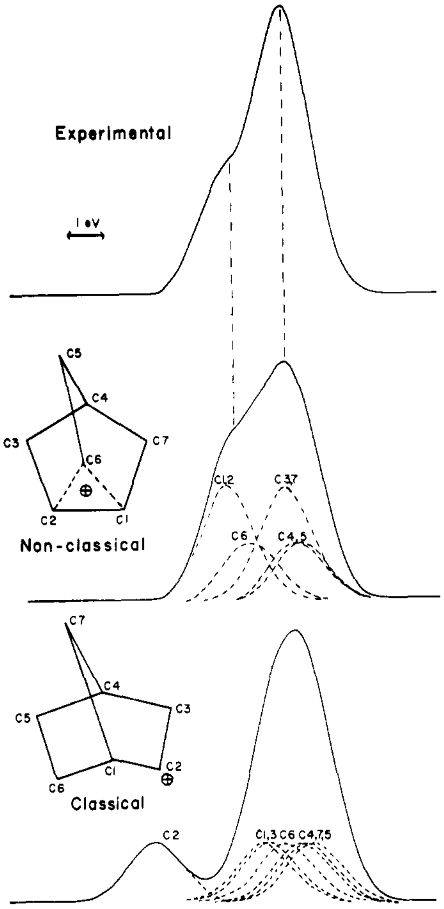

Figure 1. C 1s core-hole-state spectra for the 2-norbornyl cation, simulated using a fwhm of 1.8 eV for composite line widths.

4.31G basis). Further, the hole-state and ab initio equivalent cores results are in excellent agreement, with regard to both the span in binding energy and relative ordering, whereas the recently published MINDO/3[19] results are strikingly different in both these aspects.

Core hole-state spectra may be synthesized by taking components of appropriate line shape and line width. Figure 1 shows such simulated spectra for the ΔSCF STO-4.31G basis, the STO-3G equivalent cores spectra being essentially identical. Even with relatively poor resolution, a clear-cut distinction exists between the classical and nonclassical species. An interesting feature of the nonclassical spectrum is the intermediate binding energy calculated for C-6, which implies that any attempt to deconvolute the experimental spectrum into just two components is untenable.[5,6] For the classical spectrum, the high binding energy calculated for C-2 leads to a well-resolved spectrum with intensity ratio 1:6.

When considering the experimental data, contamination problems suggest that emphasis should be placed on shifts rather than relative intensities.[2] Even a cursory perusal of the synthesized spectra suggests that the experimental data are not interpretable in terms of a classical parent 2-norbornyl cation. Comparison between the calculated nonclassical spectrum and a smoothed version (normalized to a flat baseline) of the experimental data, however, is quite striking. The most logical conclusion to draw is that the published spectra pertain to a nonclassical 2-norbornyl cation, for which the surface has been contaminated by extraneous hydrocarbon.[23] With a knowledge of electron mean free paths[24] (~20 Å for kinetic energies appropriate to the experimental data) and taking a monolayer as ~5 Å thick, the experimental data would be quantitatively described in terms of the calculated line profile for the nonclassical ion with a fractional (~0.6) monolayer coverage of hydrocarbon contamination. To this extent, the calculations outlined here resolve experimental ambiguities.

The distinction between classical and nonclassical energies is so fine as to be sensitive to minor electronic perturbations. Thus, a methyl substituent, stabilizing a positive charge, might be anticipated to prefer a classical structure. From calculations on 2-propyl and *tert*-butyl cations,[25] a decrease in C-2 binding energy of ~0.9 eV is expected, giving a shift of ~3.5 eV for a classical 2-methylnorbornyl cation, in good agreement with the reported ESCA shift of 3.7 eV.[5,6]

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(26) Thanks are due to the Science Research Council for provision of a research studentship, and to the Atlas Computing Laboratory for computing facilities.

