Introduction of an electron-withdrawing substituent in the alcohol destabilizes the protonated zwitterionic species in the upper left corner of the diagram. This causes the transition state to "slide" downhill and to the right, that is to a transition state involving less proton transfer, and an expected lower value of α is seen.

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Registry No. $CH_3CH_2OCOS^-\cdot K$, 35832-93-0; $CH_3OCOS^-\cdot K$, 34520-64-4; $CH_3OCH_2CH_2OCOS^-\cdot K$, 85319-49-9; $CH_3CH_2OCS_2^-\cdot K$, 140-89-6; $CH_3OCH_2CH_2OCS_2^-$, 65944-33-4; cyanoacetic acid, 372-09-8; chloroacetic acid, 79-11-8; formic acid, 64-18-6; acetic acid, 64-19-7; cacodylic acid, 75-60-5; dihydrogen phosphate, 14066-20-7.

Supplementary Material Available: Tables V (pH and k_0 values for alkyl xanthates and monothiocarbamates) and VI (rate constants for D_3O^+ catalysis for xanthates and monothiocarbamates) (4 pages). Ordering information is given on any current masthead page.

Electroorganic Reactions on Organic Electrodes. 1. Asymmetric Reduction of Prochiral Activated Olefins on a Poly-L-valine-Coated Graphite†

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Abstract: The electrochemical asymmetric reduction of citraconic acid (**1**) and 4-methylcoumarin (**3**) was carried out at a poly-L-valine-coated graphite cathode. Maximum optical yields of methylsuccinic acid (**2**) and 3,4-dihydro-4-methylcoumarin (**4**) were 25 and 43%, respectively, in a phosphate-buffered solution (pH 6).

Some methods for electrochemical asymmetric reduction of prochiral ketones, imines, and olefins had been reported: As summarized by Tilborg and Smit,[1] the use of chiral solvents, chiral supporting electrolytes, chiral electrode surface-active materials, and chiral chemically modified electrodes could result in asymmetric induction. Although the use of chiral solvents[2] and supporting electrolytes[3] gave 6 and 20% optical yields, respectively, in each best case in the reduction of acetophenone, these methods inherently need large amounts of optically acitive materials as asymmetry-inducing reagents. In contrast to these, the other two methods should be characterized by the efficient use of extremely small amounts of the inducing reagents A pioneer work in the field of electrochemical asymmetric synthesis was made by Gourley et al.[4] using optically active alkaloids. They obtained a 17% optical yield in the reduction of 4-methylcoumarin (**3**) in the presence of sparteine (5 mM). Afterward, Miller and his co-workers[5,6] reported surprisingly high optical yields, close to 50%, in the reduction of 2-acetylpyridine in the presence of strychinine (0.5 mM). They also prepared chemically modified electrodes with optically active amino acids and attempted asymmetric induction in both reduction and oxidation.[7–9] The highest optical yield (14.5%)[7,10] seemed to be obtained in the reduction of 4-acetylpyridine on a graphite cathode modified with (*S*)-(−)-phenylalanine methyl ester.

Asymmetric reduction using chiral chemically modified electrodes should be an excellent method, since very small amounts of inducing reagents can act efficiently. However, there may be a disadvantage in this method due to low coverage of chiral species on electrode surface. This point may be able to improved by using polymer-coated electrodes[11–13] including a polypeptide.[14] Miller et al.[11b] reported an interesting electrolysis using a polymer-coated electrode. The electrocatalyzed reduction of *meso*-1,2-dibromo-1,2-diphenylethane at a poly-*p*-nitrostyrene-coated platinum cathode gave *trans*-stilbene in high yields, and the turnover number for catalyst sites was estimated to be 10^4.

In this work, as a part of a larger program for highly selective electrosyntheses of organic compounds using electrodes modified with organic materials, we first examined the asymmetric reduction of activated olefins on an optically active polymer-coated electrode. A number of works dealing with the asymmetric reduction of ketones[1–3,5–8,13,15] and imines[15k,16] had been reported, while only

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† Stereochemical Studies of the Electrolytic Reactions of Organic Compounds. 19.

