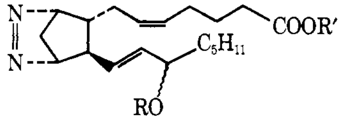
function and the PGH_2 carboxylic appendage, depended upon a crucial ordering of individual steps and careful selection of reagents and reaction conditions. Among the constraints which had to be reckoned with were (1) interference of N—COOEt groups with reagents such as R_2AlH, $LiBH_4$, and the ylide $Ph_3P{=}CHCH_2CH_2CH_2COO^-$ (under the usual conditions[16]), (2) acid sensitivity of azo-bridged intermediates, and (3) lability of **9** and **13** to base-catalyzed β-elimination of the nitrogen bridge. Under carefully selected conditions, the ester **9** was converted to the corresponding acid **10** (10 equiv of potassium hydroxide in H_2O-CH_3OH(1:2) at 0 °C for 18 h) and thence to the alcohol **11** by sequential treatment with ethyl chloroformate–triethylamine (1 equiv each, in THF at 0 °C for 30 min) and sodium borohydride (6 molar equiv in 6:1 THF-H_2O at 10-15 °C for 2 h). More vigorous base treatment of **11** (6.75 equiv of KOH in ethylene glycol at 115 °C for 4.5 h) removed both ethoxycarbonyl groups to form the corresponding free hydrazine which after extraction but without purification was directly oxidized by air in the presence of cupric acetate catalyst to the azo-bridged alcohol **12** (70% yield). oxidation of **12** by chromium trioxide–pyridine (1:2) reagent (8.5 equiv) in CH_2Cl_2 at 0 °C for 1.5 h yielded the corresponding (azo-bridged) aldehyde (**13**), which was directly converted to the enol ether **14** (70% from **12**) using 3 equiv of methoxymethylenetriphenylphosphorane (generated using lithium diisopropylamide in THF) in 3.4:1 toluene–THF at 0 °C for 0.5 h. The aldehyde **15** could only be obtained in poor yield from enol ether **14** by mild acid-catalyzed hydrolysis in water at 0 to 25 °C (even aqueous acetic acid) because of an extraordinary sensitivity to acid. However, the aldehyde was generated cleanly from **14** under *neutral* conditions (10:1 THF-H_2O, 3 equiv of mercuric acetate as catalyst at 23 °C for 10 min followed by addition of excess aqueous potassium iodide and extraction). Reaction of **14** with the Wittig reagent from (4-carboxybutyl)triphenylphosphonium bromide in Me_2SO[16] at 25 °C afforded the desired acid **16** (66% from **14**). Treatment of **16** with ethereal diazomethane followed by THP cleavage using 3:1:1 HOAc-THF-H_2O at 45 °C for 3 h gave a mixture of 15-epimeric (PG numbering) hydroxy esters **17** (99% yield) which were readily separable by chromatography on silica gel into 15α- (natural configuration) and 15β-alcohols (R_f values 0.33 and 0.42, respectively, on silica gel plates with ether for development). Hydrolysis of the methyl ester of the 15α-alcohol (0.15 N lithium hydroxide in 2.5:1 THF-H_2O at 0 °C for 2.5 h) afforded upon isolation the (±)-azo analogue (**1**) of PGH_2 (99% yield), spectroscopically and chromatographically identical with an authentic sample synthesized from PGA_2.[1] The same product was obtained from the 15β-epimer of the ester **17** by mesylation (1.2 equiv of methanesulfonyl chloride and 1.2 equiv of triethylamine in CH_2Cl_2 at −25 °C for 1 h) followed by reaction with potassium superoxide[15,17] (6 equiv in 1:1:1 Me_2SO-DME-DMF containing 18-crown-6 for 20 min at 0 °C) (72% overall yield).[18,19]



16, R′ = H; R = THP
17, R′ = CH_3; R = H

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(6) For multistep syntheses of this substance see (a) E. J. Corey, T. K. Schaaf, W. Huber, U. Koelliker, and N. M. Weinshenker, *J. Am. Chem. Soc.*, **92**, 397 (1970); E. J. Corey and G. Moinet, *ibid.*, **95**, 6831 (1973); (c) E. J. Corey and J. Mann, *ibid.*, **95**, 6832 (1973).

