clopropene yields the less stable vinyl carbene, in contrast to the analogous thermal reaction.[16] In such cases the efficiency of funneling to the ground-state surface is usually held responsible for the observed products.[4,16] However, it is quite conceivable that triplet cyclopropene is unsymmetrical. Substituent effects on this structure may again determine the nature of the α-cleavage product. Interestingly, Johnson et al.[17] have recently considered an explanation other than that based on the funneling process. They have speculated that the π bond strength in the excited state may be reversed, leading to the difference between thermal and photochemical cleavage products. Our proposal is a variation of this suggestion. The results of the theoretical study initiated by Johnson et al. on cyclopropene chemistry are eagerly awaited.

The present calculations are not meant to be definitive, although the MINDO/3 method has been successfully used in earlier studies of photoreactions[18] and Jahn–Teller systems.[19] Our results merit further investigation at higher levels employing configuration interaction.[20]

The current study has yielded a variety of unusual substituted Jahn–Teller forms. The unsymmetrical structure F found for the triplet of the parent as well as substituted cyclopropenethione represents an especially interesting Jahn–Teller distorted geometry.

The alternative geometries adopted by triplet cyclopropenone and -thione represent a particularly striking example of orbital isomerism.[21] A systematic study of the effect of other substituents in preferentially stabilizing different "lumomeric" structures will be of considerable interest.

Acknowledgment. V.R. thanks the Department of Science and Technology, Government of India for financial support.

Registry No. 2-Methyl-3-phenyl-2-cyclopropene-1-thione, 56764-07-9; 2-ethyl-3-phenyl-2-cyclopropen-1-one, 5909-87-5; 3-phenyl-3-propyl-2-cyclopropene-1-thione, 97703-38-3; 2-(1-methylethyl)-3-phenyl-2-cyclopropene-1-thione, 97703-39-4; 2-cyclopropene-1-thione, 69903-36-2; 2-cyclopropen-1-one, 2961-80-0; cyclopropanol (anion), 72507-73-4; cyclopropanethiol (anion), 100840-42-4; 2-methyl-2-cyclopropene-1-thione, 103422-48-6; 2,3-dimethyl-2-cyclopropene-1-thione, 103422-49-7.

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(20) A quantitative theoretical treatment of Jahn–Teller systems should include extensive configuration interaction. See Ref 10c and: Borden, W. T.; Davidson, E.; Feller, D. *J. Am. Chem. Soc.* **1980**, *102*, 5302.
(21) Dewar, M. J. S.; Kirschner, S.; Kollmar, H. W. *J. Am. Chem. Soc.* **1974**, *96*, 5240.

Diastereoselective Synthesis of Chiral Secondary Amines with Two Chiral Centers Directly Attached to the Nitrogen Atom

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The synthesis of the amines **1a–f** by hydrogenation of the corresponding imines **4a–f** occurs with a diastereoselectivity ranging from 33% to higher than 90%. The absolute configurations of **1b–f** have been determined by either X-ray analysis (**1b** and **1c**), chemical correlation (**1e** and **1f**), or correlation via ^{1}H NMR shifts (**1d**). The difference in the observed diastereoselectivities is rationalized by a mechanism in which the hydrogenation occurs exclusively at the less hindered side of the imines, which results in the formation of amines **1** from the anti and of amines **2** from the syn imines.

Chiral amines constitute a class of compounds that have a wide application in organic chemistry as resolving agents[1] and chiral building blocks,[2] as well as chiral auxiliaries in stereoselective synthesis.[3] Naturally occurring amines such as brucine, ephedrine, and amino acids, as well as synthetic amines such as α-methylbenzylamine and 2-amino-1-butanol, are frequently used. An advantage of the use of natural chiral amines is that they occur in an optically pure form, while for the synthetic amines a resolution procedure or a stereoselective synthesis is necessary. However, a drawback of the first class is that they often are only available in one enantiomeric form.

The most successfully used method of synthesis of chiral amines involves hydrogenation of imines, in which the chiral center can be induced in various ways.[4–9] However, for the synthesis of amines with two chiral centers directly attached to the nitrogen atom the preferred method consists of condensation of prochiral ketones with chiral primary amines to afford chiral imines, which after hydrogenation yield secondary amines, possessing tow chiral centers.[6] Although a great deal of work has been done on this type of reaction it has mostly been restricted to the

(1) See, for example: Wilen, S. H. in *Topics in Stereochemistry*; Allinger, N. L., Eliel, E. L., Eds.; Wiley-Interscience: New York, 1971; Vol. 6, pp 107–176.
(2) See, for a review about amino acids as chiral building blocks: Drausz, K.; Kleeman, K.; Martens, J. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 584.
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(9) Fiaud, J. C.; Kagan, H. B. *Tetrahedron Lett.* **1977**, 1019.

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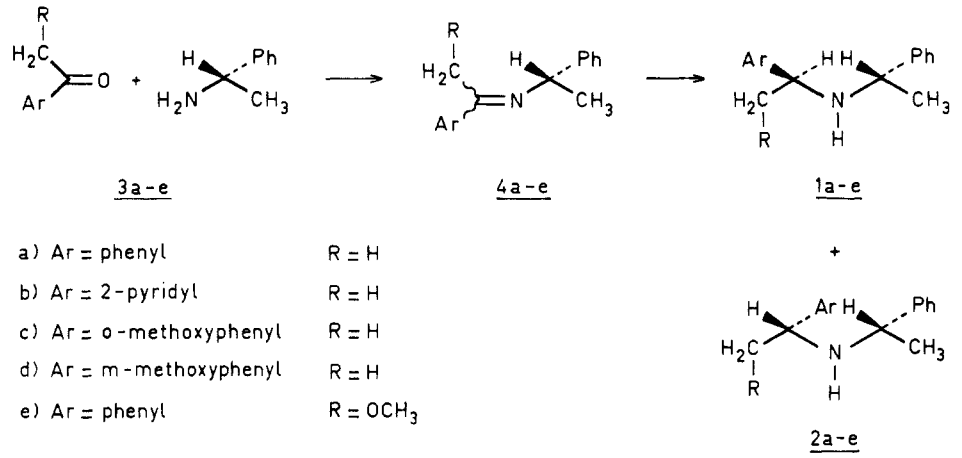
Scheme I



3a-e 4a-e 1a-e + 2a-e

a) Ar = phenyl R = H
b) Ar = 2-pyridyl R = H
c) Ar = o-methoxyphenyl R = H
d) Ar = m-methoxyphenyl R = H
e) Ar = phenyl R = OCH_3

Table I. Anti/Syn Ratio and ^1H NMR Data of 4a–e

		δ_{CH_2R}		δ_{CH_3}		δ_H[a]		δ_{OCH_3}	
imine	anti/syn ratio	anti	syn	anti	syn	anti	syn	anti	syn
4a	7/1	2.17	2.50	1.50	1.30	4.75	4.01		
4b	>19/<1	2.35		1.50		4.80			
4c	0.5/1	2.15	2.23	1.53	1.36	4.73	4.17	3.70	3.70
4d	9/1	2.16	2.27	1.50	1.38	4.73	4.00	3.78	3.68
4e	1.4/1	4.18	5.53	1.42	1.32	4.50	4.03	3.45	3.28

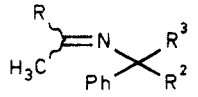
[a] The hydrogen on the chiral carbon atom of the α-phenylethyl group.

stereoselective synthesis of amino acids.[6]

Results

Synthesis of *N*-(1-Arylalkyl)-(*S*)-α-methylbenzylamines (1). The amines **1** have been synthesized according to Scheme I. The synthesis of **1a** has already been described.[10] Very recently—while we had finished our experimental work[11] —the synthesis of compounds **1b** and/or **2b** was also reported, but remarkably enough the authors do not mention the possibility of the formation of diastereomers; moreover, no physical data, with the exception of an elemental analysis, was given.[12]

The imines **4a–e** have been prepared, starting from (*S*)-α-methylbenzylamine and ketones **3a–e**, in refluxing benzene by azeotropic water removal. The syn/anti ratio of imines **4a–e** is greatly influenced by the Ar group as well as the R group, as is shown in Table I. The anti/syn isomer ratio was determined by the integration of the appropriate ^1H NMR signals, whereby the identification of syn and anti is largely based on a study of Vögtle et al.[13] They reported that in compounds of type **5** the methyl group when placed syn gives a resonance at a higher field than when it is placed anti, this as a result of the ring current effect of the phenyl group.



