

subsequently trapped by reaction with the nucleophilic phosphine; the possibility remained, however, that the ethylidene complex  $10^+$  was the initial product of hydride abstraction and that it was subsequently converted to  $9^+$  by an intramolecular hydride transfer (Scheme III). This ambiguity was resolved by reacting  $[W(\eta-C_5H_5)_2(CD_3)_2C_2H_5]PF_6$  with  $Ph_3C^-$  in the presence of  $PMe_2Ph$ . The exclusive isolation of  $[W(\eta-C_5H_5)_2(CD_2PMe_2Ph)C_2H_5]PF_6$  ( $^1H$  NMR, Scheme II) showed that hydride abstraction occurred solely from the methyl group to form  $9^+$ .

Since  $\alpha$ -H atom abstraction from the paramagnetic alkyl  $8^+$  is facile, the transition state leading to  $9^+$  is probably stabilized by significant development of the metal-carbon  $\pi$  interaction;<sup>17</sup> this would not be surprising in light of recent NMR evidence for ground-state spin delocalization via metal-carbon  $\pi$  interactions in paramagnetic vanadium alkyls.<sup>18</sup> Such delocalization may

(17) This could explain the formation of the methylidene complex  $9^+$  in preference to the ethylidene  $10^+$ . The ethylidene ligand in the isoelectronic molecule  $[Ta(\eta-C_5H_5)_2(CHCH_3)CH_3]$  is unable to achieve the electronically optimal orientation for  $\pi$  overlap as a result of unfavorable steric interactions with the rings: (a) Sharp, P. R.; Schrock, R. R. *J. Organomet. Chem.* **1979**, *171*, 43 and references therein. (b) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729. (c) Goddard, R. J.; Hoffmann, R. *Ibid.* **1980**, *102*, 7667.

generally facilitate  $\alpha$ -H atom abstraction from paramagnetic transition-metal alkyls, and we suggest that the methyl selectivity observed for hydride abstraction from **6** by an electron-transfer/hydrogen atom transfer mechanism reflects an intrinsic  $\alpha$  selectivity in the second step.<sup>19</sup>

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**Registry No.** 1-PF<sub>6</sub>, 72427-27-1; 3-BF<sub>4</sub>, 82917-93-9; 4, 39333-53-4; 5, 73210-66-9; 6, 82917-94-0; 7-BF<sub>4</sub>, 63469-56-7; 7-PF<sub>6</sub>, 53806-23-8; 8-PF<sub>6</sub>, 82917-96-2; 11-PF<sub>6</sub>, 82917-98-4; Ph<sub>3</sub>C BF<sub>4</sub>, 341-02-6; Ph<sub>3</sub>C PF<sub>6</sub>, 437-17-2; Ph<sub>3</sub>C<sup>+</sup>, 2216-49-1;  $[W(\eta-C_5H_5)_2(CD_3)_2C_2H_5](PF_6)$ , 82918-00-1;  $[W(\eta-C_5H_5)_2(CD_2PMe_2Ph)(C_2H_5)](PF_6)$ , 82918-02-3; EtBr, 74-96-4; P Me<sub>2</sub> Ph, 672-66-2.

(18) Köhler, F. H.; Hofmann, P.; Prössdorf, W. *J. Am. Chem. Soc.* **1981**, *103*, 6359.

(19) Definitive demonstration of  $\alpha$  regioselectivity in this system will require the observation of ethylidene formation from a substrate such as  $[W(\eta-C_5H_5)_2(C_2H_5)_2]$ . The synthesis of this molecule is currently being attempted in these laboratories.

## Additions and Corrections

**Absolute Stereochemistry of Palytoxin** [*J. Am. Chem. Soc.* **1982**, *104*, 3776]. R. E. MOORE,\* G. BARTOLINI, J. BARCHI, A. A. BOTHNER-BY, J. DADOK, and J. FORD.

Page 3777: In the structural formula of palytoxin (**1**), there should be a heavy dot on C(70), C(101), C(113), and C(115) to indicate the absolute stereochemistries shown by degradation products **2** and **12-16**.

Page 3779, column 1, lines 6, 11, 13, 16, 26, and 27: The *R* and *S* designations in these lines should read—16*R*,17*R*,19*R*,20*S*,21*R*,22*S*,23*S*,24*S*,25*S*,26*R*,27*R*,28*S*;... 34*S*,36*R*,37*R*,39*S*,41*S*,49*S*...; ...49*S*,51*R*,52*S*,53*R*,54*R*,55*S*...; 76*R*,77*R*,78*S*,79*S*,81*S*...; 96*S*,97*R*,98*S*,99*R*,101*R*,102*S*,103-*R*,104*R*,105*R*,108*R*,109*R*,111*S*,113*R*,115*S*,116*R*,119*R*,120*R*,122*S*...

## Book Reviews

**Operational Organic Chemistry.** By John W. Lehman (Lake Superior State College). Allyn and Bacon, Inc., Boston, Mass. 1981. xi + 671 pp. \$20.95.

This reviewer knows of no currently available textbook for the undergraduate course in laboratory organic chemistry that he would prefer to adopt over "Operational Organic Chemistry". An examination of the excellently prepared index reveals that this book covers the material most organic chemistry laboratory teachers would want it to cover. The experiments are varied and range from familiar ones to advanced research projects. The last part of the book is a collection of 36 essays describing the experimental operations used in the organic chemistry laboratory. These essays will make this textbook useful as a reference after the laboratory course is over.

The chemistry department chairman at a large state university was quoted in the November 23, 1981, issue of *Chemical and Engineering News* as saying "that real costs for chemicals and glassware have doubled over the past 2 years and the chemistry department is used as an example of how badly things are inflating". Therefore, those who adopt Lehman's text will be pleased to find that the experiments were chosen because they use moderate quantities of comparatively inexpensive chemicals and only require the glassware in a typical 19/22 organic lab kit. As in most modern laboratory manuals, safety is strongly emphasized throughout the text and while hazardous chemicals are used in some of the experiments,

the hazards are clearly pointed out to the students.

The students in the organic chemistry laboratory course in the reviewer's department have been using this laboratory textbook since the beginning of the 1981 Fall quarter. A poll of the students finds that they have a high opinion of the book. The teaching assistants (who are familiar with other laboratory texts) agree that "Operational Organic Chemistry" is excellent.

David H. Kenny, Michigan Technological University

**Food Chemicals Codex. Third Edition.** Committee on Codex Specifications, Food and Nutrition Board, National Research Council. National Academy Press, Washington, D.C. 1981. xxxi + 735 pp. \$45.00.

This volume provides revised and updated specifications and test methods for the 663 food-grade substances included in the previous edition plus 113 new entries. Infrared spectra for about 400 substances are included, together with guidelines for "good manufacturing practice".

This edition also contains a description of the procedures for developing and revising CODEX specifications and a tabular section of specifications for flavor aromatic chemicals and isolates.

This latest edition should continue to be of value to a variety of food technologists and others who have an interest in the quality and purity of food-grade substances.

William C. Kuryla, Union Carbide Corporation