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The high-pressure [4+2]cycloaddition of 1-methoxybuta-1,3-diene to the glycolaldehyde-derived heterodienophiles, catalyzed by chiral metallosalen complexes

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Abstract—A high-pressure (ca. 10 kbar) reaction of 1-methoxybuta-1,3-diene **1** with variously *O*-protected glycolaldehydes **2**, catalyzed by the chiral (salen)Cr(III)Cl **4a–d** and **5** or (salen)Co(II) **6a–f** and **7** complexes, has been studied. The best results were obtained for *tert*-butyldimethylsilyloxyacetaldehyde **2a**. The reaction afforded, in good yield (up to 90%) and with very good diastereoselectivity (up to 92%) and enantioselectivity (up to 93% ee), the [4+2]cycloadducts **3a**, which are compounds of significant synthetic interest. The stereochemical model of the cycloaddition reaction is discussed.

1. Introduction

The application of chiral catalysts to the hetero-Diels–Alder reactions of 1,3-dienes with carbonyl compounds opens a useful route to optically active dihydropyranone and dihydropyran derivatives, valuable intermediates in the total synthesis of natural products.[1] The enantioselective version of this reaction has been intensively investigated since 1990.[2] The attention of synthetic chemists has focussed mostly on the reaction of simple aldehydes with Danishefsky's diene, which led to the formation of the dihydropyranone system.[3] Chromium and cobalt salen-type complexes were also applied in this reaction, which was investigated by research groups of Jacobsen et al.,[4] and Yamada et al.[5] However, the asymmetric version of the [4+2]cycloaddition of simple 1,3-dienes, for example, 1-methoxybuta-1,3-diene, 2,3-dimethylbuta-1,3-diene and cyclohexa-1,3-diene required the application of activated carbonyl compounds such as, for example, alkyl glyoxylates. This subject was mostly investigated by the research groups of Mikami et al.,[6] Jørgensen et al.[7] and Oi et al.,[8] by applying BINOL-titanium(IV), bisoxazoline-copper(II), BINAP-palladium(II) and -platinum(II) complexes, respectively. A similar approach has also been presented by Wu et al.[9] using the (salen)cobalt(II) complex as a catalyst in the reaction of 1-alkyl-3-silyloxybuta-1,3-diene with ethyl glyoxylate. However, the enantioselectivities were moderate.

We have recently shown that the commercially available (salen)chromium(III) **4a** and cobalt(II) **6a** complexes are useful for the reaction of alkyl glyoxylates with simple 1,3-dienes.[10] However, when the non-activated heterodienophiles, such as acetaldehyde or benzaldehyde, were used in the [4+2]cycloaddition even with activated 1-methoxybuta-1,3-diene, carried out under ambient conditions, the reaction failed. In such cases, the application of high-pressure techniques led to a successful reaction. This methodology has recently been applied to the Lewis-acid-catalyzed [4+2]cycloaddition of 1-methoxybuta-1,3-diene **1** to non-activated heterodienophiles derived from glycolaldehyde **2**, leading to racemic 1-methoxy-5,6-dihydro-2*H*-pyran derivatives in moderate yields.[11] The enantioselective version of this cycloaddition using *tert*-butyldimethylsilyloxyacetaldehyde as a

