(mofd, 1, =CH) 6.63–6.82 (m, 2, =CH). We thank Dr. A. Kumar[2] for this work.

Ethyl 5,8-Dimethoxy-1-naphthoate, 4. A well-stirred mixture of 29.4 g (0.112 mol) of **3** and 17.9 g (0.123 mol) of DDQ in 500 mL of benzene was held at reflux for 5 h. The $DDQH_2$ was filtered and washed with hot benzene. The filtrate and washings were concentrated and passed over a column of basic alumina. The benzene was removed and the residue was crystallized from hexane to yield 27.1 g (93%) of colorless prisms of **4**: mp 86–87 °C; NMR 1.36 (t, 3, CH_3), 3.74 (s, 3, OCH_3), 3.87 (s, 3, OCH_3), 4.26–4.51 (q, 2, CH_2), 6.70 (s, 2, ArH), 7.42–7.57 (d, 2, ArH), 8.25–8.36 (t, 1, ArH). Anal.[8] Calcd for $C_{15}H_{16}O_4$: C, 69.3; H, 6.2. Found: C, 69.7; H, 6.2.

5,8-Dimethoxy-1-naphthoic Acid, 5. A mixture of 57.5 g of **4** in 500 mL of alcohol containing 500 mL of 20% KOH was held at reflux for 1 day. After much of the alcohol was removed by rotary evaporation, any unreacted ester was extracted with ether–benzene and the acid liberated by acidification to yield 51.3 g (93%) of **5**: mp 208–209 °C as colorless prisms from benzene–methanol; NMR 3.8 (2 close s, 6, OCH_3), 6.9 (s, 2, ArH), 7.6 (m, 2, ArH), 8.3 (m, 1, ArH). Anal.[8] Calcd for $C_{13}H_{12}O_4$: C, 67.2; H, 5.2. Found: C, 67.3; H, 5.4.

***N,N*-Diethyl-5,8-dimethoxy-1-naphthamide, 6.** A mixture of 59.16 g of **5**, 56 g of PCl_5, and 100 mL of CH_2Cl was held at reflux for 1 h while no more HCl was evolved. After rotary evaporation, the acid chloride was added dropwise to a solution of 58 g of diethylamine in 250 mL of CH_2Cl_2 at 0 °C. After standing overnight at ambient temperature, the mixture was washed with cold water and 10% $NaHCO_3$ and worked up as usual. On distillation 68.1 g (93%) of **6**, bp 195–199 °C at 1 mm, was obtained. Crystallizations from hexane yield colorless prisms, mp 90–91 °C. Anal.[8] Calcd for $C_{17}H_{21}NO_3$: C, 71.1; H, 7.4; N, 4.9. Found: C, 71.2; H, 7.5; N, 4.6.

5,8-Dimethoxy-2-(α-methylbenzyl)-1-naphthoic Acid, 8. To a stirred solution at −78 °C of 17.22 g of **6** in 450 mL of ether and 150 mL of THF containing 9 g of tetramethylethylenediamine (TMEDA) was added dropwise a solution of 1.25 M *sec*-butyllithium (Aldrich) in cyclohexane. After 1 h a solution of 12 g of acetophenone in 100 mL of ether was added in 30 min. After 2 h at −78 °C the mixture was allowed to come to room temperature overnight. After treatment with dilute HCl, the product was worked up as usual and gave a product which was heated with 600 mL of 4 M HCl for 4 h. The product was chromatographed over silica gel and eluted with 3:1 benzene/ethyl acetate to yield 15 g of a noncrystalline lactone, **7**; IR 1760 cm^{-1}, one spot on TLC. A stirred mixture of this lactone, 90 g of activated zinc dust (3-min treatment with 180 mL of water and 20 mL of concentrated HCl, and then 100 mL of 5% $CuSO_4$), 800 mL of 10% KOH, and 60 mL of pyridine was refluxed for 1 day. The acid product isolated as usual was crystallized from benzene–hexane to yield 10.9 g (72%) of **8**, mp 204–205 °C. Anal.[8] Calcd for $C_{21}H_{20}O_4$: C, 75.0; H, 6.0. Found: C, 74.8; H, 5.9.