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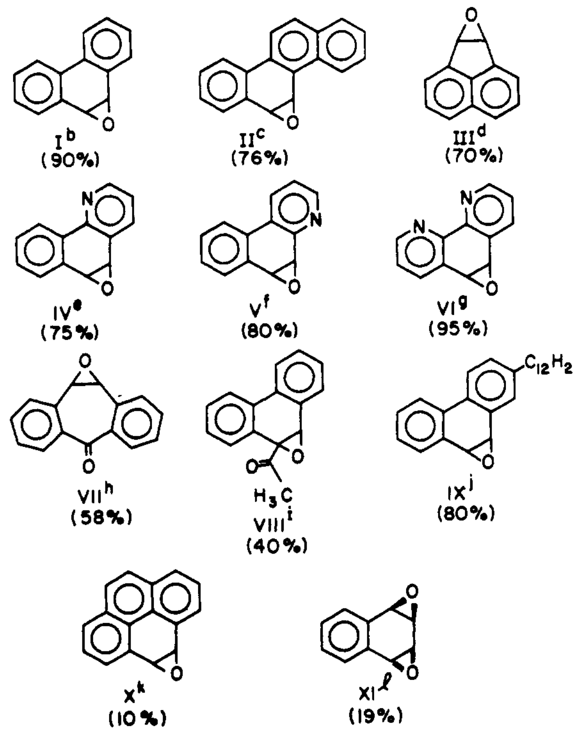
Direct Oxidation in High Yield of Some Polycyclic Aromatic Compounds to Arene Oxides Using Hypochlorite and Phase Transfer Catalysts[1]

Sir:

Because arene oxides,[2] or their subsequent metabolites,[3] have been implicated as the intermediates responsible for the carcinogenicity and mutagenicity of polycyclic aromatic hydrocarbons,[4] there has been considerable interest in developing convenient methods for their synthesis[5] and in understanding how they are formed physiologically. As part of a continuing program to investigate oxygen atom transfer (oxenoid) reactions[6] in model and enzymic systems, we have been exploring[7,8] the use of several reagents for the direct oxidation of arenes to arene oxides.[9] In this communication we report that various arene oxides can be prepared under mild conditions and in high

Chart I. Epoxides and Their Yields Formed by Direct Oxidation of the Respective Arenes by the Hypochlorite–Phase Transfer System[a]

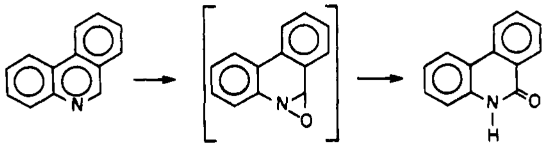


[a] See text for the experimental procedure; the numbers given in parentheses are isolated yields. [b] Identical by NMR, IR, UV, and melting point with authentic samples prepared by two independent literature procedures.[5a,b] [c] NMR spectrum was identical with that reported;[5b] II also gave expected IR and mass spectra. [d] Compound gave identical melting point, NMR, and IR data as those reported: T. Kinstle and P. Ihrig, *J. Org. Chem.*, **35**, 257 (1970). [e] IV had mp 111–112 °C; NMR ($CDCl_3$) δ 4.48 (s, 2 H), 7.1–8.7 (m, 7 H); IR ($CHCl_3$) 1020, 920 cm^{-1}; UV (EtOH) 302, 292, 269 nm; mass spectrum (% of base) 195 (100), 179 (31), 167 (86), 166 (84); ^{13}C NMR (see H. Gunther and G. Jikeli, *Chem. Ber.*, **106,** 1863 (1973), for a discussion of the chemical shifts of benzene oxides) ($CDCl_3$) (relative to TMS) 56.42, 56.08 ppm. [f] V had mp 167–168 °C; NMR ($CDCl_3$) δ 4.57 (d, 1 H, $J = 4$ Hz), 4.68 (d, 1 H), 7.1–8.5 (m, 7 H); IR ($CHCl_3$) 1025, 895 cm^{-1}; UV (EtOH) 301, 290, 285, 266 nm; mass spectrum (% of base) 195 (100), 179 (37), 167 (93), 166 (92); ^{13}C NMR (see reference in footnote *e*) ($CDCl_3$) (relative to TMS) 57.22, 57.77 ppm. [g] VI had mp 163–165 °C; NMR ($CDCl_3$) δ 4.55 (s, 2 H), 7.3–8.8 (m, 6 H); IR ($CHCl_3$) 1425, 880 cm^{-1}; UV ($CHCl_3$) 298, 289 (sh), 266 nm; mass spectrum (% of base) 196 (81), 180 (38), 168 (100). [h] VII had mp 100–105 °C; NMR ($CDCl_3$) δ 4.42 (s, 2 H), 7.2–8.2 (m, 8 H); IR ($CHCl_3$) 1670, 930 cm^{-1}; UV (EtOH) 258 nm. [i] VIII had mp 87–88 °C dec; NMR ($CDCl_3$) δ 2.39 (s, 3 H), 4.54 (s, 1 H), 7.2–8.2 (m, 8 H); IR ($CHCl_3$) 1715 cm^{-1}; UV (EtOH) 302, 287, 276, 268 nm. [j] IX had NMR ($CDCl_3$) δ 1.0–2.5 (m, 25 H), 4.5 (s, 2 H), 7.2–8.2 (m, 7 H); mass spectrum (% of base) 362 (100), 334 (71), 333 (63). [k] X had melting point and NMR identical with those reported.[5b] [l] Compound gave identical melting point and NMR data as those reported.[11]