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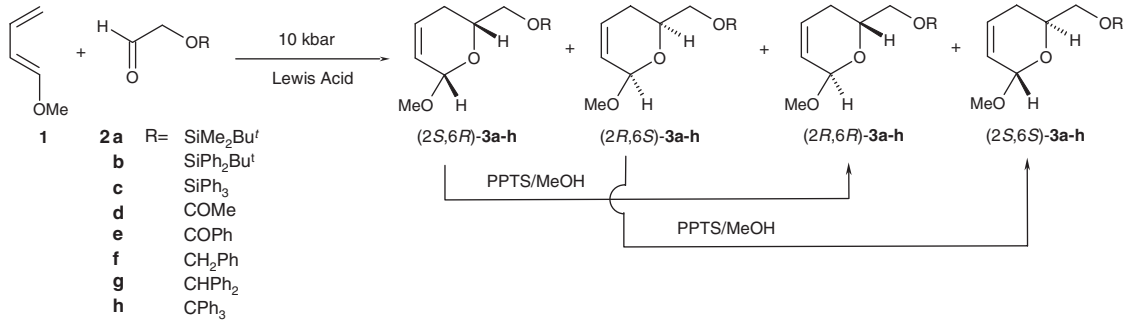
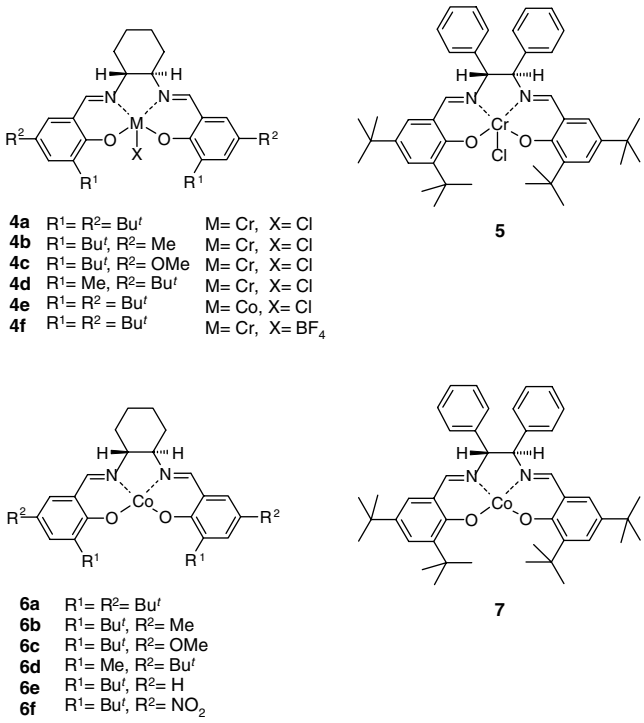


1 **2a** R= $SiMe_2Bu^t$; **b** $SiPh_2Bu^t$; **c** $SiPh_3$; **d** COMe; **e** COPh; **f** CH_2Ph; **g** $CHPh_2$; **h** CPh_3

(2*S*,6*R*)-**3a-h** (2*R*,6*S*)-**3a-h** (2*R*,6*R*)-**3a-h** (2*S*,6*S*)-**3a-h**

Scheme 1.



4a $R^1 = R^2 = Bu^t$ M= Cr, X= Cl
4b $R^1 = Bu^t$, R^2= Me M= Cr, X= Cl
4c $R^1 = Bu^t$, R^2= OMe M= Cr, X= Cl
4d R^1= Me, $R^2 = Bu^t$ M= Cr, X= Cl
4e $R^1 = R^2 = Bu^t$ M= Co, X= Cl
4f $R^1 = R^2 = Bu^t$ M= Cr, X= BF_4

5

6a $R^1 = R^2 = Bu^t$
6b $R^1 = Bu^t$, R^2= Me
6c $R^1 = Bu^t$, R^2= OMe
6d R^1= Me, $R^2 = Bu^t$
6e $R^1 = Bu^t$, R^2= H
6f $R^1 = Bu^t$, $R^2 = NO_2$

7

Figure 1. The (salen)Cr(III), Co(II) and (III) complexes used.

heterodienophile and chiral (salen)chromium(III) and cobalt(II) complexes as catalysts was also published.[12]

Herein, we report an extension of our high-pressure approach to the [4+2]cycloaddition of 1-methoxybuta-1,3-diene (**1**) to variously *O*-protected glycolaldehydes **2** (Scheme 1). The reaction was catalyzed by various (salen)chromium(III) and cobalt(II) complexes, as shown in Figure 1.

