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Transition Metal Catalysis on Olefins: Some Considerations Relative to Migratory Insertion

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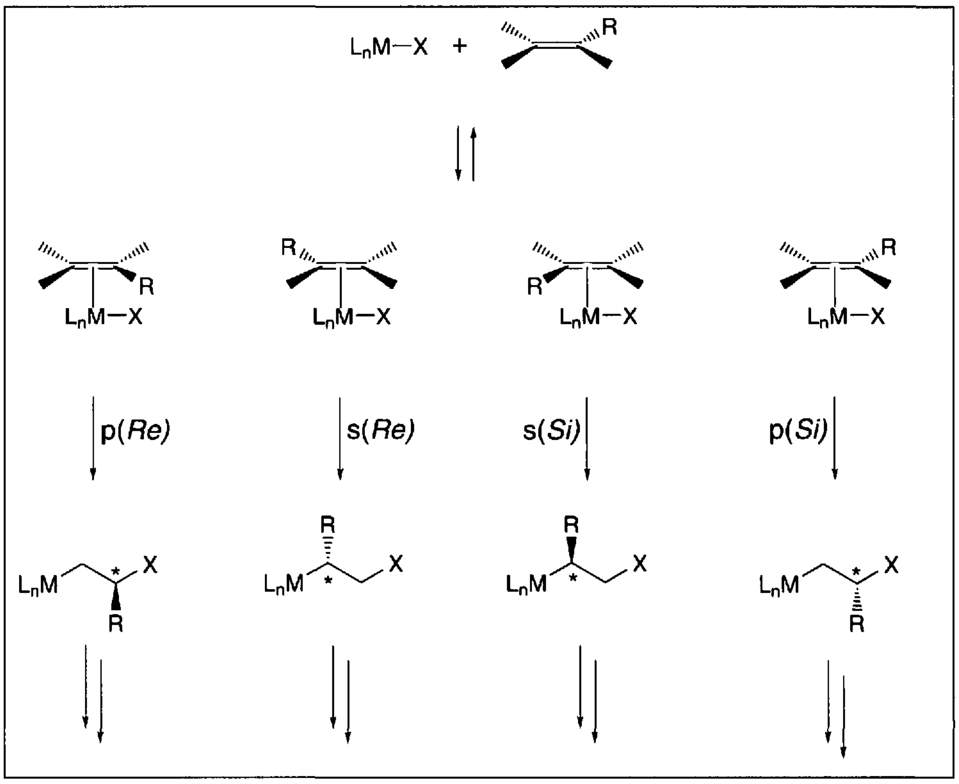
Abstract: Olefin migratory insertion into a metal–hydrogen or a metal–carbon bond is an ubiquitous step in olefin coordination catalysis by transition metal complexes. When the catalytic system has element(s) of chirality, and when the two carbon atoms of the substrate are not symmetry-related, the nature of the reaction products will be determined by the capacity of the catalytic system for enantioface selection and by the direction of the insertion. Despite some progress having been made, good control of this important catalytic step is far from being realized. Considerations concerning this step are presented with particular reference to the work of the author in the field of hydrocarbonylation and olefin (co)polymerization reactions.

Keywords: Carbonylation · Migratory insertion · Olefins · Polymerization · Transition metal catalysis

Introduction

Olefins are the most important starting materials for modern industrial organic chemistry; they are used as the substrate in very important catalytic reactions, in which the addition of groups to the unsaturated double bond take place (*e.g.* polymerization, carbonylation, hydrogenation, *etc.*). When the two carbon atoms of the substrate are not symmetry-related, the problem of control of the regio-chemistry and the stereochemistry arises, depending on the groups added to the double bond. In general, for transition metal catalyzed reactions, coordination of the olefinic substrate on the metal complex catalyst precedes migratory insertion (Scheme 1) [1]. When the rate of the successive transformation is rapid, the nature of the reaction products will reflect the relative composition of the intermediates formed after migratory insertion.

