Journal of

The Chemical Society,

Chemical Communications

NUMBER 20/1980

Asymmetric Codimerization of Cyclohexa-1,3-diene with Ethylene Catalysed by Chiral Aminophosphine-nickel Complexes

By GÉRARD BUONO,[a] GILBERT PEIFFER,[a] ANDRÉ MORTREUX,[b] and FRANCIS PETIT[b]*

([a]*Laboratoire de l'Ecole de Chimie de Marseille et des Organophosphorés, Université d'Aix-Marseille III, rue H. Poincaré,* 13397 *Marseille, France* and [b]*Laboratoire de Chimie Organique Appliquée, ERA CNRS* 458, *Ecole Nationale Supérieure de Chimie de Lille,* BP 40, 59650 *Villeneuve d'Ascq, France*)

Summary The asymmetric codimerization of cyclohexa-1,3-diene with ethylene is catalysed by the Ni(cyclo-octa-1,5-diene)$_2$–AlEt$_2$Cl–L system where L are chiral aminophosphines; optimization of this catalytic system (−70 °C; L/Ni = 10) gives (+)-(*S*)-3-vinylcyclohexene with 73·5% optical purity in 87% chemical yield when (−)-(*R*)-*N*-methyl-*N*-(1-phenylethylamino)diphenylphosphine is used.

IN recent years much interest has been shown in the synthesis of optically active substances catalysed by transition metal complexes containing chiral ligands.[1,2] In many instances, catalytic processes to form C–H bonds with simultaneous creation of chirality give almost quantitative optical yields.[3] For the formation of C–C bonds, however, such reactions have been much less successful. Important reactions of this type are the codimerizations of 1,3-dienes with ethylene in dichloromethane catalysed by Wilke's (π-$C_3H_5NiX)_2$–AlX_3–P*R^{1}R^{2}R^3 system.[4] Utilization of (−)-dimenthylphenylphosphine afforded increasing optical yields of (−)-(*S*)-3-vinylcyclo-octene with decreasing temperatures (23·5%, 0 °C; 53%, −75 °C) when a 1/2·5/1·2 molar ratio was employed. The highest enantiomeric excess (e.e.) (70%) was attained at 0 °C using an Ni/P ratio of 1/3·8,[5] in which case, however, the observed chemical yields were low.[3b]

We have previously shown[6,7] that active species prepared from the bis(cyclo-octa-1,5-diene)nickel–diethylaluminium chloride–aminophosphine system were able to catalyse the above-mentioned condensation with good rates at low temperatures; we now report that chiral aminophosphines are effective in creating chirality in the catalysed synthesis of pure 3-vinylcyclohexene in almost quantitative yields.

The optically active aminophosphines (**3**) ($[\alpha]^{20}_{\mathrm{D}}$ −58·2°; *c* 1·1, CHCl$_3$) and (**4**) ($[\alpha]^{20}_{\mathrm{D}}$ −69·9°; *c* 1·7, CHCl$_3$) were synthesized, following a standard procedure, from PPh$_2$Cl and (+)-(*R*)-phenylethylamine and the (+)-(*R*)-*N*-methyl derivative, respectively.[8,9] The diaminodiphosphine (**5**) ($[\alpha]^{20}_{\mathrm{D}}$ −21·7°; *c* 1·04, CH$_2$Cl$_2$; 70 °C) was synthesized

TABLE 1. Effect of the nature of the chiral ligand on the optical yields.[a]

Ligand	Conversion/%[b]	Selectivity/%[c]	$[\alpha_{\mathrm{D}}]$[d]	Optical yield/%[e]
(**3**)	98·5	99	22·1	13
(**4**)	99·5	98·5	45·9	27
(**5**)	97·5[f]	97	11·2	6·6

[a] All codimerizations were run in a bomb (300 ml) with 144 mmol of cyclohexa-1,3-diene under an initial ethylene pressure of 12 atm, 0·36 mmol of Ni(1,5-cod)$_2$, 0·36 mmol of (**4**) and 1 ml of AlEt$_2$Cl for 6 h at 0 °C. After hydrolysis, pure hydrocarbon (**2**) was isolated by vacuum distillation. [b] Conversion based on the amount of (**1**) used was determined by g.l.c. [c] 99—97% of (**2**), 1—3% of *cis*- and *trans*-3-ethylidenecyclohexenes. [d] All rotations (in degrees) were measured after dilution in CHCl$_3$. [e] Calculated on the basis of the value for the optically pure enantiometric 3-vinylcyclohexene (see text). [f] 50% for 2 h.

