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POLYVINYLPYRIDINES AS CATALYSTS FOR THE REDUCTION OF KETONES BY SODIUM BOROHYDRIDE UNDER TWO-PHASE CONDITIONS

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INTRODUCTION

Various kinds of organic compounds containing heteroatoms such as oxygen and nitrogen which coordinate strongly to alkali metal ions have been known to work as phase-transfer catalysts as well as quaternary onium salts. Representative catalysts are crown ethers, cryptands, and *t*-alkylamines [1–5]. In most cases the catalytic activity has been estimated by the degree of acceleration for the reaction of alkyl halides with nucleophiles. However, in these systems a catalyst amine often functions as a nucleophile to afford an ammonium salt which is known as a phase-transfer catalyst. Thus, in amine-catalyzed phase-transfer reactions, there has been a discussion whether or not an amine has catalytic activity [6–8]. In order to obtain the solution to this problem, we think that an investigation of the reduction of carbonyl compounds by sodium borohydride is suitable.

Meanwhile, little attention has been given to tertiary heteroaromatic bases, pyridine and polyvinylpyridines, as phase-transfer catalysts [9]. We have recently found that polymeric analogs of dipolar aprotic solvents serve as phase-transfer catalysts, though the monomeric analogs are inactive [10–13]. Therefore, it is of interest to examine the catalytic activity of polyvinylpyridines for the reduction of carbonyl compounds in two-phase systems. This article describes the utility of polyvinylpyridines as phase-transfer catalysts.

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EXPERIMENTAL

Materials

2-Vinylpyridine, 4-vinylpyridine, styrene, acetophenone, 2-octanone, cyclohexanone, benzaldehyde, and solvents were used after distillation. Azobisisobutyronitrile (AIBN) was recrystallized twice from methanol. Other reagents were obtained commercially and used without further purification.

Preparation of Catalysts

Polyvinylpyridines were prepared by the polymerization of 2-vinylpyridine or 4-vinylpyridine, and copolymerization of these monomers with styrene. Polymerization was carried out in the presence of AIBN in benzene at 60°C by the same method described previously [14]. The homopolymers obtained were purified by reprecipitation with ether from methylene chloride. On the other hand, copolymers were purified by reprecipitation by using petroleum ether as a poor solvent.

Extraction of Sodium Picrate

The extraction ability was evaluated by a modified procedure of the methods reported by Pedersen [15], Frensdorff [16], and Smid [17]. To a 20-mL benzene solution of the polymer containing 2.5×10^{-5} mol of the pyridine unit was added 5 mL of an aqueous picric acid solution (5×10^{-5} *M*) containing excess sodium hydroxide (1×10^{-2} *M*). The mixture was stirred magnetically for 1 h at 20°C. After separation, the aqueous solution was analyzed for picrate absorption at 355 nm by spectrophotometry.

Reduction of Ketones

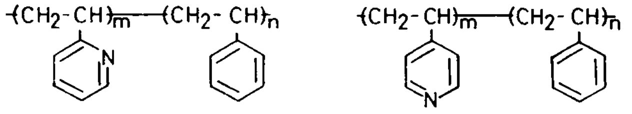
To a 20-mL round bottomed flask, a solution of ketone (1.5 mmol) in 4 mL benzene, sodium borohydride (1.2 mmol), 1% aqueous sodium hydroxide (0.1 mL), and a catalyst containing pyridine unit (0.1 mmol equivalent) were added. The mixture was stirred magnetically at room temperature or 50°C for a given time. Then the solution was acidified by 10% HCl to pH 5–6 and poured into petroleum ether to precipitate the polymer. The organic layer was analyzed by GLC.

Measurements

UV spectra were taken on a Hitachi 124 spectrometer. The separation and purification of products were performed by the use of GLC (Hitachi 063). The internal standard method was used in yield determinations. The column used included 20% Carbowax 20 M (1 m × 3 mm) on Celite 545.

