corresponds to −1.05 V vs. SCE) with the full visible output of a 200-W Hg lamp yielded a stable ~2.4 mA/cm^2 photocurrent. During an irradiation period where enough electrons were passed to consume >150% of the electroactive $S_n{}^{2-}$ we found that the Ag_2S vs. Pt potential changed only slightly from −0.126 to −0.132 V. Moreover, optical density of the $S_n{}^{2-}$ electrolyte changed from only 0.455 to 0.480 at 501.7 nm and 0.579 to 0.591 at 496.5 nm. Significantly, no H_2 evolution was observed. The small changes that are observed are likely due to a redistribution of the $S_n{}^{2-}$ species, an effect previously observed.[3]

Photoelectrode stability is evidenced by (1) constant photocurrents, (2) no obvious change in the electrode surface, and (3) constant weight of the CdTe before and after significant photoelectrochemical action, Table I. Thus, the electrode and electrolyte are stable for the p-type CdTe-based photoelectrochemical cell employing the $S_n{}^{2-}$ electrolyte. The p-type CdTe-based cell, however, inefficiently converts light to electricity, since the open-circuit photopotential has been found to be only ~150 mV and short-circuit quantum yields for electron flow are of the order of only 0.002. These low values may be due, in part, to the low carrier concentration (~10^{14} cm^{-3}) in the p-type CdTe.

The results above afforded us the opportunity of demonstrating the first double photoelectrode-based cell for the conversion of light to electricity, since it had been previously demonstrated that CdSe (E_{BG} = 1.7 eV) is a stable photoanode in the $S_n{}^{2-}$ electrolyte.[1,3] For the conversion of light to electricity, a key advantage in a double photoelectrode cell is that the maximum output voltage, V, can be higher. The ideal energetic situation is as sketched in Scheme I where the valence band position, E_{VB}, for the n-type material is just below the electrolyte redox level, E_{redox}, and the conduction band position, E_{CB}, for the p-type material is just above E_{redox}.[12] For fairly high carrier concentration the Fermi level in the n-type material, E_f, is close to E_{CB}, and in the p-type material the Fermi level, E_f', is close to E_{VB}. Consequently, the value of V upon illumination, $E_f - E_f'$, can approach the sum of the band gaps of the two materials $E_{BG} + E_{BG}'$.

The n-type CdSe-, p-type CdTe-based cell is far from ideal but is illustrative. First, irradiation of the CdSe and CdTe does yield a stable photocurrent with neither change in the electrolyte or the electrodes, Table I. The maximum open-circuit potential difference between CdSe and CdTe upon simultaneous irradiation is larger than for either CdSe or CdTe against a Pt electrode. However, the total energy conversion efficiency of the cell is less than for CdSe alone, since the p-type CdTe provides relatively little driving force (maximum of 150 mV) and yet it still must be irradiated in order for any current to flow. Qualitatively, the CdSe/CdTe based cell is at most a little over one-half as efficient as the n-type CdSe-based cell alone, since twice as many photons are required to raise the maximum output potential from ~700 mV for CdSe[1,3] alone to ~850 mV for the double photoelectrode-based cell. A mismatch in the photocurrent efficiencies in p-type CdTe and n-type CdSe contributes further to inefficiency.[15]

Though the p-type CdTe-based cell efficiency is disappointing, we are encouraged by the fact that we have demonstrated that substances other than H_2O can be reduced with 100% efficiency at p-type photocathodes. Preliminary results with other p-type materials (p-GaAs, GaP) in polychalcogenide electrolytes show similar behavior and these will be discussed in the full paper.[19]

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(15) The optimum efficiency of the double photoelectrode-based cell depends on a number of factors including the relative intensity at the two photoreceptors. These features will be elaborated in the full paper.

(16) Fannie and John Hertz Fellow.

(17) Work performed while a Visiting Scientist at M.I.T. on sabbatical leave from the Department of Chemistry, California State University, Long Beach, Calif.

(18) Recipient of a Dreyfus Teacher-Scholar Grant, 1975–1980.

