121. Asymmetric Catalysis by Vitamin B_{12}

The Isomerization of Achiral Epoxides to Optically Active Allylic Alcohols

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Achiral epoxides are isomerized to optically active allylic alcohols under the influence of catalytical amounts of cob(I)alamin in protic polar solvents.

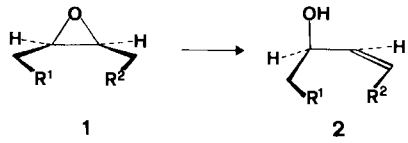
Introduction. – The isomerization of epoxides to allylic alcohols is an important transformation in organic synthesis and an industrial process [1]. Many reagents and catalysts are known to promote *non-enantioselective* isomerization [2]. Isomerizations with strong bases such as lithium amides [3–5] and potassium alkoxides [6], or *Lewis* acids like dialkylaluminium amides [7], dialkylboron triflates [8], trialkylsilyl triflates [9], and trialkoxytitanium chloride [10] are procedures requiring equimolar amounts of reagents. Mild two-step procedures are based on nucleophilic displacement followed by elimination as *e.g.* nucleophilic ring opening by phenylselenide, oxidation, and elimination of phenylseleninic acid [11] or electrophilic ring opening by (*t*-Bu)Me_2SiI followed by base-induced dehydroiodination [12]. Isomerization is also achieved by homogeneous or heterogeneous catalysis. As dissolved catalysts sulfonic acides [13], electrogenerated acids [14] and Pd(0)-phosphine complexes (in case of 1,3-diene mono-epoxides) [15] proved to be useful. Isomerization by heterogeneous catalysis also occurs with several solid acids and bases [6a] [10] [16].

Enantioselective isomerization of achiral epoxides to optically active allylic alcohols with chiral lithium amides (from BuLi and enantiomerically pure secondary amines) has recently been described by *Whitesell* and *Felman* [17] and *Asami* [18]. The yield and enantiomeric excess strongly depend on the epoxide, the base, and the solvent.

Continuing our investigations on the application of vitamin B_{12} [19] as catalyst in organic synthesis [20], we report here on preliminary results on the B_{12}-catalyzed isomerization of achiral epoxides to optically active allylic alcohols. This work was stimulated to a considerable extent by earlier findings of *Fischli et al.* on the cob(I)alamin-catalyzed enantioselective hydrogenation of *Michael*-olefins [21] and the work of *Golding* and coworkers on the stereochemistry of the alkylation of cob(I)alamin by racemic epoxides [22].

Results and Discussion. – If achiral epoxides like **1a, b, d** are dissolved in a polar protic solvent containing a catalytic amount of vitamin B_{12s} [23], the corresponding optically active allylic alcohols **2a, b, d** are formed on standing at room temperature *(Scheme)*. The

Scheme



1 2

	R^1	R^2
a	$-(CH_2)-$	
b	$-(CH_2)_2-$	
c	$-(CH_2)_4-$	
d	H	H

yield and the enantiomeric excess of the (*R*)-enantiomer strongly depend on the structure of the epoxide and may show remarkable values (*cf.* the *Table*).

The catalytically active species is vitamin B_{12s} (cob(I)alamin), obtained from vitamin B_{12} (hydroxocobalamin hydrochloride or cyanocobalamin) by *in-situ* two-electron reduction by a chemical reducing agent like Zn (in presence of NH_4Cl), $NaBH_4$, or the cathode at *ca.* –0.9 V *vs.* SCE in electro-chemical reduction. Since usually only 1 to 3 mol-% of B_{12} (with respect to epoxide = 100 mol-%) are used, the amount of consumed reducing agent is negligible small. For complete isomerization in a solvent like MeOH at room temperature under inert atmosphere, usually several hours to days are needed. On workup in presence of air, B_{12} is easily regenerated and might be re-used as such without significant loss of catalytic activity.

