Variation in the *halide* species used in oxidation reactions proved to be the most intriguing parameter affecting product distributions (see Table I). Reactions between $Cp_2Zr(PPh_2Me)_2$ and 2-halobutanes illustrate this selectivity pattern: 2-iodobutane reacted rapidly to produce $Cp_2Zr(n\text{-butyl})I$ as the major product,[14] while the analogous chloride reacted more slowly to generate zirconocene dichloride as the predominant species. To elucidate this phenomenon, reactions between $Cp_2Zr(PPh_2Me)_2$ and *sec*-butyl chloride, bromide, and iodide were qualitatively followed by ^{1}H NMR. We note that reaction occurs immediately on mixing the zirconium species with each of these halides. For the iodide rapid growth of oxidative adduct is recorded; for the bromide, somewhat slower growth is observed; and, for the alkyl chloride, much slower growth is noted. Variation in formation rates for Cp_2ZrRX as a function of halogen atom *abstracted* is reminiscent of results reported for tin radicals[15] or for Cr(II) species.[16] These observations exclude significant participation of a recombination scheme such as the one shown in Scheme II: Here alkyl iodides would be expected to yield the *greatest* relative amount of Cp_2ZrX_2 and alkyl chlorides the least.

We conclude that whereas propagation depends dramatically on R·, L, and X, initiation is apparently not highly sensitive to variation in X.[17,18] It seems then that it is this discrepancy in discrimination profiles (iodides vs. bromides vs. chlorides) between these two competing routes, both of which involve attack of a metallic species upon an alkyl halide, which determines the overall outcome of these competitive oxidation processes.

Acknowledgments. The authors acknowledge generous support for this research provided by the National Science Foundation (CHE-790096).

References and Notes

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(5) Very high capture rates by a vanadium species have been noted: Kinney, R. J.; Jones, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1978,** *100,* 637. Kinney, R. J.; Jones, W. D.; Bergman, R. G. *Ibid.* **1978,** *100,* 7802.
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(11) Cp_2Zr bis(phosphine) is considerably more reactive than the other "Cp_2Zr^{II}" complexes [$Cp_2Zr(CO)_2$,[12] $Cp_2Zr(CO)(PMe_3)$[13]].
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(14) The probable first formed species, $Cp_2Zr(sec\text{-butyl})I$, can rapidly rearrange to the observed product: Hart, D. W.; Schwartz, J. *J. Am. Chem. Soc.* **1974,** *96,* 8115.
(15) Carlsson, D. J.; Ingold, K. V. *J. Am. Chem. Soc.* **1968,** *90,* 7047.
(16) Kochi, J. K.; Powers, J. W. *J. Am. Chem. Soc.* **1970,** *92,* 137.
(17) Initiation as a function of R· and L was not studied.
(18) Initiation may proceed by electron transfer in alkyl halide complexes of Zr(II). Electrochemical potentials for alkyl halides complexed to this or similar species have not been measured.

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Received January 14, 1980

Additions and Corrections

Statistical Phase Space Theory of Polyatomic Systems. Application to the Unimolecular Reactions $C_6H_5CN^{\cdot+} \rightarrow C_6H_4^{\cdot+} + HCN$ and $C_4H_6^{\cdot+} \rightarrow C_3H_3^+ + {}^{\cdot}CH_3$ [*J. Am. Chem. Soc.*, **99,** 1705 (1977)]. By WALTER J. CHESNAVICH and MICHAEL T. BOWERS,* Department of Chemistry, University of California, Santa Barbara, California 93106.

The right-hand side of eq 6 should be divided by σ_a. Also, eq 7 should read

$$R_{\mathcal{J}}(\mathrm{b}\rightarrow\mathrm{a}) = \frac{S_r'}{\sigma_b} \iint \bar{k}_{\mathcal{J}}(\mathcal{E}_r^{\,b},\mathcal{E}_t)\rho_t(\mathcal{E}_t)\rho_r(\mathcal{E}_r^{\,b}) \times \rho_b(E - \mathcal{E}_0 - \mathcal{E}_{tr}^{\,b})\, d\mathcal{E}_t d\mathcal{E}_{tr}^{\,b} \quad (7)$$

eq 8 should read

$$k_{\mathcal{J}}(E)_a = \frac{S_r'}{\sigma_b S_r \rho_a(E - \mathcal{E}_r^{\,a})} \iint \bar{k}_{\mathcal{J}}(\mathcal{E}_r^{\,b},\mathcal{E}_t)\rho_b(\mathcal{E}_t) \times \rho_r(\mathcal{E}_r^{\,b})\rho_b(E - \mathcal{E}_0 - \mathcal{E}_{tr}^{\,b})\, d\mathcal{E}_t d\mathcal{E}_{tr}^{\,b} \quad (8)$$

and equation (9a) should read

$$\bar{k}_{\mathcal{J}}(\mathcal{E}_r^{\,b},\mathcal{E}_t) = \mathcal{P}_b(\mathcal{E}_t,\mathcal{E}_r^{\,b},\mathcal{J})/2\pi\hbar\rho_t(\mathcal{E}_t)\rho_r(\mathcal{E}_r^{\,b}) \quad (9a)$$

where $\rho_r(\mathcal{E}_r^{\,b})$ is the density of rotational states of the separated fragments at rotational energy $\mathcal{E}_r^{\,b} = \mathcal{E}_{tr}^{\,b} - \mathcal{E}_t$. Equation 10a is correct as published.