(7) The azo analogue **1** and intermediates **4** through **17** were obtained by the route described herein in racemic form.

(8) Prepared by addition of cyclopentadienyl sodium (Arapahoe Chemical Co.) in THF to a mixture of excess dry ice (small pieces) and THF to form a dimeric mixture of cyclopentadiene carboxylic acids (see, J. Thiele, *Chem. Ber.*, **34**, 68 (1901)) and subsequent esterification using 4% sulfuric acid–methanol (4% by vol) at reflux for 4.5 h. See also, W. E. Franklin, C. H. Mack, and S. P. Rowland, *J. Org. Chem.*, **33**, 626 (1968).

(9) At shorter reaction times **4** was accompanied by substantial amounts of the isomeric adduct having the methoxycarbonyl group at the bridgehead carbon. At higher reaction temperatures yields of **4** were considerably lower, and appreciable contamination by the isomeric adduct was observed.

(10) Satisfactory infrared, proton magnetic resonance, and mass spectral data were obtained using chromatographically homogeneous samples for all synthetic intermediates described herein. All reactions except those involving acidic reagents were conducted under an atmosphere of argon.

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(12) See G. P. Pollini, A. Barco, and G. De Guili, *Synthesis*, 44 (1972).

(13) Crude **4** taken directly from the Diels–Alder process can be used for the reaction with nitromethane, in which case pure **6** can be isolated after chromatography in 42% yield (overall for both steps).

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(18) The biological activity of racemic azo analogue **1** was one-half that of the optically active material synthesized as described in ref 1 from PGA_2 with regard to human platelet aggregation and release reactions. The racemic 15β-epimer of **1** showed essentially no biological activity in these tests. We are indebted to Drs. Bengt Samuelsson and Curt Malmsten of the Karolinska Institutet, Stockholm, for the biological data.

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Optical to Electrical Energy Conversion: Cadmium Telluride-Based Photoelectrochemical Cells Employing Telluride/Ditelluride Electrolytes

Sir:

We wish to report a new result concerning the stabilization of n-type semiconductor photoelectrodes used in electrochemical cells for the conversion of optical energy to electricity.[1] In recent reports[2,3] we outlined in detail the stabilization of CdS- and CdSe-based photoelectrochemical cells by use of a sulfide or polysulfide containing electrolyte. The key result is that oxidation of the *added* sulfide or polysulfide occurs at the photoelectrode at the expense of photoanodic dissolution of the electrode which normally occurs as in reaction 1.

$$_{\text{(photoanode)}}CdX_{(s)} \xrightarrow{2h\nu} Cd^{2+}_{(aq)} + X_{(s)} + 2e^- \qquad (1)$$

$$X = S, Se$$

Thinking that CdTe would be derivative, we attempted to use n-type CdTe as a photoelectrode and found it to be *unstable* even in a polysulfide electrolyte capable of stabilizing CdSe. The decomposition of a CdTe photoanode occurs according to reaction 1 for X = Te.[4] We now report that CdTe can be stabilized by an electrolyte additive. Importantly, we show that a stable CdTe-based cell is superior to CdS or CdSe in terms of wavelength response (onset at 865 nm vs. 520 and 750 nm

Table I. Stability of n-type CdTe Photoelectrodes[a]

Expt no.	mol × 10^4 CdTe before	 CdTe after ±0.02[b]	 Electrons passed	Av i, mA[c]	V_{appl}[d]
1	6.26	6.24	9.79	0.30	0.00
2	4.76	4.75	2.16	0.30	−0.50

[a] Cf. ref 6 for general procedures. [b] The error in weighing CdTe before electrode fabrication is negligible. But after electrochemical action the CdTe must be demounted and with the very brittle CdTe we invariably lose some of the crystal in this process. Therefore, we assign the error of $\pm 0.02 \times 10^{-4}$ mol. [c] Current monitored by measuring the potential drop across a 100 Ω resistor in series in the external circuit. Multiply by 4 cm^{-2} to get average current density. [d] V_{appl} is the applied potential difference between the Pt and CdTe using a power supply in series in the external circuit. A negative applied potential means that the negative lead of the power supply was attached to the CdTe. For negative V_{appl} the power supply represents an electrical load in the external circuit and the *power output* is Av $i \times V_{\mathrm{appl}}$.

