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Various aspects of the reaction of a chiral catalyst or reagent with a racemic or enantiopure substrate

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Dedicated to the memory of André Collet, who deceased October 26, 1999

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Abstract—A chiral catalyst or reagent may be used to create an asymmetric center on the components of a racemic mixture. The quantitative relationships between the various experimental data (ee's, fractional amounts of products, conversion) are given, and extended to the formation of regioisomeric products. The cases when products are not isomeric are also considered. The meaning of 'kinetic resolution' in these processes is discussed. Finally, it is shown that above results can be used to safely predict the behavior of a chiral substrate versus either enantiomers of a chiral catalyst or reagent. Indeed, regio-, diastereo- or chemoselective reactions on a chiral substrate can be achieved by the choice of the absolute configuration of an external chiral controller.

1. Introduction

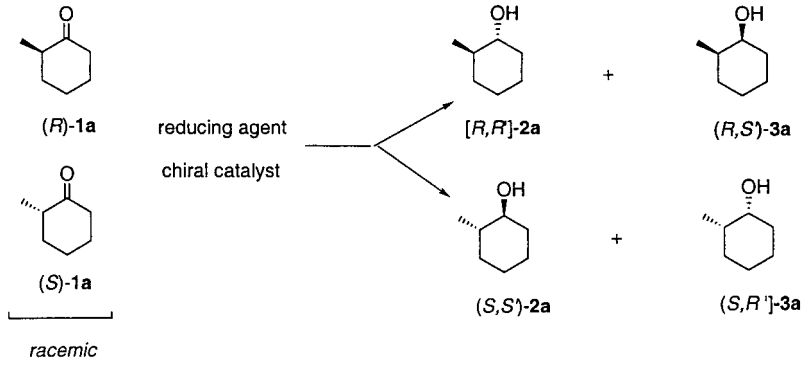
The efficient control of asymmetric induction during the creation of a new chiral unit has been one of the key issues in synthesis for the last three decades.[1] The problem has been studied both theoretically and experimentally, and immense progresses have been realized. Before 1970, very few asymmetric reactions were known with ee's or de's higher than 80%.[2] Chiral reagents or catalysts have been progressively improved,[3] giving rise to the modern generation of chiral auxiliaries of extremely high efficiency.[4] These powerful tools are increasingly finding applications, especially in the synthesis of small chiral functionalized building blocks prepared from achiral precursors. Many applications are dealing with the kinetic resolution of a racemic mixture, while traditionally only enzymatic approaches were envisaged.

It is the purpose of this article to show that a good asymmetric reagent or catalyst may generate interesting chemistry when applied to a racemic mixture (we have excluded classical kinetic resolution).

2. Creation of an asymmetric center in a racemic mixture

2.1. General discussion

Let us consider the reduction of a racemic ketone (Scheme



Scheme 1. Reduction of racemic 2-methyl-cyclohexanone.

Keywords: diastereomers; regioisomers; asymmetric induction; kinetic resolution; asymmetric catalyst; regioselectivity; chemoselectivity; chiral control; enantiodivergence.

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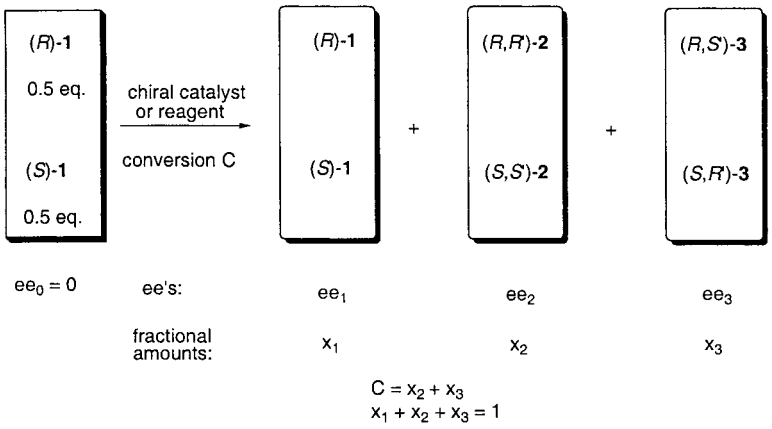


Scheme 2. General scheme of transformation of a racemic mixture into diastereomeric products by a chiral catalyst or reagent.

1). The carbonyl group will generate an asymmetric center labelled R' or S'. If the reagent is *achiral* the (*R*)-ketone **1a** will be transformed into a mixture of (*R*,*R'*)- and (*R*,*S'*)-alcohols, the (*R*) resident asymmetric center giving some asymmetric induction favoring R' or S' configuration for a given set of experimental conditions. Of course the same diastereomeric excess (de) or diastereomeric ratio (dr) will operate for the (*S*)-ketone **1a**, but with the opposite absolute configuration. Then the amount of the asymmetric induction may be evaluated either on one enantiomer or on the corresponding racemic mixture.[5] When a *chiral* reagent or catalyst is used, the situation is more complex. The diastereomeric products can be enantiomerically enriched, for a partial or total conversion of the initial racemic mixture. For example racemic **1** will give a mixture of *cis* and *trans* alcohols **2** and **3** of enantiomeric excesses ee_2 and ee_3, respectively, together with some remaining ketone **1** (enantiomeric excess ee_1). Conversion C ($C \leq 1$) is a useful parameter to consider. It can also be expressed into conversion % ($C\%$) by multiplying by 100. A schematic representation of the reactions of Scheme 1 is shown in Scheme 2. This allows to make a general discussion of the transformations of a racemic mixture under the influence of an external chiral auxiliary. The case of the full conversion ($C=1$) has been discussed by Guetté and Horeau.[7] These authors demonstrated that a simple relationship correlates the absolute values of the ee's of the two diastereomers (ee_2 and ee_3) and their relative amounts x_2 and x_3: $ee_2/ee_3 = x_3/x_2$. The ratio of the ee's of the two diastereomers is equal to the inverse ratio of their relative amounts.

