

# Additions and Corrections

**Mass Spectral Studies of Alkaloids Related to Morphine** [*J. Am. Chem. Soc.*, **89**, 4494 (1967)]. By DESMOND M. S. WHEELER, THOMAS H. KINSTLE, and KENNETH L. RINEHART, JR., Department of Chemistry, University of Nebraska, Lincoln, Nebraska, and Department of Chemistry and Chemical Engineering, University of Illinois, Urbana, Illinois 61801.

In the Acknowledgment we should have thanked Dr. Y. Sawa, Shionogi Research Laboratory, Shionogi & Co. Ltd., for the samples of sinomenine and isosinomenine.

**The Photochemical Decomposition of Geminal Diazides. I. Dimethyl Diazidomalonate** [*J. Am. Chem. Soc.*, **89**, 5958 (1967)]. By ROBERT M. MORIARTY, JONATHAN M. KLIEGMAN, and CATHERINE SHOVLIN, Chemistry Department, The Catholic University of America, Washington, D. C.

We have recently described dimethyl diazidomalonate as being quite stable to shock. This was based upon rather qualitative observations. C. O. Parker, Rohm and Haas Co., Redstone Research Laboratories, Huntsville, Ala., has obtained the following more quantitative data on the stability of dimethylmalonamide and dimethyl diazidomalonate: (1) amide, mp 153° dec, 50% fire level was greater than 38 kg in.; (2) amide, mp 157° dec (crystallized from water), 50% fire level 2.8 kg in.; (3) amide, mp 153.5° dec, 60% fire level 4 kg in.; sample made from dibromomalonamide; (4) ester, extracted into CCl<sub>4</sub> but undistilled, clean H<sup>1</sup> nmr, 50% fire level 11.3 kg in.; (5) ester, distilled at 60° under vacuum, 20% fire level (one out of five samples) 4 kg in. RDX on above scale, 10.2 kg in.

Although the impact sensitivities of these compounds vary with their states of purity, these substances are clearly hazardous and proper caution should be exercised in handling them.

**A Mass Spectrometric Investigation of the Low-Pressure Pyrolysis of Diphosphine-4** [*J. Am. Chem. Soc.*, **89**, 6477 (1967)]. By T. P. FEHLNER, Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556.

The third equation on page 6480 should read

$$R = Sgbz$$

where  $z$  is the wall collision frequency.

The third equation on page 6481 should read

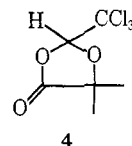
$$\log h(T) = 20.4 - 4800/T \text{ molecules cm}^{-2}$$

Finally, line 14 of paragraph 2 on page 6482 should read, "some three powers of ten..."

**Cycloaddition Reactions of 2,2-Dimethylcyclopropane** [*J. Am. Chem. Soc.*, **90**, 1926 (1968)]. By NICHOLAS J. TURRO, SIMON S. EDELSON, JOHN R. WILLIAMS, and THOMAS R. DARLING, Department of Chemistry, Columbia University, New York, New York 10027.

On page 1927, column 1, line 2, delete the word (reflux).

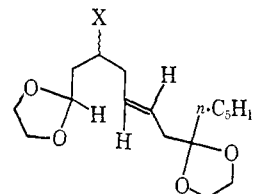
Structure 4 should appear as shown below.



4

**A New Total Synthesis of Prostaglandins of the E<sub>1</sub> and F<sub>1</sub> Series Including 11-Epiprostaglandins** [*J. Am. Chem. Soc.*, **90**, 3247 (1968)]. By E. J. COREY, ISIDOROS VLATTAS, NIELS H. ANDERSEN, and KENN HARDING, Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138.

The drawing of formulas 5 and 6 should be



**A Semiempirical Molecular Model for Cr(CO)<sub>6</sub>, Fe(CO)<sub>5</sub>, and Ni(CO)<sub>4</sub>** [*J. Am. Chem. Soc.*, **90**, 3366 (1968)]. By A. F. SCHREINER and THEODORE L. BROWN, Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois 61801.

In Table III, footnote *b* should read: C-O axial = 1.2886, C-O trigonal = 1.332.

Table IV contains a number of errors. The corrected table, in entirety, is printed below.

Table IV. Metal-Carbon Overlap Populations

Bond	Metal orbitals	—Overlap populations—	
		$\sigma$	$\pi$
Cr-C	3d	0.9696	0.7428
	4s	0.4416	...
	4p	0.5412	0.0808
Fe-C	3d	0.6300	0.5872
	4s	0.4672	...
	4p	0.4085	0.3032
Ni-C	3d	0.1386	0.1752
	4s	0.1700	...
	4p	1.062	0.0908

Table V contains a few corresponding errors. The corrected table is given below. The  $2p\pi$  (C) populations are given on a per orbital basis.

The M-C overlap population for Ni(CO)<sub>4</sub> in Tables III and VI should be changed to 0.4076.

The only conclusion which requires modification as a result of these corrections relates to the relative importance of metal 3d and 4p orbitals in  $\pi$  bonding. It now appears that the 3d orbitals, in sum (Table IV), are more important in bonding in all three compounds,

**Table V.** Overlap Populations of Metal and Carbon Orbitals in M-C and C-O Bonds, Respectively, of Cr(CO)<sub>6</sub> and Ni(CO)<sub>4</sub>

Bond	Orbital	$\sigma$	$\pi$
Cr-C	3d ( $e_g$ )	0.4848	...
	3d ( $t_{2g}$ )	...	0.2476
	4s	0.4416	...
	4p	0.1804	0.0268
C-O	2p $\sigma$ (C)	0.4327	...
	2p $\pi$ (C)	...	0.3029
	2s (C)	0.3335	...
Ni-C	3d ( $e$ )	...	0.0444
	3d ( $t_2$ )	0.0288	0.0293
	4s	0.2008	...
	4p	0.3538	0.0303
C-O	2p $\sigma$ (C)	0.4260	...
	2p $\pi$ (C)	...	0.3685
	2s (C)	0.4265	...

although their *relative* importance is very great only for the octahedral Cr(CO)<sub>6</sub>.

