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Heterogeneous asymmetric reactions Part 38. Enantioselective hydrogenation of fluoroketones on Pt–alumina catalyst☆

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Abstract

The enantioselective heterogeneous hydrogenation of 2,2,2-trifluoroacetophenone (**1**), 4-(trifluoroacetyl)biphenyl (**5**) and other fluoroketones (**2**–**4**, **6**–**8**) on modified (by cinchonidine) Pt–alumina (E4759) in toluene solution with and without trifluoroacetic acid (TFA) has been investigated. The effects of the modifier concentration (0–10 mmol/l), hydrogen pressure (1–50 bar), temperature (263–301 K) and conversion on the reaction rate and the enantioselectivity (ee) were studied. The achieved ee was 85% in case of **1**, however 67% ee was achieved in case of **5**.

It has been proposed that the compounds responsible for chiral induction are the intermediate complexes, the structure of which depends on whether hydrogenation is performed with or without TFA.

Keywords: Hydrogenation; Enantioselective; Platinum–alumina; Fluoroketones; Cinchonidine; Intermediate complexes

1. Introduction

Pt/Al_2O_3 modified by cinchona alkaloids is a suitable system for the enantioselective hydrogenation of so-called activated ketones (including trifluoromethyl ketones). The significance of the subject is demonstrated by the great number of pertinent reviews (the most recent of which was published this year [1]). Optically active, fluor-containing alcohols are highly valued compounds both in the pharmaceutical and agricultural industries. Moreover, some have been successfully utilized as precursors of liquid crystalline compounds. Enantiomers of chiral trifluoromethyl alcohols may be prepared by resolving racemates [2], by chiral chemical reagents [3], by microbiological methods [4] and by reduction on homogeneous chiral transition metal catalysts [5]. The first time heterogeneous cinchona-modified Pt/Al_2O_3 catalyst system was applied for the preparation of chiral trifluoromethyl alcohols was the enantioselective hydrogenation of 2,2,2-trifluoroacetophenone and the corresponding alcohol was obtained in an ee of 50–60% [6–8]. Later the optimization of experimental conditions enabled the achievement of 74% [9] and 92% ee [10] (Scheme 1).

When using polymer-stabilized nanoclusters, ee could not be increased over 30% even after the optimization of experimental conditions [11]. In a recently published work, Baiker and coworkers [12] report that, by theoretical calculations, "a correlation between the carbonyl orbital energy and the hydrogenation rate has been found", which can also be applied to trifluoroacetophenones [12].

Enantioselective reduction of **5** has been attained biologically [13]. Reduction by baker's yeast produces (*R*)-alcohol in high (96% ee) enantioselectivity, whereas reduction with *Geotrichum candidium* acetone powder yields the corresponding (*S*)-alcohol in excellent (99% ee) enantioselectivity. Knowing the advantages of heterogeneous enantioselective catalysis (for the sake of the same advantages, catalytically active metal complexes are also heterogenized [14–16]), it seemed promising to study the hydrogenation of **5** under such conditions.

This manuscript presents the results of the hydrogenation of trifluoroacetophenone and other fluor-containing aromatic

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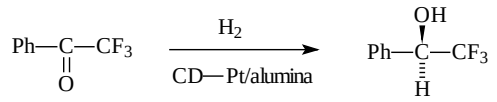

Scheme 1.

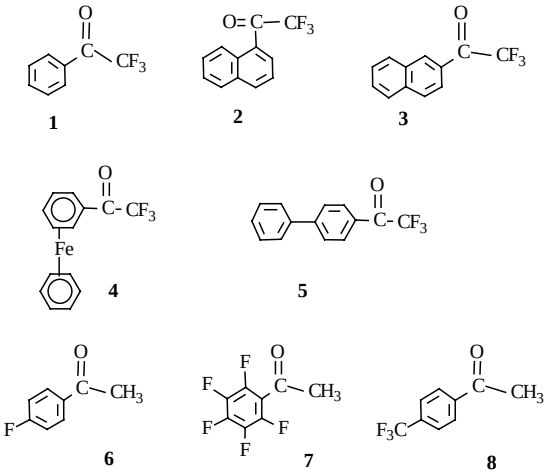

Fig. 1. Structure of investigated fluorinated ketones.

