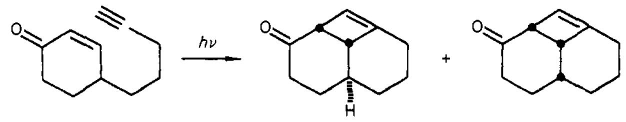
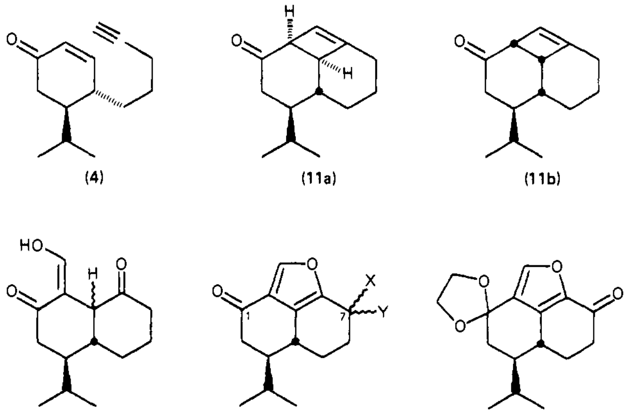
Scheme I



(5) (6a) (6b)

Chart I



(4) (11a) (11b)

(12) (13a): X = OH, Y = H (14)
(13b): X, Y = O

25 °C, 1 h) regenerated **13b**, which could be recycled.[21b]

From the outset our strategy for hibiscone C called for introduction of an axial C(6)-methyl substituent as the penultimate step. Our confidence that in fact the axial configuration would obtain derived from examination of molecular models of the enolate of **14**. In particular, axial approach of an electrophile to the α or undesired face of this enolate results in considerable tortional strain of the furan–C(7)-carbonyl π system during product development. In contrast, axial approach to the desired β face permits maintenance of a high degree of overlap throughout the bond forming process.

In practice, deprotonation of **14** [$\mathrm{LiN(Me_3Si)_2}$/THF, −50 °C] followed by addition of excess methyl iodide and acidic hydrolysis (10% HCl/THF, 25 °C, 1 h) afforded racemic hibiscone C in 64% yield, accompanied by less than 7% of the equatorial methyl epimer. That indeed hibiscone C was in hand derived from careful spectral (e.g., NMR, IR, MS, and UV) and TLC comparisons to authentic material kindly provided by Professor Thomson.[22]

In summation, the first total synthesis of hibiscone C has been achieved. Central to the successful strategy was the intramolecular [2 + 2] photocycloaddition of an enone (i.e., **4**) to an acetylenic bond. Studies to explore and extend the utility of this process are under active investigation in our laboratory and will be reported in due course.

Acknowledgment. It is a pleasure to acknowledge the support of this investigation by the National Institutes of Health (National Cancer Institute) through Grant No. 22807. In addition, we thank S. T. Bella of the Rockefeller University for the microanalyses and Drs. G. Furst and T. Terwilliger of the University of Pennsylvania Spectroscopic Facilities for aid in obtaining the high-field NMR and MS spectral data, respectively.

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(21) (a) That in fact the major product was the desired monoketal **14** was deduced from the NMR spectral data. In particular, ketalization of the C(1)-carbonyl of **2** results in a 0.46-ppm upfield shift of the furan hydrogen (δ 7.82 to 7.36). A similar effect upon ketalization of **13b** to give **14** would lead to a predicted value of δ 7.64 for the same hydrogen. In the event the observed value was δ 7.56. In the case of the C(7)-monoketal the resonance for the furan hydrogen would not be expected to undergo a significant shift from the δ 7.82 value. (b) In our initial approach to **14**, we attempted to oxidize the C(7) position of the ketal of **2** via both the NBS/hydrolysis and the $CrO_3 \cdot 2py$ sequences. These procedures resulted in the loss of the ketal functionality.

(22) We thank Professor R. H. Thomson of the University of Aberdeen for providing us with a generous sample of hibiscone C as well as copies of the spectral data (i.e., ^1H and IR).

