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ENANTIOSELECTIVE REFORMATSKY REACTION INDUCED BY CHIRAL β-AMINO ALCOHOLS§

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Abstract: Reformatsky reagent derived from tert-butyl α-bromoacetate adds to carbonyl compounds in the presence of chiral amino alcohols leading to β–hydroxy tert-butyl esters with good e.e. The enantioface differentiation depends on the reaction conditions and on the structure of the chiral auxiliary. The best chemical yields and e.e. are obtained for aromatic aldehydes by using the C-2 symmetrical chiral bis-amino alcohol (**5**) derived from m-xylylene diamine.

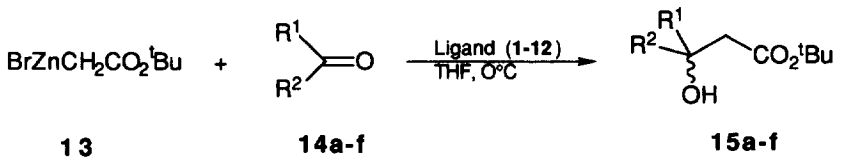
The addition of Reformatsky reagents to carbonyl and related derivatives is a very common reaction directed to the synthesis of β-functionalized esters,[1] and development of an enantioselective approach, allowing the preparation of non racemic substrates is desirable because of its synthetic utility. To this end, a diastereoselective version has been developed by addition of Reformatsky reagents to chiral substrates[2] or by using chiral α–haloacetates.[3]

A more interesting approach is the creation of a chiral environment by coordination with a chiral complexing agent or by modification of the Reformatsky derivative with a protic optically active compound. In the first way, diamines,[4] sparteine[5] and cinchonine or cinchonidine[6] have been used as chiral ligands, whereas a few examples on the use of amino alcohols[7-9] or aminodiols[10] as chiral modifiers have been also described. More recently, the method was extended to the synthesis of enantioenriched α,α-difluoro-β-hydroxy esters.[11,12]

In this paper, we present some details of the reaction of the Reformatsky reagent generated from tert-butyl α–bromo acetate and zinc with prochiral carbonyl compounds **14a-f** in the presence of different chiral amino alcohols **1-12**.

Benzaldehyde **14a** reacts with *tert*-butoxy carbonylmethylzinc bromide **13**, in the presence of the (+)-(1S,2R)-ephedrine-derived bis-amino alcohol **5**[13] leading to (S)-t-butyl-3-hydroxy-3-phenylpropionate **15a**. Both the chemical yields and the extent of the enantioface discrimination depend on the experimental conditions, and are summarized in Table 1.

These results indicate that the best combined chemical yields and optical purity (op) were obtained by using benzaldehyde, half equivalent of difunctionalized chiral bis-amino alcohol, and three-fold excess of



13 **14a-f** **15a-f**

14 and 15	a	b	c	d	e	f
R^1	Ph	2-naphthyl	4-Cl-Ph	n-Pr	PhCH=CH-	Ph
R^2	H	H	H	H	H	Me

Scheme 1

Reformatsky reagent (entry 1). When only a two-fold (entry 2) or slight excess (entry 3) of zinc derivative was used, the op was maintained, but a great depression on the chemical yield was observed.

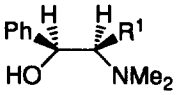
The chemical yield also decreases when one equivalent of the chiral additive, with respect to the aldehyde, was employed (entry 4); whereas the use of catalytic amount of the chiral amino alcohol (entry 5) implies a decrease in the enantioface discrimination (22% op, entry 5). The temperature does not play an important role on the enantioselection (compare entries 6 versus 1 or 7 versus 2), but under 0°C the chemical yield was highly decreased.

