

Additions and Corrections

The Stereochemistry of 9-Decalyl Free Radicals [*J. Amer. Chem. Soc.*, **87**, 2590 (1965)]. By PAUL D. BARTLETT,* RICHARD E. PINCOCK, JOHN H. ROLSTON, W. G. SCHINDEL, and L. A. SINGER, Department of Chemistry of Harvard University, Cambridge, Massachusetts 02138, and of the University of British Columbia, Vancouver 8, British Columbia.

In Table II, the column headings *cis* and *trans* should be interchanged.

Oxygen and Sulfur Chemistry of Methyltrifluoromethylphosphines [*J. Amer. Chem. Soc.*, **92**, 1901 (1970)]. By ANTON B. BURG* and DAE-KI KANG, Department of Chemistry, University of Southern California, Los Angeles, California 90007.

Dr. R. G. Cavell has noticed in our ^{19}F nmr spectra some discrepant chemical shifts, for the measurement of which the reference side bands were indeed misjudged by multiples of 21 ppm. Table I presents the

Table I. Revised Nmr Parameters for $\text{CH}_3\text{CF}_3\text{P}$ Compounds

Compd (R = $\text{CH}_3\text{CF}_3\text{P}$)	δ_{F} (J)	δ_{P} (J)	δ_{H} (J)
RCl	68.5 (73)	-76.2 (73.6)	1.5 (10, 40.5)
RI	61 (60)	-20.6 (59.6)	2.3 (11, 40.4)
ROCH ₃	71.4 (68)	-118.6 (68.7, 13.6, 6.8)	1.0 (6.8) 3.0 (13.5)
ROC(CH ₃) ₃	71.6 (74)	-93.0 (73.6)	1.01 (6.8, 40.64) 1.02 (0.59)
RSCH ₃	64.1 (65)	-11.3 (65, 12.8, 7.3)	1.3 (7.3) 2.1 (12.7)
RSC(CH ₃) ₃	63 (67)	-7.7 (66, 7.7)	1.21 (7.7, 40.4) 1.19 (0.9)
HRO	75.7 (91)	34.7 (90, 2515)	1.4 (15.7) 6.9 (516, 45.4, 43.4)
DRO	76 (92)		
CH ₃ RO	76 (84, 70.8)	-38.6 (83, 713.8)	2.0 (13.9, 40.8)
CH ₂ RS	75 (85)	-44.3 (84, 713.8)	1.9 (13.8)
R-R	53.2, 54.7	22.1, 30.1	1.2 asymm
RSR	61.8, 62.3		1.7 asymm
RSR-d ₈	61.6, 62.1	-27 ("36")	

results of a thorough restudy, with amended or additional results as well as corrected values. The chemical shifts (δ , ppm) were measured by substitution (HA-100, HR mode), upfield from Cl_3CF or H_3PO_4 , or downfield from TMS. The coupling constants (J , sec^{-1}) are given in parentheses, and refer to doublets for ^{19}F or ^1H and to quartets for ^{31}P , unless otherwise specified by superscripts. For the R-R and RSR compounds, the δ values represent optical and meso isomers; for J values, cf. D-K. Kang, *et al.*, *Org. Magn. Resonance*, 101 (1971).

The observed wide range of δ_{P} is not unusual. Most of the δ_{H} values are averages of old and new data, probably with smaller systematic errors arising from diamagnetism.

Photochemical Reactivity of Some Benzoylthiophenes. I. Electronic Absorption and Emission Spectra [*J. Amer. Chem. Soc.*, **95**, 4599 (1973)]. By D. R. ARNOLD* and R. J. BIRTWELL, The Photochemistry Unit, Department of Chemistry, University of Western Ontario, London, Ontario, Canada, N6A 3K7.

Errors which occur in Tables I and II are corrected here.

