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TETRAHEDRON: *ASYMMETRY*

Asymmetric catalysis. Part 127:[1] Enantioselective desymmetrization of 2-*n*-butyl-4,7-dihydro-1,3-dioxepin with (η^6-arene)ruthenium(II) half-sandwich complexes

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Abstract

(η^6-Arene)ruthenium half-sandwich complexes are highly active and stereoselective catalysts in the enantioselective desymmetrization of 2-*n*-butyl-4,7-dihydro-1,3-dioxepin to give 2-*n*-butyl-4,5-dihydro-1,3-dioxepin. Enantioselectivities up to 61% ee were achieved. The temperature and solvent dependence of the catalysis as well as the activation of the catalyst were investigated.

1. Introduction

4,7-Dihydro-1,3-dioxepins are readily available by reaction of the corresponding aldehyde R–CHO with *cis*-2-butene-1,4-diol. The migration of the double bond from the allyl position to the vinyl position can be carried out with KO^{t}Bu in DMSO or with transition metal catalysts. A new stereogenic center originates from this desymmetrization reaction at the acetal carbon atom. The first attempts to render this reaction enantioselective by using rhodium and ruthenium catalysts modified with diop led to only moderate enantioselectivities (max. 13% for R=*n*-butyl).[2] In a recent paper, asymmetric inductions of up to 67% ee were achieved with a Ni(chiraphos)Br_2 catalyst (R=*t*-butyl).[3] With (η^6-arene)ruthenium half-sandwich complexes, we introduce a new type of catalyst for this reaction attaining enantioselectivities of the same order of magnitude.[4]

Chiral-at-metal half-sandwich complexes have been studied with respect to their kinetically controlled formation[5,6] and their thermodynamically controlled epimerization with respect to the chiral metal atom.[6–8] They have been used to elucidate the stereochemical course of reactions at the metal center.[6,8] Their absolute configurations were determined and their chiroptical properties were investigated.[6,8]

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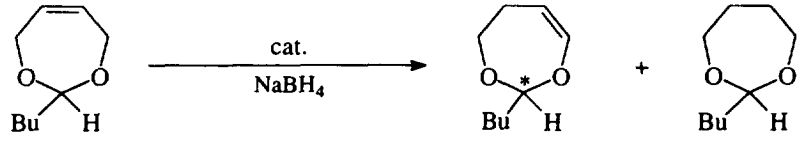
However, there are no reports that chiral-at-metal half-sandwich complexes have been used as catalysts in enantioselective reactions in which the configuration at the metal atom is retained.[9]

(η^6-Arene)ruthenium half-sandwich complexes containing an optically active unsymmetrical chelate ligand, in which the Ru atom is a stereogenic center, have been separated into diastereomers differing only in the Ru-configuration.[10–20] In these compounds, the Ru-configuration turned out to be relatively labile with half-lives of the order of minutes and hours around room temperature or even below.[14,15,17] Surprisingly, the diastereomer equilibria are usually strongly shifted to one side, e.g. 87:13 for the two diastereomers of (η^6-^{i}PrC$_6$H$_4$Me)Ru(pesa)Cl used as the standard catalyst in the isomerization reaction described below. Conditions for this olefin isomerization were such that the half-sandwich Ru complexes used are in equilibrium with respect to the chiral Ru atoms. The contributions of the major diastereomer and the minor diastereomer, which differ only in the Ru-configuration, to the enantioselectivity of the catalytic olefin isomerization must remain open as it is known that the minor diastereomer may be product-determining (compare the Halpern–Brown mechanism of hydrogenation[21]).

(η^6-Arene)ruthenium half-sandwich complexes have been used as enantioselective catalysts and catalyst precursors.[22–24] Whereas in Noyori's catalyst precursors [(η^6-arene)Ru(binap)Hal]$^+$ the arene ligand is lost during hydrogenation,[24] we present evidence that during the olefin isomerization reported here the arene ligand stays at the metal atom, although the actual mechanism of the reaction is not known. In this paper we report our results on the enantioselective isomerization of 2-*n*-butyl-4,7-dihydro-1,3-dioxepin **A** to give 2-*n*-butyl-4,5-dihydro-1,3-dioxepin **B** using known (η^6-arene)ruthenium half-sandwich complexes and, in addition, those synthezised in the preceding paper.