ketones (Fig. 1), comparing the latter ones to the hydrogenation of 2,2,2-trifluoroacetophenone (**1**). As hydrogenation of certain compounds did not take place or ee was very low under the applied experimental conditions (Table 1), the compounds discussed in detail in our manuscript are **1** and 4-(trifluoroacetyl)biphenyl (**5**). Elucidation of the reasons underlying the low reaction rate and observed ee in the case of compounds **2**–**4** and **6**–**8** necessitate further extensive studies. In the course of our studies on compounds **1** and **5**, special attention was paid to the rate and selectivity of the hydrogenation reaction, bearing in mind our earlier observations [17] as well as the latest results of Baiker and coworkers [10,18].

Table 1
Enantiomeric excesses in the hydrogenation of fluoroketones over CD modified Pt–alumina in toluene[a]

Substrate (Fig. 1)	H_2 pressure (bar)	Time (h)	Conversion (%)	ee (%)
1	1	0.5	60	50
1	10	1	100	24
2	1–50	1–5	No reaction	–
3	1–50	1–5	No reaction	–
4	1	2	No reaction	–
5	10	0.5	100	18
5	1	1	100	24
6	1	3.5	10	15
6	20	1	5	5
6	10	18	88	0
7	1–5	20	No reaction	–
7	25–50	1	No reaction	–
7	110	18	67[b]	–
8	1	5.5	50	11

[a] *Experimental conditions*: 25–45 mg E4759, 2–5 ml toluene, 298 K, 2 mg CD, 1 mmol substrate.
[b] Some unidentified compounds were formed.

2. Experimental

2.1. Materials

AcOH, toluene, naphtalene, biphenyl, ferrocene, (*R*)-(−)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride and cinchonidine (CD) were purchased from Fluka. Trifluoroacetic acid (TFA), trifluoroacetic anhydride, quinuclidine, 1,4-diazabicyclo[2.2.2]octane (Dabco) and substrates **1**, **6**, **7**, **8** were Aldrich products. These chemicals—except **1**—were used as-received. **1** was distilled before use to attain 99.5% purity. The substrates **2**–**5** were synthetized by Friedel–Crafts reaction, according to literature [4,19]. The substrates were purified by filtration through silica gel 60 (Fluka).

Pretreated 5% (w/w) Engelhard platinum–alumina catalyst (E4759) was used [20,21].

2.2. Hydrogenation

Hydrogenation was performed in an atmospheric batch reactor and in a Berghof Bar 45 autoclave. The catalytic system including the catalyst and 2–5 ml of solvent was purged three times with hydrogen after prehydrogenation (30 min) of the catalyst. The calculated amount of modifier and 1–2 mmol of substrate were introduced and stirred (1000–1200 rpm) in the presence of hydrogen for the required reaction time. Standard conditions were: 25–30 mg E4759, and 2 ml toluene (at 1 bar H_2 pressure), 42–45 mg E4759 and 5 ml toluene (at H_2 pressure > 1 bar), 293–298 K, 0.5 mmol/l CD, 1 bar H_2 pressure, 1000–1200 rpm, 1 mmol or 2 mmol substrate.

2.3. Analysis

The conversion and ee were calculated using GC data. In the hydrogenation reactions with the presence of CD, always the (*R*)-enantiomer was formed in excess. The identification of the product and the enantiomeric excesses [ee (%) = ([R] − [S]) × 100/([R] + [S])] were monitored by gas chromatography (HP 5890 GC-FID, using 30 m long Cyclodex-B capillary column, uncertainty ±2%). The enantiomeric excesses in case of **5** were determined by the Mosher esters method [22]. The product was reacted with (*R*)-(−)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride after work-up of the hydrogenation reaction mixture. The ester–methyne signal (*R*,*S*-6.29 ppm; *R*,*R*-6.37 ppm) in the ^{1}H NMR spectrum was used to determine the enantiomeric ratio, the values were obtained through routine integration processes. The major enantiomer was determined by measurement of the optical rotation [13] (*S*-enantiomer: $[\alpha]_D^{23} + 29.7$ (c 0.54, $CHCl_3$)).

