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%.

Acknowledgment. We are grateful to the National Institutes of Health (GM 28384) and to Eli Lilly for financial support. Work by R.M.H. was supported by the National Institutes of Health Research Service Award (AI 7004-02).

(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.

(12) Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543–2549.

(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

Paul F. Corey* and Frederick E. Ward[1]

Ames Division, Miles Laboratories, Inc., Elkhart, Indiana 46515

Received December 17, 1985

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

(1) Deceased, November 28, 1984.

(2) Curci, R.; Fiorentino, M.; Troisi, L.; Edwards, J. O.; Pater, R. H. *J. Org. Chem.* **1980**, *45*, 4758.

(3) Edwards, J. O.; Pater, R. H.; Curci, R.; DiFuria, F. *Photochem. Photobiol.* **1979**, *30*, 63.

(4) Montgomery, R. E. *J. Am. Chem. Soc.* **1974**, *96*, 7820.

0022-3263/86/1951-1925$01.50/0

Table I. Epoxidation of α,β-Unsaturated Acids

starting materials		reaction scale, mol	reaction time, h	products	
R^1	R^2			yield, %	mp, °C
Ph	H	0.75	2.0	92[a]	
Ph	CH_3	0.50	2.5	92	67-68[b]
Ph	Ph	0.37	2.25	90	121-123[c]
CH_3	H	0.75	2.75	62	87-88[d]

[a] Isolated as the potassium salt. [b] Reference 8; lit. mp 68-69 °C. [c] Reference 8; lit. mp 121-122 °C. [d] Reference 9; lit. mp 84.5-85.0 °C.

the reaction to be run at 24-27 °C without need to actively control pH and with no effect on yield.

This modification makes the epoxidation of unsaturated acids with potassium peroxymonosulfate simpler to perform and affords consistent yields, regardless of scale, from grams to kilograms.

Table I summarizes the results for four unsaturated acids.

Experimental Section

All materials were obtained from commercial suppliers and were used without further purification. Oxone monopersulfate compound (Du Pont, Co.) was obtained from Aldrich Chemical Co. Melting points were determined on a Buchi oil-immersion apparatus and are uncorrected.

Epoxidation Procedure. The general method is illustrated by the preparation of *trans*-β-phenylglycidic acid (isolated as the potassium salt) from *trans*-cinnamic acid.

A stirred slurry of *trans*-cinnamic acid (111.0 g; 0.75 mol) in acetone (515 mL) was treated first with $NaHCO_3$ (274 g; 3.26 mol) and then carefully with water (515 mL). The resulting thick mixture was treated dropwise, over 1.5 h, with a solution of Oxone monopersulfate compound[5] (421 g; contains 1.825 equiv of $KHSO_5$) in 4×10^{-4} M aqueous disodium EDTA[6] (1610 mL). During this addition, the reaction temperature was maintained at 24-27 °C by using a water bath and the reaction pH at ca. 7.4. After the addition was complete the mixture was stirred an additional 0.5 h and then cooled to ca. 10 °C. The reaction was acidified with concentrated HCl (ca. 140 mL) to pH 2 while the temperature was maintained at 10 °C and then treated with EtOAc (1.0 L) followed by rapid stirring. The mixture was filtered to remove insoluble salts, and the organic layer was removed. The aqueous layer was extracted with EtOAc (500 mL), and the combined organic layers were washed once with saturated aqueous NaCl (200 mL), dried over $MgSO_4$, and concentrated in vacuo from a 40 °C bath. Toward the end of the concentration, absolute EtOH was added (to keep the acid from crystallizing out), and concentration was continued until most of the solvent was removed. The yellowish oily residue was dissolved in absolute EtOH (500 mL), cooled on ice, and treated with a solution of KOH (56 g; 1.0 mol) in absolute EtOH (250 mL). The resulting thick slurry was filtered, and the solids were washed with EtOH. The filter cake was resuspended in fresh absolute EtOH (750 mL), filtered, washed with EtOH, and dried in a 50 °C oven to give the title compound (139 g; 92%) as a white powder, identical with that prepared by Harada[7] from ethyl β-phenylglycidate.

Anal. Calcd for $C_9H_7O_3K$: C, 53.44; H, 3.49. Found: C, 53.36; H, 3.74.

(5) Oxone monopersulfate compound (DuPont Co.) is $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$. Excess oxidant is used due to competing peroxide autodecomposition.

