washed, and dried in vacuo to yield 19.8 g of the crude mixture consisting of **11** and Ph_3PO. The mixture was dissolved in warm $CHCl_3$ (25 mL) and chromatographed on a 2.5 cm × 1.5 m nylon column containing dry column silica gel and using $CHCl_3$ for elution. The column was allowed to overrun by 200 mL to afford maximum separation, and the product was isolated to yield pure **11** (11.1 g, 82%). An analytical sample was recrystallized from $CHCl_3$ petroleum ether (bp 30–60 °C); mp 205–207 °C (lit.[5] mp 205–207 °C); IR (KBr) 3070 (Ar H), 1640 cm^{-1} (C=C); NMR (H_g refers to the vinyl proton geminal to the Im ring at C-1, H_c refers to the vinyl proton cis to the Im ring at C-2, H_t refers to the vinyl proton trans to the Im ring at C-2) δ 5.05 (dd, 1 H, H_g, J_{cg} = 10.0 Hz, J_{gt} = 2.0 Hz), 5.73 (dd, 1 H, H_t, J_{ct} = 18.0 Hz), 6.50 (dd, 1 H, H_c), 6.70 (s, 1 H, Im H-5), 7.20 (m, 16 H, Ar H, Im H-4). Anal. Calcd for $C_{24}H_{20}N_2$: C, 85.68; H, 5.99; N, 8.33. Found: C, 85.50; H, 6.14; N, 8.22.

A Wittig reaction was also performed in a similar manner using only 1 equiv of Ph_3PCH_3Br. Thus, reaction of 55% sodium hydride dispersion (0.570 g, 13.4 mmol), Ph_3PCH_3Br (3.62 g, 10.1 mmol), and **7** (3.41 g, 10.1 mmol) in Me_2SO (15 mL), after reaction and a workup as above, yielded **11** (0.774 g, 22.8%), **7** (0.143 g, 4.2%), and **4** (1.26 g, 36.7%), all with melting points and spectra identical with those above.

1-Benzyl-4-vinylimidazole (12) and 1-Benzyl-5-vinylimidazole (13). In an analogous manner, a solution of hexane washed 55% NaH oil dispersion (0.870 g, 20.0 mmol NaH), and Ph_3PCH_3Br (7.14 g, 20.0 mmol) in Me_2SO (15 mL) was heated for 30 min at 50 °C. To the greenish amber solution was added **8** (1.86 g 10.0 mmol) in Me_2SO (3 mL) via syringe. The red solution was stirred at 65 °C for 3 h and poured into water (200 mL). Extraction of the oil into $CHCl_3$, extraction on the $CHCl_3$ with 10% HCl, neutralization of the acid, and back-extraction of the water with $CHCl_3$ yielded pure **12**: an oil; IR (film) 3100, 3040, 2940, 1635 (vinyl), 1490, 1440, 1350, 1230, 1245, 970, 900, 820, 720 cm^{-1}; NMR δ 5.00 (s, 2 H, $CH_2C_6H_5$), 5.05 (dd, 1 H, Hg, J_{gt} = 10.0 Hz, J_{gc} = 2.0 Hz), 5.77 (dd, 1 H, H_t, J_{ct} = 18.0 Hz), 6.57 (dd, 1 H, H_c), 6.80 (s, 1 H, Im H-5), 7.43 (s, 1 H, Im H-2), 7.25 (m, 5 H, C_6H_5). Anal. [as the picrate, mp 183–185 °C] Calcd for $C_{18}H_{15}N_5O_6$: C, 52.05; H, 4.12; N, 16.86. Found: C, 52.12; H, 3.95; N, 16.98.

