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Catalytic Si–C bond formation by nucleophilic substitution at silicon by benzyl anions generated over KNH_2 loaded on alumina

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The catalytic substitution at silicon occurs in the reaction of toluene and diethylsilane in the presence of KNH_2 loaded on alumina, the yield of benzyldiethylsilane being 85% in 40 h at 329 K. Benzene also reacted with diethylsilane in the presence of the catalyst to afford a 7.5% yield of benzyl diethylsilane in 20 h at 329 K.

Keywords: solid base, KNH_2 loaded on alumina, Si–C bond formation, toluene, diethylsilane

1. Introduction

The nucleophilic substitution by a carbanion at silicon is a most conventional method for Si–C bond formation [1–5]. The substitution proceeds through penta- or hexacoordinated silicon intermediates. Various methods for activating Si–X (X: leaving group) are also discussed. The most common sources of carbanions are alkyllithium or Grignard reagents, but the reactions are not catalytic.

Carbanions can be generated on solid surfaces. Ito et al. reported that dehydrogenative coupling occurs between phenylsilanes and monosubstituted acetylenes RC≡CH over MgO or CaO [6], which is known as a strongly basic solid. Thus, the reaction of diphenylsilane and 1-hexyne ($C_4H_9C{\equiv}CH$) proceeds in the presence of MgO to give a 52% yield of 1-diphenylsilyl-1-hexyne. The reaction mechanism seems to involve $C_4H_9C{\equiv}C^-$ anions as intermediates, which are formed by the abstraction of H^+ by the basic sites of the catalyst.

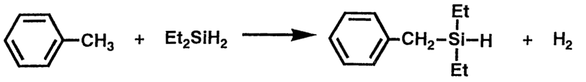
We have reported that KNH_2, which was loaded on Al_2O_3 from the ammoniacal solution followed by heating under vacuum at 573 K, is a super-base [7]. The material is denoted as KNH_2/Al_2O_3 hereinafter. KNH_2/Al_2O_3 shows very high catalytic activities for the isomerization of various alkenes [7] and olefinic amines [8], which proceeds through carbanion intermediates. For example, 2,3-dimethylbut-1-ene is readily isomerized to 2,3-dimethylbut-2-ene, even at 210 K. Moreover, the reaction of phenylacetylene over KNH_2/Al_2O_3 results in its dimerization to afford (Z)- and (E)-1,4-diphenyl-1-ene-3-yne, the ratio of (Z) and (E) being 94 : 3 [9].

We have also reported IR spectra of KNH_2/Al_2O_3 and the effect of the amount of KNH_2 supported on Al_2O_3 on the catalytic activity for the isomerization of 2,3-dimethylbut-1-ene to 2,3-dimethylbut-2-ene [7]. Thus, the OH groups on the surface of Al_2O_3 react with KNH_2 as follows:

$$\rangle\text{Al–OH} + \text{KNH}_2 \rightarrow \rangle\text{Al–OK} + \text{NH}_3$$

The $\rangle$Al–OK does not show catalytic activity, while KNH_2 loaded on alumina acts as a catalyst.

Because of the very strong basicity of KNH_2/Al_2O_3, the catalyst is expected to activate toluene, of which the pK_a value is 35 [10]. Here, we report that the dehydrogenative coupling of toluene and diethylsilane is catalyzed by KNH_2/Al_2O_3.



