In summary, we have directly established the sequence represented by eq 1–3 for the photochemical formation of $M(CO)_4L$ from $M(CO)_6$ where L is a bidentate ligand. The use of rapid-scan FT IR allows molecular specific monitoring of a photochemically generated intermediate during its thermal reaction to form an isolable product. Importantly, the rate of the monodentate to bidentate conversion, eq 3, is an example of a low activation energy process that can be studied owing to the use of light to initially extrude CO from $M(CO)_6$. Dissociative loss of CO would be the rate-determining step in the thermal formation of $M(CO)_4L$ from $M(CO)_6$ precluding the study of reaction 3, a lower activation process. Future studies will be aimed at employing vibrational spectroscopic techniques described here to study reactions involving shorter lived intermediates.

Acknowledgment. We thank the National Science Foundation for support of this research and acknowledge support from the National Institutes of Health (Grant GM 27551) for the Nicolet 7199 FT IR used in these studies.

Registry No. $W(CO)_6$, 14040-11-0; $Mo(CO)_6$, 13939-06-5; $Cr(CO)_6$, 13007-92-6; 4,4′-Me_2-2,2′-bpy, 1134-35-6; 4,4′-(n-$C_{19}H_{39})_2$-2,2′-bpy, 70268-37-0; $W(CO)_5$(2-phenylpyridine), 83005-91-8; $W(CO)_5$(4,4′-(n-$C_{19}H_{39})_2$-2,2′-bpy, 83005-92-9; $W(CO)_4$(4,4′-(n-$C_{19}H_{39})_2$-2,2′-bpy, 83005-93-0; $W(CO)_5$(4,4′-$(CH_3)_2$-2,2′-bpy), 83005-94-1; $W(CO)_4$(4,4′-$(CH_3)_2$-2,2′-bpy), 26546-43-0; $W(CO)_4$(4,7-Ph_2-1,10-phen), 83005-95-2; $Mo(CO)_5$(2-phenylpyridine), 83005-96-3; $Mo(CO)_4$(4,4′-(n-$C_{19}H_{39}$)-2,2′-bpy), 83005-97-4; $Cr(CO)_5$(2-phenylpyridine), 83005-98-5; $Cr(CO)_5$(4,4′-(n-$C_{19}H_{39})_2$-2,2′-bpy), 83005-99-6; $Cr(CO)_4$(4,4′-(n-$C_{19}H_{39}$)-2,2′-bpy), 83006-00-7.

Electrochemical Behavior of a Surface-Confined Naphthoquinone Derivative. Electrochemical and Photoelectrochemical Reduction of Oxygen to Hydrogen Peroxide at Derivatized Electrodes

Gary S. Calabrese, Robert M. Buchanan, and
Mark S. Wrighton*

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

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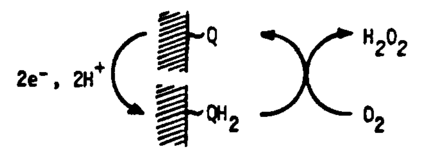
We describe the synthesis and application of a naphthoquinone reagent, I, that can be used to catalyze the reduction of O_2 to H_2O_2 at conventional electrodes or at illuminated p-type semiconducting photoelectrodes. Direct reduction of O_2 in aqueous solution to form H_2O_2, without H_2O formation and near the thermodynamic potential, does not occur readily at electrodes.[1] Much work has been directed to the catalysis of O_2 reduction at electrodes by using metal macrocycle complexes,[1a,2] but in all cases it would appear that H_2O_2, or radicals from the formation or the decomposition of H_2O_2, leads to degradation of the electrocatalyst. We were prompted to study the quinone systems, since eq 1 and 2 represent

$$Q \xrightarrow[\text{catalyst}]{H_2,\ \Delta} QH_2 \tag{1}$$

$$QH_2 + O_2 \xrightarrow{\Delta} Q + H_2O_2 \tag{2}$$

a viable pathway to the large-scale synthesis of H_2O_2,[3] where Q is a 9,10-anthraquinone derivative and QH_2 is the corresponding dihydroxy species. The electrochemical approach described here is represented by Scheme I[4,5] and the issues of concern are the (i) electrochemical potential, kinetics, and durability of the $[Q/QH_2]_{surf.}$ couple, (ii) rate of reaction of O_2 with $[QH_2]_{surf.}$, and (iii) behavior of the $[Q/QH_2]_{surf.}$ in the presence of H_2O_2. An advantage with the electrochemical synthesis of H_2O_2 is that H_2 need not be involved, and the potential necessary to reduce O_2 is 0.68 V less reducing than needed to produce H_2.

