Table II. Cleavage of Excess Substrate by *o*-Iodosobenzoate[a]

run	substrate	[substrate], M	[substrate]/[2]	$10^4 k_\psi$, s^{-1}
1	PNPA	1.0×10^{-5}	1:10	152 ± 1[b]
2	PNPA	1.0×10^{-4}	1:1	130 ± 2
3	PNPA	5.0×10^{-4}	5:1	100 ± 1
4	PNPA	1.0×10^{-3}	10:1	90 ± 2
5	PNPDPP	1.0×10^{-5}	1:10	260 ± 4
6	PNPDPP	1.0×10^{-4}	1:1	249 ± 8
7	PNPDPP	5.0×10^{-4}	5:1[c]	235 ± 5

[a] Conditions: 0.02 M phosphate buffer, 3.3 vol % DMF, pH 8.0, $\mu = 0.08$ (NaCl), 26 ± 0.5 °C; [CTACl] = 0.01 M; [2] = 1.0×10^{-4} M. Release of *p*-nitrophenoxide ion was followed at successively longer λ (lower ϵ) as [substrate] increased. [b] The lower rate constant, relative to run 6 in Table I, is due to the higher concentration of DMF (3.3 vs. 1.1 vol %). [c] Solubility problems with PNPDPP prevented us from obtaining data at 10:1 substrate/2.

~1200 for the catalysis of PNPA cleavage by micellar *o*-IBA/CTACl.

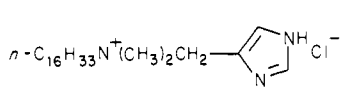
The cleavage of the active phosphate substrate, PNPDPP, is also strongly catalyzed by *o*-IBA/CTACl. At 0.01 M surfactant and 1×10^{-4} M *o*-IBA, $k_\psi = 2.38 \times 10^{-2}$ s^{-1} (run 8). Comparison with an uncatalyzed reaction in 0.02 M Tris buffer at pH 9, which gives $k_\psi = 2.9 \times 10^{-5}$ s^{-1},[8] leads to a catalytic factor of >820.

A pH-rate constant profile (not shown) was determined for reactions of 10^{-5} M PNPA with 10^{-4} M *o*-IBA in 10^{-2} M CTACl (0.02 M phosphate or acetate buffers, $\mu = 0.08$). Ten rate constants were determined over the pH range 4.5-9.55. A sharp discontinuity (abrupt decrease in slope) in log k_ψ vs. pH was found at pH 7.25, with excellent linearity on either side of the break point. Taking 7.25 as the systematic pK_a of *o*-IBA under our reaction conditions implies that **2** is ~85% converted to **3**, its catalytically active form, at pH 8.0.

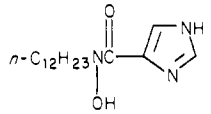
We prepared[2] **4**, the acetyl derivative of **2** and the putative intermediate in nucleophilic cleavage of PNPA by anion **3**.[9] Ester **4** decayed rapidly at pH 8 in 0.01 M micellar CTACl, with k_ψ ~0.4 ± 0.1 s^{-1}. The reaction was followed spectrophotometrically at 276 nm, λ_{max} for **4** (in DMF, ϵ 2520). Although the hydrolytic instability of **4** makes for poor precision in this determination, the rate constant for deacetylation of **4** is ~20 times larger than k_ψ for PNPA cleavage by *o*-IBA under comparable conditions (Table I, run 6). Thus **4** should not accumulate during the reaction of PNPA with *o*-IBA/CTACl. Indeed, no increase in absorbance at 276 nm could be detected during such reactions.

The behavior of *o*-IBA/CTACl in the presence of *excess* substrate was consistent with these indications of efficient turnover. The data in Table II (runs 1-4) show that the apparent value of k_ψ for liberation of *p*-nitrophenoxide ion from PNPA decreased by only ~40% as the substrate/catalyst ratio increased from 1:10 to 10:1. The kinetics remained pseudo first order, and "burst kinetics"[10] were not observed. A similar pattern held for the cleavage of PNPDPP (runs 5-7); there was no evidence for the accumulation of a phosphoryl derative of *o*-IBA.

