acetate or chloroform. The combined organic layers were washed with brine, dried with $MgSO_4$, and condensed. Capillary GC analysis (50-m DB-5 column) of various runs indicated 80–90% diastereomeric excess. Vacuum distillation from CaH_2 affords 2.55 g (92%) of **8**, which was used directly in the next step: ^1H NMR (60 MHz, $CDCl_3$) δ 0.91 (3 H, d, J = 5), 1.0 (3 H, d, J = 5), 1.5–2.15 (1 H, m), 3.24 (2 H, d, br d), 3.82–4.36 (3 H, m), 4.5 (2 H, s), 5.20–5.45 (1 H, m), 6.85–7.2 (9 H, m); ^{13}C NMR (20 MHz) δ 158.9, 140.1, 137.1, 129.9, 127.7, 127.3, 126.7, 126.4, 122.9, 122.2, 70.9, 70.4, 65.0, 53.1, 40.35, 33.6, 18.8, 18.0.

(*R*,*R*)-1,3-Dibenzyl-*N*-[(*S*)-4,5-dihydro-4-(1-methylethyl)-2-oxazolyl]-1,3-dihydroisoindole (9). The procedure is the same as described for the preparation of **8** (crude yield 100%). The major diastereomer may be isolated by trituration and recrystallization from hexanes or by careful column chromatography, eluting with 20% ethyl acetate in hexane:[17] white crystals, mp 107 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 0.98 (3 H, d, J = 7.2), 1.10 (3 H, d, J = 7.2), 1.8 (1 H, m), 3.26 (2 H, br d) and 3.32 (2 H, br d) (these signals are assigned to the benzylic methylenes—see the carbon assignments below), 4.0 (1 H, dd), 4.2 (1 H, dd), 4.4 (1 H, t), 5.0 (2 H, br d), 6.8 (2 H, m), 6.9 (2 H, m), 7.1 (10 H, br d); ^{13}C NMR (100 MHz) δ 157.9, 139.7, 137.2, 129.9, 127.7, 126.9, 126.0, 122.7, 70.9, 70.7, 64.7, 40 (v br; at 20 MHz, this line is somewhat sharper; it is assigned to the benzylic methylenes), 34.1, 19.1, 18.7. Anal. Calcd for $C_{28}H_{30}N_2O$: C, 81.91; H, 7.37. Found: C, 81.82; H, 7.41.

(*R*,*R*)-1,3-Dibenzyl-1,3-dihydroisoindole (10). A solution of 0.164 g of **9**, 0.08 g of *p*-toluenesulfonic acid, and 3 mL of hydrazine hydrate in 15 mL of 95% ethanol was refluxed for 70 h (reaction monitored by GC), then cooled, and condensed. The residue was extracted with chloroform, washed with dilute NaOH and brine, dried with $MgSO_4$, and condensed. The product was purified by radial chromatography, eluting with 20% ethyl acetate in hexane (the plate was first deactivated with 10% triethylamine in hexane and then rinsed with hexane): yield, 0.05 g, 42%; $[\alpha]_D$ −5.4°, c = 2.15 (EtOH); ^1H NMR (60 MHz, $CDCl_3$) δ 2.81–2.99 (4 H, m), 4.55–4.78 (2 H, t, br d), 7.0–7.3 (14 H, m).

Acknowledgment. We are grateful to Professor James Whitesell for graciously agreeing to delay publication of his work so that our paper could appear simultaneously. The 400-MHz NMR instrument used in this work was funded by the NIH, 1 S10 RR 03351.

Communications

A New C_2 Chiral Secondary Amine

Summary: The synthesis and application to asymmetric induction of the novel chiral tricyclic amine **2** are described.

Sir: In 1977 we reported on the preparation of enantiomerically resolved *trans*-2,5-dimethylpyrrolidine (**1**) and the intervention of this amine in enamine alkylation to form 2-alkylcyclohexanones with high levels of asymmetric induction.[1] The design feature of a pseudo C_2 symmetry axis[2] in this material, while conceived independently, follows directly from the seminal contribution of Kagan[3] and represented the first C_2 amine as well as the first monodentate, C_2 chiral auxiliary used in asymmetric induction.[4] While we[5] and others[6] have found applications for this amine in asymmetric induction schemes, its use has been severely hampered by the lack of practical routes for its synthesis, notwithstanding contributions from others.[7,8] Further, recovery of the amine **1** as well as routine manipulations are made difficult due to its low boiling point (102 °C). Recently we were motivated to overcome the practical difficulties associated with **1** by a need for a C_2 amine for incorporation into organic materials for nonlinear optical applications.[9] We report here the practical preparation of the tricyclic amine **2** (bp 97 °C (12.5 mmHg)) (Figure 1) in enantiomerically resolved form[10,11] as well as its application to asymmetric induction in the innovative sequence described by Schlessinger.[6] It should be noted that **2** is unique among C_2-symmetric, secondary amines in that the large thermodynamic preference for the cis ring fusion in bicyclo[3.3.0]octane systems[12] will effectively prevent epimerization α to nitrogen, even in processes that involve deprotonation at this position.[13]

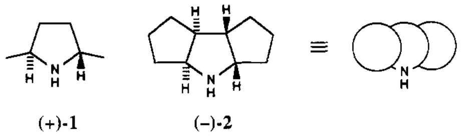

Figure 1.