In 1984, we analyzed the general situation where a racemic mixture is partially transformed into a mixture of diastereomers.[8] A mathematical treatment based on the material balance of the system allowed to find the relationships between the various parameters. The seven basic parameters are the molar fractions of the recovered starting material and the two diastereomers (x_1, x_2, x_3), the corresponding ee's (ee_1, ee_2, ee_3), and the conversion C. It is also interesting to consider the diastereomeric ratio ($dr = x_2/x_3$), which can be easily measured. In order to have a self-consistent calculation we gave arbitrarily a sign to the enantiomeric excesses, for example defining the ee's as positive when the major enantiomers are (*R*)-**1**, (*R*,*R'*)-**2** and (*R*,*S*)-**3**. In other words the (+)-sign is a label to recall that initial (*R*)-**1** is the precursor of the residual (*R*)-**1** and the diastereomers (*R*,*R'*)-**2** and (*R*,*S'*)-**3**. This allows an algebraical treatment of the calculations, Eqs. (1)–(8) have been easily established

$$ee_1 x_1 + ee_2 x_2 + ee_3 x_3 = 0, \tag{1}$$

$$dr = x_2/x_3 = [C(ee_1 - ee_3) - ee_1]/[C(ee_2 - ee_1) + ee_1], \tag{2}$$

$$ee_1 = C[dr\ ee_2 + ee_3]/[(C-1)(1+dr)], \tag{3}$$

$$ee_2 = [(C-1)(1+1/dr)ee_1]/C - ee_3/dr \tag{4}$$

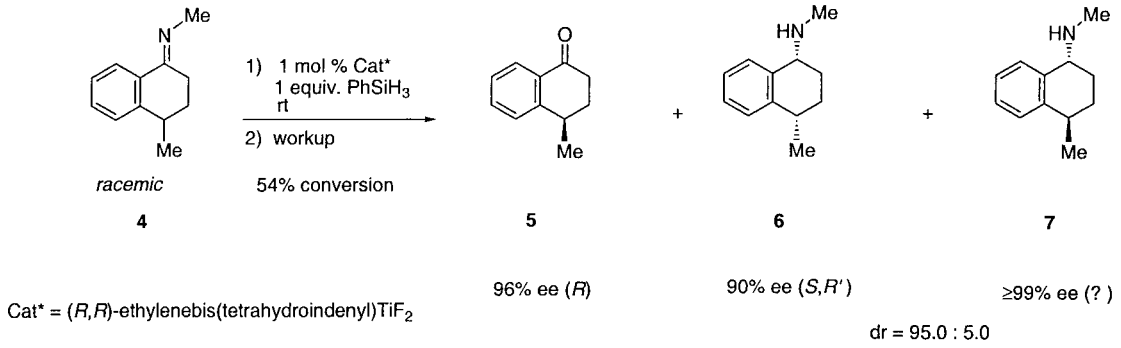
$$ee_3 = [(C-1)(1+dr)ee_1]/C - dr\ ee_2. \tag{5}$$

When the conversion of the racemic mixture is complete, Eq. (1) must be taken with the value $x_1=0$, giving $-ee_2/ee_3 = x_3/x_2$. This is the equation already found by Guetté and Horeau.[7] The (−)-sign is there because the two diastereomers must necessarily derived from the two opposite enantiomers of **1**. In addition the diastereofacial selectivities a=(*R*,*R'*)-**2**/(*R*,*S'*)-**3** and b=(*S*,*S'*)-**2**/(*S*,*R'*)-**3** can be calculated. The diastereomeric excess for the product deriving from (*R*)-**1** remains unchanged with the conversion, the ratio a of rates of attack on the two faces does not depend of the amount of (*S*)-**1**. Similarly, the diastereofacial selectivity b on (*S*)-**1** remains unchanged through the whole reaction (if the structure of the chiral reagent or catalyst remains constant). The selectivities a and b have been expressed in Eqs. (6) and (7) as a function of ee_1, ee_2 and dr (the global diastereomeric ratio x_2/x_3)

$$a = [RR']/[RS'] = dr[(1+ee_2)/(1+ee_3)], \tag{6}$$

$$a = [SS']/[SR'] = dr[(1+ee_2)/(1+ee_3)]. \tag{7}$$

In the present system, the experimental data are measured with variable accuracies. When chromatographic methods can be used, an excellent accuracy is obtained if there is a base line peak separation. Very often this applies to ee and dr measurements, leaving the major error on conversion C.



Scheme 3. Kinetic resolution of a racemic imine (Ref. 12).

This has been noticed in kinetic resolutions by chemical or biochemical ways, where one may calculate C from a relationship relating ee's of recovered starting material and product.[9,10] Similarly, one can express here the conversion C as a function of ee_1, ee_2, ee_3 and dr. For example, Eq. (3) can be rearranged to Eq. (8)

$$C = [(1 + dr)ee_1]/[dr(ee_1 - ee_2) + ee_1 - ee_3]. \quad (8)$$

Some examples will illustrate the interest of the above equations.

2.2. Applications of the basic equations (1)–(8)

Several applications of the above-mathematical treatment should be pointed out. It can be used:

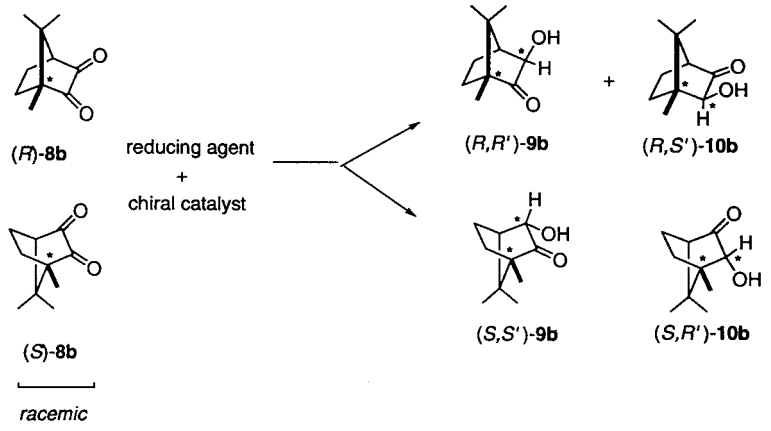
(i) to check the self-consistencies of the experimental data of asymmetric reactions performed on a racemic mixture;
(ii) calculate a missing data from the other available data;
(iii) detect or evaluate a kinetic resolution process (by calculation of the exact value of ee_1 or conversion).