Micellar reagents such as the imidazolyl surfactant **5** catalyze



5



6

cleavages of PNPA[11] and PNPDPP[12] at moderate pH with kinetic parameters similar to those of *o*-IBA/CTACl.[12] However, to our knowledge, *o*-IBA/CTACl is the only "monofunctional" O-functionalized micellar catalyst capable of both efficient cleavage *and* turnover with active ester and phosphate substrates.[13] For example, oximate ions in micellar CTABr rapidly cleave *p*-nitrophenyl esters at pH 8 and PNPDPP at pH 10, but hydrolytic regeneration of the acylated or phosphorylated oximates is very slow at pH 8.[14] Certain bifunctional O,N catalysts such as lauryl(4-imidazolecarbo)hydroxamic acid, **6**, in micellar CTABr are capable of true catalytic cleavage of activated esters[15] but lack the "off the shelf" simplicity of *o*-IBA/CTACl. Moreover, in the cleavage of PNPA, *o*-IBA in CTACl is more efficient than either **5** or **6** (in CTABr) because the deacetylation of **4** is more rapid than the acetylation of **2** and doesn't become rate-limiting when the substrate is in moderate excess.[16]

Acknowledgment. We are grateful to the U.S. Army Research Office, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for financial support.

(8) Moss, R. A.; Ihara, Y. *J. Org. Chem.*, in press.

(9) Solvent isotope effects (k_{H_2O}/k_{D_2O}) were determined for cleavages of PNPA and PNPDPP in 0.2 M phosphate buffer at pH (pD) 8.0 ($\mu = 0.54$). With [CTACl] = 0.01 M, [2] = 1×10^{-4} M, and [substrate] = 1×10^{-5} M, the solvent isotope effects were 1.03 and 1.12 for PNPA and PNPDPP, respectively. These values are consistent with nucleophilic cleavage mechanisms involving anion **3** but inconsistent with mechanisms in which **3** functions as a general base.

(10) Bender, M. L.; Kézdy, F. J.; Wedler, F. C. *J. Chem. Educ.* **1967**, *44*, 85.

(11) Tagaki, W.; Chigira, J.; Ameda, T.; Yano, Y. *J. Chem. Soc., Chem. Commun.* **1972**, 219. Tonellato, U. *J. Chem. Soc., Perkin Trans. 2* **1976**, 771. Moss, R. A.; Nahas, R. C.; Ramaswami, S. *J. Am. Chem. Soc.* **1977**, *99*, 627. With 5×10^{-3} M **5** in 0.4 M, pH 8 phosphate buffer, PNPA is cleaved with k_ψ ($=k_{acylation}$ of **5**) = 0.051 s^{-1}, followed by $k_{decylation}$ (of *N*-acetyl-**5**) = 0.015 s^{-1}. Note that deacylation is slower than acylation; the opposite is true for *o*-IBA/CTACl.

(12) Brown, J. M.; Bunton, C. A.; Diaz, S.; Ihara, Y. *J. Org. Chem.* **1980**, *45*, 4169. Brown, J. M.; Bunton, C. A.; Diaz, S. *J. Chem. Soc., Chem. Commun.* **1974**, 971. For micellar **5** and PNPDPP, $k_\psi = 0.0031$ s^{-1} at pH 8; the imidazole here functions as a general base catalyst.

(13) Reviews: O'Connor, C. J.; Ramage, R. E.; Porter, A. J. *Adv. Colloid Interface Sci.* **1981**, *15*, 25. Kunitake, T.; Shinkai, S. *Adv. Phys. Org. Chem.* **1980**, *17*, 435. Bunton, C. A.; Romsted, L. S. In "The Chemistry of Functional Groups, Suppl. B: The Chemistry of Acid Derivatives", Part 2; Patai, S., Ed.; Wiley: New York, 1979; pp 945 ff.

(14) Bunton, C. A.; Ihara, Y. *J. Org. Chem.* **1977**, *42*, 2865.

(15) Kunitake, T.; Okahata, Y.; Sakamoto, T. *J. Am. Chem. Soc.* **1976**, *98*, 7799. At pH 8 (30 °C, 0.01 M borate, $\mu = 0.01$), **6**/CTABr cleaves PNPA ~5 times faster than *o*-IBA/CTACl. However, deacetylation of *O*-acetyl-**6** is ~7 times *slower* than deacetylation of **4**.

(16) Under micellar conditions at pH 8, $k_{deacetylation}$ is ~0.4, 0.015, and 0.065 s^{-1} for acetylated **2**, **5**,[11] and **6**,[15] respectively.

