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Catalysis Today 37 (1997) 419–440

CATALYSIS TODAY

Selective heterogeneously catalyzed hydrogenations

Robert L. Augustine*

Chemistry Department, Seton Hall University, South Orange, NJ 07079, USA

Abstract

A number of catalytic hydrogenations have been discussed with emphasis on reaction selectivity. These reactions were examples of chemoselectivity, regioselectivity, stereoselectivity, diastereoselectivity and enantioselectivity. Factors such as catalyst selection, reaction conditions and the steric nature of the substrate were discussed in terms of their contribution to the selectivity of particular hydrogenations.

Keywords: Hydrogenation; Selectivity; Functional group

1. Introduction

The catalytic hydrogenation of organic functional groups is probably the most common application of heterogeneous catalysis in the synthesis of organic compounds. The usefulness of this reaction has been well covered by texts [1–10], reviews [11,12] and conference proceedings [13–30]. However, with the exception of the more recent conferences on Catalysis in Organic Chemistry [25–27] and Heterogeneous Catalysis in Fine Chemicals [29,30], an examination of the recent literature shows that catalytic hydrogenation has been the subject of only a few recent publications. Fig. 1a shows a breakdown of the non-patent abstracts that appeared in the January, 1996 issues of CA Selects, Catalysis [31]. About one-fourth of all of the papers which were abstracted during this time covered some aspect of heterogeneous catalysis which did not relate to the other areas shown in the figure. Fig. 1b shows the breakdown of the heterogeneous catalysis papers. Over three-fourths of them dealt with catalyst preparation and characterization or the mechanisms of a catalyzed process. Only about 15% of the articles covered topics of interest to the synthetic chemist and a large number of them were concerned with reactions run using solid acids. Just 5% of the papers discussed catalytic hydrogenation.

Some argument may be made that hydrogenation is a "mature" area and, thus, little additional fundamental work can be done on the topic. In fact, though, there is a great deal that can be done, particularly in developing catalysts and conditions useful for selective hydrogenations. It would be interesting to see what type of selectivity could be obtained with some of the newly prepared and characterized catalysts described in the literature. In most cases these materials were used to promote a catalytic reaction, but all too often, it was the hydrogenation of ethylene or propylene, reactions which tell very little of the potential ability of the catalyst to promote the hydrogenation of more complex substrates. An example of the use of an uncommon catalyst for a selective hydrogenation is the conversion of carboxylic acids to the

*Tel.: (1-201) 761-9033; Fax: (1-201) 761-9772; e-mail: augustro@lanmail.shu.edu

PII S0920-5861(97)00025-4

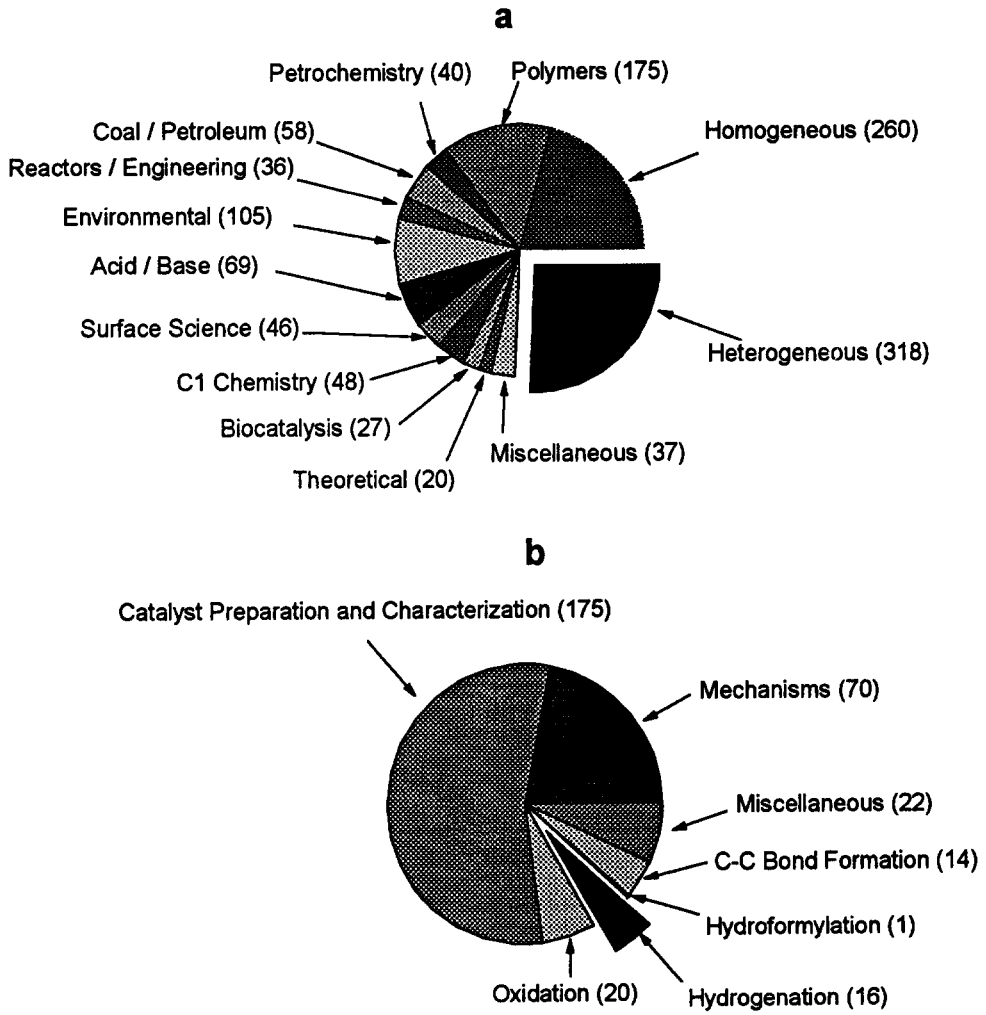
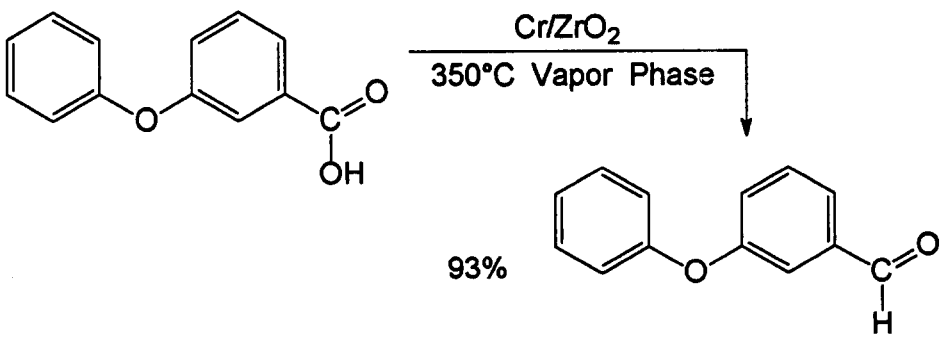


Fig. 1. (a) Categories of abstracts appearing in CA Selects, Catalysis, 8–22 January, 1996 (1239 abstracts); (b) breakdown of the heterogeneous catalysis abstracts.

corresponding aldehydes using a Cr/ZrO_2 catalyst. Excellent yields of a number of substituted benzaldehydes and aliphatic aldehydes have been obtained using this procedure (Eq. (1)) [32,33].



(1)

Hydrogenation selectivity can be influenced not only by the choice of the catalyst but also by the conditions under which the reaction is run. In general, the use of higher temperatures results in a decrease in selectivity. Thus, one should use as low a reaction temperature as possible while still maintaining a reasonable reaction rate. In many reactions, higher hydrogen pressures also cause a lessening in the reaction selectivity but, there are some enantioselective reactions in which increasing the hydrogen pressure increases the selectivity of the reaction. Other important factors are the type of solvent used and the hydrogen availability to the catalyst. This mass transport is usually related to the hydrogen pressure but, as discussed previously [34], is also influenced by the agitation of the reaction mixture and the quantity of catalyst used.

2. Selective hydrogenations

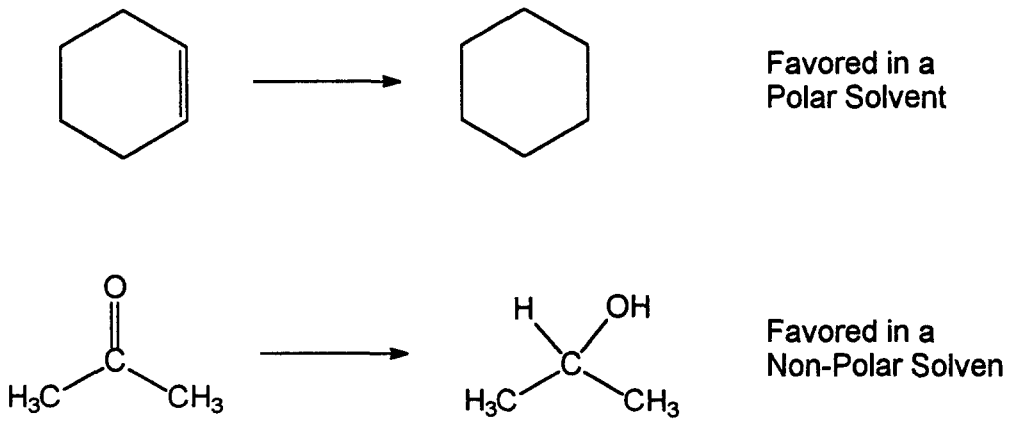
There are three basic types of selective hydrogenations [35,36].

