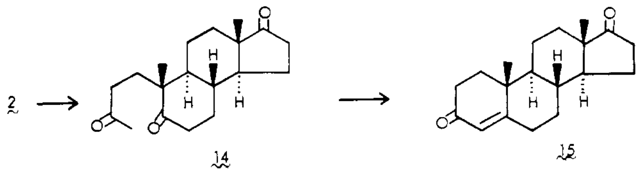
to minimize the formation of impurities showing short retention time peaks in the GC analysis, probably resulting from desilylation. The yield of **13** is probably subject to considerable improvement. Finally, treatment of the enone **13** with methyllithium yielded the substrate **1** which, because of its sensitivity, was used without purification for the cyclization studies.

Addition of the substrate **1** to a 0.5% solution of trifluoroacetic acid in dichloromethane maintained at −35 °C for 1 h produced a crystalline hydrocarbon fraction, isolated[9a] in 58% yield, containing two components in a ratio of 88:12 as shown by GC analysis. Pure crystalline specimens of these two hydrocarbons were obtained by preparative GC. The major component was assigned the structure **2** on the basis of chemical conversions (see below) and its spectral properties: mass spectra 282 (M^+, 25%), 91 (100%); IR 1965 cm^{-1}; NMR 4.68 (m, 2 H at C-21), 1.57 (s, vinylic CH_3), 0.91 and 0.88 ppm (2 s, angular CH_3). The minor component showed very similar spectral properties and was clearly an isomeric allenic compound which is presumed, by analogy to previous work,[13] to be the 13α epimer of **2** with a C/D cis ring fusion.

Unequivocal proof for structure **2** was afforded by ozonolysis [in CH_2Cl_2, pyridine, −70 °C, with reductive (Zn + HOAc) processing] of the mixture of tetracyclic hydrocarbons which gave the triketone **14** contaminated with some of the presumed 13α epimer. This product on cyclodehydration (2% NaOH/ethanol/THF 4:2:5, 25 °C, 4 h) afforded in 55% overall yield the enedione **15** contaminated with 12% (by GC) of the presumed 13α epimer. Purification[9b] readily afforded a 46% yield of *dl*-**15**, mp 127–130 °C (reported[6] 128–130 °C), which had NMR, solution IR, GC, and TLC properties that were identical with those of authentic (naturally derived) 4-androstene-3,17-dione.



Thus, the cyclization **1** → **2** has been realized in a yield that is most promising, considering that it has not been optimized; indeed, only one set of reaction conditions have been examined as yet. The removal of the presumed 13α epimeric contaminent promises to be easily accomplished by chromatography, particularly after oxygen atoms have been introduced into the molecule as shown above as well as in other examples.[13] We now look forward to examining the asymmetric cyclization of a modified form of the substrate **1** having an OH at pro-C-11[14] as well as to utilizing the allenic function for developing the cortical side chain.[5]

Acknowledgment. We thank the National Institutes of Health and the National Science Foundation for support of this research. We also thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support. R.S. is indebted to the "Stiftung für Stipendien auf dem Gebiete der Chemie", Basel for financial aid. P.L.H. was supported also by an NIH Postdoctoral Fellowship sponsored by the National Institutes of General Medical Sciences. We want to express our appreciation also to Professor P. E. Peterson for sending us a copy of his manuscript[4a] prior to publication.

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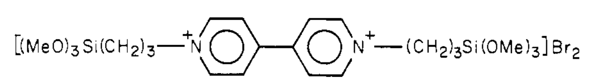
Thermodynamically Uphill Reduction of a Surface-Confined *N,N'*-Dialkyl-4,4'-bipyridinium Derivative on Illuminated p-Type Silicon Surfaces

Sir:

We wish to report the first results pertaining to a chemically derivatized p-type semiconductor photocathode surface. While p-type semiconductor electrodes do not suffer the gross decomposition typically found for their n-type counterparts,[1-3] kinetics for photocathodic H_2 evolution and surface instability are important problems that may be solved by surface modification.[4,5] Promising results for stabilizing n-type semiconductors with respect to photoanodic corrosion have previously been reported with ferrocene-centered surface modifiers.[6] Our new efforts concern the study of a p-type surface-confined *N,N'*-dialkyl-4,4'-bipyridinium derivative, since we previously showed that solution-dissolved *N,N'*-dimethyl-4,4'-bipyridinium could be photoreduced in an uphill sense at illuminated p-type Si.[4] Further, the reduced form of *N,N'*-dimethyl-4,4'-bipyridinium comes into rapid redox equilibrium with aqueous (pH <6) solutions containing suspensions of Pt to evolve H_2;[7] the H_2 evolution can also be catalyzed by hydrogenase.[8] We include results for derivatized Pt to establish the thermodynamics for the surface-confined reagent. We note possible applications in bioelectrochemistry and in electrochromic displays with reversible electrodes functionalized with the bipyridinium reagent.[9]

