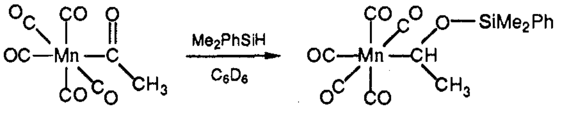
to dark red mixtures that exhibit paramagnetic broadening (and the presence of $Mn_2(CO)_{10}$ by IR spectroscopy). Excess silane stabilizes **2a**, since either adjusting the initial stoichiometry of **1**/Ph_2SiH_2 to 1:1 (even at 5 °C) or subsequently removing excess silane by size-exclusion chromatography (polystyrene beads) rapidly degrades **2a**. Conducting the reaction in the presence of CO (1 atm) slows formation of **2a** to 30 min without noticeably stabilizing the product.

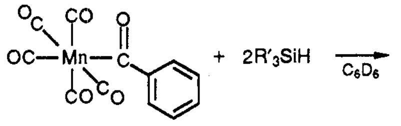
Diethylsilane exhibits similar reactivity toward **1** (eq 1) except that the bis(manganese siloxyethyl) complex **3** also forms in a 1.5–2.0:1 ratio of **2b**/**3**. Structural assignments rest primarily on ^1H and ^{13}C NMR spectral data for their ethylidene groups.[11,13] Conducting the reaction in the presence of 4–5% $Rh(PPh_3)_3Cl$ as the catalyst selectively affords **2b**, although substantial amounts of $EtOSiHEt_2$ (up to 30%) and minor amounts of unidentified organics also form.[15] In the absence of $Rh(PPh_3)_3Cl$, neither $EtOSiHEt_2$ nor $(EtO)_2SiEt_2$ are detected by ^1H and ^{13}C NMR spectroscopy.

Using the monohydrosilane Me_2PhSiH permitted isolation and full characterization of the stable α-siloxyethyl complex $(CO)_5Mn{-}CH(OSiMe_2Ph)CH_3$ (**5**) (eq 2). NMR spectral monitoring of the orange solution within 15 min of mixing **1** and Me_2PhSiH (1:1) in C_6D_6 established the presence of **5** as the only organomanganese complex in at least 83% yield (vs Cp_2Fe) and the absence of CH_3CHO, $EtOSiMe_2Ph$, and $(CO)_5Mn{-}SiMe_2Ph$.[13] Column chromatography with hexane/silica gel afforded **5** as a brown oil (67% yield).[16]



1 **5** (2)

Reactions between manganese benzoyl **4** and silanes are less straightforward. Ph_2SiH_2 rapidly and quantitatively consumes freshly recrystallized $(CO)_5MnCOPh$ (**4**) and gives the unstable siloxybenzyl complex **2c** (eq 1) (81% yield vs Cp_2Fe) and 5–8% of the silylether $PhCH_2OSiHPh_2$, but no detectable $(CO)_5Mn{-}SiHPh_2$. IR and ^1H, ^{13}C NMR spectral data for **2c**[13] closely match relevant absorptions for Gladysz's $(CO)_5Mn{-}CH(OSiMe_3)Ph$.[5a,6a] Et_2SiH_2 reacts analogously, except that the product $(CO)_5Mn{-}CH(OSiHEt_2)Ph$ (**2d**)[13] is less stable ($t_{1/2}$ = 1.5 h in the presence of 3 equiv of Et_2SiH_2). Both monohydrosilanes Me_2PhSiH and Et_3SiH cleanly transform **4** into their benzyl silyl ethers and manganese silyl complexes (eq 3). The observed yields (75–85%) under a variety of reaction conditions agree with the indicated stoichiometry. Although these reactions are slower (1–4 h), ^1H NMR spectral monitoring indicated the presence of at most trace concentrations of $(CO)_5Mn{-}CH(OSiR'_3)Ph$.