8-Hydroxy-5-methoxy-2-(α-methylbenzyl)-1-naphthoic Acid Lactone, 9. From the neutral fraction of the products resulting from heating 1.0 g of **8** with 5 mL each of acetic acid and acetic anhydride containing 0.1 g of Cl_2 for 3 h was obtained 200 mg of pure **9**: mp 130–131 °C, as pale yellow prisms; IR 1760 cm^{-1}; MS 304.1088, calcd for $C_{20}H_{26}O_3$ 304.1099. The acid portion yielded 0.3 g of **8**.

7,12-Dihydro-1,4-dimethoxy-7-methyl-12-benz[*a*]anthracenone, 10. To 60 mL of HF[6] in a polyethylene bottle was added 2.70 g of finely powdered **8** with swirling. After 1 h the mixture was poured on ice and worked up as usual to yield 2.30 g of pale yellow prisms of **10**, mp 144–146 °C. Anal.[8] Calcd for $C_{21}H_{18}O_3$: C, 79.2; H, 5.7. Found: C, 78.8; H, 5.6.

1,4-Dimethoxy-7,12-dimethylbenz[*a*]anthracene, 11. To a stirred solution of 1.70 g of **10** in 200 mL of ether under N_2 was added 10 mL of 1.7 M methyllithium in ether (Aldrich). After 1 day the mixture was worked up as usual and the crude product was chromatographed over basic alumina to yield 48% of pale yellow prisms of **11**: mp 105–106 °C; NMR 2.83 (s, 3, CH_3), 3.01 (s, 3, CH_3), 3.92 (s, 3, OCH_3), 4.00 (s, 3, OCH_3), 6.96 (q, 2, ArH), 7.55 (m, 2, ArH), 7.90 (m, 2, ArH), 8.26 (, 2, ArH). Anal.[8] Calcd for $C_{22}H_{18}O_2$: C, 83.5; H, 6.4. Found: C, 83.1; H, 6.3.

An attempt to convert 5,8-dimethoxy-2-(α-methylbenzyl)-1-acetonaphthalene, **12**, readily prepared in 80% yield from **8**, by heating at 90–100 °C for 1 h with PPA resulted in cleavage of the acetyl group to yield 5,8-dimethoxy-2-(α-methylbenzyl)-naphthalene, *m/e* 292.

Registry No. **1**, 13038-12-5; **2**, 101671-02-7; **3**, 101671-03-8; **4**, 101671-04-9; **5**, 101671-05-0; **6**, 101671-06-1; **7**, 101671-07-2; **8**, 101671-08-3; **9**, 101671-09-4; **10**, 101671-10-7; **11**, 101671-11-8; **12**, 101671-12-9; *p*-benzoquinone, 106-51-4; acetophenone, 98-86-2; 5,8-dimethoxy-2-(α-methylbenzyl)naphthalene, 101671-13-0.

Procedure for the Catalytic Asymmetric Epoxidation of Allylic Alcohols in the Presence of Molecular Sieves†

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In the original report[1] on the titanium-catalyzed asymmetric epoxidation of allylic alcohols, the general procedure called for a stoichiometric amount of the titanium tartrate "catalyst". That report also mentioned that 10% catalyst sufficed for reactive substrates, and a recent procedure[2] for the asymmetric epoxidation of (*E*)-2-hexen-1-ol prescribed 50% catalyst. Nevertheless, the numerous applications of the asymmetric epoxidation to date have been carried out almost exclusively by using stoichiometric or near-stoichiometric amounts of the titanium–tartrate catalyst.[3]

