

CHEMISTRY

Chairman: JOHN H. MEISER, Department of Chemistry
Ball State University, Muncie, Indiana 47306

Chairman-Elect: PANG-FAI MA, Department of Chemistry
Ball State University, Muncie, Indiana 47306

ABSTRACTS

Numerical Coding as a Teaching Aid for Infrared Spectroscopy. ROBERT E. VAN ATTA, Department of Chemistry, Ball State University, Muncie, Indiana 47306.—A numerical coding system for describing, filing, and retrieving infrared spectra is presented which permits systematic organization of a spectrum library for instructional use. The system, which may also be used for rapid coding of commercially available spectra, involves selection of principal absorption bands at three levels of intensity in characteristic spectral regions. The nature of the spectrum may be deduced from the numerical code, thus simplifying retrieval for qualitative comparisons. Retrieval may be accomplished via index card, rolodex systems, punched card, or computerization.

Synthesis and Reactions of Tetraethynylethylene Glycols. STEPHEN M. KELNER and KENNETH G. MIGLIORESE, Department of Chemistry, Indiana University Northwest, Gary, Indiana 46408.—In an attempt to devise an unambiguous synthetic route to tetraethynylethylenes, compounds of the general type $(RC\equiv C)_2C(OH)C(OH)C(C\equiv CR)_2$, ($R = CH_3$, $t-C_4H_9$) were



prepared by reacting the appropriate acetylenic Grignard reagent with diethyl oxalate. To date, all attempts to convert these tetraethynyl glycols to the corresponding tetraethynylethylenes has been unsuccessful. The glycols themselves do, however, exhibit some interesting chemistry which will be reported.

Chemical Modification of Human Prostatic Acid Phosphatase. JOHN J. MCTIGUE and ROBERT L. VAN ETTEN, Department of Chemistry, Purdue University, West Lafayette, Indiana 47907.—Human prostatic acid phosphatase (HPAP) catalyzes the hydrolysis of the monoanionic form of a wide range of phosphomonoesters. We considered it likely that a positively charged group at the active center of HPAP accounted for this specificity for the monoanionic form of the substrate. Since no metal ion has been found to be associated with this enzyme, we examined the possibility that a positively-charged residue such as lysine or arginine was essential for the binding of substrate. Experiments with trinitrobenzenesulfonic acid and pyridoxal 5-phosphate have excluded an active-site lysyl residue from the binding function, while treatment of the enzyme with either of the arginine-specific modifiers 2,3-butanedione or 1,2-cyclohexanedione in borate buffer at pH 8.1 leads to the loss of activity. The rate of inactivation is decreased markedly in the presence of the

competitive inhibitors L-(+)-tartrate or inorganic phosphate but not in the presence of the non-inhibitor D-(-)-tartrate.

Several reports have indicated that a phosphoenzyme intermediate is involved in the mechanism of acid phosphatases. To ascertain the identity of the amino acid residue involved in the formation of this intermediate, further chemical modification studies were undertaken. Reaction of HPAP with diethyl pyrocarbonate in succinate buffer at pH 6.0 leads to inactivation of the enzyme. Under these conditions histidine and lysine residues are modified. In the presence of competitive inhibitors the rate of inactivation is decreased. These results suggest an essential role for arginyl and histidyl residues in the mechanism of HPAP, probably with arginine in a binding site for the negatively charged phosphate group of the substrate and with histidine acting as a nucleophile in the catalytic mechanism.

A Study of the Interconversion of Human Adenosine Deaminases in Cancerous and Normal Tissues. J. ZACHARY, P. F. MA, and J. M. COERS, Department of Chemistry, Ball State University, Muncie, Indiana 47306. —Two different molecular forms of adenosine deaminase have been found in various human tissues: The high molecular weight enzyme (A form) and the low molecular weight enzyme (C form). The two forms of the enzyme are present in various proportions in different tissues and are interconvertible. There is an indication that a conversion factor is involved in this interconversion. To study this interconversion phenomena in cancerous and normal tissues, a series of incubation experiments have been attempted. A purified tissue extract containing only one of the isozymes is incubated separately with two crude tissue extracts, one normal and one cancerous. The samples, along with the appropriate controls, are subjected to thin-layer gel filtration to separate and identify the isozymes. Isozyme location on the plate is detected by measuring the enzyme activity spectrophotometrically, in eluted fractions.