Rearrangement of an Alkyl-Substituted Anthraquinone. A Model for the Biosynthetic Rearrangement of the Averufin Side Chain

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Received September 27, 1982

Various mechanisms have been proposed for the biosynthesis of aflatoxin B_1 (**1**, Chart I) a potent carcinogenic mycotoxin produced by the fungi *Aspergillus flavus* and *Aspergillus parasiticus*.[1-3] In all these biosynthetic schemes, versicolorin A (**2**), has been proposed as an intermediate, which in turn is derived from averufin (**3**). Averufin (**3**) bears an unbranched C_6 side chain on a polyhydroxyanthraquinone, and its conversion to the branched-chain aldehyde versiconal acetate (**4**) has been speculated to involve loss of the terminal acetyl unit by a Baeyer-Villiger process,[1] as well as a side-chain skeletal rearrangement proceeding

(1) Steyn, P. S.; Vleggaar, R.; Wessels, R. L. In "The Biosynthesis of Mycotoxins"; Steyn, P. S., Ed.; Academic Press: New York, 1980; pp 105-155, and references therein.

(2) Simpson, T. J.; De Jesus, A. E.; Steyn, P. S.; Vleggaar, R. *J. Chem. Soc., Chem. Commun.* **1982**, 631.

(3) Simpson, T. J.; De Jesus, A. E.; Steyn, P. S.; Vleggaar, R. *J. Chem. Soc., Chem. Commun.* **1982**, 632.

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Chart I

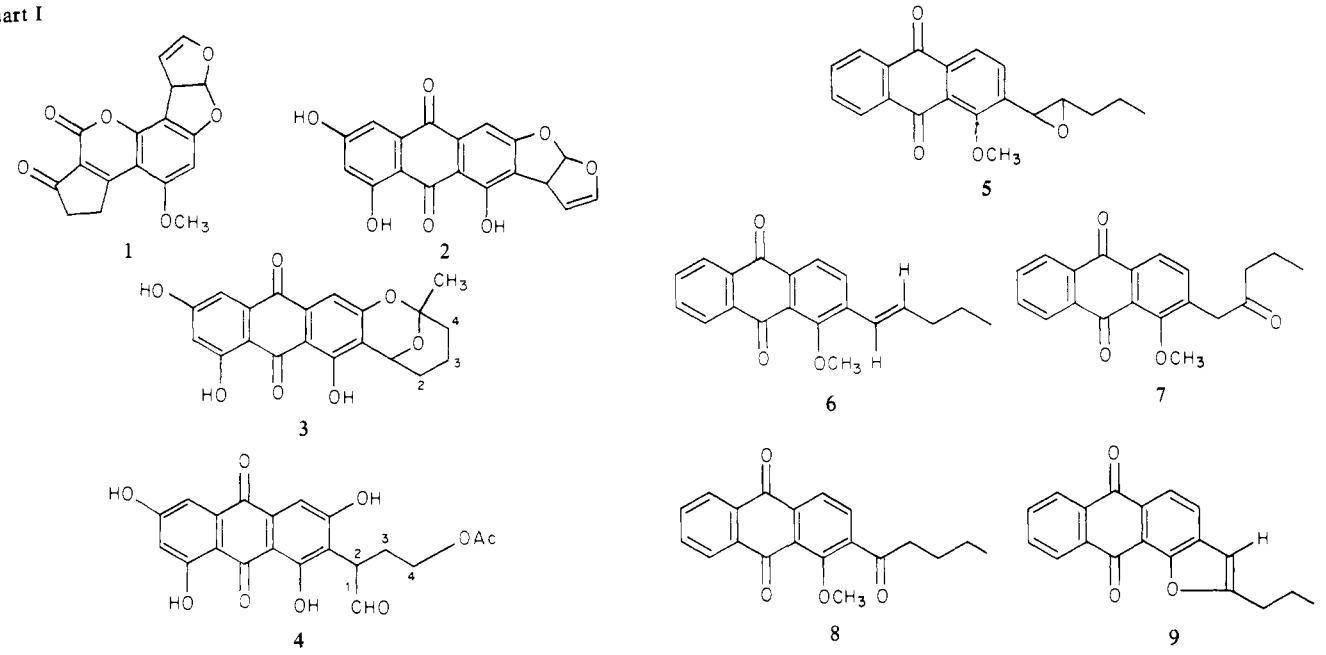
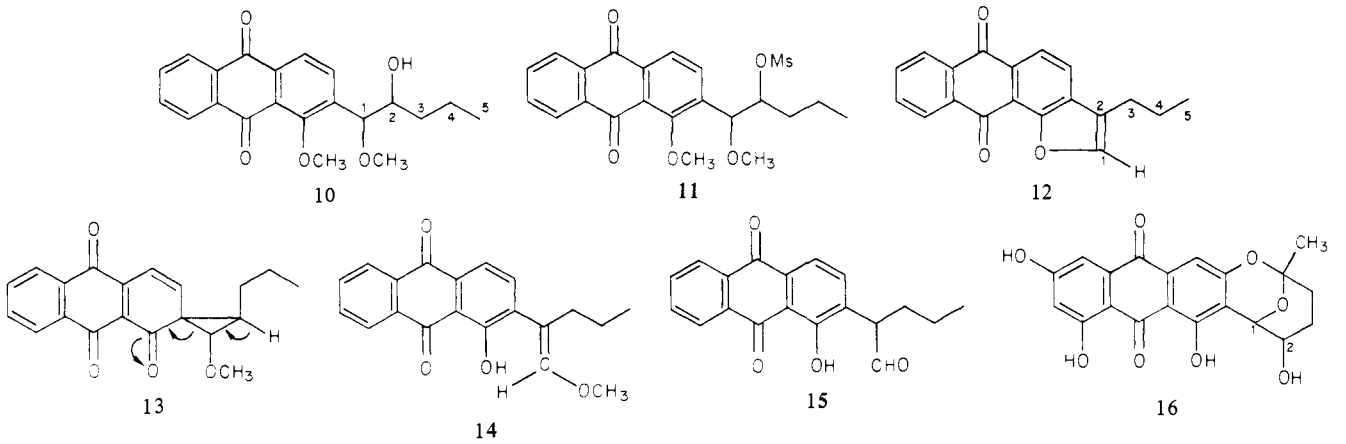


