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Asymmetric Amplification by Kinetic Resolution Using A Racemic Reagent: Example in Amine Acetylation

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Dedicated to the memory of André Rassat

Abstract: The reaction of a racemic reagent on a mixture of enantiomers with small *ee* (*ee* = enantiomeric excess) has been studied for amine acylation. A substantial asymmetric amplification could be realized, for example, from 67 to > 95.5 *ee*. The combination of asymmetric amplifications is subsequently discussed. Two sequential asymmetric amplifications, one using a racemic reagent and another using a positive nonlinear effect allowed us to start from 1.5 % *ee* and end with a large amount of a product of 97 % *ee*.

Keywords: asymmetric synthesis · chirality · kinetic resolution · nonlinear effects · racemic reagent

Introduction

Asymmetric amplification of small *ee*'s is an old problem which still of current interest because of its relevance with the origin and propagation of optical activity on earth.[1–4] Many processes have been proposed to initiate an imbalance between the distribution of two enantiomers, such as spontaneous resolution by crystallization, spontaneous resolution combined with in situ racemization, kinetic resolution or asymmetric synthesis by circularly polarized light, etc.[5–7] The asymmetric amplification of *ee*'s has been envisaged by a variety of processes. An early suggestion was the Frank model, which involves an autocatalysis coupled with an inhibition reaction between enantiomers.[8] In 1995 Soai discovered a superb and unique chemical system which is related to the Frank model.[9] Positive nonlinear effects (asymmetric amplification) are also a way to translate a small *ee* (of the catalyst or reagent) into a larger *ee* (in the product).[10,11] It can operate in the usual catalytic reactions[11,12] and in autocatalytic reactions.[13] Many other methods exist to amplify the *ee* of a compound, for example kinetic resolution[14,15] or the Horeau–Langenbeck duplication method. The coupling (statistical or not) between enantiomers has been used as a way to amplify their *ee*'s by removal of the *meso* dimer before cleavage of the homochiral dimers.[16,17] The catalytic process is especially valuable, as the product is generated both in larger amounts and with larger *ee*'s than in the starting material.

Here we wish to describe a simple way to amplify in homogeneous conditions a small *ee* (ee_0) or enantiomeric ratio (er_0) of a compound, without the use of an enantioenriched chiral auxiliary. Some examples of multiple asymmetric amplifications are subsequently described.

The usefulness of a racemic reagent: There are several facets for reactions involving a racemic substrate or a racemic reagent or catalyst.[18,19] The kinetic resolution of a racemic or enantioenriched mixture involves a chiral reagent or catalyst.[17] Usually the reagent or the catalyst are fully resolved. The use of enantio-impure reagents[18,19] or catalysts[20–23] in kinetic resolution has been discussed. The key factor for a high *ee* for the recovered starting material (ee_{sm}) is the size of the stereoselectivity factors.[14] A high $s = k_{rel}$ will allow the recovery of quite a large amount of the initial compound with excellent ee_{sm}. If s is small (< 10) then the conversion has to be increased to get a similar ee_{sm}. Mutual kinetic resolution between an alcohol and an anhydride, each one of small *ee*, led to substantial asymmetric amplifications.[24] In some special situations racemic catalysts have been used in enantioselective reactions (in presence of chiral additives)[25] or in kinetic resolution of nonracemic mixtures.[26]