Scheme I



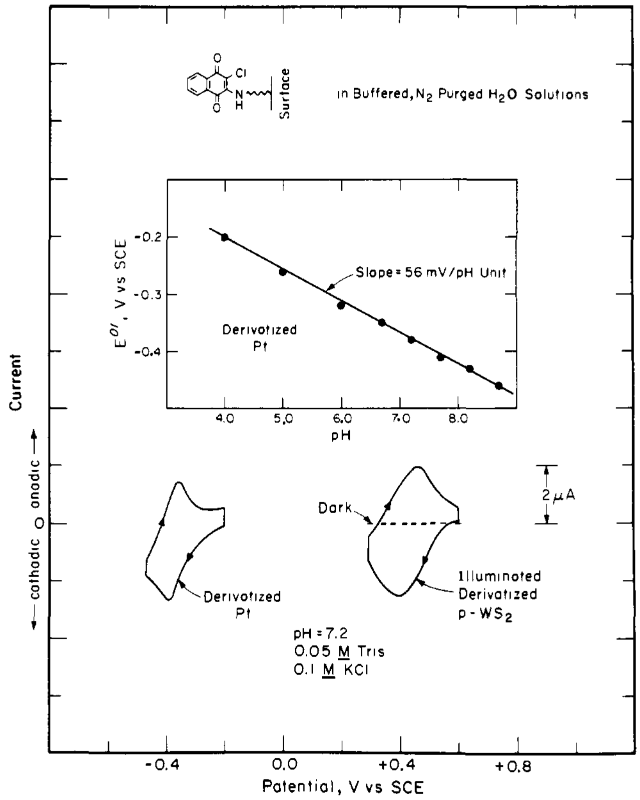


Figure 1. Cyclic voltammetry (100 mV/s) of Pt or illuminated p-WS_2 (632.8 nm, ~40 mW/cm^2) derivatized with Ib. Coverage (from integration of cyclic waves) in both cases is ~10^{-10} mol/cm^2 of the $[Q/QH_2]_{surf.}$ system. The inset shows $E°'[Q/QH_2]_{surf.}$ on Pt as a function of pH.

The synthesis of reagent I was achieved by the chemistry represented in eq 3 and 4,[6] beginning with a commercially available (Aldrich) quinone. Reagent Ib bears a $Si(OMe)_3$ group that is

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[1] (a) Yeager, E. *J. Electrochem. Soc.* **1981**, *128*, 160C. (b) Schumb, W. F.; Satterfield, C. N.; Wentworth, R. L. "Hydrogen Peroxide"; Reinhold: New York, 1955; p 90. (c) Ibl, N.; Vogt, H. In "Comprehensive Treatise of Electrochemistry"; Bockris, J. O. M., Conway, B. E., Yeager, E., White, R. E., Eds.; Plenum Press: New York, 1981; Vol. 2, 227–229.

[2] (a) Jahnke, H.; Schonborn, M.; Zimmermann, G. *Top. Curr. Chem.* **1976**, *61*, 133. (b) Collman, J. P.; Denisevich, P.; Konai, Y.; Marrocco, M.; Koval, C.; Anson, F. C. *J. Am. Chem. Soc.* **1980**, *102*, 6027. (c) Durand, R. R., Jr.; Anson, F. C. *J. Electroanal. Chem.* **1982**, *134*, 273. (d) Bettelheim, A.; Kuwana, T. *Anal. Chem.* **1979**, *51*, 2257.

[3] "Chemical and Process Technology Encyclopedia"; Considine, D. M., Ed.; McGraw-Hill: New York, 1974; p 600.

[4] A patent describes a similar objective using a "polyquinone" formed from benzoquinone, phenol, and formaldehyde adsorbed onto graphite electrodes: Grangaard, D. H., U.S. Patent 3 454 477, 1969.