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On the basis of this theory the syn and anti isomers of **4a**, **4c**, and **4d** were identified and their relative amounts determined by using the δ_{CH_2R} values in Table I. By comparison of the intensities of the other signals in the ^1H NMR spectra it became clear that the CH_3 group of **4a**, **4c** and **4d** gives a signal for the syn isomer at δ 1.3–1.4 and for the anti isomer at δ 1.5, while the H atom (attached to the chiral carbon atom of the α-phenylethyl group) absorbs for the syn at δ 4.0–4.2 and for the anti at δ 4.7–4.8. These latter correlations were used for structural identification of **4b** and **4e**, because this is impossible by comparison of the CH_2R shifts. In the case of **4b** only one isomer is formed, and based on the chemical shift of its CH_2R group δ 2.35) it is impossible to say whether it is the syn or anti isomer, while in the case of **4e** the CH_2R group is not a methyl group (R is not hydrogen). Comparison of the chemical shifts of **4b** with those of the syn and anti isomer of **4a**, **4c**, and **4d** shows that the isomer obtained has the anti configuration. By comparing the two sets of chemical shifts of **4e** it seems probable that the major isomer formed is the anti isomer. The large difference in chemical shifts of the hydrogen at the chiral carbon atom of the α-methylbenzyl moiety in the syn and anti isomers, can be rationalized by observing CPK models. The aromatic ring in the syn isomer is, due to steric hinderance, rotated out of the plane formed by the Ar–C and C=N bonds, in such a way that the hydrogen atom on the average lies above rather than in the plane of the aromatic ring and therefore absorbs at higher field. This is not the case for the anti isomer.

Table II. Formation of 1/2 on Reduction of 4 by H_2 with Pd/C as Catalyst in THF

imine	anti/syn ratio	ratio 1/2	de, %	chem yield,[a] %
4a		5.7/1.0	70	65
4b	>19/<1.0	5.6/1.0	70	61
4c	0.5/1	>19/<1.0[b]	>90	75
4d	9/1	5.0/1.0	67	45
4e	1.4/1	2.0/1.0	33	33

[a] Chemical yields of purified and isolated 1. [b] Compound **2c** was not observed as product.

The hydrogenation of **4a–e** was performed with hydrogen with palladium on charcoal (10%) as catalyst. The

(10) (a) Overberger, C. G.; Marullo, N. P.; Hiskey, R. G. *J. Am. Chem. Soc.* **1961**, *83*, 1374. (b) Yoshida, T.; Harada, K. *Bull. Soc. Chem. Jpn.* **1972**, *45*, 3706.
(11) The compounds have been referred to already in: Eleveld, M. B.; Hogeveen, H. *Tetrahedron Lett.* **1984**, 785, 5187.
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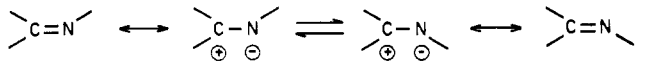
Scheme II



stereoselectivity obtained in this way is normally higher than with $LiAlH_4$ and comparable to BH_3·THF as reducing agents.[14] The chemical yields of isolated **1** (calculated on basis of consumed (*S*)-α-methylbenzylamine) as well as the diastereomeric excesses (de's) are given Table II. It is obvious that the ratios **1/2** do not correspond with the syn/anti ratios of the starting imines. Probably the imines isomerize under the used reaction conditions. It is known that this type of imines isomerizes fast since the nitrogen atom has a greater electronegativity than the carbon atom (Scheme II);[15] e.g., the syn/anti ratio of imine mixture **4a** changed after distillation.[10b] We have not investigated the factors that might influence the syn/anti ratios of the imines, because in this study only a favorable **1/2** ratio is of importance.

Compounds **1a** and **1c–e** could be isolated from the corresponding diastereomeric mixtures by crystallization of the HCl salts, on which the **1**·HCl salts preferentially crystallized out. Compound **1b** could be isolated by the same method except that the D-tartaric acid salt was used, instead of the HCl salt. The amines were obtained by treatment of the salts with sodium hydroxide. Compound **1e** has also been prepared via an independent route, starting from (*R*)-phenylglycinol (**6**). Condensation of **6** with acetophenone yielded a mixture of one of the two possible 1,3-oxazolidines (**7**) and the anti imine (**4f**) in a ratio of 3 to 1, respectively (Scheme III). An equilibrium between the 1,3-oxazolidine **7** and the anti imine **4f** during the reaction explains the yield of **1f** (73%) and the absence of **7** in the product; on reduction of the imine with hydrogen a shift of the equilibrium occurs to the imine side. The hydrogenation is performed in a highly diastereoselective way (de >90%), because only one product could be observed. The product obtained must have structure **1f**, as shown by the fact that after alkylation of the hydroxyl group only **1e** was formed. In the alkylation step, probably for steric reasons, no alkylation of the amine function took place. Attempts to change the reaction sequence, which means first alkylation of **6** and then condensation and hydrogenation, failed because in the alkylation step a certain amount of nitrogen alkylation always occurred, even when the reaction was performed under conditions that are supposed to exclude nitrogen alkylation.[16]

Attempts to synthesize (*R,R*)-bis(2-methoxy-1-phenylethyl)amine (**8**), by reaction of **6** with **3e**, failed because the 1,3-oxazolidine mixture **9** (ratio 5.6 to 1) was formed exclusively, and no trace of the isomeric imine could be detected (no IR absorption at 1640 cm^{-1} and ^{13}C NMR absorption at δ 150–170[17]). Under the applied reaction conditions it proved impossible to hydrogenate **9** to the corresponding amine **10** (Scheme IV). Probably in this case, in contrast to **7** an equilibrium between the 1,3-oxazolidine and the isomeric imine is absent.

Elucidation of the Configuration. The absolute configurations of the compounds **1a–f**, **2a**, **2b**, **2d**, and **2e**, discussed in the previous section, have been determined by different methods. The configuration of **1a**, being the major compound formed in the hydrogenation of **4a**, has to be *S,S* because, first, it possesses an optical rotation, while the compound with the *S,R* configuration (**2a**), being a meso compound, would have been optically inactive and, second, the chiral center of the starting α-methylbenzylamine has the *S* configuration. This reasoning cannot be used for elucidation of the configurations of the other products because, in principle, diastereoisomers **1b–e** as well as **2b–e** are optically active. In the cases of **1b** and **1c** the structures were established by X-ray crystallography determinations of the D-tartaric acid salt of **1b** (Figure 1) and the HCl salt of **1c** (Figure 2).

