

## CHEMISTRY

Chairman: WILMER J. STRATTON, Department of Chemistry,  
Earlham College, Richmond, Indiana 47374

RICHARD PILGER, Department of Chemistry, St. Mary's College,  
Notre Dame, Indiana 46556, was elected Chairman for 1972

### ABSTRACTS

**The Synthesis and Decomposition of Some Interesting 1-Pyrazolines.** LEO MULLINS, TERRY L. KRUGER, THERESA CHENG, and JOHN SHARP, Department of Chemistry, Ball State University, Muncie, Indiana 47306. —The synthesis of several bicyclo-1-pyrazolines through 3+2 cycloaddition has been studied. The kinetics of the decomposition of a few of these compounds has been carried out with the identification of the decomposition products. These studies have shown that the decompositions may occur by processes allowed by orbital symmetry considerations. Future work includes product analysis, kinetics, mass spectra, and comparison of photodecomposition products with thermal-decomposition products.

**Properties and Reactions of Some N, N-Diethylaniline Oxides.** TERRY L. KRUGER, NANCY E. THARP and JAMES W. KRESS, Department of Chemistry, Ball State University, Muncie, Indiana 47306. —The title compounds with a variety of ring substituents have been synthesized. The basicities of these water soluble compounds have been correlated in the Hammett Equation. These compounds undergo facile Cope elimination to the corresponding N-ethylphenylhydroxylamines. An analysis of some aspects of the mechanism of this reaction and an explanation of the effect of substituent on both this reaction and basicity was presented.

**Synthesis and Identification of p-Benzoquinones Occurring in Arthropod Defensive Secretions.** JOSEPH E. ROGERS, JR., BENJAMIN FIESELMANN and JAMES JOSE, Department of Chemistry, Earlham College, Richmond, Indiana 47374. —Eight substituted p-benzoquinones known to occur in arthropod defensive secretions have been prepared. Chromatographic methods have been explored which facilitate identification of these quinones in complex naturally-occurring secretions. The eight quinones (p-benzoquinone, methyl-p-benzoquinone, ethyl-p-benzoquinone, 2,3-dimethyl-p-benzoquinone, 2,5-dimethyl-p-benzoquinone, 2,3,5-trimethyl-p-benzoquinone, 2-methoxy-p-benzoquinone, and 2-methyl-3-methoxy-p-benzoquinone) were either purchased or in most cases were synthesized by oxidation of suitably substituted amines or phenols. The gas chromatographic behavior of these quinones has been investigated on several stationary phases over a range of temperatures. All but two of the quinones may be resolved on a five-foot by one-eighth inch copper column containing 2 per cent OV-17 on GC Q. Thin-layer and paper chromatography of the 2,4-dinitrophenylhydrazones derivatives of the quinones reveals that all eight 2,4DNP derivatives may be resolved on a silica gel layer (Eastman Chromagram K301R) upon development with a 3:1 chloroform:xylene solvent in the presence of aqueous ammonia vapors.

**A Chemical Study of the White River at Muncie.** CHARLES T. BOTKIN and ROBERT E. VAN ATTA, Department of Chemistry, Ball State University, Muncie, Indiana 47306.—Analyses for several chemical components of the White River are reported for a 50-day period during the summer of 1971. The objective of the study was to determine whether or not significant variations in dissolved oxygen, chloride, free and albuminoid ammonia, pH, calcium, magnesium, iron, and several other factors occurred and could be conveniently monitored in a flowing system of considerable volume. Results are presented for sampling points upstream and downstream of the city and are compared with climatological records for the sampling period. Time versus analyzed factor profiles are presented and, where feasible, correlated with each other and with other variables in the stream's composition.

**A New Experiment for Advanced Inorganic Chemistry.** B. N. STORHOFF and D. F. STORHOFF, Department of Chemistry, Ball State University, Muncie, Indiana 47306.—The utility of simple group-theoretical considerations in inorganic chemistry is well documented. The appreciation for such considerations has prompted the design of an experiment which illustrates their utility in vibrational spectroscopy. The experiment focuses on the infrared active CO stretching vibrations of several manganese carbonyl complexes. Probable structures are assigned to the complexes by comparing the observed and predicted spectra.