Environmental Co-carcinogens. STEPHEN R. WILSON, Department of Chemistry, Indiana University, Bloomington, Indiana 47401. —Phorbol esters, the most potent co-carcinogens known, have been isolated from a wide variety of plant sources. Co-carcinogens such as phorbol esters lower the threshold response to carcinogens at 10^{-9} molar concentrations. Since exposure of man to environmental chemical contaminants with carcinogenic potential usually involves frequent or continuous contact with minute quantities of these compounds, co-carcinogens play a decisive role in determining the carcinogenic potency of a mixture. The importance of the concentration of the carcinogen may be relatively minor even though its presence in minute amounts is obligatory. The theory of carcinogenesis and some aspects of the chemistry of phorbol will be discussed.

Isomeric 2-Substituted-1,3,2-diazaphosphorinanes. J. A. MOSBO, Department of Chemistry, Ball State University, Muncie, Indiana 47306. —Isomeric 2-methoxy- (1) and 2-dimethylamino-1,3,4-trimethyl-1,3,2-diazaphosphorinanes (2) have been prepared and their equilibrium con-

centrations determined. The distributions of 56:44 for *1* and 60:40 for *2* indicate substantially different behavior between these and the dioxo analogues. Although phosphorus stereochemistries and *cis-trans* geometries could not be identified unambiguously, ^{31}P chemical shifts and infrared phosphoryl stretching frequency data for *1* and *2* and their 2-oxo derivatives led to the speculative assignments of the more abundant isomer of *1* being *cis* and that of *2* being *trans*.

Organonitrile Complexes of Platinum. DAVID A. BLINN and BRUCE N. STORHOFF, Department of Chemistry, Ball State University, Muncie, Indiana 47306.—2-Cyanoethyldiphenylphosphine, 2-cyanocyclopentylidiphenylphosphine, and 2-cyanocyclohexyldiphenylphosphine (L) react with $1,5\text{-C}_8\text{H}_{12}\text{Pt}(\text{CH}_3)_2$ and $1,5\text{-C}_8\text{H}_{12}\text{Pt}(\text{CH}_3)\text{Cl}$ to displace the cyclooctadiene and yield monomeric complexes of the stoichiometries $\text{L}_2\text{Pt}(\text{CH}_3)_2$ and $\text{L}_2\text{Pt}(\text{CH}_3)\text{Cl}$. Spectroscopic evidence strongly suggests that in these complexes the cyanophosphine ligands function as monodentate phosphines.

Reactions of the $\text{L}_2\text{Pt}(\text{CH}_3)\text{Cl}$ complexes with AgBF_4 or AgPF_6 in acetone yield immediate precipitates along with colorless complexes of the stoichiometry $[\text{L}_2\text{PtCH}_3]_n^{n+}$. Spectroscopic evidence suggests that in these complexes one of the ligands functions as a monodentate phosphine while the other serves as a bridging group. One of the nitrile groups in each of these cationic complexes is particularly reactive and is readily attacked by alcohols.

The Synthesis and Some Reactions of 1-Bromo-2(phenylethenyl)benzene. BRUCE N. STORHOFF, Department of Chemistry, Ball State University, Muncie, Indiana 47306.—The title compound has been synthesized in good yield from readily available starting materials by utilizing Wittig reagents. The synthetic procedures are based on the reaction of benzaldehyde with a Wittig reagent prepared from *o*-bromobenzyl bromide and either triphenylphosphine or triethylphosphite, which yields the corresponding stilbene. The desired product is obtained by dehydrohalogenation of the previously brominated stilbene.