2.4. NMR measurements

Bruker Avance DRX500 NMR spectrometer was used in all experiments operating at 11.7 T magnetic field strength (500.13 MHz ^{1}H NMR and 125.77 MHz ^{13}C NMR frequency). Samples of approximately 20 mg of the carbonyl compounds (**1**, **5**) were prepared in 0.6 ml acetone (d_6) solution and the quinuclidine or Dabco was added in a five times higher molar excess [23], then the solution was transferred to a 5 mm NMR tube. J-modulated ^{13}C NMR spectra were recorded at room temperature in approximately 12 h long experiments.

3. Results and discussion

The initial aim of these experiments was to study the enantioselective hydrogenation of **1** under mild experimental conditions (H_2 pressure 1 bar, low temperature, minimal CD concentration), just like in the case of ethyl pyruvate (EtPy) [21], hoping that optimization will allow the realization of high ee. Preliminary results, however, indicated that the behavior of the two systems (EtPy, **1**) are quite different (lower reaction rates in AcOH than those measured for EtPy hydrogenation; low ee in other solvents). Observations made in the course of EtPy hydrogenation in acids of various strengths [17] were also made use of. Because the highest ee was obtained using TFA as additive, most of the experiments on both **1** and **5** were performed in a solvent mixture containing toluene + TFA.

3.1. Enantioselective hydrogenation of 2,2,2-trifluoroacetophenone (*1*)

Some characteristic results of the experiments in toluene are summarized in Figs. 2–4.

The figures show the effects of catalyst quantity, the concentration of compound **1** and temperature on the rate of hydrogenation and on ee (Figs. 2 and 3), furthermore the effect of the progress of conversion on ee (Fig. 4). The results allow the following conclusions to be drawn.

The data of preliminary experiments show that under standard experimental conditions, in the presence of catalyst in excess quantities (30 mg), at temperature range of 273–293 K and at values of 1000–1200 rpm hydrogenation takes place within the kinetic range. It has been verified [7,8] that higher ee values are attainable mainly in apolar and mildly polar solvents. The interaction between **1** and CD, which is responsible for ee, is presumably inhibited probably because of the competition of CD and **1** during adsorption. The data presented here—in agreement with the results in Fig. 2—make it obvious that the rate of hydrogenation depends on temperature, whereas ee hardly changes. It is also shown in Fig. 2 that, under identical experimental conditions, the addition of TFA greatly reduces reaction rates.

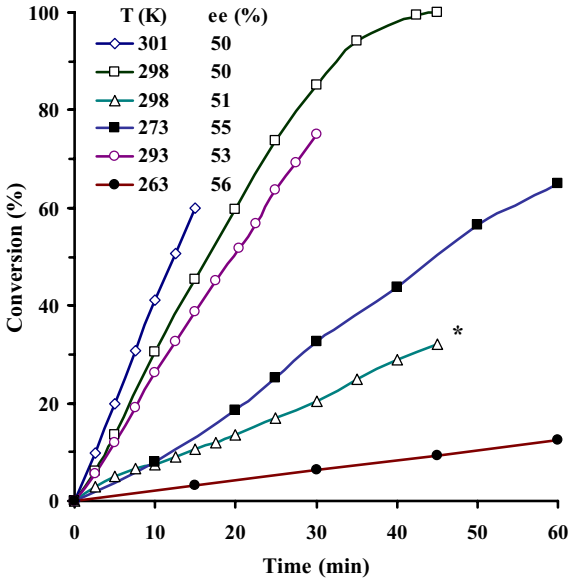

Fig. 2. Enantioselective hydrogenation of trifluoroacetophenone (**1**): the effect of temperature (standard conditions, *2 ml toluene + 0.8 μl TFA).

According to the experimental data presented in Fig. 3, a moderate CD concentration (0.5 mmol/l) was advantageous for ee, unlike the case of EtPy where the highest ee could be attained at 0.1 mmol/l CD in toluene [24] and at 0.01 mmol/l CD in AcOH [21], under similarly mild conditions. An additional difference can be observed in the rate acceleration of the hydrogenation of EtPy and **1**. The reaction rate acceleration on the modified catalyst is 10–20-fold for EtPy, but only 2–3-fold for **1**.