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Let us now consider the partial transformation of a mixture of enantiomers by a racemic reagent. Obviously the racemic reagent, like an achiral reagent, will be unable to resolve a racemic mixture, but, interestingly, it is able to modify the initial *ee* (ee_0) of a partially resolved mixture. There will be an increase in the *ee* of the recovered starting material (ee_{sm}(final) > ee_0(initial)) if each of the enantiomers of the racemic reagent displays a high enantiodifferentiation (large stereoselectivity factor $s = k_{rel}$). Ugi et al. have performed calculations on bimolecular reactions between two chiral reactants of various initial *ee*'s.[27] With the assumption of a first-order reaction in each reactant, the kinetic treatment on an equimolar mixture of reactants allowed the authors to set tables of data for various k_{rel} and conversions. The special case of a partially resolved compound versus a racemic reagent has also been treated, clearly showing an increase of ee_{sm} with conversion, with a correlation to the size of *s*. The influence of the initial *ee* of a reagent on the kinetic resolution of a racemic mixture was briefly revisited by us in 1999.[20] Plotted in Figure 1 are some curves computed as in reference [20] with $s = 30$ (initial $ee_{substrate} = 10\,\%$) and two substrate/reagent initial ratios. The general trends are seen on these curves: the *ee* of the substrate is amplified by the racemic reagent, simultaneously the racemic reagent is progressively resolved by the substrate. For example, in Figure 1a for which the initial ratio [substrate]/[racemic reagent] = 1:1 at 75.8% conversion of substrate, its initial 10% *ee* is now equal to 20.1%, while the reagent is weakly resolved ($ee_{reagent} = 17.5\,\%$). In Figure 1b for which initially [substrate]/[reagent] = 1:0.5 and $ee_{substrate} = 10\,\%$, at 49.4% substrate conversion and consequently 98.7% reagent conversion, one finds $ee_{substrate} = 17.7\,\%$ and $ee_{reagent} = 54.4\,\%$. To our knowledge there are no reports in the literature on the intriguing possibility of an increase in the imbalance between enantiomer distribution by a racemic reagent. Thus, we investigated this (see below).

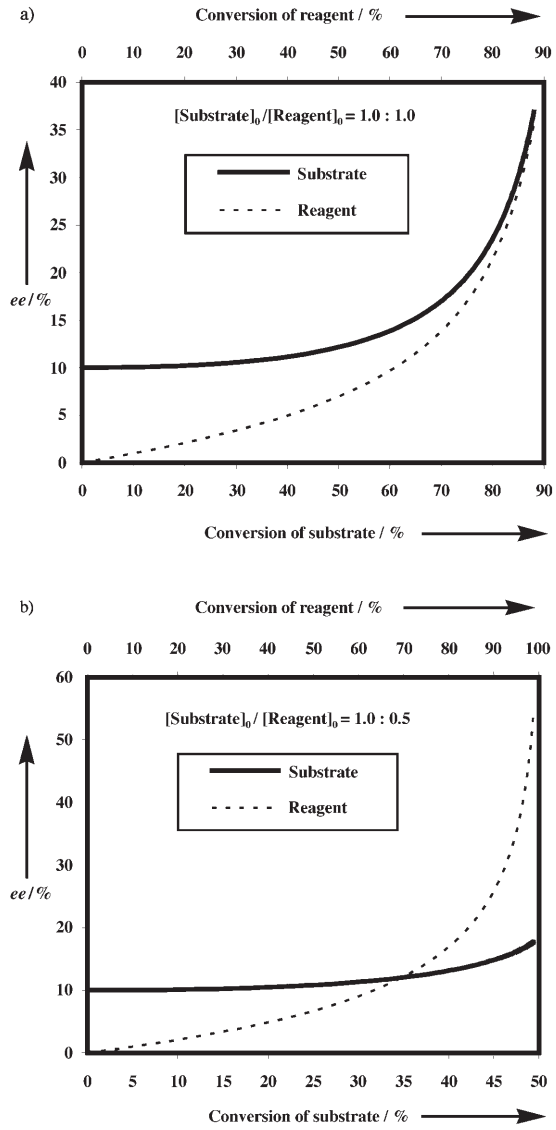
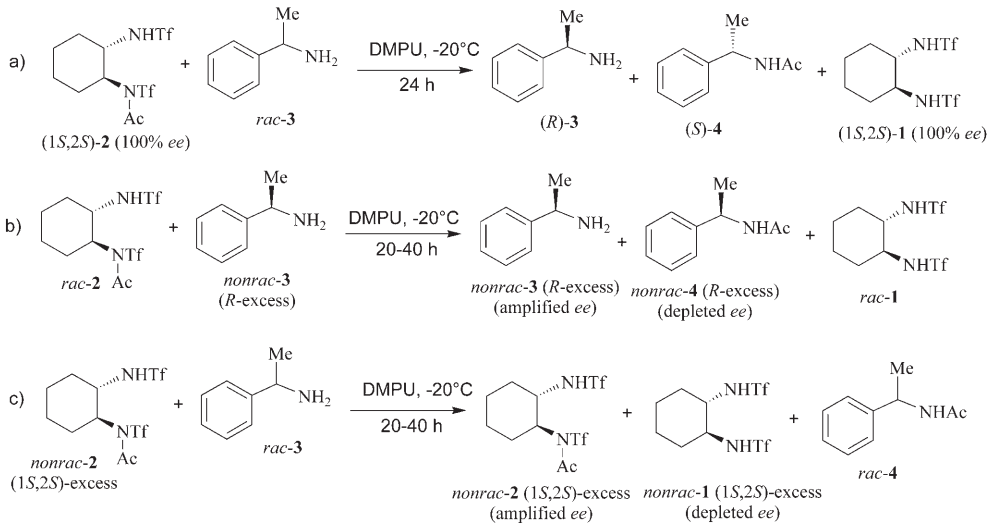