Electron-Transfer Mechanism for a Hydride-Transfer Reaction: Evidence for Selective α-Hydride Abstraction from a Transition-Metal Alkyl

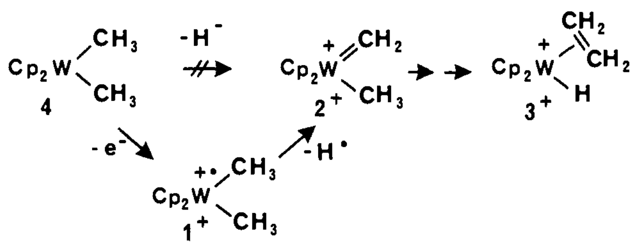
Jeffrey C. Hayes and N. John Cooper*[†]

Department of Chemistry, Harvard University
Cambridge, Massachusetts 02138

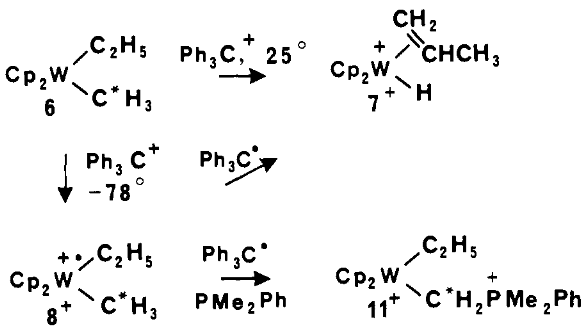
Received December 7, 1981

It has been demonstrated that transfers of alkyl anions and hydride ions from main-group organometallics and from both simple and complex hydrides to organic substrates can occur by mechanisms involving initial electron-transfer steps,[1] and there is growing interest in the general importance of electron-transfer mechanisms in reactions of organometallics.[2] We report the first examples in which hydride transfers from transition-metal alkyls to hydride acceptors occur by a two-step electron-transfer/radical-transfer mechanism and evidence suggesting that this pathway is associated with an α regioselectivity that contrasts dramatically with the normal β regioselectivity for hydride transfers from transition-metal alkyls.

Scheme I. Formation of $[W(\eta\text{-}C_5H_5)_2(C_2H_4)H]^+$ from $[W(\eta\text{-}C_5H_5)_2(CH_3)_2]$ ($Cp = \eta\text{-}C_5H_5$)



Scheme II. Reactions of $[W(\eta\text{-}C_5H_5)_2(CH_3)(C_2H_5)]$ ($Cp = \eta\text{-}C_5H_5$, *H = H or D)



[†] Fellow of the Alfred P. Sloan Foundation, 1982–1984.

(1) (a) Ashby, E. C.; Goel, A. B. *J. Am. Chem. Soc.* **1981**, *103*, 4983. (b) Ashby, E. C.; Bowers, J. R. *Ibid.* **1981**, *103*, 2242. (c) Ashby, E. C.; Goel, A. B.; DePriest, D. N.; Prasad, H. S. *Ibid.* **1981**, *103*, 973. (d) Ashby, E. C.; Goel, A. B.; DePriest, R. N. *Ibid.* **1980**, *102*, 7779. (e) Ashby, E. C.; Wieseman, T. L. *Ibid.* **1978**, *100*, 189. (f) Holm, T.; Crossland, I. *Acta Chem. Scand.* **1971**, *25*, 59. (g) Blomberg, C.; Salinger, R.; Mosher, H. *J. Org. Chem.* **1969**, *34*, 2385. (h) Fauvarque, J. F.; Rouget, E. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1968**, *257*, 1355. (i) Maruyama, K. *Bull. Chem. Soc. Jpn.* **1964**, *37*, 897. (j) Klingler, R. J.; Mochida, K.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 6626.

(2) For recent leading references see: (a) Klingler, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 5839. (b) Fukuzumi, S.; Kochi, J. K. *Ibid.* **1980**, *102*, 2141, 7290. (c) Fukuzumi, S.; Wong, C. L.; Kochi, J. K. *Ibid.* **1980**, *102*, 2928. (d) Wong, C. L.; Kochi, J. K. *Ibid.* **1979**, *101*, 5593. (e) Fukuzumi, S.; Mochida, K.; Kochi, J. K. *Ibid.* **1979**, *101*, 5961. (f) Mochida, K.; Kochi, J. K.; Chen, K. S.; Wan, J. K. S. *Ibid.* **1978**, *100*, 2927. For an introduction to earlier literature see: Kochi, J. K. "Organometallic Mechanisms and Catalysis"; Academic Press: New York, 1978.

(3) Hayes, J. C.; Pearson, G. D. N.; Cooper, N. J. *J. Am. Chem. Soc.* **1981**, *103*, 4648.