To rationalize the results of catalytic and stoichiometric reactions involving transition metal complexes and olefins as related to the direction of insertion, an empirical rule was proposed [2]: Assuming a rearrangement of the olefin complex toward a four-center transition state prior to insertion, it was proposed that the direction of the insertion is determined by the electronic structure of the reaction partners (Scheme 2), particularly for strongly polarized double bonds. Weakly polarized double bonds react similarly; however, group VIII transition metal spe-



Scheme 1. Stereo- and regiochemical pathways for olefin migratory insertion (X=H, R, COR, COOR *etc.*; p=primary, s=secondary; the descriptors apply to propene)

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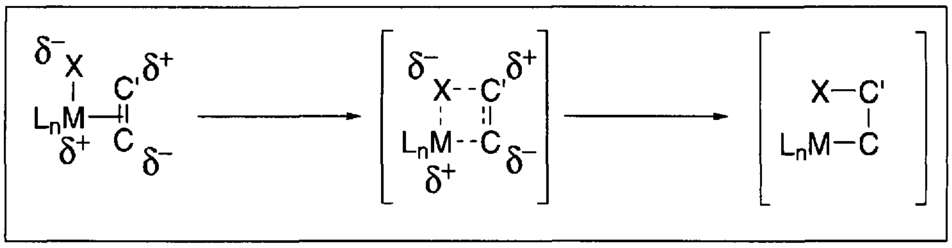
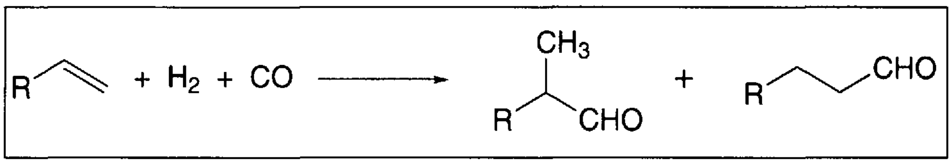
cies show a remarkable tendency to the reverse mode of insertion, steric effects being responsible for the hindering of the expected regioselectivity of the insertion step.

On the other hand, a change in the direction of the insertion implies a change in the preferred enantioface when a model of enantioface selection, based on the minimization of steric repulsion (Fig. 1) is used [3], as is the usual case [4]. Within an olefin complex, a change in the direction requires a simple rotation of the olefin around the bond between the metal and the double bond, and this does not necessarily imply olefin dissociation. In contrast, dissociation of the olefin was considered to be a prerequisite for a change in the enantioface. However, an alternative mechanism was discovered [5].



Scheme 2. Regiochemistry of the migratory insertion of an olefin controlled by polarization (X=H, R, COR, COOR *etc.*)



Scheme 3. Hydroformylation of a 1-olefin

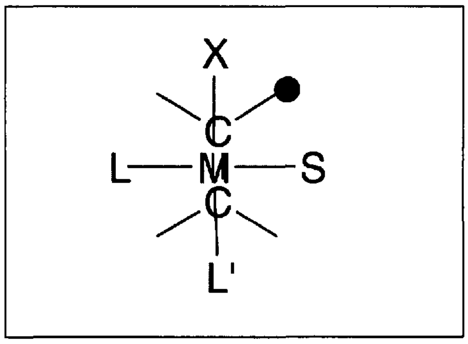


Fig. 1. Model for the analysis of the preferred enantioface for olefin migratory insertion in the M–X bond (L and S are ligands with large and small steric hindrance, respectively).

In the following discussion a distinction will be made between insertion into a metal-hydrogen and insertion into a metal-carbon bond, since for the first type of insertion reversibility through a β-hydrogen elimination step is common, as it has been shown in many cases. In contrast, β-carbon elimination occurs only rarely.

Hydrocarbonylation Reactions: Insertion into a M–H Bond

The most important and extensively investigated hydrocarbonylation reaction is hydroformylation (Scheme 3) catalyzed by complexes of cobalt, rhodium or platinum compounds. After the 63 years since its discovery, the issue of regiochemistry has not yet been resolved. Starting with aliphatic 1-olefins, the reaction can be can be carried out essentially regiospecifically toward the linear aldehyde. No system is known to achieve regioselectivity better than about 50% for the alternative branched isomer.

