Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Molecular Catalysis A: Chemical 229 (2005) 19–24
JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL
www.elsevier.com/locate/molcata

Enantioselective hydrogenation of α-hydroxyketones over cinchona-modified Pt: influence of reactant and modifier structure

Otmar J. Sonderegger, Gabriel M.-W. Ho, Thomas Bürgi[1], Alfons Baiker*

Department of Chemistry and Applied Biosciences, Swiss Federal Institute of Technology, ETH-Hönggerberg, CH-8093 Zürich, Switzerland

Received 15 October 2004; received in revised form 3 November 2004; accepted 3 November 2004
Available online 13 December 2004

Abstract

The scope of the asymmetric hydrogenation of functionalized ketones over cinchona-modified platinum was extended to achiral α-hydroxyketones. Cinchonidine showed by far the best catalytic performance affording an enantiomeric excess between 57 and 82% depending on the substrate. *O*-methoxy-cinchonidine showed poor enantioselection. *O*-phenoxy-cinchonidine favoured the opposite enantiomer compared to cinchonidine. Solvents with empirical solvent parameters E_T^N – ranging from 0.10 to 0.65 were tested. *Tert*-butylmethylether proved to be the most suitable. The highest ratio of substrate/cinchonidine where no loss in e.e. was observed was at around 540, independent of the structure of the α-hydroxyketone. The oxygen in α-position to the ketone seems to play an important role in the enantioselection as well as a phenyl ring or a rigid *cis*-conformation. The dependence of the enantiomeric excess on the modifier structure and the inversion of the sense of enantiodifferentiation is interpreted in terms of repulsive interactions, which become more evident as the steric demand of the functional group (OH, O─Me, O─Ph) of the modifier increases. The findings indicate that a hydrogen bond in the modifier reactant complex involving the hydroxyl functionality of cinchonidine is not crucial in order to achieve high enantioselectivity.
© 2004 Elsevier B.V. All rights reserved.

Keywords: Enantioselective; α-Hydroxyketones; Cinchonidine

1. Introduction

The worldwide sales of single-enantiomer drugs was more than $159 billion in 2002 and is projected to reach more than $200 billion in 2008 [1]. Heterogeneous enantioselective catalysis is a promising route for the production of enantiopure compounds because it has a lot of benefits compared to other technologies. Enantioselective catalysis has the advantage of chiral multiplication. With a small amount of optically active catalyst a large amount of a chiral product can be generated. A heterogeneous process has furthermore advantages with respect to homogeneous processes concerning catalyst handling, separation and reuse, and offers the possibility to run continuous processes [2]. Heterogeneous enantioselective catalytic systems can be prepared by different strategies. Among these, chiral modification is an easy and elegant way to combine the catalytic activity of a (supported) metal catalyst with enantiodifferentiation. The chiral information is imparted onto the catalyst simply by adsorption of a chiral molecule, the modifier. The two most investigated catalytic systems of this family are the Pt–cinchonidine (CD) [3] and the Ni–tartaric acid systems [4]. Pt/CD catalysts show good enantiodifferentiation in the hydrogenation of α-functionalized ketones, such as α-ketoesters. The scope of cinchona-modified metal systems has been steadily growing, including the enantioselective reduction of C=C bonds over Pd catalysts. Successful examples include the enantioselective hydrogenations of α,β-unsaturated acids [5,6] and 2-pyrone derivatives [7].

An interesting application of the Pt/CD system is the production of optically pure 1,2-diols, which are useful

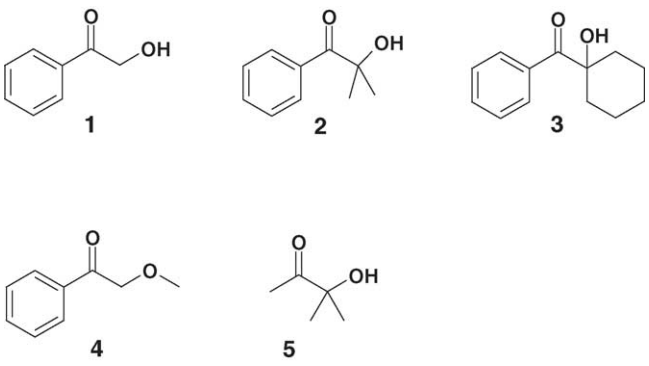
* Corresponding author. Tel.: +41 1 632 3153; fax: +41 1 632 1163.
E-mail address: baiker@chem.ethz.ch (A. Baiker).
[1] Present address: Institut de Chimie, Université de Neuchâtel, Av. de Bellevaux 51, CH-2007 Neuchâtel, Switzerland.