First example. Reduction of racemic 2-norbornanone by NDH/HLAD system.[11] The total conversion gave a mixture of *exo* and *endo*-norbornanols (in the ratio 88/12) with ee_{exo}=100% (1*R*,2*R*′) and ee_{endo}=38% (1*S*,2*R*′). With our conventions we have ee_2=1.00; ee_3=−0.38, C=1.00, x_2=0.28 and x_3=0.72. These values fit perfectly into Eq. (1).

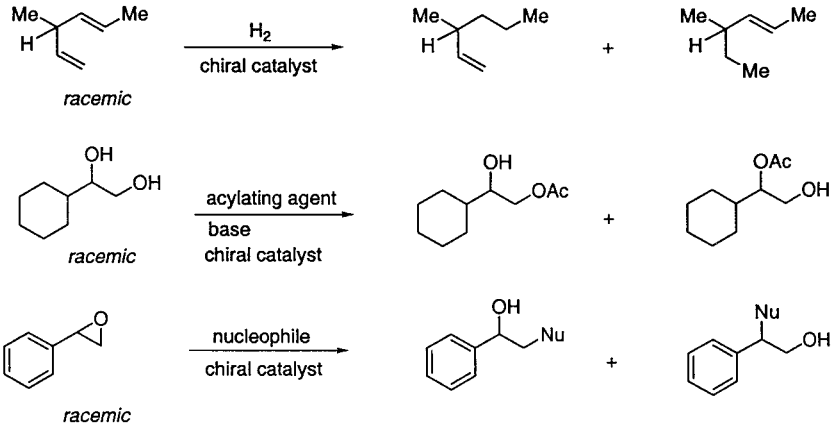
Second example. Buchwald et al. recently devised an efficient catalyst for the asymmetric reduction of imines using silanes as reducing agent. This catalyst is also able to give kinetic resolution of racemic imines.[12] For example, for a conversion of 54% (C=0.54) racemic **4** gave a 95.0/5.0 mixture of diastereomers **6** and **7** (Scheme 3). Ketone **5** was also recovered (96% ee). It comes from the hydrolytic workup of the remaining imine. In the experiment the absolute configuration of **7** could not be assigned, because of lack of material. The use of some of Eqs. (1)–(8) allowed to solve this problem. The conventions of Scheme 1 applied to data of Scheme 3; it means ee_1=+0.96, ee_2=−0.90, C=0.54, dr=17.18. Eq. (2) was checked with either ee_3=+0.99 or ee_3=−0.99. A reasonable fit (dr=22) was only obtained with ee_3=+0.99, while the impossible value dr=−2.1 was calculated for ee_3=−0.99. The plus sign implies that the minor diastereomer was generated from (*R*)-**4** and hence must have the (*R*,*R*′) configuration.

Eqs. (6) and (7) also allowed to calculate the diastereofacial selectivities on each enantiomer of imine **4**. It gives $a>10^4$, b=0.95. These values show that the (*R*,*R*)-catalyst, if used on enantiopure (*R*)-**4**, should produce **6** in very high diastereomeric purity (dr$>10^4$). The reaction on (*S*)-**4** will not be stereocontrolled (dr=0.95).

The exact knowledge of the conversion can be obtained by using Eq. (8). It gives C=54.4% (instead of 54.0% measured). The selectivity factor s may be calculated by the classical formula for pseudo first-order reactions in substrate.[9,10,13] One finds s=38.5. This value indicates an excellent efficiency for the kinetic resolution of imine **4**.



Scheme 4. Monoreduction of racemic camphoquinone in presence of a chiral catalyst or reagent.



Scheme 5. Some hypothetical examples of reactions transforming a racemic mixture into regioisomeric products.

It is important to notice that the asymmetric transformation of a racemic mixture into two diastereomeric products of high enantiomeric excess does not necessarily involve a kinetic resolution process. It is only by the study of a partial conversion of the racemic mixture that some conclusion can be reached.

3. Creation of regioisomeric products from a racemic mixture by asymmetric catalysis

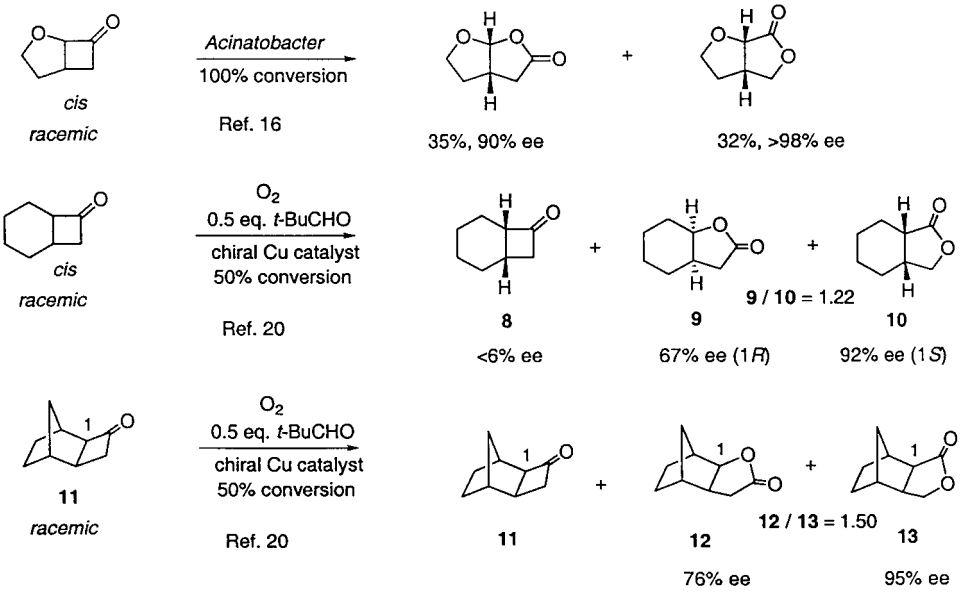
Let us consider the transformations of a racemic mixture under the influence of an external chiral auxiliary, giving rise to regioisomeric products. An example is presented in Scheme 4. The monoreduction (*endo* attack) of racemic camphoquinone **8** in presence of a chiral catalyst gives rise to a mixture of isomeric α-ketols **9** and **10**. These compounds may be enantioenriched as well as the recovered starting material. Some additional hypothetical examples are listed in Scheme 5.