[5] Murray, R. W. *Acc. Chem. Res.* **1980**, *13*, 135. See the following for use of electrodes bearing quinone functionality: (a) Degrand, C.; Miller, L. L. *J. Am. Chem. Soc.* **1980**, *102*, 5728; *J. Electroanal. Chem.* **1981**, *117*, 267. (b) Fukui, M.; Kitani, A.; Degrand, C.; Miller, L. L. *J. Am. Chem. Soc.* **1982**, *104*, 28. (c) Ueda, C.; Tse, D. C.-S.; Kuwana, T. *Anal. Chem.* **1982**, *54*, 850. (d) Tse, D. C.-S.; Kuwana, T. *Ibid.* **1978**, *50*, 1315.

[6] The HCl salt of 2-chloro-3-[[2-(dimethylamino)ethyl]amino]-1,4-naphthoquinone was prepared by the method of Cheng, C. C.; et al. *J. Med. Chem.* **1979**, *22*, 501. The free base was then prepared by treating the HCl salt with excess aqueous Na_2CO_3, followed by extraction into CH_2Cl. The solution was then dried over $MgSO_4$ and filtered and the CH_2Cl_2 was removed under vacuum. Ib was prepared by stirring 1 g of the free base in 5 mL of $BrCH_2CH_2CH_2Si(OCH_3)_3$ [prepared by reacting $HC(OCH_3)_3$ with 1-bromo-3-(trichlorosilyl)propane purchased from Petrarch Chemical Co.] at 90 °C for 12 h, after which time the product had precipitated from the solution. Filtration and repeated washings with hexane followed by drying under vacuum yileded 1.6 g (~90%) of Ib. Ia was prepared in an analogous manner by stirring the free base with n-PrBr.

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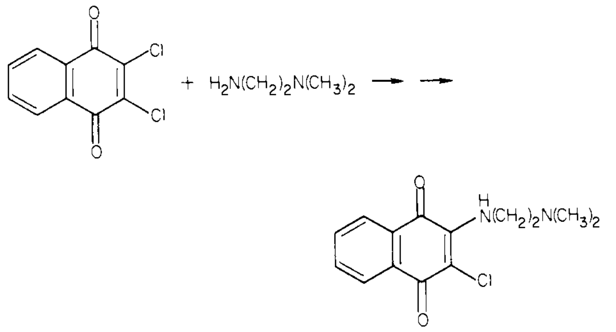
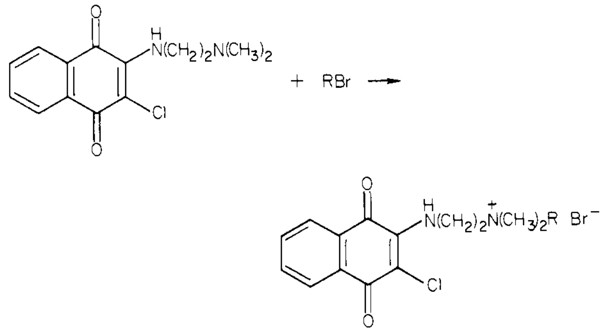


(3)



(4)

Ia, R = *n*-Pr
b, R = *n*-PrSi(OMe)$_3$

known to be useful in surface modification via reaction of the Si–O bonds with surface OH groups[7] to give $[Q/QH_2]_{surf.}$. Figure 1 shows the cyclic voltammetry[8] for a pretreated Pt electrode[9] and for a p-WS_2 photocathode[10] derivatized with Ib to yield $[Q/QH_2]_{surf.}$.[11] As expected, the $[Q/QH_2]_{surf.}$ system has an $E^{\circ\prime}$ within 50 mV of the $E^{\circ\prime}$ for Ia measured by cyclic voltammetry at Pt.[5]