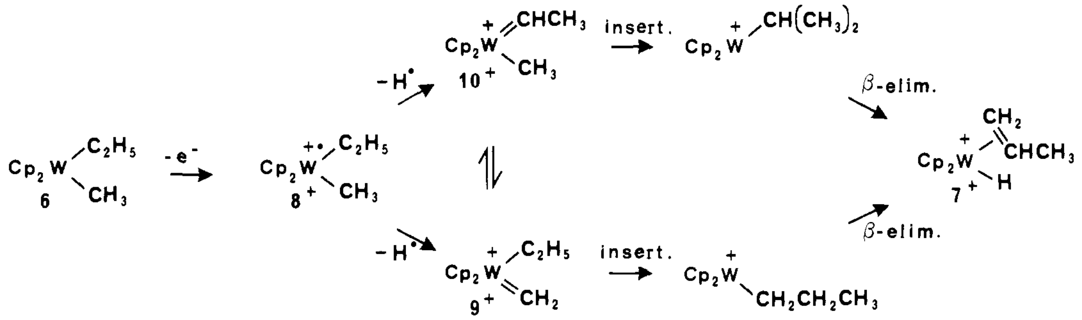
(4) Benfield, F. W. S.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1974**, 1324.

(5) IR, EPR. Quantitative ^1H NMR spectroscopy indicted that the only diamagnetic contaminant was <5% of 3^+.

(6) Cooper, N. J.; Green, M. L. H.; Mahtab, R. *J. Chem. Soc., Dalton Trans.* **1979**, 1557.

0002-7863/82/1504-5570$01.25/0 © 1982 American Chemical Society

Scheme III. Possible Pathways for the Formation of $[W(\eta\text{-}C_5H_5)_2(C_3H_6)H]^{+12}$ from $[W(\eta\text{-}C_5H_5)_2(CH_3)(C_2H_5)]$ (Cp = η-C_5H_5)



We previously reported that treatment of the 17-electron dimethyl complex $[W(\eta\text{-}C_5H_5)_2(CH_3)_2]PF_6$ (**1-PF$_6$**) with the trityl radical ($Ph_3C\cdot$) results in essentially quantitative conversion of **1-PF$_6$** into the ethylene complex $[W(\eta\text{-}C_5H_5)_2(C_2H_4)H]PF_6$ (**3-PF$_6$**) by an alkylidene insertion/β-elimination mechanism in which the key intermediate is $[W(\eta\text{-}C_5H_5)_2(CH_2)CH_3]^+$ (**2$^+$**).[3] We have now observed that attempting to form **2$^+$** directly from the neutral dimethyl $[W(\eta\text{-}C_5H_5)_2(CH_3)_2]$[4] (**4**) (a formal hydride abstraction; Scheme I) again results in formation of **3$^+$**, isolated as **3-BF$_4$** in 96% yield after treatment of **4** with Ph_3CBF_4 in CH_2Cl_2 at 25 °C. Reaction of Ph_3CBF_4 with a mixture of **4-d_0** and **4-d_6** gave a mixture of deuterated derivatives of **3$^+$** nearly identical with that previously obtained from a mixture of **1-PF$_6$-d_0** and **1-PF$_6$-d_6**,[3] as assayed by mass spectroscopic analysis of the $[W(\eta\text{-}C_5H_5)_2(C_2D_nH_{4-n})]$ formed by deprotonation.[3] We conclude that formation of **3$^+$** from **4**, like formation of **3$^+$** from **1$^+$**, is intramolecular and probably involves migratory insertion within **2$^+$**.

The formation of **2$^+$** from **4** raised the question of whether **2$^+$** is formed via a single-step hydride transfer from **4** or via an initial electron transfer to form **1$^+$** and $Ph_3C\cdot$ followed by a hydrogen atom transfer (Scheme I). EPR monitoring established that at least some $Ph_3C\cdot$ and **1$^+$** were formed in the course of the reaction, and a thermal trapping experiment was therefore attempted. Dropwise addition of 1.0 equiv of Ph_3CPF_6 to a CH_2Cl_2 solution of **4** at −78 °C resulted in oxidation of **4** to **1$^+$**, isolated as **1-PF$_6$**[5,6] in 73% yield. Efficient trapping of the intermediate showed that electron transfer was the only significant route for the hydride transfer.