Type I selectivity is that occurring when two simultaneous reactions are taking place. While such selectivity is not commonly encountered in synthetic applications, these reactions can be illustrative of the effect which the solvent can exert in determining which functional group will be selectively hydrogenated from a mixture of substrates. In the hydrogenation of a mixture of cyclohexene and acetone over a nickel catalyst, acetone is solvated in polar solvents so cyclohexene hydrogenation is favored while non-polar solvents solvate cyclohexene and acetone hydrogenation predominates (Scheme 1) [37].

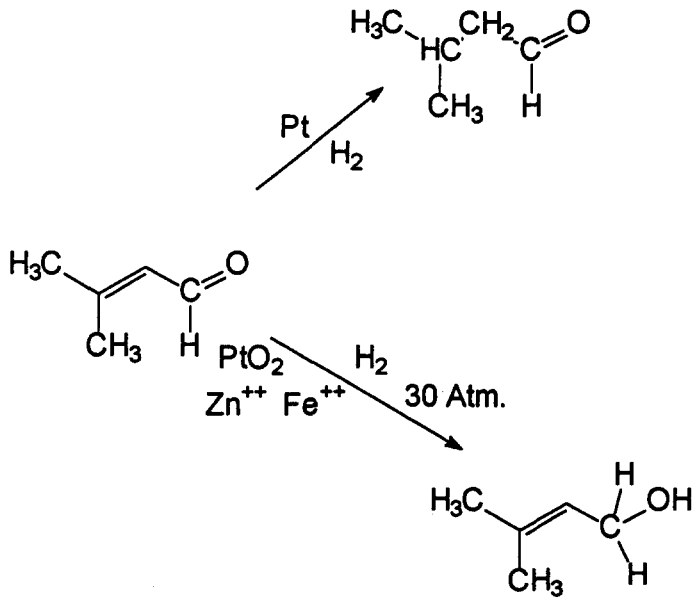
Type II selectivity is the most common in synthetic hydrogenations. This involves the differentiation between two parallel reactions in which different products can be formed from the same starting material as in the hydrogenation of an unsaturated aldehyde to give either the unsaturated alcohol or the saturated aldehyde (Scheme 2) [38].

The hydrogenations of a number of organic functional groups take place in a stepwise manner so it is frequently possible to stop the reaction at an intermediate stage and isolate a partially hydrogenated material. This selective production of an intermediate species from a sequential reaction is referred to as *Type III selectivity.* One example of this type of selectivity is the partial hydrogenation of carboxylic acids to the aldehydes mentioned above. Here, the reaction is terminated before the aldehyde is hydrogenated to the alcohol. The most common example of this type of reaction, however, is the semihydrogenation of alkynes to *cis* alkenes, a reaction of considerable synthetic importance (Scheme 3) [39].

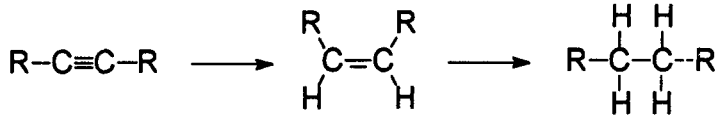
In many of these sequential reactions, selectivity can be improved by using a low hydrogen availability and a less active catalyst to minimize the complete saturation of the substrate. Selectivity can also be improved by using a catalyst on which the active component is present on or near the surface of the catalyst particles. When this is the case it is relatively easy for the substrate to reach the active sites and to be



Scheme 1. Type I Selectivity: two simultaneous reactions.



Scheme 2. Type II Selectivity: parallel reactions (two products from the same starting material).

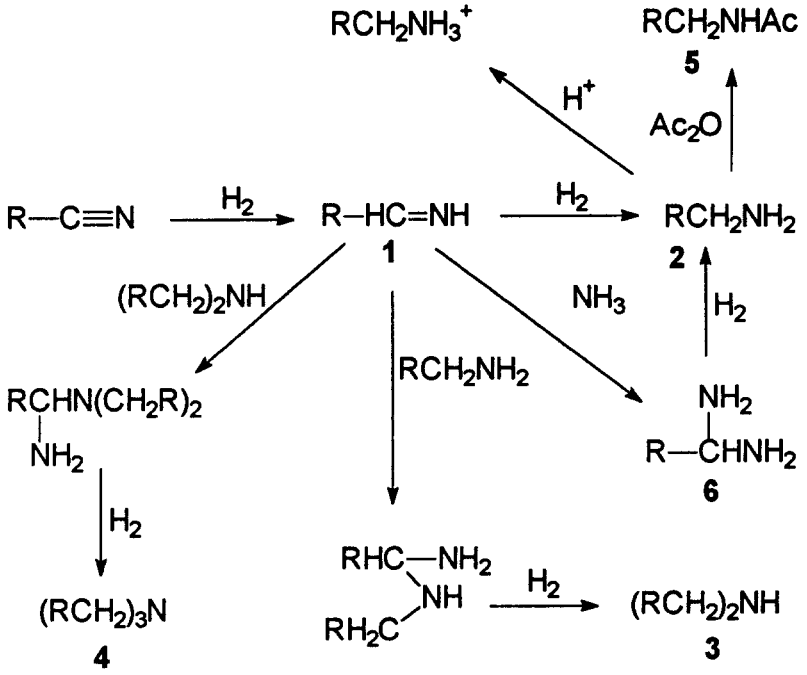


Scheme 3. Type III Selectivity: serial reactions.

displaced by unreacted substrate molecules before further saturation can occur.

The type and amount of solvent used can sometimes influence the selectivity in this type of reaction. As shown in Scheme 4, the hydrogenation of a nitrile occurs with the initial formation of an aldimine, **1**, which is then hydrogenated further to give the primary amine, **2**. Condensation of the amine with the intermediate imine, **1**, can lead to secondary amine, **3**, formation and with further condensation to tertiary amines, **4**. With a dilute solution of the nitrile these condensations are minimized and primary amine production increases. Other ways of increasing selectivity to primary amines is to add acetic anhydride to the solvent to trap the primary amine as the amide, **5**, and, thus, keep it from reacting further [40]. Acidic media can be used to protonate the product amine to prevent condensation with the imine [41]. Another approach, particularly useful with nickel catalysts, is to run the hydrogenation in ammonia which will react with the intermediate imine to form the aminal, **6**, which, on hydrogenolysis, gives the primary amine, **2**. Since the ammonia is present in a larger excess than the primary amine, secondary amine formation is suppressed [42].

As depicted in Scheme 5, the hydrogenation of aromatic nitro groups also proceeds through several stages. The first partially reduced species is the nitroso compound, **7**, which can condense with either the product aniline, **9**, or the intermediate hydroxylamine, **8**, to give dimeric products [43]. Here, too, running the reaction in a dilute solution can minimize the extent of condensation. It is not always necessary to use a large quantity of solvent to have a low concentration of substrate. Using a solvent in which the reactant is only partially dissolved will have the same effect. The nitroimidazole, **10**, was selectively hydrogenated only in concentrated ammonia, a solvent in which the

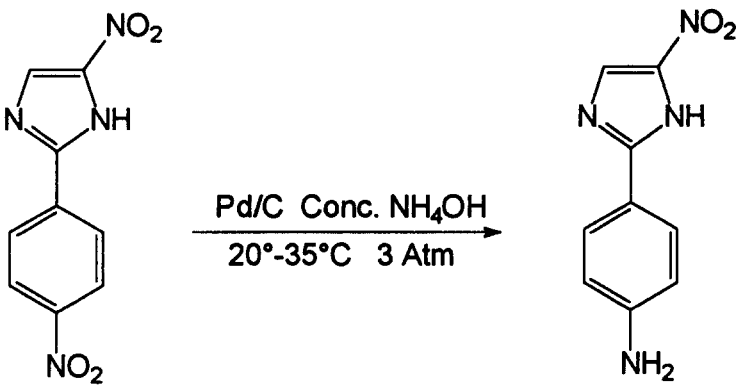


Scheme 4.

concentration of dissolved reactant was low enough that the amount of the intermediate nitroso compound in solution was minimized and condensation with the product amine was effectively prevented (Eq. (2)) [44].

In other solvents the solubility of the imidazole was too high and dimeric product formation was predominant.

Aryl hydroxylamines can be obtained by the hydrogenation of aromatic nitro compounds using



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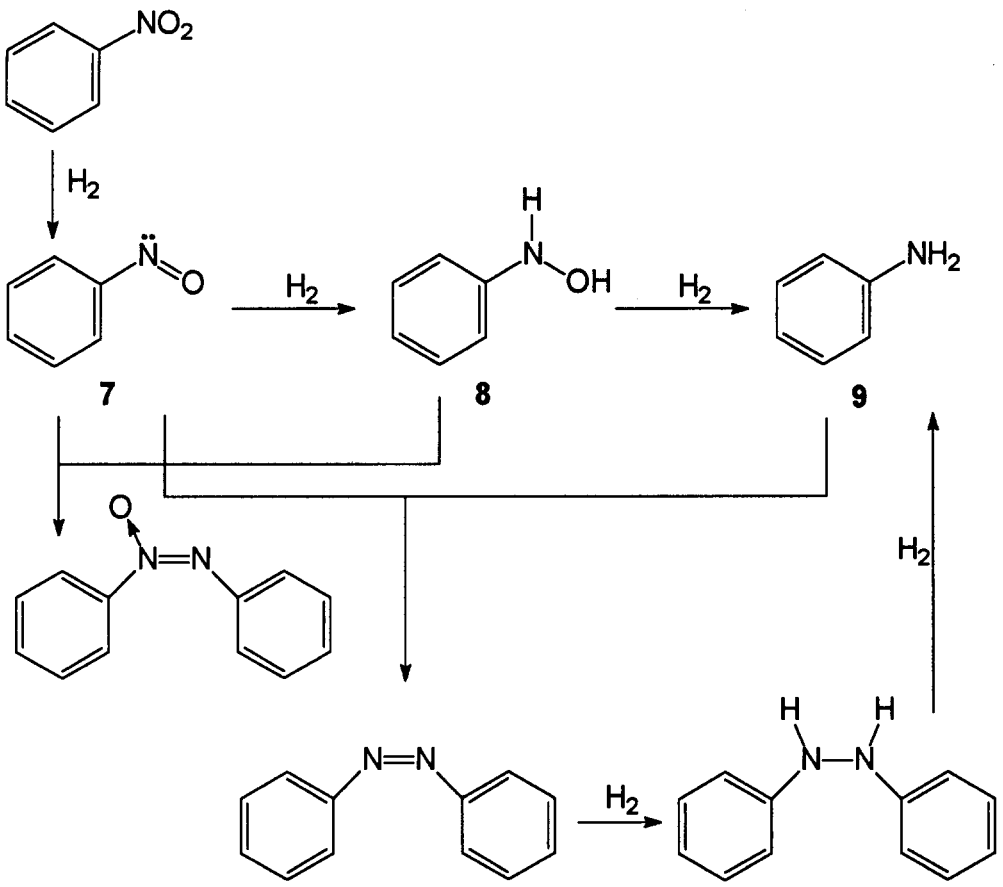
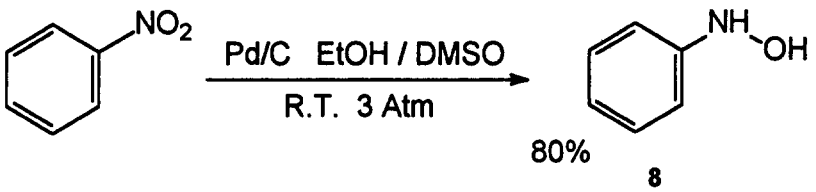
(2)



