followed by slow crystallization from methylene chloride and methanol gave colorless crystals (48 mg, mp 188–192 °C dec) which, according to ^{1}H NMR analysis (cf. Table I), consisted of **5** and **6** in a ratio of 20:1. Dimers **5** and **6** crystallize together, and we have not been able to separate the two isomers.

Irradiation of 3 To Give 1 and 5. A solution of **3** (3 mg) in benzene (4 mL) was irradiated for 2 h with light of 378 ± 8 nm (monochromator). ^{1}H NMR analysis of the residue obtained on vacuum evaporation revealed the presence of starting material (28 mol %), the formation of **1** (27 mol %), and the formation of **5** (45 mol %). There was no dimer **6** detectable.

Triplet-Sensitized Reaction of 3. A solution of **3** (10 mg) and biacetyl (90 mg) in benzene (4 mL) was irradiated for 20 min with wavelengths >440 nm (cutoff filter). The reaction mixture was analyzed by ^{1}H NMR spectroscopy and found to consist of unchanged starting material (46 mol %), styrylanthracene **1** (52 mol %), and dimer **6** (2 mol %). There was no dimer **5** detectable. (Styrylanthracene **1** was found to be stable in the presence of photoexcited biacetyl.)

Triplet-Sensitized Isomerization of 17 To Give 18. A degassed solution of **17** (6.5 mg) and biacetyl (150 mg) in benzene (12 mL) was irradiated with wavelengths >440 nm for 81 min. Vacuum evaporation of solvent and biacetyl gave a residue, which according to ^{1}H NMR analysis consisted of **18**: ^{1}H NMR δ 7.57 (d, J = 7.3 Hz, 1), 7.41 (d, J = 5.7 Hz, 1), 6.70–7.25 (m, 15), 6.68 (d, J = 5.7 Hz, 1), 5.18 (d, J = 10.7 Hz, 1), 5.0 (d, J = 10.7 Hz, 1), 4.27 (d, J = 10 Hz, 1), 4.00 (d, J = 10 Hz, 1). In the photochemical isomerization of **17** (100 mg) by direct excitation in benzene (120 mL; λ > 340 nm; 125-W mercury lamp; immersion-well apparatus; argon), **18** was isolated in 90% yield [colorless crystals, which turn yellow upon heating around 90 °C, melting around 135 °C, followed by resolidification; the final melting point is around 290 °C, which is that of *trans,trans*-1,5-bis(9-anthryl)penta-1,4-dien-3-one (cf. ref 2)].

Quantum Yield Measurements. The dimerization quantum yields are based on the potassium ferrioxalate actinometer, and they refer to measurements conducted at 20 °C in the concentration range between 0.01 and 0.1 M. However, for some unknown reason and independent of the initial concentration, at conversions below 0.05 the disappearance of **1** was found to proceed faster than is in accordance with the concentration-dependent change of quantum yield. Therefore, the measurements were evaluated iteratively for conversions ranging from 0.05 to 0.25.

The fluorescence quantum yields were determined with an Aminco Bowman SPF 500 spectrofluorometer modified for frontal illumination. The quantum yields and the fluorescence life time in dilute benzene solution were measured at 20 °C.

Registry No. **1**, 42196-97-4; **3**, 97635-20-6; **4**, 97635-19-3; **5**, 97635-21-7; **6**, 97673-32-0; **17**, 84599-82-6; **18**, 97635-22-8; *trans,trans*-1,5-bis(9-anthryl)penta-1,4-dien-3-one, 84599-83-7.

Asymmetric Nucleophilic Acylation via Metalated α-Amino Nitriles Possessing an Axially Disymmetric Tertiary Amino Group

