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Study of enantioselective hydrogenation of bulky esters of phenylglyoxylic acid on Pt-CD and Pt-β-ICN chiral catalysts: Steric effect of ester groups and inversion of enantioselectivity

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Abstract

Enantioselective hydrogenation of seven different esters of phenylglyoxylic acid was investigated by variation of the bulkiness at ester side of the substrates [Ph–C(O)–C(O)OR, R = Me (**l**), cyclohexyl (**2**), adamantyl (**3**), *cis*-decahydro-1-naphthyl (**4**), phenyl (**5**), 1-naphthyl (**6**), 2-naphthyl (**7**)] on Pt-alumina-cinchonidine (CD) and Pt-alumina-β-isocinchonine (β-ICN) chiral catalysts using mild experimental conditions (273 K and room temperature, hydrogen pressure of 1–25 bar) in solvents of AcOH and toluene. Hydrogenation on Pt-alumina-CD chiral catalyst produced high values of ee for all but the **5** and **7** compounds. The formation of (*R*)-mandelic acid esters was 86–91% in AcOH and 79–94% in toluene. The experiments verified the general applicability of the Orito reaction in the preparation of enantiomers of α-hydroxyesters. Under the experimental conditions applied, the magnitude of ee is affected by the steric size of α-ketoesters and by solvents. In the enantioselective hydrogenation of substrates over a Pt-alumina-β-ICN catalyst in toluene, inversion of enantioselectivity occurred; (*R*)-mandelic acid esters formed with a medium ee of 30–54%. The conformation of the adsorbed modifier plays a more determining role than the bulkiness of the substrate in the formation of the intermediate complex responsible for enantioselection.

Keywords: Chiral hydrogenation; Pt-alumina; Cinchonidine and β-isocinchonine; Phenylglyoxylic acid esters; Intermediate; Conformation; Inversion of enantioselectivity

1. Introduction

Optically active α-hydroxy carboxylic acid derivatives are important building blocks in organic synthesis [1]. Synthesis of these compounds by a heterogeneous catalytic method was carried out using the Orito reaction [2,3] (Table 1). Orito et al. recognized the reaction that produces (*R*)- and (*S*)-methyllactates (MeLt) in high enantioselectivity (ee) in 1979 while studying hydrogenation of methyl pyruvate (MePy) on heat-treated Pt/C catalyst in the presence of cinchona alkaloids (Fig. 1) as chiral modifiers [2,3]. By now, more than 400 publications have reported on the details of the Orito reaction. The state of research on the enantioselective hydrogenation of activated ketones has been the subject of numerous reviews since 2000 [4–9]. The main objectives of these complex research efforts have been to interpret the reaction mechanism (specifically, the origin of chiral induction), and to extend the reaction to compounds other than MePy. Industrial application of the reaction has also been realized [10]. The main model compound for these studies has been ethyl pyruvate (EtPy); the maximal ee achieved in with EtPy has been 97–98% [11,12].

Previous studies have shown that the Orito reaction produces high ee in hydrogenation of the so-called "activated ketones," compounds with an electron-withdrawing function on the carbon atom next to the oxo group [4–9]. Activated ketones of this type include α-ketoesters, α-ketoacids, α-ketoamides, α-diketones, α-ketoacetals, and α-trifluoromethyl ketones [7,13].

Regarding systematic studies on the effect of α-ketoester structure on ee, the results obtained in AcOH (the solvent found

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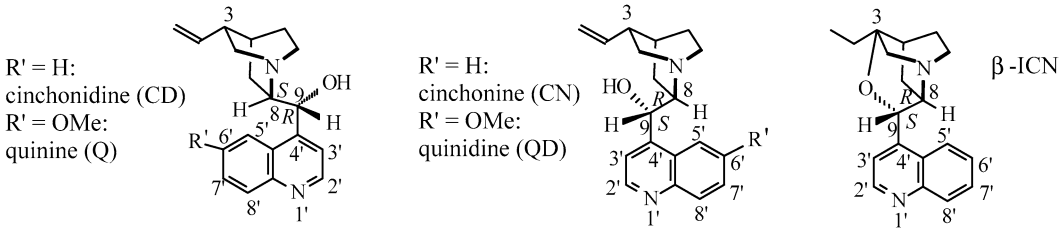
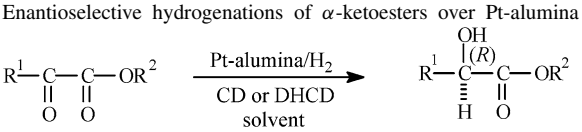