Chart II



via a Favorski-type cyclopropane intermediate[4] or the cationic rearrangement of an epoxide[5] or a 1,2-diol.[6]

All these proposed pathways involve the initial migration of an anthraquinone unit from the α-position to the β-position of the side chain, a transformation for which no synthetic analogue is known. We now report the first case of this type of rearrangement of an alkylanthraquinone system.

The epoxide **5**, available from the oxidation of olefin **6**[7] with *m*-chloroperbenzoic acid, underwent no skeletal rearrangement on treatment with boron trifluoride etherate. The ketone **7**[8] was the only product isolated, none of the regioisomer **8** being produced. When the epoxide **5** was treated with PhSeNa and the product worked up with dilute acid, a 69% yield of the condensed furan **9**[8] was obtained. The sharp singlet at δ 6.55 in its ^{1}H NMR spectrum, characteristic of the β-proton of furans, was diagnostic in establishing the structure of **9**. The β-proton in furan itself appears at δ 6.37, while the α-proton appears as a triplet at δ 7.42.[9] The furan **9** would result from an initial demethylation of the epoxide **5** followed by an intramolecular opening of the oxirane to afford a dihydrofuran that undergoes dehydration on acid workup.

When the epoxide **5** was treated with methanol in the presence of a trace of acid, the hydroxy compound **10** (Chart II) was isolated. Smooth conversion to the mesylate **11**, followed by treatment with PhSNa and acid workup afforded (75% yield) the isomeric condensed furan **12**,[8] whose ^{1}H NMR spectrum showed a sharp singlet at δ 7.79 as well as the absence of hydroxyl and methoxyl protons.[10]

(4) Tanabe, M.; Uramoto, M.; Hamasaki, T.; Cary, L. *Heterocycles* **1976**, *5*, 355.

(5) Gorst-Allman, C. P.; Pachler, K. G. R.; Steyn, P. S.; Wessels, P. L.; Scott, D.-B. *J. Chem. Soc., Perkin Trans. 1* 1977, 2181.

(6) Kingston, D. G. I.; Chen, P. N.; Vercellotti, J. R. *Phytochemistry* **1976**, *15*, 1037.

(7) The olefin **6** was prepared from the Wittig reaction of *n*-butyraldehyde and the appropriate phosphonium salt. Details will be published elsewhere.

