Diastereoselective addition of allylmetal compounds to imines derived from (*S*)-1-phenylethanamine

Giuseppe Alvaro,[a] Carla Boga,[b] Diego Savoia *,[a] and Achille Umani-Ronchi[a]

[a] *Dipartimento di Chimica 'G. Ciamician', Università di Bologna, via Selmi 2, 40126 Bologna, Italy*

[b] *Dipartimento di Chimica Organica 'A. Mangini', Università di Bologna, Viale Risorgimento 4, 40136 Bologna, Italy*

The sense of asymmetric induction and the degree of diastereoselectivity in the addition of allylmetal compounds to imines derived from aldehydes and (*S*)-1-phenylethanamine is affected by the nature of the imine and of the metal. Allyl-BBN, -MgX, -ZnBr, -Cu, and diallylcuprate attacked the *Si* face of the imine derived from 2-methylpropanal. Conversely, the *Re* face of aromatic aldimines was generally attacked, but the behaviour of the magnesium reagent was variable. Best results were achieved with allyl-BBN and diallyl cuprate (de up to 98% at −78 °C) with both aliphatic and aromatic imines. However, the use of allylzinc bromide and allyl(dichloro)iodotin was preferable with the bidentate pyridine-2-imine (de 70%, *Re* face addition). The cleavage of the chiral auxiliary (ammonium formate–palladium on carbon–methanol, 65 °C, 2 h) occurred regioselectively, with concomitant hydrogenation of the unsaturated chain, only on the dibenzylic amine obtained by the reactions of (*S*)-2,5-dimethoxybenzaldimine with allyl-BBN (de 94%) and diallyl cuprate (de 99%). This allowed the expeditious and efficient synthesis of (*R*)-(+)-1-(2,5-dimethoxyphenyl)butanamine (80% overall yield) and, at the same time, the confident assignment of the configuration to the homoallylic amines obtained from the aromatic aldimines, previously undetermined. The opposite sense of asymmetric induction observed in the reaction of aliphatic *vs.* aromatic aldimines was attributed to the isomerization of *E*- to *Z*-aromatic imines prior to the C–C bond formation. Several six-membered chair or boat cyclic transition states, featuring different dispositions of the auxiliary and π-stacking of aryl groups, have been empirically examined.

Homochiral 1-arylethanamines are widely used as auxiliaries in the asymmetric synthesis of organic compounds,[1] owing to the availability of both enantiomers and the easy removal of the auxiliary 1-arylethyl group.[2] For example, the diastereoselective addition of nucleophiles, hydrogen, and 1,3-dienes to imines and iminium ions derived from these auxiliaries has been reported.[1]

In the organometallic domain, the addition of allylmetal compounds to homochiral imines to give homoallylic amines[3] is of particular interest, owing to the many possible transformations of the C=C double bond of the allyl group. Up to now, the usefulness of 1-phenylethanamine as a chiral auxiliary in these reactions has been investigated for the imines **1–6** (Fig. 1). In the addition to **1** *B*-allyl-9-borabicyclononane (allyl-BBN) afforded a better selectivity than allylmagnesium bromide and allyl(tributyl)tin–$TiCl_4$.[4] Allyl-BBN[5] and allyl(trichloro)tin[6] added to **2** with good diastereoselectivity, whereas allylzinc bromide[5] worked unsatisfactorily.

The allylation of **1** with different allylmetal species, as well as of **2** with allyl-BBN, followed the same direction of asymmetric induction: when the configuration of the nitrogen auxiliary was *R*, the *Re* face of the imine was attacked, and *vice versa*. Conversely, allyl(trichloro)tin added to the *Re* face of (*S*)-**2**.[6] Furthermore, although the configuration of the product coming from the double addition of allylmagnesium chloride to the bis-imine **3** was not determined, it was thought likely that attack occurred at the *Re* face.[7]

The stereochemical outcome was different in allylation of the imines **4–6** which have further α- and/or β-stereocentres and oxygen substituents. In the allylation of **4**[8] and **5**[9] the chirality of the alkoxy-substituted α-stereocentre (1,2-asymmetric induction) overrode the influence of the nitrogen auxiliary (1,3-asymmetric induction), so that the diastereoselectivity could be controlled by the proper choice of either the metal or the reaction conditions (chelation *vs.* non-chelation control). On the other hand, the auxiliary chirality affected the stereocontrol on **6a,b**,[8] but the facial selectivity was the reverse of that observed with **1–3**, since the attack to the *Re* face was observed with the *S* auxiliary, and *vice versa*.

Notably, the allylation of aromatic aldimines has not been reported, apart from the Barbier reaction of the benzaldimine **7** with allyl bromide and indium powder which gave the

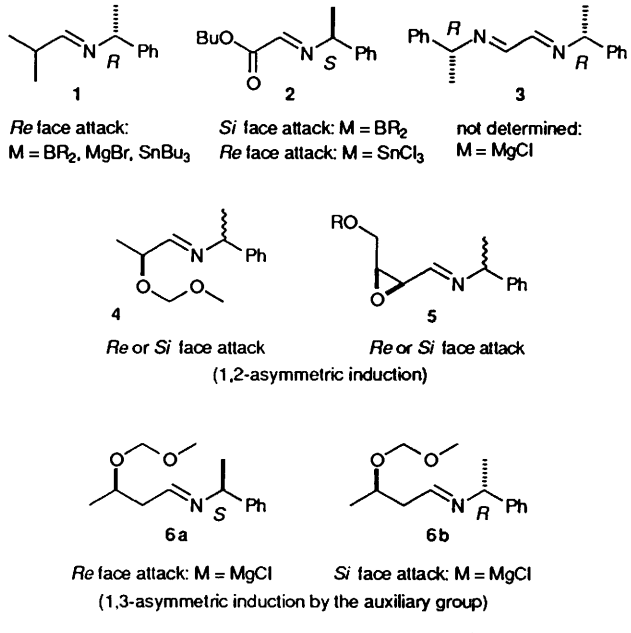
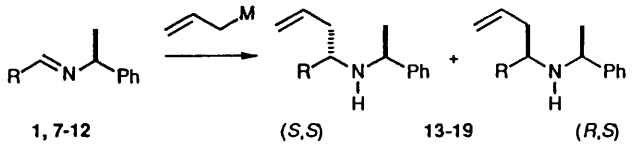


Fig. 1 Diastereoface-differentiating (*Re*/*Si*) addition of allyl-M to imines derived from (*S*)- or (*R*)-1-phenylethanamine

homoallylic amine **14** with moderate diastereoselectivity (dr 80:20), but with undetermined configuration.[10]

Results and discussion

As the influence of the structural and electronic features of the imine (the parent aldehyde) on the diastereoselectivity had not been fully investigated, we examined the reactions of the imines **1** and **7–12** with a variety of allylmetal compounds at −78 °C,[11] in which the homoallylic amines **13–19** (Scheme 1 and Table 1)



1, **13**: R = Pr^i
7, **14**: R = Ph
8, **15**: R = 4-Pyridyl
9, **16**: R = 3-Pyridyl
10, **17**: R = 2-Pyridyl
11, **18**: R = 4-MeOC$_6$H$_4$
12, **19**: R = 2-MeOC$_6$H$_4$

