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Reaction of the (111) Faces of Single-Crystal Indium Phosphide with Alkylating Agents: Evidence for Selective Reaction of the P-Rich Face

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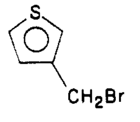
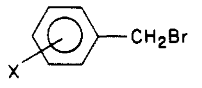
We wish to report that the P-rich, (111)B, face of single-crystal InP, but not the In-rich, (111)A, face of the same crystal, reacts with molecular reagents I and II to yield surface-bound material



I

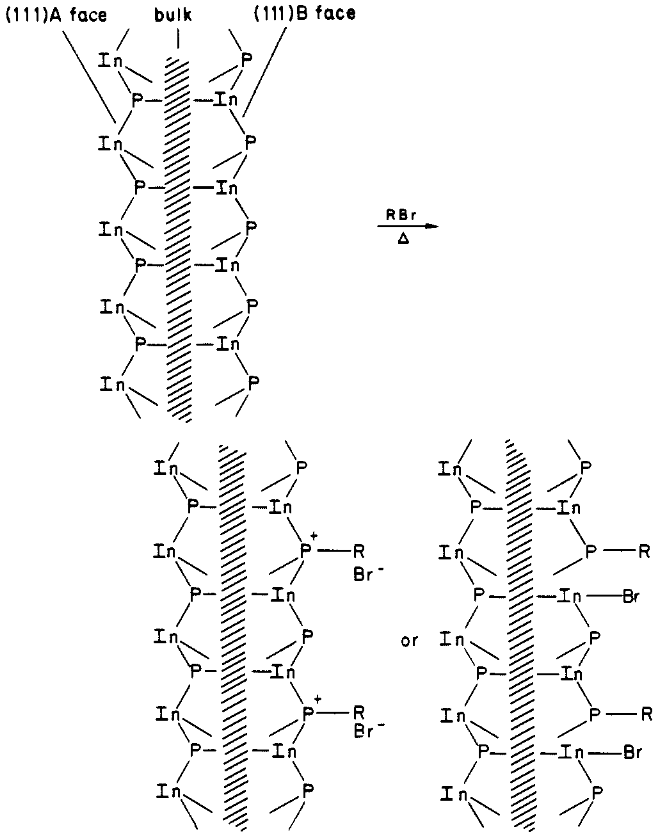


II

a X = 3-F
b X = 2,3,4,5,6-penta-F
c X = 2,6-di-Cl

derived from the apparent alkylation of a surface P atom. Exploitation of surface functional groups has been demonstrated to be very important in the attachment of molecular reagents and polymers to electrode surfaces.[1,2] Electrodes derivatized with molecules have potential uses[1,2] in analysis,[3] fuel cells,[4] electrosynthetic cells,[5] and photoelectrochemical cells.[6] We now wish to present evidence showing that an important photoelectrode material, InP,[7-10] can be functionalized with molecules by reaction of the P-rich, (111)B, face with alkylating reagents.

Scheme I. Representation of the Selective Reaction of the (111)B (P-rich) Face of Single-Crystal InP



We began our work with the view that single-crystal InP[11] with the (111) faces exposed would, if sufficiently clean, behave as a material having accessible, electron-rich, P atoms on the B face, while the P atoms on the A face, below a plane of In atoms, would be essentially inaccessible, Scheme I. Experiments were carried out using single-crystal p-type InP (Atomergic Chemetals Corporation, Plainview, NY) cut as thin slices (0.3 mm) to expose the (111) faces. The (111) faces were generally 3 mm × 10 mm in dimension and polished to 3 μm by using Al_2O_3, after which they were further smoothed by etching at 25 °C for 60 s in 1% Br_2/MeOH. After they were rinsed in MeOH, the crystals were further treated by heating in CH_3CN as described below, thoroughly rinsed in CH_3CN, and then examined by X-ray photoelectron spectroscopy (XPS) or Auger electron spectroscopy. The samples examined by XPS were transferred under Ar or in air (exposure no more than 2 min) without significant difference in the results:[12] little or no oxidized P or In could be detected on the surfaces, and the resulting P and In signals were indistinguishable from those found for InP surfaces etched with a reactive Ar^+ beam in the spectrometer.[13] The binding energy of the P 2p is, for example, at 128.5 eV and therefore easily distinguishable

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[12] (a) XPS experiments were performed on a PHI 548 spectrometer controlled by a PDP 11/04 computer. Unmounted crystals were attached to the sample holder with Ag paint. The C 1s signal was monitored to check (and correct) for sample charging; adventitious C (284.8-eV binding energy) was used as a reference. Where more than one C peak was apparent (as was usually the case) the lowest energy C peak was assigned to adventitious C. This assignment gave consistent results, and resulting values for signals of known binding energy agreed with the literature (cf. ref 13). The irradiation used was the Mg $K\alpha$ line at 1253.6 eV. Surveys were taken with 100-eV pass energy; for oxidation state information, the regions of the elements of interest were scanned with 25-eV pass energy. Resolution at this pass energy is 0.4 eV. (b) Auger electron spectra were recorded on a PDP 11/04-controlled PHI 590 Scanning Auger spectrometer employing a 5 keV, 2 μm, 100–160 nA electron beam for excitation. (c) SIMS was performed at GTE Laboratories, Inc., using a VG SIMS Lab.

