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Methylethers of cinchona alkaloids in Pt-catalyzed hydrogenation of methyl benzoylformate and pyruvaldehyde dimethyl acetal Part 2: Effect of stereochemical factors on the enantioselectivity☆

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Abstract

The enantioselective hydrogenation of methyl benzoylformate (MBF) and pyruvaldehyde dimethyl acetal (PA) was investigated under mild experimental conditions on Pt-alumina catalyst modified with MeOCD, MeOCN, MeOQN and MeOQD alkaloid derivatives in acetic acid (AcOH) and in toluene (T). Besides low rate high ee's were achieved (>90%) in the case of PA using MeOCD and MeOQN modifiers in AcOH. Under similar experimental conditions in the case of MBF the highest ee's (50–80%) were obtained in T. Hydrogenation in the presence of MeOCN and MeOQD proceeded with low ee's, namely 4–8% for MBF in AcOH and 40–50% for PA in T. Studies on the hydrogenation of MBF and PA suggested that the low ee are attributable to repulsive interactions of OMe and ethyl groups of the modifiers with the substrates and with Pt surface. The formation of the complex responsible for enantioselection and, as a consequence, for high ee may be presumed to necessitate a two-point interaction between the cinchona alkaloid and the substrate. The two-point interaction requires a closer geometrical fit as compared to a one-point interaction, while the cinchona alkaloid and the substrate are bound to active sites of the catalyst through the quinoline skeleton and the oxo group to be hydrogenated, respectively. These new experimental results can be interpreted on the basis of adsorbed 1:1 interaction model not only of electrophilic mechanism but also in toluene by the nucleophilic mechanism, too.

Keywords: Cinchona alkaloid derivatives; Enantioselective hydrogenations; Methyl benzoylformate; Pyruvaldehyde dimethyl acetal; Pt-alumina; Nucleophilic mechanism; Stereochemistry

1. Introduction

An important method of the various selective catalytic organic reactions (e.g. [1]) is the enantioselective hydrogenation of C=O and C=C bonds containing compounds on Pt and Pd catalysts modified by cinchona alakoids (Orito reaction [2], Scheme 1) and Ni catalysts modified by tartaric acids [3]. The results published in the Orito reaction [2] have been reviewed regularly (since 2005 [4,5]). In spite of the fact that about 300 manuscripts have been published on research involving ethyl pyruvate (EP), a number of questions concerning the Orito reaction are still unanswered. Finding the answers to these questions and revealing further details of a heterogeneous catalytic hydrogenation with above 90% enantioselectivities [6–8] is highly important for further practical applications of the reaction.

The main objectives of recent studies have been to expand the field of utilization of this reaction, to elucidate the reaction mechanism and to interpret chiral induction. The question we asked is this: Why does the behavior of parent cinchonas (CD, CN, QN, QD) differ from that of their methyl ethers, when the experimental data obtained using MeOCD and CD are highly similar [9]? In order to answer this question, it was also necessary to perform new measurements under entirely identical experimental conditions.

Here, we only outline recent results disclosed during the last 2 years with respect to the present state of this important area. Further catalysts [10–14] and substrates [15–20] were studied. These studies span the interpretation of the effect of solvents

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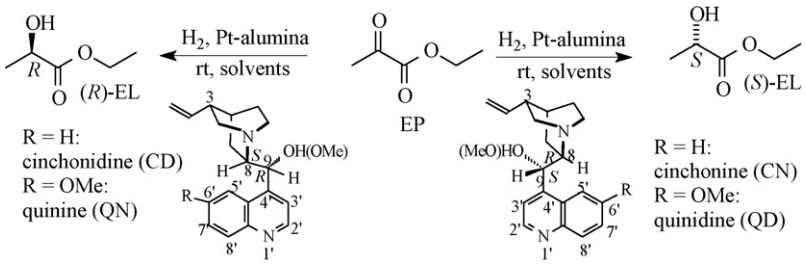


Scheme 1. Orito reaction.