2. Standard reaction and enantiomer analysis

The starting material chosen was 2-*n*-butyl-4,7-dihydro-1,3-dioxepin **A** which contains a plane of symmetry. The isomerization leads to the product 2-*n*-butyl-4,5-dihydro-1,3-dioxepin **B**, accompanied by a small amount of hydrogenation product **C** (Scheme 1). The rearranged product **B** is a suitable precursor for 2,3-substituted tetrahydrofurans and 3,4-substituted 4-butanolides.[2]



Scheme 1. Enantioselective isomerization of **A**

The standard reaction was carried out in the solvent THF:methanol (2:1) with a ratio of substrate:catalyst:$NaBH_4$=200:1:26 at room temperature (reaction time 24 h). The catalyst, here an (η^6-arene)ruthenium half-sandwich complex, was activated under nitrogen with an excess of sodium borohydride followed by addition of the substrate 2-*n*-butyl-4,7-dihydro-1,3-dioxepin **A**. In some catalyses, a relatively large portion of hydrogenated product **C** was formed. This was due to the presence of molecular hydrogen originating from the decomposition of $NaBH_4$ with methanol. This hydrogenation reaction could be suppressed almost completely by removing the hydrogen with a stream of nitrogen for about 15 min. Interestingly, the catalyses carried out with removal of the hydrogen gave much higher enantioselectivities compared to those carried out without removal of the hydrogen. The proof that molecular hydrogen is responsible for the formation of hydrogenation product **C** was furnished by the use of $CH_3OD/NaBD_4$. The decomposition of these compounds led to D_2. Consequently, only

Table 1
Enantioselective isomerization of **A** according to Scheme 1. Substrate 10 mmol, catalyst:$NaBH_4$:substrate 1:26:200, solvent (6 ml) THF:methanol=2:1, room temperature, 24 h

Entry	Catalyst	Conversion (%)	Yield of **B** (%)	ee (%) of **B**[a]
1	[(η^6-^{i}PrC$_6$H$_4$Me)Ru(pesa)Cl] **1**	100, 100, 100, 99	98, 99, 99, 96	53.0, 50.7, 49.8, 53.2
2	[(η^6-^{i}PrC$_6$H$_4$Me)Ru(pepy)Cl] **2**	17, 17	15, 16	1.2, 0.5 (-)
3	[(η^6-^{i}PrC$_6$H$_4$Me)Ru(pesa)I] **3**	100, 95	95, 91	61.0, 60.1
4	[(η^6-^{i}PrC$_6$H$_4$Me)Ru(pesam)Cl] **4**	100[b], 100[b], 100[b]	86, 87, 86	29.3, 30.3, 26.0
5	[(η^6-C$_6$H$_6$)Ru(pesa)Cl]	45[b], 96[b,c]	31, 59	4.3, 5.3
6	[(η^6-C$_6$H$_6$)Ru(pepy)Cl]	6[b]	3	3.4
7	[(η^6-C$_6$H$_6$)Ru(pesam)Cl]	63[b]	50	1.5
8	[(η^6-^{i}PrC$_6$H$_4$Me)Ru(NO$_2$pepy)Cl] **5**	19, 18[d]	16, 16	3.9, 4.1
9	[(η^6-^{i}PrC$_6$H$_4$Me)Ru(oxazsa)Cl] **6**	13, 13[e]	11, 11	0.3, 0.7

