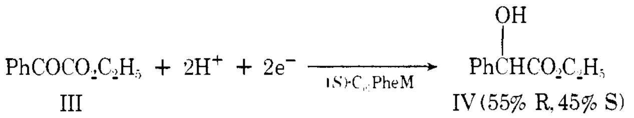
demonstrated that the reported rotation is too low and a reliable[6] absolute rotation is not available.

It was established that this electrode could be used again (isolated II, $[\alpha]^{20}\mathrm{D}$ −4.2°) and that an electrode with the *R* configuration could be synthesized. This (*R*)-$\mathrm{C_{el}}$PheM produced II, $[\alpha]^{20}\mathrm{D}$ +6.1. A further control experiment was then undertaken. It is known that optically active alkaloids in solution can lead to asymmetric induction.[7] Indeed, it has been shown that reduction of 4-acetylpyridine on a mercury electrode in the presence of alkaloids gives optically active II.[5] We, therefore, reduced I on an untreated graphite electrode in the presence of 0.015 *M* (*S*)-PheM. Although catalytic hydrogen evolution was noted from the amino acid, this was suppressed by addition of I and alcohol II was produced as the major product. After GLC purification this alcohol had a rotation $\alpha_{\mathrm{OBS}} = -0.015$. A second trial gave $\alpha_{\mathrm{OBS}} = +0.025$.

It is concluded that no asymmetric induction occurred and the origin of the activity from (*S*)-$\mathrm{C_{el}}$PheM reductions is, on the surface, not from material cleaved and in solution. The state of the amino acid during reduction is not known. In particular the ester moiety is susceptible to reaction and may not be intact.

The reduction of ethyl phenylglyoxylate (III) on this chiral electrode was also performed. Using the above procedure and (*S*)-$\mathrm{C_{el}}$PheM the alcohol IV was formed in 94% yield at −1.05 V. It was purified by GLC, characterized spectrally, and had $[\alpha]^{20}\mathrm{D}$ −12.5° ($c = 0.8$, $\mathrm{CHCl_3}$). Pure IV was prepared from optically pure (+)-mandelic acid and found to have a rotation of +128.4° ($c = 1.2$, $\mathrm{CHCl_3}$). The observed asymmetric induction corresponds, therefore, to an optical purity of 9.7%.



$$\underset{\mathrm{III}}{\mathrm{PhCOCO_2C_2H_5}} + 2\mathrm{H}^+ + 2e^- \xrightarrow[(S)\text{-}\mathrm{C_{el}PheM}]{} \underset{\mathrm{IV}\,(55\%\ R,\,45\%\ S)}{\mathrm{PhCH(OH)CO_2C_2H_5}}$$

The above results demonstrate the principle of covalently modified electrodes. The particular examples are easily and inexpensively prepared, and it would seem that such modified electrodes would have substantial applications in preparative and analytical electrochemistry and in energy conversion. In essence, one can combine the selectivity of chemical processes with the catalytic nature of an electrode for electron transfer processes to perform selective, catalytic redox processes.

Acknowledgments. Amino acid samples were supplied by G. Plume. A stimulating conversation with Professor James Bobbitt concerning the surface functionality of graphite is acknowledged.

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Stereoselective Bifunctional Catalysis of the Dedeuteration of Cyclopentanone-*2,2,5,5-d$_4$*[1]

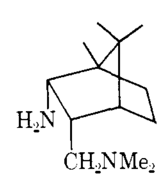
Sir:

Certain monoprotonated primary-tertiary diamines have been found to catalyze the dedeuteration of acetone-d_6 and isobutyraldehyde[2] via formation of an iminium ion, which is dedeuterated internally by attack of the tertiary amino group. We have now found marked stereoselectivity in such catalysis.

Dedeuteration of cyclopentanone-*2,2,5,5-d*$_4$ in the presence of perchloric acid or monofunctional bases follows Scheme I, in which the rate is proportional to the number of deuterium atoms present.[3] The sample kinetic plot in Figure 1 could be used for any such catalyst if the log *t* scale were renumbered to apply to the appropriate *k* value. In the presence of monoprotonated (1*R*,2*S*,3*R*,4*R*)-3-dimethylaminomethyl-1,7,7-trimethyl-2-norbornanamine (**1**),[4] however, two of the deuterium atoms exchange faster than the other two. This is explained by Scheme II, where k_{d} and k_{l} are rate constants, per deuterium atom, for removal of the two different types of deuterium atoms attached to the prochiral α carbon atoms of the ketone. Equations for the fraction of ketone present as D4, D3, etc., as a function of k_{d}, k_{l}, and the time were obtained by application of the operator method[5] and neglect of the D0, D1, and D2 present in the starting material, which was about 91% D4 and 8% D3. The results obtained in a run using **1** and the corresponding theoretical curves based on these equations are shown in Figure 2. The results are consistent with Scheme II and not with Scheme I, which demands that the D1 concentration reach a maximum before eight half-lives for the disappearance of D4 (rather than >100 D4 half-lives, as observed).