1381-1169/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.molcata.2004.11.003

intermediates and auxiliaries in organic synthesis [8]. They can be transformed into chiral epoxides, aziridines and amino alcohols [9–11]. The 1,2-diol functionality can be found in a number of pharmaceutical intermediates [12]. Such diols can be obtained through enantioselective hydrogenation of vicinal ketones. Several vicinal diketones have been hydrogenated over cinchonidine-modified Pt, such as cyclohexane-1,2-dione [13], butane-2,3-dione [14], hexane-3,4-dione [15], and 1-phenylpropane-1,2-dione [16]. In the first step of all these reactions, chiral α-hydroxyketones are formed. The observed behaviour of diketones in the enantioselective hydrogenation over Pt/CD exhibits features that are different from the behaviour of ethyl pyruvate and other α-ketoesters, which have been studied in some detail [17–20]. For instance, the overall rate acceleration can be observed only in some cases, not in general, for the hydrogenation of vicinal diketones [21]. Further, it has been proposed that in the hydrogenation of 1-phenylpropane-1,2-dione on the Pt/CD system the reaction mechanism of the first hydrogenation is different from that of the second one [22]. The first hydrogenation was proposed to involve a two-step cycle (reactant–modifier) whereas the second hydrogenation was suggested to proceed via a three-step cycle (reactant–modifier–acetic acid). In any case the mechanism of enantiodifferentiation is not well studied for this class of substrates. A better mechanistic understanding of the enantioselection in the hydrogenation of diketones would also contribute to a better general understanding of the Pt/CD system.

The enantioselectivity in the asymmetric hydrogenation of diketones depends on two subsequent hydrogenation steps, leading to two chiral centres, which complicates mechanistic investigations. In the second hydrogenation step, a chiral α-hydroxyketone reacts to a chiral diol. To the best of our knowledge till now, no achiral α-hydroxyketones have been studied.

To gain some insight how structural changes of the reactants affect their catalytic behaviour in the heterogeneous enantioselective hydrogenation over chirally modified platinum, a series of α-hydroxyketones (Scheme 1) has been investigated, including 2-hydroxyacetophenone (**1**), 2-hydroxy-2-methylpropiophenone (**2**), 1-hydroxycyclohexylphenylketone (**3**), 2-methoxyacetophenone (**4**), which is a derivative of **1** and 3-hydroxy-3-methyl-2-butanone (**5**). Three different chiral modifiers were applied: cinchonidine (CD), *O*-methoxy-cinchonidine (MeOCD) and *O*-phenoxy-cinchonidine (PhOCD).



Scheme 1. Overview of reactants.

2. Experimental

The 5 wt.% Pt/Al_2O_3 catalyst (Engelhard 4759) was prereduced in flowing hydrogen for 90 min at 400 °C. The platinum dispersion was 0.27 as determined by TEM measurements. All the solvents and reactants were used as received: *tert*-butylmethylether (*t*-BM-ether) (Fluka >99.5%), dioxane (Fluka >99.5%; over molecular sieve (H_2O <0.01%)), toluene (Fluka >99.7%), tetrahydrofuran (THF) (Riedel-de Haën; spectranal), ethyl acetate (Merck p.a.), dichloromethane (Baker >99.5%), 1-methylpyrrolidin-2-one (Fluka >99.0%), *N*,*N*-dimethylformamide (Scharlau >99.8%), acetonitrile (Fluka >99.5%), 2-propanol (Fluka p.a.), acetic acid (Fluka p.a.), cinchonidine (CD) (Fluka), *O*-methoxy-cinchonidine (MeOCD) (Ubichem >95%), *O*-phenoxy-cinchonidine (PhOCD) (Ubichem >95%), 2-hydroxyacetophenone (**1**) (Aldrich 98%), 1-hydroxy-2-methylpropiophenone (**2**) (Aldrich 97%), 1-hydroxycyclohexylphenylketone (**3**) (Aldrich 99%), 2-methoxyacetophenone (**4**) (Aldrich 95%) and 3-hydroxy-3-methyl-2-butanone (**5**) (Fluka 95%) (Scheme 1).

