

chloride (450 mL) was added a solution of **5** (6.36 g, 30 mmol) in methylene chloride (20 mL). The reaction was stirred at room temperature for 3 h, then diluted with methylene chloride (450 mL). The methylene chloride solution was decanted, and the residue remaining in the flask was washed with additional methylene chloride. The combined organic solutions were filtered through a short column of fluorisil (20 g) to remove colloidal chromates, and the filtrate was evaporated at reduced pressure to furnish 5.4 g (85%) of 2,5-diacetylcyclohexaneacetaldehyde: $^1\text{H NMR}$ (CDCl_3) δ 10.32 (br s, 1 H), 2.64-1.80 (m, 11 H), 2.16 (s, 6 H); mass spectrum, m/z 210 (M^+).

The acetaldehyde intermediate (4.2 g, 20 mmol) was taken up in tetrahydrofuran (200 mL), and water (0.5 mL) and concentrated hydrochloric acid (1.0 mL) were added. The solution was heated at reflux for 5 h, then diluted with water (10 mL), and evaporated at reduced pressure to remove most of the tetrahydrofuran. The residual aqueous solution was extracted with ether (3 \times 200 mL), and the combined ether extracts were successively washed with saturated sodium dicarbonate solution (20 mL) and brine (50 mL), then dried (MgSO_4), and filtered. Evaporation of the ether, chromatography of the residue on silica gel (25 g, CH_2Cl_2), and recrystallization of the eluate from benzene-hexane provided 2.0 g (52%) of pure **6**: mp 86-91 $^\circ\text{C}$; $^1\text{H NMR}$ (CDCl_3) δ 7.04-6.78 (m, 1 H), 6.12-5.84 (m, 1 H), 2.60-1.0 (m, 11 H), 2.16 (s, 3 H); mass spectrum, m/z 192 (M^+).

Anal. Calcd for $\text{C}_{12}\text{H}_{16}\text{O}_2$: C, 74.97; H, 8.39. Found: C, 74.95; H, 8.46.

9-Acetyl-5,12-dihydroxy-4-methoxy-6(11H)-hexahydronaphthacene (8). 7-Methoxy-3-(phenylsulfonyl)-1(3H)-isobenzofuranone (**7**) (1.82 g, 6 mmol) was added as a slurry in THF (40 mL) to a magnetically stirred, cold (-78°C) solution of lithium *tert*-butoxide (17.6 mmol) prepared from *n*-butyllithium (17.6 mmol) and *tert*-butyl alcohol (18.0 mmol). The yellow anion solution, still at -78°C , was stirred for 15 min, and then **6** (1.8 g, 0.4 mmol) was added in a single portion. The reaction

was continued at -78°C for 15 min at which point the cooling bath was removed and the reaction was allowed to come to room temperature. The reaction was allowed to stand at room temperature for 1 h and was quenched by addition of hydrochloric acid (2 mL of 6 N), whereupon bright yellow crystals of **8** precipitated. The crystals were collected by filtration and washed with methylene chloride (50 mL) to furnish 2.0 g (93% yield) of pure (**8**): mp 223-226 $^\circ\text{C}$; mass spectrum, m/z 354 (M^+). Compound (**8**) was found to be extremely sensitive to air oxidation, and a satisfactory combustion analysis could not be obtained.

9-Acetyl-6-hydroxy-4-methoxy-7,8,9,10-tetrahydronaphthacene-5,12-dione (9). Oxygen was bubbled through a solution of **8** (4 g, 11 mmol) in DMF (100 mL) at 100 $^\circ\text{C}$ for 2 h. The oxygen flow was then terminated, and water (20 mL) was added. As the reaction cooled, orange crystals of **9** precipitated, which were collected by filtration, washed with water, and dried to give 3.7 g (94% yield) of pure **9**: mp 222-225 $^\circ\text{C}$ (lit.⁴ mp 223-226 $^\circ\text{C}$), mixture melting point undepressed; $^1\text{H NMR}$ (CDCl_3) δ 13.36 (s, 1 H), 8.08-7.22 (m, 4 H), 4.07 (s, 3 H), 3.30-2.40 (m, 4 H), 2.27 (s, 3 H), 2.27 (m, 1 H), 2.0-1.4 (m, 2 H), mass spectrum, m/z 350 (M^+).

Anal. Calcd for $\text{C}_{21}\text{H}_{18}\text{O}_5$: C, 71.99; H, 5.18. Found: C, 71.70; H, 5.30.