[21–23], and the application of various instrumental techniques [22,24–30] and quantum chemical calculations [13,31–35]. New information has been presented on the relationship between modifier structure and enantioselectivity [14,22,29,36–45]. It should be noted that the relative adsorption strength of chiral modifiers has been recently studied not only by instrumental techniques [23] but in a continuous fixed-bed reactor too [46–49].

Recent studies aimed the elucidation of the relationships between the enantiomeric excess (ee) and conversion and between the rates of enantioselective and racemic hydrogenation in this context, which have been violently disputed [28,49–52]. Addressing the structure of the intermediate responsible for chiral induction has greatly contributed to the clarification of the mechanism of enantioselective hydrogenation and the origin of chiral induction [30,44,45,48,53–57]. Recognition of the unexpected inversion of enantioselectivity over 50% [58,59] gave a new impulse to research on reaction mechanisms [11,16,17,19,39,48,57,60,61].

The new results summarized above confirm previous conclusions regarding the interpretation of chiral induction. It is generally accepted that the intermediate responsible for the enantioselection is the 1:1 complex of the cinchona alkaloid as chiral modifier and the substrate (see [4,5]). No consensus has been reached, however, concerning the structure of this intermediate. According to recent evidence the activated ketones are attached to the cinchonas through the protonated N of the quinuclidine part and through the C5′-H region of the quinoline moiety of modifiers [30,53,55].

The results described in this study represent the continuation of our previous work [9] in which we addressed the chiral hydrogenation of (EP) and ketopantolactone (KPL) [9] and methyl benzoylformate (MBF) and pyruvaldehyde dimethyl acetal (PA) (this work = tw) in acetic acid (AcOH) and toluene (T) as solvent on Pt-alumina catalyst modified by parent cinchona alkaloids and their C9-*O*-methyl derivatives (Scheme 2). Studying the four activated ketones with diverse structures under identical experimental conditions, in the presence of the parent cinchona alkaloids and their hardly ever studied C9-*O*-Me derivatives as catalyst modifiers yielded further information on this most intensively researched enantioselective heterogeneous catalytic hydrogenation reaction. Our new measurements opened the way for drawing generalizable conclusions and allowed to find the answer to some of the open questions.

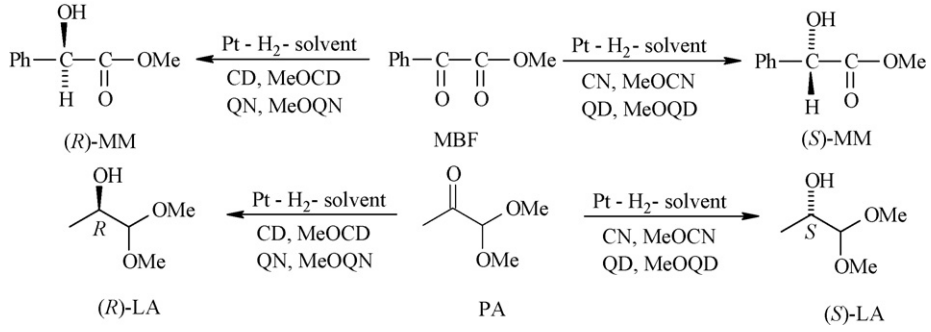
2. Experimental

2.1. Materials

MBF, PA, parent cinchona alkaloids (CD, CN, QN, QD) and solvents were from Aldrich or Fluka, and used as received. The C9-OMe cinchonas were synthesized as in ref. [9]. MBF (bp 391–393 K at 5 Hgmm) and PA (bp 325–327 K at 25 Hgmm) were distilled in vacuum using Vigreaux-column. H_2: 99.999% (Linde), D_2: 99.8% (Linde). The pretreated Engelhard E4759 Pt-alumina catalyst was used as in ref [9]. Using ultrasound treatment also improves the catalyst performance [62].