Fig. 1. The structures of parent cinchona alkaloids (CD, CN, Q, QD) and β-ICN.

Table 1
Enantioselective hydrogenations of α-ketoesters over Pt-alumina in AcOH



Entry	Substrate		ee (%)	Reference
	R^1	R^2		
1	Me	Me	97–98[a]	[11,14,15]
2	Me	Et	92–94[a]	[11,14,15]
3	Me	Pr	90–96[a]	[11,15]
4	Me	*i*-Pr	77[a]–80	[11,14]
5	Me	Bu	91[a]	[11]
6	Me	*i*-Bu	92–93[a]	[11,15]
7	Me	*t*-Bu	93	[15]
8	Me	Neo-pentyl	92	[15]
9	*i*-Pr	Et	54–95[a]	[14,15]
10	*i*-Bu	Et	91	[15]
11	*t*-Bu	Et	50–81[b]	[14,15]
12	Ph	Et	84–98[b]	[14,15]
13	$Ph(CH_2)_2$	Et	90–93[b]	[14,15]

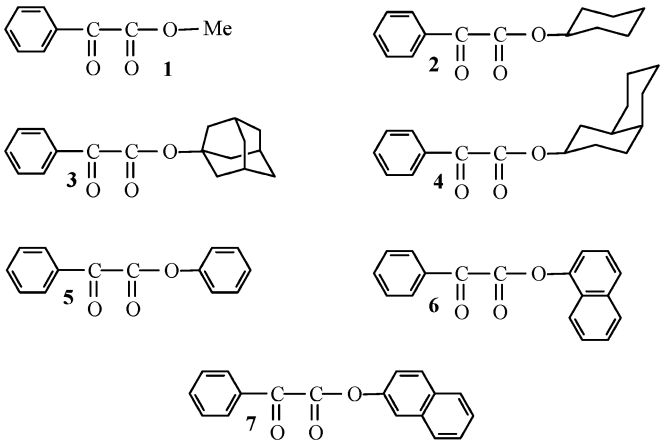
[a] Pt-colloidal cluster.
[b] In optimized conditions.

to be the best) are summarized in Table 1. Some of the compounds listed in Table 1 have also been studied by others. Because those authors did not examine the correlation of ee with substrate structure, these data are not included in Table 1. From the table, it appears that increasing the bulkiness of R^1 prevented higher ee; however, ee could be increased by optimizing the experimental conditions. Despite the fact that in the cases where R^1 = phenyl and R^2 = Et (EBF, entry 12), the hydrogenation reaction was considerably slower than that for EtPy, the highest ee was attained (98%) [16]. The high ee prompted us to study the effect of increasing the bulkiness of the ester group on ee.[1] Toward this end, synthesis and study of the new compounds outlined in Scheme 1 were initiated.

2. Experimental

2.1. Materials

The AcOH, CD, **1**, and compounds used in synthesis of **2–7** were from Fluka or Aldrich and used as received. β-isocinchonine (β-ICN) was synthesized as described previously [17–19]. The **2–7** esters were synthetised by the reaction of phenylglyoxylic acid chloride (not isolated) [20] and the appropriate alcohols (or phenols) in dichloromethane at room temperature [21].



Scheme 1. Investigated esters of phenylglyoxylic acid in Orito reaction.