The inset in Figure 1 shows the pH dependence of $E^{\circ\prime}[Q/QH_2]_{surf.}$ that parallels data for the solution species Ia. The shift in $E^{\circ\prime}$ with pH is ~56 mV/pH in the range investigated.[12] Thus, $E^{\circ\prime}[Q/QH_2]_{surf.}$ is ~400 mV more negative than $E^{\circ\prime}(O_2/H_2O_2)$ and ~300 mV more positive than $E^{\circ\prime}(H_2O/H_2)$. Electrodes bearing approximately monolayer amounts (~10^{-10} mol/cm^2) of $[Q/QH_2]_{surf.}$ show good cyclic voltammetry waves for scan rates up to 1 V/s or pHs between 4 and 8.7, but the peak current is not directly proportional to sweep rate above 50 mV/s. The $[Q/QH_2]_{surf.}$ system is durable for thousands of cycles between $[Q]_{surf.}$ and $[QH_2]_{surf.}$. Figure 1 includes the cyclic voltammetry for illuminated p-$WS_2/[Q/QH_2]_{surf.}$ showing that the $[Q]_{surf.} \rightarrow [QH_2]_{surf.}$ reduction can be effected at an electrode potential ~0.8 V more positive than on Pt, consistent with the behavior of p-WS_2 previously characterized.[10] Thus, the photoassisted reduction of O_2 to H_2O_2 should be possible with use of the derivatized p-WS_2.

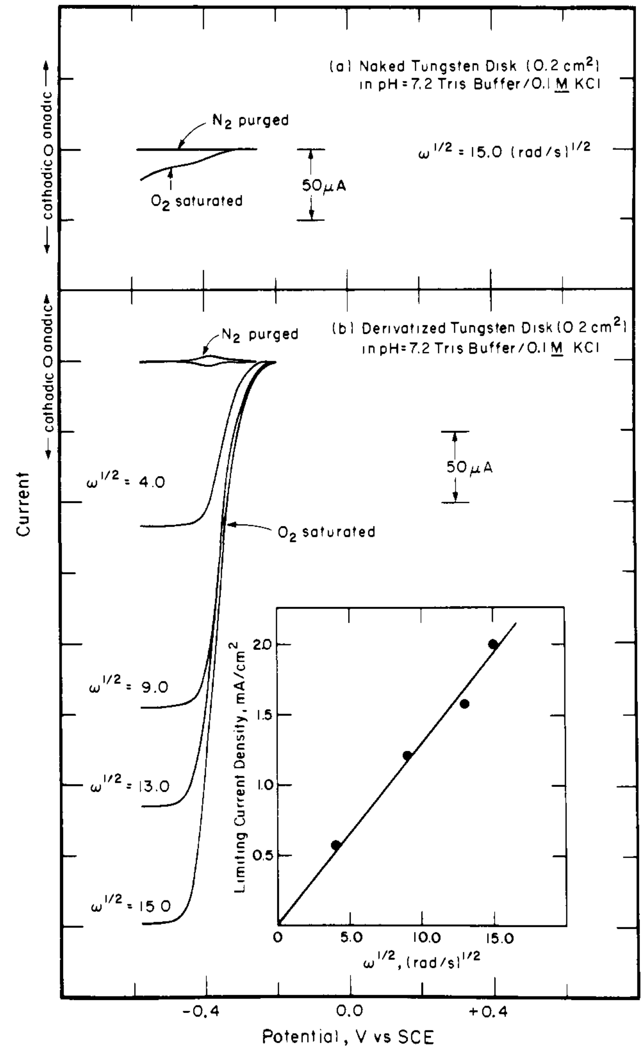


Figure 2. Electrochemical response of O_2 (saturated) (a) at a naked rotating W disk electrode and (b) at a derivatized disk with $[Q/QH_2]_{surf.}$ = ~10^{-10} mol/cm^2. The inset in b shows the limiting current density at −0.5 V vs. SCE vs. $\omega^{1/2}$. All scans are at 10 mV/s and begin at −0.2 V vs. SCE to avoid oxide growth on the W disk.