The hydrogenation reactions above 30 bar were carried out in a 100-ml stainless-steel autoclave equipped with a 50-ml glass liner and PTFE cover. The reactor was magnetically stirred ($n = 500\ min^{-1}$). The pressure was held at a constant value by a computerized constant volume–constant pressure equipment (Büchi BPC 9901). The hydrogenation reactions up to 30 bar were carried out in a multiple reactor (Argonaut Technologies) equipped with eight 10-ml glass liners, which are mechanically stirred ($n = 500\ min^{-1}$). The reaction conditions were: 21 ± 1 mg prereduced catalyst, 0.92 mmol substrate (0.46 mmol for reactant **1**), 6.8 μmol modifier and 5 ml solvent, 20 bar, room temperature (21 °C) and 6 h reaction time were chosen, if not otherwise stated. In the solvent screening reactions 0.34 μmol and 6.8 μmol modifier, respectively, were used.

The enantiomeric excess (e.e.) was determined using a MERCK LaChrom HPLC-System and a chiral column (CHIRALCEL OB or CHIRALCEL OD). The measurements were carried out at 15 °C and the UV-detector was set at 210 nm. The detector was calibrated by injecting mixtures of reactant and product of known compositions.

Enantiomeric excess is expressed as $e.e.(\%) = 100 \times (|R - S|)/(R + S)$. For phenylethane-1,2-diol (the hydrogenation product of **1**), the absolute configuration of the major enantiomer in the reaction with CD as modifier was determined as (*R*) by comparison with the commercial (*R*)-enantiomer (Fluka).

3. Results

In the first step hydrogenations of reactants **1**–**5** (Scheme 1) were carried out in different solvents aiming at finding the most suitable solvent (Table 1). Among the tested solvents *tert*-butylmethylether (*t*-BM-ether) proved to be the most suitable leading to the best results with respect to both e.e. and conversion. Dioxane also gave good e.e.s, but at lower conversion. The results obtained with the different reactants are listed according to increasing E_T^N-values (empirical parameter of solvent polarity) [23] of the solvents. With some exceptions, the e.e. decreased with increasing solvent polarity.

Table 1
Influence of solvents on enantioselectivity and conversion for the hydrogenation of **1**–**5** over Pt/alumina modified by CD

Substrate	Solvent	E_T^N[a] [23]	e.e. (%)	Conversion (%)
1	Toluene	0.10	61	97
	t-BM-ether	0.15	70	89
	Dioxane	0.16	70	41
	2-Propanol	0.55	37	100
	Acetic acid	0.65	3	89
2	Toluene	0.10	39	44
	t-BM-ether	0.15	50	91
	Dioxane	0.16	44	21
	2-Propanol	0.55	29	97
	Acetic acid	0.65	5	95
3	Toluene	0.10	49	76
	t-BM-ether	0.15	63	68
	Dioxane	0.16	84	15
	THF	0.21	33	29
	Ethyl acetate	0.23	44	52
	Dichloromethane	0.31	53	33
	1-Methylpyrrolidin-2-one	0.36	50	1
	DMF	0.40	–	0
	Acetonitrile	0.46	39	43
	2-Propanol	0.55	41	87
	Acetic acid	0.65	11	88
4	Toluene	0.10	58	56
	t-BM-ether	0.15	71	90
	Dioxane	0.16	69	20
	THF	0.21	44	34
	Ethyl acetate	0.23	53	51
	Dichloromethane	0.31	41	23
	2-Propanol	0.55	34	99
	Acetic acid	0.65	9	100
5	Toluene	0.10	11	65
	t-BM-ether	0.15	14	48
	Dioxane	0.16	10	9
	THF	0.21	9	9
	Ethyl acetat	0.23	7	23
	Dichloromethane	0.31	7	28
	2-Propanol	0.55	5[b]	67
	Acetic acid	0.65	1	25

Reaction conditions: 21 mg catalyst, 0.92 mmol substrate (0.46 mmol for reactant **1**), 6.8 μmol CD, 5 ml solvent, 20 bar, room temperature (21 °C) and 6 h reaction time.

[a] Empirical parameter of solvent polarity.

[b] Opposite enantiomer.

