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Preparation of chiral diols by the osmium-catalysed, indirect anodic oxidation of olefins

A. R. AMUNDSEN, E. N. BALKO

Corporate Research Department, Engelhard Corporation, 101 Wood Ave., Iselin, NJ 08830, U.S.A.

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Chiral diols have been prepared by the osmium-catalysed, indirect anodic oxidation of the corresponding olefin. Diol yields were high in all cases; enantiomeric selectivity was related to the bulk of substituent groups borne by the alkene. Overoxidation of the product diol to the corresponding diketone was the principal contributor to process inefficiency.

1. Introduction

The use of osmium tetroxide for the oxidation of olefins to produce vicinal diols is a well-known, reliable synthetic method in organic chemistry [1]. In this process the tetroxide reacts with the olefin to produce an osmate ester which is then hydrolysed to yield the diol and Os(VI). Osmium tetroxide is infrequently used as a stoichiometric oxidant due to its high cost; most often, OsO_4 is employed to catalyse the alkene oxidation by a less expensive primary reagent such as hydrogen peroxide or chlorate ion.

Several workers have used a primary oxidant which forms a chemically reversible redox pair, and replenished the inventory of oxidant by anodic oxidation of the reduced form of the couple. In such a system, the primary oxidant regenerated at an insoluble anode, in turn, reoxidizes the Os(VI) to form Os(VIII), the moiety which actually reacts with the organic molecule. Such electrolytic regeneration facilitates operation of the synthetic process on a continuous, rather than batch basis and has obvious advantages for automated process control. Mayell [2] considered the use of an oxygen diffusion electrode for regeneration of a ferricyanide primary oxidant in the osmium-catalysed oxidation of propylene to the glycol and reduced the idea to practice in the oxidation of acetylene to oxalic acid [3]. In similar work, Connelly [4] produced propylene glycol in a system in which the Cr(VI) primary oxidant was anodically regenerated.

Recently, Sharpless and his coworkers [5, 6] have complexed the Os(VIII) with a chiral ligand to produce an oxidation catalyst which yields optically active diols in remarkably high enantiomeric excess. These workers employed a hydroquinidine or dihydroquinine ester as the orienting ligand, N-methylmorpholine N-oxide (NMO) as the primary oxidant, and have successfully exploited the process with a large number of olefins. When modified by substitution of ferricyanide for the NMO oxidant and by the use of a two phase reaction mixture, the Sharpless process has produced, at room temperature, a number of assymetric diols in enantiomeric excess of greater than 90% [7]. Oishi and Hirama [8] have reported similar results with N,N′-dineohexyl-2,2′bipyrrolidine as the ligand using osmium tetroxide as a stoichiometric oxidant at $-78°$ C.

In this report we describe the synthesis of a number of chiral diols using the recent modification of the Sharpless process in an electrolytically regenerated system; the coupled pair of redox cycles involved in the oxidation is illustrated in Fig. 1. Octavalent osmium reacts with the chiral base to form a coordination complex soluble in an organic phase:

$$OsO_4 + L \longrightarrow \text{Complex} \qquad (1)$$

This complex is the stereoselective oxidant. It, in turn, reacts with the olefin substrate also present in the organic phase to form an osmate ester:

$$\text{Complex} + \text{Olefin} \longrightarrow \text{Osmate ester} \qquad (2)$$

The ester hydrolyses to yield a chiral diol and hexavalent osmium:

$$\text{Osmate ester} + 2(OH)^- \longrightarrow \text{Diol} + OsO_4^{2-} + L \qquad (3)$$

Ferricyanide ion is insoluble in the organic phases studied in this work and the hydroquinidine ester ligand is not soluble in a basic aqueous solution. Regeneration of Os(VIII) therefore occurs at the liquid–liquid interface or in aqueous solution between uncomplexed osmate ion and the iron(III) oxidant:

$$2\{Fe(CN)_6^{3-}\} + OsO_4^{2-} \longrightarrow 2\{Fe(CN)_6^{4-}\} + OsO_4 \qquad (4)$$