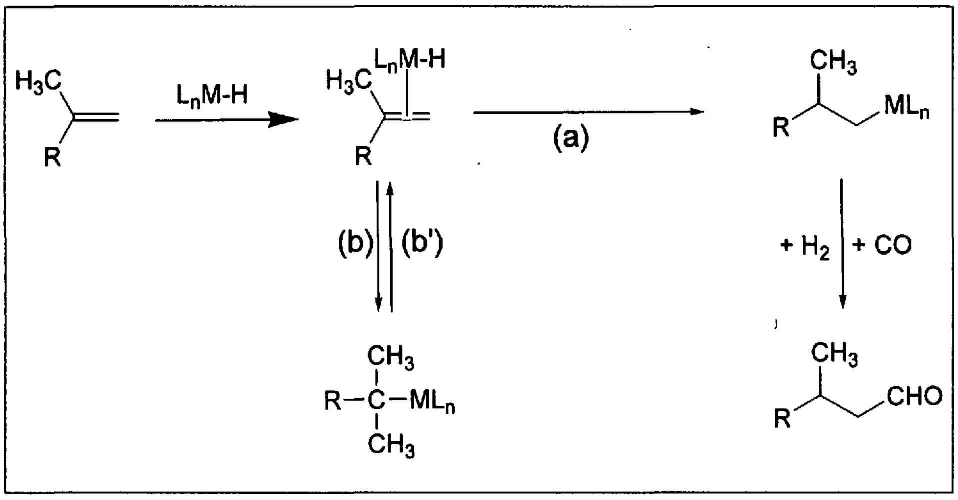
The reaction is stereospecific with rhodium and platinum catalysts modified with phosphine and diphosphine ligands [6]. Therefore, after formation of the alkyl intermediates, rapid carbon monoxide insertion into the metal-carbyl bond (Scheme 1) takes place, causing irreversible olefin migratory insertion, at least under some reaction conditions. An important aspect of this reaction is related to the possible reversibility of the olefin coordination step, particularly when enantioselective hydroformylation is carried out. In more general terms: does enantioface selection influence the regioselectivity in a catalytic process?

Enantioselectivity in hydroformylation is still unsatisfactory. The best chiral ligands developed so far for the rhodium-catalyzed reaction are (*R*,*S*)-Binaphos ((*R*)-2-(diphenylphosphino)-1,1'-binaphthalene-2'-yl-{(*S*)-1,1'-binaphthalene-2,2'-diyl}phosphite) and related systems [7]. The corresponding catalysts give good enantioselectivity for various substrates including 1-butene. The regioselectivity toward the chiral reaction product remains low. A model for the olefin migratory insertion, such as that shown in Fig. 1 [3], enabled the prediction of the results of enantioface discrimination [8] for various substrates. Therefore, a similar mechanistic evolution independent of the structure of the substrate may be assumed. Consistently, a semiquantitative theoretical model, which was later applied to the Binaphos-catalyst, gave a better definition of the catalytic species involved (*i.e.* of the chemical nature of the ligands L, L' and S) [9]; the model assumed, even if not explicitly, rapid olefin dissociation [10].

Olefin dissociation is quite slow during the catalysis of cobalt hydroformylation; in contrast to rhodium catalysts, β-hydrogen elimination after formation of the alkyl intermediate can be rapid. Therefore, despite the *syn*-addition of the cobalt and hydrogen to the double bond and the insertion of CO, which occurs with retention of the configuration, the stereochemistry of the reaction is usually not recognized [11]. Labeling studies have shown that for these catalysts, the regiochemistry of the final product may be opposite to that which occurs during olefin migratory insertion. Both cobalt and rhodium carbonyls give almost exclusively the product corresponding to formylation at the 1-position when 2,3,3-trimethyl-1-butene or 2,3-dimethyl-1-pentene are used as the substrate (Scheme 4) [12].

However, this product is formed through pathway (a) for rhodium and prevailingly through pathway (b-b'-a) for cobalt. It is noteworthy that the same low diastereoselectivity (~20%) is observed for 2,3-dimethyl-1-pentene with the two catalytic systems. Whereas the lack of carbon monoxide insertion after step (b) is understandable on the basis of steric considerations, the reason for the opposite regioselectivity exhibited by the two catalytic systems is not clear. Similarly, for 1,1-diphenylethene, rhodium carbonyls give preferential formation of the tertiary hydrocarbyl derivative, which does not undergo carbon monoxide insertion [13].

Rhodium catalysts modified with diphosphine, particularly those with C_2-symmetry, have been largely used in hydroformylation [14][10]. Diphosphines having natural bite angles close to 120°



Scheme 4. Hydroformylation of 2,3,3-trimethyl-1-butene and 2,3,-dimethyl-1-pentene with rhodium and cobalt carbonyls

favor the equatorial–equatorial coordination (see Fig. 2) [15][16], and cause preferential formation of the linear aldehyde for aliphatic olefins. However, the investigation of a series of 2,8-dimethyl-4,6-bis(diarylphosphino)phenoxathiin-ligands in which the diphosphine basicity was varied to maintain a similar steric environment [17], showed no influence on the regioselectivity of the hydroformylation of 1-octene; the ratio between the two metal complex isomers (ee/ea, Fig. 2) instead changed with these ligands from 1/1 to more than 9/1. Even if model calculations do improve the level of confidence with respect to regio-and enantioselectivity [10], it is clear that the small energy differences involved render the proposal of better ligands based on theory a very difficult task.