(8) This substance gave satisfactory elemental analysis and spectroscopic data. The melting point, mass spectral data, and ^{1}H NMR ($CDCl_3$) for the furans **9** and **12** are given here: Furan **9**: mp 167–171 °C; mass spectrum, *m/e* 291, 290, 262, 261, 233; ^{1}H NMR δ 8.34–8.2 (m, 3 H), 7.87–7.78 (m, 3 H), 6.55 (s, 1 H), 2.96–2.90 (t, J = 7.15 Hz, 2 H), 1.93–1.85 (m, 2 H), 1.11–1.05 (t, J = 7.15 Hz, 3 H). Furan **12**: mp 179–183 °C; mass spectrum, *m/e* 291, 290, 262, 261, 233; ^{1}H NMR δ 8.33–8.20 (m, 3 H), 7.79 (s, 1 H); 7.92–7.74 (m, 3 H), 2.72–2.66 (t, J = 7.15 Hz, 2 H), 1.80–1.65 (m, 2 H), 1.01–1.99 (t, J = 7.70 Hz, 3 H).

(9) Jackman, L. M.; Sternhell, S. In "Applications of NMR spectroscopy in Organic Chemistry" 2nd ed.; Pergamon Press: New York, 1969; p 209.

(10) The furan **12** was obtained by adding a DMF solution of the mesylate **11** to 1.25 equiv of sodium thiophenolate in dry DMF under N_2. The reaction was quenched after 3 h at 110 °C, followed by successive treatments with aqueous HCl (10%) and dilute aqueous NaOH. Chromatography (silica gel/methylene chloride) followed by crystallization of the isolated product from ethanol afforded a 75% yield of furan **12** as bright yellow feathery needles.

The β-propyl side chain in furan **12** results from an overall 1,2-migration of the anthraquinone unit, which we believe proceeds via the formation of a methoxycyclopropane dienone (**13**). We propose that initial O-demethylation of **11** is followed by an intramolecular expulsion of the hindered mesyloxy group to give the cyclopropane **13**, which then undergoes ring opening to the enol methyl ether **14** and subsequently condenses to **12** on acidification via the aldehyde **15**.

Very recently, Townsend[11,12] has offered convincing evidence that averufin **3** is converted in vivo to aflatoxin B_1 (**1**) via versiconal acetate **4** in such a manner that the C-1 hydrogen of **3** becomes the aldehyde hydrogen of **4**, thus ruling out a Favorski-type cyclopropanone intermediate in this transformation. Our model studies suggest that an acid-catalyzed epoxide or diol rearrangement is unlikely and that nidurufin (**16**),[13] probably as a pyrophosphate ester (OPOP at C-2), may well be the intermediate unbranched progenitor of the branched-chain aflatoxin precursors.

Acknowledgment. This work was supported by a grant from the National Institutes of Health, CA 30377-01A1.

Registry No. 5, 84066-44-4; **6**, 84066-45-5; **7**, 84066-46-6; **9**, 84066-47-7; **10**, 84066-48-8; **11**, 84066-49-9; **12**, 84066-50-2; PhSeNa, 23974-72-3.

(11) Townsend, C. A.; Christensen, S. B.; Davis, S. G. *J. Am. Chem. Soc.* **1982**, *104*, 6152.
(12) Townsend, C. A.; Christensen, S. B.; Davis, S. G. *J. Am. Chem. Soc.* **1982**, *104*, 6154.
(13) Aucamp, P. J.; Holzapfel, C. W. *J. S. Afr. Chem. Inst.* **1970**, *23*, 40.

Book Reviews

Inorganic Coordination Compounds: Nobel Prize Topics in Chemistry Series. By George B. Kaufman (California State University). Heyden & Son Ltd, London. 1981. xii + 206 pp.

This book is one of the most delightful I have had the opportunity to review. In fact, I could not lay down the book once I started reading it. I wholeheartedly endorse Sir Geoffrey Wilkinson's recommendation: "It should be compulsory reading for all students." The book deals with the historical development of inorganic chemistry leading to Werner's coordination theory.

Chapter Three reproduces Werner's address before the Société Chimique de France (1912), summarizing the definitive work on the constitution and configuration of coordination compounds by him and his associates. The address is a masterpiece of scientific presentation in its precision, brevity, and style. Chapter Six presents the gist of the classic Werner–Jørgensen controversy. The chapter also shows how experimental techniques—conductivity, molecular weight, optical activity measurements—simple by today's standards, when performed with skill and imagination can substantiate epoch-making theories.