Scheme 1

were formed. Diethyl ether was the solvent of choice for allyl-BBN, and tetrahydrofuran (occasionally diethyl ether) for all the other allylmetal reagents. The diastereoisomeric ratio (dr) of the products was determined by GC–MS analysis. The variation of the dr with time, for reactions carried out at 25 °C, indicated the reversibility of the addition of allylzinc bromide to all the imines, and of allylmagnesium chloride to the aliphatic imine **1**. We have recently reported that the addition of allylzinc bromide to the imines derived from aromatic aldehydes and methyl (*S*)-valinate is reversible.[12]

Allylation of the aliphatic imine 1

By using allyl-BBN in Et_2O we obtained (*S*,*S*)-**13** with excellent stereocontrol (dr 93:7), thus confirming an earlier report,[4] although in our work the compound was prepared by a simpler procedure and not purified by distillation. Subsequently, we observed that the reaction of allylmagnesium chloride in tetrahydrofuran gave better diastereoselectivity (dr 90:10) than the previously reported reaction of allylmagnesium bromide in diethyl ether.[4] Allylzinc bromide reacted sluggishly and with modest diastereoselectivity. Allylcopper displayed a diastereoselectivity comparable to that of allylmagnesium bromide whilst diallylcuprate proved to be a reagent superior even to allyl-BBN, and afforded the homoallylic amine (*S*,*S*)-**13** with dr 95:5.

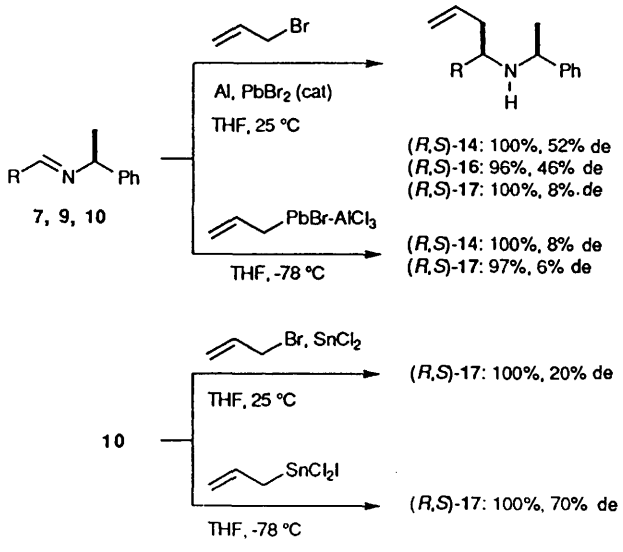
Allylation of the aromatic imines 7–12

The sense of asymmetric induction as well the degree of stereocontrol were dependent on the nature of both the metal and the imine, whilst the solvent played a role in the reactions of the Grignard reagents. In the reactions performed on the benzaldimine **7**, excellent diastereoselectivity was obtained with allyl-BBN, whereas allylmagnesium halides and allylzinc bromide (sluggish reaction) gave low diastereoselectivity. Surprisingly, allylmagnesium chloride gave the opposite sense of asymmetric induction with respect to the other allylmetal reagents, including allylmagnesium bromide in ether. Allyl-BBN was also the most selective reagent with the other aromatic imines **7–12** (Table 1), apart from the bidentate pyridine-2-imine **10**. Diallylcuprate was generally preferable to allylcopper, and moderate diastereoselectivity was generally achieved (de up to 72%).

The addition to both the azomethine group and the pyridine ring and low diastereoselectivity were observed in the addition of allylmagnesium chloride to **8** and **9**, whilst the sense of asymmetric induction was inverted in the corresponding addition to **10**. The diastereoselectivity was very low in the reaction of allylcopper with **10**. However, with this imine allylzinc bromide worked satisfactorily, even better than allyl-BBN, although the diastereoselectivity was far from good.

The reactivity of allylzinc bromide was affected by the electronic effects of the aryl substituents: an immediate reaction took place with the pyridineimines **8–10**, although no product could be observed with the 4-methoxybenzaldimine **11** at −78 °C: **18** was obtained by allowing the reaction mixture to reach 25 °C overnight, so that the diastereoisomeric ratio at equilibrium was then determined.

We also applied several different Barbier procedures to the imines **7**, **9** and **10** and always obtained a low to moderate preponderance of the *Re* face addition products. The best results were achieved by generating the allylmetal species *in situ* from allyl bromide and the bimetal redox system Al/$PbBr_2$ (cat.),[12] or from allyl iodide and tin dichloride[13] (Scheme 2).



7, **14** : R = Ph
9, **16** : R = 3-Pyridyl
10, **17**: R = 2-Pyridyl

Scheme 2

The homoallylic amines **13**, **14**, but not **17**, were obtained with moderate diastereoselectivity by the first method. Notably, the formation of **17** from **10** required the use of 1.1 equiv. of $PbBr_2$, because the complexation of the imine with this salt moves the reduction potential to a more negative value. Aiming to improve the diastereoselectivity, we performed the reaction by following the corresponding Grignard procedure. Thus, we prepared allyllead bromide from allylmagnesium chloride and $PbBr_2$, after which we added $AlCl_3$ and the imines **7** and **10** to the organometallic reagent at −78 °C; unexpectedly, **14** and **17** were obtained with low stereocontrol. Disappointing results were also achieved on replacing $AlCl_3$ with BF_3.

In contrast, when allyl(dichloro)iodotin was generated at room temperature, by the oxidative addition of tin dichloride to allyl iodide in the presence of the imine **10**, a rapid reaction took place giving **16** with moderate diastereoselectivity (Scheme 2). The corresponding reaction performed by the Grignard procedure, *i.e.* with the preformed allyltin reagent at −78 °C, gave a slightly improved diastereoselectivity. Unfortunately, no reaction occurred between allyl(dichloro)iodotin and the other imines, by following either the Grignard or Barbier procedures.

Mechanisms

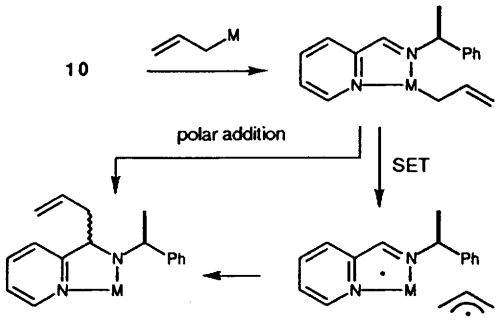
The addition of allylic organometallic reagents to imines usually proceeds through preliminary N–metal coordination, after

Table 1 Preparation of the homoallylic amines **12–17** by addition of allylmetals to the imines (*S*)-RCH=NCH(Me)Ph **1** and **7–11**[a]

		Products and diastereoisomeric ratios *S,S*/*R,S*						
Allylmetal (equiv.)	Solvent	**13** from **1** R = Pr^i	**14** from **7** R = Ph	**15** from **8** R = 4-Pyridyl	**16** from **9** R = 3-Pyridyl	**17** from **10** R = 2-Pyridyl	**18** from **11** R = 4-MeOC$_6$H$_4$	**19** from **12** R = 2-MeOC$_6$H$_4$
C_3H_5BBN (2)	Et_2O	93:7[b]	3:97[b]	3:97	7:93	25:75	7:93	3:97
C_3H_5MgCl (1.5)	THF	90:10[c]	65:35 (39:61)[d]	42:58[e]	45:55[e]	56:44	60:40[c]	30:70 (21:79)[d]
C_3H_5ZnBr (3)	THF	75:25[c,f]	33:67[c,f]	40:60[c,f]	30:70[c]	13:87[c]	75:25[g]	25:75[c,f]
$C_3H_5Cu{\cdot}MgICl$ (3)	THF	89:11	30:70	20:80	22:78	48:52	26:74	24:76
$(C_3H_5)_2CuMgCl{\cdot}MgICl$ (3)	THF	95:5	17:83	15:85	14:86	33:67	26:74	17:83

