dioxide reaction with the double bond (eq 1) and the subsequent ene reaction (eq 2) are proceeding is effectively as in the absence of water. The absence of the 1,3 rearrangement *in the presence of water* (eq 8) is probably due to the fact that the negatively charged sulfinate anion is a less efficient migrating group than a free, un-ionized sulfinic acid.[6]

We have now obtained evidence that allylic sulfinic acids are indeed very unstable species which in situ undergo smooth decomposition to sulfur dioxide and the olefin, as we suggested earlier.[1] Thus, treatment of the Grignard reagent prepared from 3-chloro-2-methylpropene[8] with liquid sulfur dioxide in ether produced a white precipitate which was filtered, washed with pentane,[9] and characterized by NMR and IR analyses as the magnesium salt of the corresponding allylic sulfinic acid.[10] Addition of dilute hydrochloric acid to an ether suspension of the salt in a reaction flask protected with a dry ice condenser led to the instantaneous liberation of sulfur dioxide and formation of isobutylene which was identified by NMR analysis (eq 9). In addition to the olefin, the ether solution contained a small amount of *tert*-butyl chloride resulting from the addition of hydrogen chloride to isobutylene.

$$\text{(9)}$$
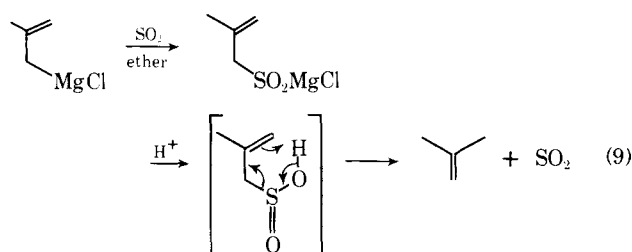
Similarly, magnesium salts of the allylic sulfinic acids, prepared by reaction of sulfur dioxide with the Grignard reagents derived from 1-chloro-3-methylbut-2-ene,[11] *trans*-1-chloro-2-butene,[13] and 2-chloromethylenecyclohexane,[14] on acid hydrolysis gave the olefin and sulfur dioxide. The following observations are noteworthy. The deuterolysis of the magnesium salt of α,α-dimethylallylsulfinic acid in the presence of deuteriosulfuric acid gave 4-deuterio-2-methylbut-2-ene (eq 10). Hydrolysis of the magnesium salt of α-meth-

$$\text{(10)}$$

$$\text{(11)}$$

$$\text{(12)}$$
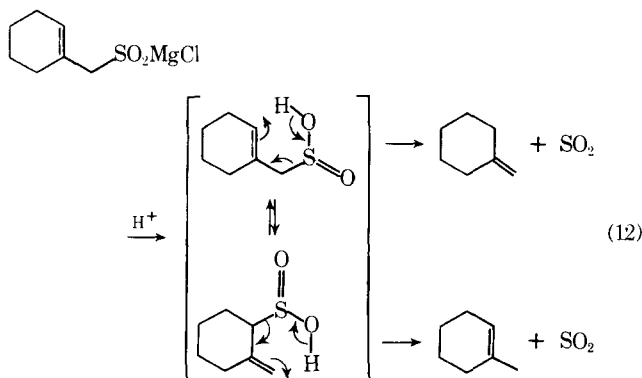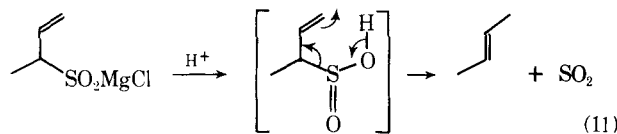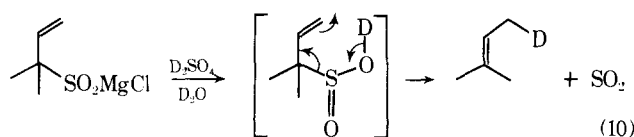
ylallylsulfinic acid gave predominently *trans*-2-butene (eq 11). Hydrolysis of the magnesium salt of the allylic sulfinic acid derived from 2-chloromethylenecyclohexane afforded ap-

proximately a 1:1 mixture of 1-methylcyclohexene and methylenecyclohexane and sulfur dioxide (eq 12).