2. Results and discussion

As mentioned above, we found that simple glycolaldehyde derivatives **2a**–**h** react with 1-methoxybuta-1,3-diene **1** in the presence of $Eu(fod)_3$ under 10 kbar pressure to afford the racemic cycloadducts **3a**–**h** in moderate to good yields, and with good *cis*-diastereoselectivities as a result of the predominance of the *endo* addition.[11] Moreover, the application of chiral (salen)chromium(III) and cobalt(II) complexes in the reaction of diene **1** with heterodienophile **2a** resulted in the formation of *cis*/*trans* diastereomeric mixtures of cycloadduct **3a** in moderate to high enantioselectivity.[12]

Initially, we decided to use the (salen)CrCl complex **4a** for the reaction of diene **1** with heterodienophile **2a** (Table 1, entries 1–4). The product **3a** was obtained in good yield (even in the case when 0.5 mol % of the catalyst was used) along with very high *endo*-selectivity, with the major *cis*-cycloadduct being formed with 84–87% ee. Similar diastereoselectivities were obtained when other silyloxyacetaldehydes **2b** and **2c** were used as heterodienophiles; however, the yields and enantioselectivities were much lower (entries 5 and 6).

Application of the modified chromium(III) catalysts **4b**–**d** (entries 7–9) and **5** (entry 10) to the reaction of **1** with **2a** afforded results similar in terms of yield, diastereo- and enantioselectivity to the results shown in entries 1–4. The use of the cobalt chloride complex **4e** (entry 11) gave a significantly lower yield as well as a slightly lowered diastereo- and enantioselectivity.

Next, we investigated the influence of catalyst **4f**, in which the counterion Cl^- was replaced by BF_4^-, on the reaction of diene **1** with two heterodienophiles **2a** and **2d** (Table 1, entries 12–15). The complex **4f**, which previously worked very well in the reactions of Danishefsky's diene with simple aldehydes,[4] turned out to be very poor in terms of both yield and enantiomeric excess. The major reaction product was the *trans*-diastereomer as a result of acidic isomerization of the initial diastereomeric mixture. The complex **4f** having a less-coordinated counterion is more active and acidic than the chloride complex, causing a partial polymerization of diene **1**, which explains low yields.

Next, we attempted to optimize the reaction of diene **1** with heterodienophile **2a** using the neutral (salen)Co(II) complex **6a** (Fig. 1 and Table 2). We found that this commercially available catalyst was stereochemically highly effective, although the yield was lower when compared to the cationic more active chromium–chloride complex **4a**.

In the beginning, we investigated the influence of the amount of catalyst and solvent on the course of the reac-

Table 1. High-pressure [4+2]cycloaddition of diene **1** to heterodienophiles **2a–d** in the presence of the complexes **4a–f** and **5**[a]

Entry	Catalyst	Mol %	Dienophile	Solvent	Yield (%)	*cis*/*trans*[b]	ee for *cis*-**3**[b] (%)	ee for *trans*-**3**[b] (%)
1	**4a**	5	**2a**	CH_2Cl_2	80	91:9	84	66
2	**4a**	2	**2a**	CH_2Cl_2	70	95:5	85	65
3	**4a**	2	**2a**	Toluene	84	96:4	87	78
4	**4a**	0.5	**2a**	CH_2Cl_2	60	96:4	85	65
5	**4a**	2	**2b**	CH_2Cl_2	55	97:3	56	32
6	**4a**	2	**2c**	CH_2Cl_2	49	96:4	52	31
7	**4b**	2	**2a**	CH_2Cl_2	82	94:6	86	73
8	**4c**	2	**2a**	CH_2Cl_2	70	93:7	86	76
9	**4d**	2	**2a**	CH_2Cl_2	59	89:11	86	66
10	**5**	2	**2a**	CH_2Cl_2	90	96:4	82	46
11	**4e**	2	**2a**	CH_2Cl_2	32	81:19	75	32
12	**4f**	2	**2a**	CH_2Cl_2	35	8:92	10	12
13	**4f**	2	**2a**	Toluene	29	8:92	10	10
14	**4f**	2	**2d**	CH_2Cl_2	31	11:89	0	2
15	**4f**	2	**2d**	Toluene	25	5:95	4	4

[a] The reactions were carried out using 1 mmol of aldehyde **2** (0.5–1 mol/L) and 1.2 mmol of diene **1** under the pressure of 10–11 kbar at 20 °C for 24 h.
[b] The *cis*/*trans* ratio and the enantiomeric excess were determined by GC on a capillary chiral column.

