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SYNTHESIS AND REACTION OF A SILICA-SUPPORTED CATALYST WITH AMMONIUM GROUPS. IMMOBILIZED AMMONIUM GROUPS ON SILICA

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ABSTRACT

The immobilization of lipophilic quaternary ammonium salts onto the large areas of the surface of silica has been accomplished. The modified silica served as a catalyst for the nucleophilic replacement of benzylic halides by cyanide.

INTRODUCTION

When metal complexes are immobilized on polymer supports, the nature of the polymer matrix affects the catalytic activity exhibited by the complex. When polyvinylpyridine was used as a catalytic support in organic solvents, it swelled and the active centers were rendered less effective by subsequent chain entanglements [1] and neighboring group effects.

Because of the reduction in activity of the metal center owing to the above reasons, silica was chosen as an alternate support. Selective oxidation of *t*-butyl hydroperoxide was observed with Br_4MoO^- immobilized on silica [2]. In that study the catalyst was found to have the same activity immobilized as it had free. This is because the active sites of the silica-immobilized catalyst are isolated on the silica surface and each site is active as in homogeneous catalysis.

This paper presents work on the immobilization of onium salts on silica which has been functionalized by silane coupling agents and on the catalytic reactivity of these immobilized onium salts for nucleophilic alkylation and substitution.

EXPERIMENTAL

a. Materials

Silica (323 m^2/g) was supplied as a gift from Nikki Chemical Co., Ltd. The silane coupling reagents [chloropropyltrimethoxysilane and 3(2-aminomethylpropyl)trimethoxysilane] were gifts from Toray Silicone Co., Ltd. Other chemicals were commercial materials and were used without further purification.

To activate the silica, it was suspended in 6 *M* HCl at 50°C for 24 h, centrifuged, washed until neutral, and dried at 80°C under vacuum before use.

b. Preparation of *II*

In a typical reaction, 3(2-aminomethylaminopropyl)trimethoxysilane (30 mL, 139 mmol) was added to the activated silica (10 g) in benzene (50 mL) and refluxed for 10 h with the aid of a Dean-Stark trap to produce the modified silica (*I*). *I* was collected and dried under vacuum. *I* (2 g), *p*-toluenesulfonylchloride (5 g, 26.2 mmol), and pyridine (10 mL) were stirred for 4 h at 60°C and 24 h at 25°C to produce the tosylate *II*.

c. Preparation of *III*

II (2 g) was treated with 1.5 *N* sodium ethoxide (1.5 mL) and filtered to obtain the sodium salt of the silica. The salt (2 g) in dimethylformamide (10 mL) (DMF) was treated over 40 min with *N*-(*p*-tosylsulfonyl)diethoxytosylate (0.83 g, 1.5 mmol) in DMF (3 mL) while heating at 100°C. After cooling to 25°C, the mixture was stirred for an additional 24 h. The mixture was filtered to produce *III*, which was dried under vacuum.

d. Preparation of *IV*

III (2.9 g), acetic acid (13 mL), and hydrobromic acid (27 mL) were stirred at 50°C for 24 h. The mixture was cooled to 25°C, ether was added, and *IV* was filtered off. *IV* was washed with ether and dried under vacuum. Elemental analysis indicated 0.65 mmol amine/g silica. The structure was examined by FT-IR. νNH = 3500 cm^{-1}, δNH = 1650 cm^{-1} (shoulder).

e. Preparation of *V* and *VI*

Chloropropyltrimethoxysilane (5.4 g, 27.2 mmol) was attached to the activated silica (2 g) as in a. The silica was then treated with (*s*)-(+)-2-(anilinomethyl)pyrolidine or (*s*)-(+)-2-(2,6-xylidinomethyl)pyrrolidine (2.5 mmol) in refluxing absolute ethanol to produce *V* and *VI*. The content of the introduced amine was 1.0 mmol/g silica, which was calculated by elemental analysis.

f. Catalytic Studies

NaOH (2 mL, 25% aqueous solution) and KCN (0.3 g, 5.1 mmol) were treated with benzyl chloride (2.0 g, 16 mmol) and benzene (1 mL) while stirring. After 20 min, *IV* was added and the mixture was stirred at 40°C for 20 h. The product, 2-cyano-1,2,3-triphenyl propane, was extracted with ether and identified by comparison with the melting point and the IR spectrum of the authentic compound. The starting material and

TABLE 1. Results of (1-Halogenoethyl)benzene with Aqueous KCN Solution[a]

Substrate (X)	Catalyst	Reaction time, h	Conversion, %	Cyanation/ hydroxylation
Br	Bu_4NCl	24	67	[b]
Cl	"	24	71	2.3
Br	*IV*	15	81	0.4
Br	*V*	15	77	0.5
Cl	*V*	24	100	0.4

[a] Substrate, 10 mmol; benzene, 2 mL, KCN, 10 mmol; H_2O, 2 mL; catalyst, 0.5 mmol; reaction temperature, 40°C.

[b] Not determined.

monobenzyl compound were checked by GC (PEG 20M, 20%, 2 m × 3 mm i.d.). Mono- and dibenzyl compounds were not obtained without *IV* in this reaction condition. Cyanation of 1-halogenoethylbenzene was carried out in the usual way. The reaction conditions are shown in Table 1. The analysis was done by GC in a manner similar to that described above.

