A New System for Catalytic Asymmetric Epoxidation Using Iminium Salt Catalysts

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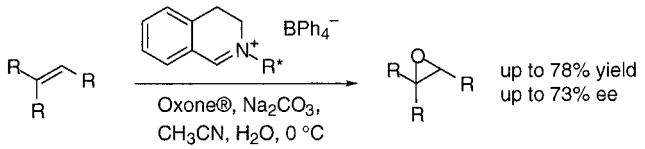
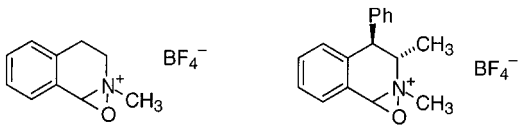
Enantiomerically pure or optically enriched chiral epoxides are widely used synthons of high versatility and are now among the most important intermediates for asymmetric carbon−carbon bond formation.[1] As a result, systems for asymmetric epoxidation remain of prime importance in organic chemistry. The most successful, even ubiquitous, techniques currently available include the Sharpless procedure, limited to allylic alcohol epoxidation,[2] and the Jacobsen procedure, most successful for cyclic *cis*-alkene, particularly arylalkene, substrates.[3] More recently, chiral dioxiranes effective for asymmetric epoxidation have been reported, although the scope and generality of these systems has yet to be established.[4] The oxaziridine reagents of Davis,[5] and related procedures,[6] are highly successful for sulfur oxidation, but are not widely applicable to epoxidation. A more general process for the enantioselective epoxidation of simple alkenes remains a tantalizing and unsolved problem. Recent reports of the use of imine derivatives as epoxidation catalysts prompt us to describe our own results in this area (Scheme 1).

The existence of oxaziridinium salts as reactive intermediates was first shown in 1976.[7a] It was not until 1987, however, that Hanquet and Lusinchi reported the generation of an oxaziridinium salt for only the second time.[7b] They subsequently showed that such salts **1**, derived from a dihydroisiquinoline, are electrophilic oxygen-transfer reagents, effective for sulfide and alkene oxidation [8] in a novel iminium ion analogue of the nitrile-mediated Payne epoxidation procedure.[9] It was further established that these oxidation reactions may be carried out catalytically using "Caroate" (Oxone) as oxidant.[10] In this remarkably simple process, addition of Oxone to an iminium ion of the correct properties under the correct pH conditions produces a highly reactive oxidative intermediate, presumed to be an oxaziridinium ion, which is able to transfer oxygen to alkene substrates with regeneration of the iminium species under the reaction conditions, giving overall a catalytic process. A variety of alkene structural types proved successful substrates. More recently, Hanquet and Lusinchi have shown that a related enantiomerically pure oxaziridinium salt **2**, prepared in five steps from norephedrine, may be used to achieve catalytic asymmetric epoxidation of alkenes by Oxone, for example of *trans*-stilbene with 33% ee.[11] Aggarwal has since reported a C2 symmetric system derived from BINAP which provides up to 71% ee, in the epoxidation of 1-phenylcyclohexene, and 31% ee with *trans*-stilbene as substrate.[12] Very recently, Armstrong has shown that even acyclic iminium slats can catalyze epoxidation by Oxone.[13]

Scheme 1





1 **2**

We now show that iminium salts **3**, also formally derived from a dihydroisoquinoline and a primary amine, but chiral at the exocyclic nitrogen substituent, may be used to achieve catalytic asymmetric epoxidation of alkenes by Oxone (Scheme 1). We have thus far achieved ees of up to 73% and good yields in very clean reactions carried out at 0 °C or at room temperature over ca. 45 min in the presence of as little as 0.3 mol % of catalyst.