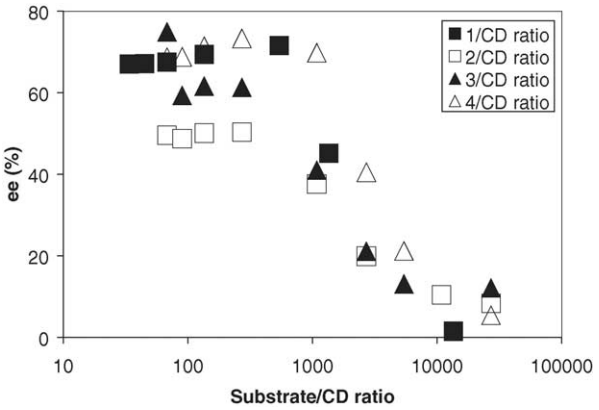


Fig. 1. Enantiomeric excess of **1**, **2**, **3** and **4** over CD modified Pt/alumina as a function of substrate/CD ratio. Reaction conditions: 21 mg catalyst, 0.92 mmol substrate (0.46 mmol for reactant **1**), 5 ml solvent, 20 bar, room temperature and 6 h reaction time.

In the next step, reactions were performed with different cinchonidine (CD) concentrations in *t*-BM-ether (Fig. 1). Interestingly, the e.e. decreased at a substrate/CD ratio higher than about 540, independent of the structure of the reactant. High modifier concentrations caused lower conversion for reactants **2–4**, whereas for reactant **1**, no significant tendency was observed. Table 2 shows the influence of the cinchonidine concentration on e.e. and conversion for reactants **1**–**5**. Hydrogenations of reactants **1**–**4** at different hydrogen pressure indicated only low hydrogen pressure dependence. The conversion slightly increased in the hydrogen pressure range 1–30 bar, whereas the e.e. was constant (**1**, **2**) or decreased slightly (**3**, **4**).

The application of lower temperature 0 °C instead of 21 °C afforded the following results: reactant **1**, 82.3% e.e. (52.6% conversion); reactant **2**, 56.6% e.e. (61.6% conversion);

Table 2
Effect of CD modifier concentration on enantioselectivity and conversion for the hydrogenation of **1**–**5** over Pt/alumina modified by CD

Substrate	CD concentration (μmol)	e.e. (%)	Conversion (%)
1	6.8	70	89
	3.4	74	87
	0.34	45	87
2	6.8	50	91
	3.4	50	91
	0.34	20	100
3	6.8	63	68
	3.4	61	77
	0.34	21	99
4	6.8	71	90
	3.4	73	93
	0.34	41	100
5	6.8	14	48
	3.4	10	58
	0.34	1	100

Reaction conditions: 21 mg catalyst, 0.92 mmol substrate (0.46 mmol for reactant **1**), 5 ml solvent, 20 bar, room temperature and 6 h reaction time.

Table 3
Performance of different modifiers in enantioselective hydrogenation of reactants **1**–**4** over modified Pt/alumina

Substrate	Modifier concentartion (μmol)	CD		MeOCD		PhOCD	
		e.e. (%)	Conversion (%)	e.e. (%)	Conversion (%)	e.e. (%)	Conversion (%)
1	6.8			5 (*R*)	49	35 (*S*)	57
	3.4	77 (*R*)	74	10 (*R*)	47	31 (*S*)	48
	0.34			7 (*R*)	54	26 (*S*)	49
2	6.8	57 (*R*)	62	11 (*S*)	43	33 (*S*)	92
	3.4			10 (*S*)	44	32 (*S*)	99
	0.34			7 (*S*)	57	16 (*S*)	98
3	6.8	76 (*R*)	42	4 (*R*)	42	26 (*S*)	74
	3.4			4 (*R*)	42	25 (*S*)	74
	0.34			3 (*R*)	86	12 (*S*)	86
4	6.8	81 (*R*)	69	5 (*S*)	31	53 (*S*)	70
	3.4			2 (*S*)	34	51 (*S*)	72
	0.34			3 (*R*)	46	33 (*S*)	19

Reaction conditions: 21 mg catalyst, 0.92 mmol substrate (0.46 mmol for reactant **1**), 5 ml solvent, 5 bar, room temperature and 6 h reaction time.

reactant **3**, 75.6% e.e. (42.4% conversion) and reactant **4,** 81.1% e.e. (69.3% conversion). Comparison of these results with those obtained at 21 °C (Table 3) shows that lower temperature favoured e.e. but lowered conversion.