Similarly, **13** was prepared by using 55% NaH oil dispersion (0.544 g, 13.0 mmol), Me_2SO (10 mL), Ph_3PCH_3Br (4.64 g, 13.0 mmol), and **9** (1.21 g, 6.50 mmol) in Me_2SO (3 mL). The solution was heated at 65 °C for 4 h and worked up as above. The crude solid was dissolved in $CHCl_3$ and precipitated with petroleum ether (bp 30–60 °C) to yield **13** (0.707 g, 59%) with the following physical properties: mp becomes a glass above 140 °C, completely melts at 210 °C; IR (KBr) 3120, 3040, 2940, 1635 (vinyl), 1490, 1440, 1350, 1230, 1110, 900, 810, 720 cm^{-1}; NMR δ 5.10 (dd, 1 H, H_g, J_{gt} = 12.0 Hz, J_{gc} = 2.0 Hz), 5.13 (s, 2 H, $CH_2C_6H_5$), 5.50 (dd, 1 H, H_t, J_{ct} = 18.0 Hz), 6.40 (dd, 1 H, H_c), 7.25 (m, 6 H, C_6H_5, Im H-5), 7.43 (s, 1 H, Im H-2). Anal. Calcd for $C_{12}H_{12}N_2 \cdot 1/2H_2O$: C, 74.46; H, 6.80; N, 14.26. Found: C, 74.58; H, 6.78; N, 14.50.

4(5)-Vinylimidazole (2). To a stirred mixture of **11** (6.72 g, 20.0 mmol) in THF (25 mL) was added 6 N hydrochloric acid (6.7 mL, 40.0 mmol). The resulting solution was refluxed for 2 h, the THF evaporated in vacuo (45 °C bath), and the resulting solid added to water (25 mL). The solid triphenylmethanol was suction filtered and washed, and the filtrate neutralized with $NaHCO_3$. The water was evaporated in vacuo (bath 45–50 °C), and the oil was treated with absolute alcohol (100 mL) and evaporated to dryness in vacuo. The solid was extracted with $CHCl_3$, and the solvent was dried (K_2CO_3) and evaporated to yield pure **2**: 1.62 g (86%); mp 80–82 °C (lit.[1a] mp 83.2–84.5 °C); NMR δ 4.85 (dd, 1 H, H_g, J_{cg} = 10.0 Hz, J_{gt} = 1.0 Hz), 5.47 (dd, 1 H, H_t, J_{ct} = 18.0 Hz), 6.47 (dd, 1 H, H_c), 6.83 (s, 1 H, Im H-5), 7.40 (s, 1 H, Im H-2).

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Registry No. **2**, 3718-04-5; **3**, 32673-41-9; **4**, 33769-07-2; **5**, 85102-84-7; **5** picrate, 86803-32-9; **6**, 80304-50-3; **7**, 33016-47-6; **8**, 85102-93-8; **9**, 85102-99-4; **11**, 86803-29-4; **12**, 86803-30-7; Ph_3PCH_3Br, 1779-49-3; benzyl chloride, 100-44-7.

Anhydrous *tert*-Butyl Hydroperoxide in Toluene: The Preferred Reagent for Applications Requiring Dry TBHP

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In 1979 we reported an azeotropic procedure for preparing anhydrous solutions of *tert*-butyl hydroperoxide in a variety of solvents.[1] We noted that azeotropically dried solutions of TBHP in benzene and toluene were very stable to storage, whereas solutions prepared by using halogenated solvents (e.g., CH_2Cl_2 and $ClCH_2CH_2Cl$) were less stable, releasing oxygen even at freezer temperatures. Benzene, in every other way the ideal solvent for this process, was rejected due to its supposed toxicity. Thus, during the past 4 years, we and others have generally used dichloroethane and methylene chloride for preparing dry TBHP solutions, in spite of the aforementioned stability problem. Drs. Lendon Pridgen and Lee Webb of Smith Kline and French (SKF) alerted us to a potential thermal hazard in using dichloroethane for azeotropic drying of TBHP (especially on a large scale).[2] The SKF scientists then kindly offered to subject dry TBHP solutions in other solvents to safety tests using their adiabatic calorimeter. Details of their tests will appear elsewhere,[3] but solutions of TBHP in toluene proved to be by far the most stable. The solutions of TBHP in halogenated solvents, especially dichloroethane, were the least stable. In fact, although we have often used dichloroethane as the azeotropic solvent for drying up to 10 mol of TBHP, we now recommend that the scale be no larger than 3 mol of TBHP if the intended solvent be any other than toluene or benzene. If the lower volatility of toluene presents a problem at the workup stage for a specific application, then the use of TBHP in benzene or methylene chloride is recommended.