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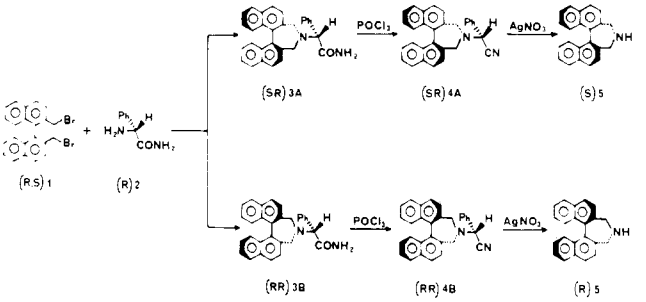
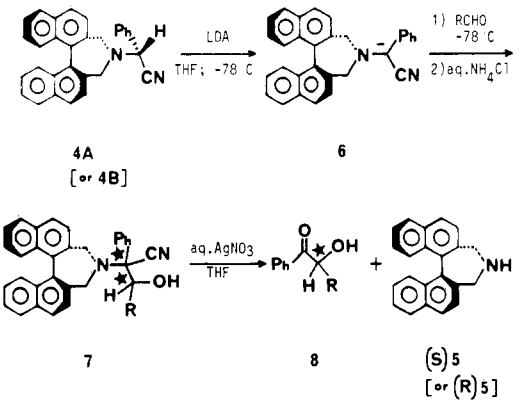
Asymmetric versions of nucleophilic acylation reactions, using metalated chiral α-amino nitriles as acyl anion equivalents in nucleophilic addition to aldehydes, have been recently developed.[1] In these reactions, the chirality information, easily introduced via the amino function, originated from secondary amines derived from natural (*S*)-proline and contained one or several asymmetric carbon atoms.

†Deceased April 21, 1984.

Scheme I



Scheme II



Considering the high interest raised for the past few years by axially disymmetric compounds in asymmetric synthesis,[2] we have been inclined to apply the known preparation of binaphthyl tertiary amines[2d,3] to the synthesis of α-amino nitriles bearing a binaphthyl unit, in order to investigate the relative efficiency of such a C_2-symmetric chiral auxiliary in asymmetric nucleophilic acylation reactions.

In the present paper, we report the synthesis of the diastereoisomerically pure α-amino nitriles **4A** and **4B** from racemic 2,2′-bis(bromomethyl)-1,1′-binaphthyl [(RS)-**1**] and their use as chiral acyl anion equivalents in nucleophilic addition to aldehydes.

Furthermore, compounds **4A** and **4B** are direct precursors of the secondary amines (*S*)-**5** and (*R*)-**5**, which are interesting key substances for the development of new binaphthyl derivatives and are obtained by this method in an optically pure state or nearly so from the racemic dibromide (*RS*)-**1**.[4]

Treatment of 2-2′-bis(bromomethyl)-1,1′-binaphthyl [(*RS*)-**1**][6] with an excess of D-(−)-α-aminophenylacetamide

(1) (a) Enders, D. In "IUPAC Current Trends in Organic Synthesis"; Nozaki, N., Pergamon Press: Oxford, 1983; p 151. (b) Enders, D.; Lotter, H.; Maigrot, N.; Mazaleyrat, J. P.; Welvart, Z. *Nouv. J. Chim.* **1984**, *8*, 747 and references cited therein.

(2) (a) Nishizawa, N.; Yamada, M.; Noyori, R. *Tetrahedron Lett.* **1981**, 247. (b) Ishiguro, M.; Koizumi, N.; Yasuda, M.; Ikekawa, N. *J. Chem. Soc. Chem. Commun.* **1981**, 115. (c) Olivero, A. G.; Weidmann, B.; Seebach, D. *Helv. Chim. Acta* **1981**, *64*, 2585. (d) Mazaleyrat, J. P.; Cram, D. J. *J. Am. Chem. Soc.* **1981**, *103*, 4585. (e) Cram, D. J.; Sogah, G. D. Y. *J. Chem. Soc. Chem. Commun.* **1981**, 625. (f) Miyashita, A.; Yasuda, A.; Takaya, A.; Toriumi, K.; Ito, T.; Souchi, T.; Noyori, R. *J. Am. Chem. Soc.* **1980**, *102*, 7932. (g) Mazaleyrat, J. P. *Tetrahedron Lett.* **1983**, *24*, 1243. (h) Sakane, S.; Fujiwara, J.; Maruoka, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1983**, *105*, 6155. (i) Amano, M.; Watanabe, M.; Baba, N.; Oda, J.; Inouye, Y. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 3672.

(3) Cottineau, F.; Maigrot, N.; Mazaleyrat, J. P. *Tetrahedron Lett.* **1985**, *26*, 421.