The formation of 1-methylcyclohexene and methylenecyclohexane, in approximately equal amounts in the last reaction, suggests that in this case the generated amounts in the last reaction, suggests that in this case the generated allylic sulfinic acid had a sufficiently long lifetime to undero the 1,3 rearrangement before the retro-ene reaction occurred.[15,16]

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(2) Note that not all allylic hydrogens exchange. Only allylic hydrogens on the carbon atoms adjacent to the generated *tertiary* carbonium ion carbon are undergoing the exchange.
(3) For a summary of general and solvent properties of liquid sulfur dioxide, see P. J. Elving and J. M. Markovitz, *J. Chem. Educ.*, **37**, 75 (1960). Water dissolves in sulfur dioxide, but the extent of its solubility is not very accurately determined. Wickert[4] reported that the equilibrium solubility of water in liqud sulfur dioxide at 22 °C is 2.3 ± 0.1 g/100 g of solvent.
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(5) Presumably, by protonation of the olefin, followed by reaction of the generated carbonium ion with water.
(6) Mechanism of the 1,3-sulfur migrations[7] is not well understood. One possibility may involve a four-membered cyclic dipolar intermediate with the negative charge localized on the sulfur oxygen and the positive chare on the tertiary carbon atom. The effectiveness with which various allylic sulfur compounds (sulfides, sulfoxides, sulfones, sulfinic acids) undergo the 1,3 rearrangement may depend on the ability of the corresponding sulfur centers to open up a new coordination site. The referee pointed out that H. Kwart and co-workers (H. Kwart and N. A. Johnson, *J. Am. Chem. Soc.*, **99**, 3441 (1977); H. Kwart and T. J. George, *ibid*, **99**, 5214 (1977); H. Kwart and N. A. Johnson, *J. Org. Chem.*, **42**, 2855 (1977); H. Kwart and K. King. "D-Orbitals in the Chemistry of Silicon, Phosphorus and Sulfur", Springer Verlag, New York, N.Y., 1977) have discussed the thiaallylic rearrangement as a well-characterized process involving a dipolar trigonal bipyramid intermediate as mentioned above.
(7) See, for example, (a) H. Kwart, N. A. Johnson, T. Eggericks, and T. J. George, *J. Org. Chem.*, **42**, 172 (1977); (b) H. Kwart and T. C. Stanulonis, *J. Am. Chem. Soc.*, **98**, 4009 (1976); (c) P. Brownbridge and S. Warren, *J. Chem. Soc., Perkin Trans. 1*, 1131 (1977); (d) D. A. Evans and G. C. Andrews, *Acc. Chem. Res.*, **7**, 147 (1974).
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(9) At this point, any hydrocarbon dimers formed during the preparation of the Grignard reagent are removed.
(10) NMR (D_2O) δ 1.81 (s, 3 H), 3.0 (s, 2 H), 4.95 (s, 2 H); IR (KBr) 1640 (C=C), 880, 1020 (SO_2^-) cm^{-1}.
(11) It is known that the Grignard reagent from this chloro olefin reacts with carbon dioxide to give 2,2-dimethyl-3-butenoic acid.[12] The reaction with sulfur dioxide, however, provided the magnesium salt of α,α-dimethylallylsulfinic acid: NMR (D_2O) δ 1.1 (s, 6 H), 4.6–6.4 (ABX, 3 H); IR (THF) 1630 (C=C), 880, 1010 (SO_2^-) cm^{-1}.
(12) H. Kwart and R. K. Miller, *J. Am. Chem. Soc.*, **76**, 5403 (1954).
(13) Reaction of the corresponding Grignard reagent with sulfur dioxide gave the magnesium salt of α-methylallylsulfinic acid: NMR (D_2O) δ 1.22 (d, 3 H), 2.84 (m, 1 H), 4.8–6.2 (ABX, 3 H); IR (THF) 1635 (C=C), 880, 1020 (SO_2^-) cm^{-1}.
(14) Reaction of 2-chloromethylenecyclohexane with magnesium apparently provides the isomerized Grignard reagent with the magnesium on the primary carbon atom and the double bond in the ring. Reaction of this Grignard reagent with carbon dioxide in tetrahydrofuran gave 2-methylenecyclohexanecarboxylic acid quantitatively. On the other hand, reaction with sulfur dioxide provided the magnesium salt of the primary sulfinic acid.
(15) The hydrolysis of the magnesium salt of this allylic sulfinic acid is not very clean. Several other as yet unidentified by-products are also formed.
(16) We are thankful to a referee who called our attention to another hydrogen–deuterium exchange published after we submitted our manuscript: T. Hori, S. P. Singer, and K. B. Sharpless, *J. Org. Chem.*, **43**, 1456 (1978).