The absolute configuration of **1e** was established by chemical correlation. In each of the two independent routes for synthesizing this compound two diastereomeric products are possible in principle, as depicted in Scheme V. The main product of reaction a appears to have a NMR spectrum identical with that of the only formed product in reaction b. Because both compounds also have the same sign of rotation, they are identical, and as a result compound **1e** must have the *S,R* configuration. Compound

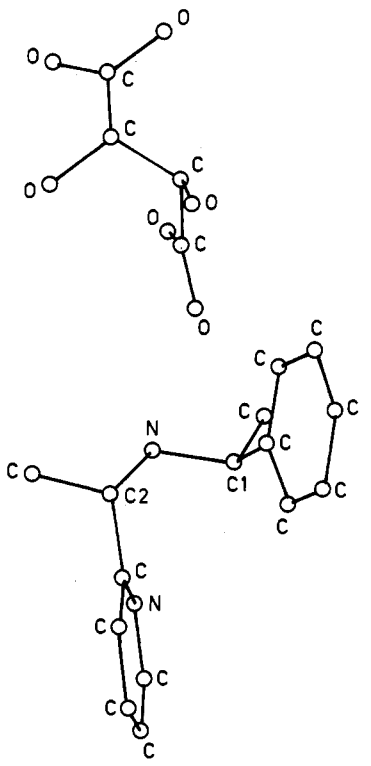


Figure 1. X-ray structure of compound **1b**–D-tartaric acid.

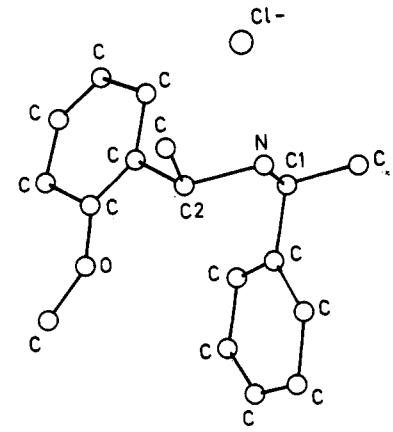
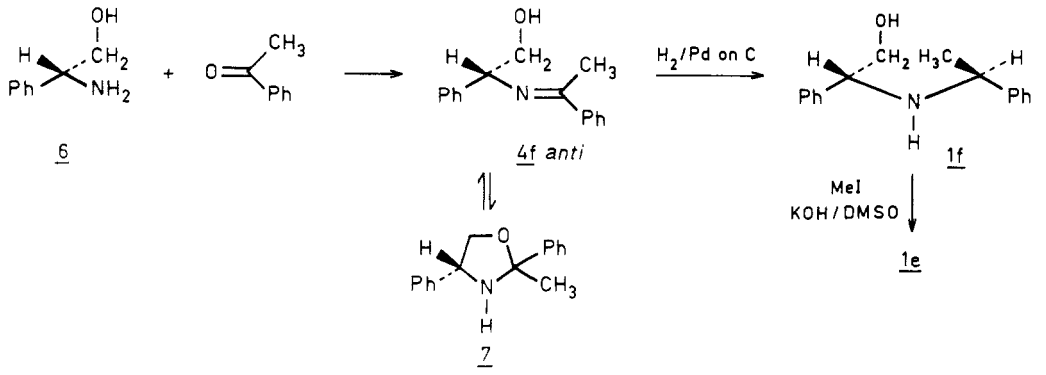


Figure 2. X-ray structure of compound **1c**·HCl.

(14) Charles, J. P.; Christol, H.; Solladié, G. *Bull. Soc. Chim. Fr.* **1970**, 4439.
(15) Sollenberg, P. Y.; Martin, R. B. In *The Chemistry of the Amino Group*; Patai, S., Ed.; Interscience: London, 1968; pp 362–364.
(16) Meyers, A. I.; Poindexter, G. S.; Brich, Z. *J. Org. Chem.* **1978**, *43*, 892.
(17) Baudet, M.; Gelbcke, M. *Anal. Lett.* **1979**, *12*(B6), 641.

Scheme III



Scheme IV

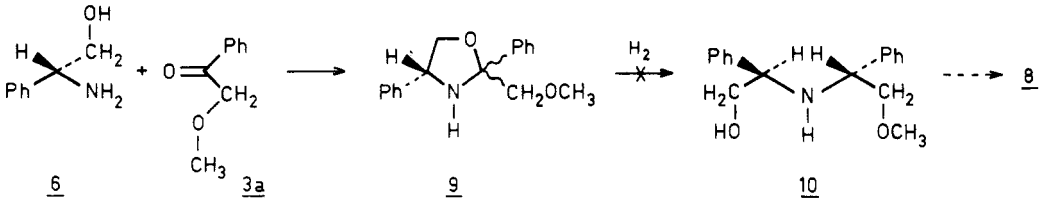
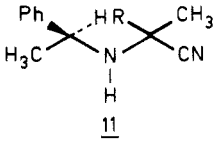


Table III. ^{1}H NMR Chemical Shifts of the Methyl Groups in 1a–e and 2a–e

compd	δ_{CH_3}	compd	δ_{CH_3}
1a	1.24	**2a**	1.34
1b	1.23/1.26	**2b**	1.37/1.37
1c	1.21/1.26	**2c**	
1e	1.27	**2e**	1.34
1d	1.21	**2d**	1.34

2e which is formed in minority in reaction a must, consequently, possess the *S,S* configuration. The *S,R* configuration of **1e** is comparable with the *S,S* configuration of the other compounds **1a–c** described before, if one takes into account that the priority numbers of the groups around the newly formed chiral center are changed.

The absolute configuration of **1d** was assigned on basis of a ^{1}H NMR chemical shift correlation in a similar way as has been done by Weinges et al.[8] for compounds of the type 11. For an assignment of the configuration of **1d** the



shifts of the methyl groups of **1a–c** and **1e**, which all possess the *S,S* configuration (**1e** has the *S,R* configuration, but this is due to the changed priority numbers), and of **2a**, **2b**, and **2e**, which all possess the *S,R* configuration (**2e** has the *S,S* configuration, due to the changed priority numbers), were compared with those of the methyl groups of **1d** and **2d**, formed in the reaction starting with *m*-methoxyacetophenone (Table III). The comparison shows that **1d** probably has the *S,S* and **2d** the *S,R* configuration, especially because from a stereoelectronic point of view, **1d** and **2d** differ scarcely from **1a**, **1c**, and **2a**, respectively.

The difference in chemical shift of the methyl group(s) in **1** and **2** can be explained by studying CPK models. For example, the conformation of **1a** with the least steric repulsion, proves to be the one depicted in Figure 3, in which the two methyl(s) groups lie in the plane formed by the two carbon(a)–nitrogen bonds and the phenyl rings lie in the planes formed by the phenyl–carbon(a) and carbon(a)–hydrogen(a) bonds. In this conformation each of the

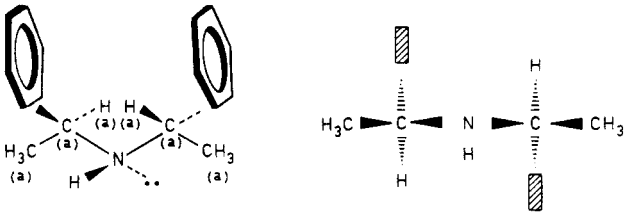


Figure 3. Most favorable conformation of **1a**.

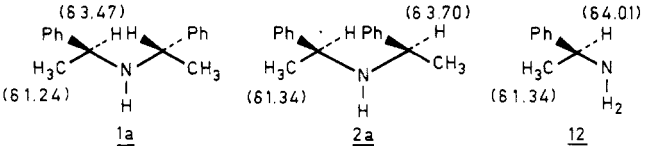


Figure 4. Some ^{1}H NMR data of **1a**, **2a**, and **12**.