RESULTS AND DISCUSSION

The functionalization of the activated silica was carried out as shown in Scheme 1. The presence of the amino groups was confirmed by elemental analysis. FT-IR spectra indicated the loss of the tosylate groups in *IV* since the S=O band disappeared and the NH peaks at 3500 and 1650 cm^{-1} were observed. FT-IR was used to propose the structures for *II–IV* shown in Scheme 1.

IV was treated with CH_3I and 10% HCl to produce immobilized ammonium salts. This material was used in the catalytic formation of 2-cyano-1,2,3-triphenylpropane as shown in Scheme 2. It is possible, in the presence of ammonium salt of *IV*, that 2-cyano-1,2,3-triphenylpropane may be synthesized in good yield by a one-pot reaction by using benzyl chloride and one-third equivalent of KCN.

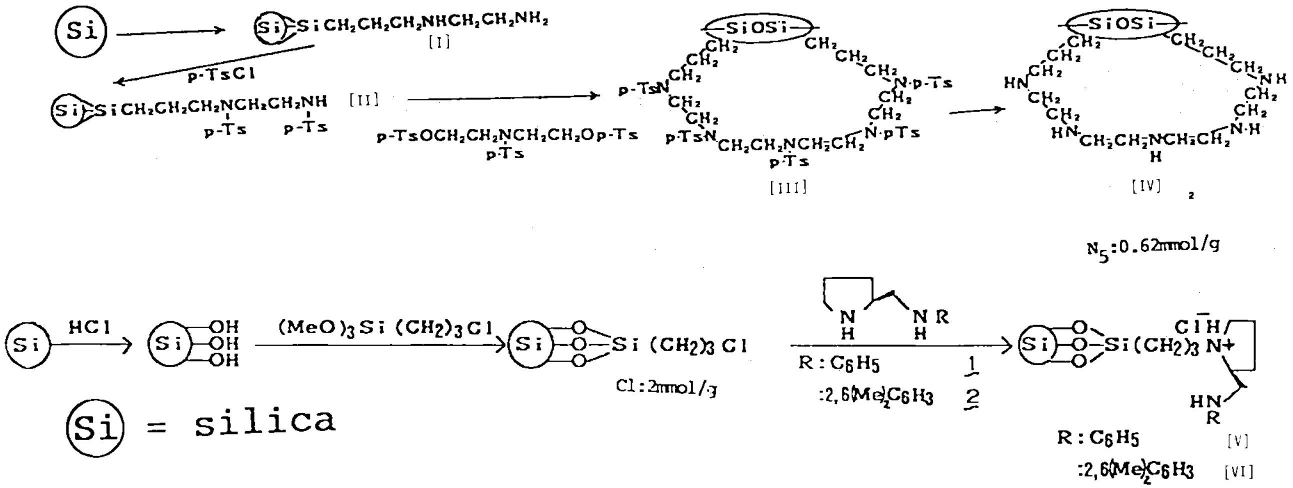
Nucleophilic substitution of halide by cyanide was carried out on 1-phenylhalogenoethane in the presence of *V* and *VI*:

$$PhCH(X)CH_3 \rightarrow PhCH(CN) + PhCHOHCH_3 + PhCH(X)CH_3$$
$$(X = Br \text{ or } Cl)$$

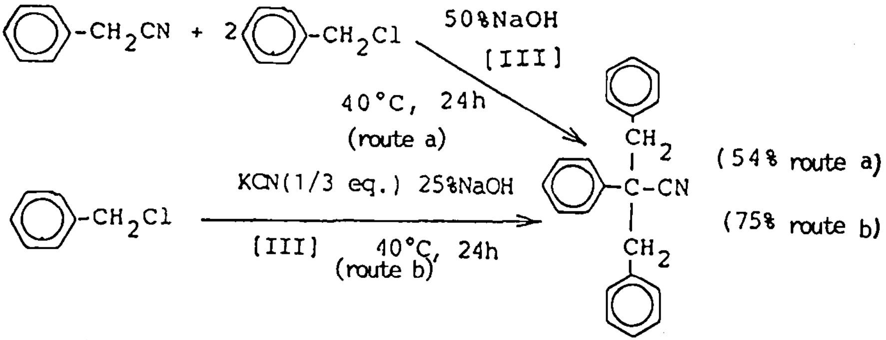
Table 1 summarizes the results. Hydroxylation is favored over cyanation in these systems.

The introduction of lipophilic groups and the reaction in nonpolar organic solvents is required to raise the level of cyanation. Catalytic systems utilizing *V* and *VI* and ammonium-group-immobilized silica derived from *IV* exhibit higher conversion rates for hydroxylation and alkylation.

An effort to increase the level of cyanation and a mechanistic study are in progress.


Si
Si Si CH₂CH₂CH₂NHCH₂CH₂NH₂
[I]
p-TsCl
Si Si CH₂CH₂CH₂NCH₂CH₂NH
p-Ts
p-Ts
[II]
p-TsOCH₂CH₂NCH₂CH₂Op-Ts
p·Ts
SiOSi
p-TsN
N·p-Ts
p·TsN
N·pTs
CH₂CH₂NCH₂CH₂
p·Ts
[III]
HN
NH
N·H
CH₂CH₂NCH₂CH₂
H
[IV]
2
N5:0.62mmol/g
HCl
OH
(MeO)3Si (CH2)3Cl
Si (CH2)3 Cl
Cl:2mmol/g
N H
N R H
R : C6H5
:2,6(Me)2C6H3
1
2
Si(CH2)3 N+
ClH
HN R
R : C6H5
:2,6(Me)2C6H3
[V]
[VI]
Si = silica

SCHEME 1.



SCHEME 2.

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