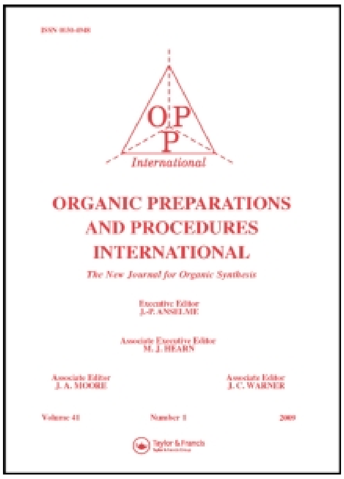

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A CONVENIENT ROUTE TO AMINOSILANES USING HYDROSILANE-RHODIUM(I) COMPLEX COMBINATIONS

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A CONVENIENT ROUTE TO AMINOSILANES USING HYDROSILANE-RHODIUM(I) COMPLEX COMBINATIONS

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Aminosilanes have long been used to convert a large variety of organic and biologically important substances into organosilyl derivatives with profoundly changed properties.[1] The most common method of preparing aminosilanes involves the reaction of chlorosilanes with amines[2] and of silicon hydrides with alkali metal salts of amines.[2,3] Besides these two methods, the dehydrogenative condensation between a hydrosilane and an amine under the catalytic action of various metals, metal salts or transition metal complexes,[4] is paricularly promising for the preparation of aminosilanes. Indeed, these reactions in many cases take place under nearly neutral conditions. Previous papers[5] from our laboratories had dealt with dehydrogenative condensations of organosilicon hydrides

$$Et_2SiH_2 + Et_2NH \xrightarrow{(Ph_3P)_3RhCl} Et_2SiHNEt_2 + H_2$$

with active hydrogen compounds such as alcohols and mercaptans in the presence of tris(triphenylphosphine)chlororhodium. As an extention of our previous work, we have studied reactions of hydrosilanes with a variety of amines in the presence of the rhodium(I) complex.

Reactions were carried out under nitrogen atmosphere, after degassing at liquid nitrogen temperature. A mixture of a hydrosilane and an amine is stirred in the presence of a catalytic amount of $(Ph_3P)_3RhCl$ at room or slightly higher

TABLE I.

Dehydrogenative Condensation of Hydrosilanes and Amines[a]

Hydrosilane	Amine	Time	Temp	Product	Yield[b]
$PhSiH_3$	Et_2NH	6 hrs.	70°	$PhSiH_2NEt_2$	98[c]
Ph_2SiH_2	Et_2NH	2 hrs.	r.t.	$Ph_2SiHNEt_2$	95
Ph_2SiH_2	$(n\text{-}Bu)_2NH$	2 hrs.	60°	$Ph_2SiHN(Bu\text{-}n)_2$	70
Ph_2SiH_2	$(CH_2)_4NH$	20 min.	r.t.	$Ph_2SiHN(CH_2)_4$	98
Ph_2SiH_2	$PhNH_2$	1.5 hrs.	60°	$Ph_2SiHNHPh$	68
Et_2SiH_2	Et_2NH	2 hrs.	r.t.	$Et_2SiHNEt_2$	98[d]
Et_2SiH_2	$(n\text{-}Bu)_2NH$	4 hrs.	45°	$Et_2SiHN(Bu\text{-}n)_2$	98[e]
Et_2SiH_2	$PhNH_2$	40 min.	r.t.	$Et_2SiHNHPh$	98[e]
Et_2SiH_2	PhMeNH	4 hrs.	50°	$Et_2SiHNMePh$	98[e]
Et_3SiH	Et_2NH	16 hrs.	70°	Et_3SiNEt_2	90[e]

a) Catalyst: $(Ph_3P)_3RhCl$; 1 mole of catalyst was used unless otherwise specified. b) Glpc yields; yields of isolated products generally amounted to 90-95 % of glpc yields. c) 0.5 mole % of catalyst. d) 0.1 mole % of catalyst. e) 0.2 mole % of catalyst.

temperature (below 70°). Aminosilanes of general formula R_3-$SiNR'_2$, $R_2SiHNR'_2$ and $RSiH_2NR'_2$ were readily prepared and the results are summarized in Table I. It should be noted that a few aminosilanes containing silicon-hydrogen bonds have been previously prepared only by the chlorosilane method.[6] However, this latter method is necessarily associated with drawbacks stemming from the separation problems of the amine hydrochlorides and the corrosive nature of chlorosilanes.

EXPERIMENTAL

Condensation of Hydrosilane with an Amine.- The general procedure used is illustrated by the reaction of diethylsilane with diethylamine. A mixture of diethylsilane (2.64 g, 30 mmoles) and diethylamine (2.19 g, 30 mmoles) was introduced into a 25 ml flask equipped with a reflux condenser which was connected to a vacuum line. The flask was immersed into a liquid nitrogen bath and the mixture degassed under vacuum (twice). It was then warmed up to room temperature under an atmosphere of nitrogen. A charge of 30 mg of tris(triphenylphosphine)chlororhodium[7] was quickly added in one portion. The mixture was stirred with a magnetic stirring bar at room temperature for 2 hrs during which time gentle evolution of hydrogen (quantitative) was observed. Glpc analysis of the resulting mixture showed the formation of diethylaminodiethylsilane (98% yield). The mixture was filtered under an atmosphere of nitrogen. The filtrate was distilled through a 7 cm column under vacuum to provide 4.50 g (94%) of the aminosilane, bp 58-58.5°/20 mm. The physical properties of aminosilanes obtained are summarized in Table II.

TABLE II.

Physical Properties of Aminosilanes

Aminosilane	bp/mm (°C)	Si-H IR(cm^{-1})	Si-H nmr(δ)	Elemental Analysis % Calcd. (Found) C	Elemental Analysis % Calcd. (Found) H
$PhSiH_2NEt_2$	50/0.2	2150	4.84(s)	66.97(67.24)	9.56(9.26)
$Ph_2SiHNEt_2$	120-3/0.75	2100	5.23(s)	75.23(74.93)	8.29(8.11)
$Ph_2SiHN(Bu\text{-}n)_2$	150-7/0.5	2120	5.30(s)	77.11(76.86)	9.38(9.17)
$Ph_2SiHN(CH_2)_4$	141-2/3.5	2120	5.28(s)	75.83(75.66)	7.56(7.38)
$Ph_2SiHNHPh$	176-7/0.26	2120	5.59(d)	78.49(78.34)	6.22(5.96)
$Et_2SiHNEt_2$	58-58.5/20	2100	4.10(q)	60.30(59.99)	13.29(12.93)
$Et_2SiHN(Bu\text{-}n)_2$	132/65	2100	4.16(q)	66.89(67.15)	13.57(13.49)
$Et_2SiHNPh$	123/32	2100	4.50(m)	66.97(66.97)	9.56(9.31)
$Et_2SiHNMePh$	96/5	2110	4.53(m)	68.33(68.45)	9.90(9.64)
Et_3SiNEt_2	44/3*	--	--	64.09(64.34)	13.45(13.17)

* Lit.[8] 199.5-201°C

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