

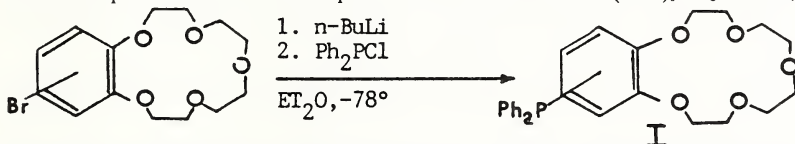
CHEMISTRY

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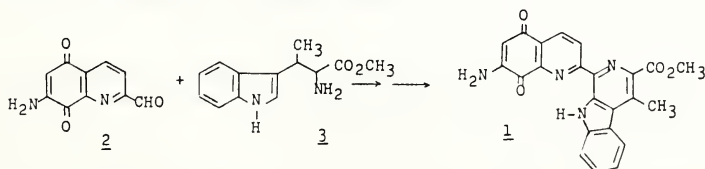
ABSTRACTS

Functionalized Crown Ethers: Benzo Crowns with P(III) Centers. JOHN BAIN, VIDA FARAZI AND BRUCE N. STORHOFF, Ball State University, Muncie, Indiana 47306.—Spectroscopic evidence indicates that the diphenylphosphine derivative of benzo-15-crown-5 has been obtained *via* the reaction scheme shown below. Bromination of the parent crown was accomplished with either NBS or Tl(OAc)₃/Br₂ in CCl₄.



Evidence has been obtained which indicates that the P(III) center reacts as expected with metal centers. (PhCN)₂PdCl₂, for example, readily reacts with I to provide a yellow colored complex which has been assigned the stoichiometry *trans*-(I)₂PdCl₂.

Studies Toward the Total Synthesis of Lavendamycin Methyl Ester, an Antitumor Antibiotic Agent. MOHAMMAD BEHFOROZ, HAMIDEH ZARRINMAYEH AND MARK A. HORN, Ball State University, Muncie, Indiana, 47306.—The objective of our studies is the synthesis of **1** through the Pictet-Spengler condensation of aldehyde **2** with β -methyltryptophan methyl ester **3**, followed by dehydrogenation. Model studies and preparation of intermediates will be described.



Applications of Chromatography/Secondary Ion Mass Spectrometry. KENNETH L. BUSCH, Department of Chemistry, Indiana University, Bloomington, Indiana 47405.—A secondary ion mass spectrometer can be used to directly analyze organic and inorganic mixtures separated by thin layer or paper chromatography, and biochemical mixtures separated by electrophoresis. A renewable sample surface is necessary to provide a stable and persistent beam of secondary ions. A phase transition matrix which is melted at the point of analysis is used to renew the surface. Spatially-resolved mass spectra are obtained when the chromatogram is moved through the point of instrument focus. The use of this spatially-resolved information for the determination of sample spot homogeneity

will be discussed. Derivatization reactions can be used with chromatography/secondary ion mass spectrometry to provide information about the distribution of organic compounds of certain functional groups distributed within a chromatogram.

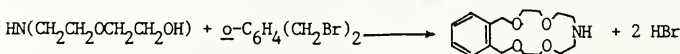
Atomic Spectroscopic and Neutron Activation Analyses of Trace Heavy Metals in Water Supplies Surrounding a Municipal Landfill. CHERYL A. BYE AND JAMES P. RYBARCZYK, Ball State University, Muncie, Indiana 47306. —The levels of 12 trace heavy metals (including toxic As, Pb, and Cd) were monitored at 20 wells and creek bed sites surrounding a closed municipal landfill. Samples were collected weekly over a 15-week period, and results will be reported as a function of geographic location, depth of sample, and rainfall amount.

A combination of several spectroscopic and nuclear techniques were utilized for the analyses, each with their own strengths and interferences. Elements in relatively high concentration were determined by simple flame AA and flame emission. Low concentration metals were measured by graphite furnace AA and ICP, which also were utilized to verify the flame data after dilution to lower concentrations. Further verifications of these concentration levels were provided by nuclear spectroscopic neutron activation analysis after a 400:1 preconcentration step.

Interaction of Some Metals and Tetrathionate Ions. S.W. DHAWALE, Indiana University East, Richmond, Indiana 47374. —The corrosion of various metals and alloys is being studied in the presence of sulfur oxyanions.