The Os(VIII) then returns to the organic phase to continue that portion of the cycle while the ferrocyanide product of this redox step is oxidized to ferricyanide at the anode:

$$2\{Fe(CN)_6^{4-}\} \longrightarrow 2\{Fe(CN)_6^{3-}\} + 2e^- \quad \text{(anode)} \qquad (5)$$

A divided cell is necessary to prevent cathodic reduction of the ferricyanide oxidant and electrodeposition of osmium. With a cell separator preventing other reagents from entering the aqueous carbonate catholyte used in this study, the cathode reaction is

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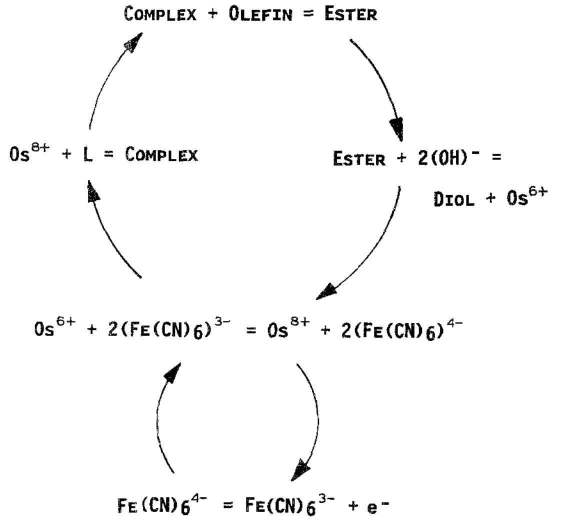


Fig. 1. Schematic representation of the coupled redox cycles in the olefin oxidation process.

water discharge:

$$2H_2O + 2e^- \longrightarrow H_2 + 2(OH)^- \quad \text{(cathode)} \qquad (6)$$

The net process, then, is:

$$\text{Olefin} + 2H_2O \longrightarrow \text{Diol} + H_2 \qquad (7)$$

We have operated this process with a number of olefins and chiral ligands and have found it to be a relatively simple method capable of producing several optically active diols in enantiomeric excess sufficiently great to be of practical interest.

2. Experimental details

2.1. *Electrochemical apparatus*

Cyclic voltammetry was conducted in a commercial Brinkman cell at room temperature under flowing nitrogen. Synthetic work was carried out in Pyrex three-compartment cells of conventional design with a Nafion® 324 membrane as the cell separator; the anode chambers of these cells had a working volume of either 175 or 400 ml and were fitted with a Luggin capillary for measurement of anode potential. A water jacket surrounding the working electrode chamber permitted anolyte temperature control. The working and counter electrodes were fabricated in the laboratory from woven platinum mesh spot-welded to CP grade titanium rod; anode mesh dimensions were 2 cm × 3 cm and 4 cm × 5 cm. Cell agitation was provided by either a Teflon stirbar or by a propellor agitator driven by an overhead stirring motor. No special precautions were taken to purge the gas space above the liquid in any of the cell compartments.

A PAR Model 273 potentiostat under control of a microcomputer operating the PAR 270 software or PAR Model 173 potentiostat with an ESC 640 digital coulometer were used for most of the work; a small number of galvanostatic runs were made using a Lambda LQ-521 power supply.