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Photochemical Upconversion in the Chlorophyll a Water Splitting Light Reaction: Causative Factors Underlying the Two-Quanta/Electron Requirement in Plant Photosynthesis

Sir:

The minimum quantum requirement in plant photosynthesis is 8 quanta/O_2 molecule evolved or 2 quanta/electron trans-
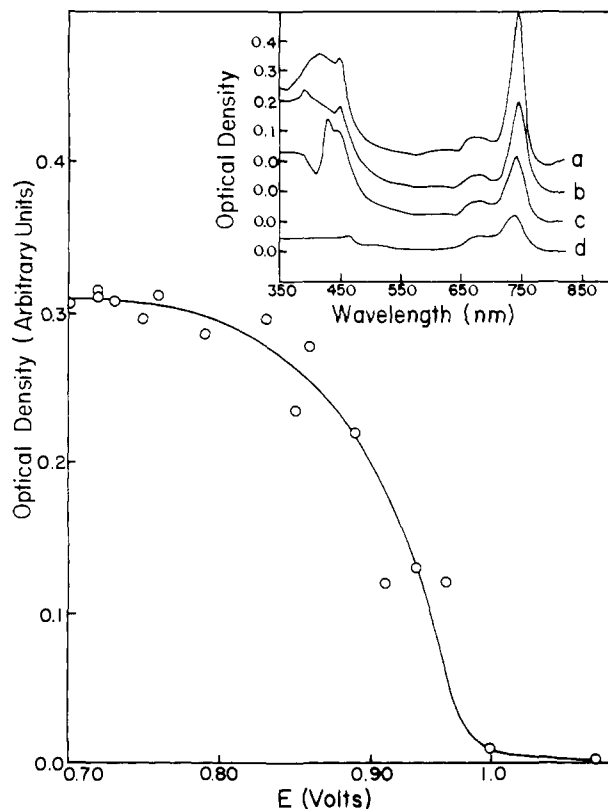
Figure 1. Redox titration of $(Chl\ a\cdot2H_2O)_n$ against standardized Fe^{3+}/Fe^{2+} couples. The data points (circles) correspond to the absorption maxima at 743 nm shown in the inset: (a) absorption spectrum of the $(Chl\ a\cdot2H_2O)_n$ solution in the absence of Fe^{3+}/Fe^{2+}; (b–d) absorption spectra of sample solution after additions of Fe^{3+} and Fe^{2+} ions in ratios corresponding to 0.76, 0.89, and 0.95 V in reduction potential, respectively, at room temperature. Chlorophyll-free solutions containing Fe^{3+}/Fe^{2+} concentrations compatible with those in sample solutions were used as blanks in the double-beam spectrophotometric measurements. The departures in the Soret regions of spectra b, c, and d from a were due to small differences in the Fe^{3+}/Fe^{2+} concentrations in correspondent sample and blank solutions.
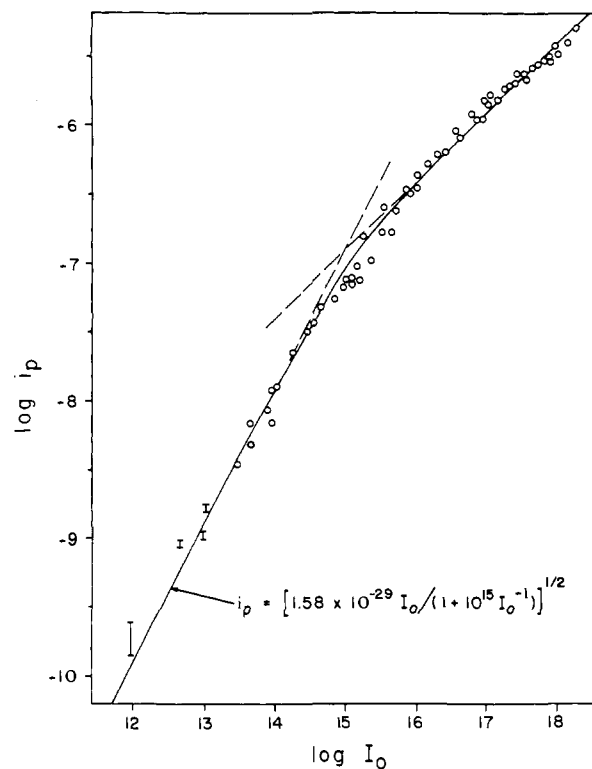