We now report the first *general* procedure for the asymmetric epoxidation of allylic alcohols employing *tert*-butyl hydroperoxide (TBHP) and *catalytic* (i.e., <10%) amounts of titanium(IV) isopropoxide and diethyl tartrate. The key element of this modification is the presence of 3A or 4A molecular sieves (zeolites) during the reaction. The advantages of using a catalytic amount of titanium include economy, mildness of conditions, ease of isolation, increased yields, and the potential for in situ derivatization of the product. In the absence of molecular sieves, reactions employing only 5 mol % titanium(IV) isopropoxide often yield product of low optical purity (39–80% ee), proceed slowly, and generally stop after achieving only 50–60% conversion. In contrast, our new procedure enables the reaction to be carried out by using only 5–10 mol % titanium(IV) isopropoxide and only 6–13 mol % of tartrate ester, giving product of high enantioselectivity (90–95% ee) at rates similar to those of the stoichiometric system. The two procedures presented below (one for disubstituted allylic alcohols and one for trisubstituted allylic alchols) are very similar and differ only in minor details of the reaction conditions and isolation technique.

Undecenol was chosen as a representative *trans*-disubstituted allylic alcohol. Decenol and hexenol have been studied also, and their reactions are quite similar, reacting completely in 1–3 h and giving products of >90% ee. In one respect undecenol is unrepresentative of its class: Optimal temperatures for *trans*-disubstituted allylic alcohols are in the range of −20 to −25 °C. However, the epoxide of undecenol is insoluble in dichloromethane below about −15 °C. Although this would not necessarily be a limitation, precipitation of the epoxide does appear to hinder further reaction, and therefore the reaction must be run at −15 °C to −10 °C.

† Dedicated to the memory of Lawrence A. Reed, III.

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Geraniol was chosen as a representative trisubstituted allylic alcohol. Such alcohols are very reactive under these new conditions, reacting completely in 15–90 min at −20 °C. It should be noted that the catalytic asymmetric epoxidation can be quite exothermic, especially for tri- and tetrasubstituted allylic alcohols. In the specific preparation detailed here, the reaction temperature is maintained at −20 °C by dropwise addition of the substrate and use of vigorous overhead stirring. Another option is to start the addition of the trisubstituted allylic alcohol at −40 °C, allowing the temperature to increase to about −30 °C during the addition. Lower temperatures result in slower reactions, but yield product of higher enantioselectivity.

The major differences between the stoichiometric and the catalytic reaction relate to concentration and product isolation. In the stoichiometric reaction substrate concentrations must be kept low (0.1–0.3 M) in order to avoid side reactions (mainly epoxide opening) due to the large amount of titanium–tartrate species and isopropyl alcohol in solution. Part of the problem in the stoichiometric reaction may be due simply to the polar nature of the medium, which facilitates epoxide opening. Higher concentrations can also lead to depressed selectivities and incomplete reaction, probably due to changes in the nature of the catalyst. In the catalytic reaction, this upper concentration limit can be increased to 0.5–1.0 M.

On the other hand, solubility is rarely a problem in the stoichiometric reaction, as the alkenols are generally drawn into solution by the titanium complex. When only a catalytic amount of titanium isopropoxide is employed, the inherent solubility of the substrate or product in dichloromethane may be the deciding factor in choice of concentration and reaction temperature. For undecenol, the choise of ca. 0.5 M is based on solubility considerations.

The simplified isolation procedure described here (the two versions are almost identical) represents a substantial improvement over those described previously for the stoichiometric reaction and should be general for most hydrophobic epoxy alcohols. Quenching of the reaction with water removes much of the complexed titanium (which otherwise tends to hinder the subsequent tartrate hydrolysis). In some cases (for example cinnamyl alcohol), it may be important to add base (10% NaOH saturated with NaCl) rather than water initially, in order to avoid epoxide opening under the slightly acidic conditions of a direct water quench. In such cases, addition of ethyl ether (ca. 10% v/v) will facilitate hydrolysis, and if it is necessary that *all* of the tartrate be removed by hydrolysis, a second treatment with NaOH/NaCl may be needed (after drying of the mixture with magnesium sulfate and filtering through Celite).