Cyclopentene oxide (**1a**) is isomerized to (*R*)-2-cyclopenten-1-ol (**2a**) in a surprisingly high ee of 65% (*Table, Entry 4*). In the conversion of cyclohexene oxide (**2a**) to (*R*)-2-cyclohexen-1-ol (**2b**) (ee *ca.* 40%), cyclohexanone is formed as a by-product (in *ca.* 20% yield, *Table, Entries 6–8*). Cyclooctene oxide (**1c**) does not undergo reaction. In a relatively fast reaction, *cis*-2-butene oxide (**1d**) is converted to (*R*)-3-buten-2-ol (**2d**), ee 26% (*Table, Entry 10*).

To explain these results, the following hypothetical mechanism seems to be plausible: Co(I) in cob(I)alamin reacts from its upper (β) side as a strong nucleophile and displaces the O-atom of the epoxide at one of the two enantiotopic C-atoms with inversion of configuration (*cf.* [22]). Two diastereoisomeric β-(hydroxyalkyl)cobalamins might be formed as short-living intermediates. Reductive elimination leads to allylic alcohol and cob(I)alamin. Assuming that the C-substituents (bearing R^1 and R^2) at the C-atom bound to Co(III) are directed towards the (less hindered) 'southern' hemisphere (ring C, D) of the β side of B_{12} (*cf.* [19]), the reductive elimination leading to (*R*)-allylic alcohol should occur from the diastereoisomer in which the hydrocarbon-chain bearing R^2 is oriented towards the 'eastern' hemisphere (ring B, C) of B_{12}.

Work on the scope and limitations of this isomerization and its mechanism – to prove or disprove our hypothesis – is in progress.

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Table. *Vitamin B_{12}-Catalyzed Isomerization of Epoxides to Allylic Alcohols*

Entry	Epoxide	Catalytic system		Solvent	Temp. [°C]	Time [h]	Product	Yield [5][b] (Purity [%])[c]	$[\alpha]_D$ [°][d]	ee [%][e]	Configuration
		mol-% of vitamin B_{12}[a]	Reducing agent								
1	Cyclopentene oxide (**1a**)	3	Zn/NH_4Cl	MeOH	*ca.* 22	40	2-Cyclopenten-1-ol (**2a**)	78 (98)	+80.9[f]	55[g]	R[h]
2		3	$NaBH_4$	MeOH	*ca.* 22	48		61 (98)	+76.4[f]	52	
3		1	C-Cathode, −1.1 V (SCE)	0.2N $LiClO_4$ MeOH	20	20		12 (91)	+34.9[i]	24	
4		3	Zn/NH_4Cl	MeOH	45	7		68 (92)	+73.1[j]	50	
5		1	Zn/NH_4Cl	MeOH[k]	*ca.* 22	168		64 (96)	+94.5[f]	65	
6	Cyclohexene oxide (**1b**)	3	Zn/NH_4Cl	MeOH	45	16	2-Cyclohexen-1-ol (**2b**)	62 (80)[l]	+45.3[m]	40[n]	R[o]
7		1.5	Zn/NH_4Cl	MeOH	60	4		52 (71)[l]	+40.1[m]	36	
8		1	Zn/NH_4Cl	MeOH	*ca.* 22	120		49 (72)[l]	+47.3[m]	42	
9	Cyclooctene oxide (**1c**)	1	Zn/NH_4Cl	MeOH	60	30	No isomerization				
10	*cis*-2-Butene oxide (**1d**)	1	Zn/NH_4Cl	MeOH	*ca.* 22	30	3-Buten-2-ol (**2d**)	57 (94)[p]	−8.80[q]	26[r]	R[r]

[a]) Hydroxocobalamin hydrochloride in mol-% with respect to epoxide. The rate of isomerization depends on catalyst concentration, however, the ee is not substantially affected.

[b]) Yield of the isolated pure allylic alcohol, calculated with respect to epoxide. Conversion of the starting material to the product was monitored by GC.