Figure 1. Amplification of 10% *ee* substrate with initial molar ratio substrate over reagent of 1.0:1.0 (a) and 1.0:0.5 (b). Computed plots according to reference [20], for reactions that are first order with respect to substrate and reagent.

Use of a racemic reagent in acylation reactions: As a model case we selected the convenient acylation of a racemic amine **3** by the monoacetyl bistriflamide **2** (Scheme 1a) which has been recently described by Mioskowski et al.[28] For example racemic **3** and **2** (100% *ee*) in DMPU (DMPU = *N*,*N*′-dimethyl-*N*,*N*′-propylene urea) gave **2** with 84% *ee* for 50% conversion. The authors calculated from these data that $s = k_{rel} = 30$. We easily reproduced this experiment. Then we allowed amine **3** (*R*) with 67% ee_0 (initial) to react with less than one equivalent of racemic reagent **2** (Scheme 1b, Table 1). When 1.0 equiv of amine **3** (*R*, 67% *ee*) was treated with 0.53 equiv of racemic reagent **2** and kept until the complete consumption of *rac*-**2** (for example, 53% conversion of **3**), the isolated residual amine **3** (*R*) had an ee_{sm} of 95%, in agreement with calculations made in reference [28] and the value of $s = 30$; the *N*-acetylamine **4** (product) was obtained in 37% *ee* ($ee_{product}$, *R*). A set of asymmetric amplifications of initial *ee*'s of amine **3** under various experimental conditions confirmed the good correlation between ee_{sm} (initial and final) and the size of *s* and conversion *C* (Table 1). Encouraged by these results and in order to evaluate the generality of this amplification strategy, we examined the alternate reaction of *N*-acetylbistriflamide **2** of small *ee* with *racemic amine* **3** (Scheme 1c, Table 2). When 1.0 equiv of acylating agent (1*S*,2*S*)-**2** (1.5% *ee*) was treated with 0.93 equiv of racemic amine **3** and kept until the complete consumption of *rac*-**3** (for example, 93% conversion of **2**), the remaining unreacted acylating agent (1*S*,2*S*)-**2** was isolated with 15.5% *ee*. The evaluation of the asymmetric amplification was conveniently done by isolation of **2** by flash chromatography and chiral HPLC or by hydrolysis of **2** into **1**, the *ee* of which was measured by ^{19}F NMR in presence of quinidine. The results of Tables 1 and 2 confirm that a racemic reagent can easily enhance the *ee* of its partner if the stereoselectivity factor is not too small.



Scheme 1. a) Kinetic resolution of *rac*-**3** by *enantiopure*-**2**. b) Enantiomeric amplification of *nonrac*-**3** by *rac*-**2**. c) Enantiomeric amplification of *nonrac*-**2** by *rac*-**3**.