(19) Note Added in Proof. Aside from the related work in ref 10–12, a number of related reports on p-type photoelectrodes have recently appeared: (a) H. Tributsch, *Ber. Bunsenges. Phys. Chem.*, **81,** 361 (1977); (b) A. J. Nozik, *Appl. Phys. Lett.*, **30,** 567 (1977); **29,** 150 (1976); (c) M. Tomkiewicz and J. M. Woodall, *Science*, **196,** 990 (1977); and (d) K. Ohashi, J. McCann, and J. O'M. Bockris, *Nature* (*London*), **266,** 610 (1977).

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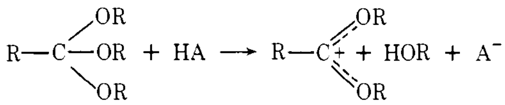
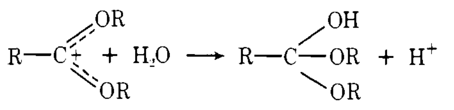
Ortho Ester Hydrolysis. The Complete Reaction Mechanism

Sir:

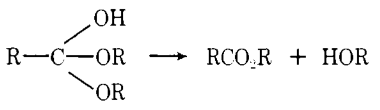
The mechanism for the acid-catalyzed hydrolysis of ortho esters is generally believed to consist of three separate reaction stages:[1] (1) generation of a dialkoxy carbonium ion, (2) hydration of this ion to a hydrogen ortho ester, and (3) breakdown of the latter to alcohol and carboxylic acid ester products (eq 1–3). Although this is a reasonable reaction mechanism, the process has invariably been studied only under conditions where the first stage is rate determining and there is therefore no direct kinetic evidence for the rest of the reaction scheme. We wish to report that we have now found conditions under which stage 3 is rate determining and that we have also observed the interconversion of the reactants and products of



$$\mathrm{R{-}C(OR)_3 + HA \longrightarrow R{-}\overset{+}{C}(OR)_2 + HOR + A^-} \qquad (1)$$



$$\mathrm{R{-}\overset{+}{C}(OR)_2 + H_2O \longrightarrow R{-}C(OH)(OR)_2 + H^+} \qquad (2)$$



$$\mathrm{R{-}C(OH)(OR)_2 \longrightarrow RCO_2R + HOR} \qquad (3)$$

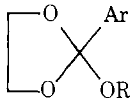
Table I. Hydronium-Ion Catalytic Coefficients for the Hydrolysis of 2-Phenyl-2-alkoxy-1,3-dioxolanes[a]

Alkoxy group	$10^2k_{H^+}$, M^{-1} s^{-1} In phosphonate buffers[b]	In HCl solutions
OCH_2CHCl_2	12.4 ± 0.2	3.05 ± 0.02
$OCH_2C{\equiv}CH$	16.6 ± 0.5	2.91 ± 0.03
OCH_2CH_2Cl	18.4 ± 0.2	2.85 ± 0.04
$OCH_2CH_2OCH_3$	26.2 ± 0.3	2.93 ± 0.10
OCH_3	54.0 ± 0.7	2.99 ± 0.03
OCH_2CH_3	81.8 ± 0.8	3.09 ± 0.01
	Av	2.97 ± 0.09

[a] At 25 °C and ionic strength of 0.10 M. [b] Obtained by extrapolation to zero buffer concentration.

stage 2. These discoveries thus provide the first direct support for the complete reaction mechanism.[2]

We performed our study using a series of cyclic ortho esters, the 2-aryl-2-alkoxy-1,3-dioxolanes, **1**. In weakly acidic phosphonate-anion buffer solutions (pH 4.5–7.5), rates of cleavage of OR from these substances (as measured by rates of loss of a radioactive label placed in the OR group) are identical with rates of appearance of carboxylic acid ester product (as measured spectroscopically by monitoring the increase in $ArCO_2R$ absorbance), and standard treatment of the kinetic data gives hydronium ion catalytic coefficients characteristic of the substrate used. The results for a series of 2-phenyl derivatives are presented in column 2 of Table I; it may be seen that k_{H^+} changes regularily, by a factor of nearly 7, as the nature of the OR group is varied in a systematic way.