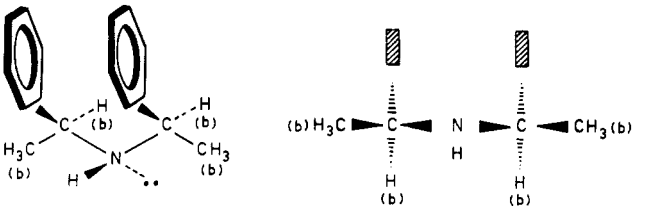
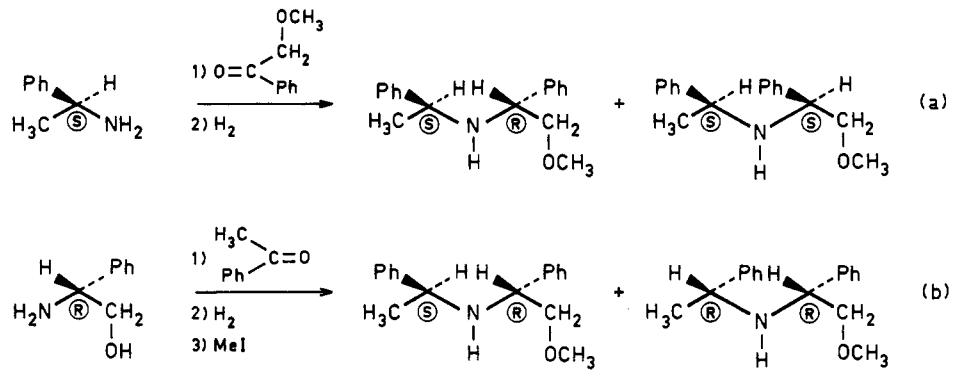


Figure 5. Most favorable conformation of **2a**.

hydrogens(a) lies above and very close to the other phenyl ring (compare also the X-ray structures of **1b**–D-tartaric acid and **1c**·HCl, Figures 1 and 2, respectively) which will cause a high-field shift of H(a) as a result of the ring current effect of the phenyl group. Indeed, when the shift of H(a) is compared with the corresponding shift of the hydrogen in (*S*)-α-methylbenzylamine (**12**) a remarkable difference is observed (δ 3.47 and 4.01, respectively; see Figure 4). This difference is too large to be caused by the change from a primary to a secondary amine, as can be seen by a comparison of various primary and secondary amines (shift differences are about 0.05 ppm; e.g., the hydrogen atom attached to the tertiary carbon atom in diisopropylamine and isopropylamine has a chemical shift of δ 2.88 and 2.92, respectively). The CPK model of **2a** shows that probably the most favorable conformer is the one depicted in Figure 5. In this conformation the hy-

Scheme V



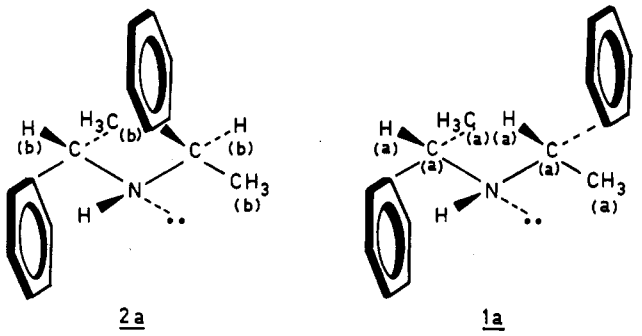


Figure 6. Favorable conformations of **2a** and **1a**.

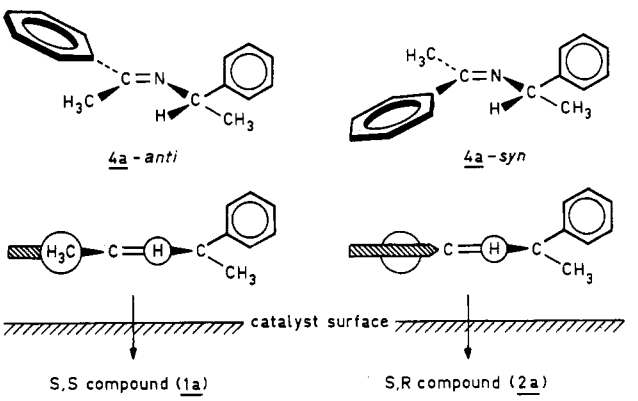


Figure 7. Preferred conformations of *anti*-**4a** and *syn*-**4a** (according to Harada et al.[10b]).

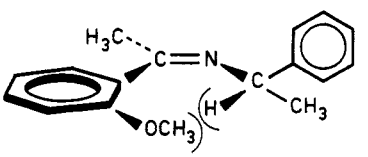


Figure 8. Structure of *syn*-**4c**.

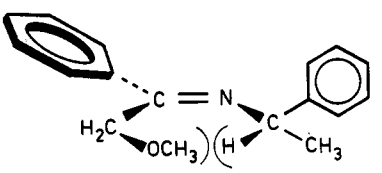


Figure 9. Structure of *anti*-**4e**.

drogens(b) do not feel a ring current effect of the phenyl group. Indeed, the H(b) (δ 3.70) resonates at a lower field than H(a) in **1a** (δ 3.47).

In order to explain the chemical shift difference of H(b) in **2a** (δ 3.70) and the corresponding hydrogen in **12** (δ 4.01) one should realize that also somewhat less favorable conformations of **1a**/**2a** may still be populated to a significant extent, namely, the ones in which one of the α-methylbenzyl groups is rotated 120° around the carbon–nitrogen bond (see Figure 6), which brings one of the H(b)'s in **2a** above a phenyl ring. However, no conformer for **2a** is possible in which at the same time both H(b)'s lie above a phenyl ring. For this reason and because this conformation of **2a** is less favorable than the one depicted in Figure 5, it has to be expected that the high-field shift of H(b) is not as large as in the case of H(a) in **1a**, and this is indeed observed (δ 3.70 and 3.47; see Figure 4). The reasoning described above for the hydrogens(a) and -(b) can be extended to the methyl(a) groups in **1a** and methyl(b) groups in **2a**. While for **2a** no favorable conformation exists in which a methyl group lies above a phenyl ring such a conformation is possible for **1a** (see Figure 6). So, it has to be expected that for the CH_3 groups in **2a** there is no high-field shift and for the CH_3 groups in **1a** there is a high-field shift, which is indeed found (CH_3 (**1a**) δ 1.24; CH_3 (**2a**) δ 1.34; CH_3 (**12**) δ 1.34; see also Figure 4). It should be noted that the transition from primary to secondary amines does not significantly change the chemical shifts (<0.02 ppm).

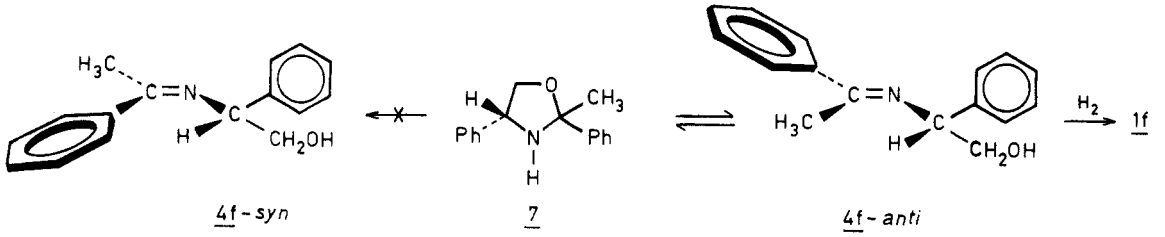
Discussion

The results described in this paper fit into a mechanism, proposed previously by Harada for compound **4a**.[10b,18] In this mechanism an equilibrium between the anti and syn isomers of **4a** (caused by the catalyst) is proposed. However, the most stable conformations of *anti*-**4a** and *syn*-**4a** are suggested to be as depicted in Figure 7, which means that the hydrogen, attached to the chiral carbon atom of the α-methylbenzyl moiety, is located in the plane of the Ph—C=N moiety. The diastereoselectivity can be explained by considering that both imine isomers, by which the anti imine is favored over the syn isomer for steric reasons, are hydrogenated from the least hindered side, that is from the side of the methyl groups.