As regards changes in reaction rate and enantioselectivity as a function of percentage conversion, according to Baiker et al.'s studies in dichlorobenzene and toluene [6,25] both

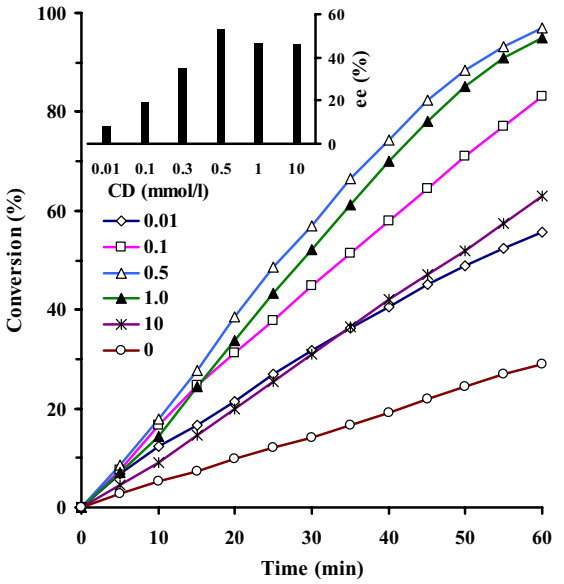

Fig. 3. Enantioselective hydrogenation of trifluoroacetophenone (**1**): the effect of CD concentration (standard conditions).

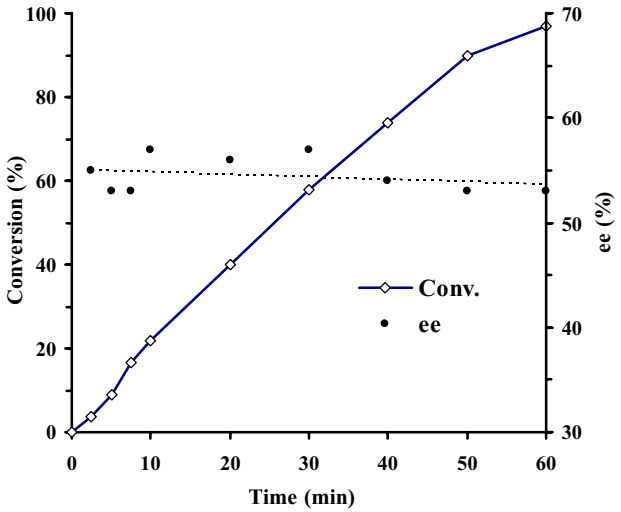

Fig. 4. Enantioselective hydrogenation of trifluoroacetophenone (**1**): the effect of conversion on ee (standard conditions).

ee and rate increased during the initial period of the reaction, below 10–20% conversion. By the evidence of the data displayed in Fig. 4, no such initial period could be observed under the standard conditions studied.

Data on the dependence of enantioselectivity on hydrogen pressure, TFA concentration and percentage conversion are summarized in Table 2. According to these measurements, increasing hydrogen pressure under identical conditions did not favor an increase in ee (entries 1–5). When TFA was added, however, hydrogen pressure was increased over 1 bar because of the slow reaction at 1 bar. For this reason hydrogenation in the presence of the additive TFA was mostly carried out at a hydrogen pressure of 10 bar. The experiments suggest that to attain higher ee values, optimal TFA concentration is necessary, which in our case is 5–15 μl/5 ml toluene. As regards optimal TFA concentration, the data in [10], TFA/CD = 9.6 mol/mol and TFA/React. = 9.6 mol/mol may lead to some confusion; the correct value is probably TFA/CD = 9.6 mol/mol. In the case of TFA/**5** = 9.6 mol/mol the reaction was very slow and racemic mixture was formed.

As shown by the data in Table 2, TFA significantly increases ee, in accordance with results published earlier [10,17]. Under these experimental conditions the progress of conversion had a favorable effect on ee (entries 13–15).

