with ammonia in DMF in the presence of CO_2: IR (neat) 3075 (C=CH), 1648 (C=C), 884 ($C=CH_2$) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.48 (m, 2 H), 1.64 (m, 3 H), 1.70 (m, 3 H), 2.00 (m, 4 H), 2.19 (s, 6 H), 2.75 (m, 2 H), 4.69 (m, 2 H), 5.32 (t, J = 7 Hz, 1 H); mass spectrum, m/e (relative intensity) 181 (2.1, $M^{+\cdot}$), 98 (10), 58 (100), 44 (33), 30 (7). Anal. Calcd for $C_{12}H_{23}N$: C, 79.49; H, 12.79; N, 7.72. Found: C, 79.66; H, 12.74; N, 7.76.

Acknowledgment. We gratefully acknowledge financial support from the "Deutsche Forschungsgemeinschaft" (DFG). Palladium and platinum salts were kindly donated by Degussa AG, Hanau. We also thank Dr. Wilhelm Meltzow for carrying out the GC work.

Registry No. 1, 77984-56-6; 2, 77984-57-7; 3, 77984-58-8; 4, 77984-59-9; 5, 77984-60-2; 6, 77984-61-3; 7, 77984-62-4; 8, 77984-63-5; ammonia, 7664-41-7; isoprene, 78-79-5; 2,7-dimethyl-1,3,7-octatriene, 36638-38-7; dimethylamine, 124-40-3; K_2PdCl_4, 10025-98-6; $P(OC_4H_9)_3$, 102-85-2; $Pd[P(OC_4H_9)_3]_4$, 77984-64-6; $P(OCH_3)_3$, 121-45-9; $P(OC_2H_5)_3$, 122-52-1; $P(O\text{-}i\text{-}C_3H_7)_3$, 116-17-6; $P(OCH_2CH=CH_2)_3$, 102-84-1; $P(OC_6H_5)_3$, 101-02-0; $P(C_4H_9)_3$, 998-40-3; $P(c\text{-}C_6H_{11})_3$, 15205-58-0; $P(C_6H_5)_3$, 603-35-0; $Ni[P(OC_2H_5)_3]_4$, 14839-39-5; $Pd[P(OC_2H_5)_3]_4$, 38266-18-1; $Pd[Ph_3P)_4$, 14221-01-3; $Pt[P(OC_2H_5)_3]_4$, 23066-15-1; $Pt[PPh_3]_4$, 14221-02-4; $Pd(acac)_2$, 14024-61-4.

Supplementary Material Available: IR spectra, ^1H NMR spectra, and mass spectra of the eight amines prepared (20 pages). Ordering information is given on any current masthead page.

Metal Catalysis in Organic Reactions. 12.[1] Asymmetric Induction Phenomena in the Isomerization of Racemic 1-Alkenes by Chiral Aluminum Solvate–Nickel Systems

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Received June 24, 1980

The isomerization of some racemic 1-alkenes in the presence of chiral amine–triisobutylaluminum solvate–bis(N-methylsalicylaldimine)nickel systems has been studied. The susceptibility to isomerization of the alkenes was found to be related to their structure and in particular to the nature of the amine used. However (E)-2-alkenes had been recovered as main products both in the absence and in the presence of the amine in the catalytic system. In most of the cases investigated, asymmetric induction phenomena take place, both in the isomerization reaction and in the competitive displacement reaction. The nature of the active species is discussed, and reasonable reaction paths are presented.

Recently we have reported the occurrence of chiral discriminating processes in the isomerization of racemic 1-alkenes by an optically active amine–i-Bu_3Al solvate–nickel system.[1] In continuing our research, we have now extended the investigations to elucidate some aspects of the isomerization of 1-alkenes by catalytic systems obtained through interaction of an i-Bu_3Al chiral solvate with bis(N-methylsalicylaldimine)nickel. The present paper deals therefore with some features of the dynamics and the stereochemistry of the reaction, along with a mechanistic approach to the mode of the action of the catalytic system.

Experimental Section

Boiling points are uncorrected. GLC analyses were performed on Perkin-Elmer F 30 and 3920B instruments (flame-ionization detectors; 200 × 0.30 cm columns packed with 5% silicone SE 301 on 80/100-mesh Chromosorb A at 40–200 °C, 8% Carbowax 20M + 2% KOH on 80/100-mesh Chromosorb W at 40–200 °C, 10% $AgNO_3$ + 30% glycerol on 80/100-mesh Chromosorb W DMCS at 20–80 °C, and 10% $AgNO_3$ + 30% ethylene glycol on 80/100-mesh Chromosorb P at 20–50 °C; nitrogen flow rate of 12–18 mL min^{-1}).