[a] The reactions, generally performed by adding the imine to the allylmetal at −78 °C, were followed by GC–MS analysis and quenched when complete by the addition of aqueous sodium hydroxide to the reaction mixture. Aliphatic and aromatic homoallylic amines had the reverse order of elution for *S,S* and *R,S* diastereoisomers. [b] Allyl-BBN was prepared from allylaluminium sesquibromide and *B*-methoxy-9-BBN following a simplified procedure and was not distilled prior to use, so that it probably contained some dissolved aluminium salts. [c] Worse ratios, sometimes inverted, were observed upon warming the reaction mixtures to 25 °C during 12 h before quenching. [d] The reaction was performed with allylmagnesium bromide in Et_2O. [e] The yield was < 50% for the addition to the pyridine ring. [f] The conversion of the imine was incomplete after 3 h at −78 °C: **13**, 10%; **14**, 40%; **18**, 0%; **19**, 60%. [g] No product was observed after 3 h at −78 °C, so the reaction mixture was warmed to 25 °C overnight before quenching.

which the C–C bond-forming step usually takes place *via* a cyclic transition state. However, the reactions between allylmetal reagents having polarized a carbon–metal bond and aromatic imines, especially those activated by electron-withdrawing substituents, can proceed through a single electron transfer (SET) mechanism. In Scheme 3 we have considered the



Scheme 3

most intriguing case of the bidentate imine **10**, which forms chelation complexes with organometallic reagents. Interestingly, when allylmagnesium halide and allylzinc bromide were added to the pyridineimines **8**–**10**, the mixtures became deep red, a phenomenon which we attributed to the presence of imine radical-anions formed by the SET mechanism. We observed the same colour at the cathode (Pt) surface during the electrochemical reduction of the corresponding acetophenone imine in THF, as well as in the electrochemically promoted allylation[14] of the imines **7**, **9** and **10** with allyl bromide in THF.† We believe that the SET mechanism, although favoured for the pyridineimines **8**–**10**, took place only partially. In general, ring-allylation products and 1,2-diamines, which should be produced by the coupling of the allyl radical and the imine radical anion, were not observed.‡

However, the complex **10**•allylzinc bromide is coloured as the result of a long wavelength charge-transfer band arising from the transition of a d electron of the metal to the LUMO orbital of the ligand; this also occurs in 2,2′-bipyridyl- and 1,2-diimine-metal complexes.[15] In the case of 1,2-diimine-dialkylzinc complexes the C–C bond-forming step occurred by a SET mechanism but required heat or irradiation.[16] For the reaction of **10** with allylzinc bromide, the homolytic cleavage of the allyl–metal bond is relatively easy, owing to the stability of the allyl radical formed; the radical coupling step then occurs most likely at the azomethine carbon rather than at the pyridine ring.

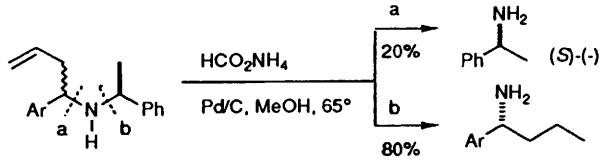
It is probable that lower stereocontrol is achieved when the reaction follows a SET mechanism: in fact, the more reducing Grignard reagents were less diastereoselective than the zinc, copper and tin reagents, especially on pyridyl imines, but proved more selective on the aliphatic imine **1**, which underwent polar addition exclusively. On the other hand, the formation of the chelation complexes generally had a beneficial effect on the diastereoselectivity.

Configuration of the newly created stereocentre

The *R*,*R* configuration of the prevalent diastereoisomer of the homoallylic amine **13** obtained from (*R*)-**1** and allyl-BBN had earlier been established by chemical correlation with authentic (*R*)-5-methylhexan-4-amine.[4] GC–MS analysis of the diastereoisomeric mixture showed that the predominant diastereoisomer (*S*,*S*)-**13** was eluted second. The same sense of asymmetric induction was observed in the corresponding reactions with allyl-magnesium, -zinc and -copper species.

Initially, we were encouraged to assume the same sense of asymmetric induction occurred in the addition of allyl-BBN to the aromatic imines, since GC–MS analysis of the homoallylic amines showed the prevalence of the second eluted diastereoisomers. However, the dr of **14** in the reactions of **7** with allylmagnesium reagents was occasionally inverted. Therefore, it became necessary to establish unambiguously the configuration of the homoallylic amines derived from aromatic imines.

We assigned the *S*,*S* configuration to the first eluted diastereoisomer of **14** because after C=C double bond hydrogenation of crude **14** (dr 65:35) obtained from **7** and allylmagnesium chloride the product was identical (GC–MS comparison) with that obtained by the addition of di-propylcuprate•BF_3 to **7**; this reaction had earlier been assumed to provide a preponderance of the *S*,*S* diastereoisomer.[11] Moreover, further studies showed that there was a preponderance of (*R*,*S*)-**18** and (*R*,*S*)-**19** (second eluted diastereoisomers) in their respective reaction mixtures, established by hydrogenolysis of the auxiliary group, which occurred with concomitant hydrogenation of the unsaturated chain (Scheme 4). However, the regioselectivity of the



18: R = 4-MeO C_6H_4, dr = 15:85
19: R = 2-MeO C_6H_4, dr = 21:79

(+)-(*R*)-**20**: Ar = 4-MeOC_6H_4
(+)-(*R*)-**21**: Ar = 2-MeOC_6H_4

Scheme 4

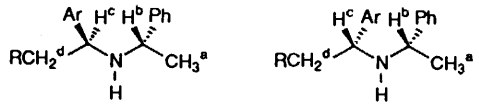
benzylic cleavage was unsatisfactory. GC–MS analysis of the reaction mixtures showed the presence of 1-phenylethanamine and of 2- or 4-butylanisole, coming from the hydrogenolysis at the undesired site, together with the desired primary amines **20** and **21**. Similar results were previously reported in the hydrogenolysis of analogous dibenzylamines [RC_6H_4(Me)CHNHCH(Me)Ph] derived from 1-phenylethanamine: the presence of only one substituent (R = Me, F) in the aryl group was not sufficient to achieve complete regioselectivity, or resulted in the cleavage at the undesired site (R = NHMe).[2b] Since, after separation of the neutral products, the crude mixtures of the bases were dextrorotatory, and (*S*)-(−)-1-phenylethanamine was present as the minor component, the amines **20** and **21** were found to be dextrorotatory and, consequently, have the *R* configuration; in this respect they were similar to known (+)-1-arylethanamines.[17]

The configuration of the diastereoisomeric homoallylic amines derived from aryl-substituted imines can then be assigned simply by GC–MS analysis, since the *S*,*S* diastereoisomers are eluted first.§ ^{1}H NMR analysis of the diastereoisomeric mixtures can also be usefully applied to determine the configuration. By analogy with the known bis(1-arylalkyl)amines **22**[11,18] and **23**[18] (Fig. 2) the *S*,*S* diastereoisomers of compounds **13**–**19** gave signals for the benzylic, allylic and methyl protons at higher fields than the *R*,*S* diastereoisomers. This was explained[18] by assuming a zig-zag conformation together with *anti* and *syn* disposition of the aryl groups in the *S*,*S* and *R*,*S* diastereoisomers, respectively. Hence, in *anti*-(*S*,*S*)-**14**–**19**, each benzylic hydrogen is subjected to the ring current effect of the non-adjacent aryl group. The ^{1}H NMR spectra of the (*S*,*S*)- and (*R*,*S*)-**13** differed signifi-

† Unpublished results from our laboratory: we used Al wire as the anode, Pt as the cathode, $PbBr_2$ as a catalyst, and tetrabutylammonium bromide as the support electrolyte. The (*R*,*S*)-homoallylic amines **14**, **16** and **17** were obtained with a low to moderate diastereoselectivity.

