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Sharpless Asymmetric Dihydroxylation: Effect of Alkene Structure on Rates and Selectivity

An Undergraduate Organic Laboratory Group Experiment

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Purpose of the Experiment

During the last decade or so a number of powerful catalytic asymmetric reactions have been developed in response to a growing demand in industry and academia for efficient and practical syntheses of single-enantiomer biologically active compounds. Among these processes Sharpless's methods for the asymmetric oxidation of alkenes, namely, asymmetric epoxidation (AE) and asymmetric dihydroxylation (AD), stand out because of their wide utility and widespread usage (*1–3*). The experiment described here is an investigation into the effect of alkene structure on Sharpless AD and is designed to introduce undergraduates to some of the concepts involved in asymmetric catalysis. We devised the experiment for our new four-year M.Chem. degree course as an experiment for the third-year laboratory. A group of six students completes the experiment during a period of four weeks (two 6-h labs per week). In the American university system this would perhaps make the experiment suitable for an advanced organic laboratory or even an upper-level integrated laboratory. Supervision of this experiment is critical, as the hazards of osmium tetroxide are well documented. During the past year six groups have successfully completed the experiment. The running costs have been comparable to those of other group experiments of a synthetic nature and the initial cost of purchase of one chiral HPLC column and one chiral GC column (see experimental section) was less than £1,200 (~U.S. $2,000).

Asymmetric Dihydroxylation

The diastereospecific cis-dihydroxylation of alkenes with osmium tetroxide is a useful procedure for the introduction of oxygen-containing functionality into a molecule in a stereodefined fashion (*4*). Potassium permanganate has been superseded by osmium tetroxide as the reagent of choice for this transformation (*5*). Osmium tetroxide is expensive and toxic, but only catalytic quantities are required if a stoichiometric secondary oxidant is also employed. The secondary oxidant effects oxidative hydrolysis of the initially formed cyclic osmate ester in situ, thereby liberating the cis-diol concomitant with regeneration of the osmium tetroxide to complete the catalytic cycle. In 1936 Criegee noticed that the rate of reaction of osmium tetroxide with alkenes was dramatically accelerated by the addition of pyridine or tertiary amines (e.g. quinuclidine) (*6, 7*). However, it was not until the 1980s that Sharpless built upon this observation as a basis for his AD protocol for the enantioselective cis-dihydroxylation of alkenes (*1–3*). The Sharpless procedure employs catalytic quantities of osmium tetroxide and single-enantiomer chiral amine ligands in conjunction with potassium ferricyanide and potassium carbonate [$K_3Fe(CN)_6$–K_2CO_3] as stoichiometric secondary oxidant in a biphasic solvent medium (Fig. 1).

Coordination of the chiral amine ligand to the osmium leads to the formation of a chiral complex. This complex can distinguish between the prochiral faces of a substrate alkene, resulting in cis-diol formation on one face of the alkene in preference to the other. The degree of enantiomeric enrichment reflects the extent to which the complex can distinguish the two prochiral faces of the alkene. This is dictated by the difference in energy between the two diastereomeric transition states leading to reaction on either face and is determined by a combination of (i) the structure of the chiral amine-containing osmate complex and (ii) the structure of the alkene substrate. Opposite enantiomers of the chiral tertiary amine give opposite enantiomers of cis-diol products.