Synthesis of racemic **2**[14,15] was accomplished in three operational steps, commencing with the radical-induced,

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[1] Whitesell, J. K.; Felman, S. W. *J. Org. Chem.* **1977**, *42*, 1663.

[2] Strictly speaking, the pyramidal nitrogen breaks the C_2 symmetry of this and related amines.

[3] Kagan, H. B.; Dang, T. P. *J. Am. Chem. Soc.* **1972**, *94*, 6429.

[4] Important contributions to this area have followed from many groups. A review of this area is in preparation by one of us (J.K.W) for *Chem. Rev.*

[5] Whitesell, J. K.; Felman, S. W. *J. Org. Chem.* **1980**, *45*, 755.

[6] Schlessinger, R.; Tata, J. R.; Springer, J. P. *J. Org. Chem.* **1987**, *52*, 708. Schlessinger, R. H.; Iwanowicz, E. J.; Springer, J. P. *J. Org. Chem.* **1986**, *51*, 3070.

[7] Harding, K. E.; Burks, S. R. *J. Org. Chem.* **1981**, *46*, 3920. Harding, K. E.; Marman, T. H. *J. Org. Chem.* **1984**, *49*, 2838.

[8] Schlessinger, R. H.; Iwanowicz, E. J. *Tetrahedron Lett.* **1987**, *28*, 2083.

[9] Chemla, D. S., Zyss, J., Eds. *Non-Linear Optical Properties of Organic Molecules and Crystals*; Academic: New York, 1987; Vols. 1 and 2. Williams, D. J., Ed. *Non-Linear Optical Properties of Organic and Polymeric Materials*; ACS Symposium Series 233; American Chemical Society: Washington, DC, 1983.

[10] The term homochiral has recently come into vogue to describe optically active materials. We prefer not to use this term as its use implies an absolute level of enantiomeric purity that is not experimentally verifiable.

[11] We have found the three-ring, abbreviated notation for **2** illustrated in Figure 1 to be quite convenient. In addition, we have coined the nickname "tricyclamine" for **2**.

[12] Dale, J. *Stereochemistry and Conformational Analysis*; Verlag Chemie: New York, 1978.

[13] For an alternate C_2 amine, see: Gawley, R. E.; Chemburkar, S. R.; Smith, A. L.; Anklekar, T. V. *J. Org. Chem.*, preceding paper in this issue.

[14] Both the anti, tricyclic amine **2** and the syn (or meso) amine **7** are new compounds. Indeed, only two previous reports on tricyclic compounds with this dicyclopentapyrrole framework have appeared. See: Posvic, H.; Dombro, R.; Ito, H.; Telinski, T. *J. Org. Chem.* **1974**, *39*, 2575. Hegedus, L. S.; Hoden, M. S. *J. Org. Chem.* **1985**, *50*, 3920.

[15] Spectral data (^{13}C and ^1H NMR) consistent with the structure of all new compounds *and* with purities greater than 95% were obtained.

0022-3263/88/1953-5383$01.50/0

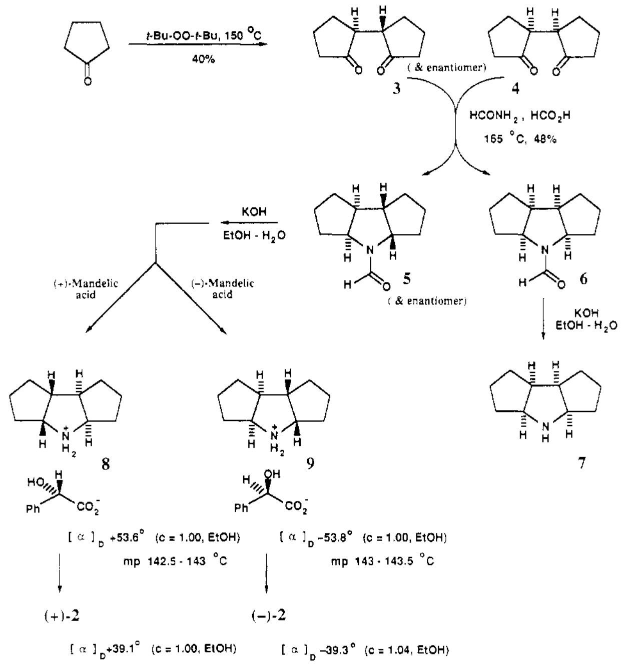

Figure 2.