Table I. Chemical Shifts (ppm) and Coupling Constants (Hz) for the Protons on Thiophene of Some 2-Benzoylthiophenes

	Ia (X = H)	Ib (X = OCH ₃)	Ic (X = CN)
H ₃	7.59	7.60	7.61
H ₄	7.14	7.11	7.18
H ₅	7.64	7.62	7.78
J _{3,4}	4.0	4.0	4.0
J _{3,5}	1.5	1.2	1.2
J _{4,5}	5.0	5.0	4.2

Table II. Chemical Shifts (ppm) and Coupling Constants (Hz) for the Protons on Thiophene of Some 3-Benzoylthiophenes

	IIa (X = H)	IIb (X = OCH ₃)	IIc (X = CN)
H ₂	7.86	7.86	8.18
H ₄	7.56	7.54	7.77
H ₅	7.31	7.33	7.76
J _{2,4}	1.4	1.5	1.4
J _{2,5}	3.0	3.3	3.3
J _{4,5}	5.2	5.0	5.4

Properties of the [4]Annulene System. Induced Paramagnetic Ring Current [*J. Amer. Chem. Soc.*, **95**, 8481 (1973)]. By S. MASAMUNE,* NOBUO NAKAMURA, M. SUDA, and H. ONA, Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada.

On page 8482, column 2 line 4 from bottom, "1.22 (18 H) and 1.05 (9 H)" should be replaced by "1.12 (9 H) and 1.05 (18 H)." Table I should be corrected accordingly.

The Photochemistry of 3-Alkylidenecyclohexanones. The Role of Olefin Geometrical Isomerization in the Triplet-State Reactivity of β,γ -Unsaturated Ketones [*J. Amer. Chem. Soc.*, **96**, 1158 (1974)]. By KENNETH G. HANCOCK* and RONALD O. GRIDER, Department of Chemistry, University of California at Davis, Davis, California 95616.

In Table I, Φ_{direct} and Φ_{quenched} for $9 \rightarrow 4$ should read 0.08 (and not 0.18 as reported).

Photoequilibrium ratios predicted by eq 1 using quantum yields from Table I and ϵ_{300} 's from Table II were within ca. 5% (and not 2% as reported) of ratios observed at 300 nm.

The statement following structure 26 on page 1164 should be deleted and replaced with: "The ordering of the quantum yields ($14 \rightarrow 5 > 5 \rightarrow 14$, but $4 \rightarrow 9 >$

9 → 4) suggests competition of two opposing effects. α -Methylation enhances α cleavage [note P. S. Engel, *et al.*, *J. Amer. Chem. Soc.*, **96**, 924 (1974)], so $\Phi_{4 \rightarrow 9} > \Phi_{9 \rightarrow 4}$ for the 1,3-shift, but the 14 → 5-(*E*) stereoselectivity suggests stereochemical preference for acyl migration across the molecular face less encumbered with methyl groups."

Organosulfur Chemistry. II. Highly Stereoselective Reactions of 1,3-Dithianes. "Contrathermodynamic" Formation of Unstable Diastereoisomers [*J. Amer. Chem. Soc.*, **96**, 1807 (1974)]. By ERNEST L. ELIEL,* ARMANDO A. HARTMANN, and ANTHONY G. ABATJOGLOU, William Rand Kenan, Jr., Laboratories of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514.

On page 1810, first column, 10 lines from bottom, for "3600 cm⁻¹ in 5a" read "3600 cm⁻¹ in 4a and 3529 cm⁻¹ in 5a."

Stereochemistry of Chloride Displacement from Silacyclobutanes [*J. Amer. Chem. Soc.*, **96**, 2637 (1974)]. By B. G. MCKINNIE, N. S. BHACCA, F. K. CARTLEDGE,* and J. FAYSSOUX, Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803.

Due to a misprint in the original literature and misinterpretation on our part, we have misrepresented the

structural assignments originally made by others for 1-chloro-1,2-dimethylsilacyclobutane and 1,2-dimethylsilacyclobutane on the basis of proton nmr. Our assignments are in fact in complete accord with those made earlier and presented in complete form by J. Dubac, P. Mazerolles, and B. Serres, *Tetrahedron*, **30**, 749, 759 (1974).

Static Structure of the Fluxional Molecule B₅H₉[P(CH₃)₃]₂, an Isoelectronic Analog of B₅H₁₁²⁻ [*J. Amer. Chem. Soc.*, **96**, 3013 (1974)]. By A. V. FRATINI, G. W. SULLIVAN, M. L. DENNISTON, R. K. HERTZ, and S. G. SHORE,* Department of Chemistry, Ohio State University, Columbus, Ohio 43210.