Sharpless has designed a chiral ligand system consisting of two naturally derived dihydroquinine (DHQD) alkaloid units linked together by a phthalazine (PHAL) linker

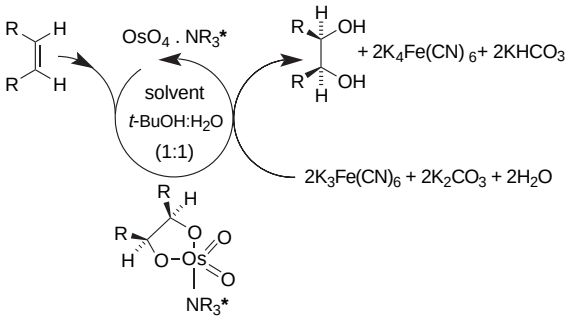
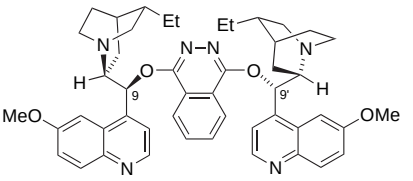
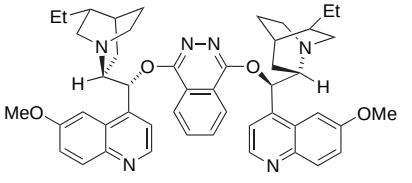


Figure 1. Catalytic cycle for Sharpless asymmetric dihydroxylation. For example, NR_3* = $(DHQD)_2PHAL$ (single enantiomer chiral ligand; see Fig. 2).



$(DHQD)_2PHAL$



$(DHQ)_2PHAL$

Figure 2. Chiral ligands for Sharpless asymmetric dihydroxylation.

[$(DHQD)_2PHAL$, Fig. 2) (*1–3*). The enantiomeric alkaloid does not occur in nature, so he had to use the naturally derived diastereomeric dihydroquinidine- (DHQ-) based analogue for this purpose [$(DHQ)_2PHAL$, Fig. 2). To all intents and purposes these two ligands behave as if it they were enantiomeric, since it is the configuration at C-9 that is crucial to the enantiodifferentiating event in cis-dihydroxylation and the difference in configuration at the quinuclidinic ethyl substituent is not important.

Sharpless has also categorized alkenes into 6 general types varying in the degree and position of substitution (Table 1) (*1–3*).

Using the above phthalazine-based ligand systems, moderate to good levels of enantioselectivity can be achieved for most of these types of alkene. That so many different types of alkenes can be efficiently dihydroxylated with high enantioselectivity is a particularly attractive feature of the AD process. Such broad substrate tolerance is rare in asymmetric catalysis.

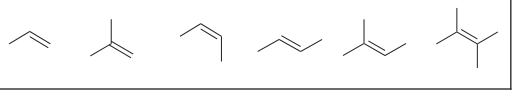
The quasi-enantiomeric ligand systems ([$DHQD]_2PHAL$ and [$DHQ]_2PHAL$) are commercially available as constituents of ready-mixed oxidizing systems known as "AD mix β", which contains $(DHQD)_2PHAL$, and "AD mix α", which contains $(DHQ)_2PHAL$.

Sharpless has provided a model for predicting the sense of enantioselectivity of dihydroxylation of a particular type of alkene with these ligands and this is most easily presented in the form of a pictorial mnemonic (R_S, R_M and R_L refer to "small", "medium", "large" substituents respectively, Fig. 3) (*1–3*). He developed this model as the result of a complex optimization process based not only upon his understanding of the reaction mechanism (which is still the focus of debate) (*1–3, 8–10*) but also upon the correlation of structural information about the chiral osmate ester complex and the substrate alkene with data relating to their rate and stereoselectivity of reaction. The process is iterative and is an essential component of any program aimed at designing and optimizing asymmetric catalytic processes.

The Experiment

This experiment involves each member of the group taking charge of one alkene from the series of six shown below (Fig. 4). The alkenes represent five[1] of the six "classes" of alkene. Each student performs three dihydroxylation reactions: two Sharpless (*11*) asymmetric cis-dihydroxylations