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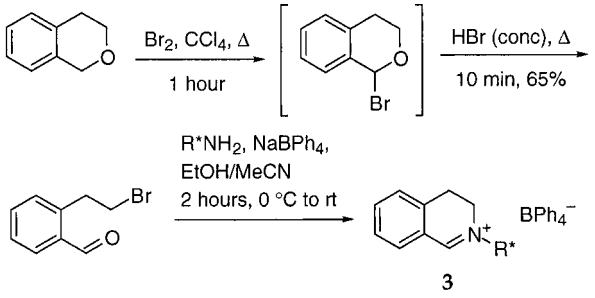
Scheme 2

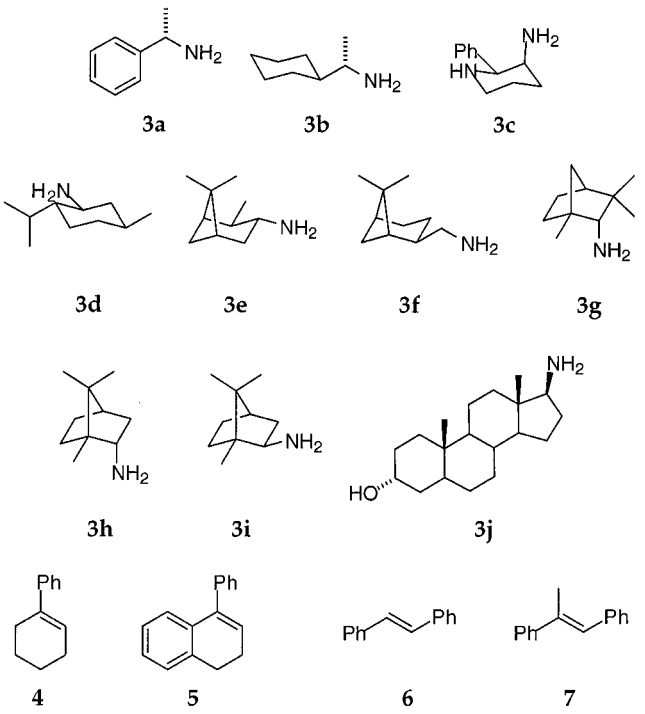


3

The iminium salts used have the advantages that they are extremely easy to prepare on any scale (Scheme 2) and that the structural variation available is large because the chirality is resident in the amine component. Treatment of isochroman with bromine in carbon tetrachloride under reflux for 1 h followed by exposure to concentrated hydrobromic acid provides 2-(2-bromoethyl)-benzaldehyde.[14] Primary amines condense smoothly and rapidly with this material at 0 °C to furnish the corresponding dihydroisoquinolinium bromides. These organic salts are oils, and the consequent difficulties encountered on attempted purification by conventional methods dictated a change of counterion. Addition of sodium tetraphenylborate to the condensation reaction mixture induces formation of the corresponding tetraphenylborate salts, which are precipitated in remarkably clean form from the reaction mixture as crystalline solids. Overall yields of catalyst are generally between 30 and 65%, limited in part as a consequence of a side reaction, elimination of hydrogen bromide from the bromoethyl moiety of the precursor. No chromatography is necessary at any point in this sequence.

Very hindered amines give inferior conversions, typically of the order of 25−30%, presumably due to an increased tendency to act as bases rather than nucleophiles, as evidenced by the increased proportion of 2-vinylbenzaldehyde and derived imine observed. Nevertheless, the small quantities required to catalyze the epoxidation reaction and the lack of any necessary purification more than compensate for reduced yields and the cost of some of the chiral amines screened. Typically, for the epoxidation of 1-phenyl 1-cyclohexene on a 420 mg scale, less than 8 mg of most catalysts were used for ca. 70% isolated yields of epoxide within a 1 h reaction time. The fact that quantitative conversions can be accomplished within 1 h using only 0.3 mol % of the catalyst is unprecedented for iminium salts involved in such a reaction. Overall, the synthesis of the catalyst and the asymmetric oxidation together takes no longer than 6 h.

Typical oxidation conditions, with Oxone (2 equiv) as oxidant, acetonitrile−water (1:2 or 1:1) as solvent, sodium carbonate (4 equiv) as base, and 0.3−5 mol % of dihydroisoquinolinium salt, were used to investigate the catalytic asymmetric epoxidation of 1-phenylcyclohexene **4**. One of the more selective catalysts, the *N*-isopinocampheyl **3e** derivative, was also used in the catalytic asymmetric epoxidation of a range of alkenes **5**−**7**, giving up to 73% ee for *trans*-stilbene as substrate. Complete retention of double bond stereochemistry is observed. This catalyst is readily accessible in both enantiomeric forms, as both enantiomers of the parent amine are commercially available. Although selectivities do not generally vary greatly with temperature, the optimum for reaction rate appears to be ca. 0 °C. A selection of the results obtained at this temperature is shown in Table 1.