2.1.1. General method for the synthesis of the 2–7 esters

To a stirred solution of 1.5 g (10 mmol) of phenylglyoxylic acid and 0.1 mL of DMF in 20 mL of dichloromethane, 1.3 mL of oxalyl chloride was added dropwise at 273 K. The mixture was stirred for 4 h at room temperature, then evaporated in vacuo at 313 K. Then 30 mL of dichloromethane was added to the residue. A small amount of 4-dimethylamino pyridine (DMAP) was added to the solution, followed by a solution of 10 mmol of alcohol (or phenol) and 4 mL of triethylamine in 10 mL of dichloromethane dropwise under stirring. The mixture was stirred at room temperature for 24 h; diluted in 20 mL of dichloromethane; washed with water (2 × 10 mL), 10% NaOH solution (1 × 10 mL) and saturated NaCl solution (15 mL); and then dried (Na_2SO_4), filtered, and concentrated in vacuo. The crude products were purified by vacuum distillation or recrystallyzation or column chromatography using hexane/acetone (5:2) as an eluent. Silica gel 60 (Fluka 60741) was used for column chromatography.

The purity and characterization of the compounds prepared were checked by TLC (Fluka 60778 silica gel TLC cards, hexane/acetone 5:2 as eluent), gas chromatography–mass spectroscopy (GC-MS) (Agilent 6890 N with 5973 MSD; temperature: 10 min → 373 K, 5 K/min → 473 K; 10 psi of He; 15-m long DB-1 column), and nuclear magnetic resonance (NMR)

[1] After submitting our manuscript an significant article was published in a similar subject (M. Maris, D. Ferri, L. Konigsmann, T. Mallat, A. Baiker, J. Catal. 237 (2006) 230.), which deals with the hydrogenation of compounds, containing R^1 = aromatic groups.

spectroscopy (Bruker Avance 500 spectrometer; ^{1}H: 500 MHz; ^{13}C: 125.8 MHz, in $CDCl_3$, with chemical shifts are expressed in ppm downfield from internal tetramethylsilane). The characterization data on the compounds (white solids or colorless oils) are summarized below. The yields concern the isolated, pure products.

2.1.2. Characterization data of the compounds

Phenylglyoxylic acid cyclohexyl ester (**2**): yield: 62%; bp. 407–409 K/1 Hgmm (lit. [22] 440 K/5 Hgmm); n_D^{20}: 1.5236; TLC: R_f 0.66; ^{1}H NMR: 7.98 (d, 2H), 7.65 (t, 1H), 7.51 (t, 2H), 5.09 (m, 1H), 2.06 (m, 2H), 1.78 (m, 2H), 1.59 (m, 3H), 1.43 (m, 2H), 1.29 (m, 1H); GC-MS (ret. time): 19.3 min.

Phenylglyoxylic acid 1-adamantyl ester (**3**): yield: 65%; semi solid; TLC: R_f 0.69; ^{1}H NMR: 8.01 (t, 2H), 7.65 (t, 1H), 7.52 (t, 1H), 2.32–2.21 (m, 9H), 1.74 (m, 6H); ^{13}C NMR: 186.6, 163.4, 134.4, 132.5, 129.8, 128.7, 84.90, 41.3, 36.0, 31.0; GC-MS (ret. time): 28.0 min.

Phenylglyoxylic acid *cis*-decahydro-1-naphthyl ester (**4**): yield: 67%; mp. 379–380 K (diethyl ether); TLC: R_f 0.68; ^{1}H NMR: 7.98 (d, 2H), 7.64 (t, 1H), 7.50 (t, 2H), 5.12 (m, 1H), 2.14 (m, 1H), 1.80 (m, 4H), 1.65–1.40 (m, 9H), 1.21 (m, 2H); ^{13}C NMR: 186.7, 163.6, 134.6, 132.6, 129.9, 128.8, 78.7, 40.1, 35.5, 31.5, 25.9, 25.8, 21.2, 19.7; GC-MS (ret. time): 28.1 min.

