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Crosslinked Polyvinylpyridine Hydrochloride as a Mild Polymeric Catalyst for Acetalization of Carbonyl Compounds and Esterification of Carboxylic Acids

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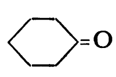
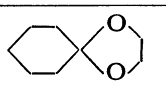
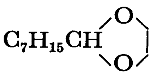
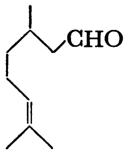
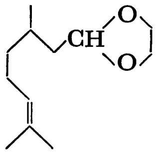
Synopsis. Crosslinked poly(4-vinylpyridine) hydrochloride was found to be an effective catalyst for acetalization of carbonyl compounds and esterification of carboxylic acids. The polymeric catalyst was inert to some acid sensitive functional groups which cannot tolerate under the influence of a strong acid cation exchange resin.

One of the advantages provided by insoluble polymeric catalyst[1)] is their easy recovery from the reaction system which prevents the leakage of toxic chemicals. The use of them may be valuable from environmental point of view. Although cation exchange resins[2)] are historically one of the earliest examples of the polymeric catalysts, there have been few works available in the literature on milder and more selective polymeric acid catalysts. We have now found that crosslinked poly(4-vinylpyridine) hydrochloride (**1**) was a mild and effective catalyst for acetalization of carbonyl compounds and esterification of carboxylic acids.

The experimental results of the acetalization of carbonyl compounds are given in Table 1. The reaction of cyclohexanone with ethylene glycol proceeded smoothly in the presence of **1** at room temperature to give the corresponding acetal in 96% yield. The spent catalyst was easily rejuvenated by washing with small amounts of organic solvents, and was reused several times with little loss of activity. Acetalization of octanal and citronellal with ethylene glycol also proceeded smoothly in the presence of **1**.

TABLE 1. ACETALIZATION OF CARBONYL COMPOUNDS WITH ETHYLENE GLYCOL CATALIZED BY POLYMERIC ACID CATALYSTS[a)]

Carbonyl compound	Catalyst	Products	Yield %[b)]
	**1**		96
	1[c)]		98
	IR-120B[d)]		95
	IRC-50[e)]		0
$C_7H_{15}CHO$	**1**		90
	**1**		62

a) Reactions were carried out with 2.0 mmol of carbonyl compound, 10.0 mmol of ethylene glycol, and 50 mg of polymeric acid catalyst at room temperature for 1 h. b) Determined by GLC analysis of the reaction mixture, and were based on the carbonyl compound. c) Fifth use. d) A strong acid cation exchange resin in the H form. e) A weak acid cation exchange resin in the H form.

The polymeric catalyst (**1**) was also effective for the esterification of acetic acid with 1-butanol, and the reaction at 80 °C gave butyl acetate in a quantitative yield. In the corresponding esterification of acetic acid with 2-butanol, however, yield of the ester was low. Results are given in Table 2.

Although pyridine hydrochloride has been known as a good catalyst for acetalization of carbonyl compounds,[3)] it is very hygroscopic and must be protected from moisture.[4)] This disadvantage can be overcome by the use of the polymeric catalyst (**1**) which is non-hygroscopic and very easy to handle in comparison with the monomeric analogue.

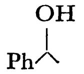
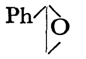
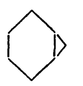
A strong acid cation exchange resin containing sulfonic acid group was also an efficient catalyst for the acetalization and the esterification. On the other hand, a weak acid cation exchange resin containing carboxyl group was almost inactive as a catalyst for the reactions. It should be noted, however, that the use of **1** as a catalyst has an advantage over the use of strong acid cation exchange resins, because the use of **1** allowed the application of reactions to the reactants having some acid sensitive functional groups which cannot tolerate the strong acid cation exchange resins. In order to demonstrate this advantage of the use of **1**, esterification of acetic acid with 1-butanol was carried out in the presence of a polymeric catalyst and an additive which contained some acid sensitive functional groups. Results are given in Table 3. For example, 1-phenylethanol used as an additive was recovered quantitatively in the reaction of acetic acid

TABLE 2. ESTERIFICATION OF ACETIC ACID WITH ALCOHOLS CATALYZED BY POLYMERIC ACID CATALYSTS[a)]

Alcohol	Catalyst	Products	Yield %[b)]
n-C_4H_9OH	**1**	$CH_3COOC_4H_9$-n	100
	IR-120B[c)]		100
	IRC-50[d)]		3
s-C_4H_9OH	**1**	$CH_3COOC_4H_9$-s	27
	IR-120B[c)]		74

a) Reactions were carried out with 5.0 mmol of acetic acid, 10.0 mmol of alcohol, and 125 mg of polymeric acid catalyst at 80 °C for 1 h. b) Determined by GLC analysis of the reaction mixture, and was based on acetic acid. c) See footnote (d) in Table 1. d) See footnote (e) in Table 1.

Table 3. Esterification of acetic acid with 1-butanol in the presence of some acid sensitive additives[a)]

Additive	Catalyst	Yield of the ester/%[b)]	Recovered additive/%[b)]
	**1**	93	100
	IR-120B[c)]	98	21[d)]
	**1**	2	20
	IR-120B[c)]	85	0
	**1**	88	100
	IR-120B[c)]	89	45

a) The reactions were carried out with 5.0 mmol of acetic acid, 10.0 mmol of 1-butanol and 2.5 mmol of additive at 80 °C for 1 h. b) Determined by GLC analysis of the reaction mixture. c) See footnote (d) in Table 1. d) Significant amounts of styrene and other unidentified products were formed.

and 1-butanol catalyzed by **1**. On the contrary, in the corresponding reaction catalyzed by the strong acid cation exchange resin, only 21% of 1-phenylethanol was recovered and significant amounts of styrene and other unidentified products were formed. Norcarane contains an acid sensitive cyclopropane ring, but was not affected under the influence of **1**. In contrast, only 45% of norcarane was recovered in the presence of the strong acid cation exchange resin. (Epoxyethyl)benzene was unable to tolerate both of the catalysts.