In eq 10b–14, in the text surrounding these equations, and in Figures 2, 3, and 5, the quantity E should be replaced by E_v, the vibrational energy of the parent ion "a" except as follows; E should be replaced by $E_v + \mathcal{E}_r^{\,a}$ in the right-hand side of eq 10b, in both sides of eq 11 and 12, and in the first argument of $\mathcal{P}_{\mathcal{J}}$ in eq 14. These replacements are based on the standard assumption that the rotational angular momentum and rotational constant of the parent neutral are unaltered by the ionization process. Also the right-hand side of eq 10b should be divided by the rotational partition function of the parent molecule, and the right-hand side of eq 14 should be divided by a (numerically determined) normalization constant.

For clarification, S_r' always equals $2\mathcal{J}$, and $\mathcal{P}_b(\mathcal{E}_t,\mathcal{E}_r^{\,b},\mathcal{J})$, $\Gamma_b(\mathcal{E}_{tr},\mathcal{J})$, $\bar{k}_{\mathcal{J}}(\mathcal{E}_r^{\,b},\mathcal{E}_t)$, $k_{\mathcal{J}}(E)_a$, and $k_{\mathcal{J}}(E,\mathcal{E}_t)_a$ are functions of both $\mathcal{J}$ and its projection on a space-fixed axis. Furthermore, if the parent molecule is treated as a spherical top, then $k_{\mathcal{J}}(E)_a$ and $k_{\mathcal{J}}(E,\mathcal{E}_t)_a$ are also functions of the projection of $\mathcal{J}$ on a body-fixed axis and $g_{\mathcal{J}}$ in eq 10b equals $(2\mathcal{J})^2$. Also, note that $\int \bar{k}_{\mathcal{J}}(\mathcal{E}_r^{\,b},\mathcal{E}_t)2\mathcal{J}_t\, d\mathcal{J} = k_L$, where k_L is the Langevin capture rate constant.

Finally, a minor error was found in our RRKM computer program which, when corrected, required minor changes (~10%) in the transition state frequencies in order to reproduce the RRKM curves plotted in Figures 3 and 5.

None of the errors or misprints affect in any way the general conclusions of this paper.

Catalytic Decarbonylation of Aldehydes [*J. Am. Chem. Soc.*, **100,** 7083 (1978)]. By D. H. DOUGHTY and L. H. PIGNO-

LET,* Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455.

On p 7083 the ligand dppp is named incorrectly and should be 1,3-bis(diphenylphosphino)propane, not 1,2-bis(diphenylphosphino)propane.

Sensitivity Enhancement in Natural Abundance Proton-Coupled ^{15}N NMR Spectra Using the Selective Population Transfer Method [*J. Am. Chem. Soc.*, **101,** 774 (1979)]. By HANS J. JAKOBSEN* and WALLACE S. BREY*, Department of Chemistry, University of Florida, Gainesville, Florida 32611.

In the caption for Figure 1, values for two of the coupling constants were interchanged. The correct assignments, with values determined by computer fitting of the ^{15}N spectrum of pyrrole to yield an rms error of 0.010 Hz, are: $^2J_{^{15}\text{N-H}(2)} = -4.53$ Hz and $^3J_{^{15}\text{N-H}(3)} = -5.35$ Hz. In the last paragraph of the text, the third sentence should conclude "until acquisition" rather than "during acquisition".

Methyl-Substituted Allyl Cations. A Comparison of Experimental Stability, Rotational Barrier, and Solvolysis Data with ab Initio Calculations [*J. Am. Chem. Soc.*, **101,** 6032 (1979)]. By HERBERT MAYR,* WOLFGANG FÖRNER, and PAUL VON RAGUÉ SCHLEYER, Institut für Organische Chemie der Universität Erlangen-Nürnberg, 8520 Erlangen, West Germany.

Page 6035, eq 10: C_2H_8 should be C_3H_8 and C_3H_6 should be C_2H_6.

Free-Energy Relationships for Electron-Transfer Processes [*J. Am. Chem. Soc.*, **101,** 6140 (1979)]. By FRANCO SCANDOLA,* Centro di Studio sulla Fotochimica e Reattività degli, Stati Eccitati dei Composti di Coordinazione del CNR, University of Ferrara, Ferrara, Italy, and VINCENZO BALZANI,* Istituto Chimico "G. Ciamician" dell'Università and Laboratorio di Fotochimica e Radiazioni, d'Alta Energia del CNR, Bologna, Italy.