Figure 2. The flux dependence of the $(Chl\ a\cdot2H_2O)_n$–H_2O photogalvanic response. The low-flux data points are given in error bars (99% confidence intervals) corresponding to $\sigma = \pm2.5$ and noise excursions about the mean. The doubling of the exponential flux dependence from semilinearity in the strong light limit to linearity in the weak light limit is attributed to the two-photon upconversion activation in step 4. The fluxes were estimated by a power integration of the lamp function.

ferred in the primary light reaction.[1] It was suggested[2] that this requirement is attributable to that for the photoreaction of $(Chl\ a\cdot2H_2O)_2$ with water.[3-6] This suggestion differs from the phenomenological scheme of two one-photon chlorophyll light reactions ("PSI" and "PSII") that operate in series, mediated by a dark bridge of electron carriers.[1] According to this "series scheme" the PSI light reaction is responsible for ferredoxin reduction, whereas the PSII reaction is associated with the water oxidation (oxygen evolution) process. There are a number of difficulties with the series scheme. The designation of the plastoquinone as the primary electron acceptor in PSII appears to be in conflict with the observation that hydrated Chl a aggregates, unlike monomeric Chl a,[7,8] preferentially photoreduce water in the presence of benzoquinone.[9] The assignment of PSI as the sole agent for the reduction of ferredoxin is not easily reconciled with the observation that electrons ending up in NADP do not appear to involve P700 directly.[10] The question of the role of biphotonic energy upconversion in photosynthesis deserves consideration in view of the observation that singlet–triplet annihilation plays a dominant role in photophysical[11] and photochemical[6] properties of the chlorophyll on account of the extensive overlap between its singlet and triplet absorption spectra.[12,13] The postulate of an obligatory sequence of two light reactions for the water splitting reaction is contrary to the observation of water photolysis by a single chlorophyll light reaction involving $(Chl\ a\cdot2H_2O)_{n\geq2}$.[2-6] In earlier communications the Chl a water splitting reaction was established by photogalvanic[2,3b] and

electron spin resonance[3a] observations of $(Chl\ a\cdot2H_2O)_{n\geq2}$ photooxidation in the presence of water, and by mass spectrometric and pyrolytic determinations of gaseous H_2 and O_2[4-6] evolution from this reaction. In this communication, we investigate into the factors responsible for $(Chl\ a\cdot2H_2O)_n$ being capable of sensitizing the water splitting reaction. We describe the flux dependence of the Chl a water splitting reaction and examine the biphotonic origin of this reaction.

Chlorophyll, prepared from spinach in the usual manner,[24,25] was dissolved in doubly distilled water in the presence of acetone. The aqueous Chl a solution was sonicated until the chlorophyll became evenly dispersed in the solution. The temperature of the solution was then increased to 70 °C to get rid of any excess acetone from the azeotropic solution. The absorption spectrum of the resulting $(Chl\ a\cdot2H_2O)_n$ preparation (3×10^{-5} M in Chl a concentration) is shown in spectrum a of the inset in Figure 1.