‡ The reaction of the imine **10** with allyllithium in THF at −78 °C produced (*R*,*S*)-**17** with 48% de and small amounts of imine dimers.

§ The reverse order of elution was observed for (*S*,*S*)- and (*R*,*S*)-**13**.



anti - S,S **14-19**: R = $CH{=}CH_2$ *syn - R,S*
22: Ar = Ph; R = H
23: Ar = 2-Pyridyl; R = H

Compd. (Ar)	Order of GC elution	Confign.	δ (ppm, 300 MHz) H_a (d)	H_b (q)	H_c	H_d
22[a]	1st	*S,S*	1.24	3.47	—	—
	2nd	*R,S*	1.34	3.70	—	—
23[a]	1st	*S,S*	1.23	3.27	3.50	1.26
	2nd	*R,S*	1.37	3.27	3.50	1.37
23	1st	*S,S*	1.24	3.45	3.59	1.32
	2nd	*R,S*	1.37	3.78	3.84	1.37
14 (Ph)	1st	*S,S*	1.30	3.50[b]	3.50[b]	2.35
	2nd	*R,S*	1.36	3.76[b]	3.76[b]	2.48
15 (4-Py)	1st[c]	*S,S*	1.31	3.39	3.48	2.27
	2nd[d]	*R,S*	1.36	3.51	3.80	2.41
16 (3-Py)	1st[e]	*S,S*	1.33	3.47[b]	3.47[b]	2.37
	2nd[f]	*R,S*	1.41	3.77	3.83	2.50
17 (2-Py)	1st[g]	*S,S*	1.29	3.47	3.52	2.42
	2nd[h]	*R,S*	1.38	3.76	3.86	2.54
18 (4-$MeOC_6H_4$)	1st	*S,S*	1.28	3.34	3.50	2.32
	2nd	*R,S*	1.35	3.72[b]	3.72[b]	2.45
19 (2-$MeOC_6H_4$)	1st	*S,S*	1.27	3.55	3.74	2.40
	2nd	*R,S*	1.33	3.68	4.15	2.50

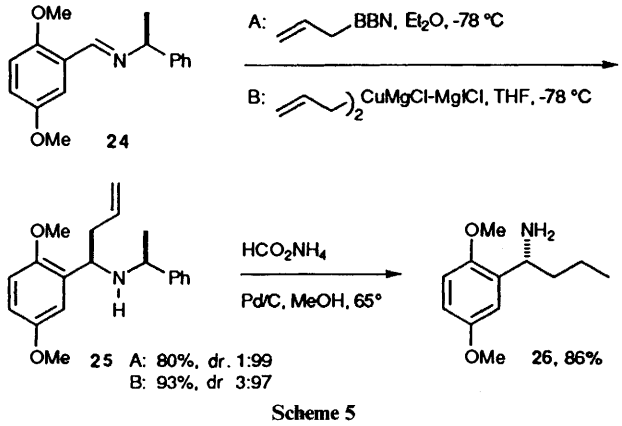
[a] 60 MHz. [b] The H_b and H_c signals (m) were not separated. [c] Pyridyl H: δ 8.76 (m, 2 H) and 7.47 (m, 2 H). [d] Pyridyl H: δ 8.62 (m). [e] Pyridyl H: δ 8.56 (m, 1 H), 7.67 (m, 1 H) and 7.38 (m, 2 H). [f] Pyridyl H: δ 8.48 (m, 2 H) and 7.63 (m, 1 H). [g] Pyridyl H: δ 8.61 (m, 1 H) and 7.62 (m, 1 H). [h] Pyridyl H: δ 8.54 (m, 1 H) and 7.65 (m, 1 H).

Fig. 2 Correlation between configuration, order of GC elution, and ^1H NMR signals of the diastereoisomers of bis(1-arylalkyl)amines

cantly only in respect of their vinylic, allylic and methine signals.

Synthesis of (*R*)-1-(2,5-dimethoxyphenyl)butan-1-amine

Aiming to develop a convenient synthetic route to optically active α-aryl substituted amines, we thought that the obstacle of the non-selective cleavage of the chiral 1-phenylethyl auxiliary could be overcome using more substituted arylimines.[2b] Therefore, we carried out the addition of allyl-BBN and diallylcuprate to 2,5-dimethoxybenzaldimine (*S*)-**24** and, in both cases, obtained the homoallylic amine (*R,S*)-**25** with excellent diastereoselectivity (Scheme 5). The successive



Scheme 5

hydrogenolysis was completely regioselective and afforded the primary homoallylic amine (*R*)-(+)-**26** in good yield.

Stereochemical models for the asymmetric induction

Aiming to explain the differences in stereochemical outcome of the reactions of aliphatic and aromatic imines, we examined several possible transition states (see Fig. 3). In the absence of

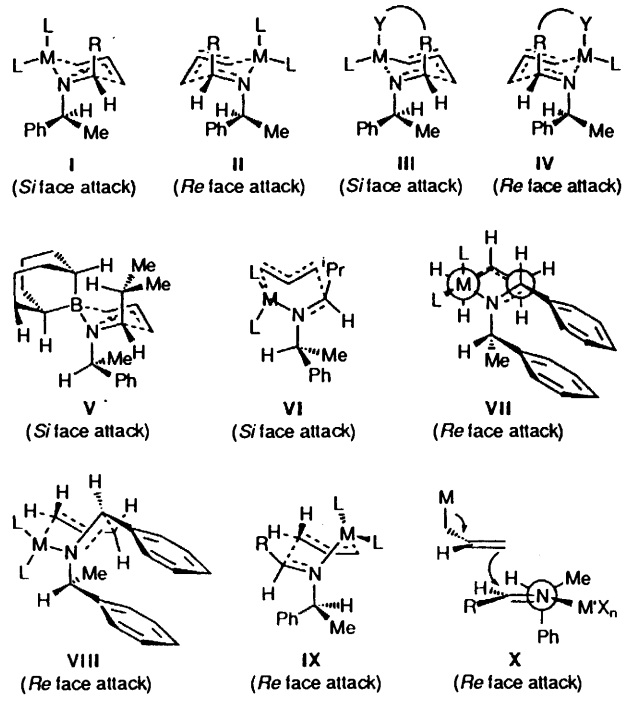


Fig. 3 Transition states for the allylation of imines derived from (*S*)-1-phenylethanamine

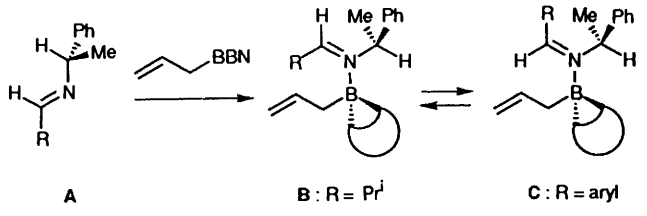
Lewis acids the homoallylic amines are produced from the allylmetal-imine complexes *via* six-membered cyclic transition states.¶

¶ For practical reasons, a tetracoordinated metal is represented in the transition states, but this is only a simplification: for example, in the reactions of allyltin trihalide with **10** the number of ligands on tin is six.