Table 2
Enantioselective hydrogenation of trifluoroacetophenone (**1**) over cinchonidine (CD) modified Pt–alumina[a]

Entry	TFA (μl)	H_2 pressure (bar)	Time (h)	Conversion (%)	ee (%)
1[b,c]	0	1	0.5	55	50
2[b,c]	0	3	0.5	100	40
3[b,c]	0	5	0.5	100	48
4[b,c]	0	10	0.5	100	24
5[b,c]	0	15	0.5	100	25
6	2.5	10	1	15	62
7	5	5	1	5	70
8[d]	5	10	1	8.5	60
9	15	10	1	18	83
10	25	10	1	15	78
11[d]	25	10	1	18	64
12[e]	5	10	1	11	85
13	5	10	2	36	77
14	5	10	3	50	80
15	5	10	8	100	84

[a] *Experimental conditions*: 42–45 mg E4759, 5 ml toluene, 273 K, 2 mg CD, 0.25 ml (**1**).
[b] 298 K.
[c] 0.3 mg CD.
[d] 5 mg CD.
[e] 258 K.

3.2. Enantioselective hydrogenation of 4-(trifluoroacetyl)biphenyl (*5*)

Enantioselective hydrogenation of **5** under the conditions of heterogeneous catalysis is not mentioned in the literature. In the case of **1**, from the solvents checked toluene was found to be a good solvent; however, high ee can only be attained in the presence of TFA as additive. Therefore the majority of measurements involving **5** were performed in a solvent mixture of toluene + TFA, under the conditions found optimal for **1** (H_2 pressure > 1 bar, 5 μl TFA). The results are summarized in Fig. 5 and Table 3.

Examination of the rates of hydrogenation reactions revealed that, unexpectedly, racemic hydrogenation is significantly faster for **5** than for **1**, whereas enantioselective hydrogenation proceeds at identical rates. The value of ee attained under identical experimental conditions is 53% for **1** but only 24% for **5**. Interpretation of these data necessitates further studies. The data in Table 3 allow to conclude that

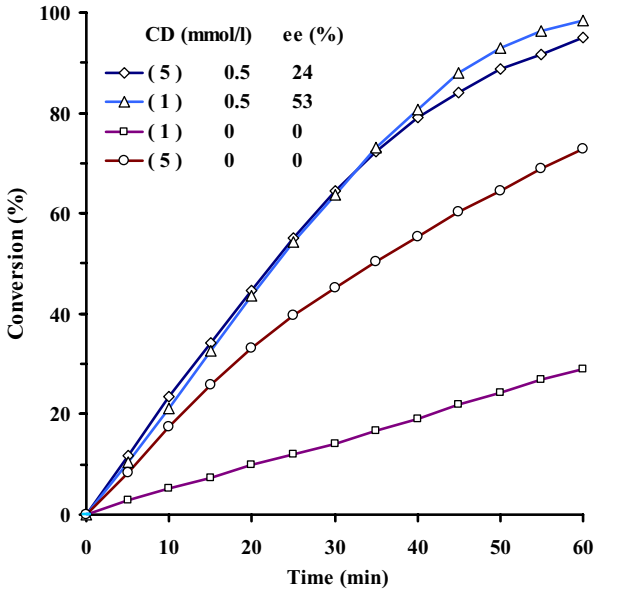

Fig. 5. Racemic and enantioselective hydrogenation of **1** and **5**: the effect of substrate structure on rate (standard conditions).

Table 3
Enantioselective hydrogenation of trifluoroacetylbiphenyl (**5**) over cinchonidine (CD) modified Pt–alumina[a]

Entry	Temperature (K)	H_2 pressure (bar)	TFA (μl)	Time (h)	Conversion (%)	ee (%)
1	298	10	0	0.5	100	18
2	298	10	5	1	24	55
3	298	20	5	1	38	47
4	273	10	5	5	33	66
5	273	20	5	2	18	67
6	273	30	5	2	13	65
7[b]	273	20	5	3	30	41
8[c]	283	8	0	2	91	38
9[c]	273	10	5	2	47	52
10[d]	273	10	1000	5	50	33
11	273	10	1000	4	30	0

[a] *Experimental conditions*: see in Table 2; 0.46 g (**5**).
[b] Solvent: toluene + 10 μl H_2O.
[c] Solvent: toluene/AcOH (1/1).
[d] Solvent: AcOH.

(i) the highest ee is 67%, in the attainment of which the additive TFA and low temperature (273 K) play a determinant role at hydrogen pressures of 10–30 bar; (ii) under similar conditions, at 298 K ee is nearly 20% lower; (iii) ee is increased and reaction rate is decreased by TFA.