In 1996, we considered and shortly discussed the transformations of a racemic mixture involving regioselectivity control.[14] We want here to give a general and detailed analysis of these systems.

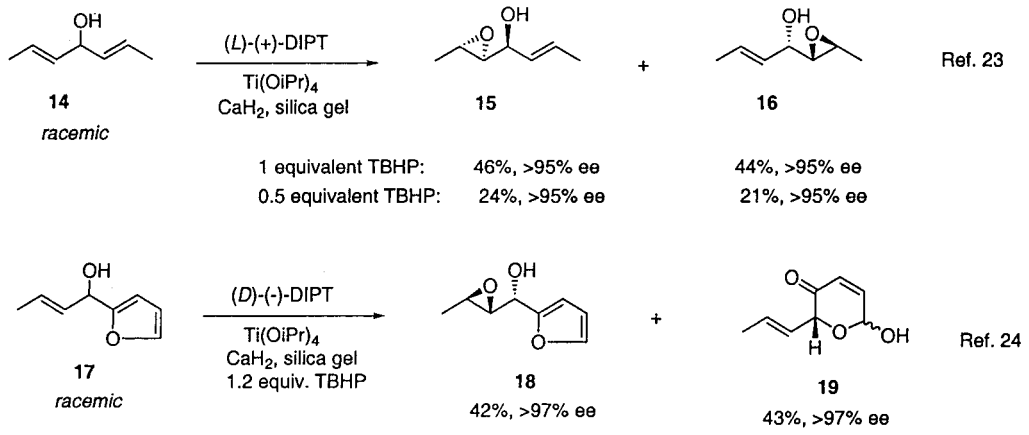
The comparison of Schemes 1 and 4 shows some similarities: two products are formed (diastereomeric or regioisomeric), each one is chiral and enantiomerically enriched.

A partial conversion in both cases leaves some starting material which can be enantioenriched. It becomes obvious that the general Scheme 2 applies as well to the formation of diastereomers (as in Scheme 1) or to the formation of regioisomers (as in Scheme 4). The only difference is that in Eqs. (2)–(8) the diasteromeric ratio (dr) has to be replaced by the regioisomeric ratio (rr). The sign convention on the ee of the regioisomers is the same as previously applied to the diastereomers: the ee's of recovered starting material and of the two regioisomers are arbitrarily defined as positive if the major enantiomer is related to the (*R*)-enantiomer of the initial racemic substrate.

Formula (1)–(8) have wide applicability shown as follows.



Scheme 6. Asymmetric Baeyer–Villiger reaction on some racemic ketones.



Scheme 7. Regioisomeric asymmetric epoxidations of unsaturated alcohols.

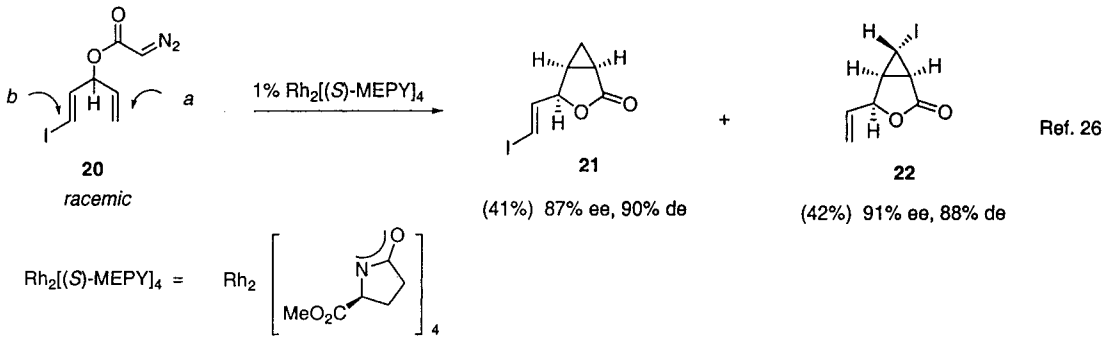
3.1. Applications of the general equations

3.1.1. Asymmetric Baeyer–Villiger reaction. Asymmetric Baeyer–Villiger enzymatic oxidation of ketones is well documented.[15–18] Sometimes two isomeric lactones with high ee's may be produced[16] (Scheme 6). A similar behavior was found for several non-enzymatic Baeyer–Villiger reactions.[19–22] Bolm et al. used a chiral copper complex as catalyst with a bis-oxazoline ligand, in the presence of molecular oxygen and pivalaldehyde.[19,20] Two experiments are detailed in Scheme 6. We had previously discussed the data of these experiments.[14] The main points will be summarized. The authors assumed that the higher ee for the 'abnormal' Baeyer–Villiger product **10**, with respect to the normal lactone **9**, could be the result of a competing uncatalyzed pathway introducing some racemic 'normal' product. By using a modification of Eq. (1), we demonstrated that the spontaneous Baeyer–Villiger oxidation may indeed account for the lower ee of lactone **9**, but in quantities not higher than 30% of the total amount of **9**.[14] Oxidation of ketone **11** led (at 50% conversion) to a mixture of the two isomeric lactones **12** and **13** of unknown absolute configurations. Based on the arbitrarily (1*R*) absolute configuration of 12 as depicted in Scheme 6, we find the following set of values: $ee_2=+0.76$, $ee_3=-0.95$, $x_2/x_3=1.50$. The unspecified value of ee_1 can now be calculated by Eq. (3), it gives $ee_1=+0.076$. It means 7.6% ee. The kinetic resolution is again very low.

