121. Asymmetric Catalysis by Vitamin B₁₂

The Isomerization of Achiral Epoxides to Optically Active Allylic Alcohols

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(3.VI.88)

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



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 NH₄Cl), NaBH₄, 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)-2cyclohexen-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 R¹ and R²) at the C-atom bound to Co(III) are directed towards the (less hindered) 'southern' hemisphere (ring C, D) of the β side of B₁₂ (*cf.* [19]), the reductive elimination leading to (*R*)-allylic alcohol should occur from the diastereoisomer in which the hydrocarbon-chain bearing R² is oriented towards the 'eastern' hemisphere (ring B, C) of B₁₂.

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

We thank the Swiss National Science Foundation for financial support. We are indebted to our colleagues Dr. P. Bigler, Mr. A. Saxer, and Mr. H. Gfeller for NMR (400 MHz), GC, and GC-MS analyses.

		Ë	able. Vitamin B ₁	2-Catalyzed	Isomerizatio	to of Epo	cides to Allylic Alcohols				
Entr	ry Epoxide	Catalytic syster	в	Solvent	Temp.	Time	Product	Yield [5] ^b)	[°] d[×]	ee [%]	Config-
1		mol-% of vitamin B ₁₂ ^a)	Reducing agent		[°C]	[q]		(Purity [%])°)	(p	(,	uration
-	Cyclopentene oxide (1a)		Zn/NH ₄ CI	MeOH	ca. 22	6	2-Cyclopenten-1-ol (2a)	78 (98)	$+80.9^{f}$)	55 ⁸)	R^{h}
~	•	3	NaBH ₄	MeOH	ca. 22	48	•	61 (98)	+76.4 ^f)	52	.
ŝ		1	C-Cathode,	0.2N LiClO	4 20	20		12 (91)	$+34.9^{i}$)	24	
			-1.1 V (SCE)	MeOH							
4		3	Zn/NH ₄ Cl	MeOH	45	7		68 (92)	+73.1 ^j)	50	
S		1	Zn/NH4Cl	MeOH ^k)	ca. 22	168		64 (96)	+94.5 ^f)	65	
9	Cyclohexene oxide (1b)	3	Zn/NH4Cl	MeOH	45	16	2-Cyclohexen-1-ol (2b)	62 (80) ¹)	+45.3 ^m)	40 ⁿ)	$R^{\circ})$
~		1.5	Zn/NH₄CI	MeOH	60	4		52 (71) ¹)	+40.1 ^m)	36	
°		1	Zn/NH ₄ Cl	MeOH	ca. 22	120		49 (72) ¹)	+47.3 ^m)	42	
9	Cyclooctene oxide (1c)	1	Zn/NH ₄ Cl	MeOH	60	30	No isomerization				
10	cis-2-Butene oxide (1d)	-	Zn/NH4CI	MeOH	са. 22	30	3-Buten-2-oi (2d)	57 (94) ^p)	-8.80^{9})	26 ^r)	R ^r)
a)	Hydroxocobalamin hydrocl	lloride in mol-%	with respect to e	spoxide. The	rate of ison	lerization	depends on catalyst concer	itration, how	ever, the ee	e is not sub	stantially
(q	attected. Yield of the isolated mire al	lvlic alcohol-calc	ulated with resn	ect to enoxic	łe Conversi	on of the	starting material to the nrc	duct was mo	nitored hv	UU UU	
ۍ ر	Pure allylic alcohol in isolat	ed material, deter	mined by GC.	and a man			and ann an mutannin Sum muc			5	
ۍ ک	Room temp. ca. 22-23°.										
6	Based on $([R - S]/[R + S])$	× 100, calculated	l for pure allylic	alcohol.							
<u>_</u>	Neat, $c = 1$ g/ml.										
(s	Determined by 400-MHz N	IMR spectra of t	oth diastereois	omeric Mosl	ier esters pr	epared fi	om $(+)-(R)$ and $(-)-(S)-3$,	3,3-trifluoro	-2-methoxy	-2-phenylp	ropionyl
	chloride according to [24].										
	For the assignment of confi	guration, cf. [25].									
<u> </u>	$c = 4.4 (\rm CCl_4).$										
<u>ج</u> .	$c = 0.86 (\text{CCI}_4).$						Ţ				
<u>.</u>	Ratio (v/v) epoxide/MeOH	ca. 1:3, in all oth	er cases ca. 1:10								
<u>_</u>	Main impurity is cyclohexai	none as determine	d by GC.								
Ē	c = 1.4 (CHCl ₃).										
(u	Determined by 400-MHz N	MR of both dias	tereoisomeric A	fosher esters	prepared fr)-(+) uo	R)- and (-)-(S)-3,3,3-triflu	oro-2-metho	xy-2-pheny	Ipropionyl	chloride
	according to [24].										
،	For assignment of configura	ttion cf. [26], ee (c	alc.) is based on	⊨ max. [α] ^{f.t.} =	= 112° [26];	according	to a recent report, max. [a	$_{ m D}$ might be c	a. 130° as c	alc. from th	ne ee of a
	precursor [26c].										
(d	Main impurity is H ₂ O (GC)										
.	Neat, $c = 0.837$ g/ml.										
<u>_</u>	For specific rotation and as	signment of confi	guration, cf. [27								