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Registry No. **3a**, 86420-17-9; **3b**, 86374-39-2; **4a**, 86391-80-2; **4b**, 86374-40-5; **4c**, 86374-41-6; **5**, 86374-42-7; **6**, 86374-43-8; **7**, 65131-09-1; **8**, 86374-44-9; **9**, 86374-45-0; 2,5-diacetylcyclohexaneacetaldehyde, 86374-46-1; 11-deoxydaunomycinone, 83962-00-9.

Communications to the Editor

Electroorganic Reactions on Organic Electrodes. 3. Electrochemical Asymmetric Oxidation of Phenyl Cyclohexyl Sulfide on Poly(L-valine)-Coated Platinum Electrodes[†]

Tetsuo Komori and Tsutomu Nonaka*

Department of Electronic Chemistry
Tokyo Institute of Technology
4259 Nagatsuta, Midori-ku
Yokohama, 227 Japan

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As summarized by Tilborg and Smit,¹ some methods for electrochemical asymmetric reduction of prochiral compounds had been reported. Among the methods, the highest optical yield was obtained in the asymmetric reduction in the presence of optically active alkaloids: Kariv and co-workers² reported a high optical yield of 47.5% in the reduction of 2-acetylpyridine to 2-(hydroxymethyl)pyridine in the presence of strychnine. Afterward, Tallec and co-workers³ obtained 44.3% of optical yield in the reduction of 1,1-dibromo-2,2-diphenylcyclopropane to 1-bromo-2,2-diphenylcyclopropane in the presence of emetine.

Recently, Osa and co-workers⁴ have reported a new method for the electrochemical asymmetric reduction: They obtained 2-6% of optical yields in the reduction of 2-hexanone to 2-hexanol

Table I. Electrochemical Asymmetric Oxidation of Phenyl Cyclohexyl Sulfide (1) to Phenyl Cyclohexyl Sulfoxide (2) on Poly(L-valine)-Coated Platinum Electrodes

type of electrode	2		
	$[\alpha]^{20}_{\text{D}}$ (c)	optical yield, %	chemical yield, %
A ^b	-54.0 ^o (0.7)	28.0	34.0
B ^c	-81.1 ^o (0.3)	40.0	14.5
C ^{d,e}	-106.2 ^o (0.7)	54.0	31.2

^a Measured in acetonitrile. ^b Poly(L-valine) was coated on a bare platinum surface. ^c Poly(L-valine) was coated on the platinum surface precoated with polypyrrole by adsorption. ^d Poly(L-valine) was coated on the platinum surface precoated with polypyrrole anchored covalently. ^e The electrolysis time was 14 h.

using Raney-nickel powder electrodes modified with optically active tartaric acid. More recently, we have found that a poly(L-valine)-coated graphite electrode was effective for the reduction of prochiral olefins.^{5,6} A high optical yield of 43% was obtained in the reduction of 4-methylcoumarin to 4-methyldihydrocoumarin.

On the other hand, a few papers dealing with electrochemical asymmetric oxidation had been published: Low optical yields of 0.3-2.5% were reported in the oxidation of aryl methyl sulfides to the corresponding sulfoxides on electrodes modified chemically with optically active compounds such as phenylalanine methyl ester⁷ and camphoric acid.⁸ In this work, the asymmetric oxi-

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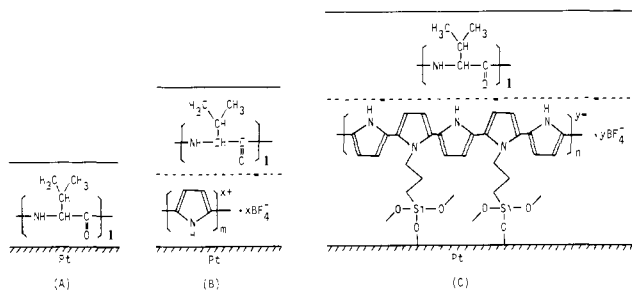
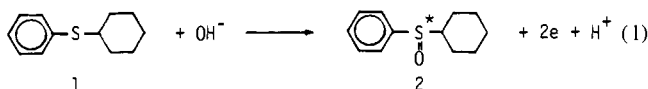


Figure 1. Poly(L-valine)-coated platinum electrodes.

duction of phenyl cyclohexyl sulfide (**1**) to phenyl cyclohexyl sulfoxide (**2**) (eq 1) was examined, and remarkably high optical



yields were obtained by using poly(L-valine)-coated platinum electrodes, as shown in Table I.