(1)

2. Experimental

γ-alumina used as a support has a surface area of 135 $m^2\ g^{-1}$. MNH_2/Al_2O_3 (M: Na, K, Rb) was prepared from an ammoniacal solution of the alkali metal by an impregnation method. The preparation of the catalyst and the catalytic reaction were carried out in the same quartz tube, which could be attached to a high-vacuum system. Alumina was heated in a quartz tube at 673 K for 3 h. A piece of K (Na or Rb) metal was then placed in the quartz tube under nitrogen with a small amount of Fe_2O_3. After evacuation of the system at room temperature, ammonia was liquefied in the quartz tube at dry ice–ethanol temperature to dissolve the metal. A blue color due to the solvated electrons developed. The color gradually faded and disappeared, indicating the transformation of the metal to the corresponding amide. Added Fe_2O_3 serves as a catalyst for the transformation. The solution was kept in contact with alumina for 1 h, and then heated under vacuum for 3 h at prescribed tem-

Table 1
Catalytic activities of various solid bases [a]

Catalyst	Amount of metal (mmol / 1.00 g of Al_2O_3)	Yield of benzyldiethylsilane (%)
KNH_2/Al_2O_3	2.6	74
		85 [b]
		64 [c]
$RbNH_2/Al_2O_3$	2.6	73
$NaNH_2/Al_2O_3$	2.6	0
KF/Al_2O_3	5.0	2
MgO		0
CaO		0

[a] Catalyst weight: 0.20 g, reaction temperature: 329 K, reaction time: 20 h, Et_2SiH_2: 1.5 mmol, toluene: 28 mmol.
[b] Reaction time: 40 h.
[c] Reaction temperature: 303 K.

peratures, which are 523, 573, and 623 K for $NaNH_2/Al_2O_3$, KNH_2/Al_2O_3, and $RbNH_2/Al_2O_3$, respectively, since the catalysts evacuated at these temperatures showed the highest catalytic activities for the isomerization of 2,3-dimethylbut-1-ene.

CaO and MgO were prepared by heating $CaCO_3$ at 998 K and $Mg(OH)_2$ at 773 K, respectively, under vacuum. KF supported on alumina (KF/Al_2O_3) was prepared by heating alumina loaded with KF under vacuum at 673 K. The loading of KF was done with an impregnation method from its aqueous solution.

The mixture of the purified reactants was put into a glass tube, which was then attached to the side arm of the reactor, and degassed with a freeze–thaw method. The reaction was started by transferring the reactants into the reactor.

The products were identified by ^1H NMR (270 MHz) and GC-mass spectroscopy. The amount of the products were determined by a gas chromatograph equipped with an OV 101 glass column, using propylbenzene as an internal standard. The yields of products were calculated based on the starting silanes.

3. Results and discussion

When Et_2SiH_2 (1.5 mmol, 0.20 cm^3) was stirred with 0.2 g of KNH_2/Al_2O_3 in excess toluene (28 mmol, 2.0 cm^3) at 329 K for 20 h, benzyldiethylsilane [1] was obtained in a 74% yield (table 1). The molar ratio of the formed benzyldiethylsilane to the amount of KNH_2 supported on Al_2O_3 was 2.1, indicating the reaction is catalytic. The yield increased by increasing the reaction time to 40 h. The yield was lower at lower temperature, being 64% at 303 K in 20 h. Other reactions such as disproportionation of Et_2SiH_2 were not observed. $RbNH_2/Al_2O_3$ was as active as KNH_2/Al_2O_3 for the dehydrogenative coupling. For this reaction, KF/Al_2O_3 showed a very low activity, while $NaNH_2/Al_2O_3$, CaO and MgO were totally inactive.

Table 2
Reactivities of alkylbenzenes with Et_2SiH_2 over KNH_2/Al_2O_3 [a]

Reactant	pK_a	Amount of reactant (mmol)	Yield (%)
toluene	35 [b]	28	74
ethylbenzene		25	23
propylbenzene		21	7.0
isopropylbenzene	37 [c]	29	2.0

[a] Catalyst weight: 0.20 g, reaction temperature: 329 K, reaction time: 20 h, Et_2SiH_2: 1.5 mmol. Amount of K metal 2.6 mmol per 1.00 g of Al_2O_3.
[b] Ref. [10].