The effectiveness and selectivity of the process is no doubt governed by a number of factors, including the structures of the catalyst and substrate, the concentration, the catalyst loading, the solvent used, and the temperature. The structural features of the catalyst which determine the pattern of enantioselectivity in our system however remain unclear; both bornyl **3h** and menthyl **3d** systems gave disappointing ees, despite the popularity and selectivity of enantioselective catalysts and chiral auxiliaries based upon these terpenes. The process is more selective than the Hanquet system presumably because the center of asymmetry is nearer to the reacting center, although the myrtanyl derivative **3f**, which has its asymmetric centers relatively remote from the reaction site, is more selective than the isobornyl system **3i**. It is clear from the cases examined that increased steric hindrance near the reaction site is important, but is evidently not the only factor which governs enantioselectivity. For example, the fenchyl derivative **3g**, which is the most sterically demanding, gave the best enantioselectivity in acetonitrile−water (1:2), albeit at the expense of the rate of the process. The *N*-isopinocampheyl salt **3e**, however, which has considerably less steric requirements, is almost as selective, but is significantly more selective than the bornyl, menthyl, and steroidal systems **3h**, **3d**, and **3j**, which are all of similar or higher steric demand. Furthermore, the rate of conversion is similar for these four systems. While it is as yet difficult to draw firm conclusions about the effects of alkene structure upon enantioselectivity, our results so far appear to suggest that the system is most effective with disubstituted substrates, thus neatly complementing currently available procedures, which commonly

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Table 1. Catalytic Asymmetric Epoxidation

catalyst	alkene	catalyst loading/mol %	yield/%	ee/%[§]	major enantiomer
3a	**4**	5	54	0	(+)−(*R*,*R*)
3b	**4**	5	70	0	(+)−(*R*,*R*)
3c	**4**	1	39	25	(−)−(*S*,*S*)
3d	**4**	0.5	63	19	(+)−(*R*,*R*)
3e	**4**	0.5	68	27	(+)−(*R*,*R*)
3e	**4**[b]	5	68	40	(+)−(*R*,*R*)
3e	**5**[b]	5	73	63	(−)
3e	**6**[b]	5	75	68[‡]	(+)−(*R*,*R*)
3e	**6**[b]	10	78	73	(+)−(*R*,*R*)
3e	**7**[b]	5	72	15	(+)−(*R*,*R*)
3f	**4**	0.5	66	12	(−)−(*S*,*S*)
3g	**4**	0.5	45	32	(+)−(*R*,*R*)
3h	**4**	0.5	60	18	(+)−(*R*,*R*)
3i	**4**	0.5	58	8	(+)−(*R*,*R*)
3j	**4**	0.5	47	14	(−)-(*S*,*S*)

[a] Determined by HPLC (Chiralcel OJ) and/or ^{1}H NMR spectroscopy in the presence of Eu((−)-hfc)$_3$. [b] Acetonitrile−water 1:1 used as solvent. [c] Recrystallized to 95% ee in one recrystallization.

exhibit highest enantioselectivities in epoxidation of trisubstituted alkenes.

Conclusion

We have developed a new catalytic procedure for asymmetric epoxidation, applicable to unfunctionalized alkene substrates. We would emphasize the extreme simplicity of the procedure described, the ease of preparation of a wide range of catalysts without need for chromatography, the absence of any sensitive materials, and the retention of double bond stereochemistry. The procedure requires no close monitoring, and provides remarkably clean reactions in an inexpensive, simple, and rapid process using minimal quantities of catalyst. Further development by modification of catalyst structure and extension to functionalized alkene substrates is in progress.