(4) Synthesis of the amine **5** by direct reaction of ammonia with the dibromide **1** is unsatisfactory because of the occurrence of a further bis alkylation reaction which is difficult to control and leads to a quaternary ammonium salt.[5]

(5) Unpublished results from our laboratory and: Wittig, G.; Koenig, G.; Clauss, K. *Justus Liebigs Ann. Chem.* **1955**, *593*, 127.

0022-3263/85/1950-3916$01.50/0

Table I. α-Hydroxy Ketones PhCOCH(OH)R 8 Obtained by Addition of the Anions of the α-Amino Nitriles 4 to the Aldehydes RCHO

α-amino nitrile		α-hydroxy ketone 8				
	abs config[a]	R	yield,[b] %	$[\alpha]^{23}_{546}$ (d, 95% EtOH)	ee,[c] %	abs config
4A	S	Me	30	−13.9° (1.7)	34	S[d]
4B	R	Me	33	+12.5° (2.4)	31	R[d]
4A	S	n-Pr	56	+10.4° (2.5)	50	R[d]
4B	R	n-Pr	46	−9.7° (2.6)	46	S[d]
4A	S	i-Pr	32	−0.7° (2.1)	4	R[e]
4A	S	t-Bu	0			
4A	S	$PhCH_2$	24	−7.4° (1.9)	56	R[f]

[a] Of the binaphthyl unit. [b] Isolated product. [c] Determined from the Mosher's esters[10] of the α-ketols 8, by ^1H NMR and GC. [d] Reference 1b. [e] Determined by treatment of L-α-hydroxyisovaleric acid obtained from L-(+)-valine[11] with phenyllithium, which led to a sample of (S)-8 (R = i-Pr) having a positive optical rotation $[\alpha]^{23}_{546}$ +20° (c 2.2, 95% EtOH). [f] Reference 12.

(2)[7] and triethylamine in refluxing benzene/acetonitrile led quantitatively to a 1:1 diastereoisomeric mixture of α-amino amides 3 (Scheme I). Crystallization from dichloromethane/ethyl acetate led to the pure isomers (*SR*)-**3A** (76% yield) and (*RR*)-**3B** (46% yield). Such fractionation, corresponding to a resolution of the binaphthyl moiety, was quickly realized because of the relative low solubility of compound **3A**. The absolute configuration of the binaphthyl unit in these two α-amino amides was established by reacting optically pure (*S*)-**1** and (*R*)-**1**[6] with (*R*)-**2**, which led to samples of (*SR*)-**3A** and (*RR*)-**3B**, respectively, having identical melting points, ^1H NMR spectra, and optical rotations as those obtained by fractionation.

The two diastereoisomeric α-amino amides were converted into the corresponding α-amino nitriles (*SR*)-**4A** (94%) and (*RR*)-**4B** (94%) with phosphorus oxychloride in dimethylformamide.[7] Treatment of **4A** and **4B** with an excess of aqueous silver nitrate in THF led to the secondary amines (*S*)-**5** (58%) and (*R*)-**5** (69%), respectively (Scheme II).

In nucleophilic acylation experiments, the α-amino nitrile **4** (**A** or **B**) was deprotonated with lithium diisopropylamide (LDA) in THF at −78 °C, and the aldehyde RCHO (R = Me, *n*-Pr, *i*-Pr, *t*-Bu, $PhCH_2$) was added to the resulting anion **6**. After 3 h at −78 °C, the reaction mixture was quenched with aqueous ammonium chloride. In order to prevent any fractionation, the mixture of diastereoisomeric β-hydroxy-α-amino nitriles **7** obtained after extraction was directly hydrolyzed with aqueous silver nitrate to the corresponding α-hydroxy ketone **8** and amine **5**.[9]

The chemical yields, optical rotations, enantiomeric excesses, and absolute configurations of the isolated α-hydroxy ketones **8** are reported in Table I.

The results show that the α-amino nitrile **4A** containing a (*S*)-binaphthyl group leads to (*R*)-α-ketols for R = *n*-Pr, *i*-Pr, and $PhCH_2$ but surprisingly to the opposite configuration for R = Me. It can also be pointed out that the use of the two diastereoisomeric α-amino nitriles **4A** and **4B** with the same aldehyde RCHO gives rise to α-ketols of opposite configuration, with similar ee's, suggesting that the corresponding anions **6** behave like enantiomers rather than diastereomers (i.e., the initial configuration of the α-carbon atom of the amino nitrile is not memorized in the corresponding anion, as expected).

