Asymmetric Synthesis in the Nickel-complex-catalysed Formation of Olefins from Allyl Alcohols and Grignard Reagents

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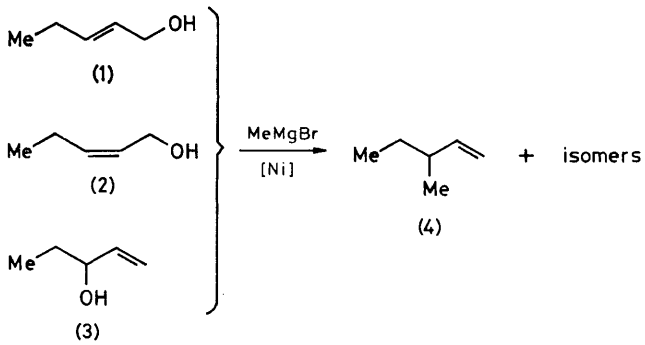
Summary The reaction of three isomeric pentenols with methyl magnesium bromide catalysed by (−)DIOP nickel dichloride [DIOP = *O,O'*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane] leads to optically active 3-methylpent-l-ene, with the optical yield and product configuration related to the configuration of the initially formed (η^3-allyl)nickel intermediates.

RECENTLY there has been a considerable amount of interest in asymmetric hydrogenation reactions catalysed by transition-metal complexes.[1,2] Relatively few examples, however, of catalytic chiral syntheses which involve carbon–carbon bond formation have been reported.[2] As expected from the involvement of (bis-phosphine)(η^3-allyl)nickel (alkyl) complexes in the nickel-catalysed substitution reactions of allyl alcohols,[3,4] it has been shown that the use in this reaction of chiral phosphines together with prochiral allyl alcohols results in the formation of optically active olefins.[5] Here we report the synthesis of optically active 3-methylpent-l-ene from three isomeric pentenols and methyl magnesium bromide in the presence of [(−)DIOP]$NiCl_2$.† The chirality of the products obtained from this series of alcohols together with the mechanism of the reaction allowed the intermediates and the factors which control the optical yields to be clearly defined.



The reaction of the three isomeric pentenols (**1**), (**2**), and (**3**) with methyl magnesium bromide catalysed by (−)DIOP nickel dichloride gave the chiral 3-methylpent-1-ene (**4**). The optical yields and configuration of the product are given in the Table.

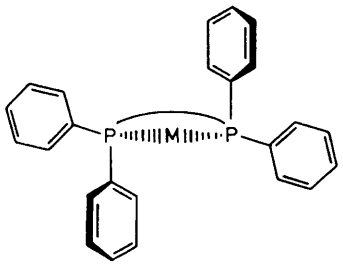
† (−)DIOP = (−)-*O,O'*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane.

TABLE. Asymmetric synthesis[a] of 3-methylpent-1-ene (**4**) catalysed by [(−)DIOP]$NiCl_2$.

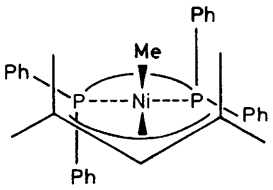
	Alcohol		
	(**1**)	(**2**)	(**3**)
(**4**) (major enantiomer)	(+)-(*S*)	(−)-(*R*)	(−)-(*R*)
Enantiomeric excess (%)[b]	1·2	14·9	8·5[c]

[a] A typical procedure is as follows: MeMgBr (95 mmol, 1·9M in Et_2O) followed by the alcohol (19·8 mmol) were added to [(−)DIOP]$NiCl_2$ (1·03 mmol) under nitrogen. After 4 d at 20 °C distillation and preparative g.l.c. gave compound (**4**). [b] Enantiomeric excesses are based on a rotation of 37·7° (neat) for pure (**4**) [P. Pino, L. Lardicci, and L. Centoni, *J. Org. Chem.*, 1959, **24**, 1399; we thank Dr. P. Pino (Zurich) for a sample of this olefin]. [c] Reaction of (**3**) with MeMgI in the presence of [(−)-(*R*)-1,2-bis(diphenylphosphino)-1-phenylethane]nickel dichloride gave (+)-(*S*)-(**4**) with 1·3% optical purity (ref. 5).