4

$$PhCH_2OSiR'_3 + (OC)_5Mn{-}SiR'_3 \quad (3)$$

6a: $R'_3 = Me_2Ph$
b: $R'_3 = Et_3$

Directly hydrosilating an acyl ligand and forming the manganese α-siloxyalkyl complexes **2a–d** and **5** represents only one facet of manganese acyl/hydrosilane chemistry. Both **1** and **4** serve as extremely efficient aldehyde and ketone hydrosilation catalysts;[17,18] all silyl ethers noted were generated quantitatively with 2–4% **1** or **4** as catalyst and a 1:1 mixture of aldehyde plus hydrosilane.[19] Manganese acyls **1** and **4** also are more active and general catalysts than is $Rh(PPh_3)_3Cl$[7] toward hydrosilation of FpCOR with mono- and dihydrosilanes.[20] A straightforward albeit speculative mechanism for hydrosilation of $(CO)_5MnCOR$ (**1** and **4**) entails oxidative addition of hydrosilane at manganese;[3-5] the resulting transient $(CO)_4Mn(H)(SiR'_3)(COR)$ rearranges first to $(CO)_4(H)Mn{=}C(OSiR'_3)R$ (via a 1,3-silatropic shift)[21] and then to the coordinatively unsaturated α-siloxyalkyl intermediate $(CO)_4Mn{-}CH(OSiR'_3)R$. Studies in progress are concerned with further applications of manganese acyls as hydrosilation catalysts and with their mechanism(s) of action.

Acknowledgment. Support from the Department of Energy, Office of Basic Energy Science is gratefully acknowledged.

Supplementary Material Available: Table I containing ^1H and ^{13}C NMR and IR spectral assignments for **2a–d**, **3**, **5**, the silyl ethers, and the silylmanganese complexes $(CO)_5Mn{-}SiHPh_2$ and $(CO)_5Mn{-}SiMe_2Ph$ and microanalytical data (4 pages). Ordering information is given on any current masthead page.

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[15] Treatment of this reaction mixture with Fp^-Na^+ (−78 °C) and workup by silica gel chromatography affords the known[7b] $Fp{-}CH(OSiHEt_2)CH_3$ in 31% yield. Similar transmetalation[15a] of $(CO)_5MnCH_2OCH_3$ provides $FpCH_2OCH_3$ (65% yield). (a) Casey, C. P.; Cyr, C. R.; Anderson, R. L.; Martin, D. F. *J. Am. Chem. Soc.* **1975**, *97*, 3053.

[16] For **5**: IR (C_6H_{12}) 2106 (w), 2044 (w), 2007 (s), 1987 (m) cm^{-1} (CO); ^1H NMR (C_6D_6) δ 7.56 (m, 2 H, Ph), 7.21 (m, 3 H, Ph), 5.07 (q, J = 6.5 Hz, MnCH), 1.74 (d, J = 6.5, $MnCHCH_3$), 0.33 (s, $SiMe_2$); ^{13}C NMR (C_6D_6) δ 133.8, 129.8, 128.0, 127.1 (Ph), 69.6 (MnCH), 35.0 ($MnCHCH_3$), −1.1, −1.6 ($SiMe_2$). Anal. Calcd for $C_{15}H_{15}O_6SiMn$: C, 48.13; H, 4.04. Found: C, 48.06; H, 4.03.

[17] (a) Both $Co_2(CO)_8$[4b] and $Co(CO)_4SiR_3$[3b] complexes induce catalytic hydrosilation of ketones,[17a] a sequence not previously documented with $(CO)_5Mn$ Complexes. Sakurai, H.; Miyoshi, K.; Nakadaira, Y. *Tetrahedron Lett.* **1977**, 2671. (b) $(CO)_5MnSiR_3/Mn_2(CO)_{10}$ systems catalytically hydrosilate alkenes and *O*-silate alcohols. Faltynek, R. A. *J. Organomet. Chem.* **1983**, *258*, C5. Hilal, H. S.; Abu-Eid, M.; Al-Subu, M.; Khalaf, S. *J. Mol. Catal.* **1987**, *39*, 1. Hilal, H. S.; Khalaf, S.; Al-Nouri, M.; Karmi, M. *Ibid.* **1986**, *35*, 137.

[18] Reviews on catalytic ketone hydrosilation: (a) Ojima, I.; Hirai, K. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1985; Vol. 5, p 103. (b) Corriu, R. J. P.; Guerin, C.; Moreau, J. J. E. *Top. Stereochem.* **1984**, *15*, 45. (c) Brunner, H. *Top. Stereochem.* **1988**, *18*, 129; *Synthesis* **1988**, 645. (d) Chaloner, P. A. *Handbook of Coordination Catalysis in Organic Chemistry*; Butterworths: Boston, 1986; Chapter 7.2. (e) Dickson, R. S. *Homogeneous Catalysis with Compounds of Rhodium and Iridium*; D. Reidel Publishing Co.: Boston, 1985; Chapter 3.11.

[19] ^1H and ^{13}C NMR spectral data[13] agree with literature values or data obtained with commercially available samples.