Table 2. High-pressure [4+2]cycloaddition of diene **1** to heterodienophiles **2a–h**, in the presence of complexes **6a–f** and **7**[a]

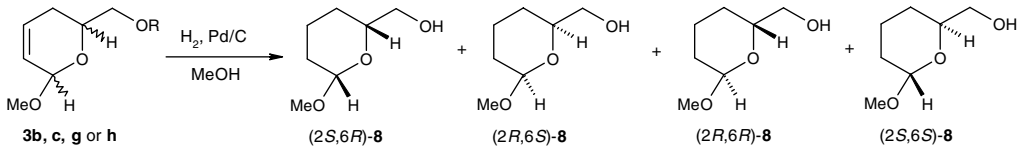
Entry	Catalyst	Mol %	Dienophile	Solvent	Yield (%)	*cis*/*trans*[b]	ee for *cis*-**3**[b] (%)	ee for *trans*-**3**[b] (%)
1	**6a**	2	**2a**	CH_2Cl_2	47	95:5	93	79
2	**6a**	2	**2a**	Toluene	38	83:17	74	59
3	**6a**	5	**2a**	CH_2Cl_2	61	93:7	93	73
4	**6a**	5	**2a**	Toluene	48	80:20	74	60
5	**6a**	2	**2b**	CH_2Cl_2	25	98:2	85	66
6	**6a**	2	**2b**	Toluene	30	98:2	66	48
7	**6a**	2	**2c**	CH_2Cl_2	32	97:3	65	31
8	**6a**	2	**2c**	Toluene	38	94:6	38	18
9	**6a**	2	**2d**	CH_2Cl_2	29	81:19	15	5
10	**6a**	2	**2e**	CH_2Cl_2	26	79:21	20	8
11	**6a**	2	**2f**	CH_2Cl_2	34	89:11	56	33
12	**6a**	2	**2g**	CH_2Cl_2	45	92:8	62	28
13	**6a**	2	**2h**	CH_2Cl_2	50	95:5	61	30
14	**6b**	2	**2a**	CH_2Cl_2	27	93:7	86	72
15	**6c**	2	**2a**	CH_2Cl_2	32	93:7	85	69
16	**6d**	2	**2a**	CH_2Cl_2	49	95:5	91	75
17	**6e**	2	**2a**	CH_2Cl_2	38	93:7	85	71
18	**6f**	2	**2a**	CH_2Cl_2	35	86:14	70	33
19	**7**	2	**2a**	CH_2Cl_2	15	88:12	58	18

[a] The reactions were carried out using 1 mmol of aldehyde **2** (0.5–1 mol/L) and 1.2 mmol of diene **1** under the pressure of 10–11 kbar at 20 °C for 24 h.
[b] The *cis*/*trans* ratio and the enantiomeric excess were determined by GC on a capillary chiral column.

tion of **1** with **2a**, catalyzed by **6a**, and found that an increase in concentration of the catalyst favourably influenced the reaction yield slightly, whereas diastereo- and enantioselectivity remained practically unchanged (Table 2, entries 1–4). In turn, the change of the solvent from methylene dichloride to toluene decreased the yield of the reaction, diastereo- and enantioselectivity (cf. entries 1–2 and 3–4). Similar effects in terms of enantioselectivity were observed for two other *O*-silyloxyacetaldehydes **2b** and **2c** (entries 5–8).

In the case of the acyl derivatives of glycolaldehyde **2d** and **2e**, the yield and diasteroselectivity of their reaction with diene **1** were substantially lower, when compared to the heterodienophiles **2a–c**; the enantioselectivity was extremely poor for both diastereomers (entries 9 and 10). Application of the *O*-benzyl-type heterodienophiles **2f–h** led again to moderate yields and enantioselectivities, whereas diastereoselectivity was very good (entries 11–13).