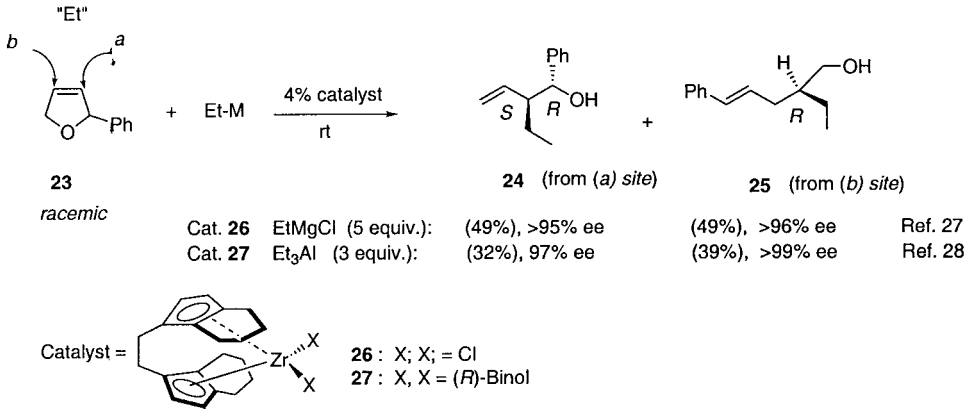
3.1.2. Asymmetric monoepoxidation of unsymmetrical divinylcarbinols. Scheme 7 describes various examples of monoepoxidation of racemic substrates.[23,24]

At 50% conversion of racemic **14** one calculates by Eq. (3) that $ee_1=4.5\%$ for recovered **14**; the kinetic resolution is quite small, despite the high ee's of the two regioisomeric products **15** and **16**. The complete conversion of the 2-furylmethanol **17** gave an epoxide **18** deriving from (*S*)-**17** and a pyranone **19** deriving from (*R*)-**17**. The pyranone originated from the initial epoxidation of a double bond located inside the furan ring of **17**. The equal amounts of **18** and **19** together with the identity of the ee's is in excellent agreement with the general Eq. (1). Independent experiments have shown that, at 70% conversion of **17**, recovered **17** (32% isolated yield) had 82% ee, showing thus a significative kinetic resolution.[25]

3.1.3. Asymmetric cyclopropanation. Martin et al. studied the intramolecular cyclopropanation of secondary allylic diazoacetates **20** (Scheme 8).[26] It yielded equimolar amounts of cyclopropanation on double bonds *a* and *b* of **20**. The chiral catalyst selectively promoted the cyclization of each enantiomer onto a different double bond. (*S*)-**20** produced **21** through preferential attack of the *b* double bond, while (*R*)-**20** reacted through the *a* double bond, giving **22**. Since the reaction was runned at complete conversion, the equimolar amounts of lactones with similar ee's agree well with Eq. (1).



Scheme 8. Regioisomeric cyclopropanation.



Scheme 9. Zirconocene-catalyzed ethylmetallation of 2,5-dihydrofurans.

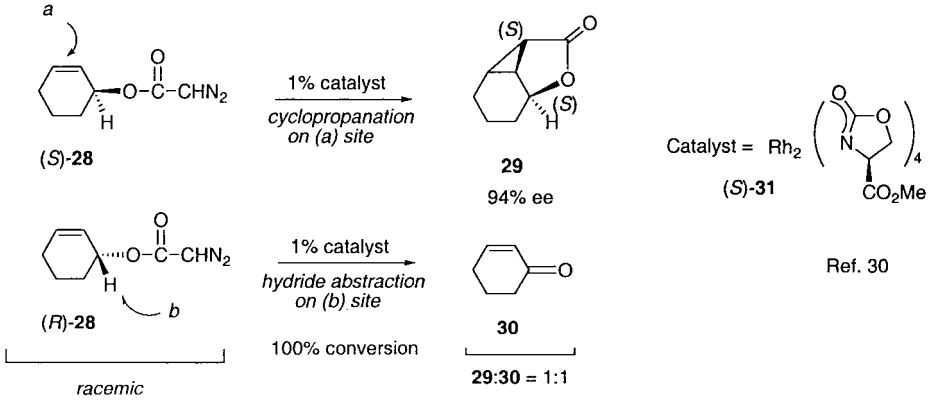
3.1.4. Ethylmetallation of C=C double bonds. Hoveyda et al. developed the zirconation-catalyzed asymmetric ethylmagnesation of various alkenes.[27] Similarly, Whitby et al. realized the ethylalumination of alkenes, using the same zirconium catalyst.[28] These authors established that dihydrofuran **23** could be transformed into a mixture (close to 1:1) of two isomeric alcohols (constitutional isomers), each one of very high ee (Scheme 9). The isolated yields were based on the recovered starting material. The process was called kinetic resolution by the authors, who did not recovered **23**. One can use the data in Scheme 9 to evaluate the ee of remaining **23** in the ethylalumination reaction.[28] Using the convention of Scheme 2 (ee_1, x_1=starting material, ee_2, x_2, ee_3, x_3=the two isomeric products) one can write: $x_2(1-x_1)=0.32$ and $x_3(1-x_1)=0.39$, since the division by $(1-x_1)$ corresponds to the correction made to calculate the isolated yields based on recovered starting material. With $ee_2=-0.97$ and $ee_3=+0.99$, Eq. (1) provides $ee_1=-0.076(1-x_1)/x_1$. Since a large excess of Et_3Al has been used, one can assume a high conversion, then a small x_1. If one takes $x_1=0.10$, it comes $ee_1=-0.69$. It means that the residual **23** has the (*S*) configuration with ee=69%. A kinetic resolution is then operating, in addition to the excellent regioselectivity of the reaction, which is specific of each enantiomer. For the ethylmagnesation reaction the conversion was complete. Then it is not possible to appreciate the amount of kinetic resolution of **23**. Hoveyda et al. previously established that kinetic resolution of dihydropyrans may occur in the zirconocene-catalyzed reaction.[29]