The surface-derivatizing agent, I, was prepared by refluxing dry 4,4'-bipyridine (Aldrich Chemical Co.) with 1-bromo-3-trimethoxysilylpropane [prepared by reacting $HC(OMe)_3$ with 1-bromo-3-trichlorosilylpropane purchased from Petrarch Chemical Co.] in rigorously dry CH_3CN solution. Reagent I was isolated as a pale yellow solid bromide salt by crystallization from CH_3CN solution by adding Et_2O.[10] UV–vis and ^1H NMR spectroscopy accords well with the structure shown, and redox behavior is consistent with isolation of a derivative of *N,N'*-dialkyl-4,4'-bipyridinium with $E°$ values of ~−0.5 and −0.9 V vs. SCE for the first and second reversible, one-electron reductions in CH_3CN, respectively.[11]



I

The hydrolytically unstable $Si(OMe)_3$ groups provide a site for attachment to surfaces bearing OH groups, and in the presence of H_2O polymerization of I is possible.[12] Figure 1 shows a

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(10) The elemental analysis for I is satisfactory. Anal. (Schwartzkopf) Calcd (found): C, 41.13 (40.63); H, 5.96 (5.81); N, 4.36 (4.23); Si, 8.74 (8.76); Br, 24.87 (24.68).

(11) Hunig, S.; Gross, J.; Schenk, W. *Justus Liebigs Ann. Chem.* **1973**, 324.

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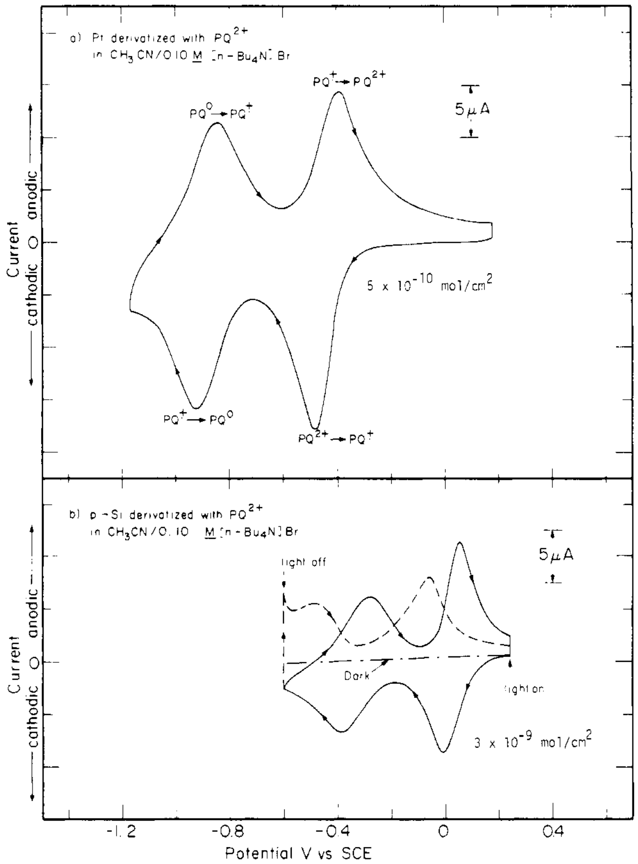

Figure 1. Cyclic voltammetry at 100 mV/s for Pt and p-Si derivatized with I under the conditions shown. Illumination of p-Si was at 632.8 nm, 5 mW/cm^2. The initial potential was the positive limit in both cases. Coverage of electroactive PQ^{2+} is given in mol/cm^2 for each electrode.