Table1. Sharpless Structural Categorization of Alkenes

	Alkene Type					
	I	II	III	IV	V	VI
Structure						

under identical conditions (but employing the two pseudoenantiomeric AD mixes, α and β) and a Warren (*12*) racemic cis-dihydroxylation in which the separate components of the reaction are added individually. The AD mixes are available commercially from Aldrich or can be prepared according to the method of Sharpless (*11*). There is no commercial premixed system for the Warren protocol, and in any case the addition of the individual components is pedagogically useful. The students set all three reactions going simultaneously so that their progress can be monitored by TLC at ~30-min intervals. The time required for each reaction to reach completion varies between 2 and 20 h (see experimental section). Although the data are only qualitative, reliable relative rate data can be inferred from the time taken for the alkene to be consumed provided that the amount of osmium added is strictly constant in all the reactions. We have found that this can be achieved by the use of accurately pre-weighed vials of AD mixes and osmate salt.

All three cis-diol samples are subjected to chiral GC or HPLC analysis to determine the purity and level of enantioselection achieved in the AD reactions. We have found that the purity at this stage is very dependent on the practitioner and that flash chromatography is sometimes necessary. The pure cis-diols are fully characterized by ^1H NMR, IR, and low-resolution MS. Optical rotations of all three samples are also recorded using a polarimeter (using the same solvent as that reported in the literature).

Analysis of Results and Assessment

We assess this practical after dividing the group into pairs of students. One pair write a word-processed report, one pair make a poster, and the third pair give a short oral presentation using overheads. The following aspects of the work form the framework for assessment.

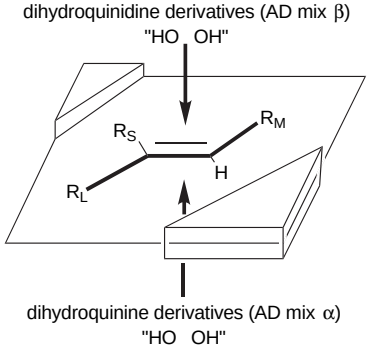


Figure 3. Sharpless's mnemonic for predicting sense of enantioselection in AD reactions.

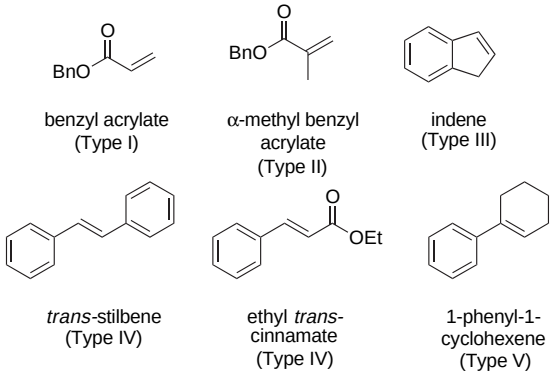


Figure 4. Alkenes for this experiment.

Quality of samples and spectroscopic/chromatographic data.

Understanding of the asymmetric dihydroxylation reaction.

Ability to correlate the results obtained experimentally (particularly rates of reaction and extent and sense of enantioselection) with those predicted by reference to the literature.

Clarity and style of presentation.

This has provided an effective vehicle for some detailed (and animated!) discussions of the reaction mechanism (e.g., relative merits of [2+2] and [3+2] cycloaddition modes) (*10*) and the molecular basis of Sharpless's mnemonic by inspection of potential transition states using molecular models.

Experimental Procedures

General

CAUTION: Osmium tetroxide is formed in situ in these reactions. This compound is volatile and highly toxic, so all the reactions and workups should be carried out in an efficient hood with the sash pulled down as low as possible. Gloves, lab coats and eye protection should be worn at all times. Any spillages should be diluted with aqueous sodium sulfite and wiped up using copious amounts of water. All aqueous waste should be collected for incineration in a "waste osmium" bottle.