Two footnotes (refs 45 and 46) are lacking. The footnotes are as follows:

(45) In this view, the α and β coefficients of eq 4 can be given as a function of ΔG and $\Delta G^{\ddagger}(0)$ as follows:

$$\alpha = 1/[1 + \exp(-\ln 2\, \Delta G/\Delta G^{\ddagger}(0))]$$

$$\beta = \Delta G/[1 + \exp(\ln 2\, \Delta G/\Delta G^{\ddagger}(0))] + \Delta G^{\ddagger}(0) \ln [1 + \exp(-\ln 2\, \Delta G/\Delta G^{\ddagger}(0))]/\ln 2$$

(46) For an example of such behavior, see: I. B. Afanas'ev, S. V. Prigoda, T. Y. Mal'tseva, and G. I. Samokhvalov, *Int. J. Chem. Kinet.*, **6,** 643 (1974).

Conformational Characteristics of Poly(methyl vinyl ketone)s and of Simple Model Ketones [*J. Am. Chem. Soc.*, **101,** 6481 (1979)]. By ULRICH W. SUTER, the Eidgenössische Technische Hochschule, Technisch-Chemisches Laboratorium, ETH-Zentrum, CH-8092 Zürich, Switzerland.

On page 6482, on the next to the last line in the formula, $f_{6-12}(r_r)$ should be replaced by $f_{6-12}(r^*)$, and the same substitution should be made on page 6483 (left-hand column), line 4.

Structure and Reactivity in Intramolecular Catalysis. Catalysis of Sulfonamide Hydrolysis by the Neighboring Carboxyl Group [*J. Am. Chem. Soc.*, **101,** 6981 (1979)]. By TEUN GRAAFLAND, ANNO WAGENAAR, ANTHONY J. KIRBY, and JAN B. F. N. ENGBERTS,* Department of Organic Chemistry, University of Groningen, Nijenborgh, 9747 AG Groningen, The Netherlands, and the University Chemical Laboratory, Cambridge, CB2 1EW, England.

In Table III the thermodynamic activation parameters for hydrolysis of **11** in 50% EtOH-H_2O (v/v) should be: $\Delta G^{\ddagger} = 26.39$ kcal mol^{-1} and $\Delta S^{\ddagger} = -18$ eu. $\Delta H^{\ddagger}$ is given correctly. The conclusions are not affected.

A New Empirical Method to Calculate Average Molecular Polarizabilities [*J. Am. Chem. Soc.*, **101,** 7206 (1979)]. By KENNETH J. MILLER* and JOHN A. SAVCHIK, Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12181.

Page 7208, second column: Equation 21 should read:

$$\sqrt{\overline{r_A{}^2}} = \sqrt{\frac{3}{2}}\,\sqrt[4]{\overleftarrow{a_0\alpha_A}} \tag{21}$$

Intramolecular Electrostatic and General Acid Catalysis in the Hydrolysis of *O,S*-Thioacetals [*J. Am. Chem. Soc.*, **102,** 292 (1980)]. By THOMAS H. FIFE* and THEODORE J. PRZYSTAS, Department of Biochemistry, University of Southern California, Los Angeles, California 90033.

Page 296, column 2, line 28: "C–O bond breaking" should read "C–S bond breaking".

Photolysis of Alkyl Azides. Evidence for a Nonnitrene Mechanism [*J. Am. Chem. Soc.*, **102,** 735 (1980)]. By EVAN P. KYBA* and RUDOLPH A. ABRAMOVITCH,* Departments of Chemistry, The University of Texas at Austin, Austin, Texas 78712, The University of Alabama, University, Alabama 35486, and Clemson University, Clemson, South Carolina 29631.

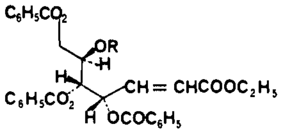
Page 740: In the Acknowledgments, reference 33 should appear after the initials R. A. A. inside the parentheses and *not* outside.

The Chemistry of Bis(fulvalene)divanadium [*J. Am. Chem. Soc.*, **102,** 1009 (1980)]. By JAMES C. SMART* and BARRY L. PINSKY, Department of Chemistry, University of California, Berkeley, California 94720.

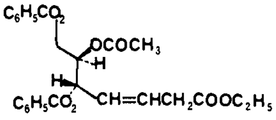
On page 1010, column 1, line 6 should read, "Bis(fulvalene)divanadium(II,III) Hexafluorophosphate, $[(\eta^5{:}\eta^5\text{-}C_{10}H_8)_2V_2{}^+](PF_6{}^-)$."

Stereospecific Total Synthesis of a "Slow Reacting Substance" of Anaphylaxis, Leukotriene C-1 [*J. Am. Chem. Soc.*, **102,** 1436 (1980)]. By E. J. COREY*, DAVID A. CLARK, GIICHI GOTO, ANTHONY MARFAT, and CHARLES MIOSKOWSKI, Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138, and BENGT SAMUELSSON and SVEN HAMMARSTROM, Karolinska Institutet, S-10401 Stockholm, Sweden.

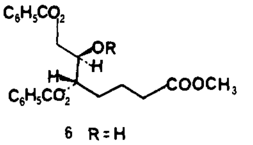
On p 1437 structures **3–9** were incorrectly drawn. The correct structures are shown below.



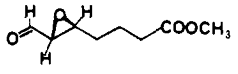
3 R= H
4 R= OAc



5



6 R=H
7 R=Tos



8 X=CH$_2$OH
9 X=CHO