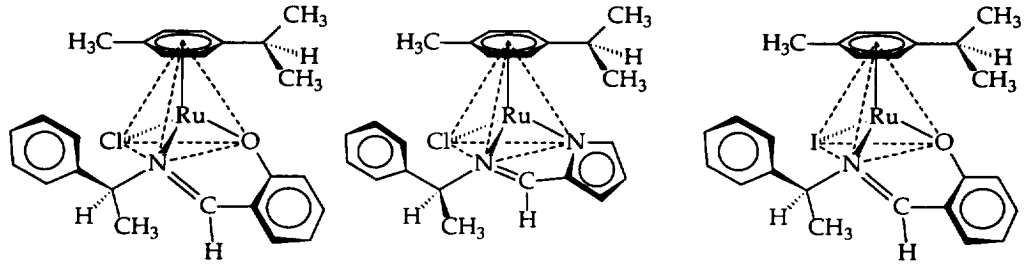
[a] the results refer to the (+)-enantiomer if not stated otherwise. [b] without removing the hydrogen by a stream of nitrogen. [c] reaction time 68 h. [d] reaction time 144 h. [e] reaction time 99 h.

deuterated hydrogenation product **C** is produced, which was identified by ^{1}H NMR spectroscopy. After 24 h the reaction was stopped by bubbling air through the solution to deactivate the catalyst. The solvent was evaporated and the oily residue was purified by Kugelrohr distillation. The conversion was measured by ^{1}H NMR spectroscopy and the enantioselectivity was determined by GC using a chiral Lipodex C column (or a chiral Rt-βDEXcst column, for which the order of elution of the enantiomers of **B** and the hydrogenation product **C** is reversed). In situ catalysts consisting of [Rh(cod)Cl]$_2$ and (−)-diop gave 11% ee at room temperature[2] and 18% ee at 0°C.[4] The standard catalysis was carried out four times with **1** as the catalyst. The conversions were quantitative and the enantioselectivities were 49.8–53.2% ee (Table 1, entry 1). Samples withdrawn from catalytic runs before completion of the reactions gave reduced asymmetric inductions. In an experiment in which the substrate was added 35 min after dissolution of catalyst **1** and sodium borohydride in THF/methanol the conversion was only 66% and the enantioselectivity 33.3% ee.

3. Screening of (η^6-arene)ruthenium half-sandwich catalysts

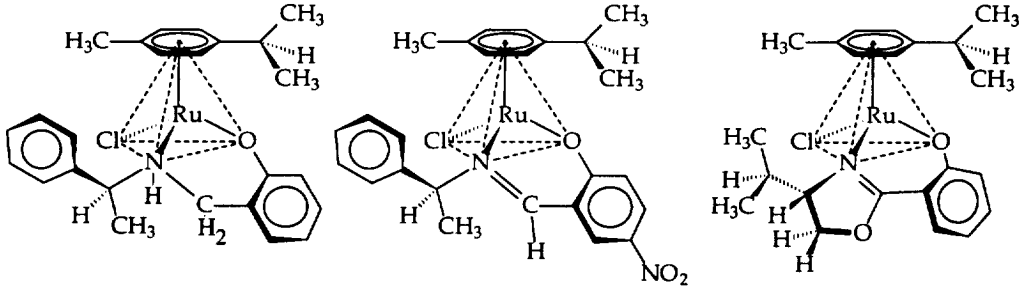
The activity and stereoselectivity of (η^6-arene)ruthenium half-sandwich catalysts in the desymmetrization of 2-*n*-butyl-4,7-dihydro-1,3-dioxepin **A** (Scheme 1) depend strongly on the arene ligand, the chelate ligand and the unidentate ligand. The cymene complexes **1**–**4** (Scheme 2) and their benzene analogs were tested extensively. The results are shown in Table 1.

Quantitative conversion within 24 h was achieved with the complexes **1**, **3** and **4** and with [(η^6-C$_6$H$_6$)Ru(pesa)Cl] (entry 5) after prolongation of the reaction time to 68 h. All of them derive from the Schiff base pesaH of salicylaldehyde and (*S*)-1-phenylethylamine or its hydrogenation product pesamH.