2.2. *General synthetic method*

A mixture containing two liquid phases, similar to that described by Sharpless [7] was used. The aqueous phase was a 0.4 M solution of potassium carbonate, which also contained the potassium ferricyanide; the organic phase was either cyclohexane or t-butanol in which was dissolved the ligand. The volume ratio of organic to aqueous phase volume was 4 : 3. These two liquid phases were added directly to the anode chamber, the neat diol added next, then finally the osmium tetroxide in the form of a 5 g dm^{-3} solution in 0.4 M aqueous potassium carbonate. Cell operation normally commenced within one minute of catalyst addition; all components of the reaction mixture were free to contact both the membrane and anode. Preparative runs were terminated manually when the coulometer indicated that the desired quantity of charge had been passed. Except where differently noted, the chiral ligand was hydroquinidine 4-chlorobenzoate; with stilbene this ester provides selectivity for oxidation to the R,R-diol. Unless otherwise specified, the reaction mixture contained 8.15 mmoles of alkene, 0.13 mmol of osmium tetroxide, 1.23 mmol of ligand, 3.20 mmol of potassium ferricyanide, and 75 ml of deionized water. Cell current behaviour with this mixture is illustrated in Figs 6 and 7.

Immediately following each electrolytic run, the reaction mixture was quenched by agitation with 10 g of solid sodium sulphite and, after the phases had been allowed to separate, the aqueous layer was extracted with three 100 ml portions of methylene chloride. The combined organic phases were then extracted with three 100 ml portions of 5% (v/v) sulphuric acid to separate the nitrogen-base ligand.

Determination of crude yield and enantiomeric excess (ee) was, in most cases, performed on the organic phase as treated above. Hydrobenzoin is one of the rare compounds that will spontaneously resolve during crystallization [9] and it was important to avoid formation of the solid diol prior to an ee determination. In those cases where purified hydrobenzoin was desired, the organic phase was then taken to dryness under reduced pressure and the resulting crude solid product recrystallized from absolute ethanol after passage through a silica gel column. Final yield was between 60 and 70% with a specific rotation of 90–92°, in good agreement with the value of 91.1° reported in the literature [10]. Some osmium was found to be retained by the silica gel sorbent; similar behaviour has been reported for alumina [11]. Further osmium removal was accomplished by either passing an ethanolic solution of the diol through a column containing a resin bearing sulphhydryl groups (Rohm & Haas Duolite GT-73) or by stirring a methylene chloride solution of the crude product with solid NaSH. Residual osmium levels of 400 and 200 p.p.b. in the final solid diol product were achieved by these treatments, respectively.

2.3. *Analytical details*

Analysis of the reaction mixture and isolated products was done by gas chromatography using a HP 5890 Series II GC, equipped with a 0.53 mm × 10 m HP-1 column (methyl silicone gum). The initial column temperature was 70° C, after 2 min it was ramped at 10° C per min to a maximum of 190° C which was held for 1 min. A flame ionization detector was employed. This method was unable to separate benzil from benzoin and determinations of the former compound were done using the liquid chromatograph.

The reaction mixture contained optically active reaction products, optically active byproducts, and an optically active ligand; polarimetry was not a practical method for determination of diol enantiomeric purity in this matrix. Enantiomeric excess data were calculated from chiral liquid chromatograms obtained using a Waters Delta Prep 3000 LC. The stationary phase consisted of a J. T. Baker Chiragel OJ column (4.6 × 250 mm) preceded by a silica guard column; the mobile phase was a mixture of 95% hexane and 5% isopropanol. Where required, peak deconvolution and area determination were carried out using a commercial computer program ('Peak Fit' software, Jandel Scientific, Corte Madera, CA). Due to detection limit restrictions, the maximum ee value which could be reliably obtained from the LC data was 95%. Determination of ee was also made from NMR spectra of Mosher's esters of the crude diol [12]. S-(+)-methoxy-alpha-(trifluoromethyl)phenylacetyl chloride (Mosher's chloride) was prepared from R-(+)-alpha-methoxy-alpha-(trifluoromethyl)phenylacetic acid using a literature method [13]. Mosher's chloride (228 mg) was added to a mixture of 4-dimethylaminopyridine (110 mg) and the respective crude diol (0.3 mmol) in methylene chloride (3 ml). The mixture was stirred overnight at room temperature. A 50 : 50 mixture of methylene chloride and ethyl acetate (3 ml) was then added, resulting in the formation of a precipitate. This was removed by passing the mixture through a 0.45 μm nylon filter. The filtrate was allowed to evaporate to dryness and a ^{1}H NMR spectrum was taken of the resulting residue dissolved in $CDCl_3$ using a Varian XL200 spectrometer. Racemic diols, either purchased or prepared in this laboratory when not available commercially, were run as standards in order to identify the appropriate peaks for ee determination.