**Rhenium(I) Complexes of 2-Cyanoethyldiphenylphosphine.** B. N. STORHOFF, Department of Chemistry, Ball State University, Muncie, Indiana 47306.—Halopentacarbonylrhenium (I) (Cl or Br) reacts with 2-cyanoethyldiphenylphosphine(L) to yield novel complexes of the stoichiometry  $[\text{Re}(\text{CO})_3\text{LX}]_n$ . Infrared data and molecular weight data suggest that these complexes are dimeric and utilize L as a bridging ligand. The complexes react with a variety of donor solvents and ligands (L') to yield complexes of stoichiometry  $\text{Re}(\text{CO})_3\text{LL}'\text{X}$ .

**Chelating Behavior of Some New Sterically Hindered Tetrafunctional Azine Ligands.** JOHN A. SCARLETT and WILMER J. STRATTON, Department of Chemistry, Earlham College, Richmond, Indiana 47374.—Two new unsymmetric azine ligands and their iron(II) complexes have been synthesized and characterized. Pyridinalpyridylphenylketazine was found to form two complexes as expected:  $[\text{Fe}_2\text{L}_3]\text{I}_4$ , with each ligand bridging two metals in a bis-bidentate fashion, and  $[\text{FeL}_2]\text{I}_2$ , with tridentate bonding of each ligand. Elemental analysis, infrared spectra, and electronic spectra were used to confirm these structures. Pyridylmethylpyridylphenylketazine also forms a bridged complex,  $[\text{Fe}_2\text{L}_3]\text{I}_4$ , but apparently does not form a 2:1 tridentate complex. Attempts to produce the latter complex resulted only in formation of a hydrazone complex. A ligand hydrolysis mechanism is proposed, in which the steric effects of the phenyl and methyl groups cause the ligands to "squeeze" out a metal ion, thus allowing proton attack on the uncoordinated C=N group.

**Conductivity Studies in Acetonitrile for a Novel Series of Metal Chelates with 2-Pyridylmethylketazine.** DAVID J. HARRIS and WILMER J. STRATTON, Department of Chemistry, Earlham College, Richmond, Indiana

47374.—Complexes of  $\text{NiCl}_2$ ,  $\text{CoCl}_2$ ,  $\text{ZnCl}_2$  with 2-pyridylmethylketazine, each of which had analyses indicating 4/5 or 5/6 of a ligand per metal, were studied in acetonitrile solution. The data obtained showed that the conductances of the three compounds are distinctly different. Empirical equivalent weights were established from the conductivity data for each complex. Comparison of the slopes of plots of equivalent conductance versus square root of concentration with similar plots for two reference compounds was used to establish the charge types of the complexes. Results for the nickel complex are consistent with a formula  $[\text{Ni}_2\text{L}_2\text{Cl}_3(\text{H}_2\text{O})_2][\text{NiCl}_4]$ . Data for the cobalt and zinc complexes do not fit this formulation and are indicative of a more highly polymeric structure.

#### A Counterdiffusion Study of Ferric and Silicate Ions in Agar Media.

JON D. NAYLOR and JOHN H. MEISER, Department of Chemistry, Ball State University, Muncie, Indiana 47306.—The development of new techniques for obtaining quantitative data used in the investigation of the counterdiffusion of ferric and silicate ions in an agar gelatin is presented. A treatment is given of the equations used for predicting the location of the band precipitates at given time intervals based on the supersaturation theory. The authors also presented a brief historical account of the Liesegang Phenomenon and a review of several theories providing explanations of this occurrence of band precipitates.

#### Liquid X-Ray Diffraction Studies of the Structures of Aqueous Metal Nitrate, Acetate, and Perchlorate Solutions Using Overviewing Techniques.