The present investigation deals with the interaction of tetrathionate ions with iron powder and nickel plates. The corrosion of nickel was quite visible from the black film formed. Some results on the attempts to use spectroscopic techniques to identify the corrosion product on the metal surface will be presented. The initial results indicated the formation of thiosulfate ions during the corrosion. Results on the estimation of thiosulfate ions will be reported.

The Preparation of Functionalized Aza Crown Ethers. VIDA FARAZI, M. BRIAN ARNOLD AND BRUCE N. STORHOFF, Ball State University, Muncie, Indiana 47306. —Aza crown ether **1** with three types of metal-binding sites has been synthesized from commercially available starting material by using the following reaction scheme. Reactions of **1** with $\text{H}_2\text{NCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH} + \text{ClCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH} \longrightarrow \text{HN}(\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH})_2 + \text{HCl}$



allylic and benzylic halides, such as $p\text{-BrC}_6\text{H}_4\text{CH}_2\text{Br}$, in the presence of sodium carbonate provided good yields of the corresponding derivatives. Strategies for functionalizing these crown ethers with P(III) centers will be discussed.

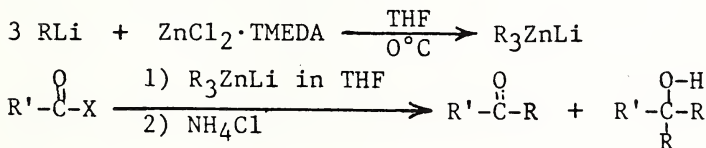
Potassium Ion Induced Enhancement of Crown Fluorescence by Displacement of a Complexed Quencher. SUSAN J. GANION, PAUL L. BOCK AND LYNN R. SOUSA, Ball State University, Muncie, Indiana 47306. —As a part of an effort to devise new types of potassium sensitive analytical reagents, a crown ether containing a fluorescent naphthalene chromophore has been synthesized and its fluorescence properties studied. In methanol solution, the presence of cesium ions causes a dramatic quenching (decreasing) of fluorescence due to a "heavy atom effect" by complexed cesium ions. When potassium ions are present in a solution containing crown ether and cesium ions, the potassium ions cause an increase in fluorescence by displacing the quenching cesium ions from the crown ether compound. Since the increase in fluorescence intensity is directly related

to the concentration of potassium ion present, the crown ether-cesium ion system can be used to determine the concentration of potassium ions present in solution.

The data has been analyzed by a nonlinear least squares curve fitting program. This analysis and its relationship to the design of more sensitive crown ether fluorescent agents will be discussed.

Electron Spin Resonance of Membranes. MARY E. HUSS, Department of Mathematics, Indiana University East, Richmond, Indiana 47374, JEROME I. KAPLAN AND STEPHEN R. WASSALL, Department of Physics and WILLIAM STILLWELL, Department of Biology, Indiana University-Purdue University at Indianapolis, Indianapolis, Indiana 46223. —Detailed analysis of ESR (electron spin resonance) spectra recorded for spin labelled lipid molecules in membranes requires the formulation of a quantum mechanical model (spin density matrix) which allows for various kinds of molecular motion, thus enabling a comparison to be made of the experimental spectra with simulated spectra. A computer program will be described which gives the simulated spectra in terms of motional parameters (correlation times and order parameters). The effects of retinoid (vitamin A and derivatives) and fatty acid incorporation on ESR spectra for nitroxide spin labeled stearic acids intercalated into phospholipid model membranes will be discussed as examples of application of the program.

Reactions of Lithium Triorganozincates with Acid Halides. RICHARD A. KJONAAS AND DOUGLAS SANQUENETTI, Indiana State University, Terre Haute, Indiana 47809. —Several lithium triorganozincates (R_3ZnLi) were prepared from zinc chloride/ N,N,N',N' -tetramethylethylenediamine complex ($ZnCl_2 \cdot TMEDA$) and organolithium reagents. These were then treated with acid halides under a variety of reaction conditions to give ketones and tertiary alcohols.



R' = alkyl or aryl

X = F, Cl, Br

The method appears to complement existing methods of synthesizing ketones from acid halides.