The $(Chl\ a\cdot2H_2O)_n$ solution is titrated against additions of mixtures of $FeCl_2$ and $FeCl_3$, in which the relative concentrations of the Fe^{3+} and Fe^{2+} ions were adjusted to provide redox potentials in the 0.7–1.1-V range. The bleaching of the chlorophyll in the presence of an oxidizing agent manifests Chl a oxidation.[24,26-28] The $(Chl\ a\cdot2H_2O)_n$ absorption maximum at 743 nm was recorded as a function of the increasing oxidation potential given, according to the Nernst equation, by the ratio of Fe^{3+} and Fe^{2+} concentrations. The concentrations of the Fe^{3+} and Fe^{2+} ions were kept in excess of the chlorophyll concentration, so that the effect of $(Chl\ a\cdot2H_2O)_n$ oxidation on the potential poised by the Fe^{3+}/Fe^{2+} couple in the sample solution was negligibly small throughout the entire range of the redox titration. From the results shown in Figure 1, it is found that the midpoint reduction potential for $(Chl\ a\cdot2H_2O)_n$ is +0.92 V, which exceeds the corresponding potential, +0.81

V, for the O_2/H_2O half-reaction at pH 7. This observation accounts for the ability of $(Chl\ a\cdot2H_2O)_n^{+\cdot}$, formed from the photooxidation of $(Chl\ a\cdot2H_2O)_n$ by water,[3] to oxidize water resulting in the evolution of molecular oxygen.[4-6] Significantly $(Chl\ a\cdot2H_2O)_n$ appears to be the only known form of Chl a to possess this property. Various other forms of Chl a complexation are characterized by reduction potentials in the <0.5–0.76-V range.[24,26-28]

The dihydrate Chl a/Pt electrode, prepared after the method described earlier,[2] was used in a photogalvanic assembly made up of two half-cells separated by a glass frit, one containing the Chl a/Pt electrode and the other a Chl a free Pt electrode. Both electrodes were immersed in a 0.1 M aqueous solution of KCl. The photogalvanic response of $(Chl\ a\cdot2H_2O)_n$ is greatly enhanced when the Chl a/Pt and Chl a free half-cells are, respectively, kept under acidic and basic conditions.[2] In the present experiment, pH values of 2.2 and 12.0 were maintained for the Chl a/Pt and Chl a free half cells using citrate–phosphate buffers. The cell assemblies were deoxygenated by bubbling argon through the individual half-cells for 1 h.

The illumination of the Chl a/Pt electrode resulted in a flow of electrons from the Chl a free electrode (anode) to the Chl a/Pt electrode (cathode). The initial ($t = 0$) readings of the photogalvanic response were recorded. The photogalvanic response indicates a linear flux dependence under weak light conditions and a sublinear dependence at higher light intensities. To establish the power dependence of the $(Chl\ a\cdot2H_2O)_n$ light reaction in the strong flux limit, we employed the total output from a 1000-W tungsten–halogen lamp. The incident flux was varied by placing a series of five neutral density filters in the path of the exciting light at several lamp power supply voltage settings. The flux at each voltage setting was calibrated by a Spectra Physics power meter. The resulting experimental points, represented as log i_p vs. log I_0, where i_p and I_0 are the photogalvanic current and incident flux, respectively, and fitted to the empirical equation

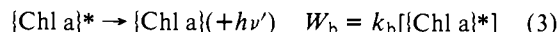$$i_p = [(1.58\times10^{-29})I_0/(1 + 10^{15}I_0^{-1})]^{1/2} \qquad (1)$$

are shown in Figure 2. It is apparent that the $(Chl\ a\cdot2H_2O)$–water photoreaction rate varies as the square root of I_0 in the strong light limit.