Scheme I

$$\mathrm{D4} \xrightarrow{4k} \mathrm{D3} \xrightarrow{3k} \mathrm{D2} \xrightarrow{2k} \mathrm{D1} \overset{k}{\rightleftharpoons} \mathrm{D0}$$



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Scheme II

$$\begin{tikzcd}
\mathrm{D4} \arrow[r, "2k_{\mathrm{d}}"] \arrow[d, "2k_{\mathrm{l}}"'] & d\text{-}\mathrm{D3} \arrow[r, "k_{\mathrm{d}}"] \arrow[d, "2k_{\mathrm{l}}"'] & d\text{-}\mathrm{D2} \arrow[d, "2k_{\mathrm{l}}"'] \\
l\text{-}\mathrm{D3} \arrow[r, "2k_{\mathrm{d}}"] \arrow[d, "k_{\mathrm{l}}"'] & \mathrm{i}\text{-}\mathrm{D2} \arrow[r, "k_{\mathrm{d}}"] \arrow[d, "k_{\mathrm{l}}"'] & d\text{-}\mathrm{D1} \arrow[d, shift right, "k_{\mathrm{l}}"'] \\
l\text{-}\mathrm{D2} \arrow[r, "2k_{\mathrm{d}}"] & l\text{-}\mathrm{D1} \arrow[r, shift left, "k_{\mathrm{d}}"] & \mathrm{D0} \arrow[l, shift left] \arrow[u, shift right]
\end{tikzcd}$$

A partly dedeuterated sample containing about 68% D2, 17% D1, and 13% D3 showed at 277 nm the largest absolute rotation (Figure 3) we are aware of for a compound whose optical activity is wholly an isotope effect. This rotation was shown to arise from the ketone rather than an impurity by the observation of racemization in the presence of 3-dimethylaminopropionitrile at a rate corresponding to a primary kinetic isotope effect ($k_{\mathrm{H}}/k_{\mathrm{D}}$) of 3.4. Application of the octant rule[6,7] in its simplest form to the positive Cotton effect in the vicinity of the uv absorption maximum of the ketone (noting the larger atomic polarizability of protium

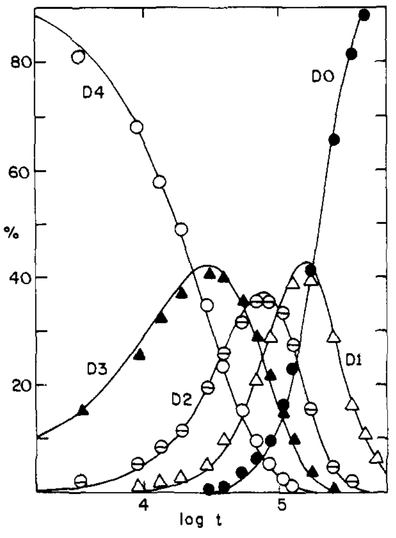

Figure 1. Kinetic plot (time in sec) for the dedeuteration of aqueous 0.206 *M* cyclopentanone-2,2,5,5-d_4 containing 0.0986 *M* total 3-dimethylaminopropionitrile at pH 7.627 and 35°. The curves are based on Scheme I with $k = 9.00 \times 10^{-6}$ sec^{-1}.

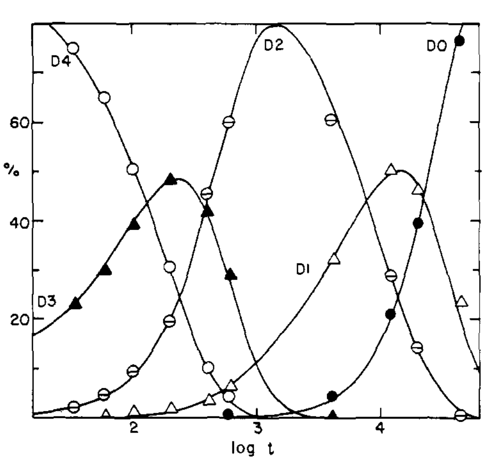

Figure 2. Kinetic plot (time in sec) for the dedeuteration of 0.206 *M* cyclopentanone-2,2,5,5-d_4 containing 0.00509 *M* aqueous **1** at pH 8.03 and 35°. The curves are based on Scheme II with $k_d = 4.77 \times 10^{-5}$ sec^{-1} and $k_l = 266 \times 10^{-5}$ sec^{-1}.