An unusual feature of the formation of **2$^+$** from **4** is the loss of the hydride from an α carbon; although abstraction of β hydrides from transition-metal alkyls is a well-documented process,[7,8] there are only two previous reports of abstraction of α hydrides.[8,9] One of these described a selective α-hydride abstraction from a ReC_2H_5 group by Ph_3C^+, and the authors suggested that this selectivity might be associated with the electron-acceptor capability of Ph_3C^+.[9] Since at this point we had demonstrated that the reaction of **4** with Ph_3C^+ proceeded by an electron-transfer mechanism, the tungstenocene metal–ligand environment offered an exceptional opportunity to test whether such a mechanism would result in α-hydride abstraction even in the presence of β hydrogens. A tungstenocene substrate containing both α and β hydrogens was accordingly prepared as shown in eq 1.

$$\underset{\mathbf{4}}{[W(\eta\text{-}C_5H_5)_2(CH_3)_2]} \xrightarrow{PhCO_2H} \underset{\mathbf{5}}{[W(\eta\text{-}C_5H_5)_2(CH_3)(OCOPh)]} \xrightarrow{EtMgBr} \underset{\mathbf{6}}{[W(\eta\text{-}C_5H_5)_2(CH_3)(C_2H_5)]} \quad (1)$$

The conversion of **4** to **5** has been reported previously,[6] and reaction of **5** in THF with 10 equiv of EtMgBr in Et_2O at 70 °C for 23 h converted **5** to **6**. Crude **6**, contaminated by 10% $[W(\eta\text{-}C_5H_5)_2H_2]$,[10] was obtained in 56% yield, and analytically pure $[W(\eta\text{-}C_5H_5)_2(CH_3)(C_2H_5)]$,[11] as used in subsequent experiments, was obtained in 35% yield after four recrystallizations from pentane.

The reaction of 1.0 equiv of Ph_3CBF_4 with **6** in CH_2Cl_2 at 25 °C resulted in formation of $[W(\eta\text{-}C_5H_5)_2(C_3H_6)H]BF_4$[12] (**7-BF$_4$**, Scheme II) in 89% yield. When the reaction of **6** with Ph_3C^+ was carried out by using Ph_3CPF_6 at −78 °C, however, **6** was oxidized to $[W(\eta\text{-}C_5H_5)_2(CH_3)(C_2H_5)]^{+}\cdot$ (**8$^+$**, Scheme II; isolated in 94% yield as **8-PF$_6$**[13,14]). The trapping of **8$^+$** indicates that the formation of **7$^+$** from **6** and Ph_3CBF_4 occurs by an electron-transfer mechanism. The intermediacy of **8$^+$** was confirmed by treating **8** PF$_6$ with 2.04 equiv of the trityl radical in CH_2Cl_2 at 21 °C to give **7-PF$_6$** in 93% yield.

The formation of **7$^+$** from both **6** and **8$^+$** rules out the possibility that hydrogen abstraction occurs from the β position in the ethyl group, since the product that would result, $[W(\eta\text{-}C_5H_5)_2(C_2H_4)CH_3]^+$, is a known molecule[15] that we have shown to be stable under these conditions. Hydrogen loss could, however, occur either from the methyl group of **8$^+$** to form the methylidene complex $[W(\eta\text{-}C_5H_5)_2(CH_2)C_2H_5]^+$ (**9$^+$**), or from the α-CH_2 of the ethyl group to form the ethylidene complex $[W(\eta\text{-}C_5H_5)_2(CH_3)CHCH_3]^+$ (**10$^+$**), since either **9$^+$** or **10$^+$** could give rise to **7$^+$** by an insertion/β-elimination sequence (Scheme III). Further experiments were required to distinguish between these two possible pathways and identify the origin of the abstracted hydride.

Reaction of **8** PF$_6$ with $Ph_3C\cdot$ in the presence of PMe_2Ph in CH_2Cl_2 at 21 °C (Scheme II) gave $[W(\eta\text{-}C_5H_5)_2(CH_2PMe_2Ph)C_2H_5]^+$ (**11$^+$**), isolated in 50% recrystallized yield as **11-PF$_6$**.[16] Formation of this phosphonium salt strongly suggested that the methylidene complex **9$^+$** had been formed and

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(7) (a) Green, M. L. H.; Nagy, P. L. I. *J. Organomet. Chem.* **1963**, *1*, 58. (b) Cohen, L.; Giering, W. P.; Kenedy, D.; Magatti, C. V. *Ibid.* **1974**, *65*, C57.

(8) Sanders, A.; Cohen, L.; Giering, W. P.; Kenedy, D.; Magatti, C. V. *J. Am. Chem. Soc.* **1973**, *95*, 5430.

(9) Kiel, W. A.; Liu, G.-Y.; Gladysz, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 3299.

(10) Green, M. L. H.; Knowles, P. J. *J. Chem. Soc., Perkin Trans. 1*, **1973**, 989 and references therein.