Electron Impact Mass Spectrometry of β -Alkylhydrocinnamate Methyl Esters. TERRY L. KRUGER, TIMOTHY T. CURRAN AND MOHAMMAD BEHFOROZ, Ball State University, Muncie, Indiana 47306. —The title compounds with alkyl = methyl-, ethyl-, isopropyl-, t-butyl- and vinyl- were subjected to mass spectrometric analysis. The fragmentation patterns were typical of β -aryl esters but still very sensitive to the nature of the alkyl group. The observed patterns arise from competition between (a) α -cleavage ($-OCH_3$), (b) McLafferty rearrangement (-74), and (c) ketene extrusion (-42). The effect of alkyl substituent on the predominant mode of reaction will be discussed.

Validation of a Test to Identify Erythro and Threo Diastereomers of RCHDCHDX Compounds: Variable-temperature NMR Studies of 2-Chloroethanol. DAVID L. MCCOLLUM AND PAUL L. BOCK, Ball State University, Muncie, Indiana 47306. —RCHDCHDX compounds have been used widely in determining the stereochemistry at carbon of organic and organometallic reactions. The use of these compounds has required the assumption

that erythro diastereomers have larger vicinal coupling constants than threo diastereomers. We previously had proposed a test, based on variable temperature nmr, that should allow one to avoid making any assumptions about which coupling constant goes with which diastereomer. In that earlier work, theoretical considerations involving the Karplus equation and semiempirical molecular orbital calculations indicated that in a variable temperature nmr study, the coupling constants of erythro compounds should change about twice as fast as the coupling constants for threo compounds. This paper describes variable-temperature nmr studies of 2-chloroethanol. The "erythro" coupling constant changed 2.90 times as fast as the "threo" coupling constant. These results are in complete accord with our previously proposed test.

A Study of Adenosine Deaminase and Its Conversion Factor in Normal and Pathological Human Serum. PANG FAI MA AND JEFFREY T. STARKEY, Center for Medical Education, Ball State University, Muncie, Indiana 47306. —A large and small molecular form of adenosine deaminase have been reported in advanced mammals, including man. The molecular weights of these enzyme forms are estimated to be 200,000 and 35,000 respectively by gel filtration column chromatography. The small form can be reversibly converted into the large form in the presence of conversion factor, a high molecular weight glycoprotein that is aggregated during this process. Previous studies have shown that the distribution of the two molecular forms of adenosine deaminase is tissue-specific (for instance, the large form of the enzyme is predominant in human liver while the small form is predominant in human heart). It follows that the conversion factor is present in higher amounts within those tissues where the large form predominates. With this in mind, an attempt is made to study the conversion process and determine whether or not the serum level of conversion factor is elevated in certain pathological conditions.

A Search for a Flashier Crown: Synthesis of a Crown Ether with Potassium Ion Enhanced Fluorescence. THOMAS E. MABRY, C. DAVID WHITESELL AND LYNN R. SOUSA, Ball State University, Muncie, Indiana 47306. —The synthesis of a new and (we hope) more sensitive crown ether that will signal the presence of potassium ions by increased fluorescence will be described. In earlier work we have synthesized and studied crown ether compounds containing a fluorescent chromophore and a quenching group across from each other on the same crown ether ring. These crown ether compounds signal the presence of potassium ions in solution by giving more intense fluorescence. Evidently the complexation of potassium ions by the crown ether ring stiffens the molecule and separates the fluorescent chromophore from the quencher thus increasing fluorescence intensity.

Our new crown ether molecule has been designed with a cavity-size and ligand-number that should improve its ability to complex potassium ions over our earlier crown ether compounds. These design changes should enhance the sensitivity of the compound, but also make the synthesis somewhat more difficult.

Three-dimensional Profiling of Matrix-interferences in the ICP. JOHN E. SHARKITT, GREGORY A. STEPHENSON AND JAMES P. RYBARCZYK, Ball State University, Muncie, Indiana 47306. —A FORTRAN program was developed to mathematically transform two-dimensional lateral emission data from an ICP source into 3-dimensional spatial data using the ABEL function. The experimental emission first had to be described by a curve-fitted mathematical formula, as performed by BMDP. This mathematical description of the lateral data was utilized by the ABEL program to produce three-dimensional radial profiles of the cylindrical ICP. The ABEL provides accurate spatial resolution of analyte atomic and emission processes.

These ABEL-resolved profiles were then utilized to describe the exact location of analyte-matrix interactions and excitations in the ICP. Easily ionized matrix elements

cause spatially-controlled enhancement suppression of analyte emission. The exact mechanism of this interference is unknown, and three-dimensional data will be provided to aid in characterizing the interference.