Preparative GLC was carried out on a Perkin-Elmer F 21 chromatograph using 300 × 0.80 columns filled with 8% Carbowax + 2% KOH on 80/100-mesh Chromosorb P (CwKOH) and 10% Ag NO_3 + 30% glycerol on 80/100-mesh Chromosorb W DMCS (Ag-G).

Spectral measurements were determined with the following instruments: IR, Perkin-Elmer Model 225; NMR, Varian XL A 100 at 100 MHz; mass spectra, Varian MAT CH7. Optical rotations were measured with a Perkin-Elmer 142 polarimeter; unless otherwise specified, rotations refer to pure liquid.

General Reagents. Triisobutylaluminum (Fluka A. G., Co., Buchs) and tris[(R)-2,3-dimethylbutyl]aluminum[2] were carefully redistilled under nitrogen and stored in sealed capillary glass vials in weighed amounts. Bis(N-methylsalicylaldimine)nickel [Ni(mesal)$_2$] and (−)-(DIOP)$NiCl_2$ were prepared and purified as reported elsewhere.[3,4] N,N-Dimethylmenthylamine (DMMA) [bp 92–93 °C (18 mmHg), $\alpha^{25}{}_D$ −46.59° (l = 1)], N,N-dimethylbornylamine (DMBA) [bp 54 °C (0.8 mmHg), $[\alpha]^{25}{}_D$ +24.94° (ethanol)], (R)-N,N-dimethyl-1-phenylethylamine (DMPEA) [bp 92–94 °C (30 mmHg), $[\alpha]^{25}{}_D$ +67.68° (heptane)] were prepared by the corresponding amines[5–7] by using a general method[8] for the methylation of amines. (L)-Sparteine was prepared from sparteine sulfate (Merck) according to a previously reported procedure.[9]

(RS)-4-Methyl-1-hexene was prepared according to established procedures.[10] (R)-4-Phenyl-1-hexene (bp 90–91 °C (18 mmHg), $[\alpha]^{25}{}_D$ −8.68°)[11] and (R)-4-phenyl-5-methyl-1-hexene (bp 97–98

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°C (13 mmHg), $[\alpha]^{25}_D$ +23.78°)[12] were obtained respectively from (*S*)-1-chloro-2-phenylbutane ($[\alpha]^{25}_D$ +5.48°)[11] and (*R*)-1-chloro-2-phenyl-3-methylbutane ($[\alpha]^{25}_D$ −0.25°)[12] via (4*S*)-1-bromo-2-ethoxy-4-phenylhexane[11] and (4*R*)-1-bromo-2-ethoxy-4-phenyl-5-methylhexane.[12] (*RS*)-4-Phenyl-1-hexene and (*RS*)-4-phenyl-5-methyl-1-hexene were prepared as reported.[11,12] (*RS*)-3-Phenyl-1-pentene [bp 79–80 °C (20 mmHg)] was prepared by pyrolysis of the oxide of (*RS*)-*N*,*N*-dimethyl-3-phenylpentylamine.[11]

Isomerization of (*R*)-4-Phenyl-1-hexene: (*R*)-(*E*)-4-Phenyl-2-hexene. $Ni(mesal)_2$ (0.0223 g, 0.068 mmol) was treated under a dry nitrogen atmosphere at 0 °C with triisobutylaluminum (0.6766 g, 3.412 mmol) in a two-necked 25-mL flask equipped with a magnetic stirrer, a Versilic silicone cap, and a glass stopcock.

(*R*)-4-Phenyl-1-hexene (5.464 g, 34.09 mmol) was then injected by hypodermic syringe through the cap, and the flask was placed in a thermostatic bath at 25 ± 1 °C. After 1 h, the residual reaction mixture was cautiously hydrolyzed with dilute sulfuric acid, extracted with pentane, and separated by means of preparative GLC (CwKOH, 120 °C, 180 mL min^{-1} of N_2). We obtained a mixture (2.34 g) of (*R*)-(*E*)- and -(*Z*)-4-phenyl-2-hexene (*E*/*Z* ratio ~8/1) and the *E* isomer was recovered by preparative GLC (Ag-G, 85 °C, 400 mL min^{-1} of N_2). The (*R*)-(*E*)-4-Phenyl-2-hexene (diasteroisomeric purity >99%) obtained showed the following: bp 74 °C (188 mmHg); $[\alpha]^{25}_D$ −43.70° (heptane); mass spectrum, *m*/*e* (relative intensity) 160 (M^+, 18), 132 (12), 131 (100), 129 (17), 128 (11), 117 (9), 116 (18), 115 (25), 103 (8), 91 (56), 77 (14), 65 (10), 53 (8), 51 (8), 41 (9), 39 (12); IR 3080–2860, 1940, 1870, 1800, 1740, 1600, 1490, 1450, 1375, 965, 910, 750, 697 cm^{-1}; NMR ($CDCl_3$, Me_4Si) δ 0.84 (3 H, t, CH_3CH_2), 1.62 (3 H, d, CH_3CH=), 1.53–1.82 (2 H, m, CH_2), 3.04 (1 H, q, *J* = 7 Hz, CHCH=), 5.34 (1 H, m, *J* = 7, 15 Hz), 5.57 (1 H, dd, *J* = 7, 15 Hz), 7.16 (5 H, m, C_6H_5).