Table 1. Enantioselective Reformatsky Reaction of benzaldehyde catalyzed by **5**

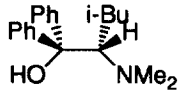
Entry	Solvent	Molar Ratio **13/14a/5**	React. Time (H)	React. Temp. (°C)	Yield (%) **15a**	op (%)[a]	Config.[b]
1	THF	3/1/0.5	24	0	(90)	(62)	S
2	THF	2/1/0.5	24	0	(56)	(78)	S
3	THF	1.1/1/0.5	24	0	(17)	(69)	S
4	THF	3/1/1	24	0	(48)	(75)	S
5	THF	3/1/0.2	24	0	(85)	(22)	S
6	THF	3/1/0.5	24	-78 to 0	(43)	(61)	S
7	THF	2/1/0.5	6	60	(53)	(72)	S
8	Et_2O	3/1/0.5	2	0	(71)	(6)	S

[a]Determined by polarimetry, based on the maximum values described for the specific rotation. [b]Assigned on the basis of the sign of the specific rotation previously described.

Finally, *tert*-butoxycarbonylmethylzinc bromide readily reacted with benzaldehyde in diethyl ether, leading to **15a** in good chemical yield but in very poor optical purity (entry 8), probably because the zinc derivative-amino alcohol complex is insoluble in that solvent.



1 R^1 = Me
2 R^1 = Ph



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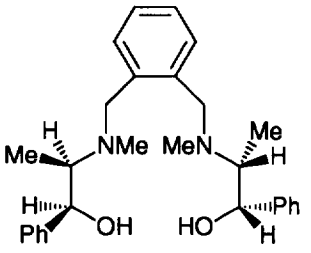

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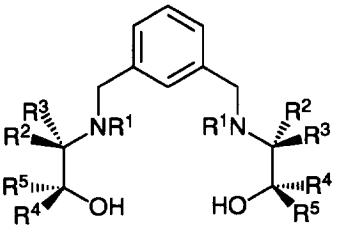

5-12

	R^1	R^2	R^3	R^4	R^5
5	Me	Me	H	Ph	H
6	Et	Me	H	Ph	H
7	Bn	H	Me	H	Ph
8	Me	Ph	H	Ph	H
9	Et	Ph	H	Ph	H
10	Me	Ph	H	Me	Me
11	Me	H	i-Bu	Me	Me
12	Me	H	i-Bu	Ph	Ph

Scheme 2

Table 2 illustrates examples of the enantioselective Reformatsky reaction of benzaldehyde in the presence of the amino alcohols **1-12** depicted in Scheme 2.

The reactions were carried out at 0° C, in THF and molar ratio Reformatsky reagent/aldehyde/ additive: 3/1/1 for amino alcohols **1-3** or 3/1/0.5 for bis-amino alcohols **4-12**. When only two-fold excess of zinc derivative was used, the op of the final β-hydroxy esters were slight better, but the chemical yields decreased (compare entries 1, 6, and 10 versus 2, 7 and 11 in Table 2).

Some facts are remarkable from the data collected in Table 2. Thus, the optical yields obtained in the reactions induced by the bis-amino alcohol **5** derived from ephedrine were quite similar than those obtained in the reaction with N-methylephedrine **1** but the chemical yields were much better for the reactions induced by **5** (compare entries 1 and 2 versus 6 and 7 in Table 2). Nevertheless, the ephedrine derived o-isomer **4** has been shown practically inefective as chiral inductor (3% op, entry 5). The role of the bulkiness of the substituent at the nitrogen atom is also important. Contrary to reported for the additions of dialkylzinc,[14] an increasing in the size of the nitrogen substituent tends to decrease the enantioface discrimination (compare entry 6 versus 8 or 9 and 10 versus 12 in Table 2).

The use of (1S, 2R)-1,2-diphenyl-2-dimethylamino ethanol **2**[15] or its bis-amino alcohol derivatives **8** and **9** as chiral inductors did not modify the chemical yields but decrease the optical yields (entries 3 and 10-12 in Table 2). The stereogenic nature of the carbon atom supporting the hydroxyl group seems to be crucial for a good discrimination. When the amino alcohols **3**,[16] **11** and **12** derived from leucinol, or **10**, prepared from

phenylglycinol, with only one stereogenic center were used as chiral additives, the β-hydroxy ester was obtained in very low op (entries 4 and 13-15 in the Table).