comparison of the electrochemical characterization of a pretreated Pt and a p-type Si electrode derivatized with I. Derivatization was accomplished by reaction of the pretreated surfaces[13] with a CH$_3$CN solution of ~1 mM I at 25 °C for 3-8 h. The data in Figure 1a are representative for Pt: clean, persistent, and reversible cyclic voltammetric waves are observed in CH$_3$CN/0.1 M [*n*-Bu$_4$N]Br. The two waves observed presumably correspond to the two one-electron reductions of the 4,4′-bipyridinium system that are confined to the surface of the electrode. The waves are very close to the position found for solution cyclic voltammetry of I in the same electrolyte solution, as expected.[14] While both reductions are reversible in CH$_3$CN, only the first reduction is reversible in aqueous electrolytes. In aqueous solutions, potentials negative enough to give the second reduction sometimes yield reversible reduction, but often the reduction leads to loss of electroactivity.[15] Integration of the cyclic voltammetric waves reveals that polymeric quantities of the reagent can be confined to the surfaces; we have observed coverages up to ~10^{-8} mol/cm^2, and this may possibly be increased by longer derivatization time. Note in Figure 1 that the two waves in CH$_3$CN have a different shape but equal area. These wave-shape differences are to be investigated further. Electrode surfaces derivatized with I are very rugged; the surface-confined reagent has been cycled between oxidized and reduced forms thousands of times without deterioration in properties.

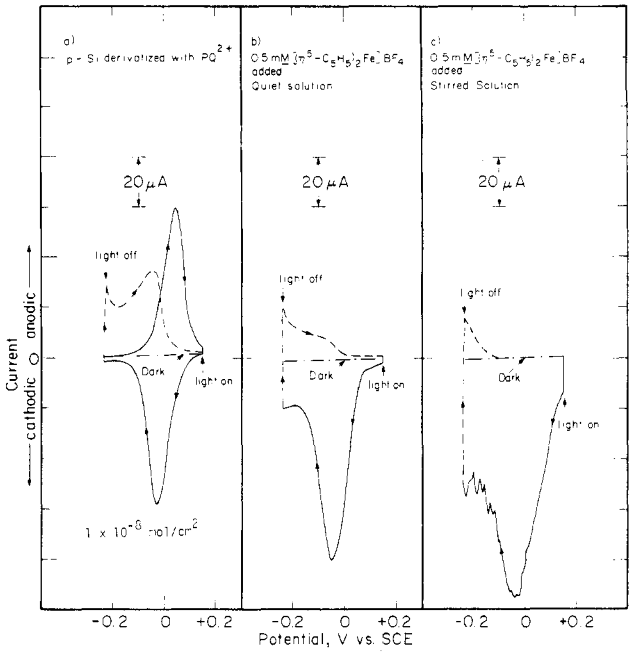

Figure 2. Cyclic voltammetry (100 mV/s) for p-type Si derivatized with I. Initial potential is +0.15 V vs. SCE in all cases, and the electrolyte solution is CH$_3$CN/0.1 M [*n*-Bu$_4$N]Br. There is no cathodic or anodic current observed in the dark. Illumination (632.8 nm, 5 mW/cm^2) during the negative scan portion gives a cathodic current. Turning off the light at the negative limit (−0.2 V vs. SCE) allows observation of anodic current peak corresponding to PQ$^{+\cdot}$ → PQ^{2+}. In quiet (b) or stirred (c) solutions of [Fe(η^5-C$_5$H$_5$)$_2$]$^+$, the wave for PQ$^{+\cdot}$ → PQ^{2+} is attenuated due to the competitive oxidation of PQ$^{+\cdot}$ by the [Fe(η^5-C$_5$H$_5$)$_2$]$^+$. The scan in (a) is for a solution containing no [Fe(η^5-C$_5$H$_5$)$_2$]$^+$ and is the same before and after the experiments in (b) and (c).

Data in Figure 1b are typical for p-type Si: a cathodic scan from +0.1 to −1.0 V vs. SCE yields no current in the dark, but irradiation with 632.8-nm light yields two cathodic waves that are more positive than on Pt by ~500 mV. The 500-mV shift of the waves compared to Pt represents the extent to which the 4,4′-bipyridinium can be photoreduced in an uphill sense by illumination of the p-Si that has a band gap of 1.1 eV.[16] The 500-mV uphill photoreduction is consistent with the output photovoltage recently reported for a p-Si-based cell where the redox active system was the *N*,*N*′-dimethyl-4,4′-bipyridinium.[4]

As shown in Figure 1, the reduction of the surface reagent is blocked in the dark on the p-type electrode, as would be expected, since the electrons are minority carriers and their availability requires band-gap (E_g) excitation. However, if the light is switched off at the negative limit of the scan, the oxidation of the reduced surface material is observable in the dark, since oxidizing equivalents (holes) are the majority charge carriers. Thus, reduction requires $\geq E_g$ illumination while oxidation processes can occur in the dark. The two-stimuli response of the p-type semiconductor can be exploited to show directly that "mediated" reduction using the surface-confined redox reagent is possible. By mediated reduction, we mean that the reduction of a solution species, A$^+$, would occur via chemistry represented by eq 1 and 2; that is, the sequence of events is electron-hole-pair generation

$$\text{p-Si-surface-PQ}^{2+} \xrightarrow[\text{potential (more negative than 0.0 V vs. SCE)}]{\text{light } (\geq E_g)} \text{p-Si-surface-PQ}^{+\cdot} \quad (1)$$

$$\text{p-Si-surface-PQ}^{+\cdot} + \text{A}^+ \xrightarrow{k_a} \text{p-Si-surface-PQ}^{2+} + \text{A} \quad (2)$$