(6) Na_2EDTA is used to prevent trace-metal-catalyzed peroxide decomposition.

(7) Harada, K. *J. Org. Chem.* **1966**, *31*, 1407.

(8) Blicke, F. F.; Faust, J. A.; Raffelson, H. *J. Am. Chem. Soc.* **1954**, *76*, 3161.

(9) Payne, G. B.; Williams, P. H. *J. Org. Chem.* **1959**, *24*, 54.

Registry No. $KHSO_5$, 10058-23-8; (*E*)-PhCH=$CHCO_2H$, 140-10-3; (*E*)-PhCH=$C(CH_3)CO_2H$, 1895-97-2; (*E*)-PhCH=C-$(Ph)CO_2H$, 833-81-8; (*E*)-H_3CCH=$CHCO_2H$, 107-93-7; *trans*-3-phenyloxiranecarboxylic acid potassium salt, 19190-78-4; *trans*-2-methyl-3-phenyloxiranecarboxylic acid, 82812-97-3; *trans*-2,3-diphenyloxiranecarboxylic acid, 53884-88-1; *trans*-3-methyloxiranecarboxylic acid, 96150-05-9.

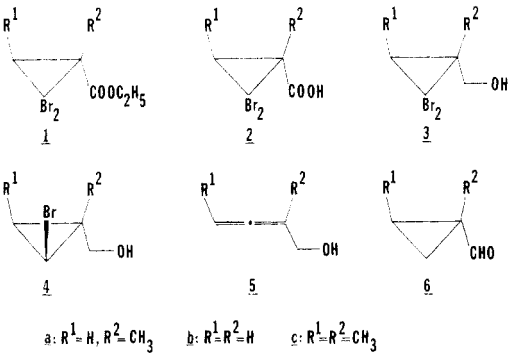
Cyclopropylidene Formation during Lithium Aluminum Hydride Reduction of Some Ethyl 2,2-Dibromocyclopropanecarboxylates and Their Corresponding Acids

Evy Jørgensen and Leiv K. Sydnes*

Department of Chemistry, University of Tromsø, N-9001 Tromsø, Norway

Received November 29, 1985

In connection with another study we needed fair amounts of (2,2-dibromo-1-methylcyclopropyl)methanol (**3a**). To make this compound we treated ethyl 2,2-dibromo-1-methylcyclopropanecarboxylate (**1a**) with an excess of lithium aluminum hydride (LAH) as previously described,[1] but to our surprise a complex reaction mixture was obtained rather than essentially one product. Since LAH gradually loses its reducing power when exposed to light and air,[2] the formation of the complex mixture was possibly due to the fact that our previous experiments were carried out with LAH from an old, frequently used sample,[3] whereas the recent reaction involved fresh hydride.[4] This prompted us to investigate the reduction of some ethyl 2,2-dibromocyclopropanecarboxylates and their corresponding acids with a fresh sample of LAH and led to the discovery of cyclopropylidene generation during treatment of *gem*-dihalocyclopropanes with LAH.



a: R^1=H, R^2=CH_3 b: R^1=R^2=H c: R^1=R^2=CH_3

Treatment of ester **1a** with fresh hydride gave reaction mixtures whose composition varied with the specific condition employed (Table I). The highest yield of alcohol **3a** (>90% based on consumed starting material) was obtained with an LAH/substrate ratio of 0.50; higher ratios increased the yields of other products, viz., monobromo alcohol **4a** and allene alcohol **5a**, at the expense of the dibromo alcohol. The product distribution is sensitive to the mode of addition as alcohols **4a** and **5a** are formed in higher yields when LAH is added as a homogeneous, eth-

(1) Sydnes, L. K.; Skattebøl, L. *Acta Chem. Scand., Ser. B* **1978**, *32*, 632.

(2) (a) Brown, W. G. *Org. React. (N.Y.)* **1951**, *6*, 469. (b) Finholt, A. E.; Jacobson, E. C. *J. Am. Chem. Soc.* **1952**, *74*, 3943.

(3) The sample, purchased from Koch-Light Laboratories, England, was about 2 years old and had been used regularly when the research reported in ref 1 was initiated.

(4) The LAH used in the present study was from a new sample purchased from Aldrich.

0022-3263/86/1951-1926$01.50/0