Reactions performed with *O*-methoxy-cinchonidine (MeOCD) and *O*-phenoxy-cinchonidine (PhOCD) as modifiers are compared to similar experiments with the standard modifier cinchonidine in Table 3. For this purpose reaction conditions optimised with CD were applied using *t*-BM-ether as solvent. From the results listed in tables 2 and 3, the following conclusions can be drawn: (i) CD provides by far highest enantioselection with all reactants; (ii) PhOCD provides opposite enantiomer and (iii) MeOCD shows poor enantiodifferentiation.

4. Discussion

Among the investigated solvents *t*-BM-ether, dioxane and toluene are most suitable for the heterogeneous enantioselective hydrogenation of **1**–**5** over CD-modified Pt. In polar solvents the e.e. is quite low. Toukoniitty et al. found the same behaviour for the 1-phenylpropane-1,2-dione system for the first reaction step [22,24]. Low reaction temperature was favourable for the e.e., but lowered conversion, as observed for other reactions catalyzed by the Pt/CD system [13].

For the reactants **1**–**4** e.e.s from 57% up to 82% with cinchonidine as modifier were obtained. This compares favourably with structurally similar systems such as 1-phenylpropane-1,2-dione [21] and substituted acetophenones [25].

With PhOCD for the reactants **1**–**4** the enantioselectivity is inversed and the (*S*)-enantiomer was obtained in excess with e.e.s in the range of 26–53%. For reactant **4** with CD 75% e.e. toward the (*R*)-enantiomer was obtained and with PhOCD 53% e.e. toward the (*S*)-enantiomer. Interestingly, this is the same inversion of enantioselectivity as has been observed for ketopantolactone [26] when changing from CD to PhOCD.

This could be an indication that the mechanism of enantioselection is similar for these systems. As a consequence, this would imply that the reactants investigated here adopt a *cis* conformation of the ketone and hydroxyl (methoxy) groups during enantioselection, since in ketopantolactone the corresponding functional groups are fixed in *cis* conformation. A *cis* conformation was also proposed for the enantioselective hydrogenation of 1-phenylpropane-1,2-dione over modified Pt [22], which shows similar behaviour concerning solvent and modifier (CD, MeOCD) as the reactants investigated here. The conformation of the reactant (*cis* versus *trans*) has important consequences on the interaction with the modifier, as has also been discussed in detail for the enantioselective hydrogenation of methyl pyruvate [27,28]. The reactants investigated here are conformationally flexible, and therefore different substitution (reactants **1**–**3**) could affect the e.e. through a change of the relative stabilities of the conformers. This could be one reason for the higher e.e.s generally obtained for reactants **1** and **4** compared to **2** and **3**. The *cis* conformation in the former is stabilized with respect to *trans* due to repulsive interactions between the hydroxyl (methoxy) group with the phenyl ring in trans conformation.

Reactants **1**–**4** show similar catalytic behaviour. The common chemical feature of the reactants is the functional group bearing an oxygen atom in α-position to the ketone that is hydrogenated. This oxygen seems to play a very important role and the reason for this may be of different kind. For the enantioselective hydrogenation of 1-phenylpropane-1,2-dione it has been proposed that this functional group interacts via a hydrogen bond with the modifier (see below). Alternatively, a stabilisation of the transition state has been proposed. Vargas et al. calculated the semi-hydrogenated species for methylpyruvate hydrogenation [29]. They found that the ester group oxygen in α-position lowers the energy needed for hydrogen uptake, through hydrogen bonding in the transition

state. It is very likely that this kind of hydrogen bonding can be formed in the transition state of reactants **1**–**4** as well. Acetophenone is the corresponding molecule to reactants **1** and **4** without oxygen in α-position. The e.e. for its enantioselection in toluene is 17% [25].

