

Chiral Discrimination in the Isomerization of Racemic 1-Olefins by an Optically Active Organoaluminium–Nickel System

By GIAMPAOLO GIACOMELLI,* LUCIANO LARDICCI, RITA MENICAGLI, and LUIGI BERTERO

(Centro di Studio del CNR per le Macromolecole Stereordinate e Otticamente Attive, Istituto di Chimica Organica dell'Università, 56100 Pisa, Italy)

Summary Racemic 1-olefins are isomerized by the homogeneous (*R*)-*NN*-dimethyl-1-phenylethylamine–AlBu₃–Ni(*N*-methylsalicylideneamine)₂ catalytic system; both the unchanged 1-olefins and the (*E*)-2-olefins formed are optically active, indicating that the reaction is stereoselective.

KINETIC resolution of a racemic mixture and simultaneous synthesis of optically active compounds can be achieved by partial transformation of racemic substrates in the presence of optically active catalysts. The two enantiomers could, in principle, have different reactivities and optically active products would be obtained in such cases.

We have previously reported that the soluble catalytic system obtained by interaction of tri-isobutylaluminium with *N*-methylsalicylideneaminonickel(II) [Ni(mesal)₂] is active in the isomerization of 1-olefins, which are rapidly converted mainly into (*E*)-2-olefins.¹ These observations suggested the possibility of using an optically active ligand in the catalytic system as a chiral discriminating agent in the isomerization of racemic olefins. Here we report some results obtained in the isomerization of a series of racemic 1-olefins using a chiral amine–AlBu₃–Ni(mesal)₂ system.

The experiments were carried out in the absence of solvent, by treating AlBu₃ with 1 equiv. of (*R*)-*NN*-dimethyl-1-phenylethylamine, α_D^{25} (*l* 1) + 59.94° (neat),² at –20 °C and then adding the nickel complex at the same temperature. The mixtures were kept at room temperature for the required time, and the products were recovered at 0.1 mmHg in a liquid-air trap† and separated by preparative g.l.c. The results are reported in the Table.

The presence of the ligand causes an appreciable decrease in the isomerization rate compared with reactions carried out in the absence of the amine.¹ The nature and the structure of the 1-olefin seem to play an important role in stabilizing the catalytic system. Using 3-methylpent-1-ene‡ or 4-methylhex-1-ene,¹ a black powder precipitates within a few minutes at room temperature and isomerization does not proceed further. In other cases, a pale yellow homogeneous solution, which does not decompose even after several days, is formed when the olefin is added. Also, whereas 3-phenylpent-1-ene³ and 4-phenylhex-1-ene³ are slowly isomerized (5% after 15 days and 29% after 3 days, respectively), 5-methylhept-1-ene⁴ isomerizes faster (29% after 3 h). In all cases, both the unchanged 1-olefin and the (*E*)-2-olefin recovered are optically active, indicating

TABLE
Isomerization of racemic 1-olefins by the (*R*)-*NN*-dimethyl-1-phenylethylamine–AlBu₃–Ni(mesal)₂ system.^a

Substrate	Isomerization /%	Unchanged 1-olefin			<i>(E)</i> -2-olefin recovered		
			$[\alpha]_{365}^{25}$ (heptane)	Optical purity/%		$[\alpha]_{365}^{25}$ (heptane)	Optical purity/%
3-Phenylpent-1-ene	5	(+)-(S)	0.56°	0.27 ^b	—	—	—
4-Methylhex-1-ene	26	(–)-(S)	0.01°	0.09 ^c	(–)-(R)	0.26°	0.18 ^d
4-Phenylhex-1-ene	29	(+)-(S)	0.02°	0.05 ^e	(–)-(R)	0.34°	0.18 ^f
	35	(+)-(S)	0.05°	0.12 ^e	(–)-(R)	0.46°	0.24 ^f
5-Methylhept-1-ene	29	(+)-(S)	0.61°	1.78 ^g	(+)-(R)	0.12°	n.d.

^a Molar ratios: amine:Al 1:1, Al:Ni 50:1, C=C:Al 10:1. ^b Optically pure olefin has $[\alpha]_{365}^{25}$ 210°(heptane). ^c Maximum rotation $[\alpha]_{365}^{25}$ 10.7°(heptane). ^d Optically pure olefin has $[\alpha]_{365}^{25}$ 146°(heptane). ^e Maximum rotation $[\alpha]_{365}^{25}$ 42.0°(heptane). ^f Maximum rotation $[\alpha]_{365}^{25}$ 192°(heptane). ^g Optically pure olefin has $[\alpha]_{365}^{25}$ 34.2°(heptane).

† From the hydrolysed reaction mixtures, the amine, having unchanged optical purity, can be recovered quantitatively.

‡ The extent of isomerization is too low to allow any accurate evaluation of the optical activity.

stereoselective processes: in the cases investigated, the (*R*) enantiomer isomerized faster than the (*S*) one in the presence of the chiral catalytic system (Table).

It is noteworthy that stereoselection is operative only when a chiral amine-AlBu¹₃ solvate is used. In fact, no optically active products were recovered when 4-methylhex-1-ene was isomerized either in the presence of the (–)-(di-*op*)NiCl₂⁵-AlBu¹₃ system or in the presence of the catalyst

obtained by the reaction of Ni(mesal)₂ with the trialkylalane and then adding the amine. The present results therefore suggest, at least in these cases, that the catalytic species responsible for the chiral discrimination is a bimetallic system,⁶ in which nickel and aluminium atoms are close together.

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