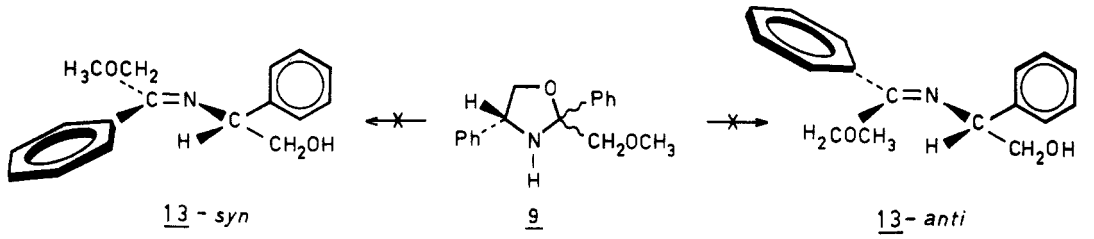
The existence of an equilibrium between the syn and anti imine during the hydrogenation is supported by the absence of a correlation between the syn/anti imine ratios and the diastereoselectivities of the hydrogenation (see Table II). The degree of diastereoselectivity is the same for **4a**, **4b**, and **4d**, which can be explained by realizing that in these cases the syn/anti imine ratio (under the reaction conditions of hydrogenation) will be the same, because they are virtually the same from a steric point of view. The increase in diastereoselectivity on hydrogenation of **4c** with respect to **4a** (de of >90% and 70%, respectively) is understood in terms of an increase of steric hindrance in

(18) In the past also another mechanism was reported.[10a] However, in this mechanism the starting hypothesis is incorrect and therefore we have ignored it.

Scheme VI



Scheme VII



syn-**4c** in comparison with *syn*-**4a** (Figure 8). Therefore, the *anti*-**4c**/*syn*-**4c** ratio will be greater than the *anti*-**4a**/*syn*-**4a** ratio and, consequently, the diastereoselectivity increases on going from **4c** to **4a**. The decrease in diastereoselectivity in the case of **4e** compared to **4a** (de of 33% and 70%, respectively) can be explained by realizing that *anti*-**4e** is less favored over *syn*-**4e** than is the case for *anti*-**4a** over *syn*-**4a**, which is due to the increase of steric hindrance in *anti*-**4e**, compared to *anti*-**4a** (Figure 9). Therefore, the *anti*-**4e**/*syn*-**4e** ratio will be smaller than the *anti*-**4a**/*syn*-**4a** ratio, and, consequently, the diastereoselectivity of the hydrogenation of **4e** will be less than that of **4a**.

The high degree of diastereoselectivity on hydrogenation of the *anti*-**4a**/**7** mixture to **1f** (de >90%) can be rationalized by assuming that there exists an equilibrium between the imine and the 1,3-oxazolidine isomer and that ring opening of **7** leads to a slow process to *anti*-**4f** which on hydrogenation affords **1f** (formation of the corresponding *syn*-**4f** isomer from **7** does not occur to a significant extent (Scheme VI)). The failure to observe hydrogenation of the 1,3-oxazolidine mixture **9** might be due to the absence of a ring opening to either *syn*-**13** or *anti*-**13** imine (Scheme VII). The reason for not forming *anti*-**13** in this case is due to an increased steric interaction compared to *anti*-**4f** (it is indeed remarkable that in the reaction mixture **9** from α-methoxyacetophenone and (*R*)-phenylglycinol (Scheme IV) no imine has been observed).

Finally, the results, reported in Table II, exclude alternative pathways, which were not taken into consideration by Harada,[10b] e.g., formation of the minor diastereomer **2** by (i) an approach of the catalyst surface by the anti imine (in the favored conformation) at its most bulky side (Figure 10, pathway I) or (ii) an approach of the catalyst surface by the anti imine in a less favorable conformation with the methyl group in the Ph—C=N plane (Figure 10, pathway II).

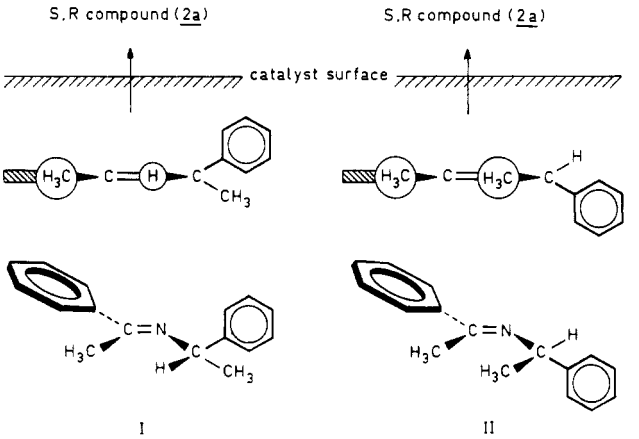


Figure 10. Possible alternative pathways for *anti*-**4a** to form **2a**.

Experimental Section

General Remarks. Melting points were determined on a Mettler FP-2 melting point apparatus equipped with a Mettler FP-21 microscope. The IR spectra were recorded on a Unicam SP-200 infrared spectrophotometer. The ^{1}H NMR spectra were recorded on a Varian A-60 or on a Hitachi Perkin-Elmer R-24B spectrometer and the ^{13}C NMR spectra at 25.2 MHz on a Varian XL-100 or at 50.3 MHz on a Nicolet NT-200 spectrometer. In the ^{1}H NMR spectra Me_4Si was used as an internal standard (δ = 0.0), and in the ^{13}C NMR spectra $CDCl_3$ was used as an internal standard (δ = 76.91 ppm). Optical rotations were measured on a Perkin-Elmer 241 polarimeter. All solvents and reagents were purified according to the usual standard methods. (*S*)-α-Methylbenzylamine, (*R*)-α-phenylglycinol, acetophenone, 2-acetylpyridine, and α-, *o*- and *m*-methoxyacetophenone were taken from commercial sources (Janssen Chimica).