With proper consideration of the two-photon activation mechanism, the present observations may be interpreted in terms of a steady-state scheme in which a generalized chlorophyll light reaction is given in a sequence of six consecutive steps with corresponding rate, W, given as follows:
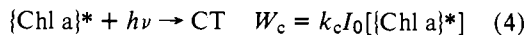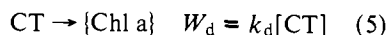
initial excitation of photoactive aggregate {Chl a}

$$\{Chl\ a\} + h\nu \rightarrow \{Chl\ a\}^* \qquad W_a = k_a I_0 \qquad (2)$$
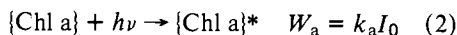
radiative or radiationless decay

$$\{Chl\ a\}^* \rightarrow \{Chl\ a\}(+h\nu') \qquad W_b = k_b[\{Chl\ a\}^*] \qquad (3)$$

upconversion to a tautomeric charge transfer (CT) state[29]

$$\{Chl\ a\}^* + h\nu \rightarrow CT \qquad W_c = k_c I_0[\{Chl\ a\}^*] \qquad (4)$$

nonradiative decay of the tautomeric state

$$CT \rightarrow \{Chl\ a\} \qquad W_d = k_d[CT] \qquad (5)$$

reaction with the primary electron acceptor A

$$CT + A \rightarrow \{Chl\ a\}^+ + A^- \qquad W_e = k_e[CT][A] \qquad (6)$$
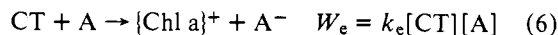
back-reaction or regeneration

$$\{Chl\ a\}^+ + A^- \rightarrow \{Chl\ a\} + A \qquad W_f = k_f[\{Chl\ a\}^+]^2 \qquad (7)$$

The steady-state solution of steps 2–7 results in the expression for the photogalvanic current

$$i_p \propto [\{Chl\ a\}^+] = \left[\frac{k_c k_e[A]}{k_f(k_d + k_e[A])} \times \frac{k_a I_0}{(k_c + k_b I_0^{-1})} \right]^{1/2} \qquad (8)$$

which reproduces the empirical fit (eq 1) for the photoresponse of $(Chl\ a\cdot2H_2O)_n$. We observe that the presence of the term $k_b I_0^{-1}$ in eq 8, resulting from the photochemical upconversion (step 4), is responsible for the *doubling* in the exponential flux dependence from semilinearity in the strong light limit to linearity in the weak light limit. In the absence of step 4 the corresponding steady-state solution yields a similinear dependence throughout the entire range of fluxes, a condition that has long been established for one-photon light reactions involving monomeric Chl a.[30]

The free energy needed for the water splitting reaction is 1.23 V. The photon energy at 743 nm is 1.67 V. After losses due to irreversibility and to the Franck–Condon activation[31,32] of photochemical conversion have been taken into consideration, it appears that the two-photon activation mechanism in step 4 may be obligatory for the observed water splitting effects. We note that all other known examples of water photolysis involve photons in the near-ultraviolet wavelength region[33,34] where the incident energy is more than twice that at 743 nm.

Earlier work has focused on the characterization of the P700 reaction center aggregate in terms of the photochemical and structural properties of the monohydrate dimer (Chl a·$H_2O)_2$.[3,24,35] The present delineation of (Chl a·$2H_2O)_{n\geq2}$,[2,35b,36] as a unique molecular assembly capable of water photolysis,[4-6] suggests that the Chl a water splitting reaction in vivo probably does not differ in essence from the corresponding reaction in vitro.[2,6] This uniqueness may be rationalized in terms of the highly specific intraaggregate-bonding interactions that influence the charge delocalization within (Chl a·$2H_2O)_n$ during photochemical activation.[25] The biphotonic origin of Chl a–H_2O reaction described in this work, along with a proper consideration[6] of the secondary dark electron flow connecting the water splitting light reaction with the P700 light reaction, provides a plausible explanation for the observed 2 quanta/electron transferred requirement for plant photosynthesis.

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reaction center preparations is expected to deprive the primary photochemistry of the upconversion mechanism which is activated by the annihilation of the antenna BChl a S_1 by the reaction center BChl a T_1.[22,23] The observed requirement of in vivo BChl a photosynthesis is 2 quanta/electron.[1a]

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Book Reviews*

Energy. Volume II, Non-nuclear Technologies. By S. S. PENNER and L. ICERMAN. Addison-Wesley, Reading, Mass. 1976. xxx + 673 pp. $19.50 (cloth); $13.50 (paper).