For the enantioselective hydrogenation of 1-phenylpropane-1,2-dione it has been claimed that the C-9 OH of the CD modifier interacts with the reactant and is, therefore, necessary for achieving high enantioselectivity. The proposal was based on the observation that only marginal e.e. was obtained with MeOCD [22]. The proposed model for enantiodifferentiation (for the first hydrogenation step) included two hydrogen bonds between CD and the dione reactant. One hydrogen bond is formed between the N–H of CD and one keto group and the second hydrogen bond between the C-9 OH of CD and the second keto group of the reactant. Such an interaction is, in principle, also feasible for reactants **1**–**4** investigated here. Furthermore, the similar catalytic behaviour (solvent dependence, slight rate deceleration) for reactants **1**–**4** and 1-phenylpropane-1,2-dione [22] indicates a similar mechanism. Even more striking to demonstrate the similarity of the catalytic systems is the observation that the achieved e.e. in the first hydrogenation step of 1-phenylpropane-1,2-dione in the presence of CD was reported as 57% in favour of the (*R*)-alcohol, whereas a slight e.e. in favour of the (*S*)-enantiomer was found in presence of MeOCD. These values are very close to what we find for reactant **2**, which is structurally very similar to 1-phenylpropane-1,2-dione.

However, the view of enantiodifferentiation involving two hydrogen bonds as outlined above is challenged by several observations. If a hydroxyl functionality was necessary in the modifier reactant complex in order to establish a second hydrogen bond to achieve high enantioselectivity, one could expect a different behaviour of reactants **1**–**3** with respect to **4**. The former reactants carry a hydroxyl functionality and could also form a hydrogen bond with the MeOCD modifier, whereas **4** and 1-phenylpropane-1,2-dione are not able to do so. The catalytic results show that reactant **4** behaves like the other reactants **1**–**3**. This, on the one hand, clearly shows that the reactant is not a hydrogen bond donor in the enantiodifferentiating interaction and on the other hand at least indicates that no second hydrogen bond is formed between reactant and modifier. Furthermore, when using PhOCD as modifier a similar argument should be valid as for MeOCD. PhOCD can also not form a second hydrogen bond with **4**, but still appreciable e.e. is observed in the hydrogenation of **4** (although in favour of the opposite enantiomer). The decrease in e.e. in the enantioselective hydrogenation of 1-phenylpropane-1,2-dione (first hydrogenation step) and **1**–**4** when using MeOCD instead of CD as modifier may therefore have another reason: When going from CD over MeOCD to PhOCD the steric requirements of the corresponding groups (H, Me, Ph) increases and correspondingly the e.e. decreases and finally switches. The increasing steric demand may influence not only the adsorption mode on the surface [30] but also direct enantiodifferentiation in opposite direction due to repulsive modifier–reactant interactions. Such a trend was also found for other reactants [31]. Note that in the hydrogenation of activated α-substituted ketones the e.e. with MeOCD is very similar to the one with CD [31].

For the reactants investigated here, not only the oxygen atom in α-position to the ketone is important as discussed above, to achieve high e.e. For reactant **5** the maximum achieved e.e. was 14%. For the structurally very similar reactant **2**, 57% were observed. This shows that for reactants **1**–**4** the phenyl ring is necessary for enantioselection as well. Finally, the difference in enantioselectivity between cinchonidine and phenoxycinchonidine for reactants **2** and **3** is significant. The cyclohexyl ring of reactant **3** seems to be sterically too demanding for appreciable enantioselectivitiy with *O*-phenoxy-cinchonidine.

5. Conclusions

Reactants **1**–**4** can be hydrogenated with appreciable enantiomeric excess. For the structurally similar reactants **1** and **4** over 80% e.e. was achieved without extensive system optimization. The behaviour of reactants **1**–**4** on a cinchona-modified Pt surface is very similar. All four reactants show the same general trend with respect to dependence on solvent, pressure and modifier. By comparison with reactant **5** we can conclude that for these reactants the phenyl ring or a fixed system is essential for enantioselection. Furthermore, the oxygen in α-position to the ketone plays a crucial role for achieving high enantiomeric excess.

Based on the comparison of the catalytic behaviour of **1**–**4** in the enantioselective hydrogenation over Pt modified with cinchonidine, *O*-methoxy-cinchonidine and *O*-phenoxy-cinchonidine it is suggested that no second hydrogen bond between the modifier and reactant is formed, as has been proposed recently for the enantioselective hydrogenation of the structurally similar 1-phenylpropane-1,2-dione. Instead, the dependence of the enantiomeric excess on the modifier structure and in particular inversion of the enantiomeric excess is interpreted in terms of repulsive modifier–reactant interactions, which become more pronounced as the steric demand of the C-9-O–R group of the modifier increases. The obvious importance of the oxygen bearing group (ketone, hydroxyl, methoxy) in α-position to the ketone that is hydrogenated is rather assigned to a lowering of the transition state energy for hydrogenation due to hydrogen bonding, as previously suggested based on calculations.