$(R_{Ru},S_C)/(S_{Ru},S_C)$-**1** $(R_{Ru},S_C)/(S_{Ru},S_C)$-**2** (R_{Ru},S_C)-**3**

[(η⁶-^{i}PrC$_6$H$_4$Me)Ru(pesa)Cl] [(η⁶-^{i}PrC$_6$H$_4$Me)Ru(pepy)Cl] [(η⁶-^{i}PrC$_6$H$_4$Me)Ru(pesa)I]



$(R_{Ru},S_C)/(S_{Ru},S_C)$-**4** $(R_{Ru},S_C)/(S_{Ru},S_C)$-**5** $(R_{Ru},S_C)/(S_{Ru},S_C)$-**6**

[(η⁶-^{i}PrC$_6$H$_4$Me)Ru(pesam)Cl] [(η⁶-^{i}PrC$_6$H$_4$Me)Ru(NO$_2$pesa)Cl] [(η⁶-^{i}PrC$_6$H$_4$Me)Ru(oxazsa)Cl]

Scheme 2. Complexes **1**–**6** used in the enantioselective isomerization of **A** and their abbreviated formulas. Only one diastereomer of each complex is shown

The catalytic activities of the pepy complexes **2** and [(η⁶-C$_6$H$_6$)Ru(pepy)Cl] which epimerize much more slowly at the Ru atom than the pesa complexes, were only small (entries 2 and 6) with conversions below 20%. Remarkably, cymene complexes proved to be more active catalysts than benzene complexes (compare entries 1/5, 2/6, 4/7).

The most active catalysts also gave the best enantioselectivities. Thus, with complex **1**, a 51.7% ee was achieved. Even better results were attained with the iodo derivative **3**, for which in the synthesis and in epimerization studies only one diastereomer could be detected (see preceding paper). With **3** as a catalyst, **B** was obtained in 60.6% ee. Complex **4** containing the hydrogenated chelate ligand of **1** and **3** gave an enantioselectivity of 28.5% ee. The asymmetric inductions of the other complexes were below 5% ee. Thus, the complexes with benzene (entries 5–7) gave only poor enantioselectivities compared to the cymene complexes (entries 1–4), indicating that the arene stays at the metal during the catalytic cycle.

Other complexes showed only low to moderate activities. With the complex [(η⁶-C$_6$H$_6$)-Ru(pepyra)Cl]PF$_6$ [pepyra=(*S*)-2-*N*-(1-phenylethyl)pyridinecarbaldimine] the conversion was 52% and the enantioselectivity 6.4% ee.[4] Two complexes were tested, which contained the Schiff base derived from salicylaldehyde and (*R*)-2-amino-1-butanol (absaH). With [(η⁶-^{i}PrC$_6$H$_4$Me)Ru(absa)Cl] in which absa is bound as an *N*,*O*-ligand, the conversion was 72% (extensive hydrogenation) and with [(η⁶-^{i}PrC$_6$H$_4$Me)Ru(absa)]PF$_6$, in which absa acts as a tridentate *N*,*O*,*O*-ligand, the conversion was 20–30%.[4] With both complexes **B** was obtained as a racemate.

Complexes **5** and **6** were prepared in order to investigate the influence of the chelate ligand upon the catalytic activity and enantioselectivity. For this purpose, we modified the ligand pesaH by substitution with a nitro group in the *p*-position of the phenol moiety, and by incorporating the C=N bond into the

oxazoline ring of the ligand oxazsaH we introduced conformational rigidity. Nitro substituents are known to improve the enantioselectivity of pesaH-type ligands in Cu-catalyzed cyclopropanation reactions[25] and oxazoline-type ligands have proven universally applicable in metal-catalyzed enantioselective transformations since their introduction in 1986.[26] The two complexes **5** and **6** were not very active showing conversions below 20%. With **5**, the enantioselectivity was small but significant (entry 8); with **6** only racemic **B** was produced (entry 9).