The *Si* and *Re* face of the imine are attacked in the chair transition states **I** and **II**, respectively, both of which are characterized by the orientation of the H atom of the auxiliary towards the inside of the chair transition structure, but differ for the non-bonded interactions of the Ph and Me groups with the metal ligand L. Analogous models and similar arguments were advanced to explain the diastereoselectivity of α-chiral boron enolate aldol reactions.[19] Although the transition state **I** attempts to explain the *Si* face addition of allyl-BBN to the aliphatic imine **1**,[4] in our opinion, transition state **II** was insufficiently taken into account since in the reaction described **I** is disfavoured with respect to **II**; this is because the Ph group, considered larger than Me, is orientated towards the bulky ligand of boron. In view of this, the observed diastereoselectivity must be explained by other transition states.

Our hypothesis was supported by the stereochemical outcome of the reactions of the bidentate imines **10** and **12**, which generally underwent *Re* face addition. We assume that the allylmetal reagents, apart from boron, and the imines **10**, **12** and **24** form chelation complexes, from which the chair transition states **III** and **IV** can be constructed.‖ These do not suffer from the 1,3-diaxial repulsive interaction (R *vs.* L) present in **I** and **II**, since it is replaced by a bonding interaction. In fact, **IV** gives a correct prediction for the configuration, *R*, of the newly formed stereocentre.** By analogy, **II** should be preferred to **I**. Hence, we believe that the *Si* face addition to the aliphatic imine (*S*)-**1**, as well as the *Re* face addition to the aromatic (*S*)-imines cannot be explained by the transition states **I** or **II**.

We propose that the reaction of imines with allyl-BBN proceeds as described in Scheme 6. The imines exists



Scheme 6

preferentially in conformation **A** where the hydrogen atoms of the azomethine and auxiliary group are *syn* orientated, as we verified by NOE experiments. However, after complexation with allyl-BBN, the imines assume conformation **II** by rotation of the N–C (auxiliary) bond in order to avoid the severe steric interactions of Me and Ph with the boron ligands. When R = Pr^i the C–C bond-forming step can take place either *via* the chair transition state **V** (Fig. 3), in which Me is orientated inside and the small H interacts with the boron ligand, or a boat transition state, *e.g.* **VI**, in which Ph is orientated outside. We prefer **VI** because all the steric interactions are apparently reduced. Conversely, when R is an aryl group (co-planar to the azomethine group), both conformations **A** and **B** are destabilized by the collision of the *ortho*-aryl hydrogen with any boron ligand. The imine should then isomerize to the *Z* configuration, while probably maintaining the conformation of the auxiliary as shown in **C** (Scheme 6). The *E*/*Z* isomerization of imines was previously proposed to explain the diastereoselective addition of crotylboranes[21] and boron enolates[22] to imines. The correct sense of asymmetric induction in the addition to the aromatic imines, *e.g.* the benzaldimine **7**, is then given by the chair and boat transition states **VII** and **VIII**, in which the two Ph groups take a quasi-parallel orientation to reduce the steric interaction, or even to achieve some stabilization by π stacking.††[23]

The boat transition state **IX** can be also examined, since theoretical studies[24] have demonstrated that analogous boat transition states are preferred in the addition of lithium acetaldehyde enolate,[24a] α-hydroxyacetic acid lithium enolate,[24b] and the Reformatsky reagent of methyl bromoacetate[24c] to methanimine. However, in the reactions of allyl-BBN transition state **IX** would suffer from the strong interaction of the bulky boron ligand with the opposing vinylic hydrogen atom.

The same arguments and transition states can be applied to the reactions of the aliphatic and aromatic aldimines with diallylcuprate, which exhibited, surprisingly, a comparable diastereoselectivity to allyl-BBN. The better diastereoselectivity of diallylcuprate with respect to allyl-copper, -zinc and -magnesium reagents can be attributed, in part, to the increased number of covalently bound ligands on the metal in the cyclic transition state(s). Furthermore, the covalent radius of copper is shorter than those of zinc and tin, so that the cyclic transition states involving copper are more compact, and the steric interactions affecting the diastereoselectivity are more effective. At the same time, the nature of the metal, and the number and the bulkiness of the ligands on the metal should also affect the degree of *E*/*Z* isomerization of the imine and, consequently, the diastereoselectivity.

Finally, the acyclic Felkin-type transition state **IX** satisfactorily rationalizes the diastereoselectivity of the addition of allyllead bromide to imines mediated by aluminum salts, but the higher stereocontrol obtained at 25 °C (Barbier procedure) rather than at −78 °C (Grignard procedure) is surprising (Scheme 2). Different orgametallic species and/or different mechanisms are, perhaps, involved in the alternative procedures.

Experimental

General conditions

Solvents were distilled in an argon atmosphere prior to use: Et_2O and THF were over distilled successively over sodium benzophenone ketyl and $LiAlH_4$. Optical rotations were measured on a digital polarimeter in methanol solution in a 1 dm cell and $[\alpha]_D$ values are given in 10^{-1} deg cm^2 g^{-1}. Elemental analyses were performed on a Model 1106 microanalyser (Carlo Erba). UV spectra were recorded on a Perkin-Elmer Lambda 6 spectrophotometer. IR spectra of neat compounds were obtained with a Nicolet 205 FT spectrometer and are expressed by wavenumber (cm^{-1}). ^{1}H NMR spectra were recorded on a Varian Gemini 300 instrument at 200 or 300 MHz in $CDCl_3$ which was stored over Mg. ^{1}H Chemical shifts are reported in ppm relative to $CHCl_3$ (δ 7.27). *J* Values are given in Hz. MS spectra were taken at an ionizing voltage of 70 eV on a Hewlett-Packard 5971 spectrometer with GC injection. Chromatographic purifications were carried on columns of silica gel Merck, 230–400 mesh) at medium pressure. (*S*)-(−)-1-Phenylethanamine (ee 99%), *B*-methoxy-9-BBN, allylmagnesium chloride (2 mol dm^{-3} in THF), and copper(I) iodide (99.999%), tin(II) chloride (99.99%) and allyl iodide (98%) were purchased from Aldrich. All the organometallic reactions were performed

‖ Several analogous bicyclic transition states were reported in the literature. However, the reaction of zinc enolates derived from α-amino esters with 1,2-diimines was assumed to proceed *via* the transition state attained from the monodentate imine-zinc enolate complex rather than from the bidentate imine complex.[20]

** Notably, the same sense of asymmetric induction that we have observed with **10** and **12** has been recently found in the addition of allyl(trichloro)tin to the bidentate imine (*S*)-**2** (*Re* face addition).[6] We also predict that the addition of allylmagnesium bromide to the bisimine (*R*,*R*)-**3** will occur to the *Si* face, the reverse of the predicted *Re* face attack.[7]

†† π Stacking effects, locking one conformation of reactants preferentially in one transition state assembly, are increasingly exploited to achieve asymmetric induction with chiral auxiliaries and catalysts.

in a flame-dried apparatus under a static atmosphere of dry nitrogen.