Table 1. Amplification of the *ee* of **3** by the use of racemic reagent **2**.[a,b]

Entry	Amine **3** Initial *ee* [%] (mol equiv)	Acylating agent *rac* **2** [mol equiv]	Conversion of **3** [%][c]	Recovered amine **3**[d] *ee*(final) [%]	Amide **4**[e] $ee_{product}$ [%]
1	85.8 (1.0)	0.23	23.0	98.0	46.3
2	67.0 (1.0)	0.28	28.0	83.0	25.0
3	67.0 (1.0)	0.53	53.0	95.5	37.0
4	67.0 (1.0)	0.64	64.0	98.0	54.0
5	67.0 (1.0)	0.83	83.0	>99.5	60.8
6	4.2 (1.0)	0.50	50.0	8.2	0.15
7	4.2 (1.0)	0.90	90	22.6	1.8

[a] Reactions were performed at −20°C for 20–48 h in DMPU until complete consumption of racemic acyl transfer reagent **2**. [b] Compounds **3** and **4** have an *R* configuration. [c] Conversion calculated from *ee*'s of **3** and **4** or measured by GC. [d] Measured by HPLC (OD-H) on the corresponding amide obtained on acetylation. [e] Measured by HPLC (OD-H).

Table 2. Amplification of the *ee* of the acyl-transfer agent **2** by the use of racemic amine **3**.[a,b]

Entry	Initial *ee* [%] of acyl-transfer agent **2** (1 mol equiv)	Mol equiv of racemic reagent (amine) **3**	Conversion of **2** [%][c]	*ee* [%] of recovered **2**[d]
1	20.0	0.65	55.0	28.0
2	5.0	0.80	80.0	31.0
3	1.5	0.93	93.0	15.5

[a] Reactions were performed at −20°C for 20–48 h in DMPU until complete consumption of racemic amine **3**. [b] Compounds **1** and **2** have an (1*S*,2*S*) configuration. [c] Complete conversion of **3** was assumed, except in entry 1. [d] Measured after isolation and hydrolysis into **1**, followed by ^{19}F NMR with quinidine as the shift reagent; in entry 3 *ee* was also measured on recovered **2** by HPLC.

Multiple asymmetric amplifications: It may be interesting to combine (one-pot when possible) various sequential processes of asymmetric amplification to get a final high *ee* from a modest initial *ee*. This is illustrated in Figure 2. The enantiomeric amplification index, a (>1), in the first step can be expressed by the ratio of *er* values $a = er_1/er_0$ or by the ratio of *ee*'s $a = ee_1/ee_0$ (for the relative advantages of both definitions see reference [12]). The overall amplification in the ith step will be $a_i = er_0$ (or ee_0) $\times a_1 \times a_2 \times \cdots \times a_i$. The sequential er_i or ee_i are of increasing values. Here we do not discuss the numerical values of this approach (some details are given in the Supporting Information),[29] instead we have illustrated these below with some experiments.

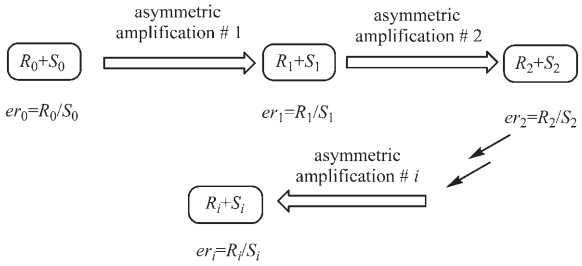


Figure 2. Sequential asymmetric amplifications. R_1 and S_1 refer to the product isolated after the first asymmetric amplification, it could be structurally identical to the starting material R_0, S_0, or of a different structure (if R_0, S_0 is a reagent or catalyst giving the product R_1, S_1). $er_i > er_{i-1}$ (or $ee_i > ee_{i-1}$).

We undertook the project to couple a first asymmetric amplification by a racemic reagent (*rac*-**3**) to a subsequent enantioselective catalytic reaction in which there is a positive nonlinear effect with respect to a catalyst (**1**).

Bistriflamide **1** is a classical and useful asymmetric catalyst for the addition of organozincs on aldehydes, when used in presence of stoichiometric amounts of $Ti(OiPr)_4$.[30] The original procedure for the catalyst preparation was devised by Ohno and Kobayashi[31] and was subsequently modified by Walsh.[32] In the Ohno and Kobayashi method, **1** and $Ti(OiPr)_4$ were first heated in toluene at 40°C for 20 min, then diethylzinc was added at −78°C, followed by benzaldehyde.

