

Book reviews

Supplements to the 2nd Edition of Rodd's Chemistry of Carbon Compounds: Volume III, Aromatic Compounds, Part H: Polycarbocyclic Compounds With More Than Thirteen Atoms in the Fused-Ring System: edited by MARTIN F. ANSELL, Elsevier, Amsterdam, or Elsevier Science Publishing Co., Inc., P.O. Box 1663, Grand Central Station, New York, NY 10163 in North America, 1988, xi + 154 pages + Subject Index, \$76.25, Dfl. 145.00.

This volume constitutes an up-to-date supplementation of the second edition of *Rodd's Chemistry of Carbon Compounds*, particularly of chapters 28, 29, and 30 of volume III H, and is concerned with aromatic compounds. The book consists of three contributed chapters, and all of the authors are authorities in their respective fields. The Editor and the contributors are to be congratulated on maintaining the high standard of the earlier volumes, and the authors, on the success of this immense task, including careful preparation of the text and formulas for photo-printing. The book discusses new chemistry of a wide range of condensed aromatic hydrocarbons and their derivatives, starting with anthracene and proceeding through the novel, fused-ring hydrocarbon kekulene ($C_{48}H_{24}$), m.p. $>620^\circ$. In addition to references on chemistry, photochemistry, and structure, the text cites key references to carcinogenic or environmentally hazardous compounds. Pertinent references on oxygenated metabolites of carcinogenic, polycyclic hydrocarbons and on intermediates useful in the synthesis of natural products, anthracyclines, and dyes have also been included. The literature survey, which is far from thorough, cites work through the year 1984, with some references through the year 1986.

A chapter by R. Bolton (University of London) presents some recent studies on the synthesis, structure, reactivity, and application of anthracene, phenanthrene, and related compounds and their derivatives; this includes substitution (*i.e.*, functionalization), halogenation, nitration, and oxidation (including ozonolysis) processes. Beginning with 9,10-anthraquinone, the synthesis of an important electron-acceptor, namely, 11,11,12,12-tetracyanoanthraquinone dimethide and its tetrathiafulvalene and tetrathioanthracene charge-transfer complexes (organic metals) is the most notable achievement. A very interesting *meso*-addition reaction of anthracenes has received special attention in this chapter. Using the approach outlined, series of triptycenes and hindered triptycenes have been synthesized by the addition of arynes across the *meso*-position of substituted anthracenes. Also, photoinduced electron-transfer oxidations of strained molecules in the presence of anthracene derivatives have been discussed. In a recent example, 9,10-dicyanoanthracene-sensitized photo-oxidation of arylvinylloxiranes in acetonitrile in the

presence of oxygen affords the corresponding 1,2,4-trioxepine [S. Futamura and Y. Kamia, *J. Chem. Soc., Chem. Commun.*, (1988) 1053–1055]. Anthracene derivatives can also be potential reagents in the polymer chemistry of cyclomalto-octaose (“ γ -cyclodextrin”), which consists of 8 D-glucosyl residues, and has been shown to be capable of including two guest molecules in its large cavity. Recent study shows that two anthracene-9-carbonyl moieties attached to the AB, AC, AD, and AE D-glucosyl units of γ -cyclodextrin undergo intramolecular photodimerization, giving unstable photodimers for the AB and AC regioisomers, and stable photodimers for the others. These regioisomers might be used as molecular switches with which host–guest complexation could be regulated by light [A. Ueno, F. Moriwaki, A. Azuma, and T. Osa, *J. Chem. Soc., Chem. Commun.*, (1988) 1042–1043]. The chapter further outlines some new reactions of phenanthrene and its derivatives. Cycloaddition occurs with phenanthrene, although less generally than with anthracenes. Photochemically induced reactions of phenanthraquinones, and their application to the preparation of photo-sensitive materials has characterized much of the recently published work. Reexamination of the classical oxidation (chromic acid–warm glacial acetic acid) of triphenylene showed that it gives a mixture of 1,4-quinone (1,4-dioxotriphenylene) (m/z 258) and phenanthrene-1,2-dicarboxylic anhydride (m/z 248) [C. Mannich, *Ber.*, 40 (1907) 163–168; A. J. Fatiadi, in print]. Hydroxylation of triphenylene (osmium tetroxide–benzene–pyridine, 48 h) gives *cis*-5,6-dihydro-5,6-dihydroxytriphenylene (m/z 262) (A. J. Fatiadi, in print). This chapter could also be supplemented by recent work on a new class of molecular hosts based on a *m*-terphenyl framework in which the other rings are orthogonal to the central ring, to give new cupped- and capped-ophanes having molecular cavities [T. K. Vinod and H. Hart, *J. Am. Chem. Soc.*, 110 (1988) 6574–6575].