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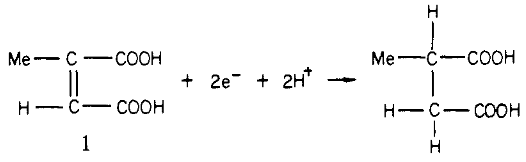
Table I. Asymmetric Reduction of Citraconic Acid (1) and 4-Methylcoumarin (3) on Poly-L-valine-Coated Graphite Cathode

							hydrogenated products (2, 4)		
run no.	olefin	concn of dip-coating solution, w/v %	supporting electrolyte	cathodic potential,[a] V vs. SCE	current density,[b] A/dm²	charge passed, F/mol	current efficiency,[c] %	chem yield,[c] %	opt yield,[d] %
1	1[e]	0.5	0.4 M H_2SO_4 (pH 0)	−1.0		2.0	19	19	0.3
2	1[e]	0.5	0.2 M NaH_2PO_4 (pH 6)	−1.0		0.2	80		25
3	1[e]	0.5	0.2 M NaH_2PO_4 (pH 6)	−1.2		0.2	56		3
4	1[e]	0.5	0.2 M NaH_2PO_4 (pH 6)	−1.0		0.6	62		12
5	1[e]	0.5	0.2 M NaH_2PO_4 (pH 6)		1.2	2.0	21	21	21
6	1[e]	1.0	0.2 M NaH_2PO_4 (pH 6)		1.2	2.0	32	32	9
7	1[e]	0.5	0.4 M $NaClO_4$ (pH 7)		1.2	2.0	0	0	
8	1[e]	0.5	0.1 M Na_2CO_3-0.05 M $NaHCO_3$ (pH 10)		1.2	2.0	0	0	
9	1[e]	0.5	0.4 M NaOH (pH 13)		1.2	2.0	0	0	
10	2[f]	0.5	0.2 M NaH_2PO_4 (pH 6)	−1.4		4.5		8	43
11	2[f]	0.5	0.2 M NaH_2PO_4 (pH 6)	−1.4		6.0		15	32

[a] For controlled potential electrolysis. [b] For constant current electrolysis. [c] For total of the enantiomeric products. [d] Percentage of enantiomer excess. In all cases the *S* configurational enantiomer was formed in excess. [e] 50 mL of 0.145 M citraconic acid solution containing ethanol in 20 v/v %. [f] 50 mL of 0.050 M 4-methylcoumarin solution containing ethanol in 50 v/v %.

two essential examples for olefins had been given. As described above, Gourley et al.[4] reported that (*R*)-(+)-3,4-dihydro-4-methylcoumarin (**4**) was obtained in 17% and 3.5% optical and chemical yields, respectively, in the reduction of 4-methylcoumarin (**3**) in the presence of sparteine. In previous works, we examined the asymmetric reductions of open-chain olefins in the presence of optically active alkaloids[17] and amino acids,[15k] and in the best case, (*R*)-(+)-methylsuccinic acid (**2**) was formed in 2.4% and 53% optical and chemical yields, respectively, from citraconic acid (**1**) in the presence of L-cysteine. The same olefins **1** and **3** were also used as starting prochiral compounds in the present work, and results obtained were compared with those reported previously.



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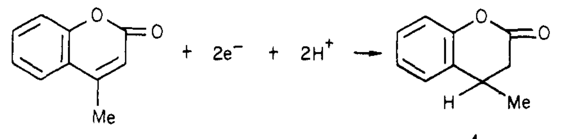

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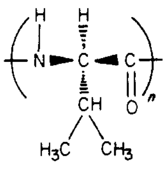
4

Results and Discussion

Poly-L-valine was chosen as an optically active polymer to coat electrodes because of its high optical rotatory power and good filming property. Generally, the properties of poly(amino acids)



poly-L-valine

are greatly affected by their preparative methods. In the present work, poly-L-valine was prepared by the *N*-carboxy anhydride (NCA) method: $[\alpha]^{20}{}_D$ −150°; M_r ca. 2000.[18] A poly-L-valine-coated graphite electrode was prepared by a dip-coating method. The film of poly-L-valine on the graphite electrode looked so thin that optical interference fringes could be observed.