(11) ^{1}H NMR (benzene-d_6) δ 4.17 (s, 10 H, 2 C_5H_5), 1.69 (t, J = 7.3 Hz, 3 H, CH_2CH_3), 0.74 (q, J = 7.3 Hz, 2 H, WCH_2), 0.17 (s, (satellites J_{W-H} = 5.5 Hz), 3 H, WCH_3). Anal. Calcd for $C_{13}H_{18}W$: C, 43.60; H, 5.07. Found: C, 43.55; H, 5.03. ^{1}H NMR showed the presence of trace amounts (1–2%) of $[W(\eta\text{-}C_5H_5)_2H_2]$.

(12) Identified by comparison of ^{1}H NMR spectra in $(CD_3)_2SO$ and $(CD_3)_2CO$ with that reported in the literature for **7-PF$_6$**.[4] The two isomers of **7$^+$** (exo and endo) were present in a 47:53 ratio.

(13) This material was contaminated by trace amounts (<2%) of diamagnetic compounds, **3-PF$_6$** and **7-PF$_6$**, as shown by quantitative ^{1}H NMR. Material of this purity is only obtained if the solvent is removed rapidly at −40 °C after the oxidation (1 h on a 1.3 mmol/50 mL scale).

(14) $\langle g \rangle$ (CH_2Cl_2) = 2.0560. IR (Nujol) 3138 s, 1442 s, 1432 s, 1415 mw, 1300 br w, 1217 mw, 1179 m, 1128 w, 1079 br w, 1023 m, 1015 m, 965 br m, 879 br s, 835 br vs, 780 m sh, 742 mw, 722 br mw. Anal. Calcd for $C_{13}H_{18}PF_6W$: C, 31.04; H, 3.61. Found: C, 30.88; H, 3.62.

(15) Benfield, F. W. S.; Cooper, N. J.; Green, M. L. H. *J. Organomet. Chem.* **1974**, *76*, 49.

(16) ^{1}H NMR (acetone-d_6) δ 8.10–7.65 (m, 5 H, C_6H_5), 4.83 (s, 10 H, 2 C_5H_5), 2.28 (d, J_{P-H} = 13.2 Hz, 6 H, $2CH_3$), 1.40 (t, J = 7.3 Hz, 3 H, CH_2CH_3), 0.92 (d, J_{P-H} = 13.2 Hz (satellites $J_{W-H} \simeq$ 6 Hz), 2 H, WCH_2P), 0.42 (q, J = 7.3 Hz, 2 H, WCH_2). Anal. Calcd for $C_{21}H_{28}P_2WF_6$: C, 39.40; H, 4.41. Found: C, 39.29; H, 4.34.

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 $[W(\eta\text{-}C_5H_5)_2(CD_3)C_2H_5)]PF_6$ with $Ph_3C\cdot$ in the presence of PMe_2Ph. The exclusive isolation of $[W(\eta\text{-}C_5H_5)_2(CD_2PMe_2Ph)C_2H_5)]PF_6$ (^1H NMR, Scheme II) showed that hydride abstraction occurred solely from the methyl group to form **9**$^+$.

Since α-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 π interaction;[17] this would not be surprising in light of recent NMR evidence for ground-state spin delocalization via metal–carbon π interactions in paramagnetic vanadium alkyls.[18] Such delocalization may generally facilitate α-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 α selectivity in the second step.[19]

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Exxon Educational Foundation, and the National Science Foundation (Grant CHE80-16162) for their support of this research.

Registry No. **1**-PF_6, 72427-27-1; **3**-BF_4, 82917-93-9; **4**, 39333-53-4; **5**, 73210-66-9; **6**, 82917-94-0; **7**-BF_4, 63469-56-7; **7**-PF_6, 53806-23-8; **8**-PF_6, 82917-96-2; **11**-PF_6, 82917-98-4; Ph_3 C BF_4, 341-02-6; Ph_3 C PF_6, 437-17-2; $Ph_3C\cdot$, 2216-49-1; $[W(\eta\text{-}C_5H_5)_2(CD_3)C_2H_5](PF_6)$, 82918-00-1; $[W(\eta\text{-}C_5H_5)_2(CD_2PMe_2Ph)(C_2H_5)](PF_6)$, 82918-02-3; EtBr, 74-96-4; P Me_2 Ph, 672-66-2.

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[17] This could explain the formation of the methylidene complex **9**$^+$ in preference to the ethylidene **10**$^+$. The ethylidene ligand in the isoelectronic molecule $[Ta(\eta\text{-}C_5H_5)_2(CHCH_3)CH_3]$ is unable to achieve the electronically optimal orientation for π 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.

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

[19] Definitive demonstration of α regioselectivity in this system will require the observation of ethylidene formation from a substrate such as $[W(\eta\text{-}C_5H_5)_2(C_2H_5)_2]$. 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*