Experimental Section

2-(2-Bromoethyl)benzaldehyde. Bromine (60 g, 0.37 mol) is added through a reflux condenser over a period of 5 min with stirring to an ice cooled solution of isochroman (50 g, 0.37 mol) in carbon tetrachloride (200 mL). After the vigorous reaction subsides, (ca. 5 min), the cooling bath is removed and the dark brown solution heated under reflux until the reaction mixture becomes pale yellow (indicative of complete consumption of bromine; ca. 1 h). The solution is then allowed to reach ambient temperature, and the solvent is removed under reduced pressure. To the yellow oil obtained (1-bromoisochroman), 75 mL of 48% aqueous hydrobromic acid is added and the reaction mixture is brought to reflux (dark green-blue). After approximately 10−15 min the solution is allowed to cool and extracted with diethyl ether (4 × 50 mL) (Care: The solution must be at room temperature or below prior to extraction with ether; first ether extract may be the lower layer as it is very concentrated with organic material). The organic extracts are washed with water (2 × 30 mL) and then with dilute sodium bicarbonate solution and dried over magnesium sulfate. Evaporation of the solvent under reduced pressure furnishes 67.5 g (65% yield) of crude 2-(2-bromoethyl)benzaldehyde as an orange oil approximately 85−90% pure. Analytically pure samples may be obtained by vacuum distillation; chromatography is not recommended. The crude material, which does not decompose when stored in a flask in the presence of light and air (do not store under nitrogen), was used for subsequent reactions. ν_{max} (neat) 2742, 1697, 1600, 1575, 1260, 1193, 755 cm^{-1}; δ_H (400 MHz, CD_3CN) 3.54−3.63 (4 H, m), 7.33 (1 H, d, *J* 7.96 Hz), 7.48 (1 H, t, *J* 7.50 Hz), 7.54 (1 H, t, *J* 7.94 Hz), 7.80 (1 H, d, *J* 7.56 Hz), 10.14 (1 H, s); δ_C (250 MHz) 33.17, 36.70, 128.10, 132.51, 134.14, 134.33, 134.88, 140.95, 193.33.

Typical Procedure for the Synthesis of Tetrahydroisoquinolinium Salts. A flask containing neat bromoaldehyde (1.1 equiv, or 1.6 equiv if crude) is cooled by means of an ice bath. The appropriate amine (1.0 equiv) is dissolved in ethanol (15 mL/g of amine) and the solution added dropwise with vigorous stirring to the cooled bromoaldehyde. After the addition is complete, stirring is continued for 1 h; then the cooling bath is removed, and the reaction mixture is stirred for a further 1 h while attaining ambient temperature (Somewhat increased yields are obtained if the reaction mixture is left to stand overnight, particularly with hindered amines). Sodium tetraphenyl borate (1 equiv) is added to the reaction mixture in acetonitrile solution (precipitation of sodium bromide may occur). After 5 min, the solvents are removed in a rotary evaporator, and the solid or viscous oil obtained is macerated in hot ethanol, causing the organic salt to precipitate. The salt is isolated by suction filtration, washed with ethanol/water (1:1) to remove sodium bromide, with ethanol to remove water, and finally with diethyl ether. The product thus obtained is of high purity and may be recrystallized from ethanol/acetonitrile (90−95/10−5) if required (crystallinity depends on parent amine).

(S)−(−)-α-Methylbenzylamine derivative: 42% yield, mp 168−169 °C. $[\alpha]^{20}_D$ −9.42°, *c* = 1.57, (CH_3CN); ν_{max} (Nujol) 1647, 1605, 1572 cm^{-1}; δ_H (400 MHz, CD_3CN) 1.82 (3 H, d, *J* 6.90 Hz), 2.99 (2 H, t, *J* 7.63 Hz), 3.65−3.71 (2 H, m), 5.24 (1 H, q, *J* 6.81 Hz), 6.82 (4 H, t, *J* 7.22 Hz), 6.97 (8 H, t, *J* 7.43 Hz), 7.25−7.29 (8 H, m), 7.37 (1 H, d, *J* 7.62 Hz), 7.45 (5 H, m), 7.54 (1 H, t, *J* 7.61 Hz), 7.75 (1 H, t, *J* 7.59 Hz), 7.83 (1 H, d, *J* 7.59 Hz), 8.97 (1 H, s); δ_C (400 MHz, CD_3CN) 17.61, 24.57, 46.96, 68.86, 117.00, 121.44, 124.34, 125.30, 127.22, 127.96, 128.10, 129.05, 129.29, 130.83, 133.77, 135.37, 136.73, 138.01, 164.57.