RICHARD M. LAWRENCE and JAN R. RELFORD, Department of Chemistry, Ball State University, Muncie, Indiana 47306.—Overviewing techniques were developed to examine the structures of liquids by x-ray diffraction. Viewing the entire scattering volume of a sample yields agreement between the forms of the observed and calculated scattering curves and permits routine calculation of a radial distribution function for the system. In these studies radial distribution functions were calculated for almost twenty aqueous solutions of silver, lead, thallium (III), mercury (I), and cerium (III) nitrates, acetates, and perchlorates. These radial distribution functions are interpreted in terms of the numbers and distances of metal-metal and metal-oxygen interactions among closest neighbors. The mercury (I) solutions are the only solutions studied in which there are significant metal-metal contacts, and the results are consistent with the presence of  $\text{Hg}_2^{2+}$ . In the other solutions studied the metal ions appear to be in contact with from four to nine oxygens of water molecules or oxy anions. The number of metal-oxygen contacts is found to vary in a consistent manner with the concentration of the solution and the nature of the cation and the anion. The metal-oxygen distances agree with the sums of the van der Waals radius of oxygen and the crystal ionic radii of the metal ions.

#### Molecular Orbital Calculations on Some Nitrogen Heterocycles.

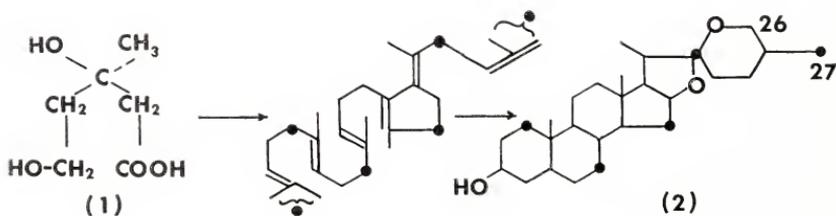
T. L. KRUGER and JAMES W. KRESS, Department of Chemistry, Ball State University, Muncie, Indiana 47306.—A CNDO/2-INDO calculation of the quantum-mechanical properties of diazomethane and some substituted pyrazoles and 1-pyrazolines was presented. Calculated and experimental

bond orders, bond lengths, ultraviolet spectra and their relationship to the physical properties of the compounds were compared. Specific emphasis was placed on comparison of HMO and CNDO/2-INDO prediction for pyrazole and substituted pyrazoles.

**An Anticholinesterase Agent and Myasthenia Gravis.** ROBERT M. BROOKER, Department of Chemistry, Indiana Central College, Indianapolis, Indiana 46227, and T. LAMAR KERLEY, Dow Human Health R and D Laboratories.—Large doses of impure para-xylene-bis (pyridinium) chloride when given to unanesthetized dogs produced a muscle weakness that progressed to complete paralysis. Small doses of the drug reversed the paralytic effects of d-tubocurarine. It was found that this latter effect was caused by an impurity present in the original salt. Attempts were made to isolate and identify this compound that exhibited this anticholinesterase activity.

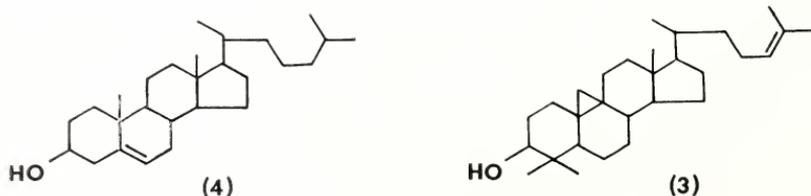
**The Biosynthesis of Steroidal Sapogenins.** PAUL ANDERMATT, University of Basel, Switzerland, and Department of Chemistry, Earlham College, Richmond, Indiana 47374.—The biosynthesis of steroids in human and animal organisms is known: acetic acid  $\rightarrow$  mevalonic acid  $\rightarrow$  squalene  $\rightarrow$  cholesterol, or a similar  $C_{27}$ -steroid.