The problem is even more complicated for aromatic substrates such as styrene. The secondary regioselectivity of the insertion contrast, that observed for aliphatic 1-olefins; an allyl-type stabilization (electronic factors prevailing) of the benzylic intermediate is assumed to play an important role [16]. However, the transition state for insertion should be of early nature [16]; due to the same direction of double-bond polarization for styrene and propene [2], the same prevailing regioisomer is, therefore, expected. In the related synthesis of esters through the hydro-carboalkoxylation reaction using palladium catalysts, it is possible to completely switch the regioselectivity of the insertion of styrene using either monophosphine or diphosphine as the modifier. The effect of the same ligands on the regioselectivity in the reaction of aliphatic olefins is similar but far weaker [18].

Polymerization Reactions: Insertion into a M–C Bond

Olefin insertion into a metal-to-carbon bond represents the growing step in all oligomerization and polymerization and is also common to various synthetically interesting reactions, such as the Heck-type reaction [19].

According to the rule mentioned in the introduction [2], the diastereoselective isotactic polymerization of propene by titanium-containing Ziegler-Natta catalysts takes place by the primary insertion of consecutive *lk*-enantiofaces. However, the analogous diastereoselective syndiotactic polymerization by vanadium systems, for which the same polarization of the catalytic species is expected, takes place by secondary insertion of *ul*-enantiofaces [20]. Does enantioface discrimination influence regiochemistry or *vice versa*?

In the last few years there has been growing interest in the use of VIII group metals for the production of olefin homo- and co-polymers [21]. We have focused on the copolymerization of olefins with carbon monoxide (Scheme 5, (b)), particularly with the aim of accessing all the possible regular and irregular microstructures from the point of view of regio- and stereocontrol [22]. A comparison of these catalysts with those based on early metals would be interesting.

Palladium catalytic systems modified with various C_2- and C_1-symmetric diphosphine ligands can produce regioregular, isotactic optically pure copolymers of aliphatic olefins, *e.g.* propene, by enantiomorphic site control [23][24]. Achiral diphosphine ligands (*e.g.* 1,3-diphenylphosphinopropane) usually give regio- and stereoirregular copolymers [25]. Recently, however, achiral diphosphine ligands were identified that produce isotactic copolymers with high regio- and stereoregularity, probably by chain-end control (Scheme 5, catalyst 1) [26]. Electronic modification of the ligands (Scheme 5, catalysts 2 and 3) enabled a switch in the regiochemistry of the olefin insertion, as determined from the ratio of the two 2-oxoglutarates produced with the same catalytic systems under slightly different reaction conditions (Scheme 5, (a)). Nevertheless, the two systems again gave the same isotactic copolymer. Thus, in contrast to the above-mentioned classical Ziegler-Natta catalysts, the regiochemistry of the olefin insertion does not influence the stereochemistry of the produced polymer. Steric modification of the ligands to produce