Hydroalumination of (*R*)-(*E*)-4-Phenyl-2-hexene. (*R*)-(*E*)-4-Phenyl-2-hexene (0.897 g, 5.60 mmol) in 10 mL of anhydrous heptane was treated, under a dry nitrogen atmosphere, with diisobutylaluminum hydride (0.876 g, 6.16 mmol) in a three-necked 50-mL flask equipped with a magnetic stirrer, a Versilic silicone cap, a dropping funnel, and a condenser. The mixture was stirred at 90 °C for 8 days; the crude product, obtained upon hydrolysis with diluted sulfuric acid, was purified by treatment with Br_2 in CCl_4. Upon distillation (*R*)-3-phenylhexane (0.59 g; bp 85 °C (18 mmHg); $[\alpha]^{25}_D$ +3.31°)[13] was obtained.

Isomerization of (*R*)-4-Phenyl-5-methyl-1-hexene: (*S*)-(*E*)-4-Phenyl-5-methyl-2-hexene. As previously reported, (*R*)-4-phenyl-5-methyl-1-hexene (3.66 g, 21.00 mmol) was treated with triisobutylaluminum (0.4168 g, 2.10 mmol) in presence of $Ni(mesal)_2$ (0.0137 g, 0.042 mmol). By the purification method previously described we obtained (*S*)-(*E*)-4-phenyl-5-methyl-2-hexene (diastereoisomeric purity >98%) having the following: bp 106 °C (18 mmHg), $[\alpha]^{25}_D$ +79.91° (heptane); mass spectrum, *m*/*e* (relative intensity) 175 (M^+ + 1, 19), 174 (M^+, 100), 132 (94), 131 (100), 130 (23), 129 (67), 128 (37), 117 (35), 116 (62), 115 (68), 104 (30), 103 (16), 92 (15), 91 (99), 77 (22), 63 (13), 52 (14); IR 3080–2860, 1940, 1865, 1795, 1735, 1600, 1490, 1380, 1365, 963, 750, 697 cm^{-1}; NMR ($CDCl_3$, Me_4Si) δ 0.73 (3 H, d, CH_3CH), 0.93 (3 H, d, CH_3CH), 1.64 (3 H, d, CH_3CH=), 1.68–2.02 (1 H, m, $(CH_3)_2CH$), 2.82 (1 H, t, *J* = 8.4 Hz, CHCH=), 5.27 (1 H, m, *J* = 8.4, 15.8 Hz), 5.54 (1 H, dd, *J* = 8.4, 15.8 Hz), 7.20 (5 H, m, C_6H_5).

Hydroalumination of (*S*)-(*E*)-4-Phenyl-5-methyl-2-hexene. As previously described, (*S*)-(*E*)-4-phenyl-5-methyl-2-hexene (0.65 g, 3.73 mmol) was reacted with diisobutylaluminum hydride (0.592 g, 4.10 mmol). After hydrolysis and purification, (*R*)-2-methyl-3-phenylhexane[12] [bp 98 °C (14 mmHg); $[\alpha]^{25}_D$ +4.54°] was obtained.

Hydroalumination of (*R*)-4-phenyl-5-methyl-1-hexene. Analogously, (*R*)-4-phenyl-5-methyl-1-hexene (0.50 g, 2.90 mmol), upon treatment with diisobutylaluminum hydride (0.460 g, 3.19 mmol), gave (*R*)-2-methyl-3-phenylhexane,[12] $[\alpha]^{25}_D$ +4.61°.

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General Procedure of Isomerization of Racemic 1-Alkenes. All reactions were carried out at least in duplicate under a dry nitrogen atmosphere.

In a typical reaction, a two-necked 25-mL flask was fitted with a stirring bar, a glass stopcock, and a Versilic silicone cap.

The vessel was charged with triisobutylaluminum (0.318 g, 1.60 mmol), and then *N*,*N*-dimethylbornylamine (0.30 g, 1.64 mmol) was added at −20 °C.