Infrared spectra were recorded as solutions in $CHCl_3$ or as Nujol mulls on a Perkin-Elmer Paragon 1000 Fourier transform spectrophotometer. Only selected absorbances (ν_{max}) are reported. ^1H NMR spectra were recorded at 250 MHz on a Bruker AM-250 instrument. Chemical shifts (δ_H) are quoted in parts per million (ppm), referenced to the residual solvent peak. Coupling constants (J) are reported to the nearest 0.5 Hz. Low-resolution mass spectra (*m/z*) were recorded on a VG platform spectrometer; only molecular ions (M^+) and major peaks are reported intensities are quoted as percentages of the base peak. For chiral GC the instrument was a Perkin-Elmer 8700; the column was a Chrompack cyclodextrin-β (60 m × 0.25 mm), with a flame detector, isothermal at the indicated temperature; the carrier gas was H_2, 18 psi. For chiral HPLC the instrument was a Gilson; the column was a Regis-Rexchrom: Pirkle Covalent D-phenylglycine (25 cm × 4.6 mm)] with a UV detector (254 nm); the flow rate was 1 mL/min, with the mobile phase as indicated. Optical rotations were recorded on a Perkin-Elmer 241 polarimeter at 589 nm (Na D-line) and 20 °C, with a path length of 1 dm. Concentrations (*c*) are quoted in g/100 mL.

The quoted durations of the experiments are approximate and represent an average value based on our experience over the past year. Similarly, the quoted specific rotations are averages (significant scatter was apparent in these readings even after clearly erroneous readings were excluded). The enantiomeric excesses determined by chiral chromatography are quoted as ranges and showed reasonably good reproducibility. They are slightly lower than those quoted in the literature by Sharpless (*1*) because the reactions were conducted at room temperature instead of the specified 0 °C.

Representative Experimental Procedures

(±)-*cis*-1,2-Dihydroxy-1-phenylethane. Powdered potassium ferricyanide ($K_3Fe[CN]_6$, MW = 329.26, 980 mg, 3.0 mmol), powdered anhydrous potassium carbonate (K_2CO_3, MW = 138.21, 410 mg, 3.0 mol), potassium osmate ($K_2OsO_2[OH]_4$, MW = 368.43, 3.6 mg, 1.0 mol% [CAUTION: highly toxic]) and quinuclidine ($C_7H_{13}N$, MW = 111.19, 5.6 mg, 5.0 mol%) were placed in a 50-mL round-bottom flask[2] containing a stir bar. Distilled water (5 mL) and *tert*-butanol (5 mL) were added and the resulting suspension was stirred (and if necessary warmed gently with a hair dryer) until two clear phases were obtained. To this mixture was added styrene (C_8H_8, MW = 104, d = 0.91, 114 μL, 1.0 mmol) dropwise by microliter syringe. The resultant heterogeneous slurry was stirred vigorously in the dark at room temperature until the reaction was complete by TLC (ca. 14 h). Anhydrous sodium sulfite (Na_2SO_3, 0.5 g) was added slowly to the reaction mixture, followed by water (20 mL), and the resulting suspension stirred at room temperature for 1 h. The reaction mixture was transferred into a 100-mL separatory funnel with two portions of chloroform (2 × 20 mL). The lower organic phase was separated off and the aqueous phase re-extracted three times with chloroform (3 × 20 mL). The combined organic phases were dried over sodium sulfate (Na_2SO_4) and filtered into a 100-mL round-bottom flask (washing the sodium sulfate twice with small portions of chloroform), and the filtrate was evaporated to leave a very pale yellow oil (100 mg, 73%).