2.2. Spectroscopy

NMR spectra were recorded on Bruker Avance 200 and 400 MHz spectrometers, using $CDCl_3$ as solvent. The ESI-MSD and ESI-MSD-ion-trap (AGILENT 1100 LC-MSD TRAP SL



Scheme 2. The Orito reaction of MBF and PA.

ion-trap MS) was operated under positive ion and auto MS–MS mode as described earlier [9,63].

2.3. Hydrogenation

Hydrogenations were performed as in ref. [9]. Standard conditions were: 12.5 mg E4759, 2.5 mL solvent (AcOH or T), 1 bar hydrogen pressure, 294–297 K, 1 mM of modifier concentration, 900–1000 rpm, 0.5 mmol of substrate. The product identification and the enantiomeric excess [ee% = ([*R*] − [*S*]) × 100/([*R*] + [*S*])] were monitored by gas chromatography (HP 6890 N GC-FID, 30 m long Cyclodex-B capillary column. Retention times (min): MBF 383 K, 25 psi He: 21.7 of MBF, 29.9 of (*R*)-MM, 30.9 of (*S*)-MM; PA 338 K, 21.65 psi He: 5.2 of PA, 8.6 of (*R*)-LA, 9.1 of (*S*)-LA; reproductibility was ±2%.

2.4. Deuteration

Deuteration was performed in the system used for hydrogenations under the following experimental conditions: 50 mg E4759, 7 mL T, RT, D_2 pressure 1 bar, CD concentration 2 mmol L^{-1}, 240 μL PA. Prior to deuteration the hydrogenating system was flushed with helium. The catalyst was stirred in T, in the presence of D_2 for 1 h. Injection of the T solution of CD was followed by stirring for a few minutes and the injection of PA. 100% conversion necessitated 6 h of deuteration. The raw product was processed in the usual way, desiccated over Na_2SO_4 and analyzed by GC–MS and ^{1}H NMR.

3. Results and discussion

3.1. Results of enantioselective hydrogenations

The results of enantioselective hydrogenations on Pt-MeO-cinchona alkaloid chiral catalysts are summarized in Tables 1 and 2 and Figs. 1 and 2. For comparison, the tables also contain the data obtained using the parent cinchona alkaloids as chiral modifiers under identical experimental conditions just like in the case of EP and KPL [9]. Experimental data obtained under substantially different experimental conditions were reported by Blaser and co-workers [64].

3.1.1. Enantioselective hydrogenation of MBF

The most widely studied model compound has been EP [4,5]. In contrast with EP, the hydrogenation of MBF and ethyl benzoylformate (EBF) has been only little studied [16,19,48,64–69], in spite of the fact that the reaction was already described by the group of Orito [70]. The experimental data in Table 1 and Fig. 1 leading to the following main conclusions: (i) just like for the parent cinchonas in the case of MeO-cinchonas differently from EP ee is higher in T than in AcOH; (ii) although smaller or larger differences exist, the tendency of the ee values are very similar to the ee values measured at a hydrogen pressure of 50 bar [64]; (iii) the hydrogenations were faster using parent cinchonas as compared to MeO-cinchonas in both solvents; (iv) the experimental data did not show unambiguous correlation between the ee and the rate; (v) similarly to parent cinchonas hydrogenation is somewhat faster in AcOH as compared to T for C6′-OMe cinchonas, however, without the C6′-OMe group the opposite results were obtained; (vi) again quite similarly to parent cinchonas, using of MeO-derivatives ee is higher in the case of MeOCD and MeOQN (C8*S*, C9*R*) than it is with the MeOCN–MeOQD pair (C8*R*, C9*S*); in the case of the latter pair (*S*)-MM is formed in excess, whereas the presence of the former leads to the formation of (*R*)-MM in excess (Scheme 2); (vii) the presence of the C6′-OMe group on the quinoline skeleton does not favor a high ee, especially with the MeO-cinchonas; (viii) the most remarkable results are the low ee values attained in both solvents when using the chiral catalysts Pt-MeOCN and Pt-MeOQD catalysts. The differences compared to EP in hydrogenation rate and in ee are presumably related to the solvation of MBF, its lower mobility and its adsorption.