The temperature was raised to 0 °C, and $Ni(mesal)_2$ (0.010 g, 0.032 mmol) was added by means of a sealed angular piece of glass tubing; after a 2-min agitation, the olefin, (*RS*)-4-phenyl-1-hexene, was injected by hypodermic syringe through the cap. The resulting mixture was stirred at room temperature (20 ± 5 °C) for 118 h. Hydrolysis was carried out with dilute sulfuric acid, and the organic phase was extracted with pentane; the combined extracts were washed with aqueous sodium bicarbonate and then dried over sodium sulfate. By distillation we obtained a crude mixture (α^{25}_D +0.34° (*l* = 1)). The components were separated by preparative GLC (3-m column, CwKOH, 120 °C, 18 mL min^{-1} of N_2), and we obtained (*S*)-3-phenylhexane ($[\alpha]^{25}_{365}$ +0.331° (heptane)), (*S*)-4-phenyl-1-hexene ($[\alpha]^{25}_{365}$ +0.069° (heptane)), and a mixture of (*S*)-(*E*)- (77%) and (*S*)-(*Z*)-4-phenyl-2-hexene (33%) ($[\alpha]^{25}_D$ +1.61°, $[\alpha]^{25}_{365}$ +6.43° (heptane)).

Results and Discussion

Isomerization of 1-Alkenes by Triisobutylaluminum Solvate–Nickel Systems. The racemic 1-alkenes we have predominately used in these isomerization experiments were 4-methyl-1-hexene, 4-phenyl-1-hexene, and 4-phenyl-5-methyl-1-hexene. According to information previously reported for 4-methyl-1-hexene,[10] the isomerization reactions of the phenyl-1-alkenes by the triisobutylaluminum–$Ni(mesal)_2$ catalytic system (molar ratio of Al/Ni = 50 and C=C/Al = 10)[10] proceeded very rapidly, conversions being complete after only 1 h at room temperature. In all cases, owing to the competitive displacement reaction,[14] the 1-alkenes were converted partially into the corresponding organoaluminum compounds (30%) and hence, after hydrolysis, into the phenylalkanes and a mixture of (*E*)- and (*Z*)-2-alkenes, the *E* isomer being, however, predominant with respect to the *Z* one (*E*/*Z* ratio of ~9). No traces of other alkenes were detected in the reaction mixtures.

The influence of a modified aluminum–nickel catalytic system[1] on the dynamics and the stereochemistry of isomerization of 1-alkenes has been investigated by using catalysts obtained through interaction of *i*-Bu_3Al solvates with $Ni(mesal)_2$. Optically active *N*,*N*-dimethylalkylamines were used as ligands to the aluminum atom in order to check, at the same time, eventual chiral discriminating processes.

The experiments were carried out in the absence of solvents by treating *i*-Bu_3Al with 1 equiv of the chiral amine at −20 °C. The nickel complex was then added at 0 °C after 5 min, followed by the 1-alkene at the same temperature, and the reaction mixtures were kept at room temperature (20 ± 5 °C) for the required time. The addition of the alkene results in the formation of red or yellow homogeneous solutions, which sometimes decompose depending on the nature of both the ligand on the aluminum atom and and the 1-alkene.

Generally, the presence of the ligand on the aluminum atom causes an appreciable decrease of the isomerization rate with respect to the reaction carried out in the absence of the amine[10] along with a decreased *E*/*Z* ratio. In the case of 4-methyl-1-hexene the reaction mixtures yielded a black precipitate within a few minutes, and the isomerization rate dropped drastically. Only when sparteine was used as the ligand were the reaction mixtures homogeneous for all the reaction time. Moreover, 4-methyl-1-hexene isomerizes faster in the presence of sparteine than in its absence:[10] the isomerization was completed within 15 min at 25 °C, and, along with the isomers of 4-methyl-2-hexene, 3-methyl-2-hexene was formed in a good yield too (35%). However, at 0 °C, the isomerization rate decreases noticeably: after 2 h, only 34% of the olefin was converted, and no 3-methyl-2-hexene was detected in the reaction mixture.[15]

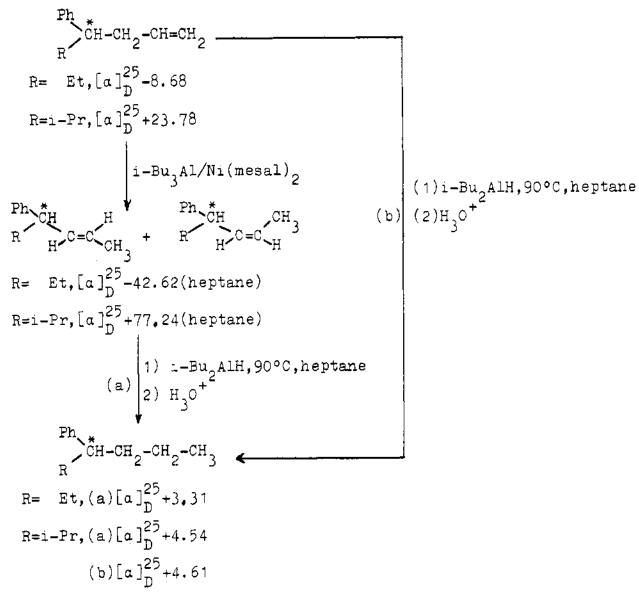
When the substrate contains a phenyl group, as in the case of 4-phenyl-1-hexene and 4-phenyl-5-methyl-1-hexene, the isomerizing reaction mixtures remain substantially homogeneous regardless of the nature of the amine bound to the aluminum atom. Even in these cases, the presence of the amine results in lowering of the isomerization rate with respect to the reaction carried out without any ligand. It is noteworthy that, contrary to what is observed for 4-methyl-1-hexene, the alkane is often present in the hydrolyzed reaction mixtures (ca. 30%), being derived from the corresponding trialkylalane formed through nickel-catalyzed displacement reaction.[14]