The Use of Pyridine to Quench the Dansylation of Amino Acids. KAY STEPHENS, SUZY POPE, ERIC R. JOHNSON AND TERRY L. KRUGER, Ball State University, Muncie, Indiana 47306.—In the derivatization of amino acids by dansylation, various amines have been used to quench the process by reaction with excess dansyl chloride (1-(N,N-dimethylamino)naphthalene-5-sulfonyl chloride). The most frequently used quenchers are small alkyl amines. While the resulting dansylated quencher peak can serve as a qualitative internal standard, its presence frequently complicates the separation and identification of the dansylated amino acids, especially when high sensitivity is desired. In this study, pyridine was found to efficiently quench the dansylation reaction without producing a dansylated quencher peak. With pyridine as the quencher, only dansic acid, which elutes well before the dansylated amino acids in the reverse phase HPLC separation, was increased, which greatly simplified the development of the HPLC separation system for the dansylated amino acids.

Magnetic Resonance Investigation of Metal Complexes of Antidiabetic Drugs. KIMBERLY K. STROUSE AND ABAS PEZESHK, Department of Chemistry, Ball State University, Muncie, Indiana 47306.—In the course of our studies of metal binding properties of various antidiabetic drugs we have prepared copper and zinc complexes of tolbutamide and acetohexamide and studied their structures using ESR and NMR techniques. The spectroscopic data indicate that the metal ion is bound to deprotonated nitrogen atom of the drug to form 2:1 drug:metal complexes. The ESR spectra also indicates that both copper complexes have tetragonal symmetry ($g_{11} > g_{\perp} > g_c$) with the unpaired electron in the $d_{x^2-y^2}$ orbital. The results of NMR, ESR, and X-ray analysis will be discussed and interpreted in terms of proposed structures.

Spectroscopic Studies of Spin-labeled Tetracycline Metal Complexes. STEPHEN C. SWINNEY AND ABAS PEZESHK, Department of Chemistry, Ball State University, Muncie, Indiana 47306.—We report a new method for determining metal binding properties of tetracycline antibiotics using spin-labeling technique. The spin-labeled tetracycline (SLTC) was prepared and its interactions with metal ions were studied using electron spin resonance (ESR) and nuclear magnetic resonance (NMR) spectroscopy. We have investigated the interaction between SLTC and copper ions in aqueous and DMSO solutions at both room temperature and liquid nitrogen temperature using ESR spectroscopy. Analysis of the ESR data in DMSO solution indicates that the amide group is involved in metal complexation, and an exchange interaction was found between the unpaired electrons of the copper ion and the nitroxyl radical. In aqueous solution, on the other hand, a weak exchange coupling was found between the unpaired electrons. The results on ESR and NMR studies will be presented.

Reactions of Phenyl (β -N-benzenesulfonyl indolyl) Iodonium Chloride with Soft Anions. ATILLA TUNCAI, Department of Chemistry, Indiana University Northwest, Gary, Indiana 46408 and ROBERT M. MORIARTY, Department of Chemistry, University of Illinois at Chicago, Chicago, Illinois 60607.—The reactions of phenyl (β -N-benzenesulfonyl indolyl) iodonium chloride with soft anions such as nitroethyl anion afforded N-benzenesulfonyl-3-iodoindole in excellent yields. The role of catalysts (copper salts), solvent and temperature was examined. The exclusive formation of the iodo compound is explained by a single electron transfer pathway. The present transformation will be discussed within the general context of nucleophilic displacement upon iodonium salts.

The Mechanism of L-Ascorbic Acid Entrapment in Human Erythrocytes. WILLIAM E. WHITE AND EUGENE S. WAGNER, Center for Medical Education, Ball State University, Muncie, Indiana 47306.——L-ascorbic acid-1-¹⁴C when incubated with human blood migrates irreversibly into red blood cells. Isolation and characterization via IR of the moiety trapped within the cells established its identity as apparently unchanged L-ascorbic acid. When dehydroascorbic acid-1-¹⁴C was incubated with human blood the results were identical including the identity of the entrapped moiety, L-ascorbic acid. Evidence will be presented to support the hypothesis that L-ascorbic acid is oxidized on the surface of the red blood cell to dehydroascorbic acid which migrates through the lipid portion of the cell membrane and is reduced back to L-ascorbic acid within the cell by glutathione reductase. The resulting L-ascorbic acid can not pass through the cell membrane and is therefore entrapped.