Table 1
Experimental data on enantioselective hydrogenation of MBF on Pt-alumina catalyst modified by parent cinchona alkaloids and their C9-OMe derivatives (standard conditions)

Entry	Modifier	Solvent	Time (min)	Conversion (%)	ee (%)
1	CD	AcOH	30	50	76 R
2	CD	T	30	94	88 R
3	MeOCD	AcOH	60	26	43 R
4	MeOCD	T	60	87	57 R
5	CN	AcOH	60	55	55 S
6	CN	T	60	77	77 S
7	MeOCN	AcOH	60	47	4 S
8	MeOCN	T	60	100	24 S
9	QN	AcOH	45	80	35 R
10	QN	T	60	61	67 R
11	MeOQN	AcOH	70	57	46 R
12	MeOQN	T	50	76	58 R
13	QD	AcOH	60	76	12 S
14	QD	T	60	42	50 S
15	MeOQD	AcOH	60	39	8 S
16	MeOQD	T	60	29	14 S

Table 2
Experimental data on enantioselective hydrogenation of PA on Pt-alumina catalyst modified by parent cinchona alkaloids and their C9-OMe derivatives (standard conditions)

Entry	Modifier	Solvent	Time (min)	Conversion (%)	Ee (%)
1	CD	AcOH	60	34	93 R
2	CD	T	60	42	65 R
3	MeOCD	AcOH	60	20	95 R
4	MeOCD	T	60	51	70 R
5	CN	AcOH	60	21	89 S
6	CN	T	60	21	50 S
7	MeOCN	AcOH	60	17	91 S
8	MeOCN	T	60	26	48 S
9	QN	AcOH	45	44	96 R
10	QN	T	60	41	61 R
11	MeOQN	AcOH	60	24	95 R
12	MeOQN	T	90	17	46 R
13	QD	AcOH	60	32	91 S
14	QD	T	60	20	46 S
15	MeOQD	AcOH	60	6	84 S
16	MeOQD	T	90	16	48 S

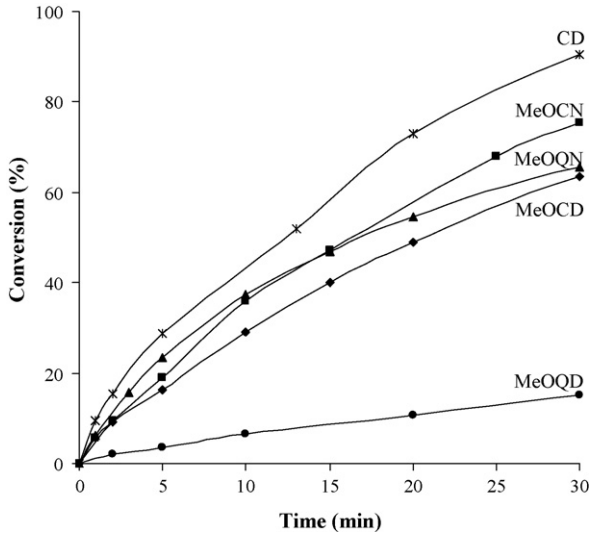


Fig. 1. The enantioselective hydrogenation of MBF on modified Pt in toluene (since $ee_T > ee_{AcOH}$, standard conditions).