The isomerization rate depends on both the nature of the amine and the structure of the 1-alkene. In fact, 4-phenyl-1-hexene is isomerized faster in the presence of *N*,*N*-dimethylmenthylamine (DMMA; 45% after 22 h) than of *N*,*N*-dimethylbornylamine (DMBA; 42% after 30 h) and more slowly in the presence of *N*,*N*-dimethyl-α-phenylethylamine (DMPEA; 43% after 110 h). However, in all cases investigated, 4-phenyl-1-hexene is isomerized faster than 4-phenyl-5-methyl-1-hexene.

(*R*)-(*E*)-4-Phenyl-2-hexene and (*S*)-(*E*)-4-Phenyl-5-methyl-2-hexene. Contrary to what was reported for 4-methyl-1-hexene,[10] no data were available on the maximum rotations of the optically active isomers of the phenyl-1-alkenes used. Therefore it was necessary to undertake a prior determination of the maximum rotatory powers of the configurational isomers of both optically active 4-phenyl-2-hexene and 4-phenyl-5-methyl-2-hexene in order to evaluate accurately the extent of the asymmetric induction eventually encountered.

The preparation of these optically active 2-alkenes was easily achieved via the isomerization of the corresponding optically active 1-alkenes.[11,12] Under the experimental conditions reported,[10] (*R*)-4-phenyl-1-hexene ($[\alpha]^{25}_D$ −8.68°)[11] and (*R*)-4-phenyl-5-methyl-1-hexene ($[\alpha]^{25}_D$ +23.78°)[12] yielded 65% (*R*)-(*E*)-4-phenyl-2-hexene ($[\alpha]^{25}_D$ −42.62° (heptane)) and 63% (*S*)-(*E*)-4-phenyl-5-methyl-2-hexene ($[\alpha]^{25}_D$ +77.24° (heptane)), respectively (Scheme I).[16] To evaluate the maximum rotatory power of the (*E*)-2-alkenes recovered and consequently the extent of racemization during the isomerization procedures, we converted samples of these alkenes into the corresponding optically active alkanes via hydroalumination with diisobutylaluminum hydride in boiling heptane.[17] While hydroalumination of (*R*)-(*E*)-4-phenyl-2-hexene gave a sample of (*R*)-3-phenylhexane,[11] having the same optical purity of the starting 1-alkene,[11] from (*S*)-(*E*)-4-phenyl-5-methyl-2-hexene was recovered a sample of (*R*)-2-methyl-3-phenylhexane[12] having a rotatory power higher (23%) than the maximum rotatory power reported in the literature[12,18] (Scheme I). Because of this discrepancy, a

Scheme I



sample of (*R*)-4-phenyl-5-methyl-1-hexene[12] was converted into (*R*)-2-methyl-3-phenylhexane by a reaction sequence not affecting the chiral carbon atom[17] (Scheme I). Thus, it was possible to establish, in addition to the maximum rotatory power of the phenylalkane, that the sample of (*S*)-(*E*)-4-phenyl-5-methyl-2-hexene recovered had substantially the same optical purity as the starting 1-alkene.[12]

The overall results obtained indicate that, even in these cases, the isomerization process is stereospecific and that the syntheses of optically active 2-alkenes can be conveniently achieved also through preparation and isomerization of the corresponding 1-alkene.[11]

Chiral Discriminating Phenomena in the Isomerization of Racemic 1-Alkenes. Up to now, stereoselective processes have been observed in the isomerization of a series of racemic 1-alkenes[19] or allyl alcohols[20] by suitable chiral catalytic systems, containing, however, the chiral ligand directly bound to the transition metal atom.

We have previously showed that chiral discriminating phenomena are operative also when a chiral amine–*i*-Bu_3Al solvate is used as a cocatalyst.[1] In fact, by using the DMPEA–*i*-Bu_3Al–Ni(mesal)$_2$ catalytic system, both the unchanged 1-alkene and the (*E*)-2-alkene recovered were optically active, indicating that one enantiomer is isomerized faster than the other.[1] This finding prompted us to investigate the factors responsible for the asymmetric induction phenomena and to verify if such a reaction could be generally extended to other chiral amine–*i*-Bu_3Al solvates.