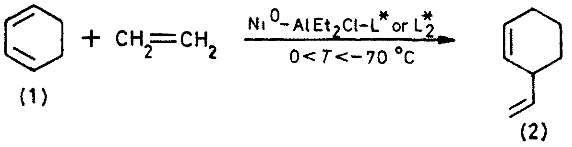
TABLE 2. Asymmetric codimerizations with (**4**). Effect of temperature.[a]

T/°C[b]	Conversion/%[c]	Selectivity/%	Optical yield/%
0	99·5	99	27[d]
−20	98	99	32
−30	96·5	99	34
−40	95	99	36·5
−50	92·5	97·5	40·5
−70	88·5	97	48

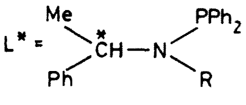
[a] Identical experimental conditions to those described in Table 1 (except for temperature). [b] ±1 °C. [c] Based on (**1**). [d] At 0 °C, cyclo-octa-1,3-diene was converted into (+)-(R)-3-vinylcyclo-octene by the catalytic system Ni⁰–AlEt$_2$Cl–(+)-(**4**) (1/4/1) with the surprisingly low optical yield of 9%.

similarly in excellent yields (80—90%) from the (−)-(R)-1,2-diaminopropane.[8,9] In contrast with many other chelating phosphines, all enantiomers of the amino phosphines (**3**), (**4**), and (**5**) are readily available, so both configurations of 3-vinylcyclohexene are accessible.

Thus, it appears (Table 1) that the asymmetric aminophosphine (**4**) is the most efficient for inducing chirality in the catalysed cyclohexa-1,3-diene–ethylene codimerization and this reaction occurs almost without isomerisation, as expected.[6]

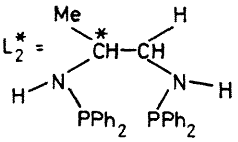


(1) (2)



(3) R = H

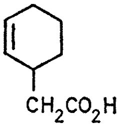
(4) R = Me



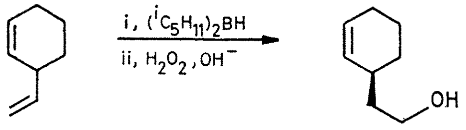
(5)

Tables 2 and 3 show clearly that the optical yields are greatly improved without alteration of the chemical yields by carrying out the catalysis at low temperature or in the presence of an excess of (**4**). This is in contrast with the results of Bogdanovic who observed deactivation of the catalyst when an excess of phosphine was used.[3b] Optimized conditions (−70 °C, P/Ni = 10) furnished the best optical yield (73·5%) with the formation of 87% of (+)-(S)-3-vinylcyclohexene ($[\alpha]_D^{25}$ +125·8°; c 3·2, CHCl$_3$).

The optical yields were determined in two ways. (a) From application of Brewster's method,[10] which can be used as a more general form of Mill's empirical rules[11] for alkylcyclohexenes; a calculated value of +170° for the specific rotation was predicted for (+)-(S)-3-vinylcyclohexene. (b) Stereoselective hydroboration of the most optically active (+)-3-vinylcyclohexene sample ($[\alpha]_D^{25}$ +125·8°; c 3·2, CHCl$_3$) with di-isopentylborane[12] led to (+)-(S)-3-(2-hydroxyethyl)cyclohexene (**7**) ($[\alpha]_D^{25}$ +62·8°; c 1·5, CHCl$_3$). This compound was quantitatively converted into the corresponding diastereomeric mixture of (+)-(R)-α-methoxy-α-trifluoromethylphenylacetic acid esters by Mosher's procedure.[13] Eu(dpm)$_3$-induced shift of the methoxy signal[14] permits the determination of enantiomeric purity (73 ± 1%) by simple integration of MeO peak areas.† There is an excellent correlation between the highest optical yields (74 $vs.$ 73%) calculated from these two independent methods.



(6)



(+)-(S)-(2) (+)-(S)-(7)

To prove its (S) absolute configuration, (**2**) ($[\alpha]_D^{25}$ +44°; c 1, CHCl$_3$) was selectively reduced[15] by homogeneous hydrogenation using Vaska's catalyst[16] to (+)-3-ethylcyclohexene ($[\alpha]_D^{25}$ + 12·6°; c 1, CHCl$_3$) known to have the (R) absolute configuration.[17]

TABLE 3. Asymmetric codimerizations with (**4**). Effect of changing the ratio P/Ni at −35 °C.

Ratio P/Ni	Conversion/%[a]	Selectivity/%[b]	Optical yield/%
1	96·5	99	34·5
3	98·5	98·5	42
5	98	96	52
7	97·5	86·5	56·5
9	97·5	88	61
11	96·5	87	61·5

[a] Based on (**1**); lower when calculations are based on ethylene (formation of butenes). [b] Remaining 1—13% made up of 3-ethylidenecyclohexenes.