RESULTS AND DISCUSSION

Polymers 1 and 2 were prepared by the free radical polymerization of the corresponding vinyl monomers and copolymerization with styrene. See Scheme 1.



1 2

	$\frac{m}{m+n}$
1a	1
b	0.5
c	0.25

	$\frac{m}{m+n}$
2a	1
b	0.5
c	0.25

SCHEME 1.

These polymers are soluble in benzene and methylene chloride, but insoluble in water. If these polymers work as phase-transfer catalysts, the polymers should extract alkali metal ions from the aqueous phase. Therefore, in order to obtain information on this point, extraction of sodium picrate was examined. The results are summarized in Table 1.

As can be seen from the table, Polymers 1 and 2 extract sodium ion, but the monomeric compound, pyridine, does not do so to any detectable degree. Furthermore, the extraction ability increases with an increase of the density of the active site in the polymers. The results can be explained by the mechanism involving chelation of a sodium ion with several pyridine rings. A similar phenomenon has been observed in polymeric analogs of dipolar aprotic solvents such as dimethyl

TABLE 1. Extraction of Sodium Picrate by Polyvinylpyridines

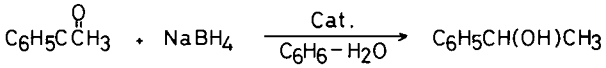
Catalyst	Extraction, %
Pyridine	0
1a	5
1b	2
1c	1
2a	12
2b	5
2c	4

sulfoxide [10], *N,N*-dimethylformamide [12], and hexamethylphosphoramide [18]. In addition, the extraction ability of Polymer 2 is much higher than that of Polymer 1 when they are compared under the same composition. This might be because the active site of Polymer 2 can interact more readily with the aqueous phase than that of Polymer 1.

The catalytic activity of these polymers was tested for the reduction of acetophenone by sodium borohydride. This reaction was carried out in benzene–water solutions, and the results are shown in Table 2.

TABLE 2. Polyvinylpyridine-Catalyzed Reduction of Carbonyl Compounds by Sodium Borohydride under Two-Phase Conditions

Carbonyl compound	Catalyst	Time, h	Temperature, °C	Yield, %
Acetophenone	—	24	50	14
Acetophenone	1a	24	50	51
Acetophenone	1b	24	50	62
Acetophenone	1c	24	50	33
Acetophenone	2a	24	50	82
Acetophenone	2b	24	50	99
Acetophenone	2c	24	50	69
2-Octanone	—	36	50	12
2-Octanone	1a	36	50	91
2-Octanone	2a	36	50	92
Cyclohexanone	—	1	Room temperature	12
Cyclohexanone	1a	1	Room temperature	57
Benzaldehyde	—	3	Room temperature	18
Benzaldehyde	1a	3	Room temperature	99



$$C_6H_5\overset{O}{\overset{\|}{C}}CH_3 + NaBH_4 \xrightarrow[C_6H_6-H_2O]{Cat.} C_6H_5CH(OH)CH_3 \qquad (1)$$

The reaction in the presence of Polymers 1a and 2a afforded 1-phenylethyl alcohol in moderate yield, but was not catalyzed by pyridine. It should be noted that the activity of the polymeric catalyst is superior to that of the monomeric analog. Further, the catalytic activity of Polymer 2 is generally higher than that of Polymer 1 in agreement with the extraction ability. Interestingly, based on the composition of Polymer 1, the activity decreases in the order 1b > 1a > 1c. The same tendency was observed for Polymer 2. This finding indicates that the activity is also affected by liphophilicity around the active site.

Based on above results, we are convinced that the lone pair electrons of nitrogen in pyridine polymers coordinate to sodium ion at the water–benzene interface, and the anion as a gegenion is transferred together with the sodium ion to the organic phase, where it attacks the substrate.

Moreover, these polymers can serve as phase-transfer catalysts for the reduction of other carbonyl compounds such as 2-octanone, cyclohexanone, and benzaldehyde.

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