We have found that TBHP in toluene is excellent for *all*[1,4,5] applications requiring anhydrous TBHP and, therefore, now use only these toluene solutions in our laboratory. For those accustomed to following the earlier azeotropic drying procedure, please note that the new one calls for a Dean–Stark apparatus. The higher boiling point of toluene leads to large loses of TBHP if the previous nonequilibrium distillation technique is used. However, with the Dean–Stark unit in place only the few percent of TBHP soluble in the separated water is lost.

The most common use for anhydrous TBHP solutions is in the titanium-catalyzed asymmetric epoxidation,[4] and these toluene solutions are perfect for that application. While the asymmetric epoxidation can be performed in other solvents, including toluene, we still prefer to use methylene chloride as the bulk solvent to which the TBHP/toluene solution is added. In one case where an asymmetric epoxidation was run in pure toluene, the rate was noticeably slower than that for the same epoxidation with methylene chloride as the bulk solvent.[6]

(1) Sharpless, K. B.; Verhoeven, T. R. *Aldrichimica Acta* **1979**, *12*, 63.
(2) Private communication to K.B.S.
(3) Lendon N. Pridgen and Lee Webb, unpublished results.
(4) Sharpless, K. B.; Behrens, C. H.; Katsuki, T.; Lee, A. W. M.; Martin, V. S.; Takatani, M.; Viti, S. M.; Walker, F. J.; Woodard, S. S. *Pure Appl Chem.* **1983**, *55*, 589. This is currently the best source of information about the titanium-catalyzed asymmetric epoxidation.
(5) Miyano, S.; Lu, L. D.-L.; Viti, S. M.; Sharpless, K. B. *J. Org. Chem.*, communication in this issue.
(6) J. Gordon Hill, unpublished result.

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Finally, while on the subject of asymmetric epoxidations we note that the importance of achieving anhydrous conditions in these reactions cannot be overemphasized. We recently examined the effect of adding known amounts of water to a standard asymmetric epoxidation reaction using (*E*)-α-phenylcinnamyl alcohol as substrate. The enantiomeric excess was 99% with no water added and plummeted to 48% with 1 equiv of added water.[7] We believe that when substandard results are obtained in an asymmetric epoxidation, the first suspicion should be that water has somehow crept in. Small-scale and catalytic epoxidations will obviously be most vulnerable to the deleterious effect of adventitious water.

Experimental Section

Preparation of Anhydrous *tert*-Butyl Hydroperoxide (TBHP) in Toluene. CAUTION.[8] To a 1-L separatory funnel was added 325 mL of TBHP-70 (Aldrich or ARCO) [70% TBHP, 30% H_2O], and then 400 mL of reagent-grade toluene was added and the solution swirled (do not shake, otherwise an emulsion may form). The aqueous layer (75 mL) was separated and the organic layer transferred to a 1-L two-necked flask equipped with a Dean–Stark trap (15-mL side arm), a reflux condenser, and a thermometer (all set up in a well-ventilated hood). After addition of several boiling chips, the solution was refluxed by using a heating mantle (caution: prevent overheating the TBHP by avoiding high power settings and by not allowing the solvent level to drop below the level of the top of the mantle).

After 1 h of reflux, about 20 mL of water was removed (note: side arm must be emptied at least once). At this point there was no further accumulation of water. Water begins accumulating at a pot temperature of 84 °C, and after less than 1 h, a constant pot temperature at 107 °C was reached. After visible accumulation of water had stopped, the system was protected from atmospheric moisture by use of a drying tube filled with Drierite, and ca. 20 mL of distillate was removed through the side arm to ensure removal of the last traces of water. After cooling, the remaining (ca. 600 mL) TBHP/toluene solution was transferred to a brown glass bottle (polyethylene cone cap)[9] and stored at *room temperature*[10] over activated 4-Å molecular sieves (sieves optional, but *do not* use larger pore size sieves). This solution was approximately 3.3 M in TBHP,[11] and no change in titer was observed after storage for 3 months under these conditions.[12]

This procedure has been performed on up to four times this scale.