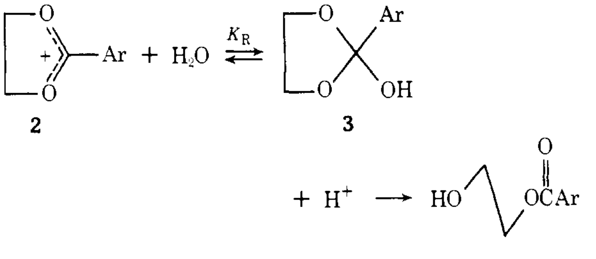


1

In more strongly acidic solutions (0.005 to 0.050 M HCl), on the other hand, all of these 2-phenyl-2-alkoxy-1,3-dioxolanes give carboxylic acid ester at precisely the same rate: the values of k_{H^+} measured under these conditions (column 3, Table I) show an extreme variation of only 8% and the standard deviation of the entire group is ±3%. This rate constant, moreover, is 4 to 30 times *less* than k_{H^+} measured in the weakly acidic solutions. It is apparent that the same quantity is not being measured at high as at low acidities, and that suggests that different steps of the overall process are being observed under the two sets of reaction conditions. This idea is reinforced by the fact that, at intermediate acidities, the appearance of product shows an induction period, and that data gathered in this region give a good fit to the standard expression for the rate of two consecutive first-order reactions containing rate constants estimated from the measurements made at low and at high acidities.

Thus, whereas dialkoxycarbonium ion formation (eq 1) is rate determining at low acidities, some subsequent step becomes slower at high acidities. This new rate determining step has the same specific rate for all members of the 2-phenyl-2-alkoxy-1,3-dioxolane series, and it must therefore involve further reaction of some intermediate which is common to the entire group, such as the 2-phenyl-1,3-dioxolenium ion, **2**, or the hydrogen ortho ester derived from it, **3**.

We have found, in fact, that these two species exist in the reaction mixture in equilibrium with one other and that the new slow step is breakdown of the hydrogen ortho ester (eq 4). Better evidence for this comes from the case where Ar = 4-methoxyphenyl instead of phenyl. The dioxolenium ion in this system, prepared by a standard method,[3] has a characteristic UV spectrum with λ_{max} at 300 nm. Stopped-flow experiments on the parent ortho ester at $[H^+]$ = 0.01 to 0.1 M reveal a transient absorption at this wavelength whose disappearance shows a striking biphasic behavior: an initial fast drop, whose magnitude decreases with increasing acid concentration, is followed by a second more gradual change. We attribute this initial fast drop in absorbance to the fast reaction of dioxolenium ion with water giving hydrogen ortho ester. Once the equilibrium concentration of the latter has been reached, the rapid drop ceases and is replaced by a slower decrease as the dioxolenium ion is siphoned off through the slower breakdown of the hydrogen ortho ester.



(4)

This hypothesis is supported by the relationship between acid concentration and the size of the fast initial drop: at lower acidities the position of the equilibrium will be further to the right and more dioxolenium ion will have to react in order to set up equilibrium concentrations. Further support comes from the fact that rate constants calculated using the second more gradual drop in dioxolenium ion concentration are identical with specific rates determined from the rate of appearance of carboxylic acid ester (λ_{max} 245 nm). These rate constants, moreover, are not linear functions of $[H^+]$ but show a leveling off at higher $[H^+]$ where the equilibrium of eq 4 is driven over to the left. Standard reciprocal treatment of these data gives pK_R = 1.2 for the 2-(4-methoxyphenyl)-1,3-dioxolenium ion, and the initial fast drop in absorbance gives the estimate k = 3×10^2 sec^{-1} for the specific rate of combination of this ion with water.