Phenylglyoxylic acid phenyl ester (**5**): yield: 48%; bp. 421–423 K/1 Hgmm; n_D^{20}: 1.5723; TLC: R_f 0.55; ^{1}H NMR: 8.10 (dd, 2H), 7.68 (m, 1H), 7.54 (m, 2H), 7.43 (m, 2H), 7.28 (m, 3H); ^{13}C NMR: 185.2, 161.7, 149.9, 135.1, 132.4, 130.1, 129.7, 129.0, 126.7, 121.2; GC-MS (ret. time): 18.9 min.

Phenylglyoxylic acid 1-naphthyl ester (**6**): yield: 35%; mp. 364–365 K; TLC: R_f 0.52; ^{1}H NMR: 8.17 (d, 2H9, 8.01 (m, 1H), 7.88 (m, 1H), 7.79 (d, 1H), 7.69 (t, 1H), 7.57–7.49 (m, 5H), 7.45 (d, 1H); ^{13}C NMR: 184.9, 161.6, 145.3, 134.9, 1345, 132.0, 129.7, 128.7, 127.6, 126.5, 126.4, 126.3, 124.8, 120.5, 117.4; GC-MS (ret. time): 29.3 min.

Phenylglyoxylic acid 2-naphthyl ester (**7**): yield: 41%; mp. 359–360 K; TLC: R_f 0.53; ^{1}H NMR: 8.15 (d, 2H), 7.92–7.83 (m, 3H), 7.76 (d, 1H), 7.70 (t, 1H), 7.58–7.48 (m, 4H), 7.38 (dd, 1H); ^{13}C NMR: 185.2, 161.9, 147.6, 135.2, 133.7, 132.8, 132.4, 130.2, 129.8, 129.1, 127.9, 127.8, 126.9, 126.2, 120.3, 118.5; GC-MS (ret. time): 30 min.

Catalyst: 5% Pt-alumina catalyst from Engelhard (E 4759) was pretreated before being used in a fixed-bed reactor (or a quartz vessel) by flushing with 30 mL min^{-1} of helium at 298–673 K for 30 min and with 30 mL min^{-1} of hydrogen at 673 K for 100 min. After cooling to room temperature in hydrogen, the catalyst was flushed with helium for 30 min.

2.2. Hydrogenation

The hydrogenation was performed in a conventional atmospheric batch reactor or hydrogenation autoclave. The catalytic system including the catalyst and the solvent was flushed with hydrogen several times and filled to the desired pressure and stirred (∼1000 rpm). After the prehydrogenation (30 min), first the modifier and then the reactant were introduced and stirred in the presence of hydrogen for the required reaction time. Standard conditions were 12.5 mg of E4759, 1 mmol L^{-1} of modifier concentration, 1.9 mL of solvent (toluene [T] or AcOH), 30 min of hydrogenation time, and 100 mg of substrate (total liquid volume, 2 mL).

The ee was measured as methyl mandelate [PhCH(OH)COOMe = MeMt]. In case of AcOH the crude product was treated with 10 mL of saturated $NaHCO_3$ solution. The mixture was extracted by 3 × 10 mL diethyl ether. The combined extraction was dried by Na_2SO_4, and the ether was evaporated. For transesterification, this mixture was refluxed with MeOH in the presence of a small amount of H_2SO_4 for 1 h, after which it was evaporated, neutralized with $NaHCO_3$, extracted with 2 × 10 mL of ether, and analyzed by GC. MeMt was identified, and enantiomeric excess [ee% = ([$R - S$] × 100/[$R + S$])] was monitored by GC (30-m long cyclodex-B Agilent 6890 N + FID capillary column, 393 K, 21.65 psi of He; uncertainty ±2%). Retention times were 16.9 min for methyl benzoylformate (**1**), 22.6 min for (*R*)-MeMt, and 23.2 min for (*S*)-MeMt.