The results obtained here may suggest the synthetic utility of **1** as a mild and efficient polymeric acid catalyst which provides an attractive alternate to the commercially available cation exchange resins.

Experimental

General. ^{1}H NMR spectra were recorded on a Varian T-60A spectrometer in carbon tetrachloride using tetramethylsilane as internal standard. IR spectra were recorded on a Hitachi 215 grating spectrometer. GLC analyses were performed on a Shimadzu GC-4B or GC-4C gas chromatograph.

Materials. 4-Vinylpyridine provided by Koei Chem. Co. Ltd., Osaka and commercial ethanol were purified by distillation before polymerization. A commercial product of divinylbenzene (*ca.* 55%) was washed with 5% aqueous sodium hydroxide and with deionized water, dried over potassium carbonate, and distilled. Dry hydrogen chloride was prepared by dropping concentrated sulfuric acid on dry lumps of ammonium chloride, and dried by passing through concentrated sulfuric acid. Other chemicals and nitrogen were used as obtained commercially.

*Preparation of Crosslinked Poly(4-vinylpyridine) Hydrochloride (**1**).* Crosslinked poly(4-vinylpyridine) containing 75 mol% 4-vinylpyridine was prepared by a copolymerization of 4-vinylpyridine with divinylbenzene followed by grinding and sifting to 60—80 mesh as was described elsewhere.[5)] The dry copolymer (1.500 g) was placed in a glass tube (5.0 mm diam × 180 mm) and excess dry hydrogen chloride was passed through the tube. To remove excess hydrogen chloride in the resin layer, nitrogen was passed through the tube until no hydrogen chloride was detected at the other end of the tube. After drying *in vacuo*, 1.845 g of **1** was obtained. Elemental analysis of the polymer showed the content of 6.82% of N and 17.98% of Cl, suggesting that the pyridyl group in the resin was quantitatively converted to the hydrochloride form (5.1 mequiv of HCl/dry g).

Resins. For comparison, two commercial resins were used in this work. Amberlite IR-120B and Amberlite IRC-50 supplied by Rohm & Haas Co., Philadelphia, Pa., U.S.A., were used as a strong acid cation exchange resin and a weak acid cation exchange resin, respectively. They were preconditioned and transferred to the H form in usual manners, and were dried *in vacuo* before use. The ion exchange capacity of IR-120B was 4.76 mequiv/dry g, which was determined by titration with standard 0.1 mol/l aqueous NaOH using phenolphthalein as indicator in 1 mol/l aqueous NaCl. The ion exchange capacity of IRC-50 was 10.0 mequiv/dry g, which was determined by back titration with standard 0.1 mol/l aqueous HCl using phenolphthalein as indicator after treatment with a large excess of 0.1 mol/l aqueous NaOH overnight at room temperature.

Acetalization of Carbonyl Compounds. A mixture of carbonyl compound (2.0 mmol), ethylene glycol (10.0 mmol), and a polymeric catalyst (50 mg) was stirred at room temperature for 1 h. After the reaction, the mixture was analyzed by GLC. After removal of the polymeric catalyst by filtration, the products were isolated and identified by comparison of their spectral data with those of authentic materials.

Crosslinked poly(4-vinylpyridine) (**1**) can be reused several times with little loss of activity. In this case, the spent polymeric catalyst was recovered by filtration, and was washed with benzene, methanol, and ether. After dried *in vacuo*, the recovered polymeric catalyst was reused for the acetalization.

Esterification of Carboxylic Acids. A mixture of carboxylic acid (5.0 mmol), an alcohol (10.0 mmol) and a polymeric catalyst (125 mg) was stirred at 80 °C for 1 h, and the mixture was analyzed by GLC. After removal of the catalyst by filtration, the products were isolated and identified by comparison of their spectral data with those of authentic materials.

The esterification reactions of acetic acid with 1-butanol in the presence of an additive were carried out in a similar manner.

References

1) For example, D. C. Neckers, *J. Chem. Educ.*, **52**, 695 (1975).

2) a) R. Kunin, E. Meitzner, and N. Bortnick, *J. Am. Chem. Soc.*, **84**, 305 (1962); b) G. F. Vesley and V. I. Stenberg, *J. Org. Chem.*, **36**, 2548 (1971); c) V. I. Stenberg, G. F. Vesley, and D. Kubik, *ibid.*, **36**, 2550 (1971).

3) a) J. Egyed, P. Demerseman, and R. Royer, *Bull. Soc. Chim. Fr.*, **1972**, 2287; b) R. Rausser, A. M. Lyncheski, H. Harris, R. Grocela, N. Murrill, E. Bellamy, D. Ferchinger, W. Gebert, H. L. Herzog, E. B. Hershberg, and E. P. Oliveto, *J. Org. Chem.*, **31**, 26 (1966).

4) M. D. Taylor and L. R. Grant, *J. Chem. Educ.*, **32**, 39 (1955).

5) N. Kawabata and K. Ohira, *Environ. Sci. Technol.*, **13**, 1396 (1979).