
The desilylation of the resulting silyl enol ethers was also studied. The method commonly employed for the desilylation involves acid- or base-catalyzed hydrolysis.[2] However, this method would be inconvenient in the present case, because such procedure would result in the formation of a complex mixture of siloxanes. This

Table 1. Reduction of ketones and aldehydes *via* the hydrosilylation by triethoxysilane (A) or trimethoxysilane (B) in the presence of $[RhCl(PPh_3)_3]$ or $[RuCl_2\ (PPh_3)_3]$[a)]

Carbonyl compound	Silane	Conditions[b]	Product	Yield/%
$CH_3CH_2COCH_2CH_3$	A	Ru, 100 °C, 3 h	$CH_3CH_2CH(OH)CH_2CH_3$	88
	A	Ru, 60 °C, 5 h		89
	A	Ru, 100 °C, 10 h		86
$C_6H_5COCH_3$	A	Ru, 120 °C, 10 h	$C_6H_5CH(OH)CH_3$	84
CH_5CHO	A	Ru, 120 °C, 6 h	CH_5CH_2OH	89
	A	Rh, 50 °C, 2 h		84
	B	Rh, 60 °C, 4 h		84(79)
	A	Rh, 70 °C, 3 h		93
	B	Rh, 70 °C, 5 h		88(75)
	B	Rh, 80 °C, 4 h		90

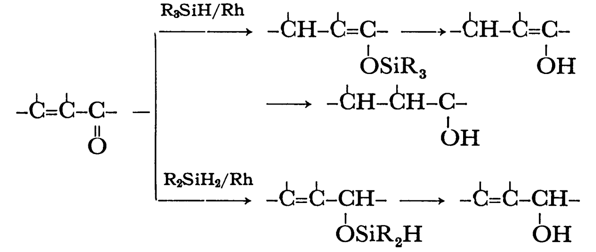
a) [Substrate]/[hydrosilane]/[catalyst] = 1/1.2/0.005. b) For hydrosilylation. c) Determined by GLC (based on the carbonyl compound charged); in parentheses are given isolated yields.

complication arises as a consequence of the high susceptibility of the ethoxyl and methoxyl groups on silicon to hydrolysis.[6] In fact, Kagan and coworkers obtained 1-Phenylethanol in at most 60% chemical yield (*via* GLC) from the reduction of acetophenone with $(EtO)_3SiH$ in the presence of a supported chiral rhodium complex after the treatment of the resulting silyl ether with an aqueous HCl–acetone solution.[3a] We found that the clean desilylation of the adducts of $(EtO)_3SiH$ or $(MeO)_3SiH$ can be achieved by ethanolysis or methanolysis in the presence of a catalytic amount of HCl or NaOH. The counter product, $(EtO)_4Si$ or $(MeO)_4Si$ can be readily removed by simple distillation in many cases. Thus, the corresponding alcohols were obtained in excellent yields *via* the hydrosilylation with the trialkoxysilanes.



$$\underset{\mathrm{OSi(EtO)_3}}{\text{-CH-}} + \mathrm{EtOH} \longrightarrow \underset{\mathrm{OH}}{\text{-CH-}} + (\mathrm{EtO})_4\mathrm{Si}$$
$$\underset{\mathrm{OSi(OMe)_3}}{\text{-CH-}} + \mathrm{MeOH} \longrightarrow \underset{\mathrm{OH}}{\text{-CH-}} + (\mathrm{MeO})_4\mathrm{Si} \qquad (3)$$

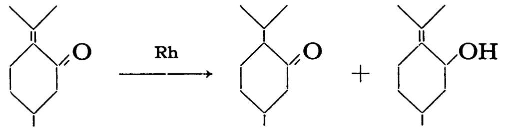
An attempt was also made to reduce α,β-unsaturated terpene carbonyl compounds with the trialkoxysilanes. The regioselective reduction of α,β-unsaturated terpene ketones and aldehydes *via* hydrosilylation catalyzed by $[RhCl(PPh_3)_3]$ was reported by Ojima and coworkers who found that the reduction with monohydrosilanes (*e.g.*, Et_3SiH) gave only or mainly saturated ketones *via* 1,4-addition while dihydrosilanes (*e.g.*, Et_2SiH_2) afforded allylic alcohols *via* 1,2-addition.[7] More recently, it has been also reported by Lappert and Nile that the hydrosilylation of *trans*-crotonaldehyde with $(EtO)_3SiH$ in the presence of $[RhCl(PPh_3)_3]$ proceeds through 1,4-addition while the same reaction in the presence of $[Ni(COD)_2]$ takes place *via* 1,2-addition.[3b]



(4)

We found that the rhodium(I)catalyzed hydrosilylation of several conjugated terpene enones with $(EtO)_3SiH$ or $(MeO)_3SiH$ also proceeded smoothly in a manner of 1,4-addition as in the case of the rhodium-catalyzed reduction of crotonaldehyde. Thus, the reduction of α-ionone, β-ionone, citral, and pulegone gave exclusively α-dihydroionone, β-dihydroionone, citronellal, and menthone in over 80% yields, respectively.

Incidentally, the reduction of α,β-unsaturated terpene ketones with trialkoxysilanes seems to show somewhat higher regioselectivity compared to that with triorganohydrosilanes; it was reported that the reduction of pulegone with Et_3SiH or $PhMe_2SiH$ gave a mixture of menthone and the allylic alcohol in a ratio of 50 : 50 or 75 : 25, respectively.[7]



(5)

$PhMe_2SiH$	75	25
$(MeO)_3SiH$	100	0

Experimental

$(EtO)_3SiH$ and $(MeO)_3SiH$ were supplied by Mitsubishi Kasei Industry Co., Ltd. Ketones and aldehydes were commercially available and used without further purification. Ethanol and methanol were purified by standard methods.[8] The complexes $[RhCl(PPh_3)_3]$[9] and $[RuCl_2(PPh_3)_3]$[10] were prepared according to literature directions.

The following reduction products were identified by comparison of their physical properties (GLC retention times, and IR and NMR spectra) with those of commercial authentic samples or literature;[11] 3-pentanol, cyclopentanol, cyclohexanol, 1-phenylethanol, benzyl alcohol, α-dihydroionone, β-dihydroionone,[11] citronellal, and menthone.

General Procedure for the Reduction of Ketones and Aldehydes. All runs were conducted in essentially the same manner; therefore, only the reduction of β-ionone by $(MeO)_3SiH$ is described in detail.

A mixture of 9.7 g (50 mmol) of β-ionone, 7.4 g (60 mmol) of $(MeO)_3SiH$, and 0.23 g (0.25 mmol) of $[RhCl(PPh_3)_3]$ was heated at 60 °C for 4 h under nitrogen with stirring. The reaction mixture was then poured into methanol (30 ml) containing a small amount of sodium hydroxide, and the resulting mixture was stirred at room temperature for 12 h. GLC analysis of the mixture disclosed the formation of β-dihydroionone in 84% yield. Evaporation of the alcohol and subsequent distillation gave 7.3 g (79% yield) of the product boiling at 93 °C/5 mmHg[12] (lit,[11] bp. 105 °C/10 mmHg).

We thank Mitsubishi Kasei Industry Co., Ltd., for gifts of trialkoxysilane.

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12) 1 mmHg = 13.595 1 × 980.665 × 10^{-2} Pa.