Only 1.5 equiv of TBHP are used in these reactions instead of the 2 equiv of TBHP previously recommended for asymmetric epoxidations. (Not all cases will tolerate this reduction in the amount of TBHP employed. Less reactive substrates may require 2–3 equiv of TBHP.) One notes that the approximately $^1/_2$ equiv of excess TBHP which remains in the reaction mixture is ignored in both isolation procedures. In the geraniol case, TBHP is much more volatile than the product; in the undecenol case, TBHP is left behind during recrystallization. We feel that in most cases, even on a large scale, this strategy of ignoring the TBHP will be both safe and also the most convenient option. If one feels that the excess TBHP must be reduced, for whatever reason, this should be possible in one of two ways: Trimethyl phosphite [$P(OMe)_3$, 1–1.3 equiv based on excess TBHP remaining] may be added to the crude CH_2Cl_2 extract. (For large scale reactions, slow addition of the phosphite and cooling are necessary.) Alternatively, the crude extract may be washed with a solution containing 10% $FeSO_4 \cdot 7H_2O$ and 10% tartaric acid in *distilled* water (2–3 mol equiv of Fe based on excess TBHP remaining). The ferrous sulfate alternative is not recommended for epoxy alcohols having substantial water solubility.

Our experience with the asymmetric epoxidation leads us to believe that the principal culprits in unacceptable rates for specific reactions have been the following inhibitors: (1) Water from incompletely dried reagents, solvents, or equipment, (2) the diol ethers (and triols if water is present) generated by in situ opening of the epoxy alcohol products, (3) unidentified contaminants contained in the hydroperoxide solutions, and (4) improper preparation of the catalyst.

We have for some time believed that adventitious water might be the culprit in the less than satisfactory selectivity of some reported epoxidations. It is now clear that the presence of water contributes to the lowering of enantioselectivity and reaction rate *by interacting both reversibly and irreversibly with the catalyst.*

Several experiments were carried out in order to better define the effect of water on a reaction employing 10% catalyst. In one experiment involving no sieves, 10 mol % of water was added to the catalyst/dichloromethane solution at 2 °C. After being stirred for 30 min, the *homogeneous* solution was cooled to −10 °C and treated with TBHP and (*E*)-2-undecen-1-ol. After 20 h the reaction was only 30% complete. Product of 4% ee was obtained, indicating that just 1 equiv of water is enough to destroy the catalyst *in the absence of molecular sieves.* In an otherwise identical experiment, powdered 4A molecular sieves were added just prior to the TBHP addition. Though slow, the reaction proceeded to greater than 90% completion after 20 h. Material of 88% ee was obtained. Thus sieves can at least partially "resurrect" a water-treated catalyst.

Although the use of a catalytic amount of titanium(IV) isopropoxide minimizes the risk of undesired in situ epoxide opening, such reactions can still be a problem for sensitive products such as the epoxide of cinnamyl alcohol. Epoxide opening by alcohols inhibits the reaction by producing diols which effectively sequester the titanium. Opening by alcohols can be minimized, and hence catalyst lifetime increased, by lowering the concentration (e.g., in the case of cinnamyl alcohol, to 0.1 M) and by carefully maintaining low reaction temperatures, especially at the beginning of the reaction (dropwise addition of the alkenol *after* addition of the TBHP and/or addition of the alkenol at −35 to −40 °C).

Inhibition may also arise from the use of contaminated TBHP solutions. In the past, we have recommended either toluene or dichloromethane as solvent for the preparation of anhydrous solutions of TBHP. Neither of these solvents is ideal—toluene solutions have been observed to develop a contaminant (possibly benzoic acid) which inhibits epoxidation whereas dichloromethane solutions are not stable at room temperature. We have stored solutions of TBHP in dichloromethane for several months at 0–5 °C with minimal loss of titre and no loss of effectiveness. Prelim-

(1) Katsuki, T.; Sharpless, K. B. *J. Am. Chem. Soc.* **1980**, *102*, 5974–5976.

(2) Hill, J. G.; Sharpless, K. B.; Exon, C. M.; Regenye, R. *Org. Synth.* **1984**, *63*, 66–78.

(3) For a review, see: Rossiter, B. E. In *Asymmetric Synthesis*, Morrison, J. D., Ed.: Vol 5, pp 193–246 (Academic Press, 1985). See, however: Roush, W. R.; Brown, R. J. *J. Org. Chem.* **1983**, *48*, 5093–5101. (This paper describes the use of 12–20 mol % catalyst for a variety of kinetic resolutions.)

inary results indicate that isooctane is a better solvent for anhydrous TBHP.