[20] Aldehyde and FpCOR substrates inhibit hydrosilation at the manganese acyl catalyst (**1** or **4**) until all substrate is consumed. Results of ^1H and ^2H NMR spectral studies with **1** and **1**-d_3 (5–18% of reaction mixture) are particularly definitive. Reference 11 and unpublished observations.

[21] Brinkman, K. C.; Blakeney, A. J.; Krone-Schmidt, W.; Gladysz, J. A. *Organometallics* **1984**, *3*, 1325.

π-Bond Energies in Protonated Schiff Bases

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Received June 1, 1990

The increased stretching frequency observed upon protonation of Schiff bases in the retinoids and other related systems is well documented.[2] Because the protonated Schiff base (PSB) has been thought to have a weaker π bond than its parent Schiff base (SB)

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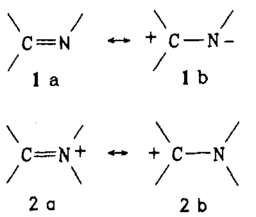
[2] Rao, C. N. R. *Chemical Applications of Infrared Spectroscopy*; Academic Press: New York, 1963 and references cited therein.

Table I. Total Bond Energy and σ- and π-Bond Energies for the Carbon–Nitrogen Bonds (kcal/mol)

molecule	total bond energy E^a	$D^{\circ\,b}$	expt[c]	E_σ	E_π[d]
$H_3C{-}NH_2$	–	79.1	87.8[e]		
$H_3C{-}NH_3^+$	–	107.4[f]	114.2[g]		
$H_2C{=}NH$	157.6	145.2	156.0[h]	79.1	78.0
$H_2C{=}NH_2^+$	194.5	202.8	213.7[i]	107.4	87.1

[a] See ref 6 for method of calculation. The data was obtained at the restricted MP4SDTQ/6-311G**//6-311G** level corrected for differences in zero-point vibrational energies. [b] Bond-dissociation energies employing data at the unrestricted and restricted MP4SDTQ/6-311G**//6-311G** corrected for differences in zero-point vibrational energies. [c] Bond-dissociation energies employing data from ref 9 except where otherwise noted. [d] Difference between the total energy calculated by the Schleyer method and the ab initio D°. [e] ΔH_f (CH_3NH_2) of −7.5 kcal/mol is from Yaws and Chiang: Yaws, C. L.; Chiang, P. Y. *Chem. Eng.* (*N.Y.*) **1988**, *95*(13), 81–88. [f] An experimental value of 114 kcal/mol is reported in ref 11. [g] ΔH_f ($CH_3NH_3^+$) of 146 kcal/mol is from Lias et al.: Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695–808. [h] We used ΔH_f ($CH_2{=}NH$) of 26.4 kcal/mol from DeFrees and Hehre: DeFrees, D. J.; Hehre, W. J. *J. Phys. Chem.* **1978**, *82*, 391–393. A value of 25 ± 3 kcal/mol has also been reported in the literature: Grela, M. A.; Colussi, A. J. *Int. J. Chem. Kinet.* **1988**, *20*, 713–718. [i] ΔH_f ($CH_2{=}NH_2^+$) of 178 kcal/mol was taken from Stams et al.: Stams, D. A.; Thomas, T. D.; MacLaren, D. C.; Ji, D.; Morton, T. H. *J. Am. Chem. Soc.* **1990**, *112*, 1427–1434.

(the singly bonded **2b** is assumed to make a greater contribution to the overall bonding picture than **1b**), considerable effort has been expended in an attempt to explain this divergent result.[3] Initially, this result was rationalized by postulating a coupling interaction between the N—H bending frequency and the C=N stretch. In these and other papers, workers in the field have assumed that the C=N stretching force constants for the iminium ion were smaller than those of the imine.[4]



Recently, Lopez-Garriga et al.[5] have shown that this shift also occurs when the base is complexed with Lewis acids, thus precluding the opportunity for N–H bend coupling. On the basis of these results and ab initio calculations,[5c] they proposed that an increase in the force constant caused by a change of hybridization at the nitrogen atom was the origin of the increased stretching frequency.