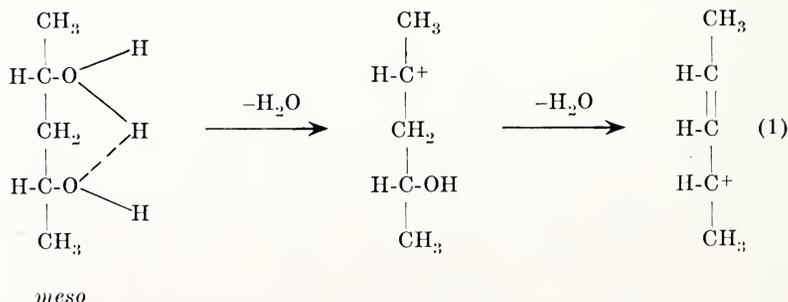
The bromine in the title compound is metalated by *n*-butyllithium at low temperature. Some reactions of the metalated product were investigated.

Chemical Education for Artists, Philosophers, Economists, and Politicians. TERRY L. KRUGER and FREDERICK K. AULT, Department of Chemistry, Ball State University, Muncie, Indiana 47306.—Trends in chemical education for nonscience majors from Sputnik to the present were discussed. During the past ten years, two widely different chemical education philosophies have evolved and now seem to dominate courses designed for nonscience majors. The two philosophies differ primarily on the issue of principles and relevance versus relevance without substance. The emphasis on relevance can result in a serious neglect of fundamental chemical concepts. The authors expressed a preference for course organization that makes basic chemical concepts the heart of the course with excursions into relevance at a depth to illustrate the application of concepts.

Understanding the pedagogical issues involved in course design requires consideration of psychological, philosophical, and economic factors which affect our lives. The alienation of modern man from his technological surroundings has been enhanced through misunderstanding of scientific concepts and as a result of advertising promises on products which fail to deliver as claimed. The modern citizen reacts predictably when faced with devices of limited lifetime and utility while experiencing decreasing economic power. The reaction has been an expression of resentment and hatred toward the scientific-technological community.

The authors proposed to offer relevance in the nonscience major course through a nonmathematical treatment of basic chemical concepts using many examples illustrating the utility of the concepts. Concepts treated in the course include elemental organization, structure and function, temperature and disorder, stoichiometry related to resource utilization, properties of solutions, and thermodynamics.

Stereoisomeric Studies in the Gas Phase on the MIKES. T. L. KRUGER and J. A. MOSBO, Department of Chemistry, Ball State University, Muncie, Indiana 47306, and R. G. COOKS, Department of Chemistry, Purdue University, West Lafayette, Indiana 47907.—Mass Analyzed Ion Kinetic Energy Spectrometry (MIKES) has been developed for studying the behavior of ions in the gas phase. Extension of the technique has been made to organic analysis and to the determination of gas phase equilibrium constants. Isomers of the functional group position type have shown large differences in gas phase ion fragmentations (Anal. Letters, 1976). We will discuss the application of the method to the determination of the stereochemistry of ions in the gas phase. The systems studied thus far are the 2,4-disubstituted pentanes, where the substituent is hydroxy-, amino-, and N-methylamino-. The decompositions (metastable) of the dihydroxy are loss of one and two water molecules. The *meso* compound loses the second water with three times the frequency in comparison with the first (water loss) and the *d,l* pair. The initial conclusion is that MIKES will prove useful in stereochemical studies in at least some cases.



The Reaction of Methyl Vinyl Ether with Chlorine. T. C. SCHWAN and CURTIS R. WILLE, Department of Chemistry, Valparaiso University, Val-

paraiso, Indiana 46383.—The reaction of chlorine with methyl vinyl ether would be expected to be a simple and straightforward addition. However, in addition to the expected product, 1,2-dichloromethoxyethane, appreciable quantities