Some chelate ligands of the pesaH family were tested in situ together with $[(\eta^6\text{-}^i\text{PrC}_6\text{H}_4\text{Me})\text{RuCl}_2]_2$ as the procatalyst in order to investigate whether the preparation of the half-sandwich complexes is necessary at all. The ratio of ruthenium:ligand was 1:2.5. The results are in agreement with those of the isolated complexes, although the enantioselectivities are somewhat lower. The conversion was quantitative with pesaH and its *p*-methoxy substituted derivative MeOpesaH. With the 4-nitro and the 2,4-dinitro derivatives, only 15 and 5% conversion was achieved, respectively. With pesaH as the ligand, **B** was obtained in 41.8% ee, compared to ca. 51% ee with **1**. The nitro compounds gave only low enantioselectivities. On the contrary, asymmetric inductions up to 42.9% ee were attained with the in situ catalyst $[(\eta^6\text{-}^i\text{PrC}_6\text{H}_4\text{Me})\text{RuCl}_2]_2$/MeOpesaH indicating that electron donating substituents in the salicylaldimine system may improve the stereoselectivity.[4]

4. Temperature and solvent dependence

All the experiments concerning the solvent and temperature dependence of the olefin isomerization **A**→**B** (Scheme 1) were carried out using complex **1** as catalyst. During the standard catalysis, started at room temperature, an increase of the temperature was observed. In order to investigate the influence of the temperature, experiments at constant temperatures were carried out. The results obtained at 20°C were hardly reproducible, the conversions varying between 5 and 94% with asymmetric inductions below 15% ee. At 25°C and higher temperatures the conversion was quantitative. At 25°C, the isomerization product **B** was obtained in 39.7% ee. A temperature of 30°C led to an increase of the enantioselectivity to 49.8% ee, whereas 40°C resulted in a decrease of the asymmetric induction to 36.4% ee.

We then tested mixtures of various solvents with methanol (2:1). The results are shown in Table 2. There are solvent mixtures in which the conversion was quantitative and the product **B** showed a high enantiomeric enrichment (entries 1–5). In addition, the formation of hydrogenation product **C** was almost completely suppressed in these solvents. The application of toluene/methanol and ethyl acetate/methanol led to an improvement of about 5% ee (entries 2 and 4) compared to the standard mixture THF/methanol (51.7% ee, Table 1, entry 1). With ethyl acetate/methanol (2 ml/4 ml) an increase to 60.5% ee was observed. With 52.8 and 51.3% ee, benzene/methanol and chlorobenzene/methanol (entries 1 and 3) gave approximately the same asymmetric induction as the THF/methanol mixture. Surprisingly, the enantioselectivity in dioxane/methanol (31.8% ee, entry 5) was much lower than in THF/methanol, although dioxane and THF are both cyclic ethers.

No isomerization was observed in chloroform/methanol and CCl_4/methanol, respectively (entries 6 and 7). In these solvent mixtures, some hydrogenation product **C** was found. In nitromethane/methanol the substrate was totally inert (entry 8). A common feature of these solvents is their oxidizing power. If a metal hydride species is involved in the catalytic cycle, originating from the activation of the (η^6-arene)ruthenium complex with sodium borohydride, it would be destroyed immediately by these solvent mixtures. In pyridine and acetonitrile the conversion is almost quantitative, but only racemic product is formed (entries 9 and 10). Both solvents have good coordinating properties. Possibly, they displace the optically active chelate ligand in the complex depriving the catalyst of its chiral information.