---

[12] Pt electrodes have been previously derivatized with polymeric quantities of a redox reagent via Si(OR)$_3$ hydrolysis reactions: Wrighton, M. S.; Palazzotto, M. C.; Bocarsly, A. B.; Bolts, J. M.; Fischer, A. B.; Nadjo, L. *J. Am. Chem. Soc.* **1978**, *100*, 7264.

[13] Smooth Pt was pretreated according to: Lenhard, J. R.; Murray, R. W. *J. Electroanal. Chem.* **1977**, *78* 195; p-Si was pretreated according to ref 6a.

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[15] Solutions of *N*,*N*′-dimethyl-4,4′-bipyridinium chloride yield polymers when reduced at Au electrodes in aqueous solutions. Such material could be related to that formed upon complete reduction of surfaces derivatized with I in aqueous media: Landrum, H.; Salmon, R. T.; Hawkridge, F. M. *J. Am. Chem. Soc.* **1977**, *99*, 3154; see also ref 9e.

[16] Wolf, H. F. "Silicon Semiconductor Data", Pergamon Press: Oxford, 1969, p 111.

by $\geq E_g$ light followed by reduction of the surface-confined reagent, PQ^{2+} to $PQ^{+\cdot}$, that then in turn reduces A^+, regenerating surface-confined PQ^{2+}. Kinetics and energetics for A^+ reduction therefore depend on the reducing power and reducing rate of $PQ^{+\cdot}$. Proof for the mediated reduction of solution species comes from cyclic voltammetry experiments in the presence of A^+. Representative data are given in Figure 2 for $A^+ = [Fe(\eta^5\text{-}C_5H_5)_2]^+$. The key is that the positive sweep reveals the amount of surface $PQ^{+\cdot}$; in the absence of A^+, the anodic wave corresponding to $PQ^{+\cdot} \rightarrow PQ^{2+}$ is equal in area to the photocathodic wave corresponding to $PQ^{2+} \rightarrow PQ^{+\cdot}$. But when solutions of A^+ are used, the photocathodic current increases, since it is no longer only limited by the surface concentration of the PQ^{2+}. Upon turning off the light at the negative limit and scanning in the positive direction at 100 mV/s, we find only a small $PQ^{+\cdot} \rightarrow PQ^{2+}$ oxidation wave. An even smaller wave is observed upon stirring the solution to bring more A^+ to the surface. Apparently, chemistry according to eq 2 is sufficiently fast that A^+ regenerates PQ^{2+}. Fast $[Fe(\eta^5\text{-}C_5H_5)_2]^+$ reduction by $PQ^{+\cdot}$ is expected, since $E°[PQ^{2+}/PQ^{+\cdot}] = -0.45$[10] and $E°([Fe(\eta^5\text{-}C_5H_5)_2]^{+/0}) = +0.45$ V vs. SCE.[17] Additional data suggest that this mediated photoreduction of the $[Fe(\eta^5\text{-}C_5H_5)_2]^+$ is the only mechanism for its reduction, i.e., there are no pinholes in the coverage precluding direct reduction of the $[Fe(\eta^5\text{-}C_5H_5)_2]^+$ as at the naked surface.[4b]

Functionalized p-type Si is also durable in $H_2O/NaClO_4$ electrolyte solution for the first one-electron reduction. Potentials sufficiently negative to yield the second reduction generally result in irreversible chemical change to yield a new surface species that has not yet been identified. Mediated reduction of $Ru(NH_3)_6^{3+}$ in aqueous solution has been demonstrated with p-type Si derivatized with I. Again, $Ru(NH_3)_6^{3+}$ should be rapidly reducible with $PQ^{+\cdot}$, since the formal potentials indicate an ~0.5-V driving force for reaction.[11,18] Experiments directed toward mediating H_2O reduction are in progress.

Acknowledgments. We thank the Department of Energy, Office of Basic Energy Sciences, and the M.I.T. Laboratory for Computer Science I.B.M. Fund for support of this research. M.S.W. acknowledges support as a Dreyfus Teacher-Scholar Grant recipient, 1975-1980.