In systems whose aryl groups are less strongly electron supplying than 4-methoxyphenyl, dioxolenium-ion intermediates can be observed only at somewhat higher acid concentrations. With Ar = phenyl, for example, no transient at λ 265 nm (λ_{max} for the 2-phenyl-1,3-dioxolenium ion) can be seen up to $[H^+]$ = 0.1 M and the specific rate of appearance of carboxylic acid ester (λ 232 nm) remains linear in $[H^+]$. Above this point, however, a transient may be seen and the catalytic effect of $[H^+]$ on the rate of hydrolysis begins to drop off. Analysis of the data in this region provide the estimate pK_R = −0.5 for the 2-phenyl-1,3-dioxolenium ion.

The shift in rate-determining step which this system undergoes comes about because the first stage of the reaction, loss of an alkoxy group from the ortho ester (eq 1), can be catalyzed only by acids, whereas the last stage, breakdown of hydrogen ortho ester (eq 3), can occur by a base-catalyzed as well as by an acid-catalyzed path. At low acidities basic catalysis of stage three combines with a low acid-catalyzed rate of stage 1 to make stage 1 rate determining. As the acidity is increased, however, basic catalysis (of stage 3) diminishes while acid catalysis (of stage 1) grows stronger until stage 3 becomes slower than stage one.

Acknowledgment. We are grateful to the National Research Council of Canada and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their financial support of this work.

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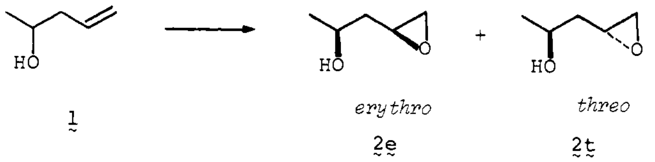
"Phosphate Extension". A Strategem for the Stereoselective Functionalization of Acyclic Homoallylic Alcohols

Sir:

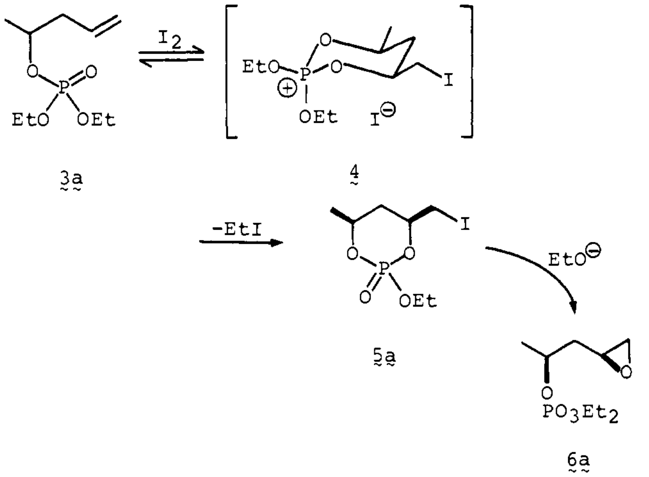
Configurational control in the introduction of chiral centers is one of the paramount considerations in the design of a natural product synthesis. While chemists have developed many versatile methods for the stereocontrolled synthesis of rigid or conformationally well-defined molecules, stereochemical control in the elaboration of acyclic or conformationally heterogeneous systems remains an elusive goal. Attention is now being directed toward the synthesis of compounds, such as the macrocyclic natural products, whose construction will require such methodology, and the need for appropriate stereoselective transformations is becoming increasingly important.[1]

In spite of considerable work in this area,[2] reactions which exhibit high 1,2- or 1,3-asymmetric induction in the generation of chiral centers in acyclic systems are relatively rare. Among the more consistently successful in this regard are reactions of chiral alcohols and amines in which the heteroatom is intimately involved in the transition state, either by coordinating and directing the incoming reagent or by stabilizing a particular conformation of the substrate.[2b,c,3] For example, both epoxidation of allylic alcohols[3] and the addition of organometallic reagents to α-hydroxy or α-amino ketones[2b] proceed with high stereoselectivity in many acyclic cases.