3.1.2. Enantioselective hydrogenation of PA

Hydrogenation of α-ketoacetals under the conditions of the Orito reaction was first realized 20 years after the discovery of the reaction [8]. Only a few studies have since presented further information about the hydrogenation of α-ketoacetals [64,68,69,71]. The results of the enantioselective hydrogenation of PA (Table 2) call attention to the following: (i) under conditions identical with those of MBF hydrogenation, PA is hydrogenated in considerably higher enantioselectivities and at a lower rate than MBF in the presence of either chiral modifier, which is probably due to its different adsorption; (ii) unlike in the case of MBF, ee values are lower in T than in AcOH; (iii) similarly to MBF the hydrogenation is faster using parent cinchonas as compared to MeO-cinchonas in both solvents; (iv) the induction period of the hydrogenations differed, phenomenon that cannot be interpreted on the basis of the experimental data published up to now; (v) in the presence of cinchonas not containing a C6′-OMe group, the reactions are generally faster in T than in AcOH; (vi) however, in the presence of cinchonas that do contain a C6′-OMe group, hydrogenation rates in the two solvents are nearly identical, or hydrogenation is somewhat faster in AcOH than in T; (vii) beside excellent ee's the most unexpected result is the low enantioselectivity observed in T especially with the C8*R*, C9*S* cinchona alkaloids. These differences are presumably related to the different modes of adsorption of the substrates as well as to the solubility of cinchonas.

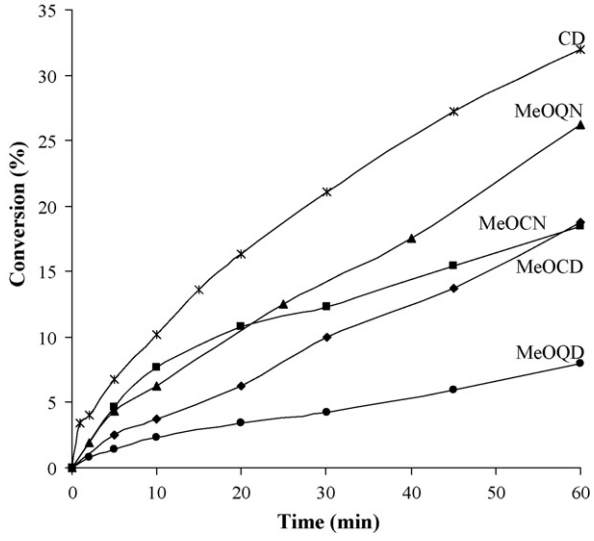


Fig. 2. The enantioselective hydrogenation of PA on modified Pt in AcOH (since $ee_{AcOH} > ee_T$, standard conditions).

The unexpected new experimental observations regarding the Pt-MeO-cinchona chiral catalysts that, in the same conditions (RT, 1 bar of H_2 pressure) have never been studied before (namely, that ee in the hydrogenation of both substrates is considerably different in both solvents), raise several new questions, that needs further studies to be answered (e.g. initial transient period, adsorption of modifiers).

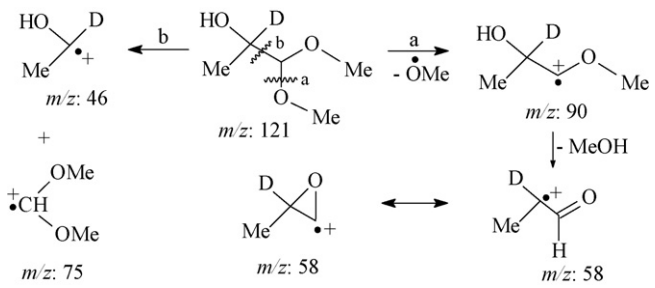
3.2. Deuteration

Because of the diverse behaviors of substrates under the conditions of the Orito reaction – with especial regard to PA, in the case of which an outstandingly high ee (91–96%) was observed at a low reaction rate – it appeared important to perform further studies using the available methods. In view of the theoretical possibility of the enolizations, D-tracer studies of PA were deemed suitable.

In the reaction of PA with D_2 over modified E4759, at 296 K $CH_3CD(OD)CH(OCH3)_2$ is formed, as verified by EI fragmentation (Scheme 3). The formation of $CH_2DCD(OH)CH(OCH_3)_2$ or $CH_3CD(OH)CD(OCH_3)_2$ indicative of enolization were not observed. This experimental observation not only indicates that the hydrogenation takes place on the C=O group, as in the case of EP hydrogenation [72], but also suggests that the mechanism of the Orito reaction is different from that in the case of EP. Namely, the rate of EP hydrogenation is manifold faster than that of PA hydrogenation. Consequently, it can be supposed that the origin of chiral induction and that of reaction rate may be different and both adsorption and interaction between substrate and modifier may be different for each substrate to be hydrogenated.