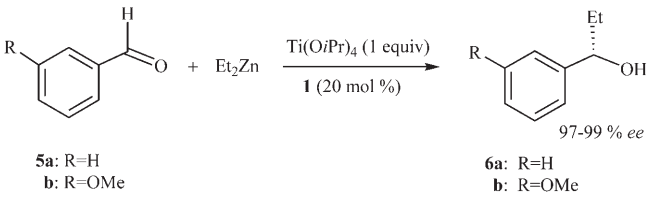
The alternate procedure of Walsh et al. was to combine **1** and Et_2Zn at 23 °C in toluene, this was followed by the sequential addition at −50 °C of $Ti(OiPr)_4$ and benzaldehyde. In 2002 we found that the Ohno and Kobayashi protocol gave a strong positive nonlinear effect in contrast with the Walsh procedure where there was a strict linearity.[33] For example, catalyst **1** with 10 % *ee* provided **6a** (Scheme 2) in 51 % *ee*. We reinvestigated these experiments and combined it with the asymmetric amplification of **2** by racemic amine **3**.

Racemic **3** amplified the low *ee*, ee_0, of a sample of *N*-acetyl bistriflamide **2** until a value of ee_1 (Table 2) had been reached. **2** was easily recovered by flash chromatography from the reaction mixture and quantitatively hydrolyzed into bistriflamide **1** (ee_1) which was taken as catalyst (20 % mol equiv) in the addition of Et_2Zn on benzaldehyde **5** according to the Ohno–Kobayashi protocol or to a slightly modified protocol, both affording an asymmetric amplification. The results are collected in Table 3 and highlight the efficiency of the combinations of asymmetric amplifications (Scheme 2). By taking an initial compound **2** of 1.5 % *ee* and after an amplification by racemic amine **3**, which generates the catalyst **1** of 15 % *ee*, this reagent was able to produce large quantities of carbinol **6b** in >97 % *ee* (Table 3, entry 6).

Table 3. Asymmetric amplification in the formation of **6**.

Entry	*ee* of catalyst **1** [%]	Amount of catalyst [mol equiv][a]	*ee* of (*S*)-**6** [%][b]
1	10.0	0.02	51 **6a**
2	10.0	0.20	89 **6a**
3	10.0	0.40	87 **6a**
4	10.0	0.20	93 **6b**
5	15.0	0.20	88 **6a**
6	15.0	0.20	97 **6b**
7	31.0[c]	0.02	84 **6a**
8	100	0.02	98 **6a**
9	100	0.02	>99.5 **6b**

[a] The catalyst precursor (1*R*,2*R*)-**1** was heated in toluene with $Ti(OiPr)_4$ (1.2 mol equiv) at 55 °C for several hours. After cooling and addition of **5a** or **5b** the reactions were run for 3 h (entry 1) or 8 h (entries 2 and 3) at −20 °C. See details in Experimental Section. [b] Measured by HPLC (OD-H), All products are of *S*-configuration except entry 7. [c] Sample (1*S*,2*S*)-**1** obtained by hydrolysis of **2**, itself isolated as in Table 2, entry 2.



Scheme 2. Catalyzed asymmetric addition of diethylzinc.

Conclusion

We established experimentally on several examples the possibility to amplify a small *ee* by using a racemic reagent. If the stereoselectivity factor is large enough the process can be quite efficient. The coupling of this type of asymmetric amplification with a second amplification process in a catalytic reaction has been realized. By this approach a small initial *ee* (in the range of 1–5 %) can give rise to a product in large amounts with *ee* >95–97 %. We are currently investigating the scope and various aspects of the use of racemic reagents in the kinetic resolution and strategy of sequential asymmetric amplifications.

Experimental Section

Apparatus and solvents: All the apparatus used were flame-dried and cooled under an argon atmosphere. Toluene was freshly distilled over CaH_2. DMPU was distilled and stored over molecular sieves (4 Å).

Determination of enantiomeric excess:

*For amide (**4**)*: The *ee* was determined by using HPLC on Chiralcel OD-H (*n*-pentane/ethanol 98.7:1.3, flow = 1.0 mL min^{-1}, retention times = 47 min (*R*), 55 min (*S*)).

*For amine (**3**)*: The *ee* was determined on the corresponding amide (**4**) obtained by acylation following similar analysis conditions to those described above.