The results obtained have shown that in the case of 4-methyl-1-hexene, the crude reaction mixtures, upon hydrolysis, showed defined optical activities only when DMPEA was used as the chiral amine,[1] while, in the case of the phenylalkenes, optically active products were recovered from the hydrolyzed reaction mixtures (Table I). Contrary to what was previously reported for the DMPEA–*i*-Bu_3Al–Ni(mesal)$_2$-catalyzed isomerizations,[1] when DMBA–ligand systems were used, the phenylalkane

(15) This result seems to indicate that 3-methyl-2-hexene arises from successive isomerization of 4-methyl-2-hexene.

(16) Because of the low concentration of the *Z* isomers in the reaction mixtures, it was impossible to recover chemically pure samples of the (*Z*)-2-alkenes. However, it should be reasonably to attribute $[\alpha]^{25}_D$ −185° (heptane) and +167° (heptane) to (*R*)-(*Z*)-4-phenyl-2-hexene and (*S*)-(*Z*)-4-phenyl-5-methyl-2-hexene, respectively, on the basis of the optical rotations of mixtures containing known amounts of the *E* isomers.

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(18) This erroneous value might be due to racemization phenomena encountered during conversion of the 1-alkene into the corresponding phenylalkane by hydrogenation over Raney Ni.[12]

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Table I. Isomerization of Racemic 1-Alkenes by the L-i-Bu_3Al–Ni(mesal)$_2$ Catalytic System[a]

			recovered alkane			recovered 1-alkene			recovered 2-alkenes			
entry	ligand (L)	substrate	config	$[\alpha]^{25}_{365}$,[b] deg	op, %	config	$[\alpha]^{25}_{366}$,[b] deg	op, %	% E isomer in sample	config	$[\alpha]^{25}_{365}$,[b] deg	op, %[c]
1[d]	DMBA	3-phenyl-1-pentene				(−)-(R)	0.670	0.32[e]				
2		4-phenyl-1-hexene	nd	nd	nd	(+)-(S)	0.154	0.37[f]	79.7	(+)-(S)	2.07	0.67[g]
3			(+)-(R)	0.331	2.97[h]	(+)-(S)	0.069	0.16[f]	76.9	(+)-(S)	6.43	1.96[i]
4[j]			(−)-(S)	1.38	12.4[h]	(−)-(R)	1.03	2.45[f]	nd	(+)-(S)	0.13	nd
5		4-phenyl-5-methyl-1-hexene	(−)-(S)	0.096	0.77[k]	(+)-(S)	0.054	0.06[e]	72.6	(+)-(S)	3.27	0.76[m]
6[n]	DMMA	4-phenyl-1-hexene	(−)-(S)	0.377	3.38[h]				nd	nd	nd	nd
7			(−)-(S)	0.190	1.71[h]		0	0	85.2	(−)-(R)	0.476	0.17[o]
8[p]			(−)-(S)	0.079	0.71[h]		0	0	85.2	(−)-(R)	0.476	0.17[o]
9		4-phenyl-5-methyl-1-hexene	(−)-(S)	0.020	0.16[k]	(+)-(R)	0.089	0.10[l]	73.8	(−)-(R)	0.524	0.12[q]

[a] Reactions carried out at room temperature: $[i\text{-}Bu_3Al]/[Ni(mesal)_2] = 50$; $[RCH{=}CH_2]/[i\text{-}Bu_3Al] = 10$; nd = not determined; op = optical purity. [b] In heptane. [c] Determined by comparison with the maximum rotatory power, in heptane, of mixtures having the same percentage composition of the optically pure E and Z isomers. [d] The 1-alkene was 35% isomerized. [e] $[\alpha]^{25}_{365}$(max) 210°. [f] $[\alpha]^{25}_{365}$(max) 42.0°. [g] $[\alpha]^{25}_{365}$(max) 311°. [h] $[\alpha]^{25}_{365}$(max) 11.14° (c 9.80). [i] $[\alpha]^{25}_{365}$(max) 328°. [j] Tris[(R)-2,3-dimethylbutyl]aluminum ($[\alpha]^{25}_{D}$ −34.20° (toluene)) was used instead of i-Bu_3Al; the mixture contained 12.4% of the alkane, 62.6% of 1-alkene, and 25% of the 2-alkenes. [k] $[\alpha]^{25}_{365}$(max) 12.49° (c 6.22). [l] $[\alpha]^{25}_{365}$(max) 93.3°. [m] $[\alpha]^{25}_{365}$(max) 438°. [n] The 1-alkene was completely isomerized. [o] $[\alpha]^{25}_{365}$(max) 277°. [p] The mixture contained only 12% of the 2-alkenes. [q] $[\alpha]^{25}_{365}$(max) 434°.