3. Results and discussion

3.1. Hydrogenation on Pt-CD chiral catalyst

Table 2 summarizes results obtained in enantioselective hydrogenation of the α-ketoesters shown in Scheme 1. Standard experimental conditions were selected on the basis of experimental data described previously [15]. The enantioselective hydrogenation of phenylglyoxylic acid esters was significantly slower than that of EtPy, as was shown for EBF [16,23]. This is a good example of the lack of a close correlation between the reaction rate and high ee. Although substrate hydrogenations in AcOH and in T were carried out under nonidentical experimental conditions (AcOH-T, 25 bar; T, 1 bar), high ee can be attained in both solvents. Values of conversion as a function of substrate type took a similar course in both solvents; however, in the case of **1** and **6**, under identical experimental conditions and at 1 bar hydrogen pressure, the reaction was significantly faster in T than in AcOH, producing an increase in ee.

Based on previous findings, for compounds containing bulky and aromatic groups (e.g., compounds **1**–**7**), solvents can be ex-

Table 2
Experimental data of enantioselective hydrogenation of esters of phenylglyoxylic acid on Pt-CD chiral catalyst (standard conditions: see Section 2)

Substrate	AcOH[a]		Toluene[b]	
	Conversion (%)	Ee (*R*%)	Conversion (%)	Ee (*R*%)
1	100	96	94	84
2	80	88	27	80
3	88	91	83	92
4	76	89	20	82
5	65	86	16	23
6	97	86	95	80
7	55	44	4	28
1[b]	50	73	94	84
6[b]	40	70	95	80

[a] 273 K, 25 bar of hydrogen, reaction time: 10 min.
[b] 298 K, 1 bar of hydrogen pressure; reaction time: 30 min.

pected to play significant roles in solvation, in the adsorption–desorption equilibrium [24–26], and especially in directing substrate adsorption (e.g., in determining the character of adsorption). For example, the solvent and the size of the ester group may promote the η^1(O)-type (end-on fashion [27,28]) adsorption of the substrate, which can be a prerequisite of intermediate complex formation in T [27,28]. Earlier hypotheses have been verified by recent significant experimental data on the determinant role of solvents in the enantioselective hydrogenation of α-ketoesters [25,29–31].

The experimental conversion and ee data suggest that both electronic and steric factors may affect the rate of enantioselective hydrogenation and ee. In compounds containing methyl (**1**) and cycloalkyl groups (**2–4**), steric factors predominate, whereas in aromatic groups (**5–7**), mainly electronic factors naturally predominate. Although the experimental conditions were not optimized, it can be established that under the conditions applied, ee is not reduced even in compounds containing bulky ester groups; ee values of 86–91% in AcOH and 79–92% in T were obtained. Thus, it appears that the size of the ester group has no significant effect on ee (except for **5** and **7**); in other words, the increased size does not hinder formation of the intermediate complex responsible for enantioselection.

Regarding the exception, in both solvents the highly divergent value of the hydrogenation rate, and even more so of the ee, observed in the case of compounds **5**, **6**, and **7** [containing phenyl (**5**), 1-naphthyl (**6**), and 2-naphthyl (**7**) groups, respectively], is quite remarkable and the interpretation of these results requires further consideration. For compounds **5** and **7**, the presence of microcontaminants not detectable by GC analysis could also contribute to the decreased ee.

3.2. Hydrogenation on Pt-β-ICN chiral catalyst

The unexpected results of research on the inversion of enantioselection [32–43] have prompted studies on the hydrogenation of phenylglyoxylic acid esters (**1–7**) on Pt-alumina-β-ICN chiral catalyst. It has been shown that on this catalyst in T, because of inversion, EtPy gave rise to (*R*)-EtLt in 50% ee [41,44]. Based on earlier experience, in the presence of cinchona alkaloids containing C8(*R*) and C9(*S*) chiral carbon atoms (cinchonine and quinidine), an ee of (*S*)-EtLt should have formed [4–7]. To study the possibility of inversion, phenylglyoxylic acid esters **1–7** were hydrogenated on Pt-alumina catalyst modified with β-ICN in T at 1 bar hydrogen pressure and room temperature (Table 3).