Preparation of the imines

Anhydrous $MgSO_4$ (10 g) and the aldehyde (50 mmol) were added to a solution of (*S*)-1-phenylethanamine (50 mmol) in THF (50 cm^3) at 0 °C and the mixture was stirred by a magnetic bar for 3 h. The solid phase was filtered off and the filtrate was evaporated under reduced pressure to leave the crude (*E*)-imine, which was obtained both in almost quantitative yield and pure, as inferred by GC–MS and ^1H NMR analyses. The imines were generally used in subsequent reactions without purification. The imines **1**,[4] **7**,[10,25,26,27,28] **8**,[26] **9**,[26,29] **10**,[26,30] **11**[26,28] and **12**[25,27] are known compounds.

(*S*)-*N*-(2-Methylpropylidene)-1-phenylethanamine 1. This compound was 93% pure by GC analysis, the main impurities being the starting reagents: $[\alpha]_D^{25}$ −76 (*c* 1.89 in $CHCl_3$); ν_{max}/cm^{-1} 1665 (C=N); δ_H(200 MHz) 7.60 (1 H, d, *J* 5.6, CH=N), 7.4–7.2 (5 H, m, Ph), 4.26 (1 H, q, C*H*Ph), 2.48 (1 H, m, C*H*Me_2), 1.48 (3 H, d, *J* 6.7, CH*Me*Ph), 1.10 and 1.07 (6 H, 2 d, *J* 7.2, CH*Me*$_2$); *m*/*z* 105 (100), 106 (14), 77 (14), 79 (11), 103 (9), 147 (7), 104 (6) and 132 (4).

(*S*)-*N*-Benzylidene-1-phenylethanamine 7. This compound had $[\alpha]_D^{25}$ +75 (*c* 0.88 in $CHCl_3$) {lit.,[23] +73.3 (*c* 1.6 in $CHCl_3$), lit.,[28] $[\alpha]_D^{22}$ −76 (*R* enantiomer)} λ_{max}(hexane)/nm 246 (ε/dm^3 mol^{-1} cm^{-1} 20 769); ν_{max}/cm^{-1} 1640 (C=N); δ_H(300 MHz) 8.30 (1 H, s, CH=N), 7.72 (2 H, m, ArH) 7.4–7.1 (8 H, m, ArH), 4.49 (1 H, q, C*H*Me) and 1.55 (3 H, d, *J* 6.7, CH*Me*); *m*/*z* 209 (M^+, 41%), 105 (100), 77 (20), 51 (10), 167 (5) and 165 (5).

(*S*)-*N*-(4-Pyridylmethylidene)-1-phenylethanamine 8. This compound had $[\alpha]_D^{25}$ +27.1 (*c* 1.1, $CHCl_3$); ν_{max}/cm^{-1} 1645 (C=N); δ_H(200 MHz) 8.70 (2 H, d, *J* 4.5, pyridyl), 8.36 (1 H, s, CH=N), 7.67 (2 H, d, *J* 4.5, pyridyl), 7.5–7.2 (m, 5 H, m, Ph), 4.60 (1 H, q, C*H*Me), 1.85 (1 H, br, NH) and 1.61 (3 H, d, *J* 6.6, CH*Me*); *m*/*z* 210 (M^+, 4%), 105 (100), 106 (8), 79 (7), 77 (6) and 51 (5).

(*S*)-*N*-(3-Pyridylmethylidene)-1-phenylethanamine 9. This compound had $[\alpha]_D^{25}$ +62.1 (*c* 2.1 in $CHCl_3$) {lit.,[28] $[\alpha]_D^{24}$ +65.6 (*c* 1.0 in $CHCl_3$)}; ν_{max}/cm^{-1} 1645 (C=N); δ_H(300 MHz) 8.87 (1 H, s, CH=N), 8.63 (1 H, m, pyridyl), 8.40 (m, 1 H, pyridyl), 8.17 (1 H, m, pyridyl), 7.42 (1 H, m, pyridyl), 7.40–7.20 (5 H, m, Ph), 4.55 (1 H, q, C*H*Me), 1.59 (3 H, d, *J* 6.7, CH*Me*); *m*/*z* 210 (M^+, 10%), 105 (100), 77 (25), 79 (20) and 51 (18).

(*S*)-*N*-(2-Pyridylmethylidene)-1-phenylethanamine 10. This compound had $[\alpha]_D^{25}$ +37 (*c* 2.24 in $CHCl_3$) {lit.,[28] $[\alpha]_D^{20}$ +44.6 (*c* 1.0 in MeOH)}; λ_{max}(hexane)/nm 235 (ε/dm^3 mol^{-1} cm^{-1} 13 540); ν_{max}/cm^{-1} 1645 (C=N); δ_H(300 MHz) 8.66 (1 H, m, pyridyl), 8.49 (1 H, s, CH=N), 8.12 (1 H, d, *J* 7.5, pyridyl), 7.75 (1 H, m, pyridyl), 7.46 (1 H, m, pyridyl), 7.40–7.25 (5 H, m, Ph), 4.67 (1 H, q, C*H*Me) and 1.64 (3 H, d, *J* 6.7, CH*Me*); *m*/*z* 210 (M^+, 2%), 195 (100), 105 (99), 77 (46), 51 (41), 79 (38), 168 (10) and 166 (8).

(*S*)-*N*-(4-Methoxybenzylidene)-1-phenylethanamine 11. This compound had $[\alpha]_D^{20}$ +93.5 (*c* 1.09 in $CHCl_3$); ν_{max}/cm^{-1} 1635; δ_H(300 MHz) 8.32 (1 H, s, CH=N), 7.74 (2 H, d, *J* 8.7, ArH), 7.50–7.20 (5 H, m, Ph), 6.92 (2 H, d, *J* 8.7, ArH), 4.53 (1 H, q, C*H*Me), 3.85 (3 H, s, OMe) and 1.60 (3 H, d, *J* 6.8, CH*Me*); *m*/*z* 239 (M^+, 40%), 105 (100), 224 (53), 238 (26), 77 (22) and 79 (17).

(*S*)-*N*-(2-Methoxybenzylidene)-1-phenylethanamine 12. This compound had $[\alpha]_D^{25}$ −5.4 (*c* 1.70 in $CHCl_3$) {lit.,[25] $[\alpha]_D^{22}$ +20 (*R* enantiomer)}; ν_{max}/cm^{-1} 1635; δ_H(300 MHz) 8.86 (1 H, s, CH=N), 8.08 (1 H, m, ArH), 7.50–7.20 (6 H, m, ArH), 7.05–6.90 (2 H, m, ArH), 4.60 (1 H, q, C*H*Me), 3.90 (3 H, s, OMe) and 1.62 (3 H, d, *J* 6.7, CH*Me*); *m*/*z* 105 (100), 224 (53), 134 (40), 77 (10), 51 (9) and 226 (2).