Proper preparation of the catalyst is essential for optimal rates and selectivity. We have never been successful with premixed stock solutions of the titanium tartrate complex. The complex is not stable at room temperature, especially in the presence of molecular sieves, and optimal results are only obtained when reagents are mixed at temperatures below about 0 °C. *The tartrate–titanium ratio is critical* and should *always* be in the range of 1.2–1.5 (even for stoichiometric reactions).[4] Use of too little tartrate will result in a lowering of selectivity; too much tartrate will slow the reaction unnecessarily. Furthermore, the catalyst mixture should be aged at −10 °C to −20 °C for 10–20 min prior to addition of the alkenol.

Preliminary experiments indicate that in the presence of molecular sieves, the kinetic resolution of secondary allylic alcohols by enantioselective epoxidation[3,4] can be successful by using as little as 15 mol % titanium(IV) isopropoxide, but it is not clear that this is *generally* true. In addition, we have yet to find an attractive general procedure for the isolation of hydrophilic epoxy alcohols, especially when dealing with large scale epoxidations. However, since only catalytic amounts of tartrate and titanium species are present at the end of the epoxidation, in situ derivatization is possible. In situ esterification was used in this work for the analysis of product enantiomeric purity (preparations of esters using acid chlorides or anhydrides). Related in situ procedures involving certain modifications (temperature, oxidant, and workup) have also worked well for molar scale preparations of the 4 nitrobenzoates and/or tosylates of glycidol, 2-methylglycidol, epoxycrotyl alcohol, and epoxyprenyl alcohol.

Finally, we would like to emphasize that the reported stoichiometric procedure[1,2] will *in general* produce material of somewhat higher enantiomeric purity than will the catalytic procedure described here. Differences in selectivity will be most noticeable in cases of slowly reacting substrates, e.g., hindered or *cis*-disubstituted allylic alcohols.[5] Nonetheless, we feel that this new procedure offers great advantage, especially with respect to product isolation and especially on a large scale. The scope of the catalytic asymmetric epoxidation, including in situ derivatization procedures, will be the subject of a future publication.

Experimental Section

Materials. Activated powdered 4A molecular sieves were used as received from Aldrich Chemical Co. Activation of crushed or pellet 3A molecular sieves involved heating in a vacuum oven at 160 °C and 0.05 mm pressure for at least 3 h. Activated crushed 3A and powdered 4A molecular sieves are similar in effect. The choice of 4A sieves for this work was based on convenience, as they are available from Aldrich Chemical Co. preactivated and powdered. Upon workup, the powdered 4A sieves remain with the aqueous phase and no filtration is generally necessary. Only in the case of allyl alcohol have crushed 3A molecular sieves been observed to be more effective than 4A. Dichloromethane (EM Reagent) was not distilled but was stored over activated 3A molecular sieve pellets. (4A sieves should not be used—we have observed pressurization of bottles of dichloromethane containing 4A sieves.) Diethyl tartrate was used as obtained from Aldrich Chemical Co. Diisopropyl tartrate is equally effective. Titanium(IV) isopropoxide was distilled under vacuum and stored under inert atmosphere. Neither the tartrate esters nor the titanium isopropoxide should be stored over sieves. Reagents handled by syringe were measured by weight rather than by volume. Aqueous 70% *tert*-butyl hydroperoxide (TBHP) was obtained from the Aldrich Chemical Co. (*E*)-2-Undecen-1-ol was prepared from 2-undecyn-1-ol (Farchan Chemical Co.) by reduction with sodium bis(2-methoxyethoxy)aluminum hydride (Red-Al).[7]

Equipment. Flasks used in reactions involving more than 25 mL of solvent were three-necked round bottomed flasks fitted with overhead mechanical stirrer, thermometer, and either a septum or an addition funnel. Internal temperature was carefully monitored. Single-necked flasks with magnetic stirbars were used in smaller reactions, and no attempt was made to monitor the internal temperature. All equipment was either flame dried under vacuum or cooled under vacuum after storage in an oven at 125 °C. All reactions were carried out under an inert atmosphere (nitrogen or argon) in order to exclude atmospheric moisture. All additions were made either by addition funnel or syringe. Cooling was effected by using a water/ethylene glycol (70/30)/dry ice bath.