---

† This result [73·5% e.e. for (+)-(S)-(**2**)] was confirmed also because the $[\alpha]_D^{25}$ of pure (+)-alcohol (**7**) was found independently to be +85·4°. This latter value was determined by initial resolution of cyclohex-2-enylacetic acid (**6**) by the best resolving agent, brucine, which afforded the (+)-(S) acid (**6**) ($[\alpha_D^{25}]$ + 65°; c 2·66, CHCl$_3$). Subsequent reduction of (**6**) by LiAlH$_4$ gave (+)-(S) alcohol (**7**) ($[\alpha]_D^{25}$ + 71·7°; c 1·02, CHCl$_3$) with 84% e.e. (found by the lanthanoid-induced shift n.m.r. technique). The use of quinine, phenylethylamine, and cinchonine was less successful in our hands.

We can conclude that the virtue of the present study consists mainly in two points. (i) The most optically active aminophosphine ligands are easily prepared and both enantiomers of 3-vinylcyclohexene are available. (ii) The side-reactions such as olefin isomerisation are limited so that the optically active products, which could be used for further synthetic application in producing chirality on a C_6 ring, are produced catalytically in nearly quantitative yields.

(*Received*, 19*th May* 1980; *Com.* 543.)

[1] W. S. Knowles, M. J. Sabacky, and B. D. Vineyard, *Chem. Technol.*, 1972, 590.

[2] J. D. Morrison and H. S. Mosher, 'Asymmetric Organic Reactions,' Prentice Hall, Englewood Cliffs, N.J., 1971.

[3] (a) W. S. Knowles, M. J. Sabacky, B. D. Vineyard, and D. Weinkauff, *J. Am. Chem. Soc.*, 1975, **97**, 2567; W. S. Knowles, M. J. Sabacky, and B. D. Vineyard, *Adv. Chem. Ser.*, 1974, **132**, 274; T. P. Dang, J. C. Poulin, and H. B. Kagan, *J. Organomet. Chem.*, 1975, **91**, 105; H. B. Kagan and T. P. Dang, *J. Am. Chem. Soc.*, 1972, **94**, 6429; N. Takaishi, H. Imai, C. A. Bertelo, and J. K. Stille, *ibid.*, 1976, **98**, 5400; H. Brunner and W. Pieronczyk, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 620; (b) B. Bogdanovic, *Angew. Chem., Int. Ed. Engl.*, 1973, **12**, 954; (c) G. Consiglio, *Helv. Chim. Acta*, 1976, **59**, 124. (d) For a stoicheiometric case see B. M. Trost and T. J. Dietsche, *J. Am. Chem. Soc.*, 1973, **95**, 8200.

[4] G. Wilke, *Angew. Chem., Int. Ed. Engl.*, 1966, **5**, 151.

[5] B. Bogdanovic, B. Henc, B. Meister, H. Pauling, and G. Wilke, *Angew. Chem., Int. Ed. Engl.*, 1972, **11**, 1023.

[6] G. Peiffer, X. Cochet, and F. Petit, *Bull. Soc. Chim. Fr.*, 1979, **2**, 415.

[7] X. Cochet, A. Mortreux, and F. Petit, *C.R. Hebd. Seances Acad. Sci.*, 1979, **288**, 105.

[8] The n.m.r. and i.r. spectra were consistent with the assigned structures, nevertheless the specific rotation of $[\alpha]_D^{20}$ $-69{\cdot}9$; *c* 1·7, $CHCl_3$ for (**4**) is different from $[\alpha]_D^{26}$ -93; *c* 1, $CHCl_3$ previously reported (M. Fiorini, F. Marcati, and G. M. Giongo, *J. Mol. Catal.*, 1978, **4**, 125).

[9] F. P. Dwyer, F. L. Garvan, and A. Shulman, *J. Am. Chem. Soc.*, 1959, **81**, 290. The absolute configuration of (+)-(*S*)-1,2-diaminopropane has been determined by X-ray analysis (Y. Saito and H. Isawaki, *Bull. Chem. Soc. Jpn.*, 1962, **35**, 1131).

[10] J. H. Brewster, *J. Am. Chem. Soc.*, 1959, **81**, 5475, 5483.

[11] J. A. Mills, *J. Chem. Soc.*, 1952, 4976.

[12] H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, 1961, **83**, 1241.

[13] J. A. Dale and H. S. Mosher, *J. Am. Chem. Soc.*, 1973, **95**, 512.

[14] F. Yasuhura and S. Yamayuchi, *Tetrahedron Lett.*, 1973, **47**, 4085.

[15] S. Jacobson, W. Clements, H. Hiramoto, and C. U. Pittman, *J. Mol. Catal.*, 1976, **1**, 73.

[16] L. Vaska and J. W. Diluzio, *J. Am. Chem. Soc.*, 1962, **84**, 679.

[17] J. H. Brewster, *J. Am. Chem. Soc.*, 1959, **81**, 5493.