3.3. Transient behavior of modifier mixtures

In order to interpret our results, experiments were carried out addressing the stability of the chiral modifiers under the condi-



Scheme 3. EI mass fragmentation of PA.

tions of hydrogenation [9] as well as their nonlinear behavior [9]. According to our new results MeO-cinchonas exhibit differences in stability under the conditions of hydrogenation and characteristic differences also exist in adsorption strength [9].

Studying the nonlinear behavior of chiral modifiers has proved to be useful in the enantioselective hydrogenation of activated ketones [61,73–75]. In our previous manuscript [9] on the research of EP and KPL hydrogenation in the presence of the rarely studied C9-OMe cinchona alkaloid derivatives, their different adsorption strengths were presented and compared to those of the parent alkaloids. Although there were differences between the data sets of both substrates in both solvents (T, AcOH), which may be due to a variety of reasons, the following order could be established for the adsorption strengths of the cinchonas: CD > MeOCD > QN > CN > MeOQN > MeOCN > QD ~ MeOQD. This order of adsorption strengths proved to be in agreement with the ee values, i.e. the stronger the adsorption, the higher the ee%. The experimental data presented in ref. [9] may be used in the interpretation of the data obtained in the enantioselective hydrogenation of MBF and PA.

The results of the numerous spectroscopic studies and theoretical calculations on adsorbed chiral modifiers published in the literature can also be utilized for the interpretation of the observed phenomena. At the time of the initiation of our studies on the four MeO-cinchonas the majority of the latters were as yet unknown.

4. Interpretation of the results and conclusion

The effect of C9-OMe cinchona alkaloid chiral modifiers on the enantioselectivity of the hydrogenation of four activated ketones (EP and KPL [9], MBF and PA (tw)) was studied under identical, mild experimental conditions (RT, hydrogen pressure 1 bar, modifier concentration 1 mM). The objective of these studies was to find a relationship between the structure of the substrates and modifiers (substituents of the rubane skeleton: two OMe groups and one ethyl group) and ee, in order to obtain further information on the stereochemistry of the Orito reaction. The results obtained are suitable for this purpose, since it has been verified by deuteration that, similarly to EP [72], hydrogenation of PA also does not involve an enol intermediate, i.e. in the case of all four activated ketones it is the oxo group that is hydrogenated.

The experimental data regarding ee in both manuscripts (ref. [9] and tw) are summarized in Figs. 3 and 4. Attention is called to the following: (i) hydrogenation of EP and KPL is faster than that of MBF and especially than that of PA; (ii) ee values are usually higher in AcOH, with exceptions mainly in the case of KPL and MBF, depending on the modifiers present; (iii) the more substituents on the rubane skeleton, the lower the ee values (with some exceptions); (iv) hydrogenation of EP and PA in AcOH may produce ee values in excess above of 90%; (v) ee values are conspicuously low in the presence of MeOCN, QD and MeOQD (with the exception of PA), especially in T.

The slow rate of PA hydrogenation, which is significantly different from the three α-ketoesters, together with the outstandingly high ee may indicate the operation of a different reaction mechanism. The slow hydrogenation rate of PA may presumably be related to its adsorption mode and to the desorption of the product (LA in Scheme 2). This phenomenon, unusual in the Orito reaction [76] – slow reaction rate and high ee – calls for further studies. As regards the ee values, in the case of EP, MBF and PA substrates outstandingly high, medium and low ee values were also obtained. In the case of KPL the ee values are lower and can be classified to two groups in both solvents (39–63 and 2–28%). The lowest ee values mainly occured with the use of MeOCN and MeOQD. The highest ee values could be attained in hydrogenations of PA and EP in the presence of cinchonas with C8(*S*), C9(*R*) configuration. Hydrogenation of KPL and especially that of MBF usually resulted in higher ee values in T.