3.3. NMR measurements

The zwitterionic adducts were studied by NMR spectroscopy. **1** as well as **5** were used as strong electrophile agents and adducts were created with tertiary amines quinuclidine and Dabco in acetone solution. Since the adduct formation is an equilibrium process, the amine molar amount was five times higher than that of the carbonyl compound. The interaction was monitored by the chemical shift change of the carbonyl signal in the ^{13}C NMR spectrum (Fig. 6).

The carbonyl signal has a quartet multiplet structure due to the heteronuclear coupling to three fluor atoms in the methyl group with a chemical shift of 181.2 ppm in **1** and 180.7 ppm in **5**. The decrease in the chemical shift can be attributed to the presence of the zwitterionic form. **1**-Dabco adduct was reported earlier [23] and was not studied here. As the adduct forms a 87.7 ppm upfield shift takes place to 93.5 ppm in case **1** and quinuclidine. Similar tendency was observed when **5** was used to produce the adduct, a 87.2 ppm upfield shift was detected. The same upfield shift was recorded when Dabco was used as a substrate.

These considerable changes in the carbonyl chemical shift confirm unambiguously the presence of the zwitterionic form when both **1** and **5** were used as electrophile agents.

3.4. Interpretation of the enantioselective hydrogenation of trifluoromethyl ketones

The majority of authors assume (see [1] and the references cited therein) that chiral induction of heterogeneous

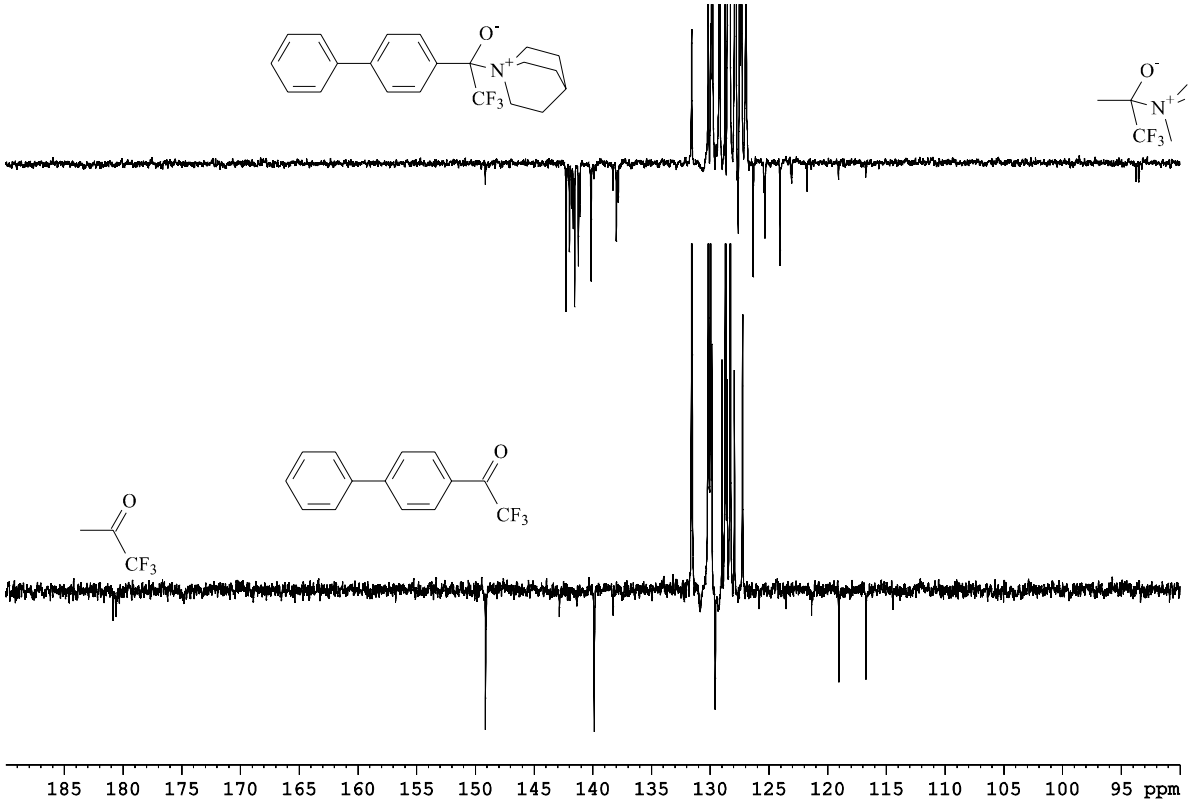

Fig. 6. J-modulated ^{13}C NMR spectra of 4-(trifluoroacetyl)biphenyl (**5**, bottom) and its zwitterionic adducts with quinuclidine (top).