Acknowledgement

Financial support by the Swiss National Science Foundation is kindly acknowledged.

References

[1] A.M. Rouhi, Chem. Eng. News 81 (18) (2003) 45.
[2] N. Künzle, R. Hess, T. Mallat, A. Baiker, J. Catal. 186 (1999) 239.
[3] Y. Orito, S. Imai, S. Niwa, J. Chem. Soc. Jpn. (1979) 1118.
[4] Y. Izumi, Angew. Chem. Int. Ed. Engl. 10 (1971) 871.
[5] Y. Nitta, K. Kobiro, Y. Okamoto, Stud. Surf. Sci. Catal. 108 (1997) 191.
[6] K. Borszeky, T. Mallat, A. Baiker, Tetrahedron: Asymmetry 8 (1997) 3745.
[7] W.-R. Huck, T. Mallat, A. Baiker, Catal. Lett. 80 (2002) 87.
[8] J. Seyden-Penn, Chiral Auxiliaries and Ligands in Asymmetric Synthesis, John Wiley, New York, 1995.
[9] H.C. Kolb, K.B. Sharpless, Tetrahedron 48 (1992) 10515.
[10] B.B. Lohray, J.R. Ahuja, J. Chem. Soc., Chem. Commun. 95 (1991).
[11] K.C. Nicolaou, X. Huang, S.A. Snyder, P.B. Rao, M. Bella, M.V. Reddy, Angew. Chem. Int. Ed. 41 (2002) 834.
[12] W.L. Nelson, J.E. Wennerstrom, S.R. Sankar, J. Org. Chem. 42 (1977) 1006.
[13] O.J. Sonderegger, T. Bürgi, A. Baiker, J. Catal. 215 (2003) 116.
[14] M. Studer, V. Okafor, H.-U. Blaser, J. Chem. Soc., Chem. Commun. (1998) 1053.
[15] W.A.H. Vermeer, A. Fulford, P. Johnston, P.B. Wells, J. Chem. Soc., Chem. Commun. (1993) 1053.
[16] E. Toukoniitty, P. Mäki-Arvela, M. Kuzma, A. Villela, A.K. Neyestanaki, T. Salmi, R. Sjöholm, R. Leino, E. Laine, D.Y. Murzin, J. Catal. 204 (2001) 281.
[17] M. Studer, H.U. Blaser, C. Exner, Adv. Synth. Catal. 345 (2003) 45.
[18] A. Baiker, J. Mol. Catal. A 163 (2000) 205.
[19] P.B. Wells, K.E. Simons, J.A. Slipzenko, S.P. Griffiths, D.F. Ewing, J. Mol. Catal. A 146 (1999) 159.
[20] A. Baiker, J. Mol. Catal. A 115 (1997) 473.
[21] E. Toukoniitty, V. Nieminen, A. Taskinen, J. Päivärinta, M. Hotokka, D.Y. Murzin, J. Catal. 224 (2004) 326.
[22] E. Toukoniitty, I. Busygin, R. Leino, D.Y. Murzin, J. Catal. 227 (2004) 210.
[23] C. Reichardt, Solvents and Solvent Effects in Organic Chemistry, VCH, Weinheim, 1988.
[24] E. Toukoniitty, P. Mäki-Arvela, J. Kuusisto, V. Nieminen, J. Päivärinta, M. Hotokka, T. Salmi, D.Y. Murzin, J. Mol. Catal. A 192 (2003) 135.
[25] R. Hess, T. Mallat, A. Baiker, J. Catal. 218 (2003) 453.
[26] S. Diezi, A. Szabo, T. Mallat, A. Baiker, Tetrahedron: Asymmetry 14 (2003) 2573.
[27] T. Bürgi, A. Baiker, J. Catal. 194 (2000) 445.
[28] D. Ferri, T. Bürgi, A. Baiker, J. Chem. Soc., Perkin Trans. 2 (2000) 221.
[29] A. Vargas, T. Bürgi, A. Baiker, J. Catal. 222 (2003) 439.
[30] N. Bonalumi, A. Vargas, D. Ferri, T. Bürgi, T. Mallat, A. Baiker, 2004 manuscript in preparation.
[31] S. Diezi, T. Mallat, A. Szabo, A. Baiker, J. Catal. 288 (2004) 162.