[c]) Pure allylic alcohol in isolated material, determined by GC.

[d]) Room temp. *ca.* 22–23°.

[e]) Based on $([R - S]/[R + S]) \times 100$, calculated for pure allylic alcohol.

[f]) Neat, $c = 1$ g/ml.

[g]) Determined by 400-MHz NMR spectra of both diastereoisomeric *Mosher* esters prepared from (+)-(*R*) and (−)-(*S*)-3,3,3-trifluoro-2-methoxy-2-phenylpropionyl chloride according to [24].

[h]) For the assignment of configuration, *cf.* [25].

[i]) $c = 4.4$ (CCl_4).

[j]) $c = 0.86$ (CCl_4).

[k]) Ratio (*v*/*v*) epoxide/MeOH *ca.* 1:3, in all other cases *ca.* 1:10.

[l]) Main impurity is cyclohexanone as determined by GC.

[m]) $c = 1.4$ ($CHCl_3$).

[n]) Determined by 400-MHz NMR of both diastereoisomeric *Mosher* esters prepared from (+)-(*R*)- and (−)-(*S*)-3,3,3-trifluoro-2-methoxy-2-phenylpropionyl chloride according to [24].

[o]) For assignment of configuration *cf.* [26], ee (calc.) is based on max. $[\alpha]_D^{r.t.} = 112°$ [26]; according to a recent report, max. $[\alpha]_D$ might be *ca.* 130° as calc. from the ee of a precursor [26c].

[p]) Main impurity is H_2O (GC).

[q]) Neat, $c = 0.837$ g/ml.

[r]) For specific rotation and assignment of configuration, *cf.* [27].

Experimental Part

1. *General.* Vitamin B_{12} (hydroxocobalamin hydrochloride, pyrogen-free *Fr. Ph. BP,* 10.7% loss on drying, < 2% cyanocobalamin) from *Roussel Uclaf.* Cyclopentene oxide (98%) cyclooctene oxide (98%), and *cis*-2-butene oxide (97%) from *Aldrich;* cyclohexene oxide (*purum,* 99%) from *Fluka;* NH_4Cl (*purum*) from *Siegfried;* $NaHB_4$ (*purum*) from *Fluka;* MeOH (*puriss.*) from *Fluka* was flushed with Ar before use. Zn-wool (*puriss.*) from *Siegfried,* 'activated' before use: Zn (*ca.* 1 g) in 5% HCl/H_2O (*ca.* 10 ml) for 10 min at r.t. followed by washing with H_2O (5 × 10 ml), MeOH (2 × 30 ml), and Et_2O (30 ml). (*R*)- and (*S*)-3,3,3-trifluoro-2-methoxy-2-phenylpropionyl chloride (ee 99%) from *JPS Chimie,* Neuchâtel. The electrochemical procedure was carried out in a H-type cell with glass frit separation using graphitized carbon felt as cathode material under potentiostatic conditions [28]. GC: *Hewlett-Packard 589* gas chromatograph, 20-m *Duran* glass cap. column coated with *SE-54,* temp. programme from 40° to 200° by a rate of 3°/min. $[\alpha]_D$: *Perkin-Elmer 241* polarimeter. ^{1}H-NMR: *Varian EM 360L* (60 MHz) and *Bruker AM-400WB* (400 MHz) spectrometer for the determination of ee by integration of the spectra of the diastereoisomeric *Mosher* esters measured in (D_6)acetone with TMS (= 0 ppm) as internal standard. The structures of **2a**, **b**, **d** were confirmed by comparison of their ^{1}H-NMR spectra with those from [29] and/or authentic material.

