For the synthesis of pentalenic acid (**1**), enyne **8** was prepared in 78% overall yield by propargylation of ethyl isobutyrate, reduction with $LiAlH_4$, silylation, oxidation with $(COCl)_2$ and DMSO, and vinylation with vinylmagnesium bromide. After benzylation, Zr-promoted bicyclization–carbonylation[5] gave a 68% yield of **9a**, the stereochemistry of which was firmly established by NMR spectroscopy (J_{H^5,H^6} = 9.8 Hz) and X-ray analysis. For the eventual synthesis of **1**, it was necessary to use *p*-methoxybenzyl chloride[10] in place of benzyl chloride for protecting the OH group of **8** due to the difficulty in debenzylation. The bicyclization–carbonylation reaction for producing >98% diastereomerically pure **9b** proceeded in 84% yield.

For selective annulation of the C ring with control of the stereochemistry of the 9-Me group, **9b** was treated at −78 °C for 15 min with the lithio derivative of (Z)-$CH_3CH{=}CHCH_2PO(OEt)_2$[11] generated by its reaction with *n*-BuLi in THF at −78 °C. Crudely isolated conjugate addition product was treated with $(n\text{-Bu})_4NF$ (0 °C, 5 min) to give a 94% yield of **10b**, which was of ≥98% stereoisomeric purity. After ketalization of **10b** with $(CH_2OH)_2$, hydroboration with BH_3·THF[12] overnight at 20 °C followed by oxidation with 30% H_2O_2 and NaOAc at 50 °C yielded the corresponding (α-hydroxyalkyl)phosphonate, which was crudely isolated and treated with $NaHCO_3$ in MeOH–H_2O at 50 °C to give **11b** in 57% yield.[13] In addition to the conjugate addition of allylphosphonate anions, the base-promoted reaction of aldehydes with $CH_2[PO(OEt)_2]_2$ readily produces (E)-alkenylphosphonates in good yields,[14] typically 80–95%. Coupled with hydroboration–oxidation–elimination, one-carbon homologation of aldehydes can be achieved in good yield, as shown in Table I.

Treatment of **11b** with 1 equiv of pyridinium *p*-toluenesulfonate (PPTS) in boiling acetone–water for 16 h not only deprotected the carbonyl group but also induced aldolization in 82% yield. After mesylation with MsCl and NEt_3, treatment with DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) in refluxing benzene yielded the desired enone, which was hydrogenated over Pd/C to give isomerically pure **12b** in 71% yield based on the aldol intermediate. Conversion of **12b** into **13** using 2,6-di-*tert*-butyl-4-methylpyridine and triflic anhydride for generation of alkenyl triflates[1d] followed by Pd-catalyzed carbomethoxylation[15] led to a 75:25 mixture of **13** and its regioisomer. On the other hand, treatment of **12b** with lithium diisopropylamide (LDA) and Tf_2NPh in DME (dimethoxyethane) for triflate generation[16] followed by deprotection of the (*p*-methoxyphenyl)methyl (MPM) group with DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) gave isomerically pure **13**, the spectra data of which were in excellent agreement with those obtained by other workers.[1] The Me ester **13** was quantitatively converted to (±)-**1** by hydrolysis with methanolic KOH.

Acknowledgment. We thank the National Institutes of Health (GM36792) and the National Science Foundation (CHE-9023728) for support of this research. We also thank Professors H. C. Brown, M. T. Crimmins, T. Hudlicky, and H. Seto for providing us with useful information and Dr. P. E. Fanwick and Mr. M. Piotto for spectral measurements.

Supplementary Material Available: Experimental procedures and analysis data for the compounds in this communication and an ORTEP view of **9a** (9 pages). Ordering information is given on any current masthead page.

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General Acid Catalysis of the Reduction of *p*-Benzoquinone by an NADH Analogue

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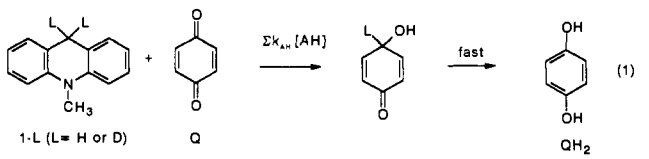
Received May 2, 1991

We report that the third-order term for acetic acid catalyzed reduction of *p*-benzoquinone, Q, by an NADH analogue, 9,10-dihydro-10-methylacridine (**1**-L, L = H or D; eq 1), displays primary isotope effects k_H/k_D = 1.5 in H_2O and D_2O and solvent isotope effects k_{H_2O}/k_{D_2O} = 1.3 for H or D transfer. Substituted RCOOH catalysts show a Brønsted slope α = 0.85. These results provide evidence for concerted hydron and hydride transfer to benzoquinone and are not consistent with a mechanism involving the semiquinone radical, QH•.[1]



Extensive studies of thermal 1,4-dihydronicotinamide reductions using isotope effects,[2] as well as kinetic and thermodynamic data,[3-6] have largely settled the question of whether the transfer of a hydride equivalent involves sequential one-electron transfers (e^-–H^+–e^-) or the transfer of a hydride ion in a single step.[7] In definitive cases where the e^-–H^+–e^- mechanism has been established, the electron acceptor has a one-electron reduction potential $E°$ > 0.4 V (NHE), much larger than that of most carbonyl compounds.[3,8-10] Nevertheless, the interaction of carbonyl compounds with Lewis acids may enhance their electron affinity[1,11] by stabilization of the developing substrate radical anion in a pathway that avoids the high-energy intermediates involved in either electron transfer to or Lewis acid complexation with the substrate.[15] Because such complexation is known to catalyze NADH-dependent reductions of the carbonyl group in enzyme[16] and non-enzyme[1,17,18] reactions, it is of interest to establish the