Reaction of Et_2SiH_2 with other alkylbenzenes such as ethylbenzene also proceeded in the presence of KNH_2/Al_2O_3 to selectively afford the corresponding benzylsilanes, as shown in table 2. Ethylbenzene gave a 23% yield of diethyl-1-phenylethylsilane [2]. Propylbenzene and isopropylbenzene reacted with Et_2SiH_2 to give diethyl(1-phenylpropyl)silane [3] and diethyl(1-phenyl-1-methylethyl)silane [4] in 7 and 2% yield, respectively. As shown in table 2, alkylbenzene with more acidic protons showed higher reactivity towards Et_2SiH_2, indicating that the abstraction of a proton from alkylbenzene by basic sites on the solid base is the rate-determining step. The reactions proceed through carbanion intermediates, which cause nucleophilic substitution at silicon.

Toluene (28 mmol) also reacted with Et_3SiH (3.2 mmol) in the presence of KNH_2/Al_2O_3 (0.2 g) to afford a 32% yield of benzyltriethylsilane [5] in 20 h at 363 K. The reaction of toluene (28 mmol) with phenylsilane (4.2 mmol) gave only 1% yield in 20 h at 373 K. In this case, the disproportionation of phenylsilane was accompanied.

Benzene has a pK_a value of 37 comparable to propylbenzenes [10] and therefore is expected to undergo the similar reaction. When Et_2SiH_2 (3.1 mmol, 0.4 cm^3) was stirred with 1.0 g of KNH_2/Al_2O_3 in benzene (68 mmol,

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[1] Benzyldiethylsilane: ^1H NMR ($CDCl_3$) 0.60 (4H, dq, $J = 3.3, 7.9$, $-SiCH_2$), 0.96 (6H, t, $J = 7.6$, CH_3), 2.18 (2H, d, $J = 3.3$, $-SiC\underline{H}_2C_6H_5$), 3.76 (1H, tquint, $J = 3.3, 3.3$, $-SiH$), 7.00–7.22 (5H, m, $-C_6H_5$). MS(m/e) 178(41), 149(49), 121(98), 87(100), 59(92).

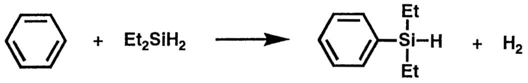
[2] Diethyl-1-phenylethylsilane: ^1H NMR ($CDCl_3$) 0.49 (2H, dq, $J = 3.0, 7.6$, $-SiCH_2$), 0.58 (2H, dq, $J = 3.0, 7.6$, $-SiCH_2$), 0.88 (3H, t, $J = 7.9$, $-CH_3$), 0.96 (3H, t, $J = 7.9$, CH_3), 2.35 (1H, dq, $J = 3.3$, 7.4, $-SiCH$), 3.64 (1H, d quint, $J = 3.0, 3.0$, $-SiH$), 7.09–7.28 (5H, m, C_6H_5). MS(m/e) 164(22), 153(56), 107(100), 86(18).

[3] Diethyl(1-phenylpropyl)silane: MS(m/e) 206(17), 177(9), 149(9), 135(6), 118(100), 105(13), 87(61), 59(67).

[4] Diethyl (1-phenyl-1-methylethyl)silane: MS(m/e) 206(21), 118(100), 87(50), 59(50).

[5] Benzyltriethylsilane: MS(m/e) 206(22), 177(7), 149(21), 115(100), 87(99), 59(33).

6 cm^3), diethylphenylsilane[6] was obtained in a 7.5% yield in 20 h at 329 K.



(2)

In conclusion, strongly basic catalysts such as KNH_2/Al_2O_3 offer a novel route to form Si–C bonds directly from alkylbenzenes and silanes.

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[6] Diethylphenylsilane: ^1H NMR ($CDCl_3$) 0.86 (4H, dq, $J = 3.3, 7.9$, $-SiCH_2$), 1.00 (6H, t, $J = 7.9$, $-CH_3$), 4.20 (1H, quint, $J = 3.3$, –SiH), 7.34–7.37 and 7.51–7.55 (5H, m, C_6H_5). MS(m/e) 164(22), 153(56), 107(100), 86(18).