From *Digitalis lanata*, an European plant, tigogenin (2) was isolated. After the incorporation of ( $2-^{14}C$ )-mevalonic acid (1) the molecule showed the expected distribution of radioactivity:



The distribution of radioactivity was determined by chemical degradation of the molecule.

The cyclisation and ring closure are strictly stereospecific. One fifth of the radioactivity was located at C-27, while C-26 showed no radioactivity. To explain this stereospecific ring closure, a  $\Delta^{24}$ -steroid as desmosterol or cycloartenol (3) may be a possible precursor of tigogenin. To clarify this problem, radioactive cycloartenol (3) and cholesterol (4) were fed to the plants. Whereas cholesterol was incorporated, tigogenin showed no radioactivity after the application of cycloartenol.



These results show, that the biosynthesis of tigogenin involves the following steps: mevalonic acid  $\rightarrow$  squalene  $\rightarrow$  cholesterol  $\rightarrow$  tigogenin.

**Thin-Layer Gel Filtration Studies of Adenosine Deaminases from Beef and Beef Fetus Livers<sup>1</sup>.** BRUCE A THORNBURGH and PANG FAI MA, Department of Chemistry, Ball State University, Muncie, Indiana 47306. —The chromatographic patterns of adenosine deaminase in beef liver and beef fetus liver showed that the enzyme exists in two forms in these tissues. The high molecular weight enzyme (Type A) was the predominant form in the beef liver and the low molecular weight enzyme (Type C) was the predominant form in the beef fetus liver. The Type-A enzyme was found to partially dissociate to the Type-C enzyme when it was rechromatographed on a Sephadex column.

A rapid method for detecting the presence of the Type-A and Type-C enzymes was needed to study the dissociation of the Type-A enzyme under various conditions. This led to the development of a thin layer gel filtration chromatographic technique which was applicable to adenosine deaminase. The technique involved the detection of the ammonia that is given off in the deamination reaction with Nessler's Reagent.

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**A Comparative Study of Adenosine Deaminase in Human Tissues.<sup>1</sup>** THOMAS A. MAGERS and PANG FAI MA, Department of Chemistry, Ball State University, Muncie, Indiana 47306. —Multiple forms of adenosine deaminase were first observed and studied in many species of lower animals by Ma and Fisher. Three relative molecular sizes were observed: 200,000, 100,000, 30,000, and designated as enzyme forms A, B, and C, respectively. Evidence by Ma has shown the smallest multiple form to be a monomeric unit of the largest.

Akedo, Nishihara, Shinkai, and Komatsu, have since studied similar multiple forms corresponding to the A and C forms in certain human tissues. They have reported that while normal human lung tissue contains only the A form adenosine deaminase, cancerous lung tissue contains both A and C forms.

The present study enlarges the survey of multiple forms in both normal and cancerous human tissues. Kinetic, physical, and immunological parameters are presented by way of comparison of the multiple enzyme forms extracted from various tissues. Thin-layer gel filtration and electrophoretic techniques have been applied to the study and characteristic patterns were discussed. Partial purification of the monomeric adenosine deaminase from the cerebrum has been achieved and pertinent data were reported.

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**Photochemical Synthesis and Destruction of Oxaziranes.** M. L. DRUELINGER and S. R. LAMMERT, Department of Chemistry, Indiana State University, Terre Haute, Indiana, 47809. —The irradiation of a series

of nitrones was studied. The compounds selected for this study possessed N-aryl or N-t-alkyl groups, while the nitrone carbon was either unsubstituted (methylene) or carried a single phenyl group. The reactions were carried out in a nuclear magnetic resonance tube using a medium pressure mercury arc. In all cases the initially formed product was the oxazirane whose photochemical stability was dependent upon its substituents and the irradiation wavelength. Subsequent reaction occurred via rearrangement to give amides or fragmentation to give nitrenes and carbonyl compounds. Mechanistic studies indicate a singlet excited state for the former and a triplet excited state for the later reaction.