Because hydrogenation of **1** in AcOH was accompanied by very little enantioselectivity, studying the hydrogenation of compounds **2–7** in AcOH seemed pointless. According to Table 3, in T, hydrogenation of all compounds but **5** and **7** yielded products of (*R*) configuration in a medium ee; compounds **5** and **7** produced low ee values. That is, in T, inversion of enantioselection occurred. The rate of hydrogenation on Pt-β-ICN chiral catalyst and the magnitude of ee depend on the substituent, but the tendencies are similar to those for hydrogenation on Pt-CD chiral catalyst; the reaction is faster and ee is higher for compounds **1–4** than for compounds **5** and **7**, and

Table 3
Inversion of enantioselectivity in the hydrogenation of **1–7** on Pt-alumina-β-ICN chiral catalyst in toluene (for conditions, see Section 2; [β-ICN] = 0.1 mmol L^{-1}, 1 bar of hydrogen pressure, reaction time: 30 min)

Substrate	Solvent	Temperature (K)	Conversion (%)	Ee (*R*%)
1	T	298	98	50
1	AcOH	295	60	0–3
2	T	294	15	46
3	T	294	38	50
4	T	298	36	35
5	T	295	5	8
6	T	298	70	54
7	T	298	3	20

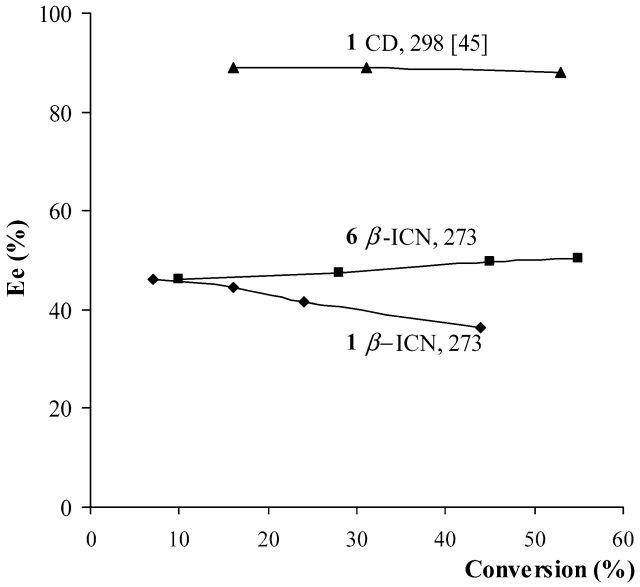
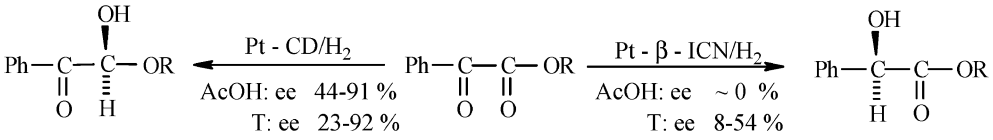


Fig. 2. Enantioselective hydrogenation of **1** and **6**: effect of modifiers (CD, β-ICN) on relationship between conversion and ee (conditions: see Section 2, 2.5 mL of toluene, 1 bar of hydrogen pressure, reaction time: 5–45 min (in case of β-ICN), 2–10 min (in case of CD)).

the behavior of compound **6** is markedly different. We see the absence of enantioselection in AcOH and the inversion observed in T as confirming the earlier supposition of different mechanisms in these two solvents [40,41,44]. Experimental results obtained so far do not allow interpretation of the low ee achieved in hydrogenation of compounds containing phenyl and 2-naphthyl groups (**5** and **7**).

Taking into account the experience of earlier studies [45], we examined the relationship between ee and conversion in the enantioselective hydrogenation of compounds **1** and **6** under the conditions of inversion, that is, in T using the chiral catalyst Pt-β-ICN (Fig. 2). No differences between the ee versus conversion relationship in inversion-free hydrogenation and in hydrogenation accompanied by inversion were seen.