We also studied the effect of the ligand structure with respect to the substituted salicylidene moieties (Table 2, entries 1 and 14–18). These simple modifications had a small influence on the diastereo- and enantioselectivity of the process. When R^1 are *t*-Bu or Me and R^2 are alkyl or methoxyl groups, the resulting enantioselectivities were in the range of 85–93%. The presence of the NO_2 group (entry 18) resulted in a drop in both diastereo- and enantioselectivity. A change in the diamine part resulted in a significant loss of both enantioselectivity and yield in the case of the cobalt catalyst **7** (Table 2,



Scheme 2.

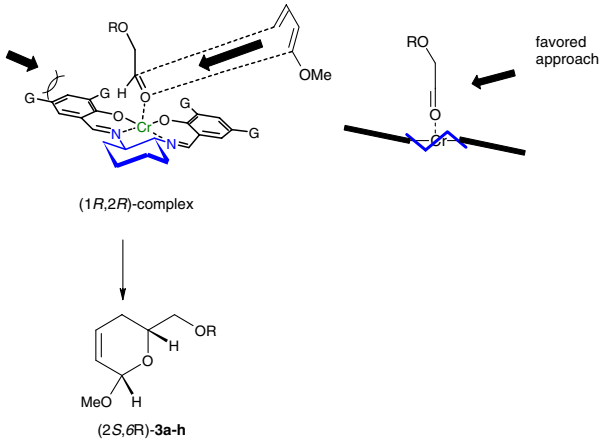
entry 19), while this was not observed in the case of the cationic chromium catalyst **5** (Table 1, entry 10).

The ratio of four [4+2]cycloadducts **3** obtained (Scheme 1) was measured by gas chromatography using chiral columns. In the case of cycloadducts **3a** and **3d**–**f**, the measurements were performed using crude reaction mixtures, after removal of the solvent and catalyst. In these cases, a chiral column α-dex 120 was applied. The stereoisomeric ratio of the four remaining cycloadducts **3b**,**c**,**g**,**h** was measured after hydrogenation of initial mixtures, catalyzed by 10% Pd/C, which resulted in a mixture of four stereoisomeric alcohols **8** (Scheme 2). After removal of the catalyst and solvent, the crude mixture was treated with a commercial trimethylsilylating reagent and subjected to gas chromatography on a chiral β-dex 120 column.

The absolute configuration of the major products was determined by chemical correlation. The formation of the diastereomers (2*S*,6*R*)-**3** predominated in the presence of all (1*R*,2*R*)-chiral catalysts used. The post-reaction mixture containing the cycloadducts **3** was isomerized in the presence of a catalytic amount of pyridinium *p*-toluenesulfonate (PPTS) in methanol (Scheme 1), while the resulting mixtures of *trans*-**3a**–**c**,**f**,**g** or **h** were hydrogenated using 10% Pd/C to yield the enantiomeric mixture of *trans*-alcohols (2*R*,6*R*)-**8** and (2*S*,6*S*)-**8** (Scheme 2). In the case of cycloadducts **3d** and **3e**, following isomerization and hydrogenation, the mixtures of *trans*-products were reduced with $LiAlH_4$ to afford the desired *trans*-alcohols **8**. The specific rotations indicated unequivocally in all cases that the major enantiomer was (2*R*,6*R*)-**8**, corresponding to the cycloadducts (2*S*,6*R*)-**3** as the major products of the original post-reaction mixture.[13]

Rationalization of our results obtained in this work is based on the stereochemical model shown in Scheme 3.

Our model originates from two sources: 1 from the conformational analysis of metallosalen complexes and their influence on the asymmetric induction of catalytic epoxidation of olefins reported by Katsuki et al.,[14] and 2 from the X-ray analysis of the (salen)Co(III)SbF_6 complex with two molecules of benzaldehyde in the axial positions, published recently by Rawal et al.[15] The crucial conclusion given by Katsuki et al. concerns nonplanar, usually stepped conformation of the complex. In turn, the Rawal et al. proposal based on the crystal structure,[15] confirmed by theoretical consideration by Yamada et al.,[16] points out that the aldehyde molecules are not oriented perpendicularly to the complex plane but this is slightly deformed as shown in Scheme 3.



