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Asymmetric, Partial Acetylation of *dl*-1-Phenylethanol by Means of Chiral Polymers

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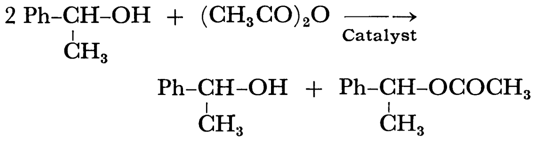
Synopsis. The partial esterification of *dl*-1-phenylethanol with acetic anhydride was carried out in the presence of poly(*O*-acryloylquinine), poly(*N*-benzyl-2-pyrrolidinylmethylacrylate), and poly(*O*-acryloyl-*N*-benzylephedrine). The propionyl esters of quinine, *N*-benzyl-2-pyrrolidinylmethanol and *N*-benzylephedrine were also used as low molecular weight catalysts. The above polymeric and monomeric catalysts showed poor, asymmetric efficiencies for this esterification.

Several synthetic polymers[1,2] derived from optically active amino alcohols have been used for the study of polymeric effects and asymmetric reactions. Some polymeric catalysts have yielded products with higher optical yields than their corresponding monomeric catalysts.

This report describes the use of poly(*O*-acryloylquinine)[2] (P-1), poly(*N*-benzyl-2-pyrrolidinylmethyl acrylate)[2] (P-2), and poly(*O*-acryloyl-*N*-benzylephedrine)[1] (P-3) in the asymmetric, partial acetylation[3-5] of *dl*-1-phenylethanol. The use of *O*-propionylquinine[2] (A-1), *N*-benzyl-2-pyrrolidinylmethyl propionate[2] (A-2), and *O*-propionyl-*N*-benzylephedrine[1] (A-3) was also examined. The acetylation was carried out in a manner similar to that reported by Wegler.[3]



$$2\,\underset{\displaystyle CH_3}{\text{Ph-}\underset{|}{\text{CH}}\text{-OH}} + (CH_3CO)_2O \xrightarrow[\text{Catalyst}]{} \underset{\displaystyle CH_3}{\text{Ph-}\underset{|}{\text{CH}}\text{-OH}} + \underset{\displaystyle CH_3}{\text{Ph-}\underset{|}{\text{CH}}\text{-OCOCH}_3}$$

Two equivalent amounts of *dl*-1-phenylethanol were allowed to react with one equivalent amount of acetic anhydride in the presence of one equivalent amount of a catalyst. The molar equivalent amount of the polymeric catalyst was calculated on the basis of that of the monomer used in the polymerization (*e.g.*, 100 mg of P-1 corresponds to 100 mg of A-1).

TABLE 1. THE OPTICAL YIELDS AND CONFIGURATIONS OF α-METHYLBENZYL ACETATE

Catalyst	O.Y.[a] (%)	Conf.[b]
A-1	1.12	*S*
P-1	0.21	*S*
P-1[c]	0.74	*S*
P-1[d]	1.13	*S*
A-2	0.14	*R*
P-2	0.08	*R*
A-3	0.09	*S*
P-3	0.00	—

a) The O.Y. (optical yield, %) was calculated with respect to the value for optically pure (*S*)-α-methylbenzyl acetate,[6] $[\alpha]^{28}_{D}=-118°$ in benzene. b) The configuration of the predominant isomer. c) P-1/acetic anhydride=5. d) P-1/acetic anhydride=10.

Table 1 shows the optical yields and configurations of α-methylbenzyl acetate obtained with these catalysts.

Table 1 indicates that asymmetric acetylation was carried out more effectively with monomeric than with polymeric catalysts.

Ten equivalent amounts of P-1 to one equivalent amount of acetic anhydride were required to obtain α-methylbenzyl acetate in a 1.13% optical yield, while one equivalent amount of A-1 was needed to obtain acetylated alcohol with the same value of optical yield. These results suggest that no favorable polymer effect with regard to stereoselectivity is observed for this esterification.

Dumont *et al.*[7] have also reported that a chiral polymeric rhodium complex catalyzed the asymmetric hydrogenation of olefins with a lower efficiency than did the corresponding monomeric complex.

Experimental

(A). To a solution of A-1 (2.28 g) and *dl*-1-phenylethanol (1.46 g) in 10 ml of carbon tetrachloride was added acetic anhydride (0.61 g). The mixture was stirred under reflux for 15 h. After removal of the solvent, the residue was dissolved in ether. The ethereal solution was washed with 1 M-hydrochloric acid to remove A-1, successively with saturated sodium hydrogencarbonate and water, and dried. The solution was evaporated to dryness under reduced pressure. The residue was distilled to give a colorless oil (1.50 g). Bp 90 °C at 13 mmHg. $[\alpha]^{17}_{D}=-0.604°$ (*c* 50, benzene). GLC and TLC of this oil showed it to be composed of two materials. The mixture was subjected to column chromatography on alumina (2×30 cm, 200 mesh, neutral).

Elution with hexane gave 0.73 g of acetylated alcohol. $[\alpha]^{13}_{D}=-1.32°$ (*c* 25, benzene). Further elution with ether gave 0.61 g of unreacted 1-phenylethanol. $[\alpha]^{16}_{D}=+0.65°$ (*c* 25, benzene).

The above acetylated and unreacted alcohols were distilled and their optical rotations were measured again. α-Methylbenzyl acetate, bp 105—108 °C at 15 mmHg. $[\alpha]^{15}_{D}=-1.34°$ (*c* 20, benzene). 1-Phenylethanol, bp 93 °C at 12 mmHg. $[\alpha]^{15}_{D}=+0.67°$ (*c* 20, benzene). The structure of acetate and unreacted alcohol was confirmed by NMR and IR.

(B). To a solution of P-1 (2.28 g) and *dl*-1-phenylethanol (1.46 g) in 10 ml of carbon tetrachloride was added acetic anhydride (0.61 g), and the mixture was refluxed with stirring. After 15 h, the solution was evaporated to dryness *in vacuo*. Ether was added to the residue, and a precipitate of P-1 was filtered off. The filtrate was evaporated to give a mixture of acetate and unreacted alcohol in a 90% yield. After having been distilled, the mixture was separated into 1-phenylethanol and α-methylbenzyl acetate by column chromatography in a manner similar to that described in (A). The use of other monomeric and polymeric catalysts was attempted according to methods similar to those described in (A) and (B).

The optical rotations of 1-phenylethanol and α-methylbenzyl acetate were measured by means of a JASCO DIP-4 automatic polarimeter (10 cm cell, *c* 20—50, benzene).

A JASCO IRA-1 (IR), a JEOL-60 MC (NMR) and a Varian M 920 (GLC) were used for the measurement of the samples in this experiment.

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