(*S*)-*N*-(2,5-Dimethoxybenzylidene)-1-phenylethanamine 24. This compound had $[\alpha]_D^{25}$ +40 (*c* 1.29, $CHCl_3$); ν_{max}/cm^{-1} 1635; δ_H(300 MHz) 8.80 (1 H, s, CH=N), 7.63–6.83 (8 H, m, aryl), 4.57 (1 H, q, C*H*Me), 3.83 (6 H, 2 s, OCH_3) and 1.59 (3 H, d, *J* 6.7, CH*Me*); *m*/*z* 105 (100), 164 (70), 149 (22), 77 (21), 79 (15), 106 (12) and 150 (10).

Preparation of the secondary homoallylic amines 13–19

The procedures for the reactions of imines with allylzinc bromide and the allyl bromide–Al–$PbBr_2$ system have been described previously.[12] The crude homoallylic amines were obtained in 80–100% yields by the various procedures described in Table 1. The significant ^1H NMR signals of compounds **13–19** are reported in Fig. 2. Since only the major diastereoisomers were obtained pure by flash chromatography (SiO_2, cyclohexane–ethyl acetate as eluent), the ^1H NMR signals for the minor diastereoisomers were deduced from the spectra of the crude reaction mixtures or from enriched chromatographic fractions.

Preparation of *N*-[(1*R*)-1-(2,5-dimethoxyphenylbut-3-enyl)]-(1*S*)-phenylethanamine 25

Reaction of *B*-allyl-9-BBN with 24: typical procedure. *B*-Allyl-9-BBN (3.24 g, 20 mmol) (prepared and purified by distillation according to the reported procedure[30] was added slowly to a solution of the imine **24** (2.69 g, 10 mmol) in anhydrous Et_2O (15 cm^3) at −78 °C under a N_2 atmosphere.[4] The reaction mixture was stirred for 3 h and then quenched at −78 °C with 10 mol dm^{-3} hydrochloric acid (5 cm^3) and stirred for further 12 h, while being allowed to reach room temperature. The ether phase was separated and the aqueous phase was extracted with Et_2O (20 cm^3 × 2). 40% Aqueous NaOH was added with caution to the aqueous phase until it reached pH 11, after which it was extracted with Et_2O (20 cm^3 × 3). The combined ether fractions were washed with brine, dried (Na_2SO_4) and concentrated at reduced pressure to leave the crude homoallylic amine **25** as an oil (2.48 g, 80%). GC–MS and ^1H NMR analysis indicated a purity >95% and a diastereoisomeric ratio 1:99. An analytical sample was obtained by column chromatography (SiO_2, cyclohexane–ethyl acetate as eluent).

Reaction of diallylcuprate with 24: typical procedure. Allylmagnesium chloride in THF (2 mol dm^{-3}; 5 cm^3, 10 mmol) was added over 5 min to a stirred suspension of 99.99% CuI (0.95 g, 5 mmol) in anhydrous THF (10 cm^3) cooled to −40 °C under a N_2 atmosphere and the mixture was stirred for a further 10 min. After this it was cooled to −78 °C, and a solution of the imine **24** (0.269 g, 1 mmol) in THF (5 cm^3) was added to it over 10 min. The reaction mixture was then stirred at −78 °C for 2 h after which it was quenched with 10% aqueous NaOH (10 cm^3) and stirred while being allowed to reach 20 °C. Diethyl ether (10 cm^3) was added to the mixture and the organic phase was separated. The aqueous phase was extracted again with ether (10 cm^3 × 3), and the collected ethereal fractions were dried (Na_2SO_4) and concentrated to leave crude **25** (0.289 g, 93% yield); GC-MS and ^1H NMR analysis indicated a purity >95% and a diastereoisomeric ratio 3:97.

N-[(4*R*)-4-(2,5-Dimethoxyphenylbut-1-en-4-yl)]-(*S*)-1-phenylethanamine **25** had *m*/*z* 166 (100), 270 (60), 105 (27), 271 (12), 79 (9) and 103 (9); δ_H(300 MHz) 7.35–7.15 (5 H, m, Ph), 6.87–6.70 [3 H, m, $(MeO)_2C_6H_3$], 5.80–5.65 (1 H, m, C*H*=CH_2), 5.08–4.96 (2 H, m CH=CH_2), 4.13 (1 H, t, C*H*CH_2), 3.73 (6 H, s, 2 OMe), 3.67 (1 H, q, C*H*Me), 2.57–2.40 (2 H, m, CHCH_2), 1.85 (1 H, br, NH) and 1.33 (3 H, d, *J* 6.5, CH*Me*) (Found: C, 77.2; H, 8.0. $C_{20}H_{25}NO_2$ requires C, 77.1; H, 8.1%).

Reaction of (*S*)-10 with allyl-$SnICl_2$: preparation of (*R*,*S*)-17

A solution of allyl iodide (0.168 g, 1 mmol) in THF (2 cm^3) was added dropwise to a magnetically stirred solution of $SnCl_2$ (0.189 g, 1 mmol) in THF (12 cm^3). After 10 min the solution was cooled at −78 °C and treated dropwise with a solution of (*S*)-**10** (0.210 g, 1 mmol) in THF (3 cm^3). After the reaction mixture had been stirred at −78 °C for 3 h, it was

quenched with 10% aqueous NaOH (10 cm^3) and extracted with Et_2O (10 cm^3 × 3). The combined extracts were washed with brine, dried ($MgSO_4$) and concentrated to give **17** as an oil (0.239 g, 95%). The diastereoisomeric ratio 15:85 was determined by GC–MS analysis, according to the order of elution.

Hydrogenolysis of 25: synthesis of (*R*)-1-(2,5-dimethoxyphenyl)butan-1-amine 26

Pd–C (0.2 g) and ammonium formate (1.5 g, 23.8 mmol) were added to the solution of the imine **25** (2.19 g, 7 mmol) in dry methanol (175 cm^3) and the mixture was magnetically stirred under reflux for 1.5 h. After cooling, the reaction mixture was filtered and evaporated under reduced pressure to leave an oil (1.70 g), containing mainly the amine **26** and some ethyl benzene (GC–MS analysis). 48% Hydrobromic acid was carefully added to the mixture until it reached pH 6–7 after which it was diluted with toluene (10 cm^3) and methanol (10 cm^3) and evaporated under reduced pressure. The residue was recrystallized from dichloromethane–cyclohexane to give the hydrobromide of **26** (1.74 g, 86%), mp 142–144 °C; $[\alpha]_D^{25}$ −3.20 (*c* 2.16, $CHCl_3$); δ_H 8.3 (3 H, br, NH_3^+), 6.98 (1 H, s, ArH), 6.84 (2 H, s, ArH), 4.52 (1 H, m, CH), 3.78 (3 H, s, OMe), 3.72 (3 H, s, OMe), 2.23–1.95 (2 H, m, $CHCH_2$), 1.40–1.12 (2 H, m, CH_2CH_3) and 0.88 (3 H, t, CH_2Me). Treatment with base (10% NaOH) of the hydrobromide followed by ether extraction and work-up gave quantitatively the free amine **26**: $[\alpha]_D^{25}$ +9.46 (2, $CHCl_3$); δ_H 6.90–6.70 (3 H, m, aryl), 4.15 (1 H, t, $CHCH_2$), 3.81 (3 H, s, OMe), 3.79 (3 H, s, OMe), 1.80 (2 H, broad, NH_2), 1.80–1.60 (2 H, m, $CHCH_2$), 1.45–1.20 (2 H, m, CH_2CH_3) and 0.92 (3 H, t, CH_2Me); *m/z* 166 (100), 167 (33), 192 (20), 151 (16), 108 (15), 136 (13) and 177 (10) (Found: C, 68.9; H, 9.1. $C_{12}H_{19}NO_2$ requires C, 68.85; H, 9.15%).