(1*R*)-*cis*-1,2-Dihydroxy-1-phenylethane. To AD mix β (1.4 g) (*11*) in a 50-mL round-bottom flask[2] containing a stir bar was added distilled water (5 mL) and *tert*-butanol (5 mL). The resulting suspension was stirred (and if necessary warmed gently with a hair dryer) until two clear phases were obtained; the lower aqueous phase appeared yellow. Stirring was maintained during dropwise addition of styrene (C_8H_8, MW = 104, d = 0.91, 114 μL, 1.0 mmol) by microliter syringe. The resultant heterogeneous slurry was stirred vigorously *in the dark*[3] at room temperature until the reaction was complete by TLC (ca. 4 h). Sodium metabisulfite ($Na_2S_2O_5$, 0.5 g) was added slowly to the reaction mixture, followed by water (20 mL), and the resulting suspension was stirred at room temperature for 30 min. The reaction mixture was then transferred into a 100-mL separatory funnel with two portions of chloroform (2 × 20 mL). The lower organic phase was separated off and the aqueous phase was re-extracted three times with chloroform (3 × 20 mL). The combined organic phases were dried over sodium sulfate (Na_2SO_4) and filtered into a 100-mL round-bottom flask (washing the sodium sulfate twice with small portions of chloroform), and the filtrate was evaporated to leave a pale yellow oil (110 mg, 80%).

Notes and Experimental Data for Individual Alkenes

(±)-2,3-Dihyroxypropanoic Acid Benzyl Ester

Substrate: benzyl acrylate[4] ($C_{10}H_{10}O_2$, MW = 162, d = 1.00, 162 μL, 1.0 mmol); *duration:* ~2 h; *product:* a colorless oil; ν_{max} ($CHCl_3$) 3421, 3067, 3034, 2933, 2883, 1740, 1456, 1213, 1119 cm^{-1}; δ_H ($CDCl_3$, 250 MHz) 2.05 (1H, t, J = 5.5, CH_2OH), 3.08 (1H, d, J = 5.5, CHO*H*), 3.83 (2H, m, CH_2OH), 4.25 (1H, q, J = 5.5, C*H*OH), 5.18 (2H, s, CH_2Ph), 7.25 (5H, m, ArH's); *m/z* (EI^+) 196 (M^+, 10%), 91 (Bn^+, 100%); chiral GC (170 °C) rt/min: 36.2 (2*R*), 36.8 (2*S*).

AD mix α gives: (2*R*)-2,3-dihydroxypropanoic acid benzyl ester: $[\alpha]_D^{20}$ +12.0° (*c* 1.0, dioxane) (lit. [*13*] +18.0° [*c* 1.2, dioxane]); chiral GC: 66–72% ee.

AD mix β gives: (2*S*)-2,3-dihydroxypropanoic acid benzyl ester : $[\alpha]_D^{20}$ −11.1° (*c* 1.0, dioxane) (lit. [*11*] −14.0° [*c* 1.02, dioxane]); chiral GC: 67–69% ee.

(±)-2,3-Dihydroxy-2-methylpropanoic Acid Benzyl Ester

Substrate: α-methylbenzyl acrylate[4] ($C_{11}H_{12}O_2$, MW = 176, d = 1.04, 169 μL, 1.0 mmol); *duration:* ~3 h; *product:* a colorless oil; ν_{max} ($CHCl_3$) 3423, 3091, 3066, 3034, 2973, 2934, 2876, 1734, 1455, 1217,1054 cm^{-1}; δ_H ($CDCl_3$, 250 MHz) 1.24 (3H, s, CH_3), 2.0 91H, bs, CH_2OH), 3.54 (1H, d, *J* = 12.0, C*H*HOH), 3.78 (1H, d, *J* = 12.0, CH*H*OH), 5.16 (2H, s, CH_2Ph), 7.32 (5H, m, ArH's); *m/z* (EI^+) 210 (M^+, 5%), 180 (20%), 131 (5%), 91 (Bn^+, 100%), 75 (55%); chiral GC (170 °C) rt/min: 28.0 (+), 28.5 (–).

AD mix α gives: (+)-2,3-dihydroxy-2-methylpropanoic acid benzyl ester: $[\alpha]_D^{20}$ +7.0° (*c* 1.0, dioxane), probably (2*S*)- by analogy with above; chiral GC: 43–54% ee.