Experiments summarized by data in Figure 2 illustrate that the $[Q/QH_2]_{surf.}$ system is capable of catalyzing the reduction of O_2. A W disk electrode was chosen as a conveniently available electrode material found to have poor kinetics for both O_2 reduction, Figure 2a, and H_2O_2 reduction (not shown). As illustrated in Figure 2b, a W disk electrode bearing ~10^{-10} mol/cm^2 of $[Q/QH_2]_{surf.}$ efficiently reduces O_2 in pH 7.2 solution. The reduction current onsets just positive of the reduction current for the $[Q]_{surf.} \rightarrow [QH_2]_{surf.}$ process and the limiting current (more negative than −0.5 V vs. SCE) is mass transport limited up to the highest rotation velocity available. The slope of the plot of limiting current vs. $\omega^{1/2}$ is consistent with a two-electron, mass transport limited reduction of O_2. Controlled potential reduction of O_2 in a two-compartment cell at a W/$[Q/QH_2]_{surf.}$ rotating disk yields H_2O_2 with >90% Coulombic efficiency.[13] The data in Figure 2 allow the conclusion that the heterogeneous rate constant for the reduction of O_2 at pH 7.2 to H_2O_2 is >0.013 cm/s for a W/$[Q/QH_2]_{surf.}$ electrode held at a potential where only $[QH_2]_{surf.}$ is present.[14] In several cases controlled potential reductions of

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(7) Arkles, B. *CHEMTECH* **1977**, *7*, 766.

(8) Bard, A. J.; Faulkner, L. R. "Electrochemical Methods", Wiley: New York, 1980; p 229.

(9) Lenhard, J. R.; Murray, R. W. *J. Electroanal. Chem.* **1977**, *78*, 195.

(10) Baglio, J. A.; Calabrese, G. S.; Harrison, D. J.; Kamieniecki, E.; Ricco, A. J.; Wrighton, M. S.; Zoski, G. D., submitted for publication.

(11) Derivatization of Pt, W, and p-WS_2 was accomplished by soaking the electrodes in ~1 mM Ib for 6–24 h at 25 °C followed by washing with CH_3CN. Similar treatment with Ia yields no electrochemically detectable surface-confined material, even though quinones are known to interact strongly with electrodes: Chambers, J. Q. In "The Chemistry of the Quininoid Compounds"; Patai, S., Ed.; Wiley: New York, 1974; pp 756–759. The mode of attachment of Ib to p-WS_2 is unclear inasmuch as it is relatively free of oxide,[10] unlike W or pretreated[9] Pt surfaces.

(12) Below pH 4 there is significant broadening of the cyclic voltammetry waves of $[Q/QH_2]_{surf.}$. High pHs are avoided to minimize hydrolysis of the Si–O links to the surface. The behavior of surface-confined quinones can be very complex, as noted in ref 5a. For clarity we represent the surface couple by $[Q/QH_2]_{surf.}$ although the actual state of protonation is not known and the mechanism for reaction with O_2 requires further study.

(13) The H_2O_2 was determined spectrophotometrically by using the procedure described in ref 1b, p 561. The current efficiency is a lower limit; losses in current efficiency could be due to a combination of direct reduction of H_2O to H_2, H_2O_2 to H_2O, O_2 to H_2O, or to thermal decomposition of H_2O_2; cf ref 1c. The error in our measurement is ±10%.

(14) This minimum value of the heterogeneous electron-transfer rate constant follows the development given in Galus and Adams (Galus, Z.; Adams, R. N. *J. Phys. Chem.* **1963**, *67*, 866) by assuming the diffusion constant for O_2 to be 1.7×10^{-5} cm^2/s from ref 2c and using our highest rotation velocity, $\omega^{1/2}$ = 15 at an electrode potential negative of $E^{\circ\prime}[Q/QH_2]_{surf.}$. Note that this heterogeneous rate constant is attributed to reaction of $[QH_2]_{surf.}$ with O_2 and is therefore not electrode potential dependent in the usual sense.[8]

O_2 were carried out for prolonged periods, ~5 h, with less than 50% loss of $[Q/QH_2]_{surf}$. Since the reduction of O_2 is mass transport limited, fractional loss of $[Q/QH_2]_{surf}$ need not lead to an equal fractional decline in observed current density. In such experiments we have determined $>10^6$ turnovers at >100 turnovers/s for the $[Q/QH_2]_{surf}$ reagent without decline in current density. Concentrations of several millimolar H_2O_2 in pH 7.2 H_2O/electrolyte have been generated with >90% Coulombic efficiency. The $W/[Q/QH_2]_{surf}$ electrodes are durable in deliberately prepared 0.1 M H_2O_2 pH 7.2 solutions and still efficiently reduce O_2 to H_2O_2 under these conditions for at least 30 min with <10% decline in current density.