(*R*)−(+)-Cyclohexylethylamine derivative: 58% yield, mp 178−180 °C. $[\alpha]^{20}_D$ +22.53°, *c* = 1.26 (CH_3CN); ν_{max} (Nujol) 1641, 1603, 1573 cm^{-1}; δ_H (400 MHz, CD_3CN) 1.00−1.04 (1 H, m), 1.18−1.27 (3 H, m), 1.44 (3 H, d, *J* 2.71 Hz), 1.60−1.79 (6 H, m), 1.92−1.94 (1 H, m), 3.16 (2 H, t, *J* 7.88 Hz), 3.83−3.87 (3 H, m), 6.83 (4 H, t, *J* 7.2 Hz), 6.98 (8 H, t, *J* 7.42 Hz), 7.25−7.29 (8 H, m), 7.44 (1 H, d, *J* 7.62 Hz), 7.51 (1 H, t, *J* 7.64 Hz), 7.74−7.79 (2 H, m), 8.67 (1 H, s); δ_C (400 MHz) 14.71, 24.41, 24.96, 25.17, 25.24, 27.89, 29.33, 39.55, 45.24, 45.41, 72.60, 117.00, 121.48, 124.21, 125.33, 128.00, 128.12, 133.48, 135.44, 136.96, 137.93, 165.15.

(+)-Isobornylamine derivative: 17% yield, mp 196−197 °C. $[\alpha]^{20}_D$ +6.88°, *c* = 1.22 (CH_3CN); ν_{max} (Nujol) 1649, 1601, 1572 cm^{-1}; δ_H (CD_3CN, 400 MHz) 0.84 (3 H, s), 0.89 (3 H, s), 1.12 (3 H, s), 1.25−1.31 (1 H, m), 1.36−1.40 (1 H, m), 1.67−1.72 (1 H, m), 1.85−1.91 (2 H, m), 1.97 (1 H, t, 4.34 Hz), 2.39−2.48 (1 H, m), 3.06−3.14 (2 H, m), 3.81−3.87 (1 H, m), 3.89−3.95 (2 H, m), 6.82 (4 H, t, *J* 7.17 Hz), 6.98 (8 H, t, *J* 7.44 Hz), 7.25−7.29 (8 H, m) 7.41 (1 H, d, *J* 7.56 Hz), 7.50 (1 H, t, *J* 7.60 Hz), 7.75 (1 H, t, *J* 7.62 Hz), 7.81 (1 H, d, *J* 7.59 Hz), 8.81 (1 H, s); δ_C (CD_3CN, 400 MHz) 11.92, 19.09, 19.92, 24.52, 25.84, 33.19, 36.95, 44.39, 47.99, 50.92, 52.00, 77.91, 116.99, 121.44, 124.64, 125.31, 127.89, 128.07, 133.71, 135.38, 135.45, 137.91, 164.20.

(−)-Bornylamine derivative: 26% yield, mp 198−200 °C. $[\alpha]^{20}_D$ −33.20°, *c* = 1.53 (CH_3CN); ν_{max} (Nujol) 1645, 1600, 1575 cm^{-1}; δ_H (CD_3CN, 400 MHz) 0.96 (3 H, s), 0.98 (3 H, s), 1.00 (3 H, s), 1.22−1.28 (1 H, m), 1.47−1.51 (2 H, m), 1.65−1.70 (1 H, m), 1.85−1.91 (2 H, m), 2.29−2.36 (1 H, m), 3.11 (2 H, t, 7.84 Hz), 3.81−3.88 (2 H, m), 4.24−4.27 (1 H, m), 6.82 (4 H, t, *J* 7.24 Hz), 6.97 (8 H, t, *J* 7.66 Hz), 7.25−7.28 (8 H, m) 7.44 (1 H, d, *J* 7.60 Hz), 7.51 (1 H, t, *J* 7.63 Hz), 7.75 (1 H, t, *J* 7.59 Hz), 7.85 (1 H, d, *J* 7.68 Hz), 8.67 (1 H, s); δ_C (CD_3CN, 400 MHz) 13.03, 17.35, 18.63, 24.59, 26.32, 26.63, 31.24, 43.85, 50.11, 51.54, 51.63, 76.34, 116.99, 121.44, 124.63, 125.31, 127.90, 128.05, 133.71, 135.38, 137.19, 137.87, 164.71.