AD mix β gives: (–)-2,3-dihydroxy-2-methylpropanoic acid benzyl ester: $[\alpha]_D^{20}$ –7.8° (*c* 1.0, dioxane), probably (2*R*)- by analogy with above; chiral GC: 57–67% ee.

(±)-*cis*-1,2-Dihydroxy-1,2-dihydroindene

Substrate: indene (C_9H_8, MW = 116, d = 1.00, 116 μL, 1.0 mmol); *duration:* ~4 h; *product:* a white solid; ν_{max} (Nujol) 3416, 2958, 2921, 1726 cm^{-1}; δ_H ($CDCl_3$, 250 MHz) 2.24 (2H, bs, 2×OH), 2.91 (1H, dd, *J* = 13.0, 5.5, C*H*H), 3.06 (1H, dd, *J* = 13.0, 7.0, CH*H*), 4.45 (1H, q, *J* = 5.5, CH_2CHOH), 4.91 (1H, d, *J* = 7.0, CHC*H*OH), 7.15–7.23 (3H, ArH's), 7.31–7.40 (1H, ArH); *m/z* (EI^+) 150 (M^+, 55%), 132 ($M–H_2O^+$, 60%), 104 (100%), 91 (45%), 77 (50%); chiral GC (160 °C) rt/min: 30.9 (1*R*, 2*S*), 31.4 (1*S*, 2*R*).

AD mix α gives: (1*S*, 2*R*)-1,2-dihydroxy-1,2-dihydroindene: $[\alpha]_D^{20}$ -13.8° (*c* 1.0, $CHCl_3$) (lit. [*14*] -51.6° [*c* 1.0, $CHCl_3$]); chiral GC: 25–34% ee.

AD mix β gives: (1*R*, 2*S*)-1,2-dihydroxy-1,2-dihydroindene: $[\alpha]_D^{20}$ +15.9° (*c* 1.0, $CHCl_3$) (lit. [*15, 16*] +44.0° [*c* 1.01, $CHCl_3$]); chiral GC: 33–40% ee.

(±)-*cis*-1,2-Diphenyl-1,2-ethanediol

Substrate: trans-stilbene ($C_{14}H_{12}$, MW = 180, 180 mg, 1.0 mmol); *duration:* ~5 h; *product:* a white solid; ν_{max} (Nujol) 3496, 3387, 1202, 1047 cm^{-1}; δ_H ($CDCl_3$, 250 MHz) 3.15 (2H, bs, 2×OH), 4.66 (2H, s, 2×C*H*OH), 7.05–7.14 (4H, ArH's), 7.17–7.23 (6H, ArH's); *m/z* (EI^+) 214 (M^+, 3%), 196 ($M–H_2O^+$, 4%), 180 (70%), 107 (100%), 79 (50%); chiral HPLC (5% IPA–95% 40–60 Petrol) rt/min: 18.3 (1*R*, 2*R*), 20.5 (1*S*, 2*S*).

AD mix α gives: (1*S*, 2*S*)-1,2-diphenyl-1,2-ethanediol: $[\alpha]_D^{20}$ –94.7° (*c* 1.0, EtOH) (lit. [*11, 17*] –90.0° [*c* 1.2, EtOH]); chiral HPLC: 94–100% ee.

AD mix β gives: (1*R*, 2*R*)-1,2-diphenyl-1,2-ethanediol: $[\alpha]_D^{20}$ +92.0° (*c* 1.0, EtOH) (lit. [*11, 17*] +90.0° [*c* 1.2, EtOH]); chiral HPLC: 94–100% ee.