*For acylating agent (**2**)*: A method was setup in which *ee* was determined by HPLC on a (*S*,*S*)-ULMO column (*n*-hexane/*i*PrOH 95:5, flow = 0.5 mL min^{-1}, UV detection at both 254 and 215 nm, retention times = 10 min (1*S*,2*S*), 12 min (1*R*,2*R*)).

*For bistriflamide (**1**)*: The *ee* was determined by ^{19}F NMR employing quinidine as chiral-shift reagent (bistriflamide (**1**)/quinidine 1:≥2) and $CDCl_3$. Chemical shifts (CF_3) = −77.34 ppm (1*S*,2*S*), −77.90 ppm (1*R*,2*R*).

GC conditions for determination of conversions for the kinetic resolution of amine: Column: DB1701 (Phase: 14 % cyanopropylphenyl 86 % methylpolysiloxane, dimensions: 30 m × 0.32 mm × 0.25 μm). Conditions: 70 °C isotherm for 10 min, 10 °C min^{-1} rate, 150 °C isotherm for 10 min, 10 °C min^{-1} rate, 250 °C isotherm for 15 min.

Kinetic resolution of amine (3)

Detailed experimental procedure for entry 5 (Table 1): (*R*)-1-Methylbenzyl amine **3** (67 % *ee*, 0.80 mmol, 0.097 g) was added to a racemic acylating agent **2** (0.66 mmol, 0.277 g) dissolved in freshly distilled DMPU (2 mL) at −20 °C. The reaction mixture was stirred at the same temperature with regular monitoring by TLC and GC. After complete consumption of the acylating agent **2** (in 2 d), the reaction mixture, as such, was loaded onto a silica-gel-packed column and flashed with 30–100 % EtOAc in pentane to provide 101 mg (77.7 %) of pure amide **4** (30 % EtOAc in pentane) and 9.1 mg (9.4 %) of pure amine **3** (100 % EtOAc).

*Amide **4***: 60.8 % *ee* (*R*) (determined by HPLC).

*Recovered amine **3***: 99.5 % ee (*R*) (converted to amide **4** by acylation and the *ee* was then determined by HPLC).

Kinetic resolution of acylating agent (2)

Detailed experimental procedure for entry 3 (Table 2): *rac*-1-Methylbenzyl amine **3** (0.93 mmol, 0.112 g) was added to (1*S*,2*S*)-acylating agent **2** (1.5 % *ee*, 1.0 mmol, 0.42 g) dissolved in freshly distilled DMPU (2 mL) at −20 °C. The reaction mixture was stirred at the same temperature for 40 h and then at 0 °C for another 8 h to ensure the complete consumption of *rac*-**3**. After this time, the reaction mixture, as such, was loaded onto a silica-gel-packed column and flashed with 3–15 % EtOAc in pentane to provide the isolated (1*S*,2*S*)-acylating agent **2** (3 % EtOAc in pentane) and bistriflamide **1** (15 % EtOAc in pentane).

Recovered ***2***: 3.6% (0.015 g, isolated yield); 15.5% *ee* (1*S*,2*S*) (determined by HPLC).

*Bistriflamide (**1**)*: 91% (0.344 g, isolated yield); ~0% *ee* (determined by ^{19}F NMR).

Experimental procedure for asymmetric amplification in diethylzinc addition to aromatic aldehydes: Freshly dried toluene (1.0 mL) and $Ti(OiPr)_4$ (1.5 mmol, 0.426 g) were added to bistriflamide **1** (15% *ee* (1*R*,2*R*), 0.25 mmol, 0.0945 g, 20 mol%) in a flame-dried Schlenk under an argon atmosphere. This mixture was stirred at 55–57°C for several hours and then cooled to −78°C. After the addition of Et_2Zn (1.5 mmol, 1.5 mL of a 1.0 M solution in hexane) and aromatic aldehyde (1.25 mmol), the reaction mixture was left to warm, while stirring, slowly to −20°C. This mixture was then stirred for 12–18 h. The reaction was quenched by adding 1 N HCl and the product was extracted into diethyl ether. The solvent was evaporated and crude product was purified by column chromatography to provide the pure alcohol. Enantiomeric excess was determined by HPLC analysis with a Chiralcel OD-H column (*n*-hexane/*i*PrOH 98:2, flow = 0.6 mL min^{-1}).

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