(R)-2-Cyclopentene-1-ol (**2a**, *reducing agent: Zn, Table, Entry 1*). Into a 100-ml flask under Ar containing MeOH (15 ml), hydroxocobalamin hydrochloride (0.84 g, 0.54 mmol) and NH_4Cl (1.08 g), a magnetic stirrer bar wrapped in Zn wool (1.00 g) was placed. After stirring for several min, the colour changed from red (B_{12}) to dark-green (B_{12s}). To this mixture, *cyclopentene oxide* (= *6-oxabicyclo[3.1.0]hexane;* **1a**; 1.72 g, 20.0 mmol) was added by syringe. The colour immediately changed to red-brown (alkyl-Co(III)). After stirring for 40 h at r.t., the colour of the soln. had returned to dark green (B_{12s}). The flask was opened, and Et_2O (80 ml) was added. A brown-red precipitation (B_{12}) was formed. The colourless soln. was decanted and the precipitation extracted 5× with Et_2O (*ca.* 20 ml each). The combined soln. was washed with sat. $NaCl/H_2O$ (3 × 10 ml), dried (Na_2SO_4), and the solvent evaporated. The remaining colourless oil **2a** (1.34 g, 78%; purity 98% (GC)) was submitted to the analysis without further purification. $[\alpha]_D^{r.t.} = +80.9°$ (neat). The ee of 55% was determined independently by integration of the ^{1}H-NMR (400 MHz, (D_6)acetone) of the two diastereoisomeric *Mosher* esters prepared according to [24] from (+)- and (−)-3,3,3-trifluoro-2-methoxy-2-phenylpropionyl chloride.

2a (*Reducing agent: $NaBH_4$, Table, Entry 2*). In a 100-ml flask with magnetic stirrer, hydroxocobalamin hydrochloride (0.84 g, 0.54 mmol) was dissolved in MeOH (15 ml) under Ar. After cooling to 0°, $NaBH_4$ (0.113 g, 3.0 mmol) was added in 3 portions. To the dark-green soln., **1a** (1.68 g, 20.0 mmol) was added by syringe. After stirring the brown soln. for 48 h at r.t. under Ar, the flask was opened, and Et_2O (80 ml) was added. A brown-red precipitate was formed. The usual workup as described above (*Entry 1*) afforded 1.56 g **2a** as a colourless oil. Bulb-to-bulb distillation (60° (oven temp.)/*ca.* 11 Torr) afforded 1.06 g (61.8%) of **2a** (purity 98% (GC)). $[\alpha]_D^{r.t.} = +76.4°$ (neat); $[\alpha]_D^{r.t.} = +75.4°$ ($c = 1.1$, CCl_4), corresponding to ee of 52%.

2a (*Electrochemical reduction, Table, Entry 3*). The cathodic and anodic compartment of the H-type electrochemical cell was charged with 0.2N $LiClO_4$/MeOH (35 and 20 ml) and the cathodic compartment flushed with Ar. Hydroxocobalamin hydrochloride (0.28 g, 0.18 mmol) was added to the catholyte. Then, a constant cathodic potential of −1.1 V (*vs.* SCE) was applied. The initially high current of *ca.* 50 mA decreased to *ca.* 5 mA, when B_{12} was reduced to the dark-green B_{12s}. Compound **1a** (1.68 g, 20 mmol) was added by syringe, whereby the colour changed to red-brown, and the current first raised to *ca.* 20 mA and then again decreased to *ca.* 5 mA. After 16 h at 20° under irradiation with VIS light (500-W halogen lamp), the current was switched off. The catholyte was transferred into H_2O-ice (50 ml) and extracted with Et_2O/pentane 3:1 (5 × 100 ml). The org. soln. was washed with brine (2 × 100 ml), dried (Na_2SO_4), and concentrated *in vacuo* to *ca.* 3 ml. Column chromatography on 140 g of silica gel with Et_2O/pentane 4:6 gave 3 fractions: 1st: 35 mg (unknown), 2nd: 337 mg of **2a**, 3rd: 235 mg of *trans*-2-methoxycyclopentan-1-ol. *Fract. 2* was purified by bulb-to-bulb distillation (70° (oven temp.)/*ca.* 40 Torr) and afforded 220 mg (12%) of colourless oil **2a** (purity 91% (GC)). $[\alpha]_D^{r.t.} = +34.9°$ ($c = 4.4$, CCl_4), ee 24%.