Table 2. Enantioselective Reformatsky Reaction of benzaldehyde catalyzed by **1-12**

Entry	Ligand (**L***)	Molar Ratio **13/14a/L***	React. Time (H)	Yield (%) **15a**	op (%)[a]	Config.[b]
1	**1**	3/1/1	24	(62)	(64)	S
2	**1**	2/1/1	24	(49)	(73)	S
3	**2**	2/1/1	22	(62)	(67)	S
4	**3**	3/1/1	23	(67)	(30)	R
5	**4**	3/1/0.5	4	(88)	(3)	R
6	**5**	3/1/0.5	24	(90)	(62)	S
7	**5**	2/1/0.5	24	(56)	(78)	S
8	**6**	3/1/0.5	5	(92)	(48)	S
9	**7**	3/1/0.5	6	(79)	(13)	R
10	**8**	3/1/0.5	16	(92)	(57)	S
11	**8**	2/1/0.5	24	(68)	(55)	S
12	**9**	3/1/0.5	15	(98)	(35)	S
13	**10**	3/1/0.5	24	(42)	(3)	S
14	**11**	3/1/0.5	48	(53)	(3)	S
15	**12**	3/1/0.5	20	(77)	(2)	S

[a]The optical purity (op) was determined by polarimetry based on the maximum values reported for the specific rotation. [b]Assigned by comparisson with the sign of the specific rotation previously described.

The described stereochemical results indicate that the sense of the asymmetric induction for the Reformatsky reaction can be referred, only in part, to that previously described for the addition of dialkylzincs.[14] Thus, the enantioface differentiation is governed by the stereochemistry at the carbon atoms were the hydroxyl and amino groups are attached. The addition occurs preferentially from the *si* face of the benzaldehyde when the configuration of the carbon atoms bearing the hydroxyl and amino groups are *S* and *R* respectively.

Nevertheless, the presence of only one stereocenter at the chiral inductors (**3**, **10-12**) decreased the enantioselection, and the same effect was noted when the bulkiness of the substituents at the nitrogen increases. The main difference betwen the enantioselective addition of dialkylzincs and Reformatsky reaction induced by chiral amino alcohols refers to the reactivity of the organometallic. Whereas catalytic quanties of inductor

accelerates the reaction rate and enhances the enantioselection for dialkylzinc additions, the Reformatsky reagent reacts slower in the presence of chiral amino alcohols, and it is necessary half equivalent of inductor to get reasonable discrimination.

An increase in the molar ratio Reformatsky reagent/ amino alcohol increases the reactivity but diminishes the enantioselectivity, probably because the uncoordinated specie reacts quickly by the uncatalyzed achiral pathway.

The enantioselective Reformatsky reaction, catalyzed by the (+)-ephedrine derived bis-amino alcohol **5**, was extended to some other aldehydes **14a-e** and acetophenone **14f**, and the results are summarized in Table 3. The observed enantioselection was better for aromatic aldehydes **14a-c** than for butanal **14d** or cinnamaldehyde **14e**, althought the presence of an electron-withdrawing group at the *para* position reduces the op (compare entries 5 and 6 versus 1 and 2 in Table 3). Finally, it is interesting to note that acetophenone led to the β-hydroxy ester **15f** in good enantiomeric excess.