(+)-Fenchylamine derivative: 61% yield, mp 153−155 °C. $[\alpha]^{20}_D$ +12.53°, *c* = 1.50 (CH_3CN); ν_{max} (Nujol) 1649, 1605, 1577 cm^{-1}; δ_H (CD_3CN, 400 MHz) 1.04 (3 H, s), 1.29 (6 H, s), 1.40−1.93 (7 H, m), 3.15 (2 H, t, 8.07 Hz), 3.89−3.92 (2 H, m), 3.65 (1 H, s), 6.83 (4 H, t, *J* 7.15 Hz), 6.98 (8 H, t, *J* 7.45 Hz), 7.25−7.29 (8 H, m) 7.43 (1 H, d, *J* 7.56 Hz), 7.52 (1 H, t, *J* 7.62 Hz), 7.76 (1 H, t, *J* 7.62 Hz), 7.91 (1 H, d, *J* 7.57 Hz), 8.75 (1 H, s); δ_C (CD_3CN, 250 MHz), 24.18, 26.00, 30.04, 30.64, 32.22, 36.44,

46.26, 49.95, 53.77, 54.99, 56.95, 89.18, 122.70, 127.20, 130.06, 131.03, 133.63, 133.80, 139.73, 141.57, 142.79, 143.68, 170.64.

(−)-Isopinocampheylamine derivative: 70% yield, mp 238−240 °C. $[\alpha]^{20}_D$ −24.70°, c = 1.36 (CH_3CN); ν_{max} (Nujol) 1639, 1600, 1574 cm^{-1}; δ_H (CD_3CN, 400 MHz) 1.12 (3 H, s), 1.18 (3 H, d, J 7.02 Hz), 1.33 (3 H, s), 1.95−2.00 (3 H, m), 2.12−2.15 (2 H, m), 2.42−2.60 (2 H, m), 3.24 (2 H, t, J 7.60 Hz), 4.08 (2 H, t, J 7.65 Hz), 4.54 (1 H, m), 6.86 (4 H, t, J 7.20 Hz), 7.01 (8 H, t, J 7.43 Hz), 7.28−7.32 (8 H, m) 7.49 (1 H, d, J 7.50 Hz), 7.56 (1 H, t, J 7.58 Hz), 7.80−7.84 (2 H, m), 9.09 (1 H, s); δ_C (CD_3CN, 400 MHz) 18.71, 22.15, 25.00, 26.95, 31.38, 33.06, 38.72, 39.66, 40.76, 46.73, 44.62, 89.18, 117.03, 121.46, 124.71, 125.32, 127.93, 128.12, 133.42, 135.49, 136.96, 137.89, 166.44.

(−)-Menthylamine derivative: 38% yield, mp 166−168 °C. $[\alpha]^{20}_D$ −28.10°, c = 1.71 (CH_3CN); ν_{max} (Nujol) 1643, 1605, 1576 cm^{-1}; δ_H (CD_3CN, 400 MHz) 0.79 (3 H, d, J 6.90 Hz), 0.94 (3 H, d, J 6.81 Hz), 0.96 (3 H, d, J 6.51 Hz), 1.21−1.25 (1 H, m), 1.45−1.49 (1 H, m), 1.51−1.68 (2 H, m), 1.70−1.82 (3 H, m), 1.84−2.00 (2 H, m), 3.13 (2 H, t, J 7.94 Hz), 3.83−3.89 (3 H, m), 6.81 (4 H, t, J 7.14 Hz), 6.98 (8 H, t, J 7.41 Hz), 7.25−7.28 (8 H, m) 7.42 (1 H, d, J 7.13 Hz), 7.50 (1 H, t, J 7.27 Hz), 7.74−7.77 (2 H, m), 8.74 (1 H, s); δ_C (CD_3CN, 400 MHz) 14.30, 19.87, 20.81, 22.33, 24.56, 26.01, 31.23, 32.93, 72.97, 117.00, 121.47, 124.47, 125.31, 127.99, 128.13, 133.50, 135.44, 137.09, 138.06, 165.76.