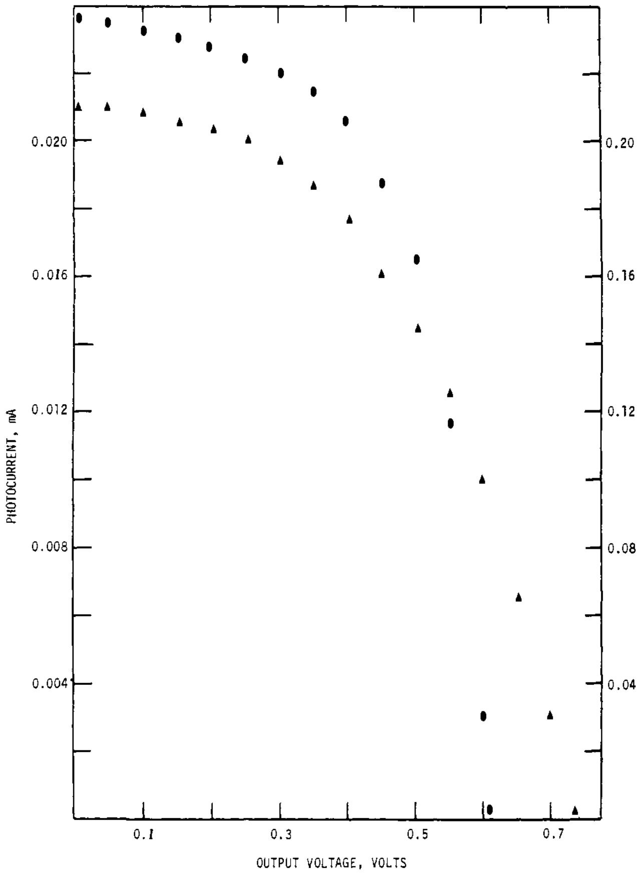

Figure 1. Photocurrent against output voltage upon 633-nm irradiation at 0.079 mW (●) and left scale and at 1.60 mW (▲) and right scale for a CdTe-based photoelectrochemical cell with a stirred 5.0 M NaOH Te^{2-}/Te_2^{2-} (0.024 M/0.003 M) electrolyte under Ar. Maximum power output (photocurrent × output voltage) occurs at 0.50 V (6.8% efficiency) for 1.60 mW irradiation and at 0.45 V (10.7% efficiency) for 0.079 mW irradiation. The exposed electrode area is 0.25 cm^2.

for CdS and CdSe, respectively) and in the output voltage at the maximum energy conversion efficiency. These properties make the CdTe-based cell the best demonstrated photoelectrochemical cell for the conversion of light to electricity.

Using irradiation wavelengths shorter than that corresponding to the band gap energy of CdTe (865 nm),[5] irradiation of an n-type CdTe electrode short-circuited to a Pt electrode results in flow of electric current such that electrons flow towards the Pt. In 5.0 M NaOH (and many other electrolytes) the photocurrent rapidly falls and significant changes in the CdTe electrode surface are visible. Elemental Te is formed on the CdTe from reaction 1 for X = Te, while H_2 evolution obtains at the Pt electrode. These observations are typical for n-type CdX-based photoelectrochemical cells when the photoelectrode is undergoing photoanodic dissolution. We have discovered that the photoanodic dissolution of CdTe can be completely quenched in the 5.0 M NaOH by adding Na_2Te which dissolves to give Te^{2-} ions oxidizable at the CdTe.