yield by treating an organic solution of the corresponding arene with aqueous sodium hypochlorite in the presence of a phase transfer catalyst.[10]

In a typical procedure, 5 mmol of the arene, dissolved in 100 mL of chloroform, is added to 250 mL of 0.6 M aqueous sodium hypochlorite (commercial bleach), the pH of which has been adjusted to between 8 and 9 with concentrated HCl. Tetrabutylammonium hydrogen sulfate (0.2–1 equiv) is added and the mixture is stirred at room temperature (water bath cooling) until TLC indicates that all of the arene has reacted (15 min to 24 h). The layers are separated and the organic layer is washed with a large excess of cold water, dried (K_2CO_3), and evaporated at room temperature. Compounds I–VIII (Chart I) were purified by recrystallization from either methylene chloride/pentane or chloroform/hexane. Compounds IX and X were purified by rapid high pressure liquid chromatography on a cyanosilica column (8 mm × 50 cm Varian CN-10 column, elution with 15% CH_2Cl_2, 0.1% isopropyl alcohol in hexane). Compound XI was recrystallized according to the reported procedure.[11]

As indicated in Chart I, the system gives high yields of epoxides not only from aromatic hydrocarbons but also from azaarenes. Surprisingly, none of the corresponding *N*-oxides could be detected in the reactions giving IV, V, and VI. Assignment of arene oxide structures to IV, V, and VI was made by spectral analysis and by comparison with the quite different spectra and physical properties of authentic samples of the *N*-oxides.[12] When phenanthridine (XII) is oxidized by the hypochlorite system only the amide 5(6*H*)-phenanthridone (XIV) is isolated from the reaction. Presumably, XIV is formed via the rearrangement of the oxaziridine XIII (eq 1).[13]



(1)

XII XIII XIV

None of the corresponding *N*-oxide could be detected under the reaction conditions, and XIV is not formed from the *N*-oxide because an authentic sample of this compound, prepared by the *m*-chloroperbenzoic acid oxidation of XII, was found not to yield the amide (XIV) under the reaction conditions.

To obtain good yields of the epoxides, it is important that the pH of the aqueous hypochlorite is 8–9. At higher pHs (above 10) very little epoxidation occurs, and at lower pHs (below 7) other oxidation products are observed. Some preliminary experiments using different organic solvents indicate that similar yields are obtained with methylene chloride instead of chloroform, but when ethyl acetate or ether is used the epoxidation proceeds more slowly (it still occurs however). In the absence of the phase transfer catalyst, no arene oxide is formed. Higher concentrations of the ammonium salt leads to more rapid arene oxide formation. Replacement of the tetrabutylammonium salt with benzyltrimethylammonium chloride results in similar yields but also a slower reaction. Also, comparable yields of phenanthrene 9,10-oxide were obtained at both 10 °C and room temperature. The use of sodium hypobromite in place of sodium hypochlorite leads to a reduced yield of phenanthrene 9,10-oxide.

The procedure outlined here is a simple, convenient, and inexpensive method for making relatively large quantities of the arene oxides I–IX. The system is not adaptable to the synthesis of all types of arene oxides; as indicated by the results in Chart I, products from reaction at the most reactive region (usually the K region) of complex arenes are expected. However, the ready synthesis of the new compounds IV–IX indicate that the method has considerable potential for the synthesis of substituted aromatic epoxides (especially of the azaarene oxides) not easily available by other methods. In addition to its utility for the preparation of arene oxides, the mechanism of this novel epoxidation reaction[14,15] is currently under investigation and will be reported shortly.

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Book Reviews

Correction: In the review of "Stereochemistry of Heterocyclic Compounds" (W. L. F. Armarego) that appeared in this Journal [99, 5841 (1977)], it was erroneously stated that the book marked the beginning of a new series, "General Heterocyclic Chemistry". In fact, there are four other volumes in the same series, each of which has been reviewed here previously.