Scheme 3. Stereochemical model.

Therefore, the approach of diene **1** to the complexed dienophile **2** should occur from the outer side. The observed direction of the asymmetric induction [(2*S*,6*R*)-**3** are always formed as the major products by the use of (1*R*,2*R*)-catalysts] is in good agreement with our tereochemical model.

3. Conclusion

In conclusion, we have shown a convenient high-pressure method of synthesis of 2-methoxy-5,6-dihydro-2*H*-pyran derivatives **3** from 1-methoxybuta-1,3-diene **1** and non-activated aldehydes **2**, carried out in the presence of 2 mol % of the commercially available chiral (salen)Cr(III) **4a** and (salen)Co(II) **6a** complexes. In the case of chromium catalysts, the yield (up to 90%) and enantioselectivity (82–87% ee) are satisfactory. The complex **6a** catalyzes the reaction more effectively as concerns enantioselectivity (up to 93% ee), although the yields are substantially lower (25–61%). The best results were obtained with *tert*-butyldimethylsilyloxyacetaldehyde **2a**. This high-pressure approach reveals higher enantioselectivity and diastereoselectivity of the studied reaction, compared to the analogous reaction of *n*-butyl glyoxylate under normal conditions catalyzed by the same (salen)chromium and cobalt complexes.[10b,c]

The stereochemical results are well rationalized on the basis of the model proposed. The present results open up a rational and efficient way to the optically active 6-substituted 2-methoxy-5,6-dihydro-2*H*-pyrans, which are valuable intermediates in the synthesis of modified sugars and other natural products.

4. Experimental

4.1. General

All chemicals were used as received unless otherwise noted. The reagent-grade solvents (CH_2Cl_2, toluene, hexane and AcOEt) were distilled prior to use. Flash chromatography was performed on silica gel (Merck Kieselgel 60, 230–400 mesh). Optical rotations were recorded using a JASCO DIP-360 polarimeter.

Enantiomeric excess of products was determined by gas chromatography performed using a Hewlett–Packard GC unit equipped with a capillary chiral column α- or β-dex 120 (30 m × 0.25 mm I.D., Supelco, Bellefonte, USA).

4.2. Materials

1-Methoxy-1,3-butadiene **1**, (*R*,*R*)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminochromium(III) chloride **4a** (if contains solvents should be dried before use) and (*R*,*R*)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminocobalt(II) **6a** were purchased from Aldrich. Other chromium(III) **4b**–**d** and **5** and cobalt(II) **6b**–**f**, **7** and **4e** salen complexes were prepared according to the known procedures, starting from an appropriate salen ligand and $CrCl_2$ or $Co(OAc)_2$ salts.[17] Salen ligands were synthesized according to the method described by Larrow and Jacobsen.[18] The *O*-protected glycolaldehydes (**2**) were prepared from the corresponding allyl ethers for **2a**–**c** and **2f**–**h** or esters for **2d**, **e** via ozonolysis.

4.3. General procedure for the catalytic high-pressure [4+2]cycloaddition[19]

A 2 ml Teflon ampoule was charged with the chromium or cobalt catalyst (usually 2–5 mol %), a solution of the appropriate *O*-protected glycolaldehyde **2** (1 mmol) in CH_2Cl_2 or toluene, 1.2–1.5 equiv of 1-methoxybutadiene, and the ampoule filled with an appropriate solvent, sealed and placed in a high-pressure vessel and the pressure was then slowly increased to 10–11 kbar at 20 °C. After stabilization, the reaction mixture was kept under these conditions for 24 h. After decompression, the mixture was subjected to column chromatography.

The NMR data of compounds **3a**–**f** were published in our earlier paper concerning the high-pressure synthesis of racemic cycloadducts **3a**–**h**.[11]

4.4. Determination of the stereoisomeric ratio of the reaction mixture

The chromatographic parameters of the enantiomeric separation of the investigated compounds were determined by GC on α- or β-dex 120 column. Chromatography conditions: carrier gas—argon, 120 or 160 kPa; injection temperature 200 °C; detector temperature 250 °C.