Scheme 5.

platinum catalysts in the presence of a small amount of dimethyl sulfoxide as an inhibitor (Eq. (3)) [45,46].



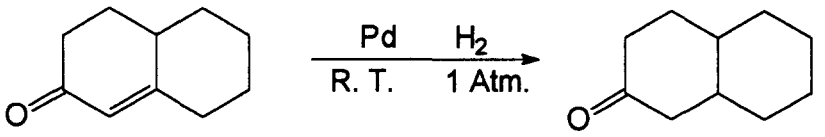
(3)

A maximum yield of 80% was obtained when the hydrogenation was interrupted after the absorption of two equivalents of hydrogen. Phenyl hydroxylamine formation is favored by low metal loading, small amounts of catalyst and rapid agitation; all factors favoring the rapid diffusion of the reactant through the reaction medium. This rapid diffusion enhances the displacement of the phenyl hydroxylamine by the nitrobenzene before hydrogenolysis of the N–OH bond can take place [45].

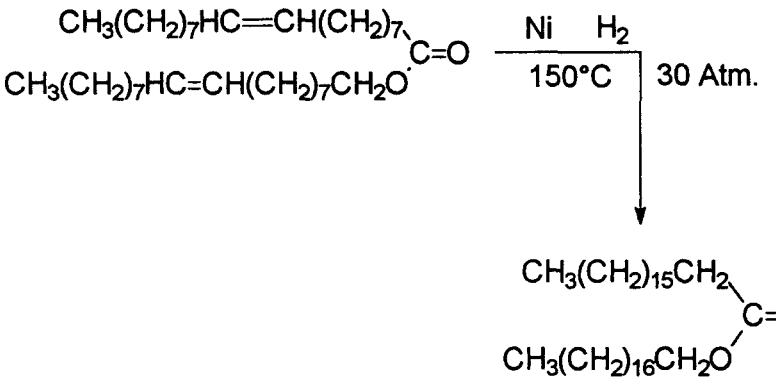
Generally, in these reactions, the use of alkaline media favors the formation of the dimeric products. In neutral solvents the partially reduced monomeric products are formed and in acid, aniline production is predominant.

Most synthetically important selective hydrogenations are combinations of Type II and Type III selectivity. Such reactions can be defined as being chemoselective, regioselective or stereoselective. A chemoselective reaction is one in which one functional group on the starting material is hydrogenated in preference to another, potentially hydrogenatable, group which is also present in the molecule. A regioselective hydrogenation is one in which one functional group is hydrogenated in the presence of another, identical, functional group in the molecule. A stereoselective hydrogenation is one which gives predominantly one stereoisomeric product. In cases where the substrate already has a chiral center which directs the hydrogenation of a prochiral group, the reaction is termed diastereoselective. Hydrogenations which produce a chiral product from a non-chiral substrate are enantioselective.

an apparent order of decreasing ease of hydrogenation along with the typical reaction conditions used for their hydrogenations. This order can frequently be modified by changes in reaction conditions and/or the steric environment of the functionalities. It is usually simple to affect the selective hydrogenation of a functional group listed near the top of this table in the presence of one found in the middle or bottom of the list. For example, it is relatively easy to selectively saturate the double bond of an unsaturated ketone or ester without reducing the carbonyl group (Eqs. (4) and (5)).



(4)



(5)

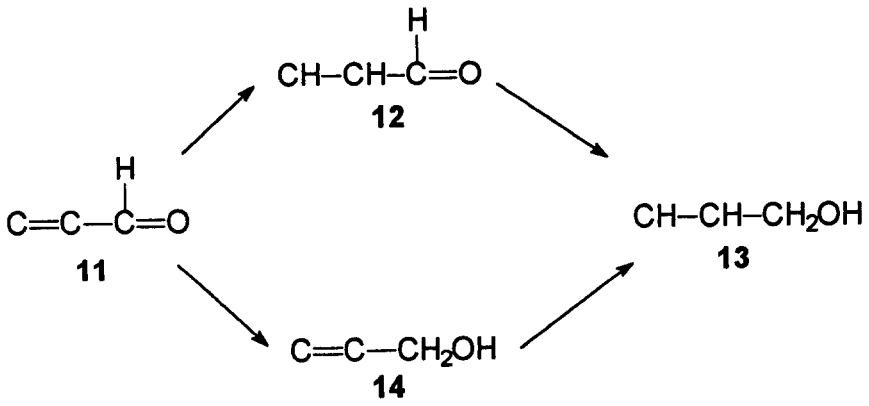
3. Chemoselectivity

The degree of difficulty in attaining a chemoselective reaction depends largely on the functional groups involved and the steric environment around each one. Table 1 lists the common organic functional groups in an apparent order of decreasing ease of hydrogenation along with the typical reaction conditions used for their hydrogenations. This order can frequently be modified by changes in reaction conditions and/or the steric environment of the functionalities. It is usually simple to affect the selective hydrogenation of a functional group listed near the top of this table in the presence of one found in the middle or bottom of the list. For example, it is relatively easy to selectively saturate the double bond of an unsaturated ketone or ester without reducing the carbonyl group (Eqs. (4) and (5)).

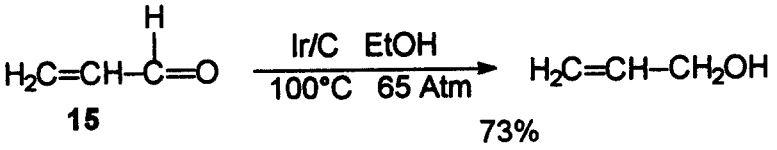
Normally the hydrogenation of an α,β-unsaturated aldehyde, **11**, over a platinum catalyst gives almost exclusively the saturated aldehyde, **12**, or, on further hydrogenation, the saturated alcohol, **13**, (Scheme 6). The unsaturated alcohol, **14**, however, can be obtained when the hydrogenation is run under the proper reaction conditions. A number of factors are important in directing this reaction toward the formation of the unsaturated alcohol [47]. The choice of catalyst is one of the most important. Over a palladium catalyst, the only reaction observed is the saturation of the double bond to give **12**. With an iridium or osmium catalyst, however, the unsaturated alcohol is formed almost exclusively (Eqs. (6)–(8)) [48].

Table 1
Hydrogenation of common organic functional groups

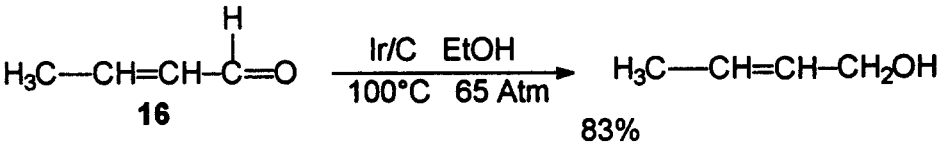
Group	Product	Catalyst	Reaction Conditions
—C≡C—	—C=C— (H, H)	Pd	Room temp, 1 atm, low catalyst ratio, deactivated catalyst
C=C—C=C	C—C=C—C (H, H)	Pd	Room temp, 1 atm
C=C—C=C	C=C—C—C (H, H)	Pd	Room temp, 1 atm Low catalyst ratio, deactivated catalyst
—NO_2	—NH_2	Pt, Pd, Rh	Room temp, 1 atm
>C=C<	>CH-CH<	Pd, Ni	Room temp, 1 atm
—C≡N	—CH_2NH_2	Raney Ni Raney Co	Room temp, 1–4 atm, NH_3 Room temp, 1–4 atm
>C=N—	>CH-NH—	Pt, Pd	Room temp, 1–4 atm
ϕ, >C=O	ϕ, CH_2	Pd	Room temp, 1–4 atm
>C=O	>CH-OH	Pt, Rh Ru	Room. temp, 2–4 atm Room temp, 1–3 atm, H_2O
Heterocyclic and Carbocyclic Aromatics	X = C, N, O	Rh Raney Ni Ru	Room temp, 2–4 atm 100–120°C, 100 atm 150°C, 100 atm
—CO_2H (R)	—CH_2OH	Ru, CuCrO	High temperature and pressure
—CO_2NR_2	—CH_2NR_2	Ru, CuCrO	High temperature and pressure



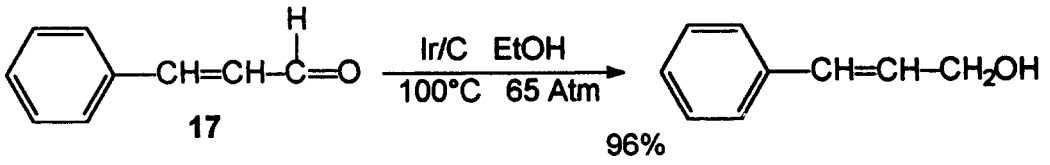
Scheme 6.