Table 2
Enantioselective isomerization of **A** according to Scheme 1 using catalyst **1**. Substrate 10 mmol, catalyst:$NaBH_4$:substrate=1:26:200, solvent 6 ml, room temperature, 24 h

Entry	Solvent/methanol 2:1	Conversion (%)	Yield of **B** (%)	ee (%) of **B**[a]
1	benzene/methanol	100, 100	99, 98	56.1, 49.4
2	toluene/methanol	100, 100	99, 99	55.3, 57.1
3	chlorobenzene/methanol	100 ,100	98, 97	47.6, 54.9
4	ethyl acetate/methanol	100, 100	99, 99	57.0, 55.2
5	1,4-dioxane/methanol	100, 100	98, 98	30.5, 33.0
6	chloroform/methanol	8	0	-
7	CCl_4/methanol	2	0	-
8	nitromethane/methanol	0	-	-
9	pyridine/methanol	100, 95	97, 93	1.2 (-), 0.3
10	acetonitrile/methanol	94, 89	83, 81	0.7, 0.4

[a] The results refer to the (+)-enantiomer if not stated otherwise.

Table 3
Enantioselective isomerization of **A** according to Scheme 1 using catalyst **1**. Substrate 10 mmol, catalyst:$NaBH_4$:substrate=1:26:200, solvent 6 ml, room temperature, 24 h

Entry	THF/methanol (v/v)	Conversion (%)	Yield of **B** (%)	ee (%) of **B**[a]
1	0 : 6	6, 5	6, 5	2.6, 6.7
2	1 : 5	80, 62	79, 61	57.3, 55.1
3	2 : 4	100, 100	>99.5, 99	60.4, 61.0
4	3 : 3	100, 100	>99.5, 99	56.4 60.0
5	4 : 2	100, 100, 100, 99	98, 99, 99, 96	53.0, 50.7, 49.8, 53.2
6	5 : 1	100, 100	94, 93	29.3, 32.3
7	6 : 0	100, 96	96, 91	racemate

[a] The results refer to the (+)-enantiomer if not stated otherwise.

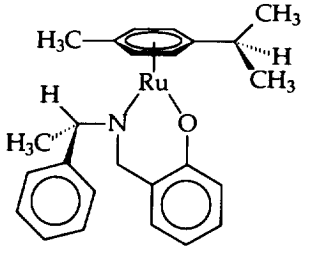
In a second test series, the influence of the ratio of THF/methanol was investigated. The results are shown in Table 3. In 100% methanol, both the activity and the stereoselectivity of the catalysis were very low. The isomerization product **B** was obtained in 6% yield with an asymmetric induction of 4.7% ee only (entry 1). An increase of the THF content to 17% improved the conversion to

70% and the enantioselectivity to 56.2% ee (entry 2). The best results were achieved with a ratio of THF:methanol=2:4. The reaction afforded **B** with 99% yield and 60.7% ee (entry 3). A further increase of the THF content to 50, 67, and 83% led to a decrease in the asymmetric induction from 58.2 via 51.7 to 30.8% ee, respectively (entries 4–6), the conversion being quantitative. Only racemic product was formed in 100% THF. Similarly, pure dioxane and ethyl acetate, respectively, led to racemic **B** (conversion ca. 50%).

Furthermore, we investigated the replacement of methanol in the THF/methanol solvent mixture by other alcohols, such as ethanol and 2-propanol (catalyst **1**). In these 2:1 THF:alcohol mixtures (6 ml), the substrate **A** was isomerized quantitatively in 24 h, hydrogenation product **C** being formed with 7–13% yield. Astonishingly, there was no enantioselectivity when ethanol or 2-propanol were used instead of methanol. The application of ethyl acetate/ethanol and dioxane/ethanol led to racemic **B** (quantitative conversion).