On the basis of investigations into the hydrogenation of the bulkier α-ketoesters, it seems that steric effects are more important in the inversion of enantioselection than in hydrogenation without inversion. In our opinion, this new finding may point to the directional effect of ester groups on substrate adsorp-



R: Me, cyclohexyl, adamantyl, *cis*-decahydro-1-naphthyl, phenyl, 1-naphthyl, 2-naphthyl

Scheme 2. Enantioselective hydrogenation of bulky esters of phenylglyoxylic acids on Pt-CD and Pt-β-ICN chiral catalysts.

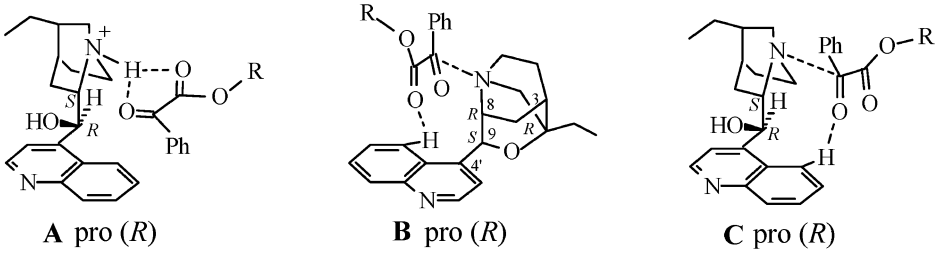


Fig. 3. The proposed structures of adduct complexes of CD (**A**, **C**) and β-ICN (**B**) with esters of phenylglyoxylic acids.

tion, presumably by promoting η^1-type substrate adsorption on the one hand and by the fact that the relatively bulky cycloalkyl group of the ester is situated not on the surface, but in the solution solvated by T, on the other hand. To be able to draw unambiguous conclusions regarding the role of steric factors in the Orito reaction, specifically designed and accurately arranged studies should be carried out, such as those reported previously [46], in which case a significant difference could be detected even between MePy and EtPy.

4. Conclusion

The Orito reaction for bulky esters of phenylglyoxylic acid was investigated on Pt-CD- and Pt-β-ICN chiral catalysts. The results are shown in Scheme 2. The experimental data listed in Table 1 and discussed herein lead to the conclusion that the Orito reaction may be used for the enantioselective hydrogenation of α-ketoesters, that is, for the synthesis of α-hydroxyesters in general, independent of the steric size of the molecule.

The results on the enantioselective hydrogenation of phenylglyoxylic acid esters are interpreted through a somewhat supplemented/modified variation of the intermediate complexes of the type proposed earlier [41]. For a Pt-CD-chiral catalyst in AcOH, the intermediate is generated through the interaction of the protonated CD [47–50] acting as electrophilic agent with the nucleophilic oxygen atom of the keto group of compounds of **1**–**7** (Fig. 3, **A**). As reported previously [41], the hydrogenation of **1**–**7** to an appropriate (*R*)-compound on a Pt-β-ICN chiral catalyst in T (when inversion occurs) is assumed on the formation of surface intermediates **B** (Fig. 3). The surface complex responsible for the enantioselection is probably formed by interaction between the nucleophilic N atom of the quinuclidine skeleton and the electrophilic C atom of the keto group of the substrate. The assumed intermediate on a Pt-CD chiral catalyst in T is shown in Fig. 3 (**C**) as well. In our opinion, the H-bridge(s) linking the C5′-H and/or C6′-H of the quinoline skeleton with the carbonyl group of the substrate plays a determinant role in the formation of intermediates **B** and **C**, responsible for enantioselection. The formation of an H-bridged surface complex of this type has been experimentally verified in the ultrahigh vacuum conditions [51]. More recent studies [52] do not support the role of intermediates of types **B** and **C**, because the nitrogen atom of quinuclidine is capable of removing a proton from the surface under nonreducing conditions; that is, as reported previously [52], even in aprotic solvents, the formation of type **A** intermediates is responsible for enantioselection.

These findings reconfirm previous suggestions regarding the effect of solvents and the sense of enantioselection. The reaction mechanism may differ depending on solvent, and the sense of enantioselection is controlled by the conformation of the modifier–substrate–Pt surface intermediate complex.

Acknowledgments

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