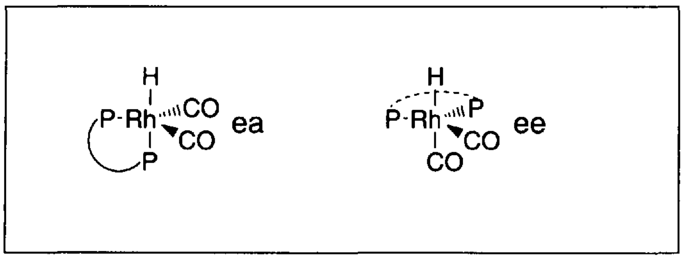
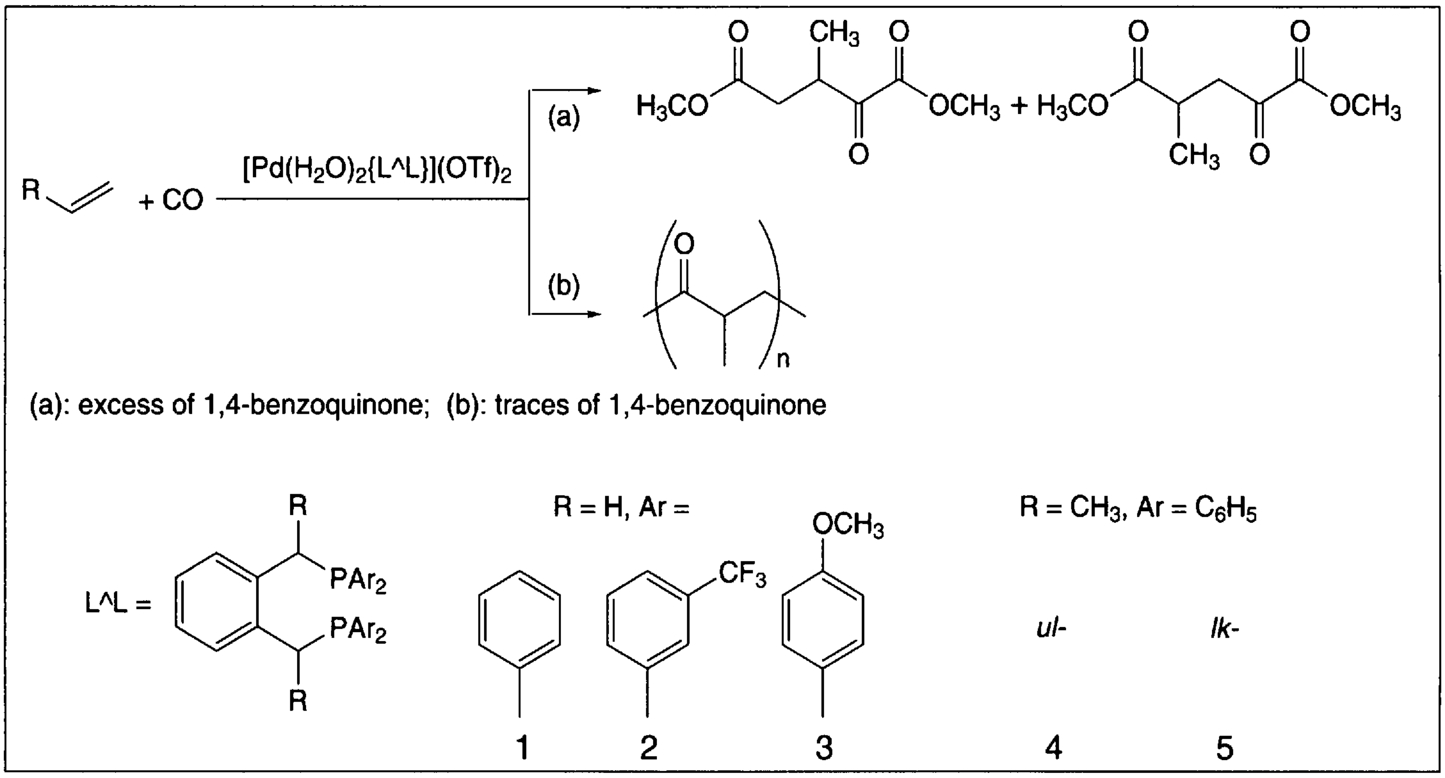


Fig. 2. Isomeric diphosphine-rhodium catalyst precursors for hydroformylation



(a): excess of 1,4-benzoquinone; (b): traces of 1,4-benzoquinone

Scheme 5. Oligo- and copolymerization of propene with carbon monoxide

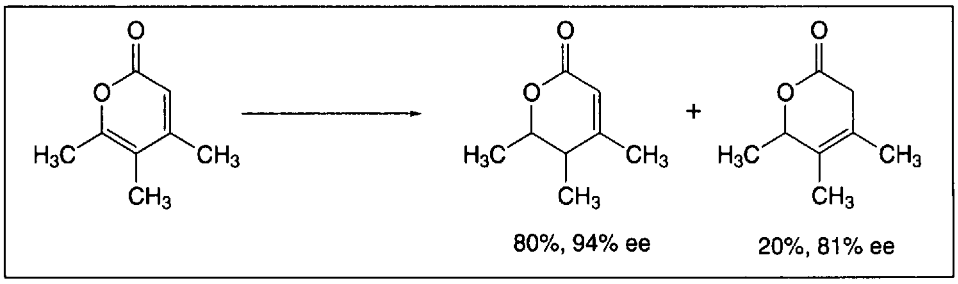
C_2- and C_s-symmetric catalysts (Schemes 3–5), brought about again no change in the microstructure of the copolymers (always isotactic), in contrast to the metallocene catalysts for polypropene that have the same symmetry [27]. The very large difference in catalytic activity of these diastereomeric systems for propene (activity ratio 1/84) but not for ethene (activity ratio ~1/2) indicates the importance of enantioface selection for efficient olefin insertion [28].