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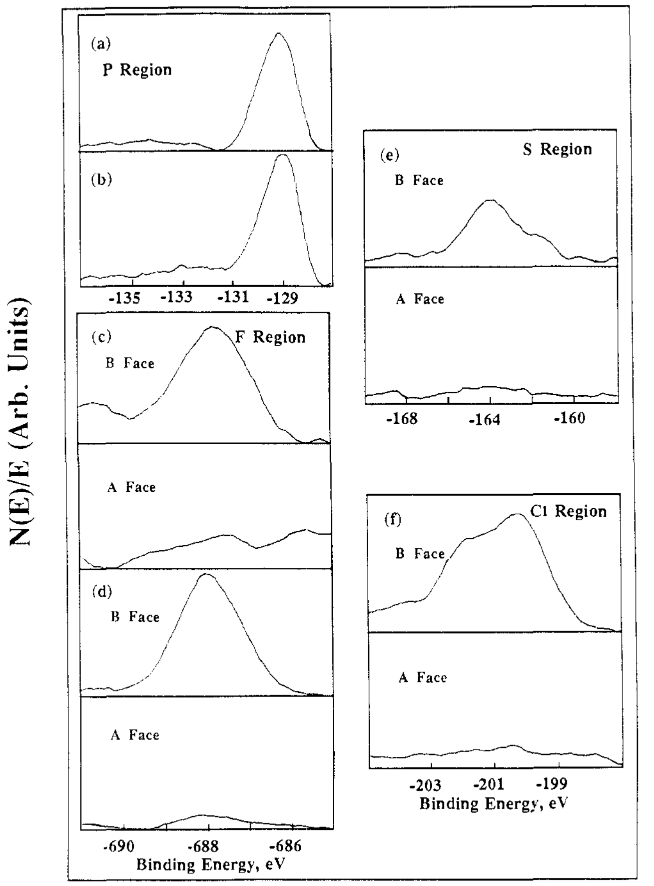


Figure 1. XPS spectroscopy of InP surfaces: (a) P region after pretreatment with Br_2/MeOH and hot CH_3CN; (b) P region after Ar^+ ion etching of InP in the vacuum chamber; (c) F region after derivatization with IIa; (d) F region after derivatization with IIb; (e) S region after derivatization with I; (f) Cl region after derivatization with IIc.

from that of the highly oxidized P (134 eV) from the oxidative etch.[14] Assuming that the density of a phosphorus oxide on InP is similar to that of P_2O_5, calculations[15] using XPS intensities show that less than 0.2 monolayers of this oxide are present on the surface of InP after our pretreatment. The conclusion is that our pretreatment removes surface oxidized material and reveals a reduced P surface like that uncovered by Ar^+ etching of InP in the vacuum chamber. We do not claim that the surface of InP can be made "atomically clean" by heating in CH_3CN, since all samples examined by XPS do show signals due to C and O impurities, including samples etched with an Ar^+ beam in the spectrometer. The appearance of C and O signals after etching a sample in the spectrometer reveals that there are impurities in the spectrometer that bind to the surface of InP, but the conclusion that the pretreatment yields a reactive surface in situ is supported by the experiments described below.

The crucial finding is that treatment of the Br_2/MeOH-etched (111) InP in CH_3CN containing 2 M I or II for 1 h at 50–60 °C yields evidence that the P-rich, (111)B, InP reacts to bind the thiophene or halogenated benzyl groups, whereas the (111)A InP does not react. The evidence is that elements unique to the thiophene, S, or the halogenated benzyl, F or Cl, can be detected by XPS or Auger electron spectroscopy on the B, and not the A, face of the same crystal, Figure 1. The face specificity is at least five to one for any case shown. The positions of the S 2p, F 1s, and Cl 2p signals in the XPS are consistent with retention of the chemical composition of the functional groups. At least 20 independent reactions and analyses show the same result: the B face reacts and the A face does not. Control experiments with 3-methylthiophene or *m*-fluorotoluene yield no detectable S or F signals on InP. The control experiments establish the importance of the reactive C–Br bond in I and II in functionalizing the InP. Calculations of coverage, based on the relative intensities of the signals arising from the InP substrate and the surface bound functionalities,[15] establish that about 1 monolayer of I or II covers the (111)B face after derivatization. The reaction of the B, and not the A, face leads to the hypothesis that much of the P-rich surface of (111) InP can be alkylated with I or II.