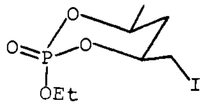
Stereocontrolled epoxidation[4] of a double bond promises to be a useful transformation in the construction of conformationally mobile systems,[5] because it generates one or two asymmetric centers and facilitates further stereospecific carbon-carbon bond-forming reactions. We have investigated a variety of methods for effecting 1,3-asymmetric induction in the epoxidation of homoallylic alcohols, and initially focused our attention on 4-penten-2-ol (**1**).[6] In view of the simplicity of the structure and the distance of the chiral center from the double bond, it is not surprising that only low asymmetric induction is observed in the direct epoxidation of **1** (reagent, conditions, ratio of **2e**/**2t**):[7] *m*-chloroperbenzoic acid, chloroform at 25 °C, 1.2; *t*-BuOOH-VO(acac)$_2$, benzene at 25 °C, 2.0; *t*-BuOOH-Mo(CO)$_6$, benzene at reflux, 0.8. Although the vanadium and molybdenum catalysts show opposite selectivities, the diastereomer ratios clearly are not synthetically useful.



Williams and co-workers have shown that the rate of attack of electrophilic halogen species on a double bond is significantly increased by concomitant attack by an appropriately positioned nucleophile.[9] We sought to extend the nucleophilic character of the hydroxyl group of 4-penten-2-ol so that it could assist electrophilic attack on the double bond and involve the chiral center in a more predictable fashion.[10] To this end, we prepared the diethyl phosphate **3a** and studied its reaction with iodine. We felt that formation of the cyclic tetraalkoxyphosphonium ion (**4**), by addition of iodine and the phosphoryl oxygen to the double bond, would be readily reversible and would heavily favor the cis diastereomer. Dealkylation of this intermediate would then furnish a cyclic phosphate (**5a**) which would be amenable to further transformation.



Treatment of the homoallylic phosphate **3a** with 2.2 equiv of iodine in acetonitrile at 25 °C for 2 days affords an 87% yield of the desired cyclic phosphate **5a**, which is predominantly (>90%) one isomer by VPC and by ^{13}C NMR. The long-range couplings of 2.0 and 2.3 Hz between phosphorus and the iodomethyl and methyl protons,[11] respectively, and an IR absorption of 1305 cm^{-1} for the P→O group[12] indicate that it is the anticipated most stable isomer **7a**. This compound rapidly reverts to acyclic olefinic material on treatment with bromotrimethylsilane in chloroform,[13] which is consistent with our prediction of ready reversibility in the formation of **4**. At present it is not clear whether the high selectivity for the axial ethoxy configuration results from selective dealkylation of **4** or from subsequent equilibration of **5a** by adventitiously produced hydrogen iodine. Treatment of the cyclic phosphate mixture (**5a**) with 1 equiv of sodium ethoxide in tetrahydrofuran at 0 °C gives the dialkyl phosphate of the erythro epoxide (**6a**) in 75% yield, contaminated with <2% isomeric material by ^{13}C NMR analysis. The cyclic phosphates **5a** must therefore be epimeric at phosphorus, because only this chiral center is lost on conversion to the epoxide.



7a

We have explored the generality of this strategy with a variety of acyclic homoallylic alcohols, as shown in Table I. Of particular interest are the results obtained with the diastereomeric 3-methyl-4-penten-2-ol derivatives **3c** and **3d**,[14] which demonstrate that 1,3-asymmetric induction takes precedence over the 1,2 effect. Although the acyclic methyl is forced into an axial position in **5d**, the stereoselectivity in the epoxidation of **3d** is still exceptionally high for 1,3-asymmetric induction.[2] Stereochemical control by the asymmetric carbon more remote from the site of reaction thus appears to be a useful aspect of this strategy.

The introduction of two chiral centers by epoxidation of a disubstituted olefin was studied with the diethylphosphate of *trans*-5-hepten-3-ol (**3e**). While the stereoselectivity of the epoxidation sequence is still excellent, the iodocyclization of this material has proceeded only in low yield so far. The cy-