The copolymerization of styrene with carbon monoxide posed a different problem: due to the regiospecific secondary insertion of this olefin, regioirregular copolymers seemed inaccessible [29]. Catalytic systems $[Pd(H_2O)_2\{L^\wedge L\}](OTf)_2$ having C_{2v}-symmetry (L^L is *e.g.* 1,10-phenanthroline) produce a syndiotactic regioregular copolymer. C_2-systems (L^L is *e.g.* 2,2'-propanediylbis(4,5-dihydro-4-(1-methylethyl)-2-oxazole)) give isotactic regioregular copolymers, as do the C_1-systems (L^L phosphino(dihydroxazole)). Analogous phosphino(dihydroxazole) systems with C_s-symmetry produce atactic but still regioregular copolymers. Modification of the phosphine moiety (different aryl substituents) of the phosphino(dihydroxazole)-ligands enabled us to modify, at least partially, the regiochemistry of the insertion to produce regioirregular copolymers. However, the change is probably caused by steric factors, as proposed for the codimerization reaction of propene with nickel-based catalytic systems [2]. A primary regioselectivity of the insertion of styrene was recently observed with a cationic palladium complex modified by the afore-mentioned (*R*,*S*)-Binaphos ligand. This is the only system containing a chelating phosphorus ligand able to produce alternating styrene-carbon monoxide copolymers [30].

Conclusions

The regiochemistry of the olefin migratory insertion step is very important, even in the cases in which, as for hydrogenation, the two groups eventually added to the double bond are equal. Depending on the regioselectivity of the insertion, some consecutive reactions may occur and influence the chemoselectivity of the process. In the enantioselective reduction of 2-pyrones (Scheme 6), the partial formation of the isomeric 3,6-dihydro-derivative is assumed to be a consequence of an insertion with a regiochemistry such to enable for the formation of an allyl intermediate [31].

The regiochemical aspect is also significant for heterogeneous catalysts, not only for the hydrogenation of double and triple bonds [32], but also of aromatic substrates. When *ortho*-disubstituted substrates are used, together with the com-



Scheme 6. Chemoselectivity in the enantioselective hydrogenation of pyrones

pletely reduced cyclohexane derivatives, a tetrahydro-product is usually formed, which is not an intermediate for the complete reduction (Scheme 7) [33]. The formation of this product might arise from the different regioselectivity of the attack.

The above discussion shows that we are still lacking a good theory which takes into account small energy differences to explain (and to force) regiochemistry during transition metal addition catalysis to olefinic substrates. Enantioface discrimination appears to be easier to steer. As a consequence, more experiments are needed in the hope to reach a better control of the direction of the olefin migratory insertion; this will also result in a better understanding of the mechanism of this important step. Such information will help us to develop a better and more useful theoretical interpretation to design new and more efficient catalysts.

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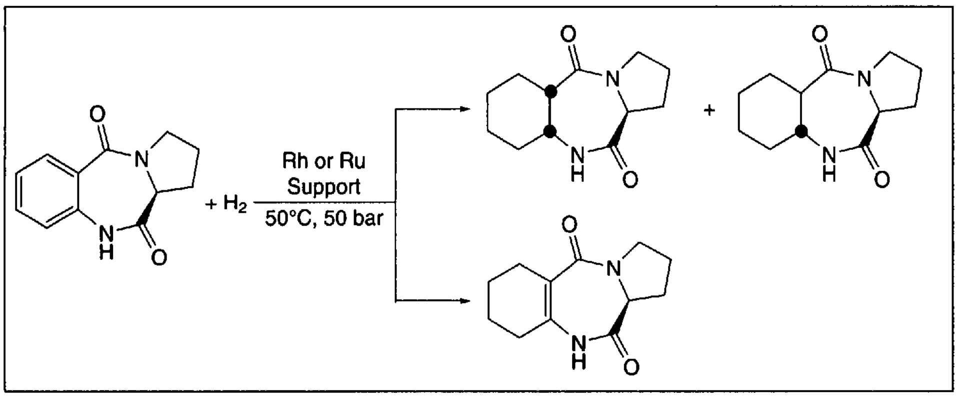

Scheme 7. Chemoselectivity in the diastereoselective hydrogenation of disubstituted aromatics

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