Three kinds of the poly(L-valine)-coated platinum electrodes (A, B, and C) shown in Figure 1 were used for the asymmetric oxidation. The coated electrode A was prepared by dipping a platinum plate (3 × 4 cm) into 0.5% (w/v) poly(L-valine) (M_w ca. 2000⁵)/trifluoroacetic acid, similarly to preparation of a poly(L-valine)-coated graphite electrode in a previous work.⁵ To prepare the coated electrode B, the platinum plate was first coated with polypyrrole by anodic polymerization at 1.5 V vs. Ag/AgCl for 2 min in 0.01 M pyrrole–0.1 M Bu_4NBF_4 /acetonitrile and then with poly(L-valine) in layers by a dipping method similar to above. The coated electrode C was also prepared by double coating with polypyrrole and poly(L-valine). A polypyrrole film in this case was covalently bound by Pt–OSi(CH₂)₃N (pyrrole nucleus) bondings to the platinum surface. Coating of the polypyrrole film was carried out by a modified method of Simon et al.,⁹ who developed the original method for the protection of n-type silicon photoanodes: The platinum plate was chemically modified with monomeric pyrrole by the reaction of its surface oxides with *N*-[3-(trimethoxysilyl)propyl]pyrrole in ethanol and then was anodically treated at 1.5 V vs. Ag/AgCl for 2 min in 0.01 M pyrrole–0.1 M Bu_4NBF_4 /acetonitrile. The polypyrrole-coated platinum plate prepared thus was also coated with poly(L-valine) by the dipping method.

Phenyl cyclohexyl sulfide (**1**) (2 mmol) was oxidized by passing 386 C of charge at 1.75–1.85 V vs. Ag/AgCl at 0 °C in 70 mL of 0.1 M Bu_4NBF_4 /acetonitrile (containing 1% water), using a potentiostat (Hokuto Denko Ltd., Model HA-201). After the electrolysis, phenyl cyclohexyl sulfoxide (**2**) was purely separated from the anodic solution by column chromatography (Kieselgel 60, chloroform–ethyl acetate, 9:1 v/v), and the optical rotation was measured in acetonitrile with a highly sensitive polarimeter (Union Co., automatic digital polarimeter Model PM-101). Because the optical rotating power of optically pure **2** has not been reported, the optical yield was calculated from NMR spectra of **2** measured in the presence of tris[3-[(trifluoromethyl)hydroxymethylene]-D-camphorato]europium(III) as an enantiomer-shift reagent.

The polypyrrole film is electronconductive, because it was doped with tetrafluoroborate ions.¹⁰ The thickness of poly(L-valine) films is estimated as ca. 10^{−4} cm by analogy with poly(L-valine)-coated graphite electrodes prepared in the previous work,⁶ and the films are not electroconductive. Therefore, electron transfer between **1** and the electrode seems to occur on and/or in the polypyrrole film.

The coated-electrode B gave a higher optical yield than the coated-electrode A. The higher optical yield may be due to a

tighter adhesion of the poly(L-valine) film to the polypyrrole-coated platinum surface of the coated-electrode B. The coated-electrode C gave a much higher optical yield of 54%. This may be also rationalized as due to the very strongly (covalently) bound adhesion of the polypyrrole film to the platinum surface of the coated-electrode C, comparing with that of the coated-electrode B.

In with the previous works^{5,6} dealing with asymmetric reduction on poly(amino acid)-coated electrodes, this asymmetric oxidation using the platinum electrodes coated doubly with polypyrrole and poly(L-valine) clearly demonstrates the advantageous utilization of polymer-coated electrodes in electroorganic syntheses.

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Registry No. Phenyl cyclohexyl sulfide, 7570-92-5; phenyl cyclohexyl sulfoxide, 3324-82-1; poly-L-valine, 25609-85-2; *N*-[3-(trimethoxysilyl)propyl]pyrrole, 80906-67-8; pyrrole, 109-97-7; tetrafluoroborate ion, 14874-70-5; polypyrrole, 30604-81-0; (*S*)-poly[imino[1-(1-methyl-ethyl)-2-oxo-1,2-ethanediy]]], 25667-19-0.

Clay-Modified Electrodes

Pushpito K. Ghosh and Allen J. Bard*

Department of Chemistry
The University of Texas at Austin
Austin, Texas 78712

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We report here the modification of an electrode surface by coverage with a thin layer of a treated clay and describe the electrochemical behavior of several substances incorporated into this clay film. The modification of electrode surfaces, for example by covalent attachment or with polymer films, is currently an active area of research.¹ Clay and other inorganic layers on electrode surfaces have the advantage of high chemical stability and special structural features and, to our knowledge, have not previously been described.

Colloidal clays have recently attracted considerable attention because of their appreciable surface area and unusual intercalation properties. Clays are employed in many commercial processes² and are important as catalysts³ or catalyst supports.⁴ The immobilization of complex catalysts in clay structures is an area of growing interest, since apart from the obvious advantages of heterogeneous catalysis, clay colloids have been found to influence the specificity of catalysts as well.⁵ Clay colloids have also been used in photocatalytic systems.⁶

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