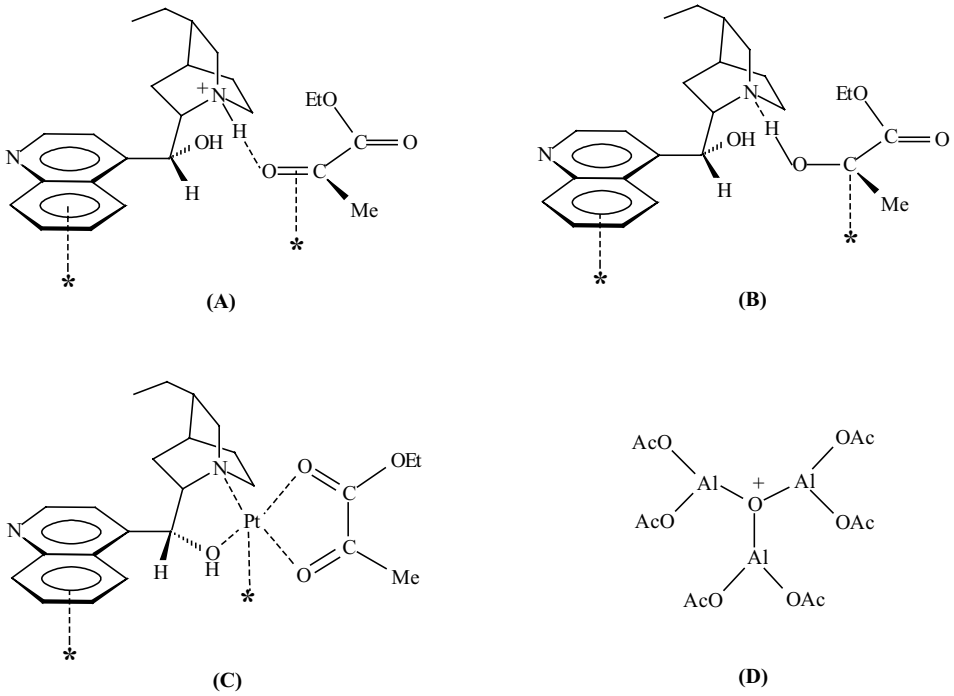

Fig. 7. Proposed adsorbed adduct complexes between DHCD + EtPy (**A**, **B**, **C**) and structure of oxonium cation (**D**) (Ac: acetyl; lactoyl: MeCH(OH)CO; pyruvoyl: MeC(O)C(O)).

catalytical enantioselective hydrogenation of activated ketones takes place on the chirally modified platinum surface (adsorption model).

In the case of EtPy hydrogenation, the adsorption model gives an identical explanation for the chemical events taking place in the two different solvents; the only difference is the structure of the intermediate complex. In AcOH, EtPy is bonded to the protonated quinuclidine via a hydrogen bond (Fig. 7**A**), whereas in toluene, half-hydrogenated EtPy is bonded to the nitrogen of the quinuclidine, also via hydrogen bond (Fig. 7**B**).

Moreover, we assumed that in AcOH the stabilization of the intermediate is also promoted by the oxonium cations (Fig. 7**D**) and their dendrimers generated on the surface under these conditions [21,26]. Besides, it cannot be excluded that the reaction mechanism in toluene is entirely different from that operating in AcOH. In toluene we proposed [24,27] that the modifier and the substrate (in the present case, EtPy) participate in the formation of the surface complex as ligands of the surface Pt atoms (Fig. 7**C**). These "ligands" bind to Pt via their unbonded electron pairs.

As regards studies aimed at the interpretation of the enantioselective hydrogenation of trifluoroacetyl ketones, considerably fewer works have been published in the literature on these than on EtPy. The results published by Baiker et al. [8–10,12,18] and our own experimental observations ([7,17], this work) are all that can be referred to. On this basis it appears that there is a significant difference between the mechanism of the enantioselective hydrogenation of this type of compound in toluene and that in toluene + TFA.