(±)-*cis*-Ethyl-2,3-dihydroxy-3-phenylpropionate

Substrate: ethyl-*trans*-cinnamate ($C_{11}H_{12}O_2$, MW = 176, d = 1.05, 168 μL, 1.0 mmol); *duration:* ~7 h, *product:* a white solid; ν_{max} (Nujol) 3446, 1694 cm^{-1}; δ_H ($CDCl_3$, 250 MHz) 1.22 (3H, t, *J* = 6.0, CH_3), 2.71 (1H, bs, OH), 3.11 (1H, bs, OH), 4.27 (2H, q, *J* = 6.0, CH_2), 4.32 (1H, d, *J* = 3.5, C*H*OH), 4.96 (1H, d, *J* = 3.5, C*H*OH), 7.32 (5H, m, ArH's); *m/z* (EI^+) 210 (M^+, 3%), 104 (100%), 91 (30%), 76 (75%); chiral GC (180 °C) rt/min: 26.2 (2*R*, 3*S*), 27.1 (2*S*, 3*R*).

AD mix α gives: (2*R*,3*S*)-ethyl-2,3-dihydroxy-3-phenylpropionate: $[\alpha]_D^{20}$ +8.0° (*c* 1.0, EtOH) (lit. [*11*] +6.3° [*c* 0.95, EtOH]); chiral GC: 91–100% ee.

AD mix β gives: (2*S*, 3*R*)-ethyl-2,3-dihydroxy-3-phenylpropionate: $[\alpha]_D^{20}$ –7.1° (*c* 1.0, EtOH) (lit. [*11, 18*] –3.8° [*c* 1.01, EtOH]); chiral GC: 96–100% ee.

(±)-*cis*-1-Phenyl-1,2-dihydroxycyclohexane

Substrate: 1-phenyl-1-cyclohexene[5] ($C_{12}H_{14}$, MW = 158, d = 0.99, 159 μL, 1.0 mmol); *duration:* ~20 h, *product:* a white solid; ν_{max} (Nujol) 3418, 1066 cm^{-1}; δ_H ($CDCl_3$, 250 MHz) 1.21–1.86 (9H, 4×CH_2+OH), 2.51 (1H, bs, OH), 3.92 (1H, dd, *J* = 9.0, 5.5, C*H*OH), 7.15–7.48 (5H, ArH's); *m/z* (EI^+) 192 (M^+, 85%), 133 (100%), 105 (80%), 71 (50%); chiral HPLC (3% IPA–97% 40–60 Petrol) rt/min: 15.7 (1*R*, 2*R*), 17.3 (1*S*, 2*S*).

AD mix α gives: (1*S*, 2*S*)-1-phenyl-1,2-dihydroxycyclohexane: $[\alpha]_D^{20}$ –2.6° (*c* 1.0, benzene) (lit. [11, 17] –3.1° [*c* 1.0, benzene]); chiral GC: 92-95% ee.

AD mix β gives: (1*R*, 2*R*)-1-phenyl-1,2-dihydroxycyclohexane: $[\alpha]_D^{20}$ +2.4° (*c* 1.0, benzene) (lit. [*11*] +2.1° [*c* 1.0, benzene]); chiral GC: 90–98% ee.

Acknowledgments

We would like to thank K. Barry Sharpless and D. Nirschl of the Scripps Research Institute for their advice on the selection of alkenes for use in this experiment.

Notes

1. No type VI tetrasubstituted alkene was provided. Initially, we planned to use 3,4-dihydro-2-methyl-1-(*tert*-butyldimethylsilyloxy)-naphthalene as a type VI alkene (tetraalkyl alkenes react too slowly). However, its preparation on a large scale proved troublesome and since the product is an α-hydroxy ketone (*19*), comparison of its rate of reaction with the other alkenes is not straightforward.

2. Clean reaction flasks are essential to avoid accidental inclusion of materials known to bring about the rapid decomposition of high-energy oxidants (e.g., traces of metals).

3. During asymmetric dihydroxylation, reaction flasks should be wrapped in aluminium foil to protect from direct sunlight, which destroys the catalyst.

4. Some ester hydrolysis occurs during workup of this substrate with aqueous sodium sulfite. Sodium metabisulfite should be used instead.

5. This substrate is thermally unstable and should be kept in a refrigerator.

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