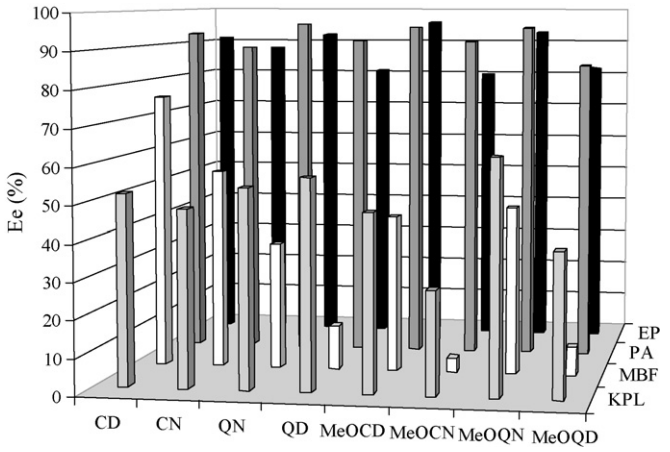


Fig. 3. Experimental data on enantioselective hydrogenation of EP, PA, MBF and KPL on Pt-alumina catalyst modified by cinchona alkaloids in AcOH (standard conditions).

It is generally accepted that the intermediate complex (IC) responsible for enantioselection is the adsorbed 1:1 complex of the cinchona alkaloid (chiral modifier) and the substrate [4,5]. No consensus has been reached, however, concerning the structure of this intermediate. The main possible types are presented

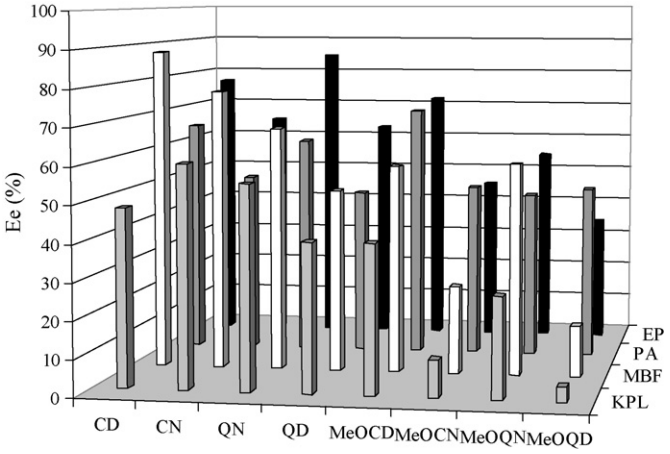
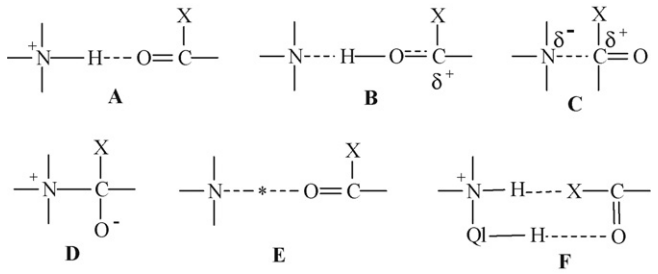


Fig. 4. Experimental data on enantioselective hydrogenation of EP, PA, MBF and KPL on Pt-alumina catalyst modified by cinchona alkaloids in toluene (standard conditions).



Scheme 4. Proposed intermediates in the Orito reaction: A [73,76], B [73,76], C [52,59], D [77], E [5a], F [53,55] (X = activating group, Ql = quinolinyl).

schematically in Scheme 4. Experimental data on IC structure have verified the following: (i) flat adsorption of the quinoline skeleton of cinchona alkaloids (see, e.g. [76,78]); (ii) open-3 conformation of adsorbed cinchona alkaloids [65]; (iii) the interaction of the protonated N of quinuclidine with the substrate, in apolar medium as well [79]; (iv) two-point interaction of the quinuclidine N and the C5′-H with the substrate [53,55].

