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HYDROSILANE-RHODIUM(I) COMPLEX COMBINATIONS AS SILYLATING AGENTS OF ALCOHOLS

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The dehydrogenative condensation of organosilicon hydrides with alcoholic substances catalyzed by rhodium(I) complex was found to furnish a convenient route for the preparation of silylated alcohols.

It has long been known that the group VIII metals and metal halides catalyze the dehydrogenative condensation(1) of silicon hydride with amines, alcohols and carboxylic acids. Although numerous studies on the scope of these processes and the mechanistic considerations have been made,(2) such a catalyst system has been used only within the limit of monohydrosilanes. This is mainly due to the disproportionation of polyhydrosilanes which is also catalyzed by these substances.(3) In fact, little has been learned(4) on the homogeneous catalysis in which mechanisms can be precisely studied and the scope of the reaction is widened. Moreover, the synthetic scope of dehydrogenative condensation has been restricted to the simple substrates and the reaction has not been extended to the protection of active hydrogen functions in terpenes, carbohydrates, amino acids and related compounds as silyl derivatives which gathers currently much interest.(5) The restriction encountered in the metal or metal halide catalysis may be due to an isomerization of other functions, e.g., olefin isomerization.(6) The limitation can be overcome since we found that the homogeneous rhodium(I) catalyst, $(Ph_3P)_3RhCl$, is exceedingly effective for these reactions(7) without any disproportionation of polyhydrosilanes and isomerization of other functions in substrates.

We show in the present communication that hydrosilane-rhodium(I) complex combinations provide powerful silylating agents of hydroxyl groups. We believe that the present agents should furnish a convenient route to the silyl-protected alcohols of terpenes, carbohydrates and related compounds, and for the preparation of silylated alcohols possessing a hydrogen atom on silicon which were rather difficult to be prepared by usual methods.[8)]

The protection of hydroxyl groups in terpenes, carbohydrates and related compounds was successfully accomplished by these agents under neutral conditions. Thus, DES-menthol (bp 147°C/0.3 mmHg), DES-borneol (bp 70°C/0.2 mmHg), DES-cholesterol (mp 139-140°C), TES-citronellol (bp 103°C/0.7 mmHg), DES-geraniol,[9)] TES-furfuryl alcohol (bp 122°C/38 mmHg), TES-diethylene glycol monomethyl ether (bp 118°C/14 mmHg), bis-TES-ethylene glycol (bp 139°C/13 mmHg) and bis-TES-mandelic acid (bp 153°C/4 mmHg) were obtained by the reactions of diethylsilane or triethylsilane with hydroxyl substances in the presence of 0.01-0.1 Mol% of $(Ph_3P)_3RhCl$ in n-hexane or benzene in almost quantitative yields without any isomerization and transfer hydrogenation by the generated hydrogen.[10)] (DES: diethylsilyl; TES: triethylsilyl)

A typical procedure is described for the silylation of cholesterol; a mixture of 1.94 g (5.0 mmol) of cholesterol and 0.50 g (5.7 mmol) of diethylsilane was dissolved in 50 ml of n-hexane and 5 mg (0.1 Mol%, 0.005 mmol) of $(Ph_3P)_3RhCl$ was added with stirring at room temperature, then a vigorous evolution of hydrogen was observed. The reaction was completed within 15 min. to give DES-cholesterol quantitatively after the catalyst was filtered off and the solvent was evaporated.

Dehydrogenative condensation of various hydrosilanes, especially polyhydrosilanes, and simple alcohols were also performed in order to see characteristics of these agents, and to test the general applicability to the preparation of alkoxysilanes which are well known precursor or monomer of siloxane polymers. Results are summarized in the Table. The rate of the reaction was substantially dependent on the nature of the alcohol and the hydrosilane, and the reactivity sequence of alcohols was found to fall in the order MeOH(100) $>$ EtOH(64) $>$ ^{i}PrOH(11) $>$ ^{t}BuOH(0.8) as indicated by a series of competitive experiments.[11)] Phenol reacts distinctly slower than do aliphatic primary alcohols, requiring heating for a rather prolonged period of time. Dihydrosilanes are much more reactive than monohydrosilanes, giving monoalkoxysilanes or dialkoxysilanes in accordance with the amount of alcohol. Slight warming was necessary for introducing of a second alkoxyl group on silicon. Trihydrosilanes are even more reactive than dihydrosilanes and reactions of methylsilane with isopropyl alcohol were found to proceed at temperature as low as -56°C, which afforded methyldiisopropoxysilane or methyltriisopropoxysilane in accordance with the amount of alcohol and the work up temperature.

The versatility of this synthetic agent will be further widened and the mechanistic considerations of these reactions are now under investigation.

Table Dehydrogenative Condensation of Hydrosilanes and Alcohols Catalyzed by $(Ph_3P)_3RhCl$

$$\equiv\text{Si-H} \quad + \quad \text{HOR} \quad \xrightarrow{(Ph_3P)_3RhCl} \quad \equiv\text{Si-OR} \quad + \quad H_2$$

Hydrosilane	Alcohol	Ratio of Reactants	Cat. (Mol%)	Conditions	Product[a]	bp(°C/mmHg)
Et_3SiH	EtOH	1:1	0.5	70°C, 30 min.	Et_3SiOEt	67/40
Et_3SiH	^iPrOH	1:1	0.5	95°C, 60 min.	Et_3SiOPr^i	69/34
$PhMe_2SiH$	MeOH	1:1	0.1	reflux, 15 min.	$PhMe_2SiOMe$	51/5
$PhMe_2SiH$	PhOH	1:1	0.1	60°C, 600 min.	$PhMe_2SiOPh$	108/2
$^nPr_3SiH$	MeOH	1:1	0.1	reflux, 15 min.	$^nPr_3SiOMe$	60/6
Ph_3SiH	EtOH	1:1	0.5	60°C, 30 min.	Ph_3SiOEt	125/0.1
Et_2SiH_2	EtOH	1:1	0.01	0°C, 10 min.	$Et_2HSiOEt$	112/760
Et_2SiH_2	MeOH	1:2	0.01	0°C, 10 min.	$Et_2Si(OMe)_2$	110/760
Ph_2SiH_2	MeOH	1:1	0.01	0°C, 5 min.	$Ph_2HSiOMe$	92.5/0.3
Ph_2SiH_2	MeOH	1:2	0.1	0°C, 5 min. then 70°C	$Ph_2Si(OMe)_2$	103/0.3
Ph_2SiH_2	PhOH	1:1	0.05	40°C, 60 min.	$Ph_2HSiOPh$	152/0.3
$PhSiH_3$	MeOH	1:2	0.01	0°C, 10 min.	$PhHSi(OMe)_2$	83/28
$PhSiH_3$	^iPrOH	1:2	0.01	0°C, 10 min.	$PhHSi(OPr^i)_2$	120/35
$PhSiH_3$	PhOH	1:2	0.01	r.t., 10 min.	$PhHSi(OPh)_2$	146/0.6

[a] Structures of silyl ethers were confirmed by comparison of their physical properties with those reported, or else by their elemental analyses and spectral characteristics.

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9) The product obtained after removal of the catalyst and the solvent was pure enough spectroscopically and gas chromatographically, but an isomerization occurred on distillation.

10) The nmr and ir spectra and elemental analyses of all new compounds were consistent with the assigned structures.

11) Two alcohols in equimolar amounts (10 equiv.) were allowed to compete for a reaction with triethylsilane (1 equiv.) at 50°C for 3-5 hr., and reactivity was determined on the basis of the relative amounts of produced alkoxysilanes by the use of glpc analyses.

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