(−)-Myrtanylamine derivative: 75% yield, mp 173−174 °C. $[\alpha]^{20}_D$ −10.66°, c = 1.80 (CH_3CN); ν_{max} (Nujol) 1651, 1604, 1574 cm^{-1}; δ_H (CD_3CN, 400 MHz) 1.13 (3 H, s), 1.28 (3 H, s), 1.57−1.58 (1 H, m), 1.94−2.05 (6 H, m), 2.47−2.49 (1 H, m), 2.65−2.67 (1 H, m), 3.13 (2 H, t, J 7.89 Hz), 3.83−3.86 (4 H, m), 6.87 (4 H, t, J 7.16 Hz), 7.02 (8 H, t, J 7.39 Hz), 7.29−7.33 (8 H, m) 7.46 (1 H, d, J 7.27 Hz), 7.54 (1 H, t, J 7.33 Hz), 7.77−7.80 (2 H, m), 8.68 (1 H, s); δ_C (CD_3CN, 400 MHz) 18.23, 22.05, 24.31, 24.95, 26.60, 32.25, 37.70, 37.91, 40.59, 42.89, 47.97, 65.62, 116.98, 121.46, 124.14, 125.32, 128.03, 128.05, 133.30, 135.76, 136.49, 137.90, 165.77.

(+)−(2*S*,3*S*)-3-Amino-2-phenylpiperidine derivative: 39% yield, mp 172−174 °C (dec). $[\alpha]^{20}_D$ +141.62°, c = 1.11 (CH_3CN); ν_{max} (Nujol) 3320, 1634, 1603, 1576 cm^{-1}; δ_H (CD_3CN, 400 MHz) 1.91−1.98 (1 H, s), 2.24−2.33 (4 H, s), 2.47 (1 H, br), 2.66−2.70 (1 H, m), 2.88−2.97 (2 H, m), 3.24 (1 H, m), 3.39 (1 H, m), 4.10 (1 H, m), 4.22 (1 H, m), 4.37 (1 H, m), 6.88 (4 H, t, J 7.01 Hz), 7.02 (8 H, t, J 7.20 Hz), 7.26−7.36 (12 H, m) 7.40−7.42 (2 H, m), 7.49 (1 H, t, J 7.24 Hz), 7.72−7.79 (2 H, m), 9.86 (1 H, s); δ_C (CD_3CN, 400 MHz) 20.28, 26.06, 28.95, 47.37, 52.94, 63.18, 69.75, 118.66, 123.17, 125.68, 126.96, 127.41, 129.38, 129.62, 129.73, 130.33, 135.31, 137.16, 137.90, 139.44, 140.67, 169.06.

Steroidal amine derivative: 11% yield, mp 125−127 °C. $[\alpha]^{20}_D$ −1.2° c = 1.33 (CH_3CN); ν_{max} (Nujol) 3420, 1644, 1605, 1578 cm^{-1}; δ_H (CD_3CN, 400 MHz) 0.74 (3 H, s), 0.79 (3 H, s), 1.11−1.93 (22 H, m), 2.44 (1 H, m), 3.13 (2 H, m), 3.87−3.92 (4 H, m), 6.82 (4 H, t, J 7.17 Hz), 6.98 (8 H, t, J 7.42 Hz), 7.25−7.29 (8 H, m) 7.47 (1 H, d, J 7.32 Hz), 7.51 (1 H, t, J 7.35 Hz), 7.76−7.79 (2 H, m), 8.78 (1 H, s); δ_C (CD_3CN, 400 MHz) 10.92, 11.24, 20.07, 22.75, 24.13, 24.87, 28.10, 28.55, 32.02, 32.64, 35.37, 35.59, 35.84, 36.68, 38.82, 46.15, 51.34, 52.88, 53.92, 65.27, 79.72, 117.21, 121.68, 124.68, 125.46, 128.18, 128.34, 133.82, 135.64, 137.37, 138.10, 164.43.