The chapter by H. F. Andrew (Glasgow College of Technology) is devoted to the fused-ring, polycyclic aromatic compounds containing one or two five-membered rings; these include the hydrocarbons benzidane, acenaphthalene, fluorene, and fluoranthene. The text presents the current state of the fundamental chemistry, recent syntheses, and reactions of these hydrocarbons and their derivatives. The following synthetic procedures merit attention: the use of “masked” α,β -unsaturated ketones (synthesis of fluoranthene), cyclodehydrogenation of 9-phenylanthracene (synthesis of benzfluoranthene), or the *o*-lithioaryl-amide route (the Harvey method) using fluorene (or substituted fluorene) as the substrate (synthesis of cholanthrene and its 3-methyl derivative). Similar methods have been applied for the synthesis of four isomers of benzaceanthrylenes [j, l, e, k]. The incorporation of a five-membered ring into polycyclic hydrocarbons generally enhances the biological activity, *e.g.* mutagenicity, of the new hydrocarbon. This is, for example, true for the powerful carcinogenicity of cholanthrene or its 3-methyl derivative, or the potent mutagen cyclopenta[*cd*]pyrene. Generally, the presence of the “bay region” in polycyclic aromatic hydrocarbons is associated with carcinogenic and mutagenic properties (compare benzo[*a*]pyrene). The “bay region” is absent from cholanthrene and cyclopenta[*cd*]pyrene, and the mechanism

of their strong carcinogenicity in the biological environment is at the moment still unclear.

The last chapter (by H. F. Andrew) is an important extension of chapter 2; it deals with polycyclic, aromatic compounds containing four or more six-membered, fused carbocyclic systems. Interest in the polycyclic aromatic hydrocarbons, in particular this group, in the past decade has focused mainly upon theoretical studies relating to aromaticity, and this chapter belongs with a discussion on the concept of "aromaticity". The chapter then examines recent advances in the chemistry of hydrocarbons containing four benzene rings; they are chrysene, naphthacene, benz[*a*]anthracene, alkylbenz- and hydrobenz-[*a*]anthracene, benzanthrene, benzo[*c*]phenanthrene, pyrene, 10b,10c-dihydro-10b,10c-dimethylpyrene, and triphenylene. The group of hydrocarbons containing five benzene rings includes pentaphene, dibenz[*a,c*]anthracene, dibenz[*a,j*]anthracene, dibenz[*a,h*]anthracene, benzochrysene, dibenzophenanthrene, benzopyrene, benzo[*e*]pyrene, benzo[*cd*]pyrene, perylene, and triptycene. The chapter concludes with a discussion of hydrocarbons having six or more benzene rings, and includes helicenes (*e.g.*, dibenzo[*b,k*]chrysene) and circulenes. Circulenes are polynuclear, aromatic hydrocarbons that may comprise, for example, six condensed benzene rings to give [6]circulene (coronene) or accommodate a ring of six or more annelated benzene rings, to form [12]circulene, namely, kekulene. The experimentally determined crystal structure of kekulene, despite its planarity, is in best agreement with the localized Clar sextet formalism rather than an annulenoid structure [E. Clar, *The Aromatic Sextet*, Wiley, London, 1972; P. M. Lahti, *J. Am. Chem. Soc.*, 53 (1988) 4590–4593]. Despite considerable interest in molecular asymmetry, and in freedom of rotation of naphthalene rings along the 1,1'-carbon bond in 1,1'-binaphthalene and its derivatives, a similar study of the next higher analog 1,1'-bipyrene [A. J. Fatiadi, *J. Org. Chem.*, 32 (1967) 2903–2904] still remains a challenge of the future.

The book concludes with an extensive Subject Index; chemical compounds have been indexed alphabetically under the names used by the authors, which sometimes fail to accord with IUPAC nomenclature.

Because of its high overall standard, and because of the Age of Interdisciplinary Chemistry in which we live, this book should be useful to synthetic organic chemists, biologists, biochemists, and chemists involved in natural products and environmental research. It is highly recommended that a copy be in every chemical library; however, for a personal copy, the price seems somewhat high.

National Institute of Standards and Technology
Gaithersburg, MD 20899

ALEXANDER J. FATIADI