One of our conclusions is that, due to the inhibition of flat adsorption, formation of the appropriate IC responsible for enantioselectivity is inhibited by OMe groups attached to the C6′, C9 atoms and by the C3-Et group. Namely different tilted structures can be formed. We assume that the extent of tiltedness (i.e. the extent of divergence from flat adsorption depending of the repulsive interactions of C6′-OMe, C9-OMe and C3-Et) increases in the following order: MeOCD < MeOQN < MeOCN < MeOQD. Different extents of divergence from flat adsorption results in different steric positions and orientations of the N-lone pair of quinuclidine. The formation of the complex responsible for enantioselection and, as a consequence, for high ee may be presumed to necessitate a two-point interaction between the cinchona alkaloid and the substrate, requiring a closer geometrical fit. The more favorable geometrical fit is produced by attractive and repulsive interactions for the formation of IC, the higher ee will result. The rigid structure of KPL prevents a close fit, therefore hydrogenation in the presence of MeOCN and MeOQD proceeds with low ee in AcOH and hardly at all in T.

In AcOH an electrophilic mechanism (N–H–O interaction, Scheme 4A and B) can be proposed (Fig. 5A), whereas in T not only an electrophilic but, in certain cases, also a nucleophilic (interaction between the quinuclidine N-lone pair and the C=O bonds) mechanism can be envisaged (Fig. 5B). Since these we have discussed in detailed in our previous works [61,75] we scetched only the IC's of electrophilic and nucleophilic interactions. The presence of these complexes are supported by experimental evidence and/or theoretical calculations [29,30,35,45,53,55–57,79]. At the present time it cannot yet be confirmed which of these complexes (depending on the modifier-substrate pair) is indeed responsible for chiral induction.

The different steric positions and orientations of the N-lone pair of quinuclidine appear to be determinant [45,55–57]. Based on the new experimental data, it may be supposed that a two-point binding between reactant and chiral modifier is a prerequisite of the formation of the substrate-modifier 1:1 IC on platinum surface [53,55]. Therefore, the stereochemical factors play a determinant role in obtaining high ee values.

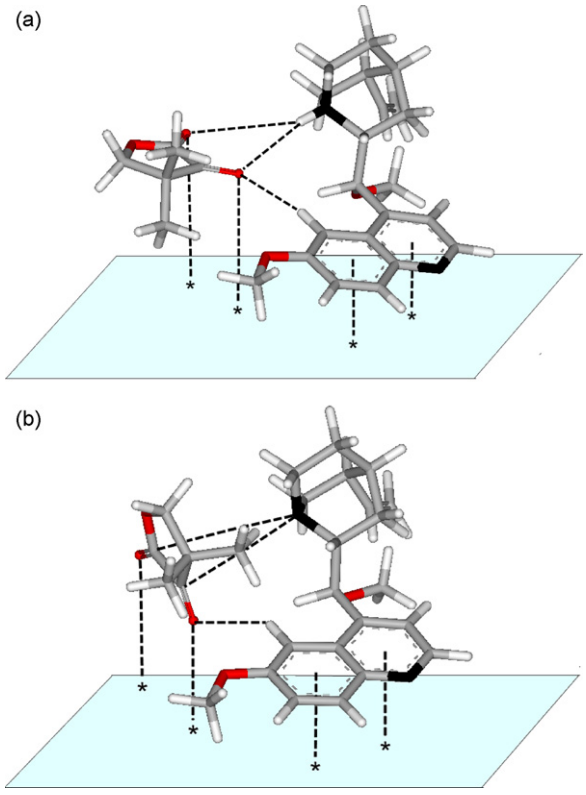


Fig. 5. The proposed structures of the pro *S* 1:1 adsorbed adducts for KPL substrate and MeOQD modifier (A, electrophilic IC; B, nucleophilic IC).

Acknowledgements

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