2a (*Table, Entry 4*). The reaction has been carried out under the indicated conditions, but otherwise analogous to *Entry 1.*

2a (*Table, Entry 5, preparative-scale isomerization*). Into a 100-ml flask under Ar containing MeOH (15 ml), hydroxocobalamin hydrochloride (0.93 g, 0.60 mmol), and NH_4Cl (0.54 g), a stirring bar wrapped in Zn wool (1.0 g) was placed. After stirring for several min, the colour changed to dark-green. Epoxide **1a** (4.97 g, 59.2 mmol) was added by syringe, and the resulting brown soln. was stirred at r.t. for 7 d (7% of **1a** was still present (GC)). Et_2O (80 ml) was added, whereby a red-brown precipitate was formed. After usual workup as described for *Entry 1,* 3.90 g of

2a (yellowish oil) were obtained (purity 94% (GC)). Bulb-to-bulb distillation (60° (oven temp.)/11 Torr) gave 3.33 g (64%) of **2a** as a colourless oil (purity 96% (GC)). $[\alpha]_D^{r.t.} = +94.5°$ (neat), corresponding to ee of 65%.

(R)-2-Cyclohexene-1-ol (**2b**; *reducing agent: Zn, Table, Entry 6*). Into a 100-ml flask under Ar containing MeOH (15 ml), hydroxocobalamin hydrochloride (0.84 g, 0.54 mmol) and NH_4Cl (1.08 g), a magnetic stirrer bar wrapped in Zn-wool (1.00 g) was placed. After stirring for several min, the colour turned to dark-green. *Cyclohexene oxide* **1b** (= *7-oxabicyclo[4.1.0]heptane;* 1.96 g, 20 mmol) was added by syringe, whereby the colour changed to brown. The soln. was stirred at 45°, and was irradiated by a 500-W incandescent bulb (distance *ca.* 10 cm, cooling by fan). After 16 h, the colour turned slowly dark-green (B_{12s}). The soln. was concentrated *in vacuo* to *ca.* 5 ml, and Et_2O (80 ml) was added. A dark-brown precipitate was formed. After usual workup as described for *Entry 1*, 1.65 g of **2b** (yellowish oil) was obtained (purity 78% (GC)). Bulb-to-bulb distillation (80° (oven temp.)/11 Torr) gave 1.53 g (62%) of **2b** as a colourless oil (purity 80% (GC), main by-product: cyclohexanon). This material showed $[\alpha]_D^{r.t.} = +36.2°$ (neat), calc. for pure allylic alcohol = +45.3°, corresponding to ee of 40% based on 112° for the pure enantiomer [26] (the ee of *(R)*-**2b** was independently confirmed by ^{1}H-NMR of the corresponding *Mosher* esters).

2b (*Table, Entries 7* and *8*). The reactions have been carried out under the indicated conditions, but otherwise analogous to *Entry 6*.

Attempted Isomerization of Cyclooctene Oxide (= *9-Oxabicyclo[6.1.0]nonane;* **1c**; *Table, Entry 9*). To the dark-green soln. of vitamin B_{12s} (prepared according to *Entry 1* from hydroxocobalamin hydrochloride (0.42 g, 0.3 mmol), NH_4Cl (1.08 g), and Zn wool (1.0 g) in MeOH (15 ml)) under Ar, **1c** (2.60 g, 20.6 mmol) in MeOH (5 ml) was added by syringe. No colour change was observed. After stirring for 5 h at 42° and irradiation with VIS light from a 500-W incandescent bulb (distance *ca.* 10 cm, cooling by fan), the reaction was stopped. According to TLC and GC, the starting material **1c** remained unchanged, no isomerization was observed.