Table 3. Enantioselective Reformatsky Reaction of carbonyl derivatives **14a-f** catalyzed by **5**

Entry	Substrate	Molar Ratio **13/14/5**	React. Time (H)	Yield (%) **15**	op (%)[a] or ee (%)[c]	Config.[b]
1	**14a**	3/1/0.5	24	**15a** (90)	(62)[a]	S
2	**14a**	2/1/0.5	24	**15a** (56)	(78)[a] (75)[c]	S
3	**14b**	3/1/0.5	26	**15b** (67)	(61)[a]	S
4	**14b**	2/1/0.5	24	**15b** (65)	(72)[a]	S
5	**14c**	3/1/0.5	24	**15c** (73)	(46)[c]	S[d]
6	**14c**	2/1/0.5	24	**15c** (60)	(67)[c]	S[d]
7	**14d**	3/1/0.5	24	**15d** (70)	(34)[a]	R
8	**14d**	2/1/0.5	23	**15d** (35)	(40)[a]	R
9	**14e**	3/1/0.5	24	**15e** (68)	(33)[a] (35)[c]	S
10	**14f**	3/1/0.5	29	**15f** (56)	(68)[a]	S

[a]The op was determined by polarimetry. [b]Assigned by comparisson with the sign of the specific rotation previously described. [c]The ee was determined by integration of the signals in the ^{19}F-NMR spectra in the Mosher derivatives. [d] The configuration was tentatively assigned by analogy to the other compounds.

In conclusion, enantioselective addition of Reformatsky reagents to carbonyl compounds is easily catalyzed by chiral β-amino alcohols. The extent of the enantioface discrimination varies with the structure of the chiral additive, whereas the sense of the induction depends on the stereochemistry at the stereocenters of the amino alcohols, and can be rationalized as previously reported for enantioselective additions of dialkylzincs.[14]

Experimental

General. The reactions were carried out in oven-dried glassware, under argon atmosphere, and using anhydrous solvents. Aldehydes and acetophenone, commercially available, were distilled prior to use. Reformatsky reagent was prepared from *tert*-butyl α-bromoacetate as previously described.[12] Chiral amino alcohols were prepared as previously described in the literature.[13, 15, 16] The ^{1}H-NMR (300 MHz) and ^{13}C-NMR (75 MHz) spectra were registered on a Bruker AC 300, using TMS as internal standard. ^{19}F-NMR spectra (282 MHz) were recorded on a Bruker ARX-300. IR spectra were recorded on a Philips PU 9706 Spectrometer, as film or KBr dispersion. Mass spectra were measured on a Hewlett-Packard 5988-A mass spectrometer by electronic impact at 70 eV. Optical rotations were measured on a Perkin-Elmer 241 Polarimeter in a 1 dm. cell. Products were isolated by column chromatography (silica gel, hexane/ethyl acetate: 5/1), and purified by bulb-to-bulb distillation or by recrystallization for **15b**.

Enantioselective Reformatsky Reaction using Chiral Aminoalcohols. A solution of carbonyl compound (2 mmol, 1 eq.) and aminoalcohol (1 mmol, 0.5 eq) in 6 mL anhydrous THF was cooled at 0°C and stirred for 20 minutes. Then the Reformatsky reagent was added via syringe and the mixture was stirred at that temperature until the reaction was finished (TLC) and then quenched with 6 mL of a 10% solution of hydrochloric acid. The organic layer was separated and the aqueous phase was extracted with ethyl acetate (3 x 10 mL). The combined organic layers were washed with brine, and dried over anhydrous Na_2SO_4. The solvents were eliminated on Rotavapor and the residue purified by column chromatography. The e.e. were determined by comparison of the specific rotations with the maximun values previously described: t-Butyl (S)- 3-hydroxy-3-phenylpropanoate (**15a**): $[\alpha]_D^{25}$ = -32.5 (c 2.0, $CHCl_3$) (75% ee).[7] t-Butyl (S)-3-hydroxy-3-(2-naphthyl)propanoate (**15b**): $[\alpha]_D^{25}$ = -26.9 (c 1.1, $CHCl_3$) (78% ee).[7] t-Butyl (R)-3-hydroxyhexanoate (**15d**): $[\alpha]_D^{25}$ = -13.6 (c 0.9, $CHCl_3$) (56% ee).[7] t-Butyl (R)-3-hydroxy-5-phenyl-4-pentenoate (**15e**): $[\alpha]_D^{25}$ = +10.2 (c 1.2, $CHCl_3$) (96% ee).[17] t-Butyl (S)-3-hydroxy-3-phenylbutanoate (**15f**): $[\alpha]_D^{25}$ = +8.2 (c 3.1, C_6H_6) (74% ee).[8] The e.e. for hydroxy esters **15c** and also **15a** and **15e** was determined by integration of the OCH_3 signals in ^{1}H-NMR spectra or CF_3 signals in ^{19}F-NMR spectra of the diastereomeric mixtures of ester derived from (R)-(+)-MTPA.[18]