As shown in Table I (runs 1–9), the reduction of citraconic acid (**1**) was carried out in a wide pH range and the highest optical yield (25%) was obtained in the controlled potential electrolysis (run 2) in an weakly acidic buffered solution. The optical yield of 25% is exceedingly higher than a value (2.4%) reported previously in the reduction of **1** in the presence of L-cysteine.[15k] A more negative potential (run 3) and a larger charge passed (run 4) in the controlled potential electrolysis resulted in the decrease of optical yields, but when a very large amount of charge was passed at a constant current density for a shorter time (run 5),[19] the decrease of optical yield was not remarkable. The use of a more highly concentrated dip-coating solution of poly-L-valine (run 6) resulted in a decrease in optical yield and an increase in chemical yield.

The lifetime of the poly-L-valine-coated electrode as an asymmetry inductor was also examined by its repeated reuse in fresh electrolytic solutions under the conditions for runs 5 and 6. The electrodes coated in 0.5 and 1.0 w/v % dip-coating solutions lost their asymmetry-inducing powers in the fourth and sixth electrolyses, respectively.

The reduction of **1** in a strongly acidic solution (run 1) gave the hydrogenated product **2** in a very low optical yield, while in the reduction in unbuffered neutral and buffered alkaline solutions the product **2** was not obtained.

In the reduction of 4-methylcoumarin (**3**) in the weakly acidic solution (runs 10 and 11), better results, which exceed the result (3.3% chemical yield and 17% optical yield) of Gourley et al.[4] in both the chemical and optical yields, could be obtained. The optical yield of 43% in run 10 also seems comparable to the highest value (49.7%)[5,6] achieved by the electrochemical asymmetric induction in the past.

Since polymer-coated electrodes can be easily prepared in general, the use of optically active polymer-coated electrodes should be a good electrochemical asymmetric induction method, if a suitable choice of polymer itself and electrode-base materials is made.

Experimental Section

Materials. Citraconic acid (**1**) was commercially supplied from Tokyo Kasei Chemical Co, while 4-methylcoumarin (**3**) was prepared by the method in the literature[20] and confirmed by the melting point and NMR spectrum. Poly-L-valine was prepared by the NCA method: L-valine monomer ($[\alpha]^{20}{}_D$ +27°) was reacted with equimolar phosgene dimer at 50 °C in THF until the monomer was completely dissolved and then

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THF was evaporated under reduced pressure. The residual *N*-carboxy anhydride (NCA) of L-valine was polymerized at 30 °C in dioxane containing 1/20 equimolar triethylamine as a catalyst. After the solution was left standing for 4 days, poly-L-valine was collected as a precipitate and washed with dioxane. The completely dried THF and dioxane were used in these procedures, because the NCA is very sensitive to moisture: yield, 33%; IR (KBr) $\nu_{C=O}$ 1630 cm^{-1}; $[\alpha]^{20}_{D}$ −150° (*c* 1, trifluoroacetic acid); M_r ca. 2000.[18]

Poly-L-valine-Coated Graphite Electrodes. A polycrystalline graphite plate (2 × 4 cm) polished with a fine emergy paper was dipped in trifluoroacetic acid solution of poly-L-valine (0.5–1.0 w/v %) for 15 min. The graphite plate was dried for 5 min under the atmospheric pressure and then for 30 min under reduced pressure.

Electrolysis. The electrolytic reduction of citraconic acid (**1**) and 4-methylcoumarin (**3**) was carried out by means of the controlled potential or constant current method at 0 °C in a divided cell. Details of electrolytic condition are given in Table I.