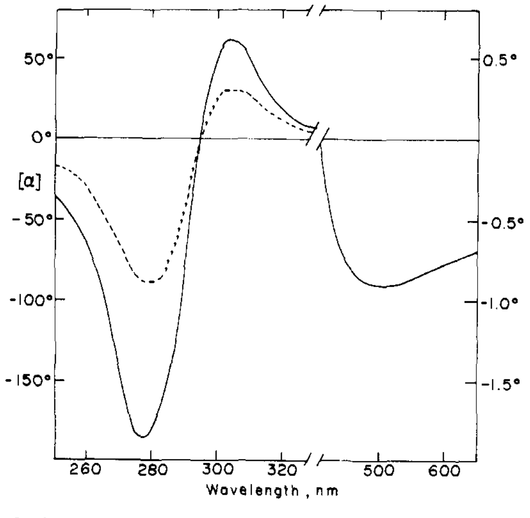

Figure 3. ORD curve for cyclopentanone extracted from aqueous 1.0 *M* cyclopentanone-2,2,5,5-d_4 containing 0.00236 *M* total **1** at pH 6.5 and 35° after 15 hr; right, neat; left, solid line, aqueous 0.092 *M* solution; dashed line, similar solution also containing 0.322 *M* free and 0.080 *M* protonated 3-dimethylaminopropionitrile after 4765 sec at 35°.

than deuterium[7]) would suggest an *R* configuration for the CO-CHD-CH$_2$ grouping in the principal products of partial dedeuteration. However, molecular models of transition states for bifunctionally catalyzed dedeuteration *strongly* indicate an *S* configuration.

Supplementary Material Available. Additional details are in the Appendix, which will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th Street, N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number JACS-75-3550.

References and Notes

(1) This investigation was supported in part by Grant GM 18593 from the National Institute of General Medical Sciences. Part XVIII in the series "Catalysis of α-Hydrogen Exchange:". For part XVII see J. Hine and S. S. Ulrey, *J. Org. Chem.*, **39**, 3231 (1974).

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(3) The reaction in water at 35° was quenched with acid; then the ketone was extracted and its deuterium content determined by mass spectral measurements. Further kinetic details are given in the Appendix.

(4) This compound was prepared from (+)-camphor, via its *endo*-3-dimethylaminomethyl derivative, whose oxime was reduced with lithium aluminum hydride. The spectral properties and other evidence for the structure of **1** are given in the Appendix.

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An Unusual Type of Organolanthanide Complex Containing the Allyl Moiety: $(\eta^5\text{-}C_5H_5)_2LnC_3H_5$

Sir:

In our work on organometallic complexes of the lanthanides, we have previously reported the preparation of σ-alkynyl derivatives from dicyclopentadienyllanthanide chlorides.[1] These contained the first metal-carbon σ bonds known for most of these elements. We subsequently prepared alkyl and aryl derivatives of these elements[2] and wished to extend the work to derivatives containing the allyl (C_3H_5) moiety. Allyl complexes of the d-block transition metals are well known,[3] and numerous non-transition metal-allyl complexes have been synthesized.[4] However, actinide-allyl complexes are rare,[3b,5,6] and lanthanide-allyl complexes have been heretofore unknown. We now report the first organolanthanide complexes to contain the allyl ligand: $Cp_2LnC_3H_5$ ($Cp = \eta^5\text{-}C_5H_5$; Ln = Sm, Er, Ho).

The complexes are prepared by the reaction of the appropriate Cp_2LnCl[7] with allylmagnesium bromide in THF-ether solution at −78° as shown in eq 1. The mixture is

$$Cp_2LnCl + C_3H_5MgBr \xrightarrow[-78^\circ]{\text{THF-ether}} Cp_2LnC_3H_8 + MgBrCl \qquad (1)$$

warmed to room temperature, and dioxane is added to precipitate the magnesium halides.[8-10]