The conformation of the phenyl rings of (−)DIOP bonded to transition metals is shown in (**5**).[6] In the (η^3-allyl)nickel complex (**6**) it can be seen that the two ends of



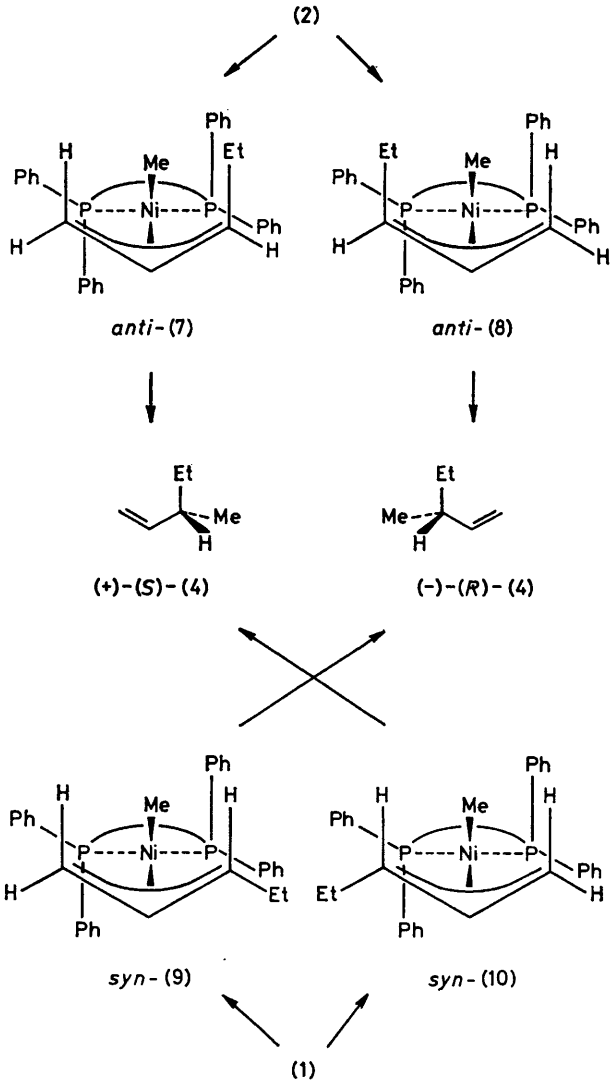
(**5**)



(**6**)

the allyl ligand are non-equivalent. At one end the *anti* and *syn* groups eclipse the phenyl rings of the adjacent phosphine whereas at the opposite end the *anti* and *syn* groups are staggered relative to the adjacent phenyl rings. The difference between the *anti* positions, which involve interaction with edge-on phenyl, is expected to be more pronounced than the difference between the *syn* positions, where a more distant interaction with face-on phenyl is present.

The *cis*-allyl alcohol (**2**) will give rise initially to the *anti*-(η^3-allyl)nickel intermediates (**7**) and (**8**). Methyl transfer will give (+)-(*S*)-(**4**) from (**7**) and (−)-(*R*)-(**4**) from (**8**). The observed (see Table) predominance of (−)-(*R*)-(**4**) is consistent with isomer (**8**) being favoured with respect to the isomer (**7**) for steric reasons. The *trans*-allyl alcohol (**1**) will give rise to the *syn* intermediates (**9**) and (**10**). A slight predominance of (+)-(*S*)-(**4**) in the coupled product is compatible, in this case, with a small energy difference between (**9**) and (**10**). The fact that the *trans*- and *cis*-alcohols (**1**) and (**2**) give rise to different optical yields of (**4**) is consistent with *anti–syn* equilibration of the η^3-allyl complexes, (**7**) ⇌ (**10**) and (**8**) ⇌ (**9**), *via* η^1-secondary complexes being



relatively slow.[3] In contrast, the fact that asymmetric synthesis is observed with the racemic alcohol (**3**) is consistent with the equilibrations (**7**) ⇌ (**8**) and (**9**) ⇌ (**10**) *via* η^1-primary intermediates occurring at appreciable rates.[4] Without such equilibration, racemic (**3**) would give racemic (**4**) since the formation of η^3-allyl complexes occurs with inversion of configuration.

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[1] J. D. Morrison and H. S. Mosher, 'Asymmetric Organic Reactions,' Prentice-Hall, 1971.
[2] D. Valentine and J. W. Scott, *Synthesis*, 1978, 329.
[3] H. Felkin and G. Swierczewski, *Tetrahedron Lett.*, 1972, 1433.
[4] H. Felkin, M. Joly-Goudket, and S. G. Davies, *Tetrahedron Lett.*, 1981, 1157.
[5] G. Consiglio, Fr. Morandini, and O. Piccolo, *Helv. Chim. Acta*, 1980, **63**, 987.
[6] S. Brunie, J. Mazan, N. Langlois, and H. B. Kagan, *J. Organomet. Chem.*, 1976, **114**, 225, and references therein.