The behavior of p-$WS_2/[Q/QH_2]_{surf}$ photoelectrodes is consistent with the conclusion that H_2O_2 can be prepared by the visible light-driven reduction of O_2. Preliminary experiments show that the derivatized, but not naked, p-WS_2 can be used to reduce O_2 to H_2O_2 at an electrode potential of ~+0.2 V vs. SCE at pH 7.2 with a power conversion efficiency of ~2% for 632.8-nm, ~10 mW/cm^2 input energy. This represents significant improvement compared to an earlier study of a p-type Si-based[15] system for photoreduction of O_2 that required electrode potentials *negative*, not positive, of $E^{\circ\prime}(O_2/H_2O_2)$.

Acknowledgment. We thank Dow Chemical U.S. for support of this research.

Registry No. 1a, 83027-25-2; **1b**, 83027-26-3; **1b** hydroquinone derivative, 83027-28-5; WS_2, 12138-09-9; O_2, 7782-44-7; H_2O_2, 7722-84-1; Pt, 7440-06-4; W, 7440-33-7; BrPr, 106-94-5; $Br(CH_2)_3Si(OMe)_3$, 51826-90-5; 2-chloro-3-[[2-(dimethylamino)ethyl]amino]-1,4-naphthoquinone, 83027-27-4.

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(15) Calabrese, G. S.; Wrighton, M. S. *J. Electrochem. Soc.* **1981**, *128*, 1014.

Diastereoselection in Intermolecular Nitrile Oxide Cycloaddition (NOC) Reactions: Confirmation of the "Anti-Periplanar Effect" through a Simple Synthesis of 2-Deoxy-D-ribose[†]

Alan P. Kozikowski* and Arun K. Ghosh

Department of Chemistry, University of Pittsburgh
Pittsburgh, Pennsylvania 15260

Received June 7, 1982

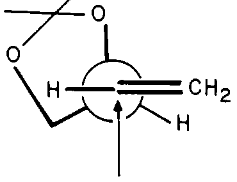
We have initiated recently a program to examine the extent to which an allylic asymmetric center can control diastereoface selection in both inter- and intramolecular additions of nitrile oxides to olefins.[1] While the extent of such diastereoselection appears to be relatively small when there is little to distinguish the allylic groups on a steric or electronic basis (except in intramolecular cyclizations where the allylic center is within the nonisoxazoline ring being formed),[2] we now report that an allylic oxygen substituent can, on the other hand, serve as a useful control element for achieving diastereoface selectivity in [3 + 2] cycloaddition reactions. We illustrate this new concept in stereocontrol through a simple synthesis of 2-deoxy-D-ribose.

Optically active (+)-(*S*)-isopropylidene-3-butene-1,2-diol, prepared from isopropylidene D-glyceraldehyde by reaction with methylenetriphenylphosphorane,[3] was reacted with (carboethoxy)formonitrile oxide[4] to afford an 80:20 mixture of diastereomeric cycloadducts. These products were separated by gravity chromatography, and the major isomer **3** (Scheme I) was heated with sodium hydroxide to effect the following transformations: (a) ester hydrolysis; (b) decarboxylative ring opening of the isoxazoline to a β-hydroxy nitrile; (c) hydrolysis of nitrile to carboxylate. Acidification and diazomethane treatment then yielded **4** (74% overall yield from **3**).[5] On converting this compound to its acetate and stirring with trifluoroacetic acid, the acetate of 2-deoxy-D-ribono-1,4-lactone (**5**) was formed (71%). The NMR of this compound was identical with that reported previously by Mukaiyama;[6] $[\alpha]^{24}{}_D = -12°$ (c 0.75, CH_2Cl_2); IR (thin film) 3450, 1785, 1740, 1240 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.07 (s, 3 H), 2.55 (dd, 1 H, J = 2.5, 18 Hz), 2.95 (dd, 1 H, J = 7, 18 Hz), 3.40–3.60 (m, 1 H), 3.85 (d, 2 H, J = 2.5 Hz), 4.40–4.60 (m, 1 H), 5.20–5.50 (m, 1 H); mass spectrum (15 eV), m/e 143, 84, 83, 53.