t-Butyl (S)-3-hydroxy-3-phenylpropanoate (15a).[7] Colorless oil, b.p. 200-205 °C (1 mm Hg). Rf 0.19 (AcOEt / hexane : 1/8). ee = 78%; $[\alpha]_D^{23}$ = -33.8 (c=2, $CHCl_3$). IR (film): 3360, 1700 cm^{-1}. ^{1}H-NMR ($CDCl_3$): 1.45 (s, 9H), 2.63 (dd, 1H, J_1 = 16.3 Hz, J_2 = 4.8 Hz), 2.68 (dd, 1H, J_1 = 16.3 Hz, J_2 = 7.9 Hz), 3.46 (br s, 1H), 5.08 (dd, 1H, J_1 = 7.9 Hz, J_2 = 4.8 Hz), 7.24-7.40 (m, 5H). ^{13}C-NMR ($CDCl_3$): 28.0, 44.3, 70.3, 81.3, 125.7, 127.6, 128.4, 142.7, 171.7. (R)-(+)-MTPA ester: ^{19}F-NMR ($CDCl_3$): -72.15 (major diastereomer (S) at C-3); -71.86 (minor diastereomer (R) at C-3). MS, m/z (%): 222 (M^+, 1); 165 (41); 147 (18); 107 (100).

t-Butyl (S)-3-hydroxy-3-(2-naphthyl)propanoate (15b).[7] Colorless solid, m.p. 64-65 °C (from hexane). Rf 0.32 (AcOEt / hexane : 1/5). ee = 72%; $[\alpha]_D^{23}$ = -24.8 (c=1.1, $CHCl_3$). IR (film) : 3400, 1700 cm^{-1} ^{1}H-NMR ($CDCl_3$) : 1.45 (s, 9H), 2.71 (dd, 1H, J_1 = 16.4 Hz, J_2 = 5.3 Hz), 2.77 (dd, 1H, J_1 = 16.4

Hz, J_2 = 7.4 Hz), 3.58 (br s, 1H), 5.25 (dd, 1H, J_1 = 7.4 Hz, J_2 = 5.3 Hz), 7.43-7.84 (m, 7H). ^{13}C-NMR ($CDCl_3$): 27.9, 44.2, 70.4, 81.3, 123.7, 124.3, 125.7, 126.0, 127.5, 127.9, 128.1, 132.8, 133.1, 140.0, 171.7. MS, m/z (%): 272 (M^+, 9); 216 (26); 199 (13); 155 (100).

t-Butyl (S)-3-(4-chlorophenyl)-3-hydroxypropanoate (15c). Colorless oil, b.p. 225-230 °C (1mm Hg). Rf 0.25 (AcOEt / hexane : 1/5). ee = 67%; $[\alpha]_D^{23}$ = -25.4 (c=2, $CHCl_3$). IR (film) : 3400, 1705 cm^{-1}. ^{1}H-NMR ($CDCl_3$) : 1.45 (s, 9H), 2.59 (dd, 1H, J_1 = 16.5 Hz, J_2 = 5.8 Hz), 2.64 (dd, 1H, J_1 = 16.5 Hz, J_2 = 6.9 Hz), 3.59 (br s, 1H), 5.05 (dd, 1H, J_1 = 6.9 Hz, J_2 = 5.8 Hz), 7.28-7.34 (m, 4H). ^{13}C-NMR ($CDCl_3$): 27.9, 44.1, 69.6, 81.5, 127.0, 128.4, 133.1, 141.1, 171.5. (R)-(+)-MTPA ester: ^{19}F-NMR ($CDCl_3$): -72.08 (major diastereomer (S) at C-3); -71.81 (minor diastereomer (R) at C-3). MS, m/z (%): 256 (M^+, 2); 141 (100); 199 (65); 183 (29).