4. The two enantiomers of a racemic mixture are transformed by different types of reaction

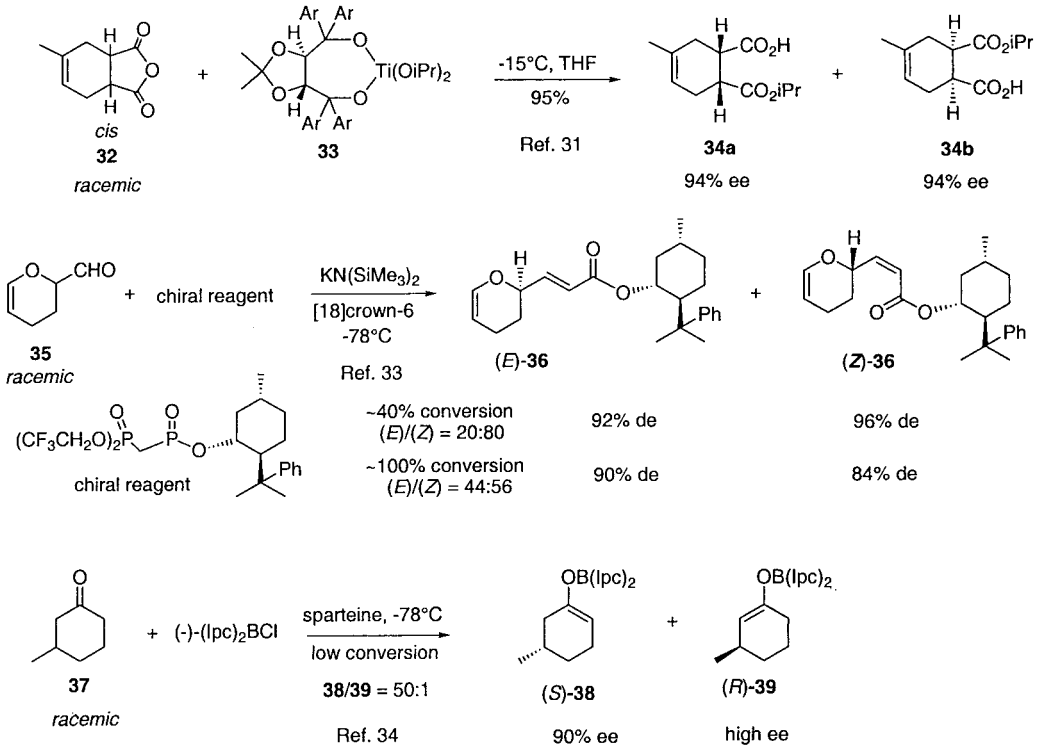
The transformation of a racemic mixture into various products under the influence of a chiral catalyst or reagent always involves competing diastereomeric transition states. One can then envisage completely different reactions when the external chirality interacts with each of the enantiomers of the racemic substrate. Very few examples are yet available. The following one is very spectacular and illustrative of what may be expected in the future.

Doyle et al. studied the intramolecular cyclopropanation of racemic secondary allylic diazoacetates in presence of a chiral rhodium catalyst.[30] They discovered that the full decomposition of racemic **28** catalyzed by **31** (Scheme 10), led to a 1:1 mixture of cyclopropane (*S*)-**29**, 94% ee coming from attack on site *a*, and cylohexenone **30**. This last compound resulted from a hydride abstraction (site *b*) with subsequent elimination of ketene. The important conclusion is that with the same catalyst the two enantiomers of racemic **28** gave divergent reactions: intramolecular cyclopropanation for (*S*) enantiomer, and hydride abstraction for (*R*) enantiomer. These divergent enantiomer preferences resulted in the formation of two very different products, **29** and **30**, which are easy to separate.

It can be hoped that, in future, additional examples of similar processes will be discovered for other types of asymmetric reactions.



Scheme 10. Formation of non-isomeric products from a racemic mixture.



Scheme 11. Action of some chiral reagents on a racemic substrate.

5. Creation of regioisomeric products from a racemic mixture by a chiral reagent

There are some cases where a racemic mixture reacts with a chiral reagent to give two regioisomeric products. Three examples are given in Scheme 11.

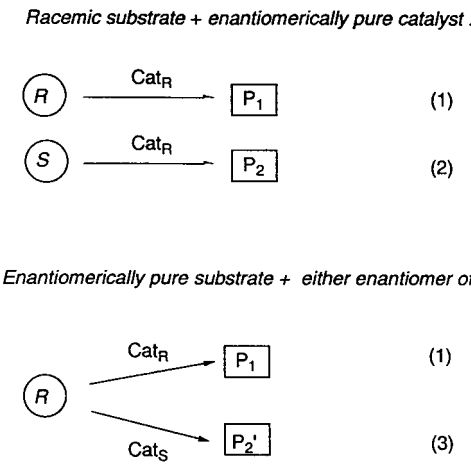
In the first example, a chiral titanium complex **33** transfers one isopropoxy group to anhydride **32**, leading to a mixture of esters **34a** and **34b** of high ee (and in unspecified relative amounts). Application of Eq. (1), by taking $x_1=0$, $ee_2=-0.94$ and $ee_3=+0.94$, immediately shows that **34a** and **34b** have been produced in equimolar amounts. Such reactions have been classified as 'enantiomer-differentiating reactions leading to constitutional isomers',[31] by analogy with the definitions proposed by Izumi and Tai.[32] In the second example, a chiral Horner–Wadsworth–Emmons reagent reacted on racemic acrolein dimer **35** (Scheme 11).[33] About 40% conversion of **35** afforded an 20:80 *E*/*Z* mixture. It was established that the (*E*) and (*Z*) products originated from different enantiomers of the starting material **35**. The high ee of each diastereomer slightly decreased for a 100% conversion. One can analyze the set of experimental data obtained at partial conversion using Eq. (3) (where ee_2 and ee_3 are replaced by de's, since the chiral auxiliary remains bound to the products). With the above conventions one write: $de_2=+0.92$, $de_3=-0.96$, dr=0.25. Eq. (3) gives with these values: $ee_1=0.58C/(1-C)$. It means that residual **35** must be of (*R*) configuration, because of the positive sign. Moreover, if one assumes a conversion close to 40% ($C=0.40$) one calculates $ee_1=+0.38$. If the actual conversion is 50% it gives $ee_1=+0.58$, meaning that the ee of the recovered (*R*)-**35** is 58%. The Horner–Wadsworth–Emmons reaction clearly gave a substantial amount of kinetic resolution of the starting material.

Ward and Lu studied the asymmetric enolborination of some racemic cyclohexanones by (−)-chlorobis-(isopinocampheyl)borane (Ipc_2BCl).[34] One example is described in Scheme 11. The reaction was performed at low conversion (15%) in the presence of sparteine, in a double stereodifferentiation process. The regioisomeric products **38** and **39** were analyzed after oxidations into the corresponding diacids. The authors calculated that 93% of the enolborination occurred from (*S*)-**37**, a good indication of a kinetic resolution, as already found by Brown et al.[35]

In conclusion, a chiral reagent can transform a racemic mixture into a variety of compounds, following the same principles that those discussed for chiral catalysts in Sections 2 and 3.