Data[6] are given in Table I showing that the CdTe undergoes no photoanodic dissolution in solutions containing a few hundredths molar Te^{2-}. We note for the two experiments given in Table I that the photocurrent is constant (±10%) for a given light intensity striking the electrode. Constant photocurrent (±10%) has been obtained for periods of 633-nm irradiation corresponding to the passage of enough current to consume >70% of the CdTe electrode, and no weight loss in the CdTe crystal was found. Oxidation of the *added* Te^{2-} occurs which yields the Te_2^{2-} ion in the presence of significant quantities of Te^{2-}.[7] The initially colorless Te^{2-} solution becomes purple as the Te_2^{2-} ($\lambda_{\max}$ 512 nm, $\epsilon \approx 1000$ l. mol^{-1} cm^{-1})[8] is formed. The Te_2^{2-} cannot increase to a concentration more than one-half that of the initial Te^{2-} concentration, but before this occurs the Te_2^{2-} becomes active at the cathode and is reduced back to Te^{2-}. Thus, a photoelectrochemical equilibrium of Te^{2-} and Te_2^{2-} is ultimately established. *Before* substantial buildup of Te_2^{2-} the evolution of H_2 is still observed at the Pt electrode.

To definitively prove that the Te^{2-}/Te_2^{2-} electrolyte is electrochemically stable we passed ~1 mA current at 0.45 V (using two Pt electrodes) through an electrolyte of 5.0 M NaOH, 0.03 M Na_2Te to yield a buildup of Te_2^{2-} which can be followed spectrophotometrically.[9] After ~24 h spectral changes cease, and in an additional 48 h enough current was passed to cycle $2Te^{2-} \rightleftarrows Te_2^{2-}$ over 16 times without any spectroscopically detectable deterioration of the electrolyte. These experiments convince us that the solution of Na_2Te will itself ultimately assume an equilibrium of Te^{2-} and Te_2^{2-} such that *no* further chemical changes will occur.

We represent the photoelectrochemical cell chemistry as in reactions 2 and 3.

Photoanode:

$$2Te^{2-} \xrightarrow{2h\nu} Te_2^{2-} + 2e^- \tag{2a}$$

or

$$Te_2^{2-} + 2Te^{2-} \xrightarrow{2h\nu} 2Te_2^{2-} + 2e^- \tag{2b}$$

Cathode:

$$2e^- + Te_2^{2-} \rightarrow 2Te^{2-} \tag{3}$$

Thus, we can stabilize CdTe to photoanodic dissolution *and* use an electrolyte which is itself undergoing no *net* chemical change. Incidentally, visible light irradiation of Te_2^{2-} does not cause any detectable change in the Te^{2-}/Te_2^{2-} solution.

Extracting electrical energy from the CdTe-based photoelectrochemical cell depends on being able to generate an open-circuit photopotential in the Te^{2-}/Te_2^{2-} electrolyte. We have obtained open-circuit photopotentials of up to ~0.7 V.

Figure 1 shows the photocurrent vs. output voltage for the CdTe-based cell employing a Te^{2-}/Te_2^{2-} electrolyte for irradiation with a known power at 633 nm. At low intensity, the short-circuit current (0.0 V output) corresponds to a quantum efficiency for electron flow $\cong 0.6$, and the maximum power output (current × output voltage) occurs at ~0.45 V. The maximum overall optical to electrical energy conversion that we have measured is 10.7% at 633 nm, and from wavelength response data we calculate efficiencies of 14 and 7% at 800 and 400 nm, respectively, at the same light intensity. As shown in Figure 1, the efficiency suffers at higher intensities as we found with CdS- and CdSe-based cells, but the main finding here is that good open-circuit voltages, respectable efficiencies at high incident intensity, excellent wavelength response, and good stability all obtain in the Te^{2-}/Te_2^{2-} electrolyte.

Acknowledgment. We thank the National Aeronautics and Space Administration for support of this work.

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(8) The molar extinction coefficient of Te_2^{2-} was obtained by monitoring current passed and optical spectral changes accompanying the electrolysis of a 0.03 M Te^{2-} solution in 5.0 M NaOH using two Pt electrodes with an applied potential of 0.45 V. We assume that 100% current efficiency for Te_2^{2-} ion generation initially obtains.

(9) For emphasis, we note that spectral changes upon photoelectrochemical generation of Te_2^{2-} are identical with those for the conventional electrochemical generation. Additionally, the current efficiency in each case is the same.

(10) Fannie and John Hertz Fellow.