t-Butyl (R)-3-hydroxyhexanoate (15d).[7] Colorless oil, b.p. 100-102 °C (0.5 mm Hg). Rf 0.24 (AcOEt / hexane: 1/8). ee = 40%; $[\alpha]_D^{23}$ = -9.7 (c=0.9, $CHCl_3$). IR (film): 3430, 1700 cm^{-1}. ^{1}H-NMR ($CDCl_3$): 0.93 (t, 3H, J = 7.0 Hz), 1.35-1.55 (m, 4H), 1.46 (s, 9H), 2.31 (dd, 1H, J_1 = 16.3 Hz, J_2 = 8.8 Hz), 2.43 (dd, 1H, J_1 = 16.3 Hz, J_2 = 3.3 Hz), 3.16 (d, 1H, J = 3.8 Hz), 3.98 (m, 1H). ^{13}C-NMR ($CDCl_3$) : 13.9, 18.5, 28.0, 38.5, 42.3, 67.7, 81.0, 172.4.

t-Butyl (S)-3-hydroxy-5-phenyl-4-pentenoate (15e).[19] Colorless oil, b.p. 230-235 °C (1 mm Hg). Rf 0.34 (EtOAc/hexane : 1/5). ee = 35 %; $[\alpha]_D^{23}$ = -3.5 (c= 1.1, $CHCl_3$). IR (film) : 3420, 1710 cm^{-1}. ^{1}H-NMR ($CDCl_3$) : 1.46 (s, 9H), 2.52 (dd, 1H, J_1 = 16.1 Hz, J_2 = 7.6 Hz), 2.59 (dd, 1H, J_1 = 16.1 Hz, J_2 = 4.6 Hz), 3.30 (br s, 1H), 4.68 (m, 1H), 6.21 (dd, 1H, J_1 = 15.9 Hz, J_2 = 6.0 Hz), 6.65 (dd, 1H, J_1 = 15.9 Hz, J_2 = 1.1 Hz), 7.20-7.40 (m, 5H). ^{13}C-NMR ($CDCl_3$): 28.0, 42.5, 68.9, 81.3, 126.4, 127.5, 128.4, 130.2, 130.3, 136.5, 171.5. (R)-(+)-MTPA ester: ^{19}F-NMR ($CDCl_3$): -72.02 (major diastereomer (S) at C-3); -71.87 (minor diastereomer (R) at C-3). MS, m/z (%): 248 (M^+, 3); 133 (100); 174 (62).

t-Butyl (S)-3-hydroxy-3-phenylbutanoate (15f).[8] Colorless oil, b.p. 145-150 °C (1 mm Hg). Rf 0.24 (CH_2Cl_2/ pentano 3:1). ee = 68%; $[\alpha]_D^{23}$ = +7.5 (c=3.1, C_6H_6). IR (film) : 3470, 1695 cm^{-1}. ^{1}H-NMR ($CDCl_3$) ; 1.28 (s, 9H), 1.52 (s, 3H), 2.70 (d, 1H, J=15.5 Hz ; 2.88 (d, 1H, J=15.5 Hz), 4.50 (br s, 1H), 7.20-7.50 (m, 5H). ^{13}C-NMR ($CDCl_3$) : 27.8, 30.7, 47.5, 72.9, 81.6, 124.6, 126.7, 128.0, 146.9, 172.0. MS, m/z (%): 236 (M^+,1); 165 (43); 121 (100).

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References and Notes

§ Dedicated to Professor Wolfgang Oppolzer, in memoriam.

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