Trifluoroacetic acid treatment of **4** followed by bis(3-methyl-2-butyl)borane reduction of the intermediate lactone gave 2-deoxy-D-ribose (**7**).[6,7] The synthetic material was identical with authentic 2-deoxy-D-ribose by the standard criteria of comparison. Alternatively, the lactone **6** was silylated to give the crystalline bis(*tert*-butyldimethylsilyl) derivative **8** (mp 76 °C). Reduction of this product with Dibal gave the disilyl derivative **9** in 92% yield [$[\alpha]^{24}{}_D = +23.6°$ (after 8 h, c 0.096, MeOH)]. The 300-MHz ^1H NMR of **9** was identical with that obtained for the product generated by silylating authentic 2-deoxy-D-ribose and chromatographically separating out the disilyl derivative.

Additionally, it was observed that acetonitrile oxide reacted with **2** to deliver after N–O bond hydrogenolysis the erythro β-hydroxy ketone as the major product (^1H NMR ratio 88:12).[8] By reacting **2** with the nitrile oxide drived from the tetrahydropyranyl derivative of 2-nitroethanol[4] and then effecting both cleavage of the THP group and hydrogenolysis of the isoxazoline by Raney nickel/$AlCl_3$/MeOH/H_2O treatment, we generated nearly a single dihydroxy ketone (>94% by HPLC analysis).[9] Sodium periodate cleavage of this α-hydroxy ketone followed by diazomethane treatment yielded **4** as the major isomer. These studies thus reveal that the sense of the addition of a nitrile oxide to **2** is independent of the nature of the nitrile oxide employed.

One can rationalize the production of 2-deoxy-D-ribose as the major product of the above scheme through the following two factors: (a) cycloaddition occurs preferentially through a transition state resembling conformer A;[10] (b) addition of the nitrile oxide occurs anti to the C–O bond (the anti-periplanar effect).[11] This latter factor is due presumably to the minimization of secondary antibonding orbital interactions as predicted on a theoretical basis by the work of Houk et al. The explanation for such stereose-



A

[†] Dedicated to the memory of Dr. Anthony Ames.

(1) Kozikowski, A. P.; Chen, Y. Y. *J. Org. Chem.* **1981**, *46*, 5248. Kozikowski, A. P.; Stein, P. D. *J. Am. Chem. Soc.* **1982**, *104*, 4023.

(2) Kozikowski, A. P.; Chen, Y. Y. *Tetrahedron Lett.* **1982**, *23*, 2081.

(3) Crawford, R. J.; Lutener, S. B.; Cockcroft, R. D. *Can. J. Chem.* **1976**, *54*, 3364.

(4) Kozikowski, A. P.; Adamczyk, M. *J. Org. Chem.*, in press.

(5) The ^1H NMR of **4** has also been compared with the ^1H NMR of the product formed from the reaction of the anion of ethyl acetate with **1**, which is known to be an 85:15 mixture of diastereomers with **4** (ethyl ester) predominating. The ABX patterns of the α-methylene protons were identical.

(6) Murakami, M.; Mukaiyama, T. *Chem. Lett.* **1982**, 241.

(7) Nakaminami, G.; Shioi, S.; Sugiyama, Y.; Isemura, S.; Shibuya, M.; Nakagawa, M. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 2624.

(8) The structure of the major isomer was verified by hydrolyzing **4** to the corresponding β-hydroxy acid and reacting this compound with excess methyllithium. The ^1H NMR of the resulting β-hydroxy ketone matched that displayed by the major isomer present in the hydrogenolysis mixture of the isoxazolines prepared from **2** and acetonitrile oxide.

(9) Kozikowski, A. P.; Adamczyk, M. *Tetrahedron Lett.* **1982**, *23*, 3123.

(10) Karabatsos, G. J.; Fenoglio, D. J. *Top. Stereochem.* **1970**, *5*, 167.

(11) Caramella, P.; Rondan, N. G.; Paddon-Row, M. N.; Houk, K. N. *J. Am. Chem. Soc.* **1981**, *103*, 2438. For a related observation in a Diels–Alder reaction, see: Franck, R. W.; John, T. V.; Olejniczak, K.; Blount, J. F. *Ibid.* **1982**, *104*, 1106. The dominance of the anti-bonding effect of an allylic oxygen substituent was first suggested by Franck in this communication.