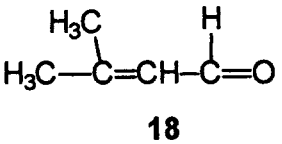
(6)



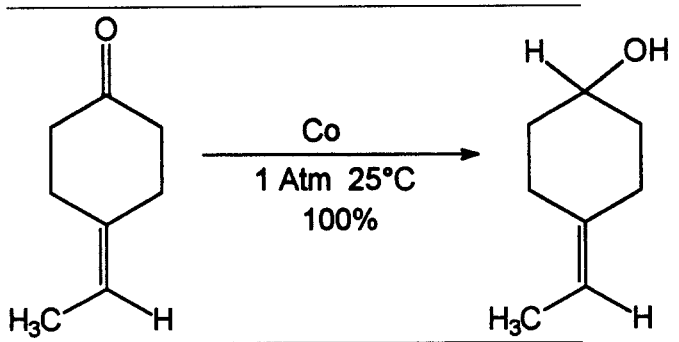
(7)



(8)



Steric hindrance around the double bond facilitates the selective hydrogenation of the carbonyl group with selectivity for unsaturated alcohol form acrolein (**15**)<crotonaldehyde (**16**)<3-methylcrotonaldehyde (**18**)<cinnamaldehyde (**17**).



(9)

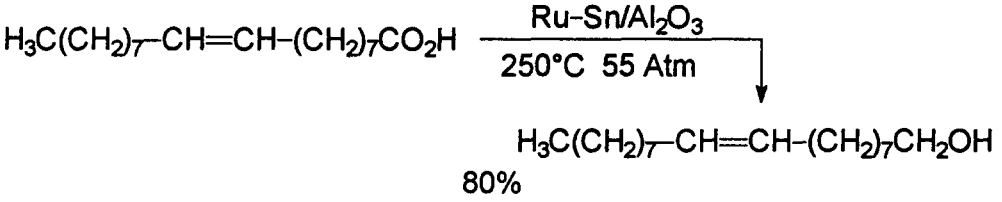
Placing a substituent on the carbonyl carbon (converting the aldehyde to a ketone) hinders the selective saturation of the carbonyl group. To date, there has been no report of the selective hydrogenation of an α,β-unsaturated ketone to an unsaturated alcohol. In molecules in which the double bond is not conjugated with the carbonyl group, the selective hydrogenation to the unsaturated alcohol takes place more easily, particularly when the double bond is highly substituted (Eq. (9)) [49].

Double bond isomerization prior to saturation will decrease reaction selectivity.

In most cases a modifier is used to enhance selectivity in the hydrogenation of α,β-unsaturated aldehydes. The most common of these are the ferrous and

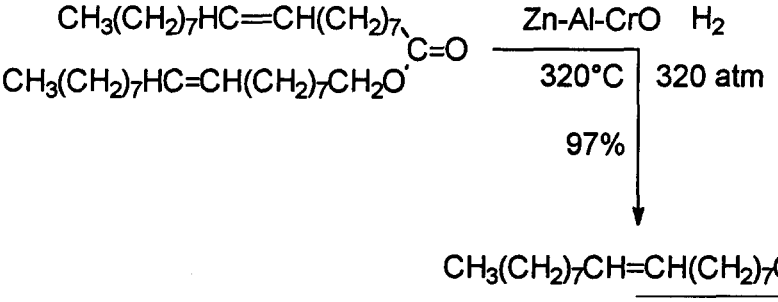
ferric salts, particularly the acetates but tin salts have also been shown to be effective [47].

Obtaining selectivity when the two functional groups are far apart in the listing shown in Table 1 is generally very difficult. Usually the hydrogenation of an unsaturated acid or ester proceeds to give exclusively the saturated acid or ester since the carboxyl group is the most difficult to hydrogenate using standard conditions. However, when a Ru–Sn catalyst was used to hydrogenate an unsaturated fatty acid, the unsaturated alcohol was obtained in about 80% yield (Eq. (10)) [50].



(10)

With a zinc–aluminum chromate catalyst, unsaturated esters were hydrogenated to unsaturated alcohols in excellent yields (Eq. (11)) [51].

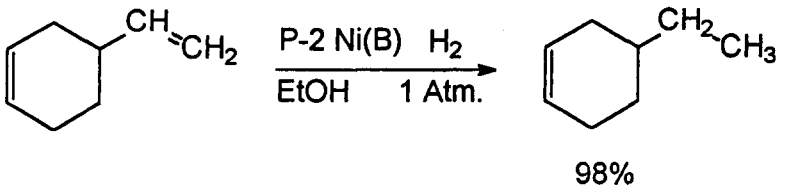


(11)

4. Regioselectivity

The selective hydrogenation of one double bond in an unconjugated diene is an example of a regioselective reaction (Eq. (12)) [52].

The selectivity in such reactions is frequently decreased by running them under conditions in which both functional groups are saturated. In these reactions steric factors also play an important role with the more accessible group being the one which is selectively saturated. In the hydrogenation of unconjugated dienes, a terminal double bond, if present, is generally saturated in preference to other, more substituted double bonds. It is sometimes necessary to hydrogenate the more hindered of the double bonds. To accomplish this the dicarbonyl iron cyclopentadienyl complex can be used as a blocking agent for the less hindered, more reactive double bond. Hydrogenation of the resulting intermediate saturates the more hindered double bond. Treating the alkenyl complex with sodium iodide regenerates the mono-olefin having the less substituted double bond intact (Eqs. (13) and (14)) [53].



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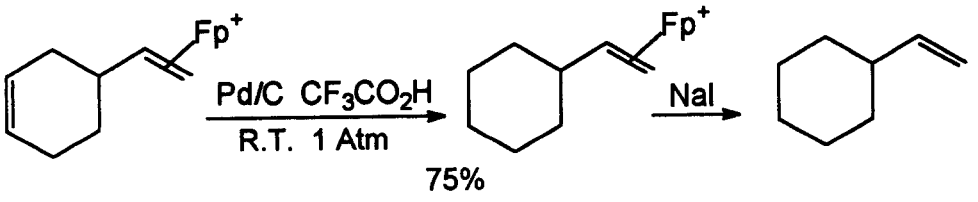

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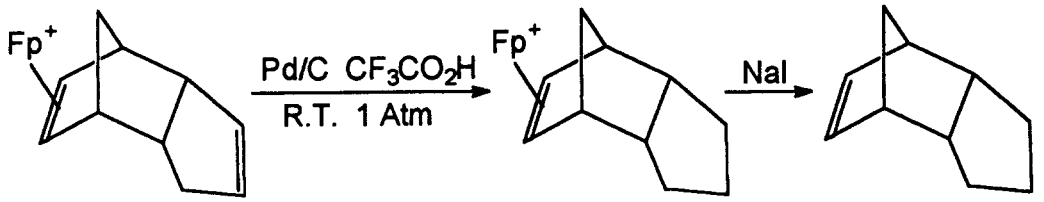


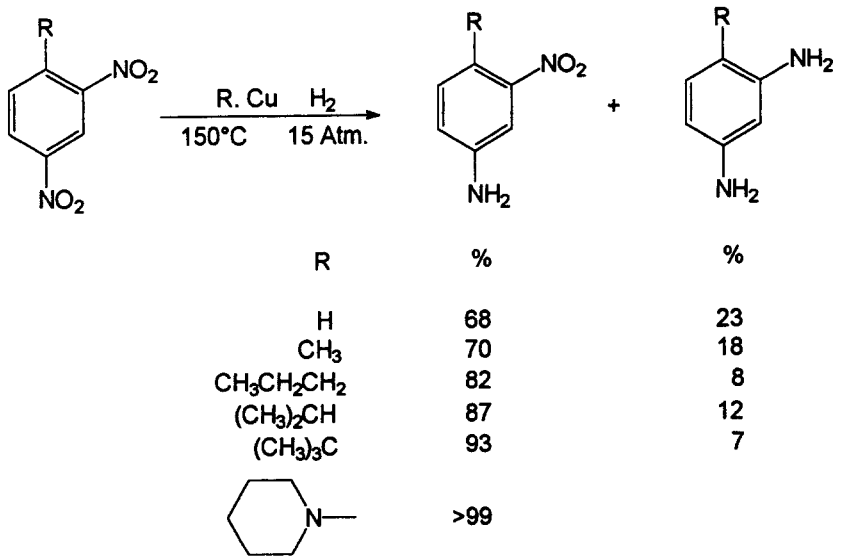
(14)

The importance of these steric factors can be illustrated by comparing the extent of the selective hydrogenation of the 4-nitro group in a series of 2, 4-dinitro-1-substituted benzenes as shown in Fig. 2 [54]. As the 1-substituent increases in size, the selectivity toward 4-nitro group saturation increases.

It is also sometimes possible to take advantage of different reactivities of apparently similar functional groups. For instance, alkyl aldehydes and ketones are not hydrogenated over a palladium catalyst but aryl carbonyl groups are converted to the methylene over such catalysts. Thus, it is possible to selectively remove an aryl ketone or aldehyde in the presence of an aliphatic ketone or aldehyde by hydrogenation over palladium (Eq. (15)) [55].

