SHORT COMMUNICATION

Asymmetric Synthesis of Methyl 2-Phenylpropionate by Means of Chiral Polyaziridines

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In order to study new catalysts and polymer effects in asymmetric reactions, the authors¹ recently carried out an asymmetric synthesis of methyl 2-phenylpropionate by means of chiral poly(*O*-acryloylaminoalcohol)s and their corresponding low-molecular-weight model compounds, which were derived from cinchona alkaloids, prolinol, and ephedrine. A distinct polymer effect with respect to stereoselectivity was observed with the polymeric catalysts described above. (A) Polymeric catalysts gave addition products with higher optical yields than did their corresponding low-molecular-weight model compounds. (B) The products with the polymeric catalysts containing conformationally rigid molecules in the side chain showed a linear relationship between $\log k_R/k_S$ and $1/T [k_R(k_S)]$, the rate constant for the *R*(*S*)-isomer].

In this paper, poly(aziridine)s having asymmetric centers in the main chain of the polymers were used as chiral catalysts for the asymmetric addition of methanol to phenyl methyl ketene (PMK).

P1_a and **P1_b** were obtained by the ring-opening polymerization of (5*S*)-1-azabicyclo[3.1.0]hexane with a catalytic amount of (5*S*)-1-

azabicyclo[3.1.0]hexane-boron trifluoride complex in bulk, and a catalytic amount of boron trifluoride etherate in benzene, respectively, according to the procedure² reported earlier (**P1_a**: MW 4000—4200; **P1_b**: MW 1400). Their corresponding low-molecular-weight model compound (**M1**)³ (bp 140—160°C at 12 mmHg, $[\alpha]_D^{20} - 103^\circ$ in ethanol) was prepared by reduction (lithium aluminum hydride) of *N*-(*N*-benzyloxycarbonyl-L-prolyl)-pyrrolidine (mp 128—132°C, $[\alpha]_D^{13} - 7.9^\circ$ in ethanol), which was made from *N*-benzyloxycarbonyl-L-proline⁴ and pyrrolidine by a mixed carbonic-carboxylic acid anhydride method.⁵

Poly[(*S*)-*N*-methylisobutylethyleneimine] (**P2**) was obtained by the method of Tsuboyama.⁶ Its corresponding low-molecular-weight model compound (**M2**) (bp 95—105°C at 4 mmHg, $[\alpha]_D^{20} + 28^\circ$ in ethanol) was prepared by *N*-methylation⁷ (HCOOH — HCHO) of *N*¹,*N*²-dimethyl-*N*¹-isopentyl-4-methyl-1,2-pentanediamine (bp 80—100°C at 4 mmHg, $[\alpha]_D^{20} + 90^\circ$ in ethanol), which was obtained by reduction (lithium aluminum hydride) of *N*-(*N*'-benzyloxycarbonyl-L-leucyl)methylisopentylamine, the latter being made from *N*-benzyloxycarbonyl-L-leucine⁸ and methylisopentylamine by a mixed carbonic-carboxylic acid anhydride method.⁵

The asymmetric addition of methanol to PMK was conducted with the above catalysts according to an earlier report.^{1a} To one equivalent amount of PMK and a small excess of methanol was added a 0.01 molar equivalent amount of the catalyst. The molar equivalent amount of the polymeric catalyst was calculated from that of the monomer used in the polymerization. The optical yield was calculated with respect to the value for optically pure (*S*)-methyl 2-phenylpropionate,^{1a} $[\alpha]_D^{22} + 109^\circ$ in toluene.

Table I indicates that **P1_a**, **P1_b**, **M1**, and **M2** gave addition products showing a preference for the *S*-isomer in the range from -78°C to $+50^\circ\text{C}$, but **P2** gave the *R*-configuration products at -40°C and -60°C . **P1_b** provided addition products with higher optical yields than did **M1** below $+25^\circ\text{C}$. The highest optical yield (10%) of the product was obtained with **P1_b** at -20°C . At -78°C , the optical yield of the product for **P1_a** was about eighteen as high as that for **M1**.

Figure 1 shows the $\log k_R/k_S - 1/T$ relation of the addition products obtained for **P1_a**, **P1_b**, and **M1**. The products for **P1_a** showed an approximately linear correlation between $\log k_R/k_S$ and $1/T$, while those for **P1_b** and **M1** exhibited only an irregular relationship. These results suggest that the increase in the molecular weight of the catalyst revealed an effect similar to that observed previously with polymeric catalysts containing conformationally rigid pendants.

However, further work and consideration are required for fully explaining these observations.

Table I. The optical yields (%) of the addition products obtained with chiral amines at various reaction temperatures ($^\circ\text{C}$)

T $^\circ\text{C}$	P1_a	P1_b	M1	P2	M2
+50	2.2	4.7	5.0	0.9	1.8
+25	3.8	5.2	3.1	1.2	2.0
0	4.2	7.3	4.9	1.5	2.7
-20	4.5	10.0	4.7	1.0	1.5
-40	5.5	2.7	2.5	1.8 ^a	3.2
-60	6.2	5.2	3.8	1.3 ^a	2.8
-78	7.2	6.2	0.4	1.8	4.3

^a Addition products of *R*-configuration.

Figure 1. Plots of $\log k_R/k_S$ against $1/T$ in case of **P1_a** (●), **P1_b** (○), and **M1** (◐).

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