Preparation of Anhydrous *tert*-Butyl Hydroperoxide (TBHP) in Dichloromethane. CAUTION.[8] Solutions of TBHP in dichloromethane were prepared essentially as described previously for toluene solutions,[2,6] with minor modifications. Two liters of aqueous 70% TBHP and 2 L of dichloromethane are shaken in a separatory funnel. The lower, organic phase is transferred to a 5-L flask fitted with a heavier-than-water solvent Dean–Stark trap ("moisture test receiver, recycle type", Ace Glass Co.) with condenser. *Although we have never experienced a problem with this procedure, all heating should be done behind an adequate blast shield in a well-ventilated fume hood.* After addition of a few boiling chips, the mixture is brought to a gentle reflux by using a heating mantle set on a low voltage. Periodically, the collected water is removed from the trap. After 10 h about 50 mL of water has been removed, and no more water is observed in the azeotrope. The TBHP solution (ca. 2.5 L) is divided into two batches, and each is finally dried in a refrigerator for several hours (usually overnight) over 200–300 g of activated 3A sieve pellets either in a flask covered with cellophane or in a polyethylene bottle. The solutions (about 50% v/v TBHP, 5–6 M) are then transferred to high density polyethylene bottles and stored over activated 3A molecular sieve pellets at 0–5 °C. When properly capped, polyethylene bottles develop negative pressure upon cooling in the refrigerator and compress. Such solutions have been stored for months without loss of effectiveness and only slight loss of titre (5–10%, possibly due to constant use, and thus warming). Assay by FT NMR is not recommended due to the problems of evaporation and pulse saturation and generally leads to values ca. 5–10% above the iodometric titre. Iodometric titration is effected as follows: A 0.1 N aqueous sodium thiosulfate solution is prepared (12.4 g of $Na_2S_2O_3 \cdot 5H_2O$ with enough water to make 500 mL will suffice for 15 to 20 titrations), and 50 mL of this solution is placed in a 50-mL graduated burette. A 250-mL Erlenmeyer flask is charged with 25 mL of isopropyl alcohol and

(4) Martin, V. S.; Woodward, S. S.; Katsuki, T.; Yamada, Y.; Ikeda, M.; Sharpless, K. B. *J. Am. Chem. Soc.* **1981**, *103*, 6237. The kinetic resolution of 2-methylenecyclohexanol is effective using 15 mol % catalyst in the presence of molecular sieves (R. C. Ronald, private communication).

(5) Using 5 mol % catalyst, the epoxidation of *cis*-crotyl alcohol is complete within 18 h at −20 °C, giving material of ca. 85% ee. S. Y. Ko, K. B. Sharpless, unpublished results.

(6) Hill, J. G.; Rossiter, B. E.; Sharpless, K. B. *J. Org. Chem.* **1983**, *48*, 3607–3608. TBHP in isooctane can also be prepared by using this procedure. Other hydrocarbon solvents have been used in this drying procedure, but most (excepting isooctane) share with toluene the unfavorable characteristic of migrating fairly rapidly *through* high density polyethylene. Such migration can lead to substantial changes in titre for TBHP solutions stored in polyethylene bottles.

(7) Denmark, S. E.; Jones, T. K. *J. Org. Chem.* **1982**, *47*, 4595–4597.

(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. When handling solutions of TBHP, the following rules should be applied: 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 to high strength TBHP solutions (Mn, Fe, and Co are particularly bad). Alkyl hydroperoxides are sensitive to metal-catalyzed radical-chain decomposition. Among other things, this produces oxygen gas. The third rule is never work with pure TBHP and avoid using very high strength solutions of it whenever possible. We do not recommend storing TBHP solutions in glass bottles due to the slight danger of gas evolution. Instead, we recommend high density polyethylene bottles, even though there may be some solvent migration through the walls of the bottle.