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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*; NH₄Cl (*purum*) from *Siegfried*; NaHB₄ (*purum*) from *Fluka*; McOH (*puriss.*) from *Fluka* was flushed with Ar before use. Zn-wool (*puriss.*) from *Siegfried*, 'activated' before use: Zn (*ca.* 1 g) in 5% HCl/H₂O (*ca.* 10 ml) for 10 min at r.t. followed by washing with H₂O (5 × 10 ml), MeOH (2 × 30 ml), and Et₂O (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. [α]_D: *Perkin-Elmer 241* polarimeter. ¹H-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 (D₆)acetone with TMS (= 0 ppm) as internal standard. The structures of **2a**, **b**, **d** were confirmed by comparison of their ¹H-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 NH₄Cl (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 (B₁₂) 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 Et₂O (80 ml) was added. A brown-red precipitation (B₁₂) was formed. The colourless soln. was decatted and the precipitation extracted 5× with Et₂O (ca. 20 ml each). The combined soln. was washed with sat. NaCl/H₂O (3 × 10 ml), dried (Na₂SO₄), and the solvent evaporated. The remaining colourless oil **2a** (1.34 g, 78%; purity 98% (GC)) was submitted to the analysis without further purification. [a]_D¹ = + 80.9^o (neat). The ee of 55% was determined independently by integration of the ¹H-NMR (400 MHz, (D₆)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: NaBH₄*, *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°, NaBH₄ (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 Et₂O (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)). $[\alpha]_{\Gamma,L}^{\Gamma,L} = +76.4^{\circ}$ (neat); $[\alpha]_{\Gamma,L}^{\Gamma,L} = +75.4^{\circ}$ (c = 1.1, CCl₄), 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 LiClO₄/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 H₂O-ice (50 ml) and extracted with Et₂O/pentane 3:1 (5 × 100 ml). The org. soln. was washed with brine (2 × 100 ml), dried (Na₂SO₄), and concentrated *in vacuo* to *ca.* 3 ml. Column chromatography on 140 g of silica gel with Et₂O/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)). [α]_D^{TL} = +34.9° (*c* = 4.4, CCl₄), 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 NH₄Cl (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)). Et₂O (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)). [α $I_D^{r,t} = +94.5^{\circ}$ (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 NH₄Cl (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 Et₂O (80 ml) 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 [α]_D^{TL} = +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 ¹H-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), NH₄Cl (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), NH₄Cl (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, Et₂O (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)).

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

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