Synthesis of (*S*,*S'*)-α,α'-Dimethyldibenzylamine (1a). A solution of 0.2 mol (24.0 g) of acetophenone, 0.2 mol (24.2 g) of (*S*)-α-methylbenzylamine ($[\alpha]^{20}_D$ −39° (neat)), and a catalytic amount of *p*-toluenesulfonic acid in 200 mL of benzene was refluxed under a nitrogen atmosphere with continuous removal of water by means of a Dean–Stark trap during 36 h. The reaction mixture was cooled in an ice bath and subsequently washed once with 25 mL of an aqueous sodium bicarbonate solution of 0 °C and twice with 25 mL of an aqueous saturated sodium chloride solution of 0 °C. After drying over magnesium sulfate and removal of the solvent, the resulting oily residue was not further purified. The imines *anti*-**4a** and *syn*-**4a** were formed in a ratio of 7 to 1. *anti*-**4a**: ^{1}H NMR ($CDCl_3$) δ 1.50 (d, J = 6.1 Hz), 4.75 (q, J = 6.2 Hz), 2.17 (s), 7.0–8.0 (br). *syn*-**4a**: ^{1}H NMR ($CDCl_3$): δ 1.30 (d, J = 6.2 Hz), 4.01 (q, J = 6.3 Hz), 2.50 (s), 7.0–8.0 (br). The imine mixture was dissolved in 200 mL of THF and 0.5 g of 10% palladium on charcoal was added. This mixture was shaken in a Parr apparatus during 16 h under 3 atm of hydrogen pressure. After removal of the catalyst by filtration, drying of the filtrate over magnesium sulfate, and evaporation of the solvent, the reaction mixture was distilled by bulb-to-bulb distillation [120 °C (0.1 torr)], giving 40.2 g of a pale yellow oil, which contained **1a** and **2a** in a ratio of 5.7 to 1.0: yield, 89%. This product mixture was treated with 500 mL of an aqueous 1 N HCl solution. After washing with 50 mL of ether, hydrogen chloride and water were removed by a rotatory evaporator at 90 °C. The resulting white

solid compound was recrystallized from water, affording 36.6 g (0.14 mol) of white crystalline **1a**·HCl, which exhibited a rotation $[\alpha]^{rt}_D$ (rt = room temperature) −84.1° (*c* 3, EtOH): yield, 70%; mp >300 °C; ^{1}H NMR ($CDCl_3$) δ 1.93 (d, 3 H)e, 3.88 (q, 1 H), 7.2–7.8 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 21.1 (q), 56.8 (d), 127.8 (d), 128.7 (d), 128.8 (d), 135.9 (s). The crystals were partly dissolved in 200 mL of water and 200 mL of diethyl ether, and subsequently 10 g of solid NaOH was slowly added. After the mixture was stirred for 2 h the solid material had disappeared, and the layers were separated. The aqueous layer was extracted with 100 mL of diethyl ether, and the combined ether extracts were dried over $MgSO_4$, filtered, and evaporated. The residual colorless oil was purified by bulb-to-bulb distillation [120 °C (0.1 torr)] affording 29.4 g (0.13 mol) of **1a**: yield, 65%; $[\alpha]^{rt}_D$ −157° (*c* 2.4, EtOH); ^{1}H NMR ($CDCl_3$) δ 1.24 (d, 6 H), 1.58 (br s, 1 H), 3.47 (q, 2 H), 7.17 (br s, 10 H); ^{13}C NMR ($CDCl_3$) δ 24.8 (q), 54.8 (d), 126.3 (d), 126.5 (d), 128.1 (d) 145.6 (s). In the NMR spectra of the crude distilled reaction mixture meso compound **2a** was also observed: ^{1}H NMR ($CDCl_3$) δ 1.34 (d), 3.70 (q), 7.15 (br s), 1.70 (br s); ^{13}C NMR ($CDCl_3$) δ 22.9 (q), 54.4 (d), 125.4, 126.7, 126.9.

Synthesis of (*S*)-*N*-[1-(2-Pyridyl)ethyl]-(*S*)-α-methylbenzylamine (1b). The same procedure as for **1a** (0.1 mol) was used. By ^{1}H NMR spectroscopy only one imine (*anti*-**4b**) was observed. *anti*-**4b**: ^{1}H NMR ($CDCl_3$) δ 1.50 (d, 3 H), 2.35 (s, 3 H), 4.80 (q, 1 H), 6.9–8.6 (m, 9 H). The amines **1b** and **2b** were formed in a 5.6 to 1.0 ratio in 80% yield. Product **1b** was obtained in a pure form, as its D-tartaric acid salt, by recrystallization of the D-tartaric acid salts of the reaction mixture from water: yield, 63%. **1b** as D-tartaric acid salt: $[\alpha]^{rt}_{578}$ −54.6° (*c* 2.1, H_2O); mp 159.2–160.4 °C; ^{1}H NMR (D_2O) δ 1.50 (d, 3 H), 1.62 (d, 3 H), 4.41 (s, 2 H), 4.16 (q, 1 H), 4.13 (q, 1 H), 7.0–7.8 (m, 8 H), 8.5 (br d, 1 H); ^{13}C NMR (D_2O) δ 19.5 (q, 2×), 56.4 (d), 57.0 (d), 73.2 (d), 123.5 (d), 124.9 (d), 128.0 (d), 129.8 (d), 130.1 (d), 135.7 (s), 139.0 (d), 154.8 (s), 176.7 (s). Anal. Calcd for $C_{19}H_{24}O_6N_2$: C, 57.86; H, 6.64; N, 7.10. Found: C, 57.45, H, 6.56; N, 7.08. Amine **1b** was obtained by treatment of an aqueous D-tartaric acid salt solution with 33% aqueous NaOH solution and extraction with dichloromethane. After evaporation of the solvent and distillation [113 °C (0.08 torr)], 13.7 g (0.061 mol) of a colorless oil was obtained: yield, 61%; $[\alpha]^{rt}_{578}$ −189° (*c* 9.6, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.23 (d, 3 H), 1.26 (d, 3 H), 2.2 (br s, 1 H), 3.27 (q, 1 H), 3.50 (q, 1 H), 6.6–7.7 (m, 9 H), 8.3 (br d, 1 H); ^{13}C NMR ($CDCl_3$) δ 23.3 (q), 25.0 (q), 55.5 (d), 56.1 (d), 121.6 (d), 121.7 (d), 126.6 (d), 128.2 (d), 140.0 (d), 145.5 (s), 149.5 (d), 164.7 (s). In the NMR spectra of the crude reaction mixture absorptions for the *S,R* isomer (**2b**) could also be observed: ^{1}H NMR ($CDCl_3$) δ 1.37 (d) [the other absorption coincide with the absorptions of **1b**]; ^{13}C NMR ($CDCl_3$) δ 21.7, 24.1, 54.9, 55.9, 119.5, 120.9, 121.8, 126.4, 128.1, 136.4, 147.9, 148.9, 164.3.

Synthesis of (*S*)-*N*-[1-(*o*-Methoxyphenyl)ethyl]-(*S*)-α-methylbenzylamine (1c). The procedure was the same as for **1a** and was performed on a 0.1 mol scale. The *anti*-**4c**/*syn*-**4c** imines were formed in a ratio of 2 to 1. *syn*-**4c**: ^{1}H NMR ($CDCl_3$) δ 1.36 (d), 2.23 (s), 3.70 (s), 4.17 (q), 6.5–7.5 (m). *anti*-**4c**: ^{1}H NMR ($CDCl_3$) δ 1.53 (d), 2.15 (s), 3.70 (s), 4.73 (q), 6.5–7.5 (m). After hydrogenation only one product (**1c**) was formed (yield; 78%), because the ^{1}H as well as the ^{13}C NMR spectrum contained only one set of absorptions: $[\alpha]^{rt}_D$ −103° (*c* 2.5, $CHCl_3$). Compound **1c** was purified by recrystallization of its HCl salt from water. **1c**·HCl: yield, 72%; $[\alpha]^{rt}_D$ −40.6° (*c* 2.5, EtOH); mp 232.7–233.2 °C; ^{1}H NMR ($CDCl_3$) δ 1.83 (d, 3 H), 1.95 (d, 3 H), 3.63 (s, 3 H), 3.0–3.4 (m, 2 H), 6.7–7.9 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 20.1 (q), 21.2 (q), 51.1 (d), 54.9 (q), 57.1 (d), 110.3 (d), 121.1 (d), 124.3 (s), 128.1 (d), 128.4 (d), 128.5 (d), 128.9 (d), 129.6 (d), 136.2 (s), 156.4 (s). Anal. Calcd for $C_{17}H_{22}ClNO$: C, 69.99; H, 7.60; N, 4.80; Cl, 12.12. Found: C, 69.91; H, 7.51; N, 4.74; Cl, 12.12. **1c**: yield, 70%; $[\alpha]^{rt}_D$ −110.0° (*c* 2.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.21 (d, 3 H), 1.26 (d, 3 H), 1.90 (br s, 1 H), 3.63 (s, 3 H), 3.3–4.1 (m, 2 H), 6.4–7.5 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 22.6 (q), 25.0 (q), 51.3 (d), 54.8 (q), 55.1 (d), 110.5 (d), 120.4 (d), 126.4 (d), 126.6 (d), 127.2 (d), 127.7 (d), 127.9 (d), 133.1 (s), 145.8 (s), 157.2 (s).