6. Predictions based on product distribution of reactions carried out on racemic mixtures

Chiral catalysts or reagents allow to transform a racemic mixture into products P_1 and P_2, such as diastereomers, regioisomers, constitutional isomers or non-isomeric compounds, as discussed in Sections 2–5. Very often one product (for example P_1) originates from one enantiomer of the starting material (for example (*R*)), while the other product P_2 comes from the transformation of the other enantiomer. Thus if the two couples (*R*)-substrate/Cat_R and (*S*)-substrate/Cat_R give, respectively, P_1 and P_2, then for symmetry reasons the new couple (*R*)-substrate/Cat_S must generate P'_2 (enantiomer of P_2) or P_2 itself if P_2 is



Scheme 12. Racemic substrate versus enantiopure substrate.

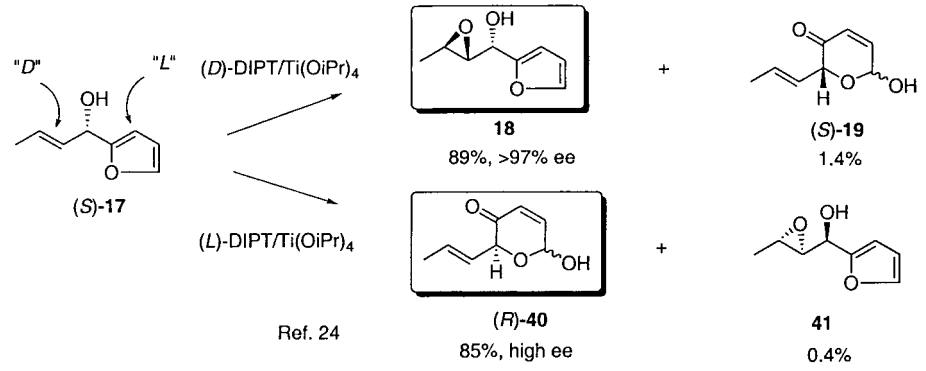
achiral (Scheme 12). The important conclusion is that one may expect an excellent *chemo- or stereo-selectivity control in the chemical transformation of a chiral compound by the good choice of the configuration of the chiral catalyst or reagent*.

As indicated in Section 2, Buchwald et al. were able to calculate that enantiopure (*R*)-**4** (Scheme 3) will lead to *cis*-amine **6** of extremely high diastereomeric excess by the use of (*R*,*R*)-catalyst.[12] On the contrary the (*S*,*S*) catalyst on (*R*)-**4** should display almost no diastereoselectivity. This is an example of matched/mismatched effects.[36]

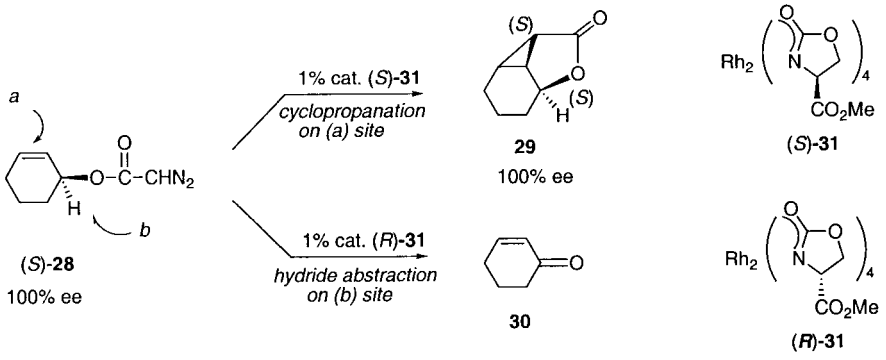
The oxidation of racemic **17** (Scheme 7) in the presence of (L)-(+)-DIPT/Ti(O*i*Pr)$_4$ catalyst gave epoxide **18** and furanone **19**.[24] The authors established that **18** and **19** derived from opposite enantiomers of **17** (see Section 2). Additional experiments showed that the reaction of (*S*)-**17** with (L)-(+)-DIPT/Ti(O*i*Pr)$_4$ or (D)-(−)-DIPT/Ti(O*i*Pr)$_4$ catalysts gave an excellent stereochemical and chemical control (Scheme 13).[24] This is a good confirmation of the usefulness of the informations collected from the reaction carried out on racemic **17**.

The transformation of racemic diazoacetate **28** in presence of a chiral rhodium catalyst gave the 1:1 mixture of products **29** and **30** (Scheme 10). One can then safely predict that (*S*)-**28** will be transformed into either (*S*)-**29** or **30** by using (*S*)- or (*R*)-catalyst **31** (Scheme 14).

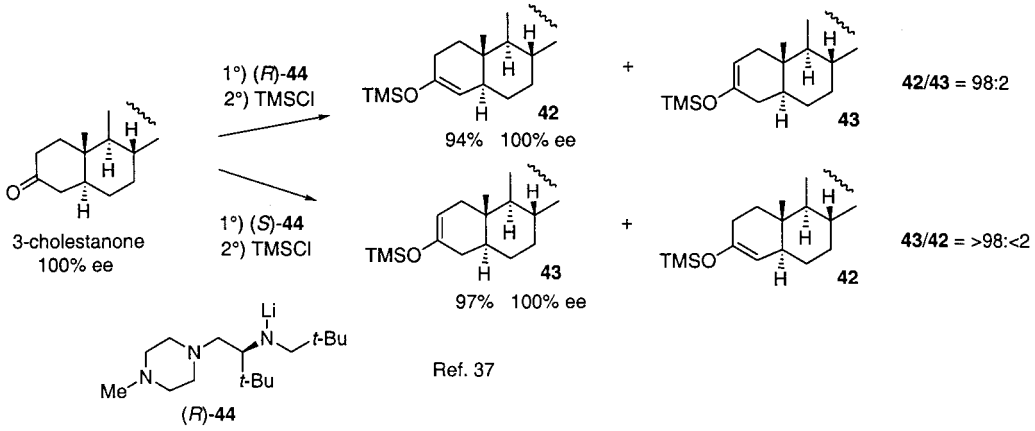
It is still unusal to find regioselective transformations of chiral compounds controlled by the absolute configuration of a chiral catalyst or reagent. One excellent example is provided by the use of chiral bases (*S*)- or (*R*)-**44** by Koga et al. to promote the regioselective formation of enol ethers of 3-cholestanone (Scheme 15).[37] Pfaltz et al. found that dimethyl malonate reacted on a dissymetric allylic acetate (100% ee) to give an almost equimolar amount of regioisomers, when the palladium complex involves an achiral ligand. However, almost full control of the regioselectivity was observed (products obtained with >98% ee), by selecting the appropriate enantiomer of a phosphino-dihydroxazole ligand.[38]