The present study constitutes the first example of asymmetric induction by axially disymmetric compounds in nucleophilic acylation reactions. Although relatively low enantiomeric excesses are obtained in these preliminary experiments, the binaphthyl unit, which is subject to structural modifications, already appears to be at least as efficient as various other chiral auxiliaries derived from natural products.[1b,13]

It can also be pointed out that the easy access to the amino nitriles **4** and to the secondary amine **5** in an optically pure state opens the way toward the synthesis of new axially disymmetric amino compounds, which may find applications to asymmetric synthesis beyond the one presently described.

Experimental Section

α-[4,5-Dihydro-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]azepinyl]-α-phenylacetamides (*SR*)-3A and (*RR*)-3B. Racemic dibromide (*RS*)-**1** (11 g; 25 mmoles) was introduced in a 500-cm^3 round-bottomed flask and dissolved in 25 cm^3 of hot benzene. (−)-α-Aminophenylacetamide (*R*)-**2**[7] (8 g; 53 mmol), triethylamine (5.1 g, 50 mmol), and acetonitrile (250 cm^3) were rapidly added to the resulting solution. The reaction mixture was magnetically stirred and refluxed for 10 h and then left at room temperature overnight. On standing a few minutes, a white precipitate deposited, and analytical TLC (SiO_2; CH_2Cl_2) of the clear upper solution showed no spot for the starting dibromide. After addition of ca. 700 cm^3 of CH_2Cl_2 and 400 cm^3 of H_2O, the organic phase was separated. The aqueous phase was extracted twice with 100 cm^3 of CH_2Cl_2. The combined organic phase was dried over $MgSO_4$ and filtered, and the solvents were removed on a rotary evaporator. The residue was dissolved in ca. 1.5 L of CH_2Cl_2 and the solution filtered on a column of SiO_2 (Kieselgel 60; 0.063–0.2 mm; 70–230 mesh ASTM; Merck) made up with CH_2Cl_2. Elution with 2 L of CH_2Cl_2/MeOH (95:5) led to 11 g (100%) of a 1:1 diastereoisomeric mixture of α-amino amides **3A** and **3B**. Another previous experiment on smaller scale starting from (*R,S*)-**1** (2.2 g; 5 mmol) and (*R*)-**2** (1.5 g, 10 mmol) gave 2.18 g (100%) of purified mixture **3A** + **3B**. The diastereoisomeric mixture (12 g; 28 mmol) was dissolved in 800 cm^3 of boiling CH_2Cl_2, and the hot solution was filtered (paper) in a 2-L Erlenmeyer flask and boiled on a hot plate. Ethyl acetate (1.4 L) was added by portions to the boiling solution, which was finally concentrated to ca 1 L. Crystallization started to occur from the boiling solution. After 48 h at room temperature, the crystals were filtered, washed with ethyl acetate, and air-dried to give 4.58 g (76%) of pure isomer (*SR*)-**3A**: mp 281–284 °C; ^1H NMR ($CDCl_3$/Me_4Si) δ 8.1–7.2 (m, 17 H, Ar H), 3.91 (s, 1 H,

(6) Hall, D. M.; Turner, E. E. *J. Chem. Soc.* **1955**, 1242.
(7) Neilson, D. G.; Ewing, D. F. *J. Chem. Soc. C* **1966**, 393.
(8) Chauffaille, J.; Hébert, E.; Welvart, Z. *J. Chem. Soc., Perkin Trans 2* **1982**, 1645.
(9) Compounds **4** could be regenerated, or other α-amino nitriles prepared, from the amine **5** by reaction with aldehyde and hydrocyanic acid.[1b]
(10) Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543.
(11) Winitz, M.; Bloch-Frankenthal, L.; Izumiya, I.; Birnbaum, S. M.; Baker, C. G.; Greenstein, J. P. *J. Am. Chem. Soc.* **1956**, *78*, 2423.
(12) McKenzie, A.; Martin, G.; Rule, H. G. *J. Chem. Soc.* **1914**, *105*, 1583.
(13) Beyond structural modifications incorporated into the reagents **4A** and **4B**, it should be possible, as suggested by the referees, to obtain enantiomerically pure ketols through purification of the diastereoisomeric adducts **7**. This has been shown previously to work in one experiment with 2-(methoxymethyl)pyrrolidine as chiral auxiliary,[1b] and the increased crystallinity brought by the binaphthyl unit in the present case should help.