In this communication, we report that the increase in the C=N stretching frequency is due (at least in part) to the fact that the C=N bond in the protonated Schiff base is stronger, not weaker, than in the unprotonated base. We have used two different methods to calculate the bond energies. The first employs the difference in heats of hydrogenation of the single and double bonds as proposed by Schleyer[6] and calculates the extent to which the π bond is stronger than the σ bond. The energies were evaluated by using ab initio energies obtained with the Gaussian 86 system of programs.[7,8] The second estimate is derived from bond-dissociation energies obtained from both experimental heats of formation[9] and ab initio calculations.[10] Neither method is free from flaws, and there is some disagreement between the results (Table I) given by the two methods. These differences notwithstanding, the trend is the same regardless of method used: both the σ- and π-bond strengths are increased when the nitrogen atom is protonated. These results are in accord with those of Boyd et al., who reported that A–B single bonds are strengthened when protonated.[11]

The increased bond energies contradict conventional wisdom in two ways. First, Table II shows that the C–N bond is longer in both $CH_3NH_3^+$ and $CH_2{=}NH_2^+$ than in the unprotonated forms whereas the reverse is predicted.[12] This modest increase in bond length that occurs when the Schiff base is protonated (0.01 Å) is accompanied by a small increase in the p character of the bond at both carbon and nitrogen. In contrast, there is a substantial increase in the p character at the carbon of CH_3NH_2 when it is protonated, which gives rise to the 0.05-Å increase in the bond length. These results support the contention of Lopez-Garriga et al.[5] that there is a change in hybridization. Armstrong and Walker have attributed this increase in bond length to a decrease in hyperconjugation in the protonated form.[13] Our calculations (Table II) also support this argument, with the hyperconjugation energy dropping from ca. 24 to 7 kcal/mol.

Second, if the bond is stronger, then why is the protonated base more reactive than the unprotonated? An examination of the eigenvalues (Table III) of the wave functions shows that the LUMO of the protonated systems has a negative energy. Examination of the natural bond orbitals[8a] (Table III) shows that the σ* in $CH_3NH_3^+$ and the π* in $CH_2{=}NH_2^+$ have the negative energies. Hence, protonation shifts both HOMO and LUMO to lower energy, and the interaction of this LUMO with an electron pair from a nucleophile is more facile than the corresponding interaction with the Schiff base.

A preliminary examination of other systems shows that an increased bond energy for both single and double bonds upon protonation is a general phenomenon and that the LUMOs of these protonated systems have negative energies. It is this property of

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[3] Kakitani, H.; Kakitani, T.; Rodman, H.; Honig, B.; Callendar, R. *J. Phys. Chem.* **1983**, *87*, 3620–3627.

[4] (a) Baasov, T.; Friedman, N.; Sheves, M. *Biochemistry* **1987**, *26*, 3210–3217. (b) Gilson, R. S.; Honig, B. H.; Croteau, A.; Zarrilli, G.; Nakanishi, K. *Biophys. J.* **1988**, *53*, 261. (c) Aton, B.; Doukas, A. G.; Narra, D.; Callendar, R. H.; Dinur, U.; Honig, B. *Biophys. J.* **1980**, *29*, 79–94. (d) Smith, S. O.; Pardoen, J. A.; Mulder, P. P.; Curry, B.; Lugtenburg, J.; Mathis, R. *Biochemistry* **1983**, *22*, 6141–6148. (e) Schiffmiller, R.; Callendar, R. H.; Waddell, W. H.; Govindjie, R.; Ebry, T. G.; Kakitani, H.; Honig, B.; Nakanishi, K. *Photochem. Photobiol.* **1985**, *41*, 563–567. (f) Smith, S. O.; Myers, A. B.; Mathis, R. A.; Pardoen, J. A.; Winkel, C.; van den Berg, L. M. M.; Lugtenburg, J. *Biophys. J.* **1985**, *47*, 653–664. (g) Ganter, U. M.; Gärtner, W.; Siebert, F. *Biochemistry* **1988**, *27*, 7480–7488.

[5] a) Lopez-Garriga, J. J.; Babcock, G. T.; Harrison, J. F. *J. Am. Chem. Soc.* **1986**, *108*, 7131–7133. (b) Lopez-Garriga, J. J.; Babcock, G. T.; Harrison, J. F. *J. Am. Chem. Soc.* **1986**, *108*, 7141–7151. (c) Lopez-Garriga, J. J.; Babcock, G. T.; Hanton, S.; Harrison, J. F. *J. Am. Chem. Soc.* **1986**, *108*, 7151–7253.

[6] Schleyer, P. v. R.; Kost, D. *J. Am. Chem. Soc.* **1988**, *110*, 2105–2109.

[7] Frisch, M. J.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Martin, R.; Stewart, J. J.; Bobrowicz, F.; DeFrees, D. J.; Seeger, R.; Whiteside, R. A.; Fox, D.; Fluder, E. M.; Pople, J. A. *Gaussian 86* (release C version); Carnegie-Mellon University: Pittsburgh, PA, 1987.