Acknowledgements

The authors are grateful to MURST (Roma) for financial support and to Prof. V. Concialini and Prof. S. Roffia for carrying out electrochemical reductions and allylations of the imines.

References

1 J. D. Morrison, *Asymmetric Synthesis*, Academic Press, New York, 1983; D. J. Hart and D.-C. Ha, *Chem. Rev.*, 1989, **89**, 1447; P. J. Cox and N. S. Simpkins, *Tetrahedron: Asymmetry*, 1991, **2**, 1; F. H. Van der Steen and G. Van Koten, *Tetrahedron*, 1991, **47**, 7503; J. d'Angelo, D. Desmaele, F. Dumas and A. Guingant, *Tetrahedron: Asymmetry*, 1992, **3**, 459; R. M. Williams and J. A. Hendrix, *Chem. Rev.*, 1992, **92**, 889.

2 (*a*) Hydrogenolysis: M. K. Anwer and A. F. Spatola, *Synthesis*, 1980, 929; S. Ram and L. D. Spicer, *Tetrahedron Lett.*, 1987, **28**, 515; (*b*) Selective hydrogenolysis of dibenzylic amines: P. Polniaszek and L. W. Dillard, *Tetrahedron Lett.*, 1990, **31**, 797; G. Bringmann and J.-P. Geisler, *Synthesis*, 1989, 608; G. Bringmann, G. Kunkel and T. Geuder, *Synlett*, 1990, 253; G. Bringmann, J.-P. Geisler, G. Kunkel and L. Kinzinger, *Liebigs Ann. Chem.*, 1990, 795; S. G. Davies and O. Ichihara, *Tetrahedron: Asymmetry*, 1991, **2**, 183; K. Hattori and H. Yamamoto, *Tetrahedron*, 1994, **50**, 2785; (*c*) Reduction with Li–NH_3–H_2O: F. X. Webster, J. G. Millar and R. M. Silverstein, *Tetrahedron Lett.*, 1986, **27**, 4941.

3 Y. Yamamoto, *Acc. Chem. Res.* 1987, **20**, 243; Y. Yamamoto and N. Asao, *Chem. Rev.*, 1993, **93**, 2207.

4 Y. Yamamoto, T. Komatsu and K. Maruyama, *J. Am. Chem. Soc.*, 1984, **106**, 5031; Y. Yamamoto, S. Nishii, K. Maruyama, T. Komatsu and W. Ito, *J. Am. Chem. Soc.*, 1986, **108**, 7778.

5 Y. Yamamoto and W. Itoh, *Tetrahedron*, 1988, **44**, 5415.

6 D. J. Hallet and E. J. Thomas, *J. Chem. Soc., Chem. Commun.*, 1995, 657.

7 W. Neumann, M. M. Rogic and T. J. Dunn, *Tetrahedron Lett.*, 1991, **32**, 5865.

8 Y. Yamamoto, T. Komatsu and K. Maruyama, *J. Chem. Soc., Chem. Commun.* 1985, 814.

9 K. J. Beresford, G. P. Howe and G. Procter, *Tetrahedron Lett.*, 1992, **33**, 3355.

10 P. Beuchet, N. Le Marrec and P. Mosset, *Tetrahedron Lett.*, 1992, 5959.

11 Some results have been reported in preliminary form: A. Bocoum, C. Boga, D. Savoia and A. Umani-Ronchi, *Tetrahedron Lett.*, 1991, **32**, 1367.

12 (*a*) A. Bocoum, D. Savoia and A. Umani-Ronchi, *J. Chem. Soc., Chem. Commun.*, 1993, 1542; (*b*) T. Basile, A. Bocoum, D. Savoia and A. Umani-Ronchi, *J. Org. Chem.*, 1994, **59**, 7766.

13 T. Mukaiyama, T. Harada and S. Skoda, *Chem. Lett.*, 1981, 1507.

14 H. Tanaka, T. Takahara, H. Dhimane and S. Torii, *Tetrahedron Lett.*, 1989, **30**, 4161.

15 J. G. Noltes and J. W. G. Van Den Hurk, *J. Organomet. Chem.*, 1965, **3**, 222. J. Reinhold, R. Benedix, P. Birner and H. Henning, *Inorg. Chim. Acta*, 1979, **33**, 209.

16 E. Wissing, E. Rijnberg, P. A. van der Schaaf, K. van Gorp, J. Boersma and G. van Koten, *Organometallics*, 1994, **13** 2609; and previous papers in the series.

17 J. J. C. Gros and S. Bourcier, in *Stereochemistry*, ed. H. B. Kagan, Georg Thieme Publishers, Stuttgart, 1977, Vol. 4.

18 M. B. Eleveld, H. Hogeveen and E. P. Schudde, *J. Org. Chem.*, 1986, **51**, 3635.

19 A. Bernardi, A. M. Capelli, A. Comotti, C. Gennari, M. Gardner, J. M. Goodman and I. Paterson, *Tetrahedron*, 1991, **47**, 3471.

20 F. H. van der Steen, H. Kleijn, A. L. Spek and G. van Koten, *J. Org. Chem.*, 1991, **56**, 5868.

21 W. R. Roush, in *Comprehensive Organic Synthesis*, ed. B. M. Trost, Pergamon Press, London and New York, 1991, vol. 2, p. 1.

22 E. J. Corey, C. P. Decicco and R. C. Newbold, *Tetrahedron Lett.*, 1991, **32**, 5287.

23 G. B. Jones and B. J. Chapman, *Synthesis*, 1995, 475.

24 (*a*) F. Bernardi, A. Bongini, G. Cainelli, M. A Robb and G. Suzzi Valli, *J. Org. Chem.*, 1993, **58**, 750; (*b*) X. Wang and C. Lee, *Tetrahedron Lett.*, 1993, **34**, 6241; (*c*) J. Maiz, A. Arrieta, X. Lopez, J. M. Ugalde and F. Cossio, *Tetrahedron Lett.*, 1993, **34**, 6111.

25 H. E. Smith, S. L. Cook and M. E. Warren, Jr., *J. Org. Chem.*, 1964, **29**, 2265.

26 F. Nerdel, K. Becker and G. Kresze, *Chem. Ber.*, 1956, **89**, 2862.

27 A. P. Terent'ev and V. M. Potapov, *J. Gen. Chem. USSR* (*Engl. Transl.*), 1958, **28**, 1220.

28 K. Hattori and H. Yamamoto, *Tetrahedron*, 1993, **49**, 1749.

29 H. Brunner, B. Reiter and G. Riepl, *Chem. Ber.*, 1984, **117**, 1330.

30 G. W. Kramer and H. C. Brown, *J. Organomet. Chem.*, 1977, **132**, 9.

Paper 5/06537B
Received 4th *October* 1995
Accepted 20th *November* 1995