Table II. Isomerization of (RS)-4-Methyl-1-hexene by the (−)-DIOP-i-Bu_3Al–Ni(mesal)$_2$ Catalytic System[a]

					recovered alkane			recovered 1-alkene			recovered 2-alkene		
entry	[DIOP]/$[NiX_2]$ ratio	reaction time, h	% alkane	% isomeriz	config	$[\alpha]^{25}_{365}$,[b] deg	op, %[c]	config	$[\alpha]^{25}_{365}$,[b] deg	op, %[d]	config	$[\alpha]^{25}_{365}$,[b] deg	op, %[e]
10[f]	1	1	nd	11					0	0		0	0
11	3	72	6	6	(+)-(S)	nd	nd	(+)-(R)	0.043	0.40	nd	nd	nd
12	3	166	24	12	(+)-(S)	0.61	1.77	(+)-(R)	0.061	0.57	(−)-(R)-(E)	0.761	0.52
13	7	166	13	6	nd	nd	nd	(+)-(R)	0.059	0.55	(−)-(R)-(E)	0.820	0.56
14	16	340	6	13	(+)-(S)	1.23	3.58	(+)-(R)	0.017	0.16	(−)-(R)-(Z)[g]	0.784[g]	0.73[g]
15	50	500	0	2[h]				(+)-(R)	0.004	0.04	(+)-(S)-(Z)[g]	1.828[g]	1.70[g]

[a] Reactions carried out at room temperature; $[i\text{-}Bu_3Al]/[Ni(mesal)_2] = 50$; $[RCH{=}CH_2]/[i\text{-}Bu_3Al] = 10$; nd = not determined; op = optical purity. [b] In heptane. [c] $[\alpha]^{25}_{365}$(max) 37.0° (heptane). [d] $[\alpha]^{25}_{365}$(max) 10.70° (heptane). [e] $[\alpha]^{25}_{365}$(max) 146.3° (heptane). [f] (−)-DIOP)$NiCl_2$ was used as the nickel salt. [g] (Z)-4-Methyl-2-hexene was recovered as the main product, $[\alpha]^{25}_{365}$(max) 107.7° (heptane). [h] Only traces of (E)-4-methyl-2-hexene were formed.

was also optically active, and the unchanged 1-alkene and the 2-alkenes recovered had the same chirality,[21] opposite that of the alkane, even if their optical purities were different (entries, 2, 3, and 5).

These findings indicate, therefore, that both isomerization and displacement reactions[14] occur with chiral discriminating phenomena, the extent of which seems to depend on the 1-alkene structure and on the reaction conversions. The result obtained by using an optically active trialkylalane, tris[(*R*)-2,3-dimethylbutyl]aluminum,[2] instead of *i*-Bu_3Al in the catalytic complex (entry 4) is worthy of note too. In this case, the reaction proceeds with an enhanced degree of asymmetric induction and with different stereochemistry, yielding the alkane and the 2-alkene with the same chirality. Moreover, the chiralities of the alkane and of the 1-alkene are opposite those of the same compounds obtained in the reaction carried out with *i*-Bu_3Al (entries 2, 3).

Chiral discrimination in both isomerization and displacement reactions was observed in the presence of the DMMA–*i*-Bu_3Al–Ni(mesal)$_2$ catalytic system too (Table I). In this context, it is to be noted that unchanged 4-phenyl-1-hexene is still racemic, and the 3-phenylhexane[11] and the 4-phenyl-2-hexenes recovered had opposite chiralities[21,22] (entries 7, 8), while 2-phenyl-3-methylhexane[12] and 4-phenyl-5-methyl-2-hexene had the same chirality[21] (opposite to that of the unchanged 1-alkene,[12] entry 9). Surprisingly, whereas the optical purity of 4-phenyl-2-hexene seems to be independent of the conversion of the reaction, the optical purity of the corresponding alkane increases as the isomerization conversion increases (Table I). This last experimental finding is highly unusual.[23]

Mechanism of the Reaction. On the basis of previous considerations,[10] the alkene isomerization by an *i*-Bu_3Al solvate–Ni(mesal)$_2$ system can also be interpreted in terms of a hydride nickel addition–elimination mechanism, as the dynamics of the isomerization process do not change substantially with respect to the reaction carried out in the absence of any ligand.[10] However, the present results suggest that the actual catalytic species is a very complex system, in which nickel and aluminum atoms are close together[1] and which contains the chiral amine too. The presence of aluminum atoms in the catalytic species is essentially confirmed by the fact that different stereochemical paths are followed with an optically active trialkylalane instead of *i*-Bu_3Al (entries 3 and 4, Table I).