[8] The wave functions obtained were analyzed with the G82NBO program: Reed, A. E.; Weinhold, F. *Quantum Chem. Program Exch. Bull.* **1985**, *5*, 141. See the following references for details of the NBO method: (a) Foster, J. P.; Weinhold, F. *J. Am. Chem. Soc.* **1980**, *102*, 7211. (b) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735. (c) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 1736. (d) Curtiss, L. A.; Pochatko, D. J.; Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1985**, *82*, 2679.

[9] Evaluated from data in the JANAF thermochemical tables: Chase, M. W., Jr.; Davies, C. A.; Downey, J. R., Jr.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. *J. Phys. Chem. Ref. Data* **1985**, *14*, 1, Suppl. 1. Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data* **1977**, *6*, 1, Suppl. 1.

[10] Whiteside, R. A.; Frisch, M. J.; Pople, J. A. *Carnegie-Mellon University Quantum Achive*, 3rd ed.; Carnegie-Mellon University: Pittsburgh, PA, 1983.

[11] Boyd, R. J.; Glover, J. N. M.; Pincock, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 5152–5155.

[12] This is not a new phenomenon. Reference 10 reports that all but three of the bonds that they studied increased in length when one of the bonded atoms was protonated. Two of those three involved protonated fluorine, and the other was hydroxylamine, which was shortened by 0.03 Å. Maksic et al. also report similar results: Maksic, Z. B.; Eckert-Maksic, M.; Skancke, P. N.; Skancke, A. *THEOCHEM* **1988**, *46*, 447–457. They attribute this to a redistribution of s-orbital density into neighboring orbitals.

[13] Armstrong, D. R.; Walker, G. T.; *THEOCHEM* **1987**, *34*, 369–389.

Table II. Bond Lengths, σ Orbital Hybridizations, and Hyperconjugative Interactions[a]

system	C–N length, Å	σ hybridization					hyperconjugation energy	
		C	N	CH σ	NH σ	lp	lp → CH σ^*	NH σ → CH σ^*
$H_3C{-}NH_2$	1.454	$sp^{2.7}$	$sp^{2.1}$	$sp^{3.0}$	$sp^{3.2}$	$sp^{4.2}$	–	–
$H_3C{-}NH_3^+$	1.507	$sp^{3.6}$	$sp^{2.2}$	$sp^{2.8}$	$sp^{3.3}$	–	–	–
$H_2C{=}NH$	1.248	$sp^{1.7}$	$sp^{1.3}$	$sp^{2.1}$	$sp^{3.6}$	$sp^{1.8}$	15.0	9.1
$H_2C{=}NH_2^+$	1.262	$sp^{1.9}$	$sp^{1.4}$	$sp^{2.0}$	$sp^{2.4}$	–	–	7.4

[a] See ref 8 for the methods used to determine the orbital hybridization and hyperconjugative interactions.

Table III. Orbital Energies

system	molecular orbitals		localized orbitals			
	HOMO	LUMO	σ	σ^*	π	π^*
$H_3C{-}NH_2$	–0.385 46	0.158 22	–0.937 82	0.643 69	–	–
$H_3C{-}NH_3^+$	–0.787 08	–0.081 46	–1.207 00	–0.281 58	–	–
$H_2C{=}NH$	–0.425 61	0.158 74	–1.215 76	0.972 22	–0.452 80	0.226 02
$H_2C{=}NH_2^+$	–0.781 65	–0.139 58	–1.501 55	0.639 01	–0.781 27	–0.071 04

the molecule that explains the enhanced reactivity toward nucleophilic addition of protonated Schiff bases or carbonyl groups and the enhanced nucleofugacity of the oxonium ion compared to the hydroxyl group. Further work is in progress to explore the chemical implications of these results.

Acknowledgment. I express appreciation to Professor William Okamura for helpful discussions and moral support. This work was made possible through a generous allotment of computer time from UCR Academic Computing and financial support from NIH Grant DK-16595.

*Book Reviews**

Molecular Dynamics in Restricted Geometries. Edited by Joseph Klafter (Tel Aviv University) and J. M. Drake (Exxon Corporation). John Wiley & Sons: New York and Chichester. 1989. x + 437 pp. $75.00. ISBN 0-471-60176-4.