oxidative dimerization[16] of cyclopentanone to a 1:1 mixture of *d,l* (**3**) and meso (**4**) diketones (Figure 2). Reductive amination of this mixture (or either separated diastereomer) with formamide (Leuckart reaction[17]) afforded a 2:1 mixture of formamides **5** and **6**. Removal of the undesired, "meso"[18] isomer was readily accomplished by selective hydrolysis with hydroxide in ethanol–water as the rate of conversion of formamide **6** to amine **7** is qualitatively 10 times faster than that for the analogous conversion of **5** to **2**. Subsequent hydrolysis of **5** after removal of **7** by simple aqueous acid extraction afforded racemic **2**. This amine was readily resolved as its mandelic acid salt, thereby providing ready and equal access to both enantiomers. Single-crystal X-ray analysis[19] of one of the diastereomeric salts[20] established the absolute configurations for (+)- and (−)-**2** to be as shown by internal reference to the mandelate residue. It is important to note that the synthesis of **2** involves no expensive reagents or solvents and that only simple distillation and aqueous–organic solvent partitioning are used for purifications.

Application of **2** to asymmetric induction is illustrated (Figure 3) by the formation of lactone **13**. The intermediate **12** was obtained with a diastereomeric excess of at least 95% (no evidence of a diastereomer by ^{13}C NMR spectroscopic analysis), and single-crystal X-ray analysis[19] established the absolute configurations of the two newly formed chiral centers (*) by internal reference to the amine subunit. Interestingly, it was found that 2 equiv of base was required for complete conversion in the alkylation step (**10** to **11**), but under these conditions, an 82% yield of recrystallized lactone **12** was obtained. Unlike the analogous sequence with dimethylpyrrolidine, the intermediate hydroxy ester **11** did not spontaneously lactonize. The final lactone (**13**) was obtained in optically pure form ($[\alpha]^{25}_D$ −96.5° (c = 1.5, $CHCl_3$), lit.[21] $[\alpha]^{25}_D$ +96° (c = 2.0, $CHCl_3$)) in 35% yield (unoptimized) from purified **12**.

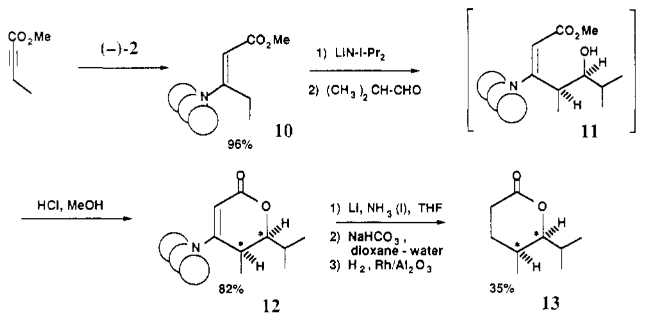

Figure 3.

There are numerous other potential applications of the amine **2** for asymmetric induction, including the use of the corresponding anion as a dialkylamide base as well as the incorporation of **2** into derived species such as bidentate ligands. We are vigorously pursuing these opportunities. In addition, we are building organic molecules from **2** for nonlinear optical applications where the chirality of the amine will enforce a noncentrosymmetric arrangement in the bulk materials.

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Supplementary Material Available: Full experimental details for the synthesis and resolution of the amine **2** (5 pages). Ordering information is given on any current masthead page.

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[16] Naarmann, H.; Beaujean, M.; Merenyi, R.; Viehe, H. G. *Polym. Bull.* (*Berlin*) **1980**, *2*, 363, 417. Gouverneur, P. *Ind. Chim. Belge* **1974**, *39*, 329, 467.

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[18] Formamide **6** is in reality a mixture of enantiomers (interconverted by rotation about the amide linkage), the result of joining subunits of C_s symmetry with the mirror planes at right angles. Interestingly, the joining of subunits, one with C_2 and one with C_s mirror symmetry, to form formamides **5** does *not* provide for geometric stereoisomers.

[19] We are grateful to Dr. V. Lynch for these analyses, the details of which will be published elsewhere.

[20] The salt used, that derived from (−)-amine and (+)-mandelic acid, was one of the more soluble diastereomers ($[\alpha]_D$ +37.0° (c = 0.99, EtOH), mp 136–7 °C).

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Modification of Photochemical Reactivity by Zeolites: Selective Photorearrangement of α-Alkyldeoxybenzoins to *p*-Alkylbenzophenones in the Cavities of Faujasites[†]

Summary: Photolysis of α-alkyldeoxybenzoins included in Li-X and Li-Y zeolites gave the corresponding rearranged *p*-alkylbenzophenones in near quantitative yields via the Norrish type I α-cleavage process. Such a striking behavior contrasts their normal reactivity in solution.

Sir: The possibility that the internal cavities of zeolites can exert topological control on organic photochemical reactions has been recently established by Turro and others.[1] In this context, we have investigated the pho-

[†] Contribution No. 4697.