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Registry No. (*E*)-α-Phenylcinnamyl alcohol, 62668-02-4; TBHP, 75-91-2; toluene, 108-88-3.

(7) M. G. Finn and Jon Ellman, unpublished results.

(8) We have carried out this procedure many times without incident. However, solutions of oxidants and oxidizable substrates are potentially hazardous and possibly subject to violent decomposition by adventitious catalysts. We have previously discussed (see section V of ref 1) the safety considerations related to handling solutions of TBHP, but it seems appropriate to repeat some of the key points here.

The first rule is never add a strong acid (not even a drop) to high-strength TBHP solutions. The second rule is never add transition-metal salts known to be good autoxidation catalysts (e.g., Mn, Fe, and Co are particularly bad) to high-strength TBHP solutions. Alkyl hydroperoxides are sensitive to metal-catalyzed radical-chain decomposition. Among other things this produces a lot of oxygen gas. The third rule is never work with pure TBHP and avoid using high-strength solutions of it whenever possible.[1]

(9) Do not use polyethylene containers as they are permeable to these solutions (preferentially to the toluene) and one observes a constantly increasing peroxide titer.

(10) These solutions are perfectly stable for many months at room temperature and do not require refrigeration. In fact, we have observed that refrigeration actually reduces their useful lifetimes by accelerating the rate at which atmospheric moisture is introduced.

(11) The active oxygen content of these ca. 3 M solutions is near 5%. One can of course prepare more or less concentrated solutions by simply adjusting the initial toluene/TBHP ratio. However, we strongly recommend that concentrations of 3–4 M be regarded as the upper limit for these TBHP solutions.

(12) The exact molarity is best determined by titration as described in footnote 58a of ref 1 above. However, as before (see note 58b in ref 1), we have found NMR analysis to be reasonably accurate (±5%) and more convenient. The equation we use for toluene solutions is molarity = $X/[0.1X + 0.32Y]$ where X = integration of the *tert*-butyl resonance ($\delta \sim 1.25$) and Y = integration of the methyl resonance ($\delta \sim 2.4$).

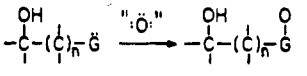
Communications

Kinetic Resolution of Racemic β-Hydroxy Amines by Enantioselective *N*-Oxide Formation

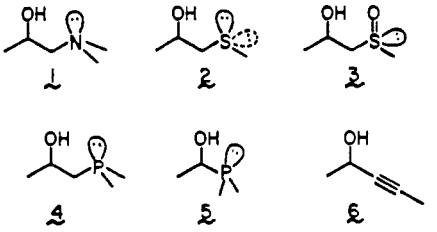
Summary: Enantioselective oxidation using TBHP and an asymmetric titanium–tartrate complex provides direct access to a variety of homochiral β-hydroxy amines.

Sir: Soon after the discovery of the asymmetric epoxidation of allylic alcohols,[1] we realized that the same titanium–tartrate catalyst might be effective for the larger class of asymmetric oxidations depicted in a most general manner in Scheme I.[2] In this conception, the only structural requirements for the substrate are a hydroxyl group for coordination to the chiral metal center and a proximate locus (G) in the molecule capable of accepting an oxygen atom.[2] Some tangible embodiments of this

Scheme I



Scheme II



(1) Katsuki, T.; Sharpless, K. B. *J. Am. Chem. Soc.* **1980**, *102*, 5974.

(2) Scheme I appears in U.S. Patent Application 175 786, "The First Practical Method for Asymmetric Epoxidation", filed August 6, 1980, assignee the Board of Trustees of Leland Stanford Junior University.

0022-3263/83/1948-3608$01.50/0