### NOTE

**Some New Approaches to Teaching Chemistry for Non-Science Majors.** LAWRENCE L. GARBER, Department of Chemistry, Indiana University at South Bend, South Bend, Indiana 46615.—If today's college student is to deal constructively with present and future social and technical problems, he must have a basic understanding of the fundamentals of science. The course described here is designed to enable the non-science oriented student to learn some of the fundamentals of chemistry but in a stimulating manner. To meet this objective, topics such as environmental pollution, polymer chemistry, chemical processes important to life, and certain aspects of drug chemistry are used to exemplify chemical phenomena. The course meets for 4 hours of lecture-discussion and 2 hours of laboratory work per week for 15 weeks.

Part I of the course emphasizes properties of atoms, electronic structure, periodic trends, oxidation numbers, simple theories of chemical bonding and the rationale behind why chemical changes take place as they do. Part I is designed to provide sufficient background for the discussion of subsequent topics. To illustrate why Part I is necessary, consider the production of sulfur dioxide which is a basic air pollutant. If the student understands electronic structure and periodic trends, the student can very easily predict that sulfur, when combined with oxygen, can have an oxidation number of plus four and thus a combustion product of sulfur will be sulfur dioxide. This type of logic can be applied to many simple, yet important, reactions that occur in pollution production and abatement.

Part II of the course emphasizes the topic of air and water pollution which obviously cannot be extremely detailed. Five main classes of air pollution; sulfur oxides and related compounds, nitrogen oxides and related compounds, hydrocarbons, carbon monoxide, and particulate matter, are included in the discussion. The student is exposed to some of the important chemical reactions that are instrumental in the production of air pollutants; chemical reactions that can be potentially harmful to life and matter; and chemical processes that might render solutions to the problems. The greenhouse effect is discussed. The factors and conditions necessary for the production of smog are emphasized.

The discussion of smog production and composition provides an excellent mechanism for the introduction of organic chemistry. The topic of

air pollution can be used to illustrate acid-base neutralization, chemical properties of acidic and basic anhydrides, pH, oxidation-reduction, colloids and colloidal properties. The discussion of water pollution very easily permits the illustration of such phenomena as ionization, electrolytes, solubility, hydrogen bonding and concentration units.

Water pollution topics include a discussion of eutrophication by phosphates and nitrates, the chemical and physical properties and biodegradability of detergents, and the essential chemical characteristics of phosphorous, nitrogen and sulfur cycles. A discussion of water hardness and the use, characteristics and effects of water softeners are easily incorporated in Part II. The topic of mercury pollution and associated controversies demonstrates readily the interrelationships of inorganic and organic chemistry.

Part III emphasizes organic and biochemistry. A discussion of polymers illustrates successfully some additional characteristics of organic compounds. A discussion of pesticides, polychlorobiphenyls and selected aspects of drug chemistry are also included. The characteristics and roles of DNA and RNA in life processes are emphasized as well as the characteristics of fats, proteins and carbohydrates.

The laboratory is designed to supplement the lecture. For 5 weeks the student investigates air and water pollution. Examples of some of the determinations are pH, color, temperature, dissolved oxygen, dissolved carbon dioxide, hardness, detergent content (ABS and LAS) and concentrations of sulfate, phosphate, nitrate, nitrite, copper, and chloride ions in local water systems. Except for temperature, color and pH measurements, Hach chemical kits, which are specifically designed for each determination, are used. The advantage of using these chemical kits, or other commercial chemical kits, is that the reagents are pre-measured, the glassware is calibrated, and the detection is simple. The amount of substance present is indicated quantitatively by either a color change or a color comparison. The detection scheme is calibrated so as to permit direct determination of concentration without the need for mathematics. Hence, the result is not masked by mathematical difficulties that the student might have. All results are collected on a data sheet. The laboratory results help to promote considerable discussion and illustrate the quality of water in the South Bend area.

In conclusion, by presenting the topics of environment pollution, aspects of drug and polymer chemistry and some of the essentials of the chemistry of life processes, important topics and concepts of chemistry can be discussed and learned by the student but in a more interesting fashion.