Synthesis of (*S*)-*N*-[1-(*m*-Methoxyphenyl)ethyl]-(*S*)-α-methylbenzylamine (1d). The same procedure as for **1a** on a 0.03-mol scale was used. The *anti*-**1d**/*syn*-**1d** imines were formed in a ratio of 9 to 1. *anti*-**1d**: ^{1}H NMR ($CDCl_3$) δ 1.50 (d), 2.16 (s), 3.78 (s), 4.73 (q), 6.0–7.5 (m). *syn*-**1d**: ^{1}H NMR ($CDCl_3$) δ 1.38 (d), 2.27 (s), 3.68 (s), 4.00 (q), 6.0–7.5 (m). After hydrogenation the amines **1d** and **2d** were formed in a 5.0 to 1.0 ratio in 80% yield. Amine **1d** was obtained in a pure form as its HCl salt by recrystallization of the HCl salts of the reaction mixture from water: yield, 54%; **1d**·HCl: $[\alpha]^{rt}_D$ −65.4° (*c* 2.3, EtOH); mp 217.1–217.7 °C; ^{1}H NMR ($CDCl_3$) δ 1.88 (d, 6 H), 3.83 (s + m, 5 H), 4.60 (br s, 2 H), 6.6–7.7 (m, 9 H). ^{13}C NMR ($CDCl_3$) δ 21.2 (q), 55.5 (q), 56.9 (d), 111.8 (d), 115.8 (d), 120.2 (d), 127.9 (d), 128.9 (d, 2 ×), 129.8 (d), 136.0 (s), 137.5 (s), 160.2 (s). Anal. Calcd for $C_{17}H_{22}ClNO$: C, 69.99; H, 7.60; N, 4.80; Cl, 12.12. Found: C, 69.75; H, 7.53; N, 4.77; Cl, 12.12. **1d**: yield, 45%; $[\alpha]^{rt}_D$ −135.8° (*c* 2.9, EtOH); ^{1}H NMR ($CDCl_3$) δ 1.21 (d, 6 H), 1.58 (br s, 1 H), 2.40 (br q, 2 H), 3.65 (s, 3 H), 6.4–7.4 (m, 9 H); ^{13}C NMR ($CDCl_3$) δ 24.8 (q), 54.9 (q + d), 111.8 (d), 112.0 (d), 118.8 (d), 126.4 (d), 126.6 (d), 128.2 (d), 129.2 (d), 145.6 (s), 147.5 (s), 159.6 (s). In the ^{1}H NMR spectrum of the crude reaction mixture an absorption for the *S,R* isomer (**2d**) could also be observed: ^{1}H NMR ($CDCl_3$) δ 1.34 (d) [the other absorptions coincide with the absorptions of **1d**].

Synthesis of (*R*)-*N*-[2-Methoxy-1-phenylethyl]-(*S*)-α-methylbenzylamine (1e). The same procedure as for **1a** on a 0.11-mol scale was used. The *anti*-**4e**/*syn*-**4e** imines were formed in a ratio of 1.4 to 1.0. *anti*-**4e**: ^{1}H NMR ($CDCl_3$) δ 1.42 (d, 3 H), 3.45 (s, 3 H), 4.18 (s, 2 H), 4.50 (q, 1 H), 6.5–7.5 (m). *syn*-**4e**: ^{1}H NMR ($CDCl_3$) δ 1.32 (d, 3 H), 3.28 (s, 3 H), 5.53 (s, 2 H), 4.03 (q, 1 H), 6.5–7.5 (m). After hydrogenation the amines **1e** and **2e** were formed in a 2.0 to 1.0 ratio: yield, 67%. Product **1e** was obtained in a pure form as its HCl salt by recrystallization of the HCl salts of the reaction mixture from ethanol/water (2:5, v/v). **1e**·HCl: yield, 34%; $[\alpha]^{rt}_{578}$ −82.2° (*c* 1.0, $CHCl_3$); mp 203.4–203.5 °C; ^{1}H NMR ($CDCl_3$) δ 1.97 (d, 3 H), 3.20 (s, 3 H), 3.5–4.5 (m, 4 H), 7.42 (br s, 10 H); ^{13}C NMR ($CDCl_3$) δ 21.2 (q), 57.0 (d), 58.9 (q), 60.3 (d), 72.7 (t), 128.0 (d), 129.0 (d), 129.2 (d), 129.4 (d), 132.4 (s), 135.9 (s). Anal. Calcd for $C_{17}H_{22}ClNO$: C, 69.99; H, 7.60; N, 4.80; Cl, 12.12. Found: C, 69.91; H, 7.60; N, 4.81; Cl, 12.07. Amine **1e** could be obtained in a pure form by treatment of its HCl salt by NaOH in a similar way as described for **1a**. **1e**: yield, 33%; $[\alpha]^{rt}_{578}$ −168.1° (*c* 2.3, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.27 (d, 3 H), 2.20 (br s, 1 H), 3.17 (s, 3 H), 3.2–3.7 (m, 4 H), 6.7–7.3 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 24.7 (q), 54.6 (d), 58.4 (q), 59.0 (d), 77.7 (t), 126.4 (d), 126.6 (d), 127.2 (d), 127.6 (d), 128.2 (2×, d + d), 140.9 (s), 145.4 (s). After the recrystallization of the **1e**·HCl/**2e**·HCl mixture, 50 mL of diethyl ether was added to the mother liquor. Subsequently, this solution was treated with an aqueous 4 N NaOH solution. After separation of the layers, washing the organic layer with brine, drying ($MgSO_4$), and evaporation of the solvent, a yellow oil resulted. This oil was subjected to a bulb-to-bulb distillation [130 °C (0.1 torr)], affording a colorless oil, which contained the amines **1e** and **2e** in a ratio of 1:2. From this mixture the following NMR data for **2e** were obtained: ^{1}H NMR ($CDCl_3$) δ 1.34 (d, 3 H), 2.2 (br s), 3.25 (s, 3 H), 3.2–3.7 (m), 6.7–7.5 (m); ^{13}C NMR ($CDCl_3$) δ 22.0 (q), 54.5 (d), 58.6 (q), 59.7 (d), 77.2 (t), 126.3 (d), 127.0 (d), 127.4 (d), 128.0 (d), 141.1 (s), 145.8 (s).