Trace osmium determinations were made by Professor Adon Gordus of the University of Michigan using neutron activation analysis.

3. Results and discussion

3.1. *Stilbene*

3.1.1. Anodic behaviour of the reaction mixture components. Figure 2 presents cyclic voltammograms of the Os(VI)/Os(VIII) and ferrocyanide/ferricyanide couples in the 0.4 M carbonate solution. It is apparent that an anodic potential of 400 mV or larger is sufficiently great to regenerate either ferricyanide or perosmate ion. This was the potential used for the potentiostatic experiments; a modest increase to 500 mV was without effect on any of the parameters measured.

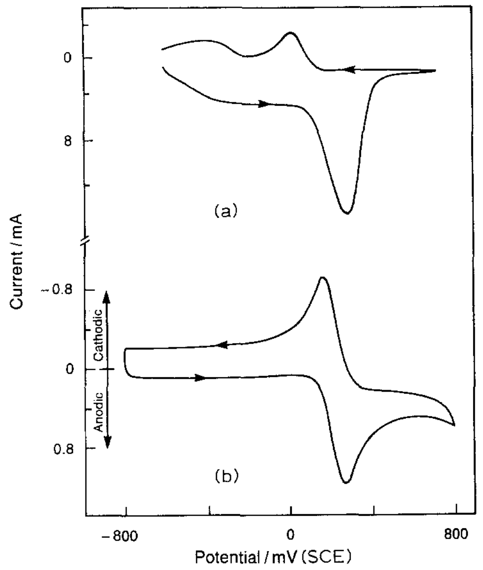


Fig. 2. Voltammograms in 0.4 M K_2CO_3 at 25° C; 6 mm diam. glassy carbon working electrode; 200 mV s^{-1} scan rate. (a) 3 × 10^{-3} OsO_4; working electrode held at −600 mV for 300 s prior to scan; (b) 1.2 × 10^{-2} $K_3Fe(CN)_6$.

At this potential, the otherwise complete reaction mixture exhibits a background current on the order of 0.1–0.5 mA cm^{-2} when an olefin is absent. Addition of stilbene immediately increases the current by two orders of magnitude.

The diol reaction product may, in principle, be consumed both by further chemical oxidation with perosmate and by direct electrochemical oxidation at the anode. Figure 3 presents cyclic voltammograms of a saturated solution of *meso*-hydrobenzoin in 0.4 M aqueous potassium carbonate. An oxidation at about −100 mV and a reduction at about −500 mV are observed; the potential of the oxidation is several hundred millivolts cathodic to the potential at which the platinum anode must be operated to regenerate ferricyanide ion. The peak currents of both processes are proportional to the square root of the scan rate, indicating diffusion control. On the basis of the observed potentials and the known electrochemistry of pinacols and benzaldehyde [14, 15], it is reasonable to assign the observed redox process to the oxidative cleavage of hydrobenzoin to benzaldehyde and the subsequent reductive dimerization to the original diol. The odour of benzaldehyde was occasionally noticed above the solid diol during product workup following preparative runs and that compound was readily detected by gas chromatography.