(R)-3-Butene-2-ol (**2d**; *Table, Entry 10*). To the dark-green soln. of vitamin B_{12s} (prepared according to *Entry 1* from hydroxocobalamin hydrochloride (0.42 g, 0.27 mmol), NH_4Cl (0.5 g), and Zn wool (1.0 g) in MeOH (10 ml)) under Ar, cis-*2-butene oxide* (= cis-*2,3-dimethyloxirane;* **1d**; 2.23 g, 30 mmol) was added by syringe. The colour immediately changed to red-brown. After stirring for 30 h at r.t., the colour turned slowly back to dark-green. Then, Et_2O (80 ml) was added, the clear soln. was separated from the brown precipitate as usual, and concentrated *in vacuo* to 5.31 g (a soln. containing 32% of **2d** (GC)). *Vigreux* distillation (55° (bath temp.)/40 Torr) gave 3.10 g of an oil, containing MeOH and **2d** (44% of **2d** (GC)). Prep. GC of 1.10 g of this fraction (20% *Carbowax*, 20 m on *Chrom. A 60/80* mesh, 60° isothermal) afforded 0.481 g (57%) of **2d** as colourless oil (purity 94% (GC)).

$[\alpha]_D^{r.t.} = -8.28°$; calc. for pure **2d**: −8.80°, corresponding to ee of 26% based on 33.9° for the pure enantiomer [27].

REFERENCES

[1] K. Weissermel, H.-J. Arpe, 'Industrielle Organische Chemie', Verlag Chemie, Weinheim, 1976, p. 245.

[2] a) M. Bartok, K. L. Lang, in 'Heterocyclic Compounds, Small Ring Heterocycles, Part 3, Oxiranes', Ed. A. Hassner, J. Wiley, New York, 1985, Vol. 42, p. 1–196; b) J. K. Crandall, M. Apparu, *Org. React.* **1983,** *29,* 345.

[3] a) A. C. Cope, H. H. Lee, H. E. Petree, *J. Am. Chem. Soc.* **1958,** *80,* 2849; b) A. C. Cope, G. A. Berchtold, P. E. Peterson, S. H. Sharman, *ibid.* **1960,** *82,* 6370; c) A. C. Cope, J. K. Heeren, *ibid.* **1965,** *87,* 3125.

[4] a) J. K. Crandall, *J. Org. Chem.* **1964,** *29,* 2830; b) J. K. Crandall, L. Chang, *ibid.* **1967,** *32,* 435, 532; c) J. K. Crandall, L. C. Lin, *J. Am. Chem. Soc.* **1967,** *89,* 4526, 4527.

[5] a) B. Rickborn, R. P. Thummel, *J. Org. Chem.* **1969,** *34,* 3583; b) R. P. Thummel, B. Rickborn, *J. Am. Chem. Soc.* **1970,** *92,* 2064; c) R. P. Thummel, B. Rickborn, *J. Org. Chem.* **1971,** *36,* 1365; d) C. L. Kissel, B. Rickborn, *ibid.* **1972,** *37,* 2060.

[6] a) M. N. Sheng, *Synthesis* **1972,** 194; b) C. C. Price, D. D. Carmelite, *J. Am. Chem. Soc.* **1966,** *88,* 4039.

[7] H. Yamamoto, H. Nozaki, *Angew. Chem.* **1978,** *90,* 180; *ibid. Int. Ed.* **1978,** *17,* 169 and ref. cit. therein.

[8] T. Inoue, T. Uchimaru, T. Mukaiyama, *Chem. Lett.* **1977,** 1215.

[9] S. Murata, M. Suzuki, R. Noyori, *J. Am. Chem. Soc.* **1979,** *101,* 2738.

[10] S. P. Tanis, P. M. Herrinton, *J. Org. Chem.* **1983,** *48,* 4572.

[11] K. B. Sharpless, R. F. Lauer, *J. Am. Chem. Soc.* **1973,** *95,* 2697.

