

Additions and Corrections

Some Very Rapid Reactions of Porphyrins in Aqueous Solution [*J. Am. Chem. Soc.*, **98**, 1908 (1976)]. By ROBERT F. PASTERNAK,* NORMAN SUTIN,* and DOUGLAS H. TURNER, Departments of Chemistry, Ithaca College, Ithaca, New York 14850, Brookhaven National Laboratory, Upton, New York 11973, and University of Rochester, Rochester, New York 14627.

Table I: The values of k_{-1} and k_2 presented in Table I were obtained from the experimental values of k_1 and k_{-1}/k_2 subject to the constraints that $k_1/k_{-1} \leq 4 \times 10^{-2}$ (otherwise a significant concentration of the nonplanar free-base form would be present) and $k_2 \leq 5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ (which is a reasonable upper limit for proton addition to the nonplanar free-base form under the conditions used).

Synthesis of Trichloroacetamido-1,3-dienes. Useful Aminobutadiene Equivalents for the Diels-Alder Reaction [*J. Am. Chem. Soc.*, **98**, 2352 (1976)]. By LARRY E. OVERMAN* and LANE A. CLIZBE, Department of Chemistry, University of California, Irvine, California 92664.

The stereochemical assignment for the major diene (kinetic preference 98:2) formed from thermolysis of the trichloroacetimidic ester of 3-buten-2-ol is incorrect in the original communication. The diene thus produced is (*Z*)-1-trichloroacetamido-1,3-butadiene. This stereochemical assignment was obvious (^1H and ^{13}C NMR, UV) when both stereoisomers became available. Treatment of the kinetically produced *cis* isomer with triethylamine (0.2 M in dioxane, 110 °C, 30 min) yielded an 85:15 equilibrium mixture of the *trans* and *cis* isomers, respectively. Geometrical isomerization also occurs in dioxane at 110 °C in the absence of triethylamine, although much more slowly. As a result, the Diels-Alder reactions reported in eq 2, in fact, do involve primarily the cycloaddition of the *trans* isomer. The preformed *trans* isomer, however, is more reactive than would be indicated in eq 2. For example, (*E*)-1-trichloroacetamido-1,3-butadiene reacts cleanly with acrolein within 4 h at 110 °C to afford **7** (95% isolated yield, a 5:1 mixture of *cis* and *trans* stereoisomers). Details of the stereochemical assignments and the mechanistic implications of the observed kinetic preference for forming the less stable *cis* isomer will be discussed in the subsequent full paper.

Molecular Orbital Studies of the Protonation of the Methylanisoles [*J. Am. Chem. Soc.*, **98**, 4061 (1976)]. By RAYMOND S. GREENBERG, MAURICE M. BURSEY,* and LEE G. PEDERSEN, William Rand Kenan, Jr.,* Laboratories of Chemistry, The University of North Carolina, Chapel Hill, North Carolina 27514.

A geometry error for the neutrals has been corrected. Energy values should be: *o*-methylanisole, -378.88438 au ; *m*-methylanisole, -378.88514 ; *p*-methylanisole, -378.88421 . The uncorrected proton affinities, by comparison with the energies of the most stable protonated forms, are 245.3, 249.7, and 246.7 kcal/mol, respectively. As the text indicates, these values must be expected to be larger than experimental values. We thank Professor Warren J. Hehre for pointing out the discrepancy in our original results.

Application of ^{13}C Nuclear Magnetic Resonance Spectroscopy to the Analysis of Charge Distribution Patterns in Unsaturated Carbonyl-Containing Compounds [*J. Am. Chem. Soc.*, **98**,

4571 (1976)]. By MELANIE J. LOOTS, LINDA R. WEINGARTEN, and RONALD H. LEVIN,* Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138.

S. Berger and A. Reiker [*Chem. Ber.*, **109**, 3252 (1976)] have recently reversed their earlier ^{13}C NMR assignments for the two olefinic carbon atoms in *o*-quinone. Therefore, the chemical shifts for C(4) and C(6) for *o*-quinone, presented in Table III of our paper, should be interchanged. The corresponding annulene correction factors now become +6.9 and +8.8, respectively, and the predicted shifts in Chart II for the parent [5]annulene become 143.8 [C(2)] and 117.5 [C(4)]. As the *o*-quinone chemical shifts have simply been interchanged, there is no effect upon Z_{Σ}^{π} for cyclopentadienone.