Although it is clear that the direct electrochemical oxidation of hydrobenzoin will occur at the anode potential used in this work, it does not make a major contribution to current inefficiency. Voltammetric measurements in saturated aqueous solutions of the

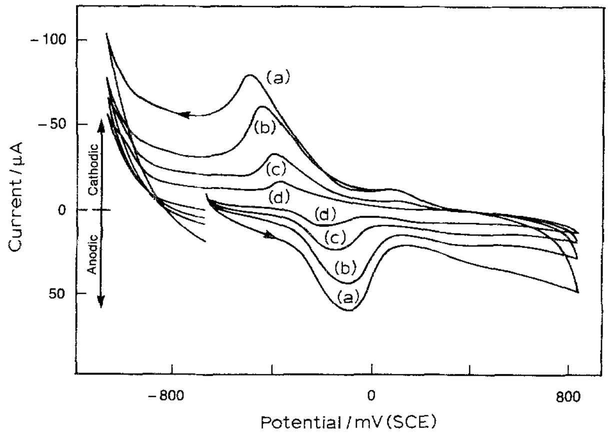


Fig. 3. Voltammograms of *meso*-hydrobenzoin in 0.4 M K_2CO_3; room temperature. The 7 mm^2 gold working electrode was held at 800 mV for 30 s prior to each scan. (a) 200, (b) 100, (c) 50, and (d) 20 mV s^{-1}.

diol found the limiting diffusion current densities to be small, about 1 mA cm^{-2}, on both gold (Fig. 3) and platinum, owing to the sparing solubility of the diol in water [16]. Reaction of perosmate with the product glycol to produce higher oxygenates consumes a far greater fraction of the cell current.

This is evident in the data shown in Fig. 4. A standard reaction mixture was altered by substituting one gram of *meso*-hydrobenzoin for the stilbene and omitting osmium tetroxide, this quantity of the diol corresponding to the mass of hydrobenzoin normally present at the end of a preparative experiment. Under these conditions, and with the anode at the usual operating potential, any increase in cell current above the background corresponds to oxidation of the diol. As is evident from the left side of Fig. 4 the steady-state oxidation current was small, about 2 mA.

Osmium tetroxide was then added to the system and the cell current immediately increased fifty-fold; the principal product of this indirect (chemical) oxidation is benzil (Fig. 5). From coulometric measurements and subsequent analysis of the extracted reaction mixture it was determined that four Faradays were consumed for each gram-mole of hydrobenzoin lost. The quantity of benzil, a four-electron oxidation product of hydrobenzoin, found in the mixture was sufficient to account for 97% of the charge passed. By contrast, in actual preparative runs where the degree of over-oxidation was considerably less, benzoin (Fig. 5) rather than benzil or benzaldehyde was the oxygenate found in the reaction mixture. Synthetic mixtures prepared from reagent hydrobenzoin and benzil were found to yield benzoin. We speculate that, under the conditions obtaining in typical preparative mixtures, the diketone formed by chemical overoxidation reacts with the large excess of diol present to produce the ketanol. No benzoic acid was found in any of the reaction mixtures.

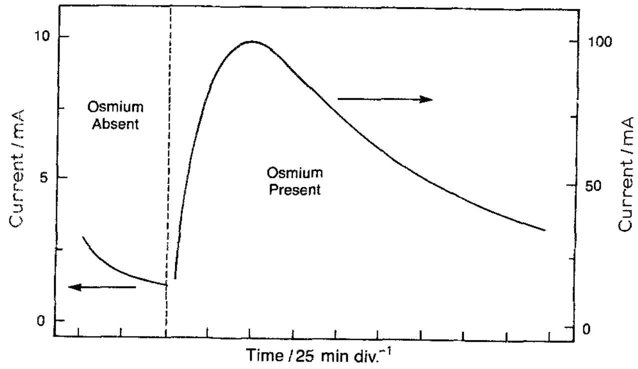


Fig. 4. Hydrobenzoin oxidation. The solution is the normal reaction mixture (Section 2.2) with *meso*-hydrobenzoin substituted for stilbene, simulating the end of run composition. For the first sixty minutes of the experiment, osmium was absent from the cell; the tetroxide was added at the 60 min point.