NC*H*(Ph)CO), 3.90 and 3.20 (dd, J = 12 Hz, 4 H, Ar CH_2N), $[\alpha]^{20}_{\lambda}$ (c 1.3, DMF) +223.1° (589), + 232.3° (578), +258.7° (546), +330.9° (436); MS, m/e 428 (M^+). Anal. Calcd for $C_{30}H_{24}N_2O$: C, 84.08; H, 5.65; N, 6.54. Found: C, 83.86; H, 5.57; N, 6.54.

The mother liquor was concentrated on a hot plate to ca. 300 cm^3 and left at room temperature. The obtained crystals [4.44 g; 74%; $[\alpha]^{20}_{546}$ −368° (c 1.2, DMF); corresponding to ca. 82% (*RR*)-**3B**, 18% (*SR*)-**3A** by ^1H NMR) were recrystallized from ethyl acetate to give 2.76 g (46%) of pure (*RR*)-**3B**: mp 263–266 °C; ^1H NMR ($CDCl_3/Me_4Si$) δ 8.1–7.2 (m, 17 H, Ar H), 4.09 (s, 1 H, NC*H*(Ph)CO), 3.62 and 3.13 (dd, J = 12 Hz, 4 H, Ar CH_2N); $[\alpha]^{20}_{\lambda}$ (c 1, DMF) −356.1° (589), −372.8° (578), −422.4° (546), −638.5° (436), +190.2° (365). Anal. Calcd for $C_{30}H_{24}N_2O$: C, 84.08; H, 5.65; N, 6.54. Found: C, 83.79; H, 5.50; N, 6.63.

A similar reaction using optically pure (*S*)-**1**[6] (0.220 g; 0.5 mmol) and (*R*)-**2** (0.16 g; 1.1 mmol) led after crystallization from dichloromethane/ethyl acetate, to (*SR*)-**3A**: 0.146 g (68%); mp 278–280 °C; ^1H NMR (vide supra); $[\alpha]^{20}_{\lambda}$ (c 1, DMF) +225.7° (589), +234.7° (578), +261.0° (546), +333.7° (436).

A similar reaction reaction using optically pure (*R*)-**1**[6] (0.220 g; 0.5 mmol) and (*R*)-**2** (0.16 g; 1.1 mmol) led after crystallization to (*RR*)-**3B**: 0.085 g (39%); mp 262–264 °C; ^1H NMR (vide supra); $[\alpha]^{20}_{\lambda}$ (c 1, DMF) −353.0° (589), −367.7° (578), −417.0° (546), −626.0° (436).

α-[2,7-Dihydrodinaphtho[2,1-*c*:1′,2′-*e*]azepinyl]-α-phenylacetonitriles (*S*,*R*)-4A and (*RR*)-4B. To 4.44 g (10.4 mmoles) of α-amino amide (*SR*)-**3A** in 100 cm^3 of DMF at 0 °C was added drop by drop a large excess of $POCl_3$ (10 cm^3) during a period of 1 h. The resulting solution was magnetically stirred at 0 °C and then at room temperature overnight and poured into water (2 L). The resulting precipitate was filtered, washed with water, air-dried, dissolved in 100 cm^3 of CH_2Cl_2, and chromatographed on a column of SiO_2 (Kieselgel 60) made up with CH_2Cl_2. Elution with CH_2Cl_2 led to pure (*SR*)-**4A** as a white crystalline solid: 4.0 g (94%); mp 215–218 °C (not recrystallized); ^1H NMR ($CDCl_3/Me_4Si$) δ 8.1–7.0 (m, 17 H, Ar H), 4.87 (s, 1 H, NC*H*(Ph)CN), 3.75 and 3.45 (dd, J = 12 Hz, 4 H, Ar CH_2N); $[\alpha]^{23}_{\lambda}$ (c 1.2, $CHCl_3$) +382.0° (589), +399.0° (578), +453.1° (546), +731.1° (436); MS, m/e 410 (M^+). Anal. Calcd for $C_{30}H_{22}N_2$; C, 87.77; H, 5.40; N, 6.82. Found: C, 86.93; H, 5.25; N, 7.00.