This book is one of a three-volume, "set of lecture notes". It contains chapters on recovery of oil from shale and tar sand, coal technologies, hydrogen fuel economy, energy storage systems, techniques for direct energy conversion, solar energy utilization, windmills, tidal energy, geothermal energy, and production and transmission of electricity. There are 20 pages of problems and an index.

Environmental Dynamics of Pesticides. Edited by R. HAQUE and V. H. FREED. Plenum Press, New York, N.Y. 1975. viii + 387 pp. $29.50.

This book is the proceedings of a symposium sponsored by the Division of Pesticide Chemistry at the April 1974 meeting of the American Chemical Society. Eighteen papers are included. They cover distribution and accumulation of pesticides, physiological effects, detoxification, and methods of chemical estimation. There is a substantial index.

La Chimie Organique, By ROBERT PANICO. Presses Universitaires de France, Paris. 1975. 128 pp. Price not stated.

This small, paperbound book provides a simple overview of organic chemistry, including general principles from bonds to physical methods, and descriptive chemistry from hydrocarbons to compounds of biological importance. A one-page bibliography contains mostly textbooks, the majority of which, curiously, are in English.

Methodicum Chemicum, Volume 6. C–N Compounds, Editor-in-Chief: F. KORTE. Edited by F. ZYMALKOWSKI. Academic Press, New York, N.Y. 1976. viii + 858 pp. $165.00.

This series, begun just a few years ago, deserves to be better known. It is a systematic presentation of reviews of proved methods, generally of analysis or synthesis, oriented toward organic chemistry. Very well known methods are generally described briefly, with references to the more important reviews that have been published, in order to allow a more detailed treatment to be given of new methods, or older ones that have not previously been adequately reviewed.

This volume is concerned with synthesis: methods by which carbon-nitrogen bonds are formed, along with some information on transformation of one type of nitrogen function into another. It is arranged according to the type of compound ultimately formed, in 18

contributed chapters. Major subdivisions of each chapter are included in the Table of Contents with their page numbers, in order to make it easy to find just what one wants. Within the chapters, there ore further logical subdivisions, with clear headings, as well as tabular presentations of types of reactions with key to the pages on which they are treated. An index of 58 pages is another great aid to easy access.

The documentation is marvelously thorough, and there must be over 10,000 references. Coverage of the literature is through 1971, but for a work of permanent reference value such as this, this fact is not detracting. Although most of the contributors are German, the text is entirely in English. This fact has produced some slightly awkward usages that occasionally require re-reading (e.g., ". . . phenolates can be reacted to cyanates . . ."). This is a trivial annoyance compared to an editorial characteristic, by which introductory phrases that are not the subject of the sentence are rarely set off by commas, even when they are quite long; this practice too often requires the reader to stop in puzzlement in midsentence.

The careful and thorough compilation of the material in this book is matched by the high quality of its production (layout, printing, paper, and binding). It is an invaluable work of reference, and no organic chemist concerned with synthesis will want to be without access to it.

Global Chemical Cycles and Their Alterations by Man. Edited by WERNER STUMM. Dahlem Konferenzen/Abakon Verlagsgesellschaft, Berlin, 1976. 347 pp. Price not stated.

This book is the report of a "workshop" conference held in Berlin in 1976 with an international group of invited participants. The goal of the conference was "to assess our understanding of the global chemical cycles and their alterations by man as a basis for describing our future environment and for projecting research needs." The content consists of a series of review papers on specific facets of chemical and energy cycles, and four "group reports", in which the available information is assessed, major questions are identified, and recommendations are made.

The papers make very sober reading, and the depth of documentation provided makes them both useful and persuasive. Such simple facts that manmade nitrogen fixation now approaches natural nitrogen fixation in magnitude, and that atmospheric CO_2 concentration is expected to double in the next 50 years, pose chemical questions of enormous importance to mankind. It is good that these serious matters have been brought to our attention in such substantial form so soon after the conference.