When molecules are confined within a restricted geometry, their static and dynamic properties are often much different from those for the same molecules in the bulk phase. Examples of such situations are fluids adsorbed in porous solids (e.g. silica, activated carbons, clays, zeolites, rocks, etc.), polymer molecules confined in thin films, and molecules in micelles, vesicles, monolayers, and Langmuir-Blodgett films. This book contains 15 chapters devoted to the study of the dynamics of molecules in such confined situations. The main emphasis of the book is on experimental studies, particularly through the use of probes such as luminescent dyes and NMR. Theoretical methods for interpreting the dynamics are also covered, including classical probability ideas, fractal treatments, and statistical mechanics. Molecular dynamics computer-simulation studies are not included. Among the topics discussed are electronic excitation transfer and photoinduced electron transfer in vesicles, micelles, silica gels, filaments, membranes, zeolites, and polymer chains; photochemical probes for orientational and translational diffusion, as well as the dynamics of reactions; cyclization of polymers; the application of NMR to study local motions in amorphous polymers, diffusion in porous media, and characterization of porous materials; orientational dynamics of supercooled liquids in porous sol-gel glasses; and the reaction kinetics of charge carrier reactions in colloidal semiconductor particles and on semiconductor films.

This book will provide an up-to-date account of experimental and theoretical research on dynamics in confined systems and will be useful to specialists in these areas. It will also be of interest to scientists and engineers doing research in porous materials and polymers.

Keith E. Gubbins, *Cornell University*

General and Synthetic Methods. Volume 11. Edited by G. Pattenden (University of Nottingham). The Royal Society of Chemistry: Cambridge. 1989. xiii + 700 pp. $260.00. ISBN 0-85186-924-6.

This long and richly illustrated volume is intended to review new and improved methods of synthesis that were reported in the literature during the year 1986. Earlier volumes cover the literature from previous years. There are 2000+ references cited in the nine subject chapters of this work. Pattenden has succeeded in the formidable task of generating a coherent review of synthetic methods and applications from the large volume of literature that was published during 1986.

The organization is inherently logical. Pattenden starts with a generous Table of Contents and then follows with five chapters devoted to the wide spectrum of functional group interconversions, three chapters on organometallics and saturated cyclic compounds, and finally a chapter on the synthesis of natural products. A list of newly (1986) published reviews on General and Synthetic Methods and an Author index complete the book. The excellent organization of the book and the detailed Table of Contents make a subject index unnecessary.

In contrast to anthologies published 5–10 years ago, this volume is weighted more toward specific examples and less toward general methodology. A particularly noticeable trend is toward asymmetric synthesis, an area that has gained importance over the last few years. There are numerous stereo- and regioselective examples cited in each chapter.

This book is not meant as a textbook, and as such it is not light reading. It is written as a reference for the practicing chemist, who wishes to maintain awareness of the directions that chemical synthesis is going. It can also help suggest solutions to problems based on the successful newer methods that are cited in the book.

James A. Thomas, *Parke-Davis Pharmaceutical Research*

Oxidations in Organic Chemistry. By Milos Hrdlicky (Virginia Polytechnic Institute). American Chemical Society: Washington, D.C. 1990. xx + 433 pp. $49.95 (softbound); $89.95 (hardbound). ISBN 0-8412-1781-5 (soft), 0-8412-1780-7 (cloth).

This is a practical book that presents a lot of experimental experience in abbreviated but carefully organized form. An opening chapter systematically summarizes the principal oxidizing agents used by organic chemists. For the most part, one paragraph suffices; it gives succinct information on the scope and principal uses, with key references. The second chapter, relatively short, is devoted to dehydrogenation. Chapter 3 (216 pages) describes oxidations of specific functional groups and also presents a lot of specific information in tables. The organization is thus according to substrate rather than oxidizing agent. This chapter is followed by one composed of preparative procedures, including preparation of reagents. Finally, there is a large group of "correlation tables", in which specific starting structures (e.g., methyl ketones) are organized according to desired product and the reagents. The whole is made even more useful by a complete author index and a thorough subject index.

Diterpenoids of Flowering Plants. Compositae (Asteraceae). By F. Seaman (University of Texas), F. Bohlmann and C. Zdero (Technical University of Berlin), and T. J. Mabry (University of Texas). Springer-Verlag: New York, Berlin, Heidelberg. 1990. vi + 638 pp. $99.00. ISBN 0-387-97058-4.

The Compositae (Asteraceae) are among the most advanced and widespread of the families of flowering plants. Their alkaloids, flavonoids, sesquiterpenoids, and polyacetylene metabolites have been extensively studied, but the diterpenoid constituents, which are also numerous

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*Unsigned book reviews are by the Book Review Editor.