

SHORT COMMUNICATIONS

New Polymeric Catalyst for the Addition Reaction
of Active Ester with Epoxy Compound

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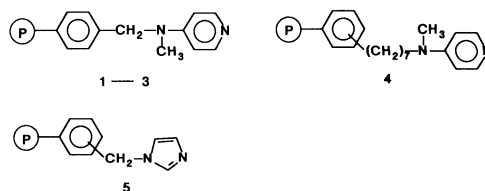
KEY WORDS Polymeric Catalyst / Polymer-Supported Base / Pendant 4-(*N,N*-dimethylamino)pyridine / Pendant *N*-Methylimidazole / Addition Reaction / 4-(*N,N*-dimethylamino)pyridine / Active Ester / Epoxy Compound /

It is well known^{1–5} that polystyrene-supported catalysts containing pendant 4-(*N,N*-dimethylamino)pyridine, 4-pyrrolidino-pyridine or *N*-methylimidazole moieties are useful catalysts for the acylation of alcohols, phospholipid synthesis, and acyl rearrangements. However, the activity of all these polymer-supported catalysts has mostly been comparable to or slightly lower than that of the corresponding low molecular weight catalysts also used.

Recently, we found⁶ that regioselective addition reaction of active ester with epoxy compound and the addition reaction⁷ of cyclic ester with epoxy compound are effectively catalyzed by insoluble polymer-supported catalyst containing pendant quaternary phosphonium or ammonium salts, and these polymeric catalysts have higher activity than the corresponding low molecular weight catalyst.

In this communication, we report new catalytic activity of polymer-supported bases for the regioselective addition reaction of active ester with epoxy compound.

Polymer-supported catalysts **1–5** were pre-



Scheme 1.

pared using the methods previously reported.^{1–5} A typical addition reaction was carried out as follows: *S*-phenyl thioacetate (PTA) [0.61 g (4 mmol)] and 0.60 g (4 mmol) of phenyl glycidyl ether (PGE) were dissolved in 2 ml of chlorobenzene, and then 0.15 g (0.2 mmol as base) of the catalyst **1** having a pendant 4-(*N,N*-dimethylamino)pyridine (DMAP) moiety was added to the solution. The mixture was stirred at 90°C for 24 h, and the yield of 1-phenoxy-3-thiophenoxy-2-propyl acetate (**6a**) was monitored by gas chromatography.

Although the reaction of PTA with PGE was expected to produce two isomers due to α - and β -cleavage of the oxirane ring using the polymer-supported catalysts **1–5**, or the corresponding low molecular weight (LMW) cat-

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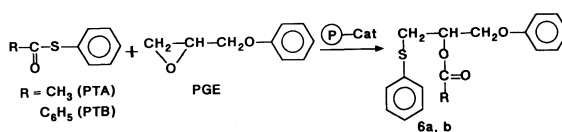
Table I. Addition reaction of active esters with PGE by polymer-supported bases^a

No.	Catalyst	Degree of cross.	Content of amino group	Active ester	Time	Yield of 6a—b	Yield of 8
		% ^b	mequiv. g ⁻¹		h	%	%
1	1	1	1.35	PTA	24	96.5	3.1
2	2	2	1.33	PTA	24	93.5	5.8
3	3^c	10	2.16	PTA	8	86.0	10.9
4	3^c	10	2.16	PTA	24	91.4	8.1
5	4	2	1.21	PTA	24	94.0	5.9
6	5	2	1.58	PTA	8	72.6	10.9
7	5	2	1.58	PTA	24	82.4	10.0
8	DMAP	—	—	PTA	24	91.4	6.7
9	MIMZ	—	—	PTA	24	84.9	3.4
10	TEA	—	—	PTA	24	7.8	3.7
11	TBA	—	—	PTA	24	4.3	3.5
12	2	2	1.33	PTB	24	82.3	6.8
13	3^c	10	2.16	PTB	24	68.7	15.0
14	4	2	1.21	PTB	24	88.9	3.1
15	5	2	1.58	PTB	24	68.6	7.8

^a The reaction was carried out with 4 mmol of active ester and 4 mmol of PGE using 5 mol% of the catalyst in 2 ml of chlorobenzene at 90°C.

^b Crosslinked with divinylbenzene.

^c Macroreticular (MR) resin.

**Scheme 2.**

alysts 4-(*N,N*-dimethylamino)pyridine (DMAP) and *N*-methylimidazole (MIMZ), only the isomer **6a** was obtained and the production of the other isomer 3-phenoxy-2-thiophenoxy-1-propyl acetate (**7a**) was not confirmed. In addition, the production of small amounts of 1-phenoxy-3-thiophenoxy-2-propanol (**8**), a hydrolysis product of **6a**, was determined. The reaction of *S*-phenyl thiobenzoate (PTB) with PGE also gave only one isomer 1-phenoxy-3-thiophenoxy-2-propyl benzoate (**6b**) with small amounts of by-product **8** (Table I). The main products **6a** and **6b**, and hydrolysis product **8** reacting active esters with epoxy compound were identified by IR and ¹H NMR spectra as reported previously.⁸

The above results indicate that this addition

reaction, catalyzed by the supported or soluble bases, proceeds regioselectively (Scheme 2).

As summarized in Table I, the reaction of PTA with PGE produced **6a** with 96.5, 93.5 and 94.1% yields using the polymer-supported catalysts **1**, **2**, and **4** containing the pendant DMAP moiety, respectively, in chlorobenzene at 90°C for 24 h. The yield of **6a** was 91.4% when the reaction was carried out using catalyst **3**, a macroreticular (MR) catalyst, under the same conditions. **6a** was also obtained with 82.4% yield when the reaction was performed with catalyst **5** having the pendant *N*-methylimidazole (MIMZ) moiety. On the other hand, **6a** was synthesized with 91.4 and 84.9% yields using LMW catalysts DMAP and MIMZ, respectively. However, the reaction of

PTA with PGE occurred only slightly using triethylamine (TEA) and tributylamine (TBA) as catalysts under the same conditions. It seems that the high catalytic activities of the polymer-supported catalysts containing the pendant DMAP or MIMZ moieties and corresponding LMW catalysts are attributable to the strong nucleophilicity of these compounds, although DMAP has a somewhat higher catalytic activity than MIMZ for the addition reaction of the active ester with the epoxy compound.

The reaction of PTB with PGE also gave the corresponding product **6b** with high yields using the same catalysts **1**–**5**; however, the yield of **6b** was lower than that of **6a**. This means that the reactivity of PTB was lower than PTA under the same conditions using the polymer-supported bases.

These results suggest that the polymer-supported catalysts containing pendant DMAP or MIMZ moieties have new and excellent catalytic activity for the regioselective addition reaction of the active ester with the epoxy compound. Furthermore, the low cross-linked polymer-supported catalysts **1** and **2** containing the pendant DMAP moiety had higher catalytic activity than that of the LMW catalyst DMAP, although the activity of the low crosslinked polymer-supported catalyst **5** with pendant MIMZ moiety was slightly lower

than that of the LMW catalyst MIMZ. In addition, it seems that the catalytic activity of the polymer-supported bases was also affected by the degree of crosslinking and content of the pendant base. That is, the catalytic activity of the 10% crosslinked polymer-supported catalyst **3** containing a large amount (2.16 mequiv. g⁻¹) of pendant DMAP moiety was lower than that of the the polymer-supported catalysts **1**, **2**, and **4** containing small amounts (1.21–1.35 mequiv. g⁻¹) of the DMAP moiety.

A study on the scope and mechanism of the polymeric support for the addition reaction is presently being conducted.

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