[12] M. R. Detty, *J. Org. Chem.* **1980,** *45,* 924.

[13] A. van Zon, R. Huis, *Recl. J. R. Neth. Chem. Soc.* **1981,** *100.* 425.

[14] K. Uneyama, N. Nishiyama, S. Torii, *Tetrahedron Lett.* **1984,** *25,* 4137.
[15] M. Suzuki, Y. Oda, R. Noyori, *J. Am. Chem. Soc.* **1979,** *101,* 1623.
[16] a) K. Arata, K. Tanabe, *Bull. Chem. Soc. Jpn.* **1980,** *53,* 299; b) K. Arata, S. Akutagawa, K. Tanabe, *ibid.* **1975,** *48,* 1097.
[17] J.K. Whitesell, S.W. Felman, *J. Org. Chem.* **1980,** *45,* 755.
[18] a) M. Asami, H. Kirihara, *Chem. Lett.* **1987,** 389; b) M. Asami, *Tetrahedron Lett.* **1985,** *26,* 5803; c) M. Asami, *Chem. Lett.* **1984,** 829.
[19] a) Z. Schneider, A. Stroinski, 'Comprehensive B_{12}', W. de Gruyter, Berlin–New York, 1987; b) D. Dolphin, 'B_{12}', 'Chemistry', J. Wiley, New York, 1982, Vol. 1.
[20] Reviews: a) R. Scheffold, *Nachr. Chem. Techn. Lab.* **1988,** *36,* 261; b) R. Scheffold, S. Abrecht, R. Orlinski, H.-R. Ruf, P. Stamouli, O. Tinembart, L. Walder, Ch. Weymuth, *Pure Appl. Chem,* **1987,** *59,* 363; c) R. Scheffold, G. Rytz, L. Walder, in 'Modern Synthetic Methods', Ed. R. Scheffold, Salle/Frankfurt, Sauerländer/Aarau, Wiley/London, 1983, Vol. 3, p. 355.
[21] a) A. Fischli, D. Süss, *Helv. Chim. Acta* **1979,** *62,* 48, 2361; b) A. Fischli, J.J. Daly, *ibid.* **1980,** *63,* 1628; c) A. Fischli, *ibid.* **1982,** *65,* 1167.
[22] a) R.M. Dixon, B.T. Golding, O.W. Howarth, J.L. Murphy, *J. Chem. Soc., Chem. Commun.* **1983,** 243; b) N.W. Alcock, R.M. Dixon, B.T. Golding, *ibid.* **1985,** 603.
[23] D. Dolphin, 'Methods Enzymol.', Vol. XVIII, 1971, Part C, p. 34.
[24] a) N. Kalyanam, D.A. Lightner, *Tetrahedron Lett.* **1979,** 415; b) S. Yamaguchi, in 'Asymmetric Synthesis', Ed. J.D. Morrison, Academic Press, New York, 1983, Vol. 1, p. 125.
[25] R.K. Hill, A.G. Edwards, *Tetrahedron Lett.* **1964,** 3239.
[26] a) R.K. Hill, J.W. Morgan, *J. Org. Chem.* **1968,** *33,* 927; b) S. Yamada, N. Takamura, T. Mizoguchi, *Chem. Pharm. Bull.* **1975,** *23,* 2539; c) H. Yamashita, *Bull. Chem. Soc. Jpn.* **1988,** *61,* 1213.
[27] a) J. Kenyon, D.R. Snellgrove, *J. Chem. Soc.* **1925,** *127,* 1169; b) H.C. Brown, G.G. Pai, *J. Org. Chem.* **1985,** *50,* 1384.
[28] L. Walder, R. Orlinski, *Organometallics* **1987,** *6,* 1606.
[29] Ch.J. Pouchert, 'The Aldrich Library of NMR Spectra', Aldrich, Co., 1983, Vol. 1.