Product Analysis. After the electrolysis, ethanol in the catholyte was distilled away under reduced pressure and the residual solution was acidified with aqueous sulfuric acid. The hydro dimer, if formed, was filtered off, and the filtrate was extracted repeatedly with ether. The combined ethereal solution was evaporated to dryness, and the recrystallization of the residual solid from an ether–benzene mixture afforded the pure hydrogenated products **2** and **4** which could be confirmed by melting points and NMR spectra.

Optical rotation of compounds was measured in 1–5-cm cells of a highly sensitive polarimeter (Union Co. automatic digital plarimeter, Model PM-101). The $[\alpha]^{20}_{D}$ of **2** and **4** were measured in ethanol and benzene, respectively, and the optical yields were calculated with reference to values reported for the optically pure enantiometers: $[\alpha]^{20}_{D}$ 17.9° (*c* 4.4, ethanol)[21] for **2** and $[\alpha]^{20}_{D}$ 32° (*c* 1, benzene)[22] for **4**.

Acknowledgment. This study was performed as a preliminary investigation for a project supported financially by the Grant-in-Aids for Scientific Researches from the Japanese Ministry of Education.

Registry No. 1, 498-23-7; (*R*)-(+)-**2**, 3641-51-8; **3**, 607-71-6; (*R*)-(+)-**4**, 30825-55-9; poly-L-valine, 25667-19-0; graphite, 7782-42-5; L-valine homopolymer, 25609-85-2.

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Isomerization of Hexamethyl(Dewar benzene) to Hexamethylbenzene Catalyzed by Electron Acceptors. Thermal Generation of an Exciplex

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Contribution from the Department of Chemistry, Roger Adams Laboratory, University of Illinois, Urbana, Illinois 61801. *Received November 15, 1982*

Abstract: The reaction of hexamethyl(Dewar benzene) (HMD) with ground-state electron acceptors and with singlet and triplet excited electron acceptors reveals parallel behavior. The thermal acceptors catalyze the conversion of HMD to hexamethylbenzene (HMB) without formation of ions free in solution. The excited-state acceptors in some cases give ions, and in others only neutral ground-state products. The behavior of these electron acceptors is interpreted to indicate that formation of an exciplex in both the thermal and photochemical reactions initiates the process responsible for isomerization. In some cases electron transfer in the exciplex and dissociation lead to ionic products.

The chemical and physical properties of strained hydrocarbons have long fascinated chemists striving to understand the details of structure and reactivity.[1] Dewar benzene (bicyclo[2.2.0]-hexa-2,5-diene) and its derivatives rank among the most noteworthy compounds in this group. The first Dewar benzene derivative was prepared by van Tamelen and Pappas[2a] and they subsequently prepared the parent hydrocarbon.[2b] Hexamethyl-(Dewar benzene) (HMD) was prepared conveniently, and in high yield, by Schäfer[3] using an aluminum chloride catalyzed cyclotrimerization of 2-butyne. The ready availability of HMD has made it the favorite substance for investigation of the Dewar ring system.

One of the remarkable properties possessed by HMD is its thermal stability. Thermolysis in inert solvent converts HMD primarily to hexamethylbenzene (HMB), eq 1.[4] At 150 °C this reaction has a half-life of over 3 h and a measured activation energy of 37 kcal/mol despite being exothermic by nearly 60 kcal/mol.[5] The high activation energy has been attributed in part to the symmetry forbiddeness of the thermal rearrangement,[6] and the nature of the reaction transition state for Dewar benzene has been extensively probed.[7] The high exothermicity of the rearrangement of the Dewar structure to its more familiar aromatic isomer provides the energy for chemiluminescence observed from some derivatives.[8] The strain of the Dewar isomer, estimated to be 45 kcal/mol,[5] raises the energy of the highest occupied molecular orbital and concomitantly lowers the ionization potential[9] and oxidation potential.[10] This feature may account for some of the metal-catalyzed rearrangements[11] and the unusual photochemistry of HMD.

(1)

Evans and co-workers[10] photosensitized the isomerization of HMD with naphthalene. They observed quantitative conversion

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