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Preliminary Communication

Dehydrogenative coupling reactions between hydrosilanes and monosubstituted alkynes catalyzed by solid bases

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Abstract

Dehydrogenative coupling reactions between phenylsilane and monosubstituted alkyne afford mono-, di- and trialkynylphenylsilane in the presence of magnesium or calcium oxide.

Key words: Hydrosilane; Dehydrogenation; Alkyne; Solid base catalyst; Magnesium oxide

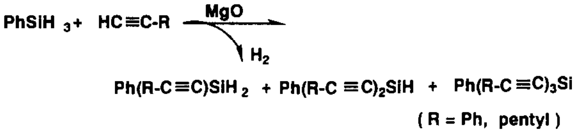
Some transition metal complexes have been described as effective catalysts for the dehydrogenative coupling reaction of monosubstituted alkenes with hydrosilanes to produce alkenylsilanes [1].

There have been few reports on the dehydrogenative coupling of monosubstituted alkynes with hydrosilanes to produce alkynylsilanes. Only H_2PtCl_6/LiI, I_2 [2]; $IrH_2(SiEt_3)(COD)(AsPh_3)$, iridium catalysts formed by adding triarylarsins or triarylphosphines to $[Ir(OMe)(diolefin)]_2$ [3]; $[IrH(H_2O)(bp)L_2]SbF_6$, $RhClL_3$ ($L = PPh_3$, bp = 7,8-benzoquinolinato) [4] have been used as catalysts. They catalyzed not only the dehydrogenative coupling reaction but also the hydrosilylation reaction, to produce corresponding alkenylsilanes. Liu and co-workers have recently found that dehydrogenative coupling reactions between phenylsilane and ethynylbenzene occurred selectively in the presence of CuCl/amine [5].

In this paper we report a new catalyst for selective dehydrogenative coupling reactions between hydrosilanes and monosubstituted alkynes.

Hydrosilane, alkyne, n-pentane as a solvent and a catalyst were transferred into a glass flask, and the reaction was carried out under a nitrogen atmosphere. Phenylsilane, diphenylsilane and phenylmethylsilane were used as hydrosilanes. 1-Hexyne and ethynylbenzene were used as alkynes. A catalyst of magnesium oxide or calcium oxide was obtained by calcining magnesium hydroxide or calcium hydroxide in a vacuum or in air at 500°C for 2 h. Silica-alumina (Al_2O_3 12wt%, commercial SiO_2-Al_2O_3 from Mizusawa Industrial Chemicals Ltd.) was treated at 500°C for 2 h before use. The size of the particles of all catalysts was 20–60 mesh. After the reaction the solid catalyst was separated from the reaction mixture by filtration. The products and unreacted monomers were analyzed by gas chromatography. The products were identified by GC-MS spectrometry, and IR, ^{1}H-NMR, ^{13}C-NMR and ^{29}Si-NMR spectroscopy.

Phenylsilane reacted with alkynes to produce monoalkynylphenylsilane, dialkynylphenylsilane and trialkynylphenylsilane with the evolution of hydrogen gas in the presence of magnesium oxide [eqn. (1)]. There were no products such as alkenylphenylsilanes, which would have resulted from hydrosilylation reactions.



$$PhSiH_3 + HC{\equiv}C\text{-}R \xrightarrow[-H_2]{MgO} Ph(R\text{-}C{\equiv}C)SiH_2 + Ph(R\text{-}C{\equiv}C)_2SiH + Ph(R\text{-}C{\equiv}C)_3Si \quad (1)$$

(R = Ph, pentyl)

The results of the reactions are shown in Table 1. High initial catalytic activity was observed, but the activity decreased rapidly. There was little change in the reaction components after 30 min. The order of conversion of silanes was

$$Ph_2SiH_2 > PhMeSiH_2 > PhSiH_3$$

Phenylsilane, which has less steric hindrance and which could be expected to be more reactive than any other silanes, showed the lowest conversion and yield. In this case a side reaction might take place and the poisoning of the active site on the magnesium oxide surface might have occurred.

Calcium oxide, which is as solid a base as magnesium oxide, showed catalytic activity, but silica-alumina, a typical solid acid, showed no activity. A reaction mechanism which brought together the Si–H bond, the

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TABLE 1. Reactions of hydrosilanes with monosubstituted alkynes [a]

Silane (mmol)	Acetylene (mmol)	Catalyst [b] (g)	Temperature (°C)	Time (h)	Conversion (%)	Product yield (%) [c]		
						Mono-	Di-	Tri-
$PhSiH_3$ (9.7)	1-hexyne (9.6)	MgO (0.5)	r.t. [d]	4	34	26	5	0
Ph_2SiH_2 (12.0)	1-hexyne (11.2)	MgO (0.5)	r.t.	4	62	52	0	–
$PhMeSiH_2$ (11.2)	1-hexyne (11.2)	MgO (0.5)	r.t.	4	49	29	1	–
$PhSiH_3$ (5.3)	1-hexyne (13.7)	MgO (1.0)	r.t.	4	97	29	50	0
$PhSiH_3$ (5.2)	EB [e] (12.3)	MgO (1.0)	80	4	88	43	24	10
$PhSiH_3$ (4.9)	EB (12.3)	MgO [f] (1.0)	80	4	31	27	5	0
$PhSiH_3$ (9.7)	1-hexyne (9.9)	CaO (0.5)	50	3	10	9	1	0
$PhSiH_3$ (9.5)	1-hexyne (9.6)	SiO_2–Al_2O_3 (0.5)	r.t.	4	0	0	0	0

[a] 10 ml of n-pentane was used as solvent.
[b] Specific surface area: MgO 323 m^2/g, CaO 34 m^2/g, SiO_2–Al_2O_3 350 m^2/g.
[c] Based on silane. Mono- = monoethynyl silane, Di- = diethynyl silane, Tri- = triethynyl silane.
[d] Room temperature.
[e] EB = ethynylbenzene.
[f] Magnesium hydroxide was calcined in air at 500°C for 2 h (158 m^2/g).

$HC{\equiv}C$ bond and the basic site on the catalytic surface has been proposed. The lower activity of magnesium oxide, which calcined in air rather than in a vacuum, might depend on the lower basicity and the lower specific surface area. More studies of kinetics and the chemical interaction between hydrosilanes and solid catalyst surface will make the reaction mechanism clear.

This report offers a new catalytic process for a dehydrogenative coupling reaction between the Si–H bond and the $HC{\equiv}C$ bond. The advantages of the reaction are its high selectivity for the dehydrogenative coupling reaction, and the easy separation of the solid catalyst.

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