Scheme 13. Regioselective epoxidation of an enantiopure substrate controlled by the configuration of the chiral catalyst.



Scheme 14. Change of reaction mechanism by reversing the absolute configuration of the catalyst.



Scheme 15. Regioselectivity of enolization of cholestanone controlled by the configuration of a chiral base.

7. Classification of asymmetric reactions performed on a racemic mixture

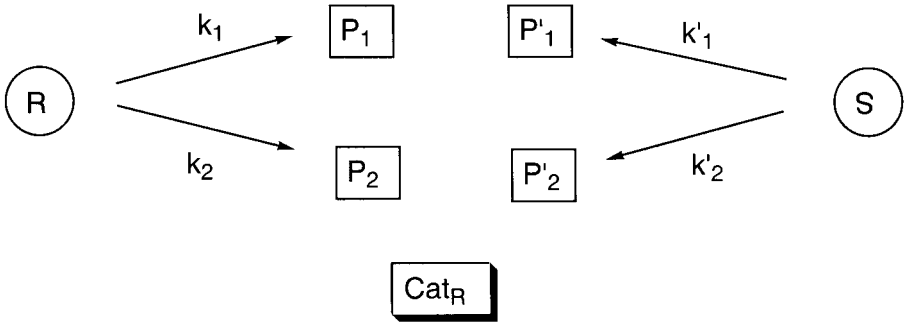
When two different (non-enantiomeric) products (P_1 and P'_2) originate from (*R*) and (*S*) substrate, respectively, one may call the process as *divergent reactions on a racemic mixture*. The word 'divergent' refers to the products: the nature and the distribution of the products are different according to the absolute configuration of the reactive substrate. This applies to the two reactions $R \rightarrow P_1$ and $S \rightarrow P'_2$ where a chiral catalyst (Cat_R) is acting. More complicated divergent reactions are depicted in Scheme 16: P_1 and P_2 (as well as the duo P'_1, P_2') can be diastereomers, regioisomers, constitutional isomers or even non-isomeric compounds. The expression divergent reaction on a racemic mixture was often used (for example see in Refs. 20 and 30). *Enantiomer-differentiating reactions leading to constitutional isomers* has been proposed, when products P_1 and P'_2 are regioisomers.[31] A similar language (selective enantiomer differentiation) has been used for the description of reactions involving racemic secondary allylic or diazoacetates (Scheme 10).[30] One may also consider the expression *enantiospecific reactions*[39] where the word 'enantiospecific' refers to the two enantiomers of the initial racemic substrate.

'Double kinetic resolution' has been proposed for the situation of Scheme 16, where P_1, P_2 and P_1', P_2' are two couples of regioisomers[23] as in Scheme 7. In this interpretation, two hypothetical kinetic resolutions were considered: $R \rightarrow P_1$ compared to $S \rightarrow P_1'$ ($k_1 > k_1'$) and $SR \rightarrow P_2$ compared to $S \rightarrow P_2'$ ($k_2 > k_2'$). The overall reaction will then generate P_1 and P'_2 as major products.[39]

In our opinion, the expression 'kinetic resolution' has to be used with much caution when a racemic mixture (*R*,*S*) is transformed such as in Scheme 16. We propose to classify the process as a kinetic resolution only if $k_1+k_2 > k_1'+k_2'$ (*R*=fast enantiomer). The existence of a kinetic resolution is easily detected by analysis of product distribution for a partial conversion. A complete transformation of racemic mixture into a mixture of products of high enantiomeric excesses may or may not be a kinetic resolution (vide supra). However, it remains a useful way to resolve a racemic mixture into enantioenriched products.[27] Obviously, some selectivities are involved here. For example, let us assume that the full transformation of racemic ($R+S$) mainly gives P_1 (high ee) and P_2' (high ee), with minor amounts of P_1' and P_2. This means that $k_1 \gg k_2$, $k_2' \gg k'_1$. There is selectivity at the level of each enantiomer, but not necessarily between enantiomers ($k_1 = k_2'$ is not forbidden). This shows why the expression enantiospecific is quite appropriated here, expressing that for a catalyst of a given absolute configuration one finds, for example, $R \rightarrow P_1$ and $S \rightarrow P_2'$.

8. Conclusions

Chemical transformations of racemic mixtures under the influence of an external chirality can produce a wide



Scheme 16. Competitive reactions acting on a racemic substrate in presence of a chiral controller. P_1 and P_1' stand for enantiomeric products as well as P_2 and P_2'. P_1 and P_2 (and P_1' and P_2') may be diastereomers, regioisomers, constitutional isomers etc.

diversity of products. The quantitative relationships between ee's and relative quantities of various products have been discussed. Some of the products may be of high enantiomeric excesses, even for a total conversion of the starting material. In cases where only two products are formed, they necessarily derived from opposite enantiomers. This provides a useful way of resolution through product separation. The enantiodivergent transformation of a racemic mixture may generate diastereomers, regioisomers or even compounds which are no longer isomeric.[40–46] The analysis of the product distribution allows to predict what products will be formed when the *enantiomerically pure substrate* is transformed under the influence of each of the enantiomers of a chiral catalyst. They are already some experimental data showing that completely different chemistry on enantiopure substrate can be obtained by changing the configuration of a catalyst or a reagent. Significant advances in this area of research are expected in the future.

Acknowledgements

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