1 mL of glacial acetic acid. To this is added 10 mL of a freshly prepared, cooled solution of 20 g of sodium iodide in 100 mL of warm isopropyl alcohol. After addition of 0.25 mL of anhydrous TBHP/dichloromethane solution, the mixture is heated to reflux (with stirring on a hot plate or with swirling above a heat gun) and refluxed for 30–45 *seconds*. Failure to reflux the solution will result in a low titre. After dilution with 100 mL of distilled water, the warm solution is titrated rapidly with 0.1 N sodium thiosulfate (25–30 mL required) to the disappearance of the yellow iodine color. Starch indicator may be used toward the end of the titration to enhance the endpoint. The concentration is calculated according to the equation [(molarity of titrant) × (mL of titrant)]/(mL of TBHP solution) × 2], i.e., 0.40 × (mL of titrant), and should be in the range of 5–6 M. The active oxygen content of a 5.0 M (45 wt %) TBHP/dichloromethane solution is about 7 wt %. Solutions of lower molarity are obtained either by dilution just prior to titration or by addition of less 70% TBHP at the start of the procedure. In any case, one should choose a flask size which ensures that the liquid level remains above the top of the heating mantle throughout the azeotropic process, adding more dichloromethane if necessary.

Catalytic Asymmetric Epoxidation of (*E*)-2-Undecen-1-ol. A mixture of powdered, commercially activated 4A molecular sieves (2.0 g, Aldrich, 15–20 wt % based on substrate) and 80 mL of dichloromethane was cooled to −5 °C. L-(+)-Diethyl tartrate (0.80 g, 3.9 mmol) and titanium(IV) isopropoxide (0.73 g, 2.6 mmol) were added sequentially. After cooling to −20 °C, *tert*-butyl hydroperoxide (12.5 mL, 78 mmol, 6.2 M in dichloromethane[9]) was added and the mixture was stirred for 10 min. *With vigorous overhead stirring*, (*E*)-2-undecen-1-ol (8.85 g, 52 mmol in 3 mL of dichloromethane) was added dropwise over about 10 min.

After being stirred for 60 min at −15 °C to −7 °C, the reaction was quenched with water (14 mL, ca. 20 times the weight of $Ti(O\text{-}i\text{-}Pr)_4$ used in the reaction), allowed to warm to room temperature, and then stirred for 30–60 min.

Hydrolysis of tartrates was effected by adding 3.5 mL of a 30% aqueous solution of sodium hydroxide saturated with sodium chloride (prepared by adding 10 g of sodium chloride to a solution of 30 g of sodium hydroxide in 80 mL of water). After 30 min of vigorous stirring, the mixture was filtered through a small plug of glass wool.[10] The organic phase was removed and combined with two extractions of the aqueous phase (dichloromethane,[11] 2 × 15 mL). Drying over magnesium sulfate and filtration through analytical grade Celite gave a clear, colorless solution. Concentration gave a TBHP-containing white solid, which was recrystallized twice from 35 mL of 30–60 petroleum ether (initial crystallization at room temperature, followed by storage at 5 °C) to give (2*S*,3*S*)-3-octyloxiranemethanol as a white solid (7.6 g, 79%, mp 58–59 °C, $[\alpha]^{25}_D$ −32.8° [*c* 1.0, $CHCl_3$]).

A 250-MHz ^1H NMR analysis of the Mosher[12] ester (derived from (+)-α-methoxy-α-(trifluoromethyl)phenyl acetyl chloride) in benzene-d_6 indicated an optical purity of >95%.

Catalytic Asymmetric Epoxidation of (*E*)-3,7-Dimethyl-2,6-octadien-1-ol (Geraniol). A mixture of powdered, commercially activated 4A molecular sieves (1.8 g, Aldrich, 15–20 wt % based on substrate) and 100 mL of dichloromethane was cooled to −10 °C. L-(+)-Diethyl tartrate (1.00 g, 4.8 mmol), titanium(IV) isopropoxide (0.91 g, 3.2 mmol), and *tert*-butyl hydroperoxide (15.6 mL, 97 mmol, 6.2 M in dichloromethane[9]) were added sequentially. After 10 min, the mixture was cooled to −20 °C and freshly distilled geraniol (10.0 g, 65 mmol, in 10 mL of dichloromethane) was added dropwise, *with vigorous overhead stirring*, over a 15-min period.