Synthesis of (*R*)-*N*-[2-Hydroxy-1-phenylethyl]-(*S*)-α-methylbenzylamine (1f). A solution of 50 mmol (6.86 g) of (*R*)-α-phenylglycinol ($[\alpha]^{24}_D$ −31.6° (*c* 0.9, 1 N HCl)), 55 mmol (6.61 g) of acetophenone, and a catalytic amount of *p*-toluenesulfonic acid was refluxed during 18 h under continuous removal of water by m eans of a Dean–Stark trap. After drying over magnesium sulfate and evaporation of the solvent, the 1,3-oxazolidine/imine mixture was obtained in a quantitative yield (98%). As shown by ^{1}H NMR spectra the two isomers **7**/*anti*-**4f** were formed in a 3.1 to 1.0 ratio: ^{1}H NMR ($CDCl_3$) δ 1.67 (s), 2.07 (s) [both signals together 3 H, ratio to each other is 3.1 to 1.0], 2.53 (br s, 1 H), 3.35–4.95 (m, 3 H), 6.8–8.0 (m, 10 H). ^{13}C NMR ($CDCl_3$): because of the complexity of the spectrum only some characteristic signals are mentioned: δ 97.9 (s) C_2 of 1,3-oxazolidine **7**,[17] δ 167.8 (s) imine carbon atom of *anti*-**4f**. The 1,3-oxazolidine/imine mixture was dissolved in 25 mL of THF, and 0.1 g of 10% palladium on charcoal was added. This mixture was shaken in a Parr apparatus during 20 h under 3 atm of hydrogen pressure. After filtration of the catalyst, drying over magnesium sulfate, and evaporation of the solvent, the reaction mixture was treated with 100 mL of an aqueous 1 N HCl solution. This solution was washed with 50 mL of ether, treated with NaOH until

pH >10, and subsequently extracted with ether (3 × 100 mL). The ethereal solution was washed with brine and dried ($MgSO_4$), and the solvent was evaporated, resulting in a colorless oil. After bulb-to-bulb distillation 8.80 g (36.5 mmol) of a colorless oil, **1f** was obtained, which slowly solidified. In the NMR spectra there was no indication of the presence of a diastereomer (**2f**). **1f**: yield, 73%; $[\alpha]^{rt}_{578}$ −186.3° (*c* 10, $CHCl_3$); mp ≈ 30 °C; ^1H NMR ($CDCl_3$) δ 1.27 (d, 3 H), 7.0–7.3 (2 × br s, 10 H), 3.27 (br s), 3.47 (s), 3.1–3.7 (m) [integration of the last three signals together is 6 H]; ^{13}C NMR ($CDCl_3$) δ 24.8 (q), 54.6 (d), 61.3 (d), 66.7 (t), 126.6 (d), 126.9 (d), 127.2 (d), 127.3 (d), 128.3 (d), 128.4 (d), 140.5 (s), 144.6 (s).

Synthesis of 1e by Methylation of 1f. To a solution of 1.0 mmol of **1** in 4 mL of freshly distilled Me_2SO was added 5.0 mmol (280 mg) of powdered potassium hydroxide. Under stirring, 2.2 mmol (0.14 mL) of methyliodide was added dropwise, and stirring was continued for 3 h. Crushed ice was added, and the solution was extracted with *n*-hexane/dichloromethane (5:1, v/v). The organic layer was washed three times with water and dried ($MgSO_4$), and the solvent was evaporated, which yielded a yellow oil that was treated with 10 mL of an aqueous 1 N HCl solution. This solution was washed with 10 mL of ether, treated with NaOH till pH >10, and subsequently extracted with ether (3 × 10 mL). The ethereal solution was washed with brine and dried ($MgSO_4$), and the solvent was evaporated, resulting in a colorless oil. This oil was purified by bulb-to-bulb distillation [120 °C (0.01 torr)], yielding 140 mg of a colorless oil: yield, 55%. **1e**: $[\alpha]^{rt}_{578}$ −155.3° (*c* 2.5, $CHCl_3$). ^1H NMR and ^{13}C NMR spectra are identical with those reported above. Amine **1e** was further purified by recrystallization of its HCl salt in a similar way as described before in the synthesis of **1e**, starting from (*R*)-phenylglycinol and acetophenone: $[\alpha]^{rt}_{578}$ −165.4° (*c* 2.4, $CHCl_3$).

Synthesis of (*R*)-2,4-Diphenyl-2-(methoxymethyl)-1,3-oxazolidines (9). A solution of 61 mmol (8.37 g) of (*R*)-α-phenylglycinol ($[\alpha]^{24}_D$ −31.6° (*c* 0.9, 1 N HCl)), 61 mmol (9.16 g) of α-methoxyacetophenone, and a catalytic amount (about 100 mg) of *p*-toluenesulfonic acid in 90 mL of benzene was refluxed under a nitrogen atmosphere under continuous removal of water by means of a Dean–Stark trap during 72 h. After the workup procedure as used for **4a** the oxazolidines were obtained in a quantitative yield (100%). The ratio of the isomers was determined by ^{13}C NMR instead of ^1H NMR spectroscopy because the latter did not give a reliable integration. The ratio of the two diastereomers **9** was 1 to 5.6. Major product: ^1H NMR ($CDCl_3$) δ 3.17 (br s), 3.37 (s), 3.52 (s), 3.3–4.8 (m), 7.0–7.8 (m). Minor product: ^1H NMR ($CDCl_3$) δ 3.17 (br s), 3.33 (s), 3.50 (s), 3.3–4.8 (m), 7.0–7.8 (m). Major product: ^{13}C NMR (C_6D_6) δ 59.3 (q), 61.8 (d), 72.6 (t),[19] 76.6 (t), 100.2 (s), 140.4 (s), 142.9 (s). Minor product: ^{13}C NMR (C_6D_6) δ 59.3 (q), 62.7 (d), 72.6 (t), 78.0 (t), 99.2 (s), 141.8 (s), 143.7 (s). The aromatic C atoms (δ 127.0–128.8) could not be assigned. IR (neat) showed very weak absorption at 3300 cm^{-1} (rather NH than OH stretch) and the absence of absorption at about 1640 cm^{-1} (characteristic for imines).

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Registry No. **1a**, 56210-72-1; **1a**·HCl, 40648-92-8; **1b**, 90933-76-9; **1b**·tartrate, 103639-23-2; **1c**, 90933-74-7; **1c**·HCl, 103621-03-0; **1d**, 90933-75-8; **1d**·HCl, 103621-05-2; **1e**, 90933-77-0; **1e**·HCl, 103621-06-3; **1f**, 103621-10-9; **2a**, 21003-57-6; **2b**, 95447-96-4; **2d**, 103621-04-1; **2e**, 95447-97-5; **2e**·HCl, 103621-07-4; **3a**, 98-86-2; **3b**, 1122-62-9; **3c**, 579-74-8; **3d**, 586-37-8; **3e**, 4079-52-1; **4a** isomer 1, 100483-17-8; **4a** isomer 2, 100483-18-9; **4b** isomer 1, 53547-68-5; **4b** isomer 2, 103667-24-9; **4c** isomer 1, 103667-21-6; **4c** isomer 2, 103667-25-0; **4d** isomer 1, 103667-22-7; **4d** isomer 2, 103667-26-1; **4e** isomer 1, 103667-23-8; **4e** isomer 2, 103667-27-2; (*E*)-**4f**, 103621-09-6; **7**, 103621-08-5; **9** isomer 1, 103621-11-0; **9** isomer 2, 103621-12-1; (*S*)-α-methylbenzylamine, 2627-86-3; (*R*)-α-phenylglycinol, 56613-80-0.

(19) The two coinciding signals of δ 72.6 (t) became separated when $CDCl_3$ instead of C_6D_6 was used as solvent (δ 72.1 (t), major product; δ 72.3 (t), minor product).