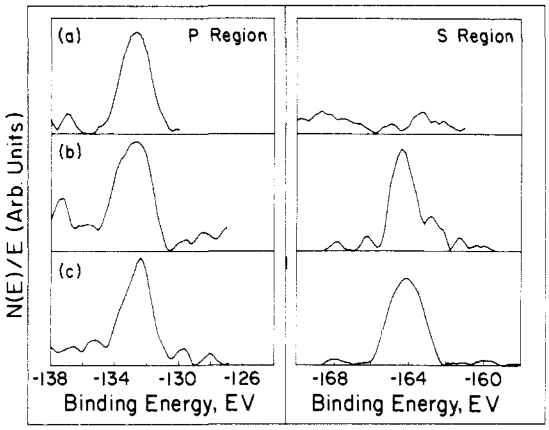


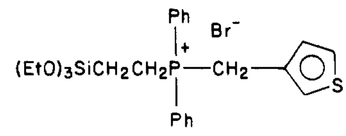
Figure 2. Comparison of P 2p and S 2p regions of the XPS spectra for (a) the polymer from III coated on ITO glass, (b) the polymer from III coated on ITO glass and subsequently treated with I, and (c) the polymer from IV on ITO glass.

Examination of RBr derivatized InP with Auger or secondary ion mass spectroscopy (SIMS) confirms the finding of a face-specific reaction of the InP with RBr, but most quantitative work has been done with XPS. One significant result from SIMS of RBr-treated InP is that molecular fragments characteristic of the R group have been detected from the B and not the A face, establishing that molecules can be immobilized on the B face of InP.

Figure 2 shows XPS data relating to indium/tin oxide, ITO, surfaces functionalized with molecular P-containing materials, potential models for the P-rich InP surface. The ITO derivatized with the silane reagent III shows a P 2p signal; subsequent reaction

$(EtO)_3SiCH_2CH_2PPh_2$

III



IV

with I in CH_3CN shows an XPS signal characteristic of S, and ITO derivatized with authentic alkylated material IV shows the same characteristic S signal. The molecular derivatizing agents thus behave as expected and the alkylation of surface-bound phosphine with I can readily be detected by XPS. Such results are similar to those found for alkylation of surface-bound pyridine moieties.[16,17] These experiments show that the binding energy for the P 2p electrons in these molecules is relatively insensitive to the change from the phosphine to the phosphonium species. The lack of an obvious shift in the P 2p peak of (111)B InP upon reaction with I or II is therefore not an indication of the nature of the surface P atoms after reaction with RBr.

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Scheme I shows two possible structures for the surface resulting from the reaction of alkylating agents with the (111)B face of InP. The issue of which, if either, of the diagrams shown is an accurate representation of this surface is presently being investigated in this laboratory, along with studies of the scope of the reaction chemistry of InP [and other group III–V (group 13–15) semiconductors].[18]

Acknowledgment. We are grateful for research support from GTE Laboratories, Inc., and the United States Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences. Use of the Central Facilities of the M.I.T. Center for Materials Science and Engineering and assistance with SIMS at GTE Laboratories, Inc., are gratefully acknowledged. Drs. Donald Dugger and Glenn D. Zoski of GTE Laboratories, Inc., are acknowledged for valuable experimental assistance and discussions.

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(18) In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise grups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

Book Reviews*

Encyclopedia of Polymer Science and Engineering. Volume 2. Second Edition. Edited by Herman F. Mark, Norbert M. Bikales, Charles G. Overberger, and Georg Menges. John Wiley & Sons: New York. 1985. xxiv + 814 pp.

This volume, prepared under the direction of J. I. Kroschwitz, contains articles ranging from anionic polymerization to cationic polymerization and includes topics such as antioxidants, automotive applications, azo polymers, biopolymers, bleaching, block copolymers, calendering, and carbon fibers, to name a few. Abbreviations, SI units, conversion factors, and unit symbols are listed in the fore pages. Standard usage of nomenclature and terminology is carefully respected. Relevant IUPAC nomenclature is summarized when appropriate as, for example, in the article on block copolymers. Bibliography sections which are provided at the end of each chapter range from brief listings consisting mainly of references to books and review articles (see chapter on anionic polymerization by S. Bywater or chapter on antibodies and antigens—polymer bound by W. J. Dreyer and A. Rembaum, for example) to what appears to be a more comprehensive compilation of general literature (as in Block Copolymers by G. Riess, G. Hurtrez, and P. Bahadur; Carbon Fibers by J. P. Riggs; or Cationic Polymerization by A. Gandini and H. Cheradame, for example). References include patent liteature when appropriate and cross-referencing appears to be adequate. In the articles on antifoaming agents, antioxidants, antiozonants, antistatic agents, azo compounds, biocides, etc., lists of commonly available products are provided along with consideration of health and safety factors.

