

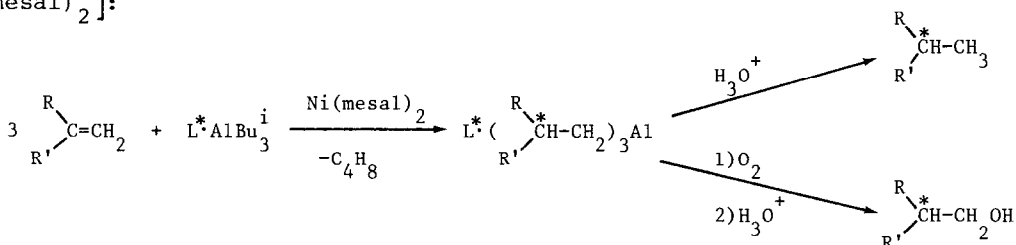
NICKEL-CATALYZED STEREODIFFERENTIATING DISPLACEMENT REACTION BETWEEN PROCHIRAL 1-ALKENES AND OPTICALLY ACTIVE ORGANOALUMINIUM SOLVATES.

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The displacement reaction between optically active AlBu_3^i solvates and vinylidene alkenes, in the presence of $\text{Ni}(\text{mesal})_2$, affords optically active trialkylalanes and hence, upon hydrolysis or oxidative procedure, alkanes or 1-alkanols.

In an earlier paper,¹ we have reported that chiral discrimination phenomena are operative in the isomerization of racemic 1-alkenes by the homogeneous (R)-N,N-dimethyl-1-phenylethylamine- AlBu_3^i - $\text{Ni}(\text{N-methylsalicylideneamine})_2$ catalytic system. This finding has prompted us to further investigate the possibility to use chiral organoaluminium solvates for converting prochiral substrates into optically active intermediates. Herein we report that a stereodifferentiating displacement reaction between prochiral vinylidene alkenes and chiral AlBu_3^i solvates occurs in the presence of N-methylsalicylideneamine nickel (II) [$\text{Ni}(\text{mesal})_2$]:



The experiments were carried out at room temperature and in the absence of solvent, by treating the chiral AlBu_3^i solvate¹ with 3 equivalents of the 1-alkene, in the presence of $\text{Ni}(\text{mesal})_2$ (molar ratio Al/Ni=50). (-)-N,N-Dimethylmenthylamine (DMMA),² (+)-N,N-dimethylbornylamine (DMBA),³ (+)(R)-N,N-dimethyl-1-phenylethylamine (DMPEA),⁴ (+)(S,S)-2,3-dimethoxy-1,4-bis(N,N-dimethylamino)butane (DDB),⁵ and (-)DIOP⁶ were used as chiral ligands. The extent of the asymmetric induction was estimated by converting the optically active trialkylalane formed into the corresponding alkane^{7,8} or alcohol,^{7,9} by hydrolysis or

oxidative procedure respectively. The results obtained are collected in the Table.

The displacement reaction of 1-alkenes with AlBu_3^i solvates is generally slow in comparison with the reaction carried out with uncomplexed triisobutylaluminium (entry 1). Nevertheless the yields are practically quantitative and high conversions can be accomplished by prolonging the reaction time. The rate of the reaction depends moreover on the nature and steric requirements of the 1-alkene and mainly on the nature of the ligand to the aluminium atom: in particular no displacement reaction occurs when the DMPEA-AlBu_3^i solvate is used (entry 4). However, in all the cases investigated, optically active products were recovered from the reaction mixtures, indicating the occurrence of enantioface differentiating processes. The enantiomeric purities of the products are generally related to the nature of the ligand used. In this context, it is noteworthy that (-)DIOP, which is reported to determine appreciable asymmetric induction values, *e.g.* in metal-catalyzed cross-coupling reactions,¹⁰ gives the lowest enantioselectivity in this kind of reaction (entry 8). Good results are obtained using DDB and DMMA; in this last case, the enantiomeric purity of the products is somewhat sensitive to the size of the substituents on the starting 1-alkene and the trend of the extent of enantioselectivity in the series of the phenylalkanes used (entries 2,3,5,6, and 10) resembles that encountered in the reduction of the analogous series of alkyl phenyl ketones by optically active trialkylalanes.¹¹

The following is a typical experimental procedure. An oven-dried 25-ml round-bottom flask, equipped with a septum-capped side arm, magnetic stirring bar, and a stopcock adaptor, was charged, under a dry argon atmosphere, with AlBu_3^i (3.42 mmol) and then (-)DMMA, $\alpha_D^{25} -46.59^\circ$ ($l=1$) was added at -20°C . The temperature was raised to 0°C and $\text{Ni}(\text{mesal})_2$ (0.068 mmol) was added by means of a sealed angular piece of glass tubing; after a 2-min agitation, 1-phenyl-2-methyl-1-butene (10.26 mmol) was injected by hypodermic syringe through the cap. The resulting mixture was stirred at room temperature for 40 h, then anhydrous heptane (10 ml) was added and dry air was bubbled into the solution for 8 h. After hydrolysis with dilute sulphuric acid, (-) (R)-2-phenyl-3-methyl-1-butanol (61% yield), $[\alpha]_D^{25} -1.41$ (neat),⁷ was recovered.

