

the oxathietane to form the olefin requires a much higher activation energy (39.1 kcal/mol).

Another relevant point concerns the relative stability of the various oxygenated compounds. The formation of cyclic intermediates and final products are much more exothermic for phosphorus than for sulfur. This fact is probably related to the larger oxygen affinity for phosphorus than for sulfur.

**Corey-Chaykovsky-Type Reaction.** Preliminary results are given on Figure 1. Transition states for the oxirane formation have been located at the STO-3G\* level and recalculated with the 4-31G\* basis. Both structures can be viewed as intramolecular S<sub>N</sub>2 transition states.<sup>16</sup> No minima have been located around these saddle points. This suggests that the trans betaines are transition structures (at least in the absence of solvent effects) and not intermediates as often proposed.

The activation energy for the sulfur is found lower than for the phosphorus. This can be understood in term of a better leaving group ability for the sulfide than for the phosphine.

Finally, our description does not support some aspects of the

conventional representations of the Wittig and Corey-Chaykovsky reactions. In the Wittig-type reactions, no zwitterionic structures (cis betaines) have been located on the reaction path. In the Corey-Chaykovsky-type reactions, the open structures look like trans betaines but correspond to saddle points and not minima on the potential energy surface.

Full details of the calculations will be given in a forthcoming paper.

**Acknowledgments.** The calculations were done at the computer centers of Orsay (CIRCE), Palaiseau (CCVR) (France), the University of Michigan, and the Institute of Molecular Science at Okazaki (Japan). We thank these computer centers for a generous allocation of computing time. We are grateful to Professor Nguyen Trong Anh, K. Morokuma, and Dr. F. Delbecq for their suggestions and stimulating discussions. O. Eisenstein thanks the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their financial support. The stay in Japan was made possible by a Rackham Research and Fellowship Grant (O.E.).

(16) The  $\angle\text{CCO}$  angle is  $91.6^\circ$  in the case of phosphorus and  $96.7^\circ$  in the case of sulfur. The  $\angle\text{PCC}$  angle is  $121^\circ$ , and the  $\angle\text{SCC}$  angle is  $130^\circ$ .

Registry No. H<sub>3</sub>P=CH<sub>2</sub>, 36429-11-5; H<sub>2</sub>S=CH<sub>2</sub>, 63933-47-1; H<sub>2</sub>CO, 50-00-0.

## Additions and Corrections

**<sup>13</sup>C-<sup>1</sup>H Coupling Constants in Carbocations. 4. Conformations of Internal Cyclopropylcarbinyl Cations (Benzobicyclo[4.1.0]heptyl Cations) and Their Rearrangements to Naphthalenium Cations** [*J. Am. Chem. Soc.* **1984**, *106*, 687]. DAVID P. KELLY,\* D. RALPH LESLIE, and BRADLEY D. SMITH

Page 693: The <sup>13</sup>C NMR assignments for compound **29** refer to a numbering scheme different from that given on structure **29** (p 692). The entry under **29** should read as follows: <sup>13</sup>C NMR  $\delta$  10.2 (t,  $J = 164$  Hz, C<sub>7</sub>), 26.6 (d,  $J = 169$  Hz, C<sub>1</sub>), 27.2 (q,  $J = 126$  Hz, CH<sub>3</sub>), 28.7 (d, d,  $J(\text{av}) = 121$  Hz, C<sub>4</sub>), 30.0 (q,  $J = 124$  Hz, CH<sub>3</sub>), 30.4 (d,  $J = 164$  Hz, C<sub>6</sub>), 30.4 (t,  $J = 127$  Hz, C<sub>3</sub>), 33.2 (s, C<sub>5</sub>), 209.0 (s, C<sub>2</sub>); etc.

**Stepwise Metal-Assisted Oxidative Decarboxylation of Vanadium(V) Ethylenebis(*o*-hydroxyphenyl)glycine). Isolation of a Possible Intermediate** [*J. Am. Chem. Soc.* **1984**, *106*, 3360]. VINCENT L. PECORARO, JOSEPH A. BONADIES, CARL A. MARRESE, and CARL J. CARRANO\*

Page 3361, line 16 should read: ...electrons, with the concomitant....

Page 3361, Scheme I: compound **5** should have no oxo group.

**Electronic Structure and Bonding of Hg(CH<sub>3</sub>)<sub>2</sub>, Hg(CN)<sub>2</sub>, Hg(CH<sub>3</sub>)(CN), Hg(CCCH<sub>3</sub>)<sub>2</sub>, and Au(PMe<sub>3</sub>)(CH<sub>3</sub>)** [*J. Am. Chem. Soc.* **1984**, *106*, 3387]. ROGER L. DEKOCK,\* EVERT JAN BAERENDS, PAUL M. BOERRIGTER, and RUDY HENGMOLEN

Pages 3387 and 3395: We refer to the Hg-CH<sub>3</sub> bonds in Hg(CH<sub>3</sub>)<sub>2</sub> as 3c-2e bonds. It is clear from the discussion and from Figure 8 that we were emphasizing that two electrons are *bonding* and two are mainly nonbonding. In that sense the bonding is not unlike that in HF<sub>2</sub><sup>-</sup>, I<sub>3</sub><sup>-</sup>, or XeF<sub>2</sub>. In the usual inorganic parlance such a bond is described as 3c-4e. We apologize for any confusion this may have caused.

**Comparative Photophysics of Platinum(II) and Platinum(IV) Porphyrins** [*J. Am. Chem. Soc.* **1984**, *106*, 4015-4017]. DONGHO KIM, DEWEY HOLTEN,\* MARTIN GOUTERMAN, and JOHANN W. BUCHLER

Page 4015, abstract, line 5: [a<sub>2u</sub>( $\pi$ ), d<sub>x<sup>2</sup>-y<sup>2</sup></sub>] should read [a<sub>2u</sub>( $\pi$ ), d<sub>z<sup>2</sup></sub>].

Page 4016, column 2, fifth line from the bottom: again [a<sub>2u</sub>( $\pi$ ), d<sub>x<sup>2</sup>-y<sup>2</sup></sub>] should read [a<sub>2u</sub>( $\pi$ ), d<sub>z<sup>2</sup></sub>].