The positions of the two-center and three-center bonds in the topological structures shown in the equilibrium on page 3014 should be reversed.

Reversible Binding of Dioxygen to Mesoporphyrin IX Derivatives at Low Temperatures. [*J. Amer. Chem. Soc.*, **96**, 5600 (1974)]. By JOSEPH ALMOG, JACK E. BALDWIN,* ROBERT L. DYER, JOEL HUFF, and CARLOS J. WILKERSON, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.

The date the manuscript was received by the Editor was inadvertently omitted in publication. The manuscript was received May 4, 1974.

Book Reviews

Unimolecular Reactions. By P. J. ROBINSON (University of Manchester Institute of Science and Technology) and K. A. HOLBROOK (The University of Hull). Wiley-Interscience, New York, N. Y. 1972. xvii + 371 pp. \$19.95.

This book is a must for anyone whose interests lie in the area of unimolecular reactions. This would include advanced students as well as research specialists. In fact, if one were limited to one book on a subject, this book would be my choice for the subject of unimolecular reactions. Although the emphasis of this book is on recent developments, especially Rice-Ramsperger-Kassel-Marcus (RRKM) theory, a clear discussion of historical developments is given in the first chapter. Chapters 2, 3, and 4 give excellent derivations of Slater theory and RRKM theory with emphasis on their basic differences. The fundamental nature of these differences has stimulated a large amount of experimental activity in the area of unimolecular reactions in the last few years.

Chapter 7 is also noteworthy in that it represents a rather extensive review of the experimental data on virtually every homogenous gas-phase unimolecular reaction known for neutral molecules. The remaining chapters deal effectively with several practical calculational details of RRKM theory as well as describing some of the important contributions made by studies of chemical activation systems as tests of various aspects of unimolecular reaction theory,

John W. Simons, *New Mexico State University*

Physical Chemistry of Organic Solvent Systems. Edited by A. K. COVINGTON and T. DICKINSON (University of Newcastle upon Tyne). Plenum Press, London and New York. 1973. x + 823 pp. \$30.00.

During the past four decades, great progress was made in understanding the behavior of electrolytes in aqueous solutions. With rapidly growing interest in nonaqueous and mixed solvents, the investigation of electrolytes has now entered a new and exciting phase. This excellent summary of the thermodynamic and kinetic

behavior of ionic solutes in organic solvent systems makes it evident that important discoveries concerning the nature of ion-solvent interactions are imminent and suggests that useful estimates of the properties of individual ionic species, such as medium effects, absolute entropies, and heat capacities, may be forthcoming in the near future.

This is the first monograph devoted in its entirety to the physical chemistry of organic solvent systems, and accordingly its impact on future directions of research will be considerable. Fortunately, it is exceedingly well done. Each of the chapters is written with authority and clarity and with a recognition of the pertinent literature through 1971. Although the contributors were 15 in number, the editors have been remarkably successful in achieving a uniformity of style that is rare in a work of this sort. Furthermore, serious instances of overlapping have been skillfully avoided.

The seven chapters are entitled "Introduction and Solvent Properties" (A. K. Covington and T. Dickinson), "Thermodynamic Measurements" (C. M. Criss, M. Salomon, R. Garnsey, J. E. Prue), "Acid-Base Behaviour" (E. J. King), "Spectroscopic Measurements" (I. R. Lantzke, D. E. Irish, T. E. Gough), "Conductance and Transference Numbers" (R. Fernandez-Prini, M. Spiro), "Reaction Kinetics and Mechanism" (D. W. Watts), and "Electrode Processes" (R. Payne, O. R. Brown). All are capably written and several are outstanding. Four of them consist of two to four parts, with different authorship, and most have substantial appendices. The chapter devoted to thermodynamic measurements, for example, comprises 103 pages of tabular data on solubilities, heats of solution, activity coefficients, solvation energies, and the like. This combination of theory with experimental results enhances greatly the value of the work.

Rigor in the theoretical treatment has been achieved without sacrifice of readability. This reviewer regards as particularly noteworthy the discussion by Criss and Salomon of single ion solvation and ionic entropies, King's brief description of the contributions of