Journal of Organometallic Chemistry Library. Volume 3. Organometallic Chemistry Reviews. Edited by D. SEYFERTH (Coordinating Editor, Massachusetts Institute of Technology), A. G. DAVIES (University College, London), E. O. FISCHER (Technische Universität, München), J. F. NORMANT (Universite de Paris VI, Paris), and O. A. REUTOV (University of Moscow). Elsevier Scientific Publishing Co., Amsterdam and New York. 1977. viii + 342 pp. $41.95.

Volume 3 in this series presents seven in-depth reviews dealing with active research areas in main-group and transition-metal organometallic chemistry. Especially timely are the treatments summarizing work on alkaline earth and lanthanide/actinide organometallic compounds. The remaining reviews explore organic peroxides of main groups II and III elements, metal complexes of polypyrazolylborates, recent advances in organotitanium chemistry, and the chemistry of η-arene-η-cyclopentadienyliron cations. All contributions to this volume bear received dates of late 1975 or early 1976, and references to literature appearing in 1976 are included in several of the reviews.

The editors are to be commended for extracting the subject reviews from the *Journal of Organometallic Chemistry* and for bringing them together in separate volumes which are available to all interested chemists. In the past, it was practically impossible for workers at schools not subscribing to the Journal to keep abreast of the subject reviews. In addition, the reviews maintain the high quality which we have come to associate with the majority of original research papers published in the Journal. This volume is therefore strongly recommended to all those working in the areas mentioned.

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The Molecular Geometries of Coordination Compounds in the Vapour Phase. By M. HARGITTAI and I. HARGITTAI (Central Research Institute of Chemistry of the Hungarian Academy of Sciences, Budapest). Elsevier Scientific Publishing Co., New York, N.Y. 1977. 276 pp. $30.25.

This book is the English version of a Hungarian book of the same title (1974). During its translation into English it was revised and updated with some references as late as 1974. The book is restricted to a discussion of vapor phase geometries of coordination compounds and claims to be the first comprehensive survey of this field.

The first chapter (approximately 10% of the text) covers general concepts of structure determination, and the remainder is a fairly systematic review and discussion of molecular structures. Later chapters cover: addition compounds (e.g., B–N, B–P, and Al–N complexes), electron-deficient molecules (e.g., boron hydrides, carboranes, metal borohydrides), halogen bridging complexes, salts of oxyacids, polymeric oxides, hydrogen-bonded complexes (e.g., dimers of organic acids, polymeric hydrogen fluoride), and transition metal complexes (complexes of π-acceptor ligands, metallocenes).

The book contains an author and a formula index but no subject index. Because of the specialized subject matter, the book will be of interest mainly to students and researchers in structural chemistry.

Walter O. Siegl, *Ford Motor Company*

Thermal Vibrations in Crystallography. By B. T. M. WILLIS (Atomic Energy Research Establishment, Harwell) and A. W. PRYOR (Australian Atomic Energy Commission, Lucas Heights). Cambridge University Press, London. 1975. xvi + 280 pp. $27.50.

This book is replete with information concerning the nature and effects of thermal vibrations in chemical crystallography. The authors have done a commendable job in presenting a fairly difficult subject area in a clear and concise manner. This book, which encompasses Willis' article (*Acta Crystallogr., Sect. A*, 25, 277 (1969)), not only contains comprehensible mathematical derivations of the essential physics involved, but also contains an abundance of graphs and illustrations which further add clarity to the subject. The refreshingly low concentration of mathematical and typographical errors illustrates the care which the authors have taken in preparing this book.

The first three chapters (Part I) deal primarily with the basic lattice dynamics of crystals—from simple alkali halide crystals to complex molecular crystals, such as hexamethylenetetramine. The reader is given a sound understanding of the manner in which the dynamical equations of motion are solved and how crystal symmetry enters into the calculations. Several sample calculations are given, along with a variety of illustrations of Brillouin zones, various dispersion relations, etc.

Part II of this book (Chapters 4, 5, and 6) is probably of more interest to the practicing crystallographer. Some of the topics which are presented and discussed are: the general expression for the intensity of x-ray scattering by a crystal in thermal motion; the anisotropic temperature-factor coefficients and their symmetry restrictions; the Debye model for the vibrational properties of crystals; anharmonic contributions to the atomic temperature factor; "forbidden reflections"; the rigid-body model for molecular crystals; and the internal mode contribution to the temperature factors of molecular crystals.