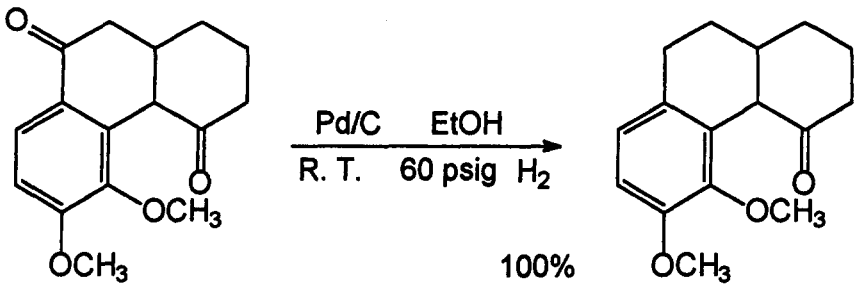
5. Stereoselectivity

The predominant formation of *cis* 1,4-disubstituted cyclohexanes in the hydrogenation of 1,4-disubstituted cyclohexenes is an example of a stereoselective reaction. Product stereochemistry in such reactions is usually predicted by estimating the relative hindrance to adsorption on the catalyst from the two faces of the



R	%	%
H	68	23
CH_3	70	18
$CH_3CH_2CH_2$	82	8
$(CH_3)_2CH$	87	12
$(CH_3)_3C$	93	7
	>99	

Fig. 2. Steric effects in the selective hydrogenation of 1-substituted-2,4-dinitrobenzenes.



(15)

double bond as depicted in Fig. 3. Adsorption and hydrogen transfer from the side A gives the *trans* product. The *cis* isomer is formed by adsorption and hydrogenation from side B. Since alkene hydrogenations have been shown to occur on the more coordinately unsaturated corner atoms and adatoms [56,57], a better estimate can be obtained on consideration of the modes of double bond adsorption on such surface atoms as pictured in Fig. 4.

The preferred direction of adsorption can also be influenced by the presence of a non-reactive functional group on the molecule. Such an influence is referred to as a haptophillic effect [58–60]. Most reactions of this type involve the interaction between a hydroxy group and the catalyst surface to fix the direction of adsorption of an alkene. Over nickel catalysts, adsorption of the double bond takes place on the side of the alkene that is *cis* to the alcohol group. When the double bond is substituted, hydrogen transfer from the catalyst gives the *trans* product as shown in Eq. (16)[61].

This effect is most pronounced with axial or pseudoaxial allylic and homoallylic secondary alcohols. The steric environment around a tertiary alcohol, even one that is axial, can minimize its interaction with the catalyst. Equatorial alcohols apparently do not easily adsorb on the catalyst, or if they do, this adsorption has little, if any, effect on product stereochemistry. Raney

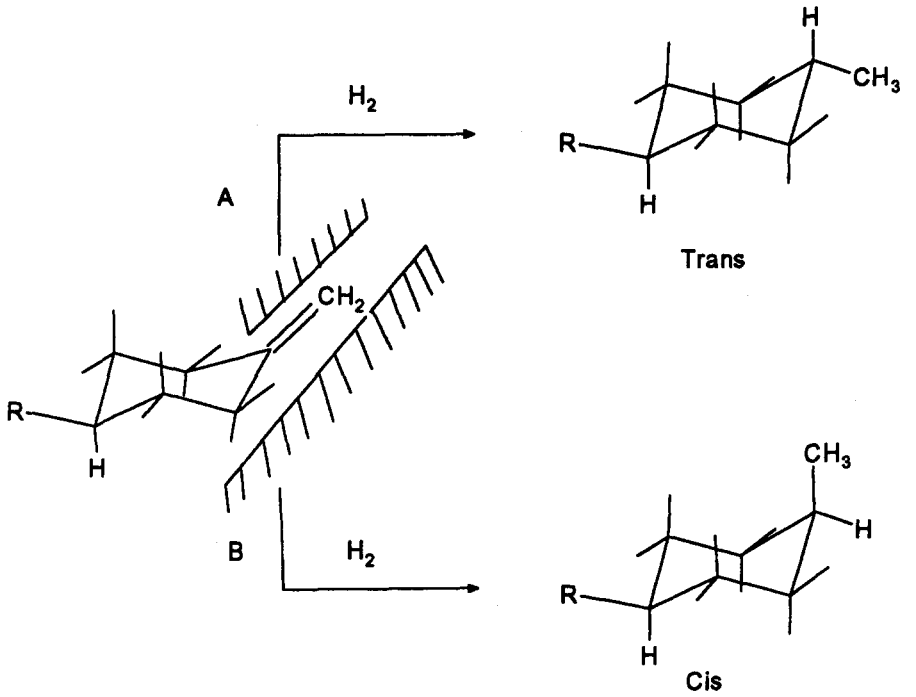
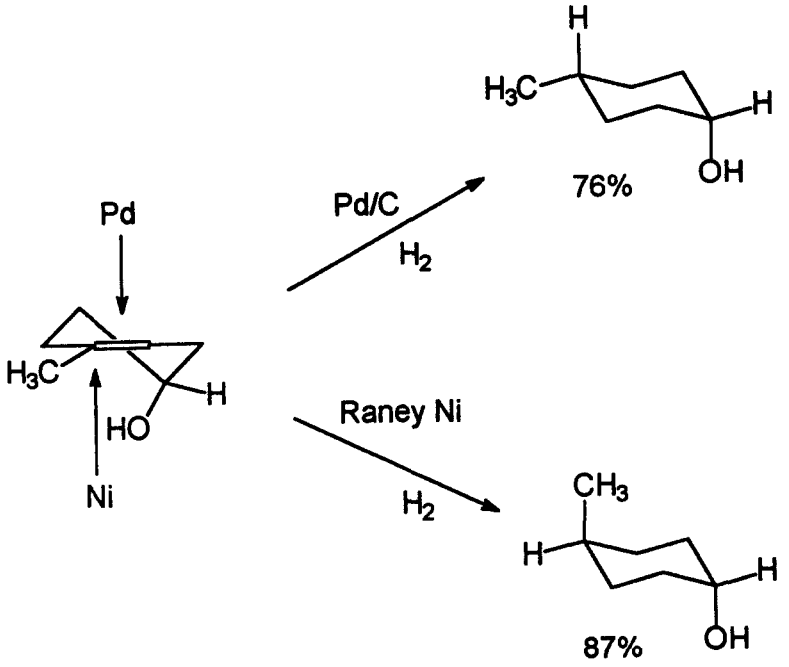
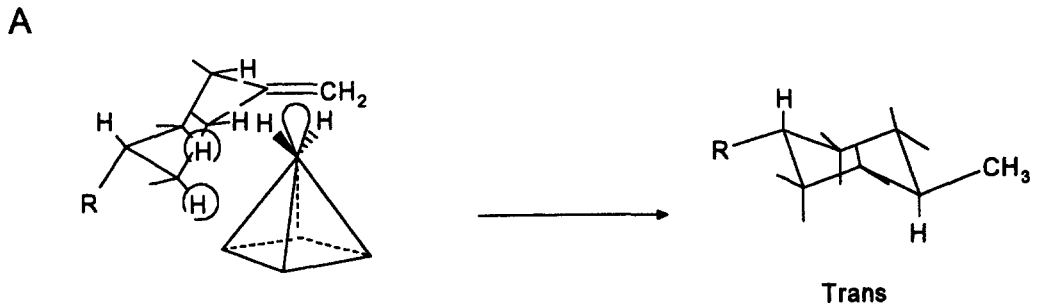


Fig. 3. Modes of 4-alkyl-methylenecyclohexane adsorption leading to *trans* and *cis* product formation.



(16)



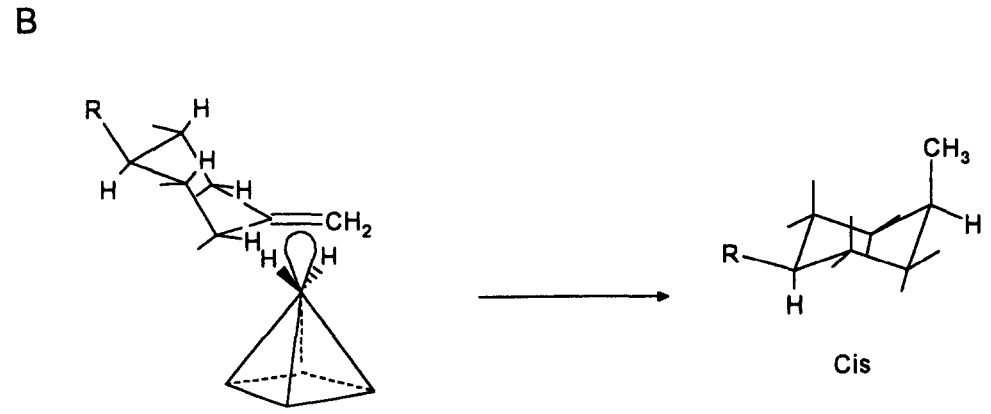


Fig. 4. Modes of adsorption of 4-alkyl-methylenecyclohexane on corner or adatom active sites.