It is apparent from comparison of the anode currents in cells in which only diol or alkene was supplied as the substrate (Figs 4 and 6) that glycol oxidation is the slower of the two processes.

3.1.2. Preparative reactions. Figure 6 illustrates the behaviour of the cell current during the course of a preparative run with stilbene. In a controlled potential electrolysis experiment of this kind, the magnitude of the current is proportional to the concentration of electroactive material in solution, in this case, ferrocyanide ion [17].

As the batch process is started, the ferrocyanide concentration increases rapidly as consumption of ferricyanide ion begins in regeneration of perosmate; a change in reaction mixture colour is noted as this occurs. The current reaches a maximum, then exhibits two regions in which the current decays such that its logarithm is a linear function of time. The rate of decay in both linear regions was less, by a factor which ranged from ten to several hundred, than the value

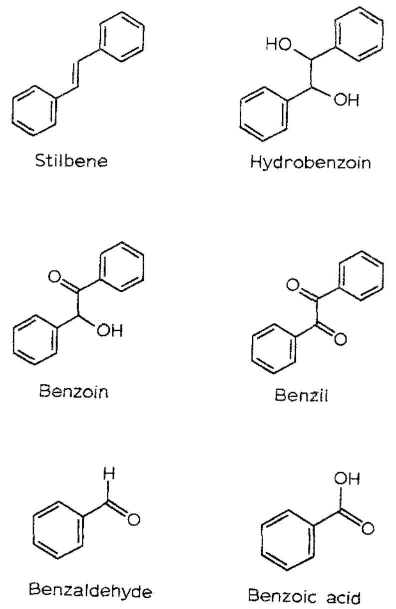


Fig. 5. Structure of stilbene and its oxygenates.

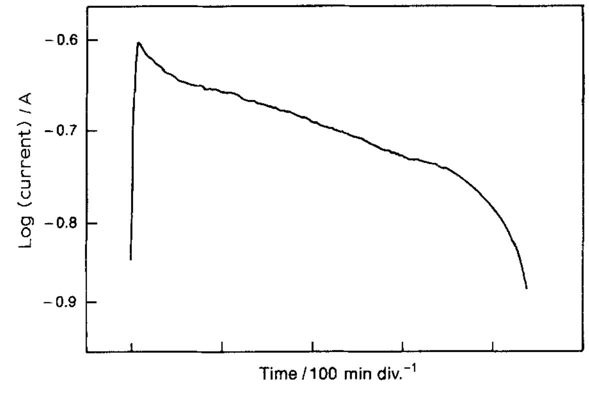


Fig. 6. Current trace during a typical preparative run; 25° C; t-BuOH solvent; cell contents as given in Section 2.2.

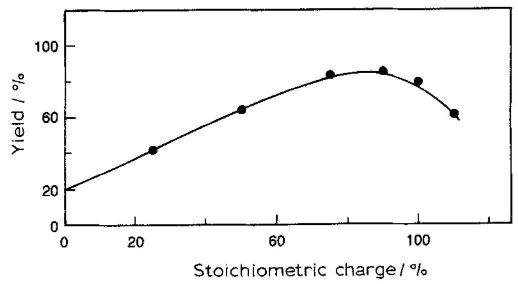


Fig. 8. Influence of charge passed at the anode on yield of hydrobenzoin; 25° C; cell contents as given in Section 2.2.

measured in the same cell and under the same hydrodynamic conditions with ferrocyanide in an osmium-free reaction mixture. The first linear region corresponds to the oxidation of olefin to glycol and exhibits the smaller slope. The second region is entered as the quantity of anodic charge supplied to the cell approaches the point of stoichiometry for diol formation and the rate of current decay increases to a larger value. Here the olefin has been nearly all consumed and the less rapid oxidation of product diol begins to moderate the ferrocyanide concentration.