Nuclear Magnetic Resonance in Pulse Radiolysis. Chemically Induced Dynamic Nuclear Polarization [*J. Am. Chem. Soc.*, **98**, 6067 (1976)]. By A. D. TRIFUNAC,* K. W. JOHNSON, and R. H. LOWERS, Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439.

The caption for Figure 1 on p 6067 is incorrect. The correct caption is:

Figure 1. Pulse radiolysis of mixtures of methanol and sodium acetate in D_2O : acetate 2.44 M (A-E); methanol 0.10 M (A), 0.25 M (B), 0.40 M (C), 0.84 M (D), 1.98 M (E).

Hydration of NH_4F [*J. Am. Chem. Soc.*, **98**, 6820 (1976)]. By PETER KOLLMAN* and IRWIN KUNTZ, Department of Pharmaceutical Chemistry, School of Pharmacy, University of California, San Francisco, California 94143.

After submission of this paper, some relevant information has come to our attention. J. O. Noell and K. Morokuma ("A Fractional Change Model in the MO Theory and Its Application to Molecules in Solutions and Solids", *J. Phys. Chem.*, **80**, 2675 (1976); this paper has a more detailed description of the methodology of ref 11 as well as more applications) pointed out that it is important to consider $\text{N}\cdots\text{F}$ variations in the distance in comparing the energies of the neutral H-bond $\text{H}_3\text{N}\cdots\text{HF}$ and the ion pair $\text{H}_3\text{N}^+\cdots\text{H}\cdots\text{F}^-$. We agree, but feel that our use of a fixed rather long ($R = 2.65 \text{ \AA}$) N-F distance, optimum for the neutral H-bonded structure will, like our neglect of correlation contributions and the neglect of three-body terms (see last part of section C), make it *harder* to form the *ion pair* compared to shorter N-F distances. For example, using the data from Figure 5 of ref 11 ($r(\text{H-F}) = 1.0 \text{ \AA}$ is the "neutral" species and $r(\text{N-H}) = 1.1 \text{ \AA}$ is "ion pair"), at $R(\text{N-F}) = 2.6 \text{ \AA}$, the energy difference (ionic-neutral) is about 7 kcal/mol; at $R(\text{N-F}) = 2.4 \text{ \AA}$, this difference is only 3 kcal/mol. The relatively crude basis set used here will, compared to a more accurate basis, have an error of the opposite sign (easier to form ion pair). The error introduced by lack of variation of the N-F distance is similar to the correlation errors, many-body errors, basis-set errors, or the necessarily limited search of the other geometrical variables for the NH_4F hydrate; this restriction will tend to make the transition from neutral \rightarrow ionic occur at a *larger* hydration number than it would if one varied $R(\text{N}\cdots\text{F})$. Whether the proton potential has a single or double well (Figure 1) will, on the other hand, be sensitive to variation of $R(\text{N}\cdots\text{F})$ so our calculations cannot be taken as evidence for the "existence" of a double-well po-

tential. In fact, the results of ref 11 suggest that there is no "double well". However, the dramatic *change* in the IR spectra we predict for $\text{H}_3\text{N}\cdots\text{H}-\text{F}$ as a function of amount of H_2O is not dependent on whether the resulting "ionic" NH_4^+F^- will have a single or double proton well.

Experimental work relevant to this study was discussed by Herschbach (D. Herschbach, Lecture at 2nd International Congress of Quantum Chemistry, New Orleans, La., April

1976). He pointed out that in crossed beams of NH_3 and HI , an ion pair was formed only when one additional NH_3 was present. This is analogous to our theoretical study, except: (1) Herschbach used HI , a stronger acid than HF ; and (2) he used NH_3 rather than H_2O as solvent. The elucidation of the solvation "forces" required for creating ion pairs thus appears to be a fruitful area for combined theoretical and experimental investigations.

Book Reviews

Principles of Electrochemical Machining. By J. A. MCGEOUGH. Wiley/Halsted, New York, N.Y. 1974. 255 pp. \$18.75.

This book is a highly specialized one which deals with a new electrochemical process of interest to all engineers. The process of electrochemical machining incorporates two fundamental fields, fluid dynamics and electrochemical engineering, in a very exciting fashion. To the conventional electrochemist it is quite a surprise to find out that the process of electrochemical machining is operating under current densities of 50 A/cm^2 , whereas most electrochemists are accustomed to rates in the order of $\mu\text{A/cm}^2$ and mA/cm^2 . The amazing thing is that the same principles hold in general although the rates of the electrochemical reactions are increased by a factor of up to sixfold. Fluid dynamics is of utmost importance in electrochemical machining because of its role in the removal of heat and mass during the high rate of metal dissolution.