In the same manner, treatment of (*RR*)-**3B** (2.63 g; 6.1 mmol) with $POCl_3$ led after chromatography to pure (*RR*)-**4B** as a white solid foam: 2.37 g (94%); mp ≃ 105–115 °C; ^1H NMR ($CDCl_3/Me_4Si$) δ 8.1–7.0 (m, 17 H, Ar H), 4.70 (s, 1 H, NC*H*(Ph)C 3.75 and 3.38 (dd, J = 12 Hz, 4 H, Ar CH_2CN); $[\alpha]^{23}_{\lambda}$ (c 1.1 $CHCl_3$) −217.5° (589), −228° (578), −258.8° (546), −391° (436). Anal. Calcd for $C_{30}H_{22}N_2$: C, 87.77; H, 5.40; N, 6.82. Found: C, 87.55; H, 5.21; N, 6.83.

2,7-Dihydrodinaphtho[2,1-*c*:1′,2′-*e*]azepine (*S*)-5 and (*R*)-5. To a solution of α-amino nitrile (*SR*)-**4A** (0.41 g; 1 mmol) in 50 cm^3 of THF was rapidly added 20 cm^3 of aqueous $AgNO_3$ (0.5 N). The mixture was stirred at room temperature overnight. After addition of CH_2Cl_2 (50 cm^3)/Et_2O (350 cm^3), the organic phase was separated, washed with water, and dried ($MgSO_4$). The solvents were removed on a rotary evaporator, and the residue was dissolved in ether. The ether solution was extracted twice with 20% HCl and the acid phase made basic with an excess of aqueous KOH. Extraction with ether led to pure amine (*S*)-**5** as a pale yellow solid foam: 0.181 g (58%); ^1H NMR ($CDCl)_3/Me_4Si$) δ 8.1–7.0 (m, 12 H, Ar H) 3.77 and 3.42 (dd, J = 12 Hz, 4 H, Ar CH_2N), 2.40 (s, 1 H, NH); $[\alpha]^{20}_{\lambda}$ (c 0.7, $CHCl_3$) +574.8° (589), +601.8° (578), +689.3° (546), +1196.7° (436); MS, m/e 295 (M^+). Anal. Calcd for $C_{22}H_{17}N$: C, 89.45; H, 5.80; N, 4.74. Found: C, 89.25; H, 5.97; N, 4.66.

In the same manner, from (*RR*)-**4B** (0.41 g; 1 mmol) was obtained pure (*R*)-**5**: 0.207 g (69%); $[\alpha]^{23}_{\lambda}$ (c 1, $CHCl_3$) −592.9° (589) −621.5° (578), −714.5° (546), −1242.5° (436). Anal. Calcd for $C_{22}H_{17}N$: C, 89.45; H, 5.80; N, 4.74. Found: C, 89.20; H, 5.86; N, 4.79.