The need for ferricyanide ion for transfer of charge to the liquid/liquid interface is evident in Fig. 7 which compares the current drawn by two otherwise identical reaction mixtures, one of which is free of the iron charge carrier. In the absence of ferri/ferrocyanide, the cell current, and consequently the rate of diol production, is diminished by about one and one-half orders of magnitude.

The yield of diol was a function of the degree of olefin conversion; this is illustrated in Fig. 8. There is a broad maximum in yield, corresponding to about 85–90% of the charge passed, for conversions between 80 and 95%, then a decrease as complete conversion is approached. The other reaction products were benzoin and benzaldehyde; this presumably reflects an increase in the rate of hydrobenzoin oxidation as the concentration of the diol increases at the end of the batch synthesis. The enantiomeric excess was large, 90 to 95%, and did not vary in any systematic way with the extent of olefin conversion. The enantiomeric purity of the products of this electrochemically regenerated synthesis was essentially the same as reported for the smaller scale, strictly chemical method [7].

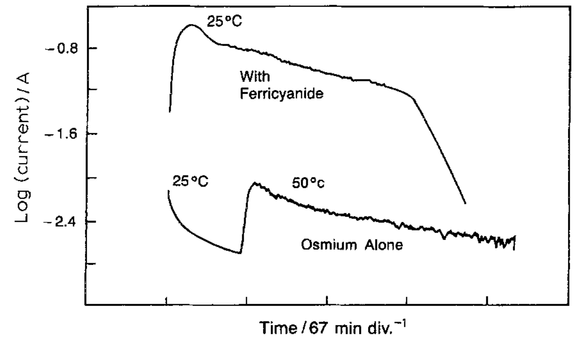


Fig. 7. Influence of the ferricyanide charge carrier on the cell current. The reaction mixture corresponding to the upper trace contained 2.2 g of hydroquinidine ester; cyclohexane as the organic solvent; and the quantities of osmium tetroxide, ferricyanide, and stilbene given in Section 2.2. Potassium ferricyanide was absent from the otherwise identical mixture for which the lower current trace was recorded. After about 1 h of operation at 25° C; the temperature of the iron free system was raised to 50° C.

The yield curve in Fig. 8 does not pass through the origin but displays an intercept of 20% yield. This represents the quantity of ferricyanide oxidant present in the initial reactor charge. That ferricyanide inventory was regenerated or 'turned over' five times in the run where 100% of the stoichiometric charge was passed. In other preparative experiments in which larger quantities of stilbene were used, the Fe(III) inventory was turned over 17 times with no evident difference in cell behaviour.

The process was notably less efficient when an achiral ligand, pyridine, replaced the hydroquinidine ester (Fig. 9). The reaction ran considerably more slowly with the former ligand, requiring about twice the time for a given conversion; accordingly, parasitic reactions had a correspondingly greater time in which to consume product diol. The nature of the ligand is known to markedly influence the rate of perosmate oxidations [1] and the observed decrease in cell current when pyridine was used suggests that the olefin oxidation reaction had become rate-limiting. The runs using pyridine produced only the expected racemic diol.

The experiments whose results are collected in Fig. 8 were obtained with a ligand : osmium ratio of 9.7 : 1 (the composition described in Section 2.2). Increasing this to 39 : 1 by reducing the quantity of osmium present did not influence the enantiomeric

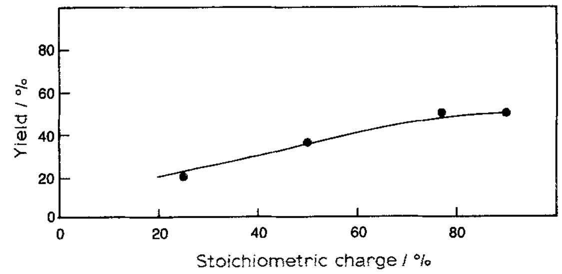


Fig. 9. Influence of charge passed at the anode on yield of hydrobenzoin in a system with 2 mol of pyridine substituted for each mole of hydroquinidine ester in the reaction mixture which is otherwise as given in Section 2.2; 25° C.

purity of the product; evidently the formation constant for the complex is sufficiently large that the osmium is fully sequestered at the lower ratio. Product enantiomeric excess remained unchanged over the temperature range of 20 to 45°; uncontrolled runs in which the temperature was allowed to peak at 60° exhibited a decrease in enantiomeric specificity. Quadrupling the quantity of olefin caused only a concomitant increase in the time required to achieve a given level of conversion; product properties were not affected.