As shown, the reaction is easy to perform and large-scale procedures do not cause any problem. Moreover, the chiral ligand may be recovered quantitatively and recycled without any noticeable racemization. Therefore, the reac-

TABLE

Entry ^a	$\begin{array}{c} R_1 \\ \diagdown \\ C=CH_2 \\ \diagup \\ R_2 \end{array}$		Ligand L*	Time (h)	Conversion % (by GLC)	X	$\begin{array}{c} R \\ \diagdown \\ CH-CH_2X \\ \diagup \\ R' \end{array}$		Optical yield %, ee (confign)
	R	R'					[α] _D ²⁵ (c, solvent)	[α] _D ²⁵ (c, solvent)	
1	Ph	Me	(-)-DMMA	1	100	H			
2			(-)-DMMA	30	69	OH	+0.76 (neat)		4 (R) ^b
3	Ph	Et	(-)-DMMA	30	46	H	-2.44 (neat)		8 (R) ^c
4	Ph	Pr ⁱ	(+)-DMPEA	250	0	H			
5			(-)-DMMA	40	67	H	-2.82 (neat)		10 (R) ^d
6			(-)-DMMA	40	68	OH	-1.41 (neat)		11 (R) ^e
7			(+)-DDB	180	33	H	+5.28 (neat)		19 (S) ^d
8	Ph	Bu ^t	(-)-DIOP	140	22	H	-0.05 (11.5, heptane)		0.2 (R) ^f
9			(+)-DMBA	200	50	H	+0.12 (10.6, heptane)		0.5 (S) ^f
10			(-)-DMMA	160	85	H	-1.63 (6.1, heptane)		7 (R) ^f
11			(+)-DDB	250	29	H	+5.30 (6.2, heptane)		23 (S) ^f
12	Me	Bu ^t	(-)-DMMA	24	76	OH	-11.02 (3.2, ethanol)		27 (R) ^g

^a The reactions were carried out at room temperature (ca 20° C), without any solvent. ^b [α]_D²⁵ (max) 10.09 (neat)(Ref.7).

^c [α]_D²⁵ (max) 29.26 (neat)(Ref.7). ^d [α]_D²⁵ (max) 28.18 (neat)(Ref.7). ^e [α]_D²⁵ (max) 12.59 (neat)(Ref.7). ^f [α]_D²⁵ (max) 23.33 (heptane). ^g [α]_D²⁵ (max) 41.4 (ethanol)(Ref.9).

tion appears to be of a potentially practical value for the preparation of optically active products from vinylidene alkenes via optically active trialkylalanes.

As regards the mechanistic aspects of the reaction,^{12,13} it is noteworthy that no stereodifferentiating process was observed in the displacement reaction between AlBu_3^i and 2-phenyl-3,3-dimethyl-1-butene in the presence of (-) DIOP NiCl_2 . The overall results suggest therefore that, according to that previously reported,¹ the actual catalyst is a complex system, in which nickel and aluminium atoms are close together, containing the chiral ligand bound to the aluminium atom too.

REFERENCES

1. G.Giacomelli, L.Lardicci, R.Menicagli, and L.Bertero, *J.Chem.Soc.,Chem.Commun.*, 633 (1979).
2. A.C.Cope and E.M.Acton, *J.Am.Chem.Soc.*, 80, 355 (1958).
3. J.Mc Kenna and J.B.Slinger, *J.Chem.Soc.*, 2759 (1958).
4. H.R.Snyder and J.H.Brewster, *J.Am.Chem.Soc.*, 71, 291 (1949).
5. D.Seebach, H.Dörr, B.Bastani, and V.Ehrig, *Angew.Chem.*, 81, 1002 (1969).
6. H.B.Kagan and T.P.Dang, *J.Am.Chem.Soc.*, 94, 6429 (1972).
7. L.Lardicci and R.Menicagli, *Atti Soc.Toscana Sci.Nat.,Pisa,Mem.,P.V.Ser.A*, 77, 25 (1970).
8. L.Lardicci, R.Menicagli, A.M.Caporusso, and G.Giacomelli, *Chem. & Ind.(London)*, 184 (1973).
9. A.M.Caporusso, G.Giacomelli, and L.Lardicci, *Atti Soc.Toscana Sci.Nat.Pisa,Mem.,P.V.Ser.A*, 80, 40 (1973).
10. G.Consiglio and C.Botteghi, *Helv.Chim.Acta*, 56, 460 (1973); Y.Kiso, K.Tamao, N.Miyake, K.Yamamoto, and M.Kumada, *Tetrahedron Lett.*, 3 (1974); T.Hayashi, M.Tanaka, and I.Ogata, *ibid*, 295 (1977).
11. G.Giacomelli, R.Menicagli, and L.Lardicci, *J.Org.Chem.*, 38, 2370 (1973).
12. L.Lardicci, G.Giacomelli, P.Salvadori, and P.Pino, *J.Am.Chem.Soc.*, 93, 5794 (1971).
13. K.Fischer, K.Jonas, P.Misbach, R.Stabba, and G.Wilke, *Angew.Chem.internat.Edit.*, 12, 943 (1973).

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