5. Transformation of the catalyst during activation

Some experiments were performed to understand the activation of the (η^6-arene)ruthenium half-sandwich complexes with $NaBH_4$. It is well known that imines are easily reduced by sodium borohydride.[27,28] Therefore, it could be assumed that the C=N bond of the chelate ligand was reduced by $NaBH_4$ during the catalysis. To test this hypothesis, complex **1** was reacted in THF:methanol (2:1) with 2 equiv. of sodium borohydride. Afterwards, no band between 1600 and 1800 cm^{-1} was observed in the IR spectrum (**1** exhibits a band at 1630/1615 cm^{-1}), confirming reduction of the C=N bond. This conclusion was corroborated by the ^1H NMR spectrum of a benzene-d_6:methanol-d_4 (2:1) solution, obtained from the reaction of **1** with $NaBH_4$, which did not show the signal for the imine proton. The mass spectroscopic analysis of the residue obtained from the reaction of **1** with 2 equiv. of $NaBH_4$ in THF:methanol (2:1) gave two peaks. The base peak was m/z=227 (the reduced ligand pesamH). The second peak at m/z=461 could be assigned to complex **7** originating from **1** by hydride addition to the carbon atom of the C=N bond followed by loss of the chloro ligand (Scheme 3). The same complex was prepared by elimination of HCl from [(η^6-^{i}PrC$_6$H$_4$Me)Ru(pesam)Cl] with KOH in CH_2Cl_2 and identified by mass spectroscopy. Complex **7** is similar to the intermediates identified in the ruthenium(II)-catalyzed transfer hydrogenation. Whether complex **7** is the isomerization catalyst, must remain open.



Scheme 3. Complex **7**

6. Experimental

2-Butyl-4,7-dihydro-1,3-dioxepin[29] and 2-butyl-4,5-dihydro-1,3-dioxepin[30] were prepared by literature methods. 2-Butyl-1,3-dioxepan: synthesis similar to 2-*n*-butyl-4,7-dihydro-1,3-dioxepin from valeraldehyde (21.2 ml, 200 mmol) and 1,4-butanediol (19.4 ml, 220 mmol). Yield 22.4 g (71%). B.p. 87–89°C/20 torr. IR (KBr): 2939, 2871 cm^{-1} (ν_{C-H}). ^1H NMR (250 MHz, $CDCl_3$): 4.64 (t, ^3J=5.7, 1H, *H2*), 3.93–3.84 (m, 2H, *H4*, *H7*), 3.66–3.55 (m, 2H, *H4*, *H7*), 1.73–1.51 (m, 6H, *H5*, *H6*, O_2CHCH_2), 1.36–1.28 (m, 4H, $CH_2CH_2CH_2CH_3$), 0.91–0.85 (m, 3H, CH_3). Anal. calcd for $C_9H_{18}O_2$ (158.24): C, 68.31; H, 11.47. Found: C, 68.19; H, 11.27. EI MS: m/z (%)=158 (M, 1), 101 (100), 71 (30), 55 (87), 41 (11).

The catalytic isomerizations were carried out under an atmosphere of dry nitrogen. The catalyst (0.05 mmol) was dissolved in the appropriate solvent (6 ml). $NaBH_4$ (50.0 mmol) was added followed by 2-*n*-butyl-4,7-dihydro-1,3-dioxepin (10.0 mmol). The developing hydrogen was removed by a stream of nitrogen for ca. 15 min. After 24 h, the reaction was stopped by bubbling air through the solution and the solvent was evaporated. The oily residue was purified by Kugelrohr distillation (60°C, 2 torr). Conversion was determined by ^1H NMR spectrocopy (250 MHz, $CDCl_3$). The integrals of the following signals were used: starting material **A**: multiplet (δ=5.7 ppm), product **B**: doublet of doublets (δ=6.4 ppm), hydrogenation product **C**: multiplet (δ=3.5–3.9 ppm). The enantiomeric analysis was carried out by GC: HP 5890 A and HP 5890 II, respectively. Method 1 (used for most of the catalyses): Macherey–Nagel Lipodex C column (50 m, 0.25 mm ID). Conditions: carrier gas H_2, 1.5 bar, 35°C isothermal. Retention times for the enantiomers of **B** 124.5 and 129.1 min and the hydrogenation product **C** 121.2 min. Method 2: Restek Rt-βDEXcst column (30 m, 0.32 mm ID). Conditions: carrier gas H_2, 0.7 bar, 82°C isothermal. Retention times for the enantiomers of **B** 15.5 and 16.3 min and the hydrogenation product **C** 17.2 min.

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