For the interpretation of hydrogenation in the presence of TFA, a certain kind of explanation for the acid effect was made possible by earlier NMR studies [17]. The recently published results of Baiker and coworkers [18] in the field of theoretical calculations and IR-spectroscopic analysis, however, not only supplemented certain statements in [17] but also led to the formulation of a novel reaction mechanism, which is also in agreement with our experimental data, inasmuch as it gives a reasonable interpretation of the chemistry in the presence of TFA additive. According to this reaction mechanism, the structure of the surface complex responsible for chiral induction has the characteristics of structure **A** outlined in Fig. 8.

The structure of the surface complex forming in the course of enantioselective hydrogenation in the absence of acids should naturally be significantly different from structure **A** in Fig. 8. Based on our present knowledge, the intermediate complexes proposed for the interpretation of EtPy hydrogenation (Fig. 7**B** and **C**) cannot be excluded either. The results of the NMR studies presented in this paper, however, prompted us to put forth again the surface complex earlier proposed by us for the hydrogenation of EtPy in the presence of the chiral modifier β-isocinchonine (β-ICN) [28]. This surface complex is shown as structure **B** in Fig. 8. In this intermediate, the nucleophilic N of the quinuclidine skeleton of DHCD interacts with the electrophilic carbon atom of the carbonyl group of the trifluoromethyl ketone.

The presence of a **B**-like intermediate is supported not only by the reactions of aldehydes and ketones with primary and secondary amines, also utilized by the organic

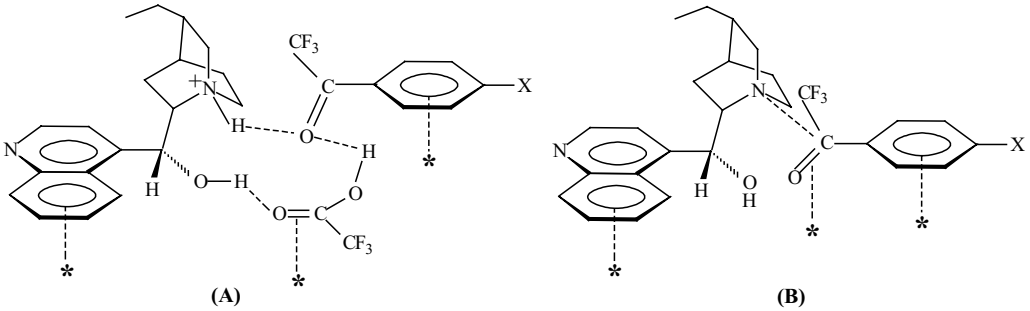

Fig. 8. Proposed adsorbed adduct complexes between DHCD + trifluoromethyl ketones with TFA additive (**A**) and without TFA (**B**) in toluene (X: H, Ph).

chemical industry, but also by the zwitterionic adducts resulting from the reaction between the compounds studied here (trifluoromethyl ketones) and tertiary amines [23]. The NMR studies of strongly electrophilic ketones and tertiary amine, presented here (see Section 3.3) also convincingly prove the formation of adducts of the zwitterionic type. By the way, compounds containing this type of bond are also found among natural alkaloids [29].

4. Conclusion

Results so far published on the enantioselective hydrogenation of fluoroketones, a group of activated ketones on chiral Pt–alumina catalysts have shown that the Orito reaction [30] is also suitable for the preparation of chiral alcohols containing trifluoromethyl groups. The available information suggests that the compounds responsible for chiral induction are different intermediates, the structure of which depends mostly on the acidic or non-acidic nature of the hydrogenation medium. In the presence of TFA, there is competition between the proton and the electrophilic carbon atom of the carbonyl group of the trifluoromethyl ketone for the unbonded electron pair of the nucleophilic nitrogen atom of the quinuclidine skeleton of CD. The results show that the winner is the proton. In toluene (in the absence of TFA) there is no such competitor; the intermediate will therefore have a different structure. Further tasks are to attempt the identification of the intermediate adducts in solution by suitable MS methods and to study the effect of the stability of zwitterion-like intermediates on enantioselectivity.

Acknowledgements

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