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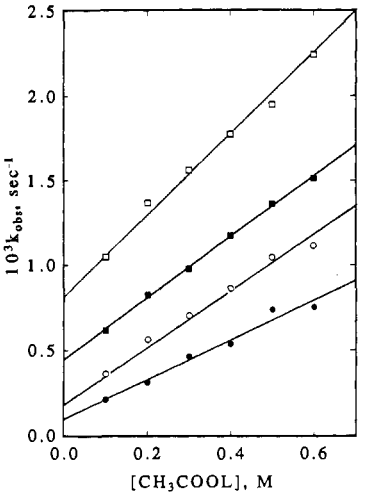

Figure 1. Dependence of the observed rate constants for reduction of 0.001 M *p*-benzoquinone by **1**-H (□, ■) and **1**-D (○, ●) on the concentration of acetic acid (fraction of acid = 0.75) in H_2O (open symbols) and D_2O (closed symbols).

conditions under which acid-catalyzed one-electron transfers can occur.

Figure 1 shows that the acetic acid catalyzed reduction of *p*-benzoquinone by **1**-L[19,20] shows small primary C–H isotope effects of $k_H/k_D = 1.48 \pm 0.11$ in H_2O and $k_H/k_D = 1.56 \pm 0.13$ in D_2O, as well as solvent isotope effects $k_{H_2O}/k_{D_2O} = 1.25 \pm 0.07$ for H transfer from **1**-H and $k_{H_2O}/k_{D_2O} = 1.32 \pm 0.13$ for D transfer from **1**-D.

The following evidence shows that the mechanism of eq 2 in which acid-catalyzed electron transfer, k_{cet}, and hydrogen atom transfer, $k_{L\bullet}$, are partially rate-limiting[1] cannot account for the experimental data. (1) General acid catalysis of electron transfer

$$\text{1-L} + \text{Q} \underset{k_{cb}[\text{A}^-]}{\overset{k_{ca}[\text{AH}]}{\rightleftharpoons}} (\text{1-L}^{\bullet+}\text{QH}^{\bullet}) \xrightarrow{k_{L\bullet}} \text{1}^+ + \text{QH}_2 \qquad (2)$$

is not expected because the hydron transfer from acetic acid to a transition state less basic than the semiquinone radical anion ($pK_a^{QH\bullet} = 4$)[14] is thermodynamically unfavorable.[15,22] (2) The C–H kinetic isotope effect (due to the second hydrogen transfer) is expected to *decrease* in D_2O, according to the multiple isotope effect criterion or concertedness developed by Hermes et al.[23] and Belasco et al.[24] This is because deuterium substitution of the acid catalyst selectively slows the initial hydron-transfer step thus partially "masking" the primary isotope effect for H atom transfer between **1**-L$^{\bullet+}$ and QH$^{\bullet}$. The C–H isotope effect that is independent of the isotopic solvent within experimental error is consistent with both hydrogen transfers occurring in a single transition state. (3) Deprotonation of **1**-L$^{\bullet+}$ by acetate ion with a second-order rate constant $\sim 10^7$ M^{-1} s^{-1} is expected to compete with the endothermic H atom transfer, in analogy to the e^-–H^+–e^- oxidation of **1**-H by $Fe(CN)_6^{3-}$, which shows a larger primary C–H isotope effect $k_H/k_D = 4.4$ for the kinetically unambiguous catalysis by acetate ion.[25]

The isotope effects indicate a small loss of both O–H and C–H zero-point energy in the transition state may reflect a reaction coordinate involving predominately heavy-atom motion[26] or hydrogen bonding to the catalyst,[27] or both. The Brønsted slope $\alpha = 0.85$ for catalysis by substituted acetic acids is consistent with a transition state resembling the protonated oxonium ion that is hydrogen bonded to the conjugate base of the catalyst.

These results show that even in cases where a Lewis acid complexed substrate has a favorable 1e$^-$ reduction potential,[11] direct hydride transfer will dominate if there is an unfavorable equilibrium for forming the Lewis acid complex.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We thank Professor M. M. Kreevoy for a gift of **1**-D.

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(20) The product 4-hydroxycyclohexa-2,5-dienone should enolize rapidly to the hydroquinone product. Similar cyclohexa-2,5-dienone intermediates have been observed spectroscopically on the millisecond time scale in the bromination of phenol.[21] A mechanism involving hydride transfer to the carbonyl oxygen with hydron transfer to the second oxygen to yield the hydroquinone product QH_2 directly cannot be excluded.[6]

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Direct Evidence for Intersystem Crossing Involving Higher Excited States of Acenaphthylene

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Received April 19, 1991
Revised Manuscript Received July 12, 1991

Despite the fact that higher excited states of aromatics in condensed media play a minor role in dictating the overall photophysics and photochemistry, studies in recent years show that photoprocesses involving higher excited states are not uncommon. Fluorescence from S_2 (abnormal fluorescence) has been found to be a general feature in systems with a large S_1–S_2 gap.[1-3] In systems with a very low S_1–S_2 gap, abnormal fluorescence is the result of thermal excitation of the S_1 state.[4] On the other hand, when T_2 is above S_1 by only a few kcals, a similar mechanism leads to emission from T_2 as well.[5] Under such a situation T_2 can participate in a variety of photophysical processes.[6] T_2 is shown

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