(11) Fellow of the Alfred P. Sloan Foundation, 1974–1976, and recipient of a Dreyfus Teacher-Scholar Grant, 1975–1980.

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Book Reviews

Atomic Absorption and Fluorescence Spectroscopy. By G. F. KIRKBRIGHT (Imperial College, London) and M. SARGENT (Shell Research, Ltd., Cheshire). Academic Press, New York and London. 1974. 808 pp. $50.00.

This book attempts to give comprehensive coverage to the theory and techniques of atomic absorption spectroscopy (AAS) and atomic fluorescence spectroscopy (AFS). Considering the tremendous difficulties of such an undertaking, especially when the techniques are still undergoing rapid development, the authors have been very successful. The material is organized in the generally accepted format with an introductory chapter, three chapters of theory, six chapters on instrumentation, two chapters on techniques, one chapter on interferences, and one long chapter on applications data.

The theory is presented with sufficient detail to prevent its being misleading but at the same time is not so comprehensive as to discourage beginning students. The instrumentation is discussed in terms of individual components (sources, flames, etc.) with the emphasis being on properties and characteristics rather than theory of operation. In this way the authors make it easy for readers to make comparisons and evaluations of various types of comonents that are available. Considerations such as optimization of parameters, sensitivity, precision and accuracy, and sample pretreatment are very adequately discussed in a chapter on techniques. A second techniques chapter includes some discussion of other nonroutine operations such as indirect analysis, isotope analysis, and laser-excited AFS. A long (176 pp) chapter on applications data should be very helpful to the new or occasional user of AAS or AFS. Important numerical data and analytical conditions along with key references are summarized for each metal that can be determined directly.

The major shortcomings of this book result almost exclusively from the still rapid pace of development in the techniques and instrumentation of AAS and AFS. Important recent developments not included are the use of vidicon and array detectors for simultaneous multielement analysis, new nonflame atomization devices, and applications of on-line computers in automating optimization of instrument parameters. Despite these shortcomings the book is of high quality and far more comprehensive than any of its current competitors and as such should become a well-known and well-used standard reference volume for AAS and AFS.

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Treatise on Analytical Chemistry. Part I. Theory and Practice. Volume 11. Edited by I. M. KOLTHOFF and PHILIP J. ELVING. John Wiley & Sons, Inc., New York, N.Y. 1975. xxiii + 697 pp. $39.50.

The "Treatise on Analytical Chemistry" is a comprehensive account in three parts: I. Theory and Practice; II. Analytical Chemistry of Inorganic and Organic Compounds; and III. Analytical Chemistry in Industry. This volume, the 11th in Part I, consists of Chapters 108 through 119 of theory and practice. These chapters have been written at a level and thoroughness consistent with those that have appeared earlier in this highly significant collection. They add to this continually expanding source of reference background material for analytical chemists. Unfortunately, it is difficult to use as a reference source because of its very size and the organizational problems presented by a series consisting of hundreds of chapters appearing over a period of years. This is not to suggest that the editors could have done more than they have in an organizational sense.

This volume consists of Chapters 108, General Laboratory Apparatus, by F. Hecht; 109, General Laboratory Operations and Techniques, by W. Prodinger and F. Hect; 110, Safety in the Analytical Laboratory, by R. F. Stalzer, J. R. Martin, and W. E. Railing; 111, Qualitative and Quantitative Chemical Analysis, by James I. Watters; 112, Qualitative Analysis: Scope and Limitations, by Richard B. Hahn; 113, Gravimetric Analysis, by Charles L. Rulfs; 114, Titrimetric Analysis: Introduction, by James I. Watters; 115, Titrimetry: Acid-Base Titration in Aqueous Solution, by John Beukenkamp and William Rieman III; 116, Titrimetry; Acid-Base Titration in Nonaqueous Solvents, by C. A. Steuli; 117, Titrimetry: Complexation Titration, by Axel Johansson and Erkki Wanninen; 118, Titrimetry: Precipitation Titration, by I. M. Kolthoff; 119, Titrimetry: Oxidation-Reduction Titration, by James A. Goldman.

Some of these chapters treat topics that were the subject of earlier