Asymmetric Nucleophilic Acylations. The following is a representative procedure for nucleophilic addition of the α-amino nitrile anions to aldehydes: In a flame-dried three-necked round-bottomed flask equipped with septums and kept under an argon atmosphere were introduced by syringe, at 0 °C, 10 cm^3 of THF freshly distilled over sodium benzophenone ketyl, 250 μL (1.8 mmol) of diisopropylamine and 1.3 cm^3 of n-BuLi (1.38 N) in hexane (1.8 mmol). The mixture was cooled at −78 °C for 0.5 h, and a solution of 0.615 g (1.5 mmol) of amino nitrile (*SR*)-**4A** in 10 cm^3 of THF was slowly added. The purified sample was submitted to ^1H NMR ($CDCl_3$; integration of the two methoxy signals) and GC (capillary column SIL S, 10 m), both methods indicating a 50 ± 2% diastereoisomeric excess. The resulting dark red solution was magnetically stirred at −78 °C for 1 h, and a solution of 0.108 g (1.5 mmol) of butyraldehyde in 5 cm^3 of THF was slowly added. The solution was stirred at −78 °C for 3 h, quenched with 20 cm^3 of saturated aqueous NH_4Cl, and allowed to warm up at room temperature. After addition of dichloromethane, the organic phase was washed with water, dried over $MgSO_4$, filtered, and evaporated. A solution of 20 cm^3 of aqueous $AgNO_3$ (0.5 N) was added to the residue, previously dissolved in 20 cm^3 of THF, and the mixture was stirred at room temperature overnight. After addition of CH_2Cl_2 (50 cm^3) and ether (250 cm^3), the organic phase was washed with water, extracted twice with 100 cm^3 of aqueous 20% HCl, washed with water, dried ($MgSO_4$), and evaporated under vacuum to give crude α-ketol 8 (R = n-Pr). The acidic extract was made basic with an excess of aqueous KOH, and extraction with ether led to the amine (*S*)-**5** (0.268 g; 61%). The crude α-ketol was chromatographed on a preparative TLC plate (SiO_2; CH_2Cl_2), giving a pure sample: 0.150 g (56%); $[\alpha]^{23}_{546}$ (c 2.5; 95% EtOH) +10.4°. According to Mosher's procedure,[10] 0.041 g (0.23 mmol) of pure ketol, 0.120 g (0.5 mmol) of (−)-α-methoxy-α-(trifluoromethyl)phenylacetic acid chloride, CCl_4 (15 drops), and dry pyridine (15 drops) were introduced in a test tube and left at room temperature for 24 h. Extraction with ether led to a crude sample, which was chromatographed on a preparative TLC plate (SiO_2; CH_2Cl_2). Care was taken in order to avoid any fractionation of the diastereoisomeric mixture of esters.

Registry No. (*S*)-1, 37803-02-4; (*R*)-1, 86631-56-3; (±)-1, 64091-25-4; (*R*)-**2**, 6485-67-2; (+)-**3A**, 97551-07-0; (−)-**3B**, 97590-56-2; (+)-**4A**, 97551-08-1; (−)-**4B**, 97590-57-3; (*S*)-**5**, 97551-09-2; (*R*)-**5**, 97551-10-5; (*S*)-**6A** (lithium salt), 97551-11-6; (*R*)-**6B** (lithium salt), 97551-12-7; **7** (R = Me), 97551-13-8; **7** (R = Pr), 97551-14-9; **7** (R = Pr-*i*), 97551-15-0; **7** (R = CH_2Ph), 97551-16-1; (*S*)-**8** (R = Me), 65646-07-3; (*R*)-**8** (R = Me), 65646-06-2; (*R*)-**8** (R = Pr), 97551-17-2; (*S*)-**8** (R = Pr), 97551-18-3; (*R*)-**8** (R = Pr-*i*), 97551-19-4; (*S*)-**8** (R = Pr-*i*), 97551-20-7; (*R*)-**8** (R = CH_2Ph), 69897-44-5; MeCHO, 75-07-0; PrCHO, 123-72-8; *i*-PrCHO, 78-84-2; $PhCH_2CHO$, 122-78-1; (*S*)-*i*-PrCH(OH)CO_2H, 17407-55-5.

Stable Simple Enols. 12.[1] Molecular Mechanics Structure and Dipole Moment of (*Z*)-1,2-Dimesityl-2-phenylethenol

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Several crowded mesityl-substituted diaryl- and triarylethenols exist in the enol form and their isomerization to the carbonyl ⇌ enol equilibrium mixture is relatively slow even under acid-catalysis.[1-3] Some noteworthy features of their chemistry are as follows: (i) When the crowding is high the enol form is *more stable* than the corresponding carbonyl[4] form. For example, (*Z*)-1,2-dimesityl-2-phenylethenol[5] (**1**) is more stable by 0.6 kcal mol^{-1} in hexane and by 1.1 kcal mol^{-1} in PhCl than the corresponding keto form (**2**).[2a] (ii) Both in solution[6] and in the solid state[7] these enols exist in a chiral propeller conformation where all the rings are twisted in the same sense. (iii) In solution the conformation of the OH is syn

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