Typical Epoxidation Procedure. Sodium carbonate (4 equiv) in water (8 mL/g) is added in one portion to an ice-cooled flask containing Oxone (2 equiv), and the effervescence manifested is allowed to subside (3 min). The tetrahydroisoquinolinium salt (5 or 10 mol %) is dissolved in the same volume of acetonitrile as that of water used and added to the reaction mixture. The alkene is dissolved in the same volume of acetonitrile and added to the reaction mixture in one portion. For alkenes that exist in the solid state and are insoluble in acetonitrile, addition should be carried out using the solid, but the appropriate volume of acetonitrile should also be added. The reaction mixture (a suspension) is stirred for 1 h (2 h for more substituted alkenes) and then transferred to a separating funnel where the acetonitrile layer is collected. The aqueous phase is diluted with water and extracted thoroughly with diethyl ether (or dichloromethane). The combined organic extracts are washed with brine and dried over sodium sulfate. Evaporation of the solvents gives a brown oil from which the epoxide is obtained by chromatography on silica gel, using 5 or 10% ethyl acetate in light petroleum ether as eluent.

1-Phenyl-1-cyclohexene oxide: 68% yield; ν_{max} (neat) 3084, 1602, 1495, 1446, 1359, 1249, 1173, 1132, 1079, 1030, 993, 974 cm^{-1}; δ_H ($CDCl_3$, 250 MHz) 1.22−1.35 (1 H, m), 1.53−1.64 (3 H m), 1.99−2.06 (2 H, m) 2.16−2.18 (1 H, m), 2.26−2.32 (1 H, m), 3.10 (1 H, t, J 2.04 Hz), 7.28−7.44 (5 H, m); δ_C ($CDCl_3$, 250 MHz) 19.78, 20.09, 24.69, 28.15, 60.13, 61.84, 125.26, 127.12, 128.20, 142.80.

1-Phenyl-3,4-dihydronaphthalene oxide: 72% yield, mp 104−106 °C. ν_{max} (Nujol) 1602, 1486, 1307, 1155, 1074, 1042, 953 cm^{-1}; δ_H ($CDCl_3$, 250 MHz) 2.1 (1 H, td, J 13.69, 5.76 Hz), 2.49−2.60 (1 H m), 2.77 (1 H, dd, J 15.53, 5.63 Hz) 2.98−3.06 (1 H, m), 3.71 (1 H, d, J 3.08 Hz), 7.11−7.31 (4 H, m), 7.45−7.61 (5 H, m); δ_C ($CDCl_3$, 250 MHz) 22.14, 25.43, 60.89, 62.98, 125.95, 127.68, 127.87, 128.07, 128.18, 128.58, 129.82, 134.99, 137.45, 138.82.

***trans*-Stilbene oxide:** 76% yield, mp 66−67 °C. ν_{max} (Nujol) 1601, 1492, 1284, 1176, 1157, 1094, 1072, 1025 cm^{-1}; δ_H ($CDCl_3$, 400 MHz) 3.84 (2 H, s), and 7.28−7.37 (10 H m); δ_C ($CDCl_3$, 400 MHz) 63.28, 125.98, 128.62, 129.31, 137.60.

***trans*-(α-Methyl)stilbene oxide:** 75% yield; ν_{max} (neat) 3061, 1602, 1495, 1449, 1381, 1279, 1157, 1118, 1065, 1027, 980 cm^{-1}; δ_H ($CDCl_3$, 400 MHz) 1.46 (3 H, s), 3.96 (1 H, s), 7.30−7.46 (10 H m); δ_C ($CDCl_3$, 400 MHz) 17.14, 63.48, 67.52, 125.57, 126.92, 127.70, 127.93, 128.60, 129.21, 136.36, 142.75.

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Supporting Information Available: A4 photocopies of ^{13}C and DEPT ^{13}C NMR spectra of products; full experimental detail (14 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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