In short, contributions in this volume provide an authoritative source of information that can be used both as reference material and as a teaching tool. This book should soon find its rightful place on the reference shelves of science libraries, as did the sixteen volumes of the predecessor first edition of this monumental Encyclopedia.

Rita B. Blumstein, *University of Lowell*

Scale up of Chemical Processes. By Attilio Bisio (Exxon Research and Engineering Co.) and Robert L. Kabel (Pennsylvania State University). John Wiley & Sons: New York. 1985. XV + 699 pages. $69.95. ISBN 0-471-05747-9.

In the words of the authors, "This book is designed to serve students, faculty, researchers, and practitioners alike." To accomplish this design, the authors have called upon 15 contributors to write all or parts of 14 of the 18 chapters. In addition to the 4 chapters written by the authors, they have done a good job of producing a relatively coherent text by organizing the book in a parallel structure at three levels. At the beginning of each chapter is a rigorous outline. At the end of the chapter is a nomenclature section and an extensive list of references (alphabetized by author). The chapter topics include mathematical modeling, reaction kinetics, reaction systems, selection of reactor types, mixing, flow, mass transfer, separations, and environmental considerations.

As one could expect from the authors' backgrounds, the book is written from an engineering perspective and contains many mathematical equations and models. The text contains clear tables and graphs which are related to the text but are also sufficiently self-explanatory such that the chapters can generally be skimmed if one desires. Many of the examples from industry deal with continuous rather than batch processes. Probably the most general but informative chapter is Gaining Experience Through Pilot Plants and Demonstration Units which ties together many of the presented concepts and theories. This chapter looks at the total picture of scaling up including use of vendor tests and necessary considerations for predicting commercial performance.

"Is there a Royal road to scale up?" the authors ask. The answer is no. However, to scale up one must understand the chemical and physical phenomena involved. This book reviews much of the art, theory, experience, and practices of scale up. And, in doing so, it adds yet more information for the process development scientist to use. This book contains something for everyone involved in scale up.

Roger N. Brummel, *Warner-Lambert Company*

The Chemistry of the Carbon–Metal Bond. Volume 3. Carbon–Carbon Bond Formation Using Organometallic Compounds. Edited by F. R. Hartley and S. Patai. John Wiley & Sons: New York. 1985. xiv + 489 pp. $160.00. ISBN 0471905577.

This volume will be welcomed by chemists interested in organic synthesis. In ten contributed chapters, the uses of tin and lead reagents (V. G. Kumar Das and C.-K. Chu), zinc, cadmium, and mercury reagents (L. Miginiac), η^3-allyl complexes of nickel, palladium, etc. (G. P. Chiusoli and G. Salerno), and transition-metal carbonyls (J. A. Davies and R. J. Shaver) are given a chapter each. There are also chapters on alkyne oligomerization (M. J. Winter), olefin oligomerization (O.-T. Onsager and J. E. Johansen), olefin and alcohol carbonylation (G. K. Anderson and J. A. Davies), olefin hydroformylation (J. A. Davies), olefin carbonylation (D. M. Fenton and E. L. Moorehead), and the Fischer-Tropsch Synthesis (G. Henrici-Olivé and S. Olivé). The several obviously missing topics, such as the use of alkali-metal and alkaline earth-metal reagents, are promised to be included in a companion volume now underway.

The chapters are supplemented by a 4-page list of abbreviations (a welcome feature), an author index, and a thorough subject index. The quality of production is up to the usual standards of the series. Structural formulas, for example, are uniform in style and very clear. The presence of running heads to the pages is admirable, but unfortunately, in the first two chapters they have been truncated to the point of uselessness and read simply "carbon–carbon bond formation". This is only a very minor detraction in such an excellent work.

Handbook of Reactive Chemical Hazards. Third Edition. By L. Bretherick. Butterworths: London, UK; and Stoneham, MA. 1985. xxvi + 1852 pp. $99.95. ISBN 0-408-01388-5.

Is it proper to think of a book about safety in the laboratory as expanding explosively? Fortunately, the price is not following suit. The author notes that since the previous edition, the work for which was completed in 1977, a very large amount of new information on chemical hazards has become available, at least partly as a result of a higher general level of concern.

This edition has been entirely reset and reorganized to include the new information. A section on specific chemicals (in formula-index order) is followed by one on classes, groups, and topics. Five appendices provide different ways for access to the information. No other work of this comprehensiveness appears to exist, and the importance of the information presented justifies having this work readily available (preferably in the laboratory rather than the library) where chemists are carrying out reactions. The prevention of one accident could save more than the price of the book, which, at less than 6¢ a page, is very reasonably priced.

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*Unsigned book reviews are by the Book Review Editor.