Compound **3a**—(column α-dex 120, $T = 120$ °C, 160 kPa): $t_{(2S,6S)} = 24.4$, $t_{(2R,6R)} = 25.5$, $t_{(2S,6R)} = 26.6$, $t_{(2R,6S)} = 27.1$ min; (column β-dex 120, $T = 130$ °C, 100 kPa): $t_{(2S,6S)} = 25.0$, $t_{(2R,6R)} = 25.6$, $t_{(2R,6S)} = 28.2$, $t_{(2S,6R)} = 29.1$ min.

Compound **3d**—(column α-dex 120, $T = 120$ °C, 160 kPa): $t_{(2S,6S)} = 16.6$, $t_{(2R,6R)} = 17.2$, $t_{(2S,6R)} = 18.6$, $t_{(2R,6S)} = 19.2$ min.

Compound **3e**—(column α-dex 120, $T = 160$ °C, 160 kPa): $t_{(2S,6S)} = 76.2$, $t_{(2R,6R)} = 78.2$, $t_{(2S,6R)} = 81.7$, $t_{(2R,6S)} = 82.9$ min.

Compound **3f**—(column α-dex 120, $T = 160$ °C, 160 kPa): $t_{(2S,6S)} = 38.5$, $t_{(2R,6R)} = 39.4$, $t_{(2S,6R)} = 42.0$, $t_{(2R,6S)} = 42.6$ min.

Compounds **3b**,**c**,**g**,**h** were hydrogenated to **8** and the alcohols converted to the trimethylsilyl ether and analyzed on GC. column β-dex 120, 120 °C, 120 kPa: $t_{(2S,6S)} = 12.9$, $t_{(2R,6R)} = 13.4$, $t_{(2R,6S)} = 16.3$, $t_{(2S,6R)} = 16.8$ min.

4.5. Chemical correlation

A mixture of cycloadducts *cis*:*trans*-**3**, obtained in the presence of chiral metallosalen complexes, was isomerized in the presence of a catalytic amount of pyridinium *p*-toluenesulfonate (PPTS) in methanol for ca. 24 h. The resulting isomer, mainly *trans*-**3**, was subjected to reduction with H_2–Pd/C. Following filtration and concentration, the mixture was chromatographed on a silica gel column using hexane/AcOEt. The specific rotation measurement indicated that the major enantiomer was laevorotatory (−)-(2*R*,6*R*)-**8** in all cases when the (1*R*,2*R*)-catalyst was used. Lit.[13] (2*S*,6*S*)-**8**; $[\alpha]_D^{20} = +129.7$ (*c* 4.3, benzene).

References

1. (a) Konowal, A.; Jurczak, J.; Zamojski, A. *Tetrahedron* **1976**, *32*, 2957–2959; (b) Danishefsky, S. J.; DeNinno, M. P. *Angew. Chem., Int. Ed.* **1987**, *26*, 15–23; (c) Bauer, T.; Kozak, J.; Chapuis, C.; Jurczak, J. *J. Chem. Soc., Chem. Commun.* **1990**, 1178–1179; (d) Golebiowski, A.; Jurczak, J. *Synlett* **1993**, 241–245; (e) Jurczak, J. In *Total Synthesis of Amino Sugars in Preparative Carbohydrate Chemistry*; Hanessian, S., Ed.; Marcel Dekker, Inc.: New York, 1997, pp 595–614.
2. For a review, see: Jørgensen, K. A. *Angew. Chem., Int. Ed.* **2000**, *39*, 3558–3588.
3. (a) Danishefsky, S. J.; Kerwin, J. F., Jr.; Kobayashi, S. *J. Am. Chem. Soc.* **1982**, *104*, 358–360; (b) Bednarski, M. D.; Danishefsky, S. J. *J. Am. Chem. Soc.* **1983**, *105*, 3716–3717.
4. (a) Schaus, S. E.; Brånalt, J.; Jacobsen, E. N. *J. Org. Chem.* **1998**, *63*, 403–405; (b) Joly, G. D.; Jacobsen, E. N. *Org. Lett.* **2002**, *4*, 1795–1798.
5. (a) Kezuka, S.; Mita, T.; Ohtsuki, N.; Ikeno, T.; Yamada, T. *Chem. Lett.* **2000**, 824–825; (b) Yamada, T.; Kezuka, S.; Mita, T.; Ikeno, T. *Heterocycles* **2000**, *52*, 1041–1045.
6. (a) Terada, M.; Mikami, K.; Nakai, T. *Tetrahedron Lett.* **1991**, *32*, 935–938; (b) Mikami, K.; Motoyama, Y.; Terada, M. *J. Am. Chem. Soc.* **1994**, *116*, 2812–2820; (c)