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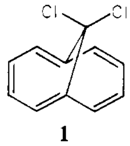
Received March 12, 1980

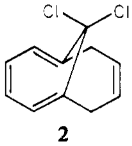
Dimerization of Bridgehead Olefins Formed from Tricyclic Cyclopropylidenes[1]

Sir:

In two recent papers, Levin[2,3] has reported the formation of dimer(s) from the treatment of 1 and 2 with MeLi. We have reported[4] that 3 affords only one dimer, which evidently is of the [2 + 2] type (presence of four olefinic carbons in the ^{13}C NMR). However, no detailed structural information regarding any of these dimers has been published. We now wish to report on some of the dimers formed from the related system, 4.[5]



1



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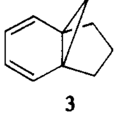

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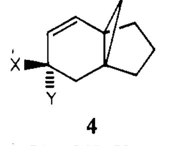
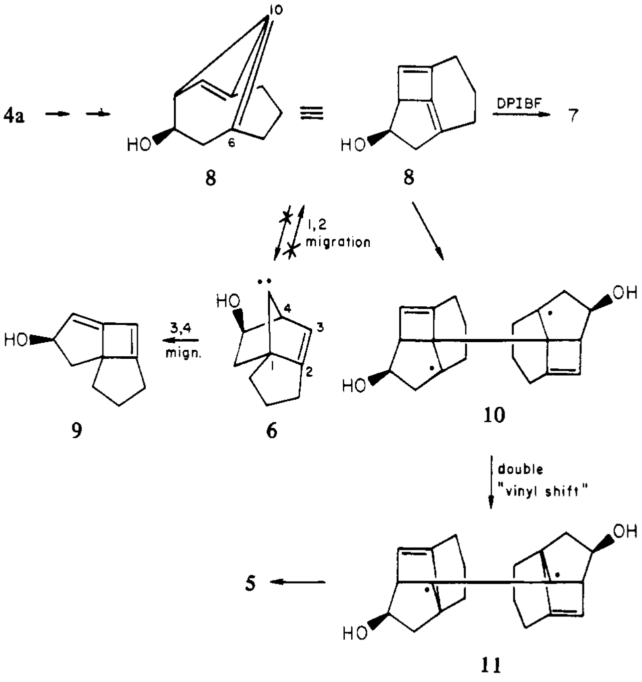
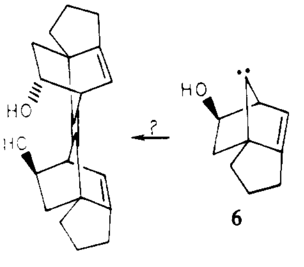


4
a, X = OH; Y = H
b, X = OMe; Y = H
c, X = H; Y = OH
d, X = H; Y = OMe

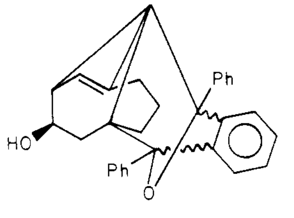
Scheme I



Treatment of **4a**[6] with MeLi at either -78 °C or room temperature affords, in addition to rearranged product,[5] only one dimer (^1H NMR, GLC analysis, 19% isolated). While the ^1H NMR spectrum is unexceptional, the ^{13}C NMR spectrum shows three *olefinic carbons*, rather than the expected two. Single-crystal X-ray analysis (see Table I) of the derived bis(*p*-bromobenzoate) (Figure 1) revealed the structure of the dimer as **5**. Stereochemically, **5** is a chiral dimer resulting from the dimerization of two *R* (or *S*) monomers to give an *E* olefin.[7] At first glance, it might appear that **5** comes from the dimerization of **6**. If this is true, the chemistry of **4a** would be quite different than previously supposed.[4,5] It thus became critical to be sure of the structures of the trapping products formed from **4a** in the presence of diphenylisobenzofuran (DPIBF). In fact, the only previous really solid structural work in this whole area is the X-ray structural analysis of but one of the two DPIBF adducts obtained from **1**.[2] As occurred previously,[4,5] reaction of **4a** with MeLi in the presence of DPIBF led to two adducts (24 and 21%). The single-crystal X-ray analysis of the derived *p*-bromobenzoate (Figures 2 and



5 **6**



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(1) We gratefully acknowledge partial support of this work by National Science Foundation Grant CHE-7618701.

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(7) The tetrasubstituted double bond of **5** is actually twisted some 8.3 ± 2.4° out of planarity.