Elsewhere the author deals with other historical developments, a number of classic experiments, and nomenclature, all done with great accuracy and little rhetoric. This reviewer was not aware that the graduate student Victor L. King, codiscoverer of optical activity in *cis*-$[Coen_2(NH_3)Cl]^{2-}$ (1912), was an American. The author also makes brief references to the developments in coordination chemistry since Werner's time, none of which of course have changed the basic postulates of Werner's theory. The book also includes a number of rare photographs, including that of King. A brief history of the Werner family and the highlights of Werner's life are also included in the book.

In concluding this review I wish to repeat Sir Geoffrey Wilkinson's recommendation, "It should be compulsory reading for all students."

Buddhadev Sen, *Louisiana State University*

Organophosphorus Chemistry. Volume 2. A Review of the Literature Published between July 1979 and June 1980. Senior Reporters D. W. Hutchinson (University of Warwick) and J. A. Miller (University of Dundee). The Royal Society of Chemistry, London. 1981. xi + 261 pp. $120.00.

This volume in the continuing series follows in the fine tradition of the previous works in that the coverage of developments in organophosphorus chemistry is excellent, but somewhat selective rather than comprehensive. There are eleven chapters: 1. Phosphines and Phosphonium Salts; 2. Quinquecovalent Phosphorus Compounds; 3. Halogenphosphines and Related Compounds; 4. Phosphine Oxides and Related Compounds; 5. Tervalent Phosphorus Compounds; 6. Quinquevalent Phosphorus Compounds; 7. Phosphates and Phosphonates of Biochemical Interest; 8. Phosphoryl Transfer from Phosphomonoesters and Adenosine 5′-Triphosphate; 9. Nucleotides and Nucleic Acids; 10. Ylides and Related Compounds; 11. Physical Methods. Chapters 1, 4, 10, and 11 are extremely well done and quite informative in terms of recent innovations. In particular, Chapter 10 clearly points out the increasing versatility of the various Wittig-type reagents for the preparation of polyenes. Chapter 11, as in earlier volumes, is most useful for those in the field for a quick perusal of spectroscopic information gleaned from a large cross section of phosphorus compounds. In view of the relatively large number of valence states that can be assumed by phosphorus, it has become of paramount importance to identify the hybridization and configuration at the phosphorus atom.

Chapter 8 also is extremely timely, since the area of phosphoryl transfer is an active one and of critical significance to the understanding of the process in biological systems. Professor Ramirez and Dr. Marecek have done well in bringing out the salient features of the fast-developing technology. This chapter and many in the book will be of interest to biological chemists as well as to phosphorus chemists or anyone working with such compounds for the first time. The discussions are well referenced with some cross citations to past volumes and other reviews which markedly increases the value of the volume. This is true for all of the chapters.

Those who have invested in the previous volumes will find this one of equal value. All of those who work in the field or who plan to work in phosphorus chemistry would do well to have it for handy reference.

K. Darrell Berlin, *Oklahoma State University*

Structure and Bonding. Volume 42. Luminescence and Energy Transfer. Contributions by G. Blasse, K. C. Bleijenberg, and R. C. Powell. Springer-Verlag, Berlin and New York. 1980. 133 pp. $40.00.

"Luminescence and Energy Transfer in Solids" is Volume 42 in the continuing series "Structure and Bonding". It consists of three reviews: The Luminescence of Closed-Shell Transition-Metal Complexes. New Developments, by G. Blasse; Energy Transfer in Concentrated Systems, by R. C. Powell and G. Blasse; and Luminescence Properties of Uranate Centres in Solids, by K. C. Bleijenberg.

The first review deals with oxides of metals in high oxidation states. The article consists primarily of statements of experimental facts although the author does provide some systematization. The general feature that emerges, that the solid-state emission spectra of these compounds consists of broad featureless bands, will probably not be of widespread interest to chemists.

The second review treats radiationless energy transfer in the absence of charge migration in inorganic solids. It reviews the relevant theory and illustrates the theory with some selected examples. The review serves the purpose of providing in a short format a guide to the theoretical and experimental literature and a survey of recent experimental results.

The final review focusses specifically on the luminescence properties of the UO_6^{6-} ion in the solid state. The contents are as specific as the title indicates.

In general, the book provides a useful guide to recent results in the specialized area of its focus. Chemists are increasingly studying the optical properties of solid-state materials. It is unfortunate that with the exception of a paragraph or two, semiconductors are not treated.

Jeffrey I. Zink, *University of California, Los Angeles*