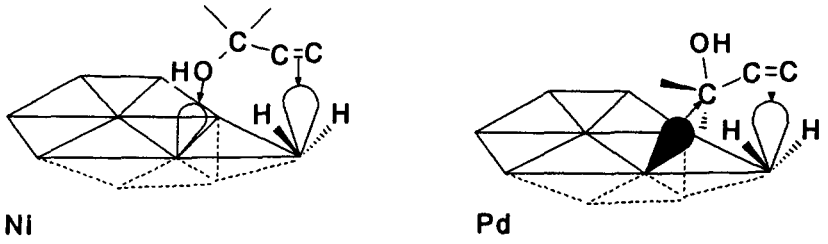


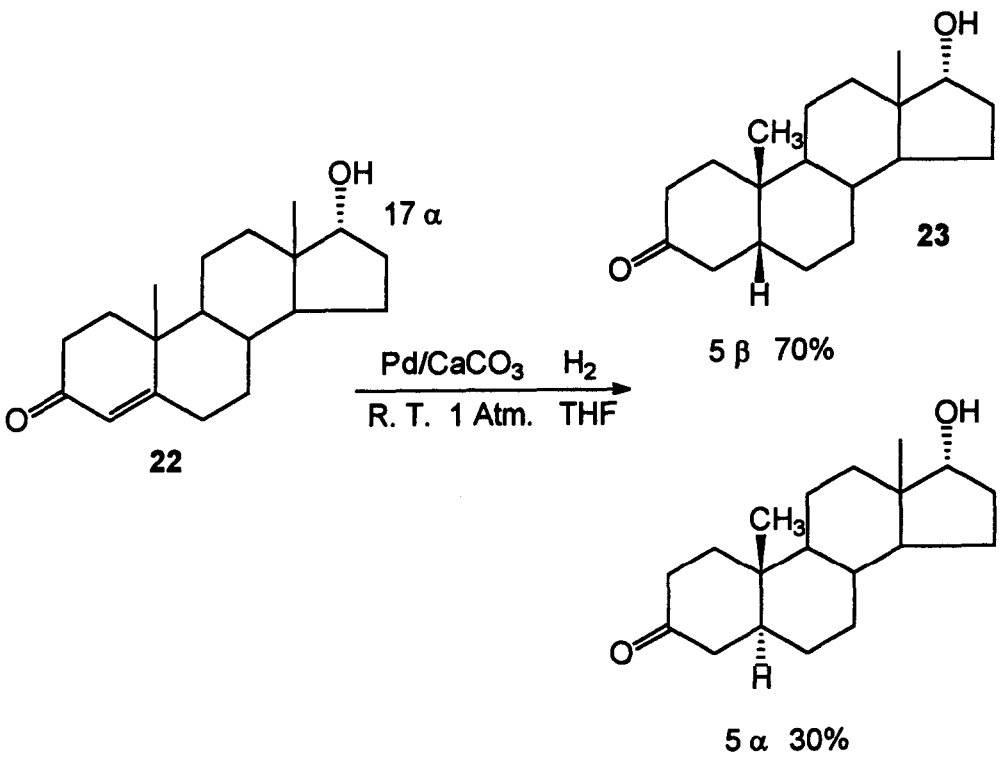
Fig. 5. Proposed adsorption modes for unsaturated alcohols on nickel and palladium catalysts.

nickel is more effective in these reactions than are supported nickel catalysts [61].

The presence of a hydroxy group can also influence the direction of alkene hydrogenation over palladium catalysts but in these reactions the effect is opposite to that observed with nickel. As depicted in Eq. (16), hydrogenation over palladium gave the *cis* product while the *trans* product was formed with a nickel catalyst. It appears that while the electron pairs on the hydroxy oxygen are involved in the adsorption on nickel, on palladium the adsorption takes place through the carbinol carbon as pictured in Fig. 5. This "palladium hydroxy group effect" [11] has had a pronounced effect in determining the stereochemistry of the hydrogenation of many steroidal double bonds. As an example, the hydrogenation of a Δ^4-3-ketosteroid such as **19** in neutral media over a palladium catalyst gave a mixture of the 5α-(**20**) and 5β-(**21**)products (Fig. 6). However, hydrogenation of the 17α-hydroxy steroid, **22**, took place predominantly from the top or β side of the molecule to give primarily the 5β product, **23** (Eq. (17)) [62].

The 5α-product, **25**, was obtained from the 17β hydroxy steroid, **24** (Eq. (18)) [62].

The nature of the reaction medium can play an important role in the stereoselective hydrogenation of



(17)

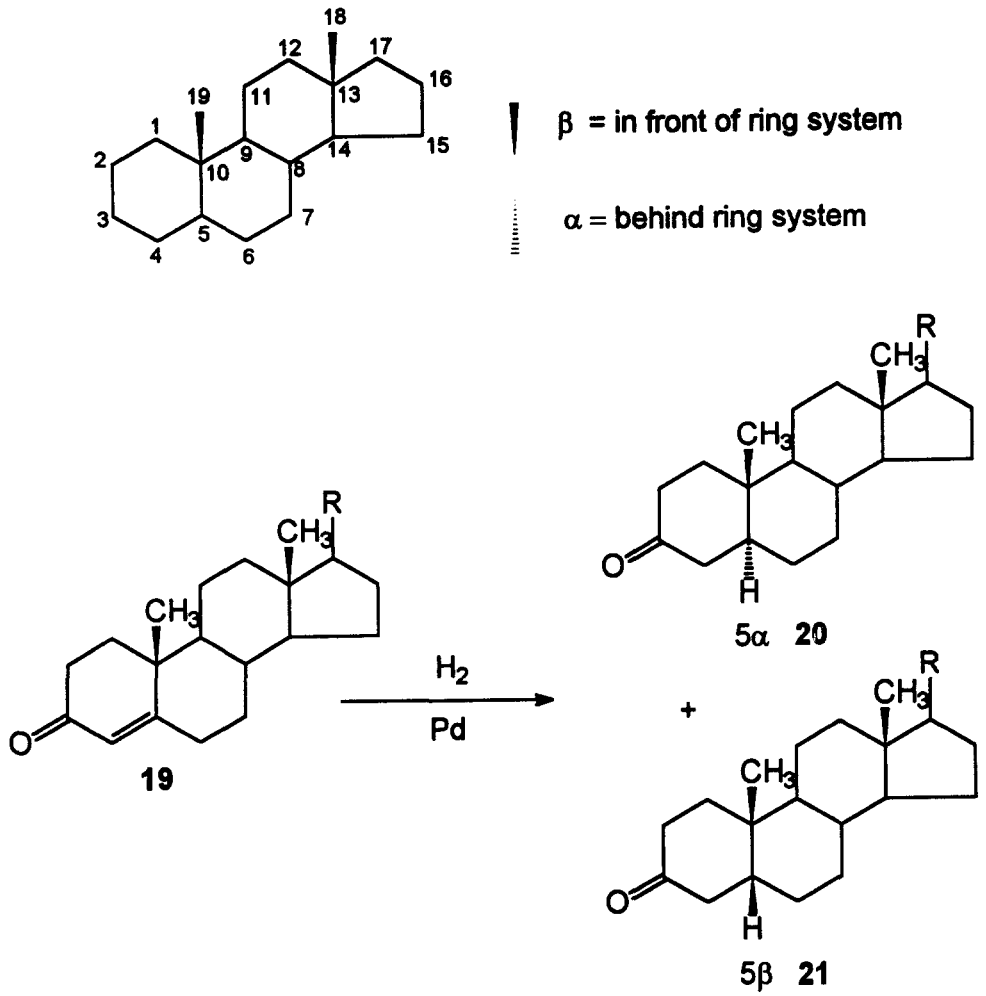


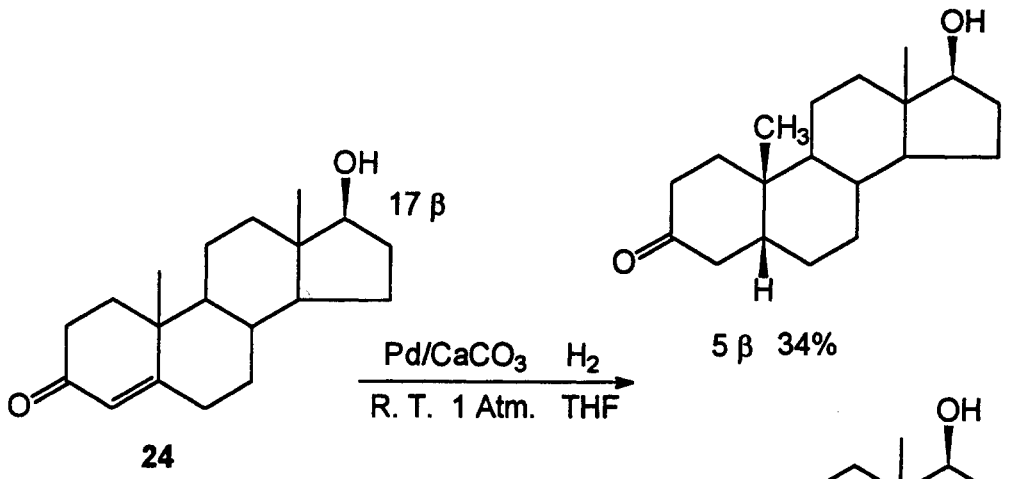
Fig. 6. Steroid numbering and stereochemical conventions. Hydrogenation of Δ^4-3-ketosteriods.

polar functional groups such as ketones. Hydrogenation of a cyclic ketone, such as a 3-keto-steroid, **26**, gives the axial alcohol, **27**, [63] in acidic medium and the equatorial alcohol, **28**, in a basic solvent [64]. If an alcoholic acid is used as the solvent, good yields of the ether, **29**, can be obtained (Eq. (19)) [65,66].