If the CO assignment of L. H. Jones and R. S. McDowell, *Spectrochim. Acta*, **20**, 248 (1964), is chosen for Fe(CO)<sub>5</sub>,  $\bar{\nu}_{CO}$  of Table VI becomes 2025 cm<sup>-1</sup>, which leads to better agreement with the calculated results. Recent work in our laboratories supports the Jones and McDowell assignment.

**The Molecular Geometry of Vanadyl Deoxyphyloerythroetioporphyrin. An Analog of Chlorophyll [J. Am. Chem. Soc., **90**, 3873 (1968)].** By ROGER C. PETTERSEN and LEROY E. ALEXANDER, Mellon Institute, Pittsburgh, Pennsylvania 15213.

In Table I, under Ring D the atoms of the last three bonds should be carbons instead of nitrogens. Thus, they should read C(16)-C(17), C(17)-C(18), and C(18)-C(19). In the same table, under Ring E the fourth bond should read C(28)-C(29).

## Book Reviews

**Enzyme Kinetics. Open and Closed Systems.** By CHARLES WALTER, University of Tennessee at Memphis. The Ronald Press Co., 15 East 26th St., New York, N. Y. 1966. vi + 102 pp. 15.5 × 23.5 cm. \$7.00.

It is a pity that the author has chosen such a general title for this small book, because readers may expect to find in it a general and balanced account of the field of enzyme kinetics. They will be disappointed, since the book treats only a very narrow aspect of the subject, namely the mathematical treatment of some of the kinetic equations that are relevant to enzyme systems.

An author certainly has a right, indeed a duty, to circumscribe his subject matter, but one expects him to deal with his chosen area in a reasonably comprehensive manner. One cannot see that this has been done in the present book, and indeed one is tempted to wonder whether the author is well versed in the literature of his subject. To give one example, on pages 42-44 he gives an account of the early-stage kinetics of enzyme systems involving two intermediates (*e.g.*, a Michaelis complex and an acyl enzyme) but makes no reference to the explicit solution of this problem given in 1959 by Stewart and Ouellet.

The effects of modifiers (activators and inhibitors) have led to valuable conclusions about enzyme mechanisms, and one finds in this book an account of the steady-state kinetics of enzyme-substrate-modifier systems as applied to the case of a single intermediate. However, it has been realized for several years that for a large group of enzymes it is unsatisfactory to neglect the interaction between the modifier and a second intermediate, such as the acyl enzyme; indeed the whole question of whether a modifier is competitive or noncompetitive can only be interpreted in terms of the two intermediates. In view of this important matter, it is surprising to find no reference to the situation. The absence of any reference to pH effects is also a serious deficiency in a book of this kind.

One finds in this book a rather formal account of the mathematical treatment of a limited number of systems, with an indication in some cases of how the experimental results can be analyzed on a computer. These cases are dealt with correctly, and research workers who happen to be involved with experimental problems to which the equations apply will find it useful to have the solutions available in this book. They will, however, often be disappointed by not finding what they want, even in the case of treatments of other systems to be found in the literature. It would have been helpful if the author had at least given references to the other treatments; relatively few references are in fact included in the present book, and there are many obvious omissions.

In view of its incompleteness, and of the fact that it does not give a balanced view of enzyme kinetics, this book could hardly be recommended to those who have not already found their way in the tangled field of enzyme kinetics; those who have may find it to be of some, if limited, use.

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## BOOKS RECEIVED, August 1968

- MELVIN CALVIN and MARGARET J. JORGENSEN. "Readings from Scientific American. Bio-Organic Chemistry." W. H. Freeman and Co., 660 Market St., San Francisco, Calif. 1968. 317 pp. \$10.00.
- MARGARET O. DAYHOFF and RICHARD V. ECK. "Atlas of Protein Sequence and Structure 1967-68." National Biomedical Research Foundation, 11,200 Lockwood Dr., Silver Spring, Md. 1968. 356 pp. \$6.00.
- ELVIN A. KABAT. "Structural Concepts in Immunochemistry." Holt, Rinehart and Winston, Inc., 383 Madison Ave., New York, N. Y. 1968. 310 pp. \$10.50.
- NOËL LOZAC'H. "la Nomenclature en Chimie Organique." Masson et Cie., 120 Boulevard Saint-Germain, Paris, France. 1967. 296 pp. 103 F.
- KAROL MAICHEL. "Guide to Russian Reference Books." Volume V. "Science, Technology and Medicine." Publications Department, Hoover Institution, Stanford University, Stanford, Calif. 1968. 384 pp. \$22.50.
- J. PERDIJON. "L'Analyse par Activation. Traitement des Informations en Spectrométrie Gamma Après Irradiation aux Neutrons." Masson et Cie., 120 Boulevard Saint-Germain, Paris, France. 1967. 156 pp. 68 F.
- ACADEMICIAN N. N. SIROTA, Editor. "Chemical Bonds in Semiconductors and Thermodynamics." Plenum Publishing Corp., 227 West 17th St., New York, N. Y. 1968. 255 pp. \$27.50.