The first 83 pages of the book are dedicated to fundamental review of fluid dynamics and electrochemistry. These reviews are well written and contain important fundamental material. It is not recommended that a newcomer into this field start from this brief review; however, the introductory review is suitable for merging various backgrounds of readers into a common starting point. The second half of the book deals with the technology and research of electrochemical machining. The types of metals, electrolytes, and the dynamics and kinematics of the process are discussed in detail. The last three chapters cover the practical aspects of electromachining: smoothing, shaping, mechanical properties, irregularities, cathode design, and flow patterns. Examples from industrial practice are brought up in the last chapter. The subject index is very useful and the pictures, especially from the studies of Muller, Tobias, and their coworkers, are educational.

In conclusion, this book is well written and incorporates together electrochemistry and fluid dynamics. Its main contribution, beside covering the process of electrochemical machining, is the demonstration that combining two fields can result in significant progress and in this particular case achieving current densities that were unheard of only a few years back.

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The Alkaloids. Chemistry and Physiology. Volume XV. Edited by R. H. F. MANSKE (University of Waterloo). Academic Press, Inc., New York, N.Y. 1975. xv + 315 pp. \$39.50.

For more than 25 years, natural products chemists and those interested in the biological properties of secondary plant metabolites have relied on the series "The Alkaloids" by Manske to help them keep pace with progress in the alkaloid field. This latest offering in the series, written in six chapters by authors active in the field of alkaloid research, surely will find similar use.

The volume is arranged according to botanical origin rather than structural type. However, within each chapter, the alkaloids are subdivided into structural classes. Structure elucidation, transformations, synthesis, biosynthesis, and varied coverage of biological properties are given attention.

Chapter 1 brings us up to date on the ergot alkaloids, which were last treated in Volume VIII. Concentrated coverage is given to the peptide alkaloids of lysergic acid and the complex state of biosynthesis.

Alkaloid chemists will welcome, in particular, Chapter 2, "The Daphniphyllum Alkaloids" since this contribution represents the first summary review of these triterpenic alkaloids. The chapter is rich in spectral data and the chemical transformations needed for structure distinction.

Chapter 3 covers the "Amaryllidaceae Alkaloids" and is the longest. Regrettably, the author's style is not always conducive to ready comprehension, and the nonexpert will find annoying the lack of numbering in diverse structures. This criticism aside, the coverage is valuable, continuing earlier treatment of these alkaloids in Volumes II, VI, and XI.

Chapter 4, entitled "The Cyclopeptide Alkaloids", is neatly organized and is easily read, the latter being a tribute to the Editor who translated the original German version. "The Pharmacology and Toxicology of the Papaveraceae Alkaloids" is offered in Chapter 5. The treatment is extensive and thorough as attested by the 691 references, the oldest from 1804, for 36 pages of text. Finally, as is characteristic of recent volumes in the series, the last chapter is committed to alkaloids of unclassified and unknown structure.

"The Alkaloids", according to the Preface, "attempts to review timely topics related to alkaloids". Overall, this volume has succeeded.

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Flame-Retardant Polymeric Materials. Edited by MENACHEM LEWIN (Israel Fiber Institute), S. M. ATLAS (Bronx Community College, CUNY), and ELI M. PEARCE (Polytechnic Institute of New York). Plenum Press, New York, N.Y. 1975. xii + 457 pp. \$45.00.

The editors state that the objectives of this series are varied, and the contributed chapters in this volume show this variability mainly in the depth of coverage given to the respective topics. Fairly extensive chapters dealing with the flameproofing of cellulose (which places much emphasis on test methods for fabrics), polyamides, and organic coatings are not quite balanced by the briefer coverage given to poly(ethylene terephthalate) or rubber flameproofing. Other chapters concern general aspects of polymer combustion and the flameproofing of protein fibers, polyurethanes, and thermoset resin systems. A treatise by C. P. Fenimore on the candle-type test for polymers is also included.

The editors are to be commended for stressing attention to chemical mechanisms of polymer degradation, combustion, and fire retardation. The varying degrees to which this goal has been met reflect, perhaps, the status of these investigations. Good mechanistic discussions were found in the chapters on polyurethanes, polyamides, and resin systems.

Since the references are generally current through 1973, this volume updates some of the discussion found in Lyons' earlier work. Whether intentional or not, this volume also appears to be directed to an area of interest not emphasized in other recent books in this field, namely the fiber-forming polymers. As a result, it should have particular appeal to scientists involved with fabric flammability.

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The Firestone Tire & Rubber Company