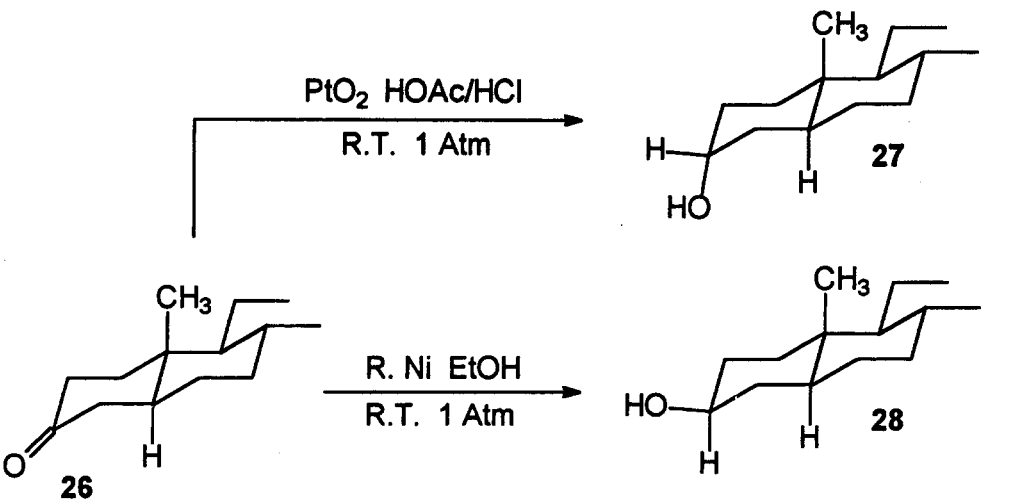
6. Diastereoselectivity

When a chiral center is present in the substrate molecule it can sometimes influence the direction from which the hydrogen is transferred to a reactive functional group, a process which leads to the formation of one diastereomer in excess of the other. The ease of determining the direction of hydrogenation in such molecules depends on the nature of the substrate. For cyclic systems, the steric factors are usually readily discernible. Alicyclic molecules, however, are more conformationally flexible so estimating the direction of attack is generally more difficult. Obviously, the closer the chiral center is to the reactive group, the more influence it will have on the direction of attack.

The preferred conformation of ketones having a chiral center adjacent to the carbonyl group is the one in which the large group on the chiral carbon lies in the same plane as the carbonyl group but is *trans* to the oxygen atom as depicted in Fig. 7a [67]. The relative ease of adsorption of the carbonyl group onto the


OH
17 β
O
24
Pd/CaCO3 H2
R. T. 1 Atm. THF
OH
CH3
O
H
5 β 34%
OH
CH3
O
H
25
5 α 66%

(18)


PtO2 HOAc/HCl
R.T. 1 Atm
CH3
H
HO
27
CH3
O
H
26
R. Ni EtOH
R.T. 1 Atm
CH3
HO
H
28
PtO2 MeOH/HCl
R.T. 1 Atm
CH3
H3CO
H
29

(19)

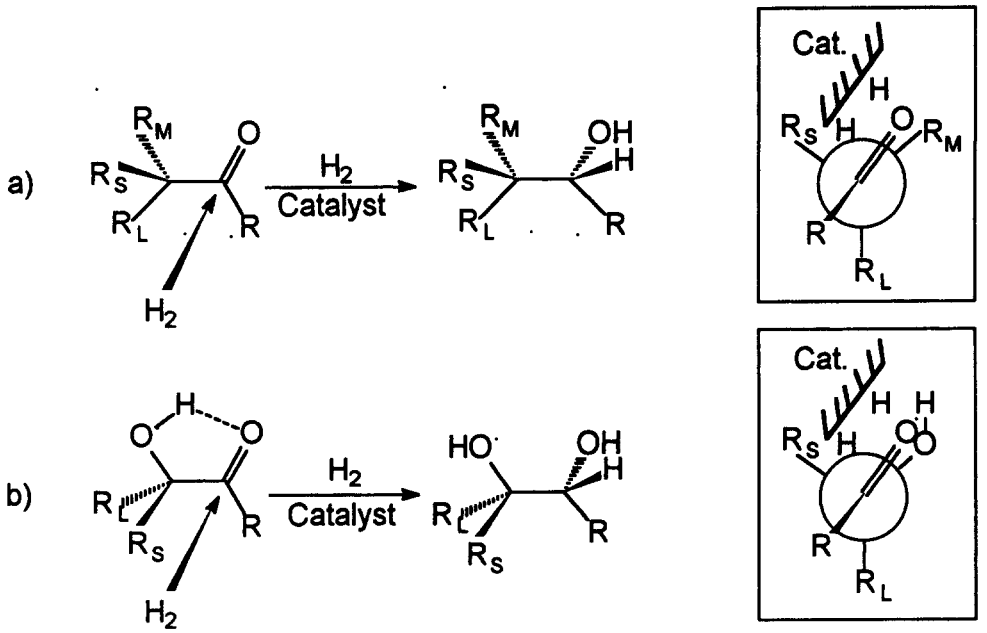
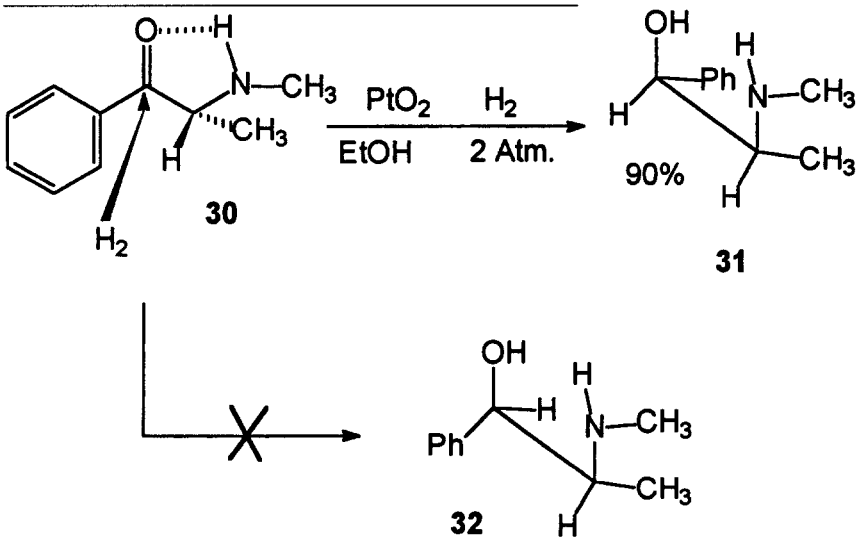


Fig. 7. (a) Preferred conformation of ketones having a chiral center adjacent to the carbonyl group. (b) Preferred conformation of ketones having a chiral center containing a group capable of hydrogen bonding with the adjacent carbonyl group. Inserts show the perspective view of the adsorption of the carbonyl group onto the catalyst.

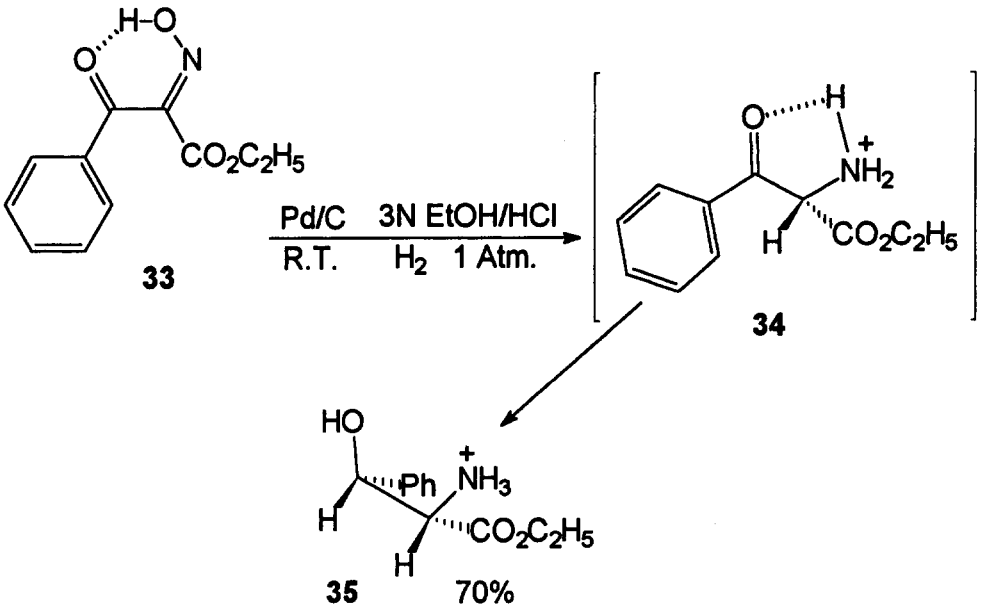
catalyst will then depend on the relative sizes of the two remaining groups on the chiral carbon. Preferred attack is from the side of the smaller group which is shown in perspective in the insert of Fig. 7a. When one of the substituents on the chiral carbon is a hydroxy or amino group which can form a hydrogen bond with the carbonyl oxygen, the conformation is more rigid, and, as depicted in Fig. 7b, preferential attack occurs from the side of the smaller of the remaining groups on the chiral carbon. Again, the direction of carbonyl group adsorption on the catalyst is shown in perspective in the insert.

Ephedrine, **31**, was formed in 90% yield on hydrogenation of the amino ketone, **30** (Eq. (20)) [68].



(20)

None of the *threo* diastereomer, **32**, was formed. Hydrogenation of the oximino ketone, **33**, gave only the *erythro* amino alcohol, **35** (Eq. (21)) [69].



(21)

Evidently the oxime was hydrogenated to the amine, **34**, which then directed the addition of hydrogen to the carbonyl group.