With regard to the influence of the amine, the question arises if the ligand responsible of the chiral discrimination may be directly coordinating the nickel atom in the catalytic system. In order to obtain further information, we have carried out some isomerization runs with the *i*-Bu_3Al–Ni(mesal)$_2$ catalytic system in the presence of variable amounts of (–)-DIOP[24] (Table II). Under the experimental conditions adopted, the isomerization rate of 4-methyl-1-hexene decreases gradually with an increasing DIOP/NiX_2 molar ratio, as does the incidence of the displacement reaction. Moreover, the (*Z*)-2-isomer is more favored than the (*E*)-2-isomer at high DIOP/NiX_2 molar ratios.

However, the main features of these reactions are that no optically active product was recovered when the 1-alkene was isomerized in the presence of (–)-(DIOP)-$NiCl_2$[4]–*i*-Bu_3Al system[1] (entry 10) and that the optical purities of both the alkane and the 2-alkene increase as the DIOP/NiX_2 molar ratio increases (entries 11–14, Table II). When the DIOP–*i*-Bu_3Al–Ni(mesal)$_2$ system is used, a reverse configuration of the 2-alkene recovered is also observed (entry 15). These stereochemical results therefore suggest that the chiral ligand responsible for the chiral discrimination should still be bound to the aluminum atom in the catalytic species. Unfortunately, the small free-energy differences involved do not permit one to rationalize accurately all the experimental data obtained, even if it is certain that both the displacement and isomerization reactions proceed with defined chiral discriminating phenomena.

Registry No. (*RS*)-3-Phenyl-1-pentene, 78086-96-1; (*RS*)-4-phenyl-1-hexene, 78086-97-2; (*RS*)-4-phenyl-5-methyl-1-hexene, 78086-98-3; (*RS*)-4-methyl-1-hexene, 13643-03-3; (*R*)-4-phenyl-1-hexene, 20068-21-7; (*R*)-(*Z*)-4-phenyl-2-hexene, 78086-99-4; (*R*)-(*E*)-4-phenyl-2-hexene, 78087-00-0; (*R*)-3-phenylhexane, 78019-43-9; (*R*)-4-phenyl-5-methyl-1-hexene, 78019-44-0; (*S*)-(*E*)-4-phenyl-5-methyl-2-hexene, 78019-45-1; (*R*)-2-methyl-3-phenylhexane, 78019-46-2; (*S*)-4-phenyl-1-hexene, 78019-47-3; (*S*)-(*E*)-4-phenyl-2-hexene, 78087-01-1; (*S*)-(*Z*)-4-phenyl-2-hexene, 78087-02-2; (*S*)-3-phenylhexane, 35216-62-7; (*S*)-2-methyl-3-phenylhexane, 36667-57-9; (*R*)-3-phenyl-1-pentene, 20068-20-6; (*S*)-4-phenyl-5-methyl-1-hexene, 36667-53-5; (*R*)-(*E*)-4-phenyl-5-methyl-2-hexene, 78019-48-4; (*S*)-3-methylhexane, 6131-24-4; (*R*)-4-methyl-1-hexene, 44565-04-0; (*R*)-(*E*)-4-methyl-2-hexene, 78087-03-3; (*R*)-(*Z*)-4-methyl-2-hexene, 78087-04-4; (*S*)-(*Z*)-4-methyl-2-hexene, 29751-21-1; triisobutylaluminum, 100-99-2; tris[(*R*)-2,3-dimethylbutyl]aluminum, 65337-63-5; bis(*N*-methylsalicylaldimine)nickel, 14322-02-2; (–)-(DIOP)-$NiCl_2$, 41677-72-9; DMMA, 54234-81-0; DMBA, 78019-49-5; DMPEA, 19342-01-9; diisobutylaluminum hydride, 1191-15-7.

(21) Here we refer to the chirality of the asymmetric carbon atom, not to the conventional configuration, attributed on the basis of the IUPAC rules for the nomenclature of organic chemistry [*J. Org. Chem.* **1970**, *35*, 2849].

(22) The optical purity of the 2-alkenes was determined on the basis of the maximum optical rotations of mixtures of the (*E*)- and (*Z*)-2-alkenes, having the same percentage composition. The accuracy of this method was tested by reacting the mixture of (*E*)- and (*Z*)-4-phenyl-2-hexene ($[\alpha]^{25}_{365}$ +6.43°, optical purity 1.96% (calcd, entry 3, Table I)) with *i*-Bu_2AlH. From the hydrolysis, (*S*)-3-phenylhexane[11] ($[\alpha]^{25}_{365}$ –0.227° (heptane), optical purity 1.97%) was recovered.

(23) A hazardous mechanistic hypothesis might tentatively be based on an enantiodifferentiating reversible shift of the nickel (or aluminum) atom from the terminal carbon atom directly to the asymmetric one of the alkyl group bound to the metal atom.

(24) Kagan, H. B.; Dang, T. P. *J. Am. Chem. Soc.* **1972**, *94*, 6429.