After 45 min of stirring at −20 °C to −15 °C, the reaction was warmed to 0 °C (5 min) and quenched with water (20 mL, ca. 20 times the weight of $Ti(O\text{-}i\text{-}Pr)_4$ used in the reaction). Upon warming to room temperature (10 min), phase separation was apparent (aqueous suspension above a clear to slightly cloudy organic phase).

Without separation, hydrolysis of tartrates was effected by adding 4.5 mL of a 30% aqueous solution of sodium hydroxide saturated with sodium chloride. After 10 min of vigorous stirring, sudden, dramatic phase separation occurred. The lower (organic) phase was removed and combined with two extractions of the aqueous phase (dichloromethane,[13] 2 × 10 mL). The combined organic phases were dried over magnesium sulfate and filtered through analytical grade Celite to give a clear, colorless solution, which turned bluish (TiO_2) on standing.[14] Concentration, followed by Kugelrohr distillation (140 °C, 1.0 mm) gave (2*S*,3*S*)-epoxygeraniol as a colorless oil (10.95 g, 99%, purity ca. 95% by NMR,[15] $[\alpha]^{25}_D$ −5.3° [*c* 3.0, $CHCl_3$]).

Acylation was carried out on a 10-mg scale by using an excess of acetic anhydride and triethylamine and a catalytic amount of 4-(dimethylamino)pyridine in 100 μL of dichloromethane. Analysis by the shift reagent Eu(III)(hfc)$_3$ (250 MHz ^1H, benzene-d_6 [hfc = 3-[(heptafluoropropyl)hydroxymethylene]-*d*-camphorate]) indicated an optical purity of 91%.

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(9) Cold stock solutions of TBHP in methylene chloride should be warmed to room temperature prior to opening (warm water baths are convenient) in order to minimize exposure to moisture. Somewhat more than the required amount of solution should then be dispensed into a small flask or graduated cylinder containing activated 3A or 4A sieve pellets and stoppered. After a few minutes, the desired volume of solution is transferred to the reaction flask, either by syringe, addition funnel, or direct addition. Syringe needles should never be inserted into any stock solution of TBHP which is to be stored.

(10) Filtration of the slightly emulsive mixture through a small pad of glass wool may aid separation by removing most of the suspended solids from the aqueous phase. However, we have found that filtration is generally unnecessary. In the event of an emulsion problem, the addition of a small amount (ca. 5% v/v) of methanol to the mixture followed by very brief shaking should be tried first. Immediate and complete phase separation generally occurs, allowing for the simple removal of the lower organic phase.

(11) Addition of methanol as described above (note 10) appears to be generally advisable, especially after the first extraction. Petroleum ether may also be used for the secondary extractions.

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(13) During any separations, if the phases do not immediately separate, ca. 5% v/v methanol should be added. After very brief shaking, clean phase separation generally occurs, leaving an almost clear organic phase below a milky aqueous phase.

(14) If the mixture is allowed to stand for a longer period after addition of magnesium sulfate, no titanium will be found in solution after filtration.

(15) The ca. 5% impurity seen in the NMR is related to an impurity in the geraniol, possibly a double-bond isomer.

Buffered Potassium Peroxymonosulfate–Acetone Epoxidation of α,β-Unsaturated Acids

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Epoxidation of α,β-unsaturated acids using the aqueous potassium peroxymonosulfate ($KHSO_5$)–acetone system reported by Curci and co-workers[2] requires careful maintenance of reaction pH at 7.5 to avoid Bayer–Villiger oxidation of acetone that occurs at lower pH.[3,4] This is commonly accomplished by performing the reaction with continuous addition of base to maintain pH. We have found that buffering the reaction with $NaHCO_3$ permits

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