Optically active alcohols have been used as chiral auxiliaries in the hydrogenation of substituted esters. The preferred conformation of an α-keto ester of a chiral alcohol is shown in Fig. 8 [70,71]. Here, too, the preferred attack is from the side of the smallest group on the chiral carbon. A similar approach has been used

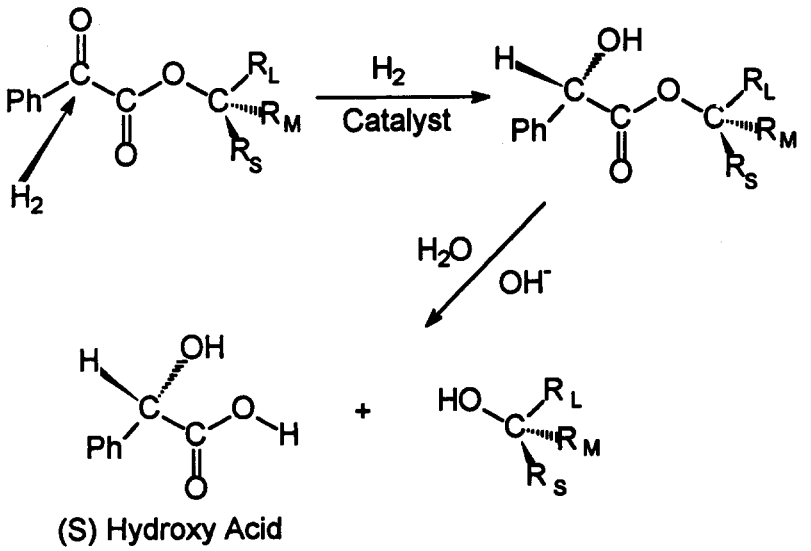
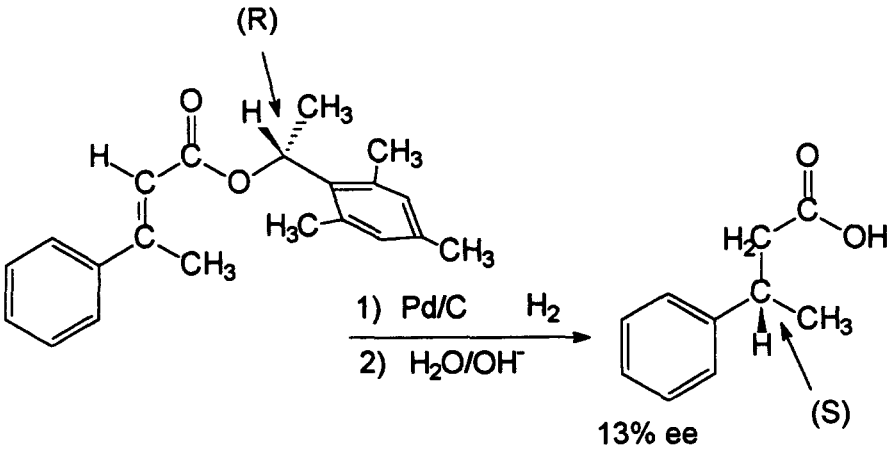
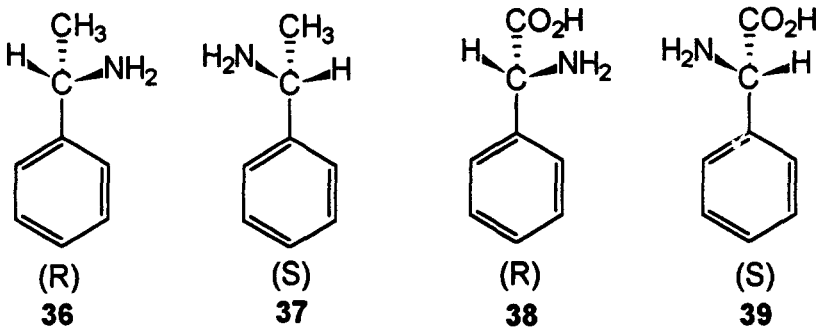


Fig. 8. Preferred conformation of α keto esters of chiral alcohols.

in the hydrogenation of α oximino esters [72] and α,β-unsaturated esters (Eq. (22)) [73].



(22)



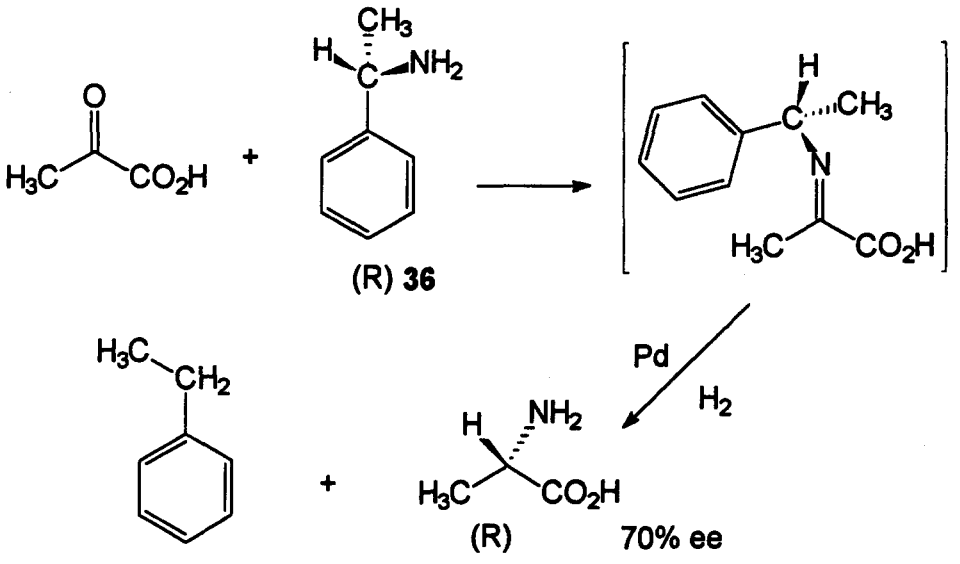
Because of the distance between the chiral center and the active group as well as the conformational flexibility of these systems, the enantiomeric excesses in these reactions range only from about 15% to 65% [74].

The optically active benzyl amines, **36–39**, have been used as chiral auxiliaries for the conversion of α keto acids to α amino acids with fairly good product ee's [75–80]. Here, not only are the amines chiral but also benzilic so hydrogenolysis of the benzyl group can take place after the saturation of the intermediate imine (Eq. (23)) [75].

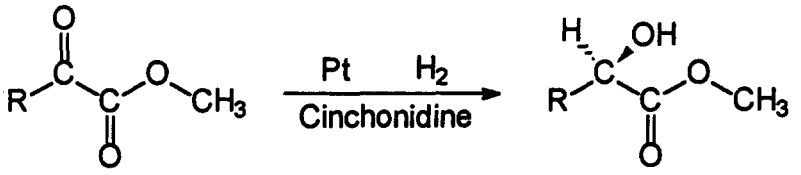
7. Enantioselectivity

In the reactions described above, the chiral directing group was a part of the reacting substrate. When a chiral auxiliary is used and subsequently removed, an enantiomeric product is obtained and reactions of this type are sometimes considered to be enantioselective. But a more direct approach to the enantioselective hydrogenation of a prochiral group involves the use of a chiral catalyst for the reaction [81]. At present, most of these reactions are run using chiral homogeneous catalysts but the earliest examples of enantioselective hydrogenations involved a metal catalyst on a chiral support such as quartz [82] or silk fibroin [83]. Another approach has been to absorb a chiral modifier onto the catalyst surface. The former concept has not been very successful but the use of chiral modifiers has been effective for some hydrogenations. Two of these systems give products with high ee's, but they appear to be very substrate specific.

Platinum catalysts which have been modified with a cinchona alkaloid are effective enantioselective catalysts for the hydrogenation of α keto esters with ee's as high as 95% (Eq. (24)) [84,85].

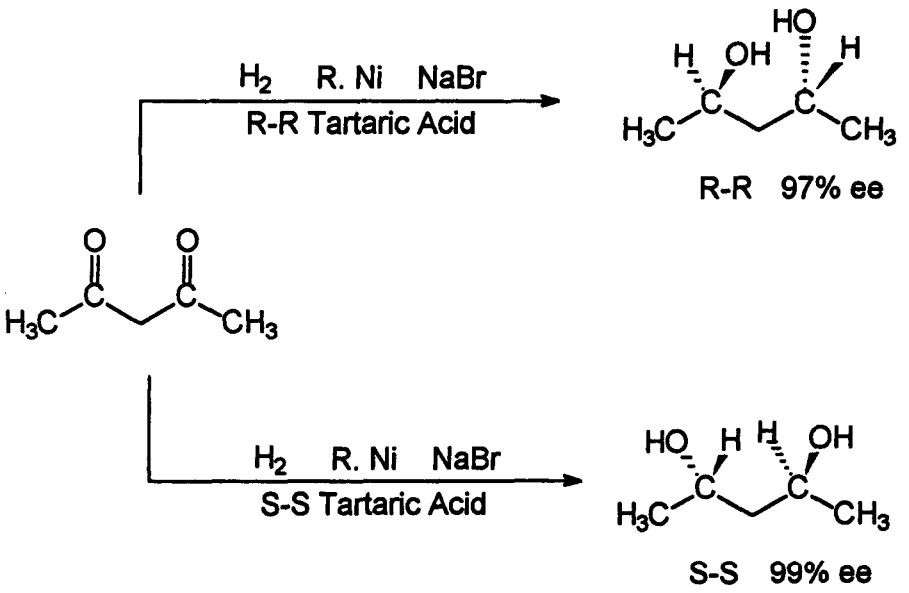


(23)



(24)

The hydrogenation of β keto esters or β diketones over tartaric acid modified nickel catalysts gives the chiral β hydroxy esters with similarly high ee's (Eq. (25)) [86].



(25)

The cinchona alkaloid modified platinum catalyzed reactions are discussed by Blaser [87] and hydrogenations run over tartaric acid modified nickel are covered by Osawa [88] in later chapters.

8. Conclusions

Heterogeneously catalyzed selective hydrogenations are effective reactions for the preparation of a number of synthetically useful compounds. At present most interest lies in the development of diastereoselective and enantioselective heterogeneous catalytic systems but, other reactions such as the selective hydrogenation of unsaturated acids and esters to unsaturated alcohols are also important, particularly if the reaction can be run without isomerization of the double bond. Other areas of interest are the partial hydrogenation of entities such as aliphatic nitro groups, nitriles, carboxylic acids and esters. The data presented here have illustrated a few of the successful approaches to these problems and, hopefully, will provide an incentive for further research in this area.

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