Both cyclohexane and t-butanol were used as the organic solvent; the alcohol is much to be preferred for this reaction. The hydrobenzoin product is of limited solubility in cyclohexane and as the dihydroxylation proceeds, the reaction mixture tended to resist dispersion of the liquid phases and separate into a paste which would adhere to the anode or membrane, breaking the current path. The problem is aggravated if an increased quantity of olefin is used. No such effects occurred with t-butanol and a greater degree of reproducibility was noted with that solvent, presumably due to more constant conditions in the reactor.

A measure of the reproducibility possible with this preparative method was provided by a series of sixteen runs carried out using t-BuOH, the mixture given in Section 2.2, but increasing the quantity of stilbene to 28 mmol. The larger of the two cell types was used without external temperature control; the liquid temperature rose from 23 to 35° C in the course of each run. With the full (100%) stoichiometric anode charge passed, the mean diol yield was 91.3% with a standard deviation of 2.4 percentage points. Enantiomeric excess was greater than 90% for all of the runs.

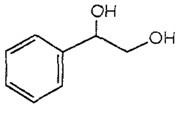
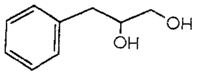
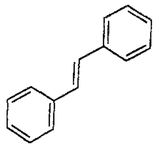
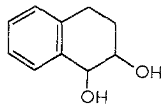
Several preparative runs were made using hydroquinine 4-chlorobenzoate as the chiral ligand to produce the S,S-hydrobenzoin enantiomer. At the same 85% stilbene conversion, the diol yield was the same as measured for R,R-isomer, 95%. The enantiomeric excess of the S,S- product was about 5% smaller than that found with the R,R-enantiomer, measured values lying in the range of 85 to 90%.

A limited number of preparations were carried out under galvanostatic conditions using a current density similar to that measured in potentiostatic experiments at the 90% conversion point. The electrode potential was monitored throughout the runs and found to remain between 400 and 500 mV. These runs were uneventful with product yields and enantiomeric purities essentially the same as measured in potentiostatic experiments taken to the same extent of stilbene conversion.

3.2. *Other olefins*

Table 1 lists the other vicinal diols prepared in this work using the hydroquinidine 4-chlorobenzoate directing ligand. No attempt was made to optimize the process for each new candidate olefin; runs were carried out potentiostatically under those conditions which earlier had led to the most efficient production of hydrobenzoin.

Table 1.

Product	*Yield*	*ee*
	88%	49%
	ca 90%	34%
	94%	90–95%
	ca 90%	>90%

Those olefins which bear the bulkiest substituent groups yield product diols with the greatest enantiomeric purity. This is not an unanticipated result given that steric interaction with the chiral ligand is the source of enantiomeric selectivity in these systems; similar results were reported earlier by Sharpless [7]. The enantiomer selectivity of the stilbene oxidation is relatively insensitive to temperature; this is not the case with all olefins. Improved enantiomeric purity in diols of the less bulky olefins may be possible by conducting the process at temperatures substantially below those used in this work.

4. Conclusions

Chiral diols have been prepared by the indirect, osmium catalysed electrolytic oxidation of the corresponding monoalkenes. The process is straightforward and has produced certain diols in enantiomeric excess of greater than 90%, following the general trends reported for the corresponding chemical synthesis. In the case of stilbene, oxidation of the product diol by Os(VIII) is the major contributor to process inefficiency.

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