Quitschalle, M.; Christmann, M.; Bhatt, U.; Kalesse, M. *Tetrahedron Lett.* **2001**, *42*, 1263–1265.
7. (a) Johannsen, M.; Jørgensen, K. A. *J. Org. Chem.* **1995**, *60*, 5757–5762; (b) Johannsen, M.; Yao, S.; Graven, A.; Jørgensen, K. A. *Pure Appl. Chem.* **1998**, *70*, 1117–1122.
8. Oi, S.; Terada, E.; Ohuchi, K.; Kato, T.; Tachibana, Y.; Inoue, Y. *J. Org. Chem.* **1999**, *64*, 8660–8667.
9. Li, L.-S.; Wu, Y.; Hu, Y.-J.; Xia, L.-J.; Wu, Y.-L. *Tetrahedron: Asymmetry* **1998**, *9*, 2271–2277.
10. (a) Kwiatkowski, P.; Asztemborska, M.; Caille, J.-C.; Jurczak, J. *Adv. Synth. Catal.* **2003**, 506–509; (b) Kwiatkowski, P.; Asztemborska, M.; Jurczak, J. *Synlett* **2004**, 1755–1758; (c) Kwiatkowski, P.; Asztemborska, M.; Jurczak, J. *Tetrahedron: Asymmetry* **2004**, *15*, 3189–3194.
11. Malinowska, M.; Salanski, P.; Caille, J.-C.; Jurczak, J. *Synthesis* **2002**, 2707–2710.
12. Malinowska, M.; Kwiatkowski, P.; Jurczak, J. *Tetrahedron Lett.* **2004**, *45*, 7693–7696.
13. Jurczak, J.; Bauer, T.; Filipek, S.; Tkacz, M.; Zygo, K. *J. Chem. Soc., Chem. Commun.* **1983**, 540–542.
14. (a) Hamada, T.; Fukuda, T.; Imanishi, H.; Katsuki, T. *Tetrahedron* **1996**, *52*, 515–530; (b) Hashihayata, T.; Ito, Y.; Katsuki, T. *Tetrahedron* **1997**, *53*, 9541–9552; (c) Yoshio, N.; Katsuki, T. *Tetrahedron Lett.* **1998**, *39*, 4325–4328; (d) Hashihayata, T.; Punniyamurthy, T.; Irie, R.; Katsuki, T.; Akita, M.; Moro-oka, Y. *Tetrahedron* **1999**, *55*, 14599–14610.
15. Huang, Y.; Iwama, T.; Rawal, V. H. *J. Am. Chem. Soc.* **2002**, *124*, 5950–5951.
16. Iwakura, I.; Ikeno, T.; Yamada, T. *Angew. Chem., Int. Ed.* **2005**, *44*, 2524–2527.
17. (a) Martínez, L. E.; Leighton, J. L.; Carsten, D. H.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1995**, *117*, 5897–5898; (b) Leung, W.-H.; Chan, E. Y. Y.; Chow, E. K. F.; Williams, I. D.; Reng, S.-M. *J. Chem. Soc., Dalton Trans.* **1996**, 1229–1236.
18. Larrow, J. F.; Jacobsen, E. N. *J. Org. Chem.* **1994**, *59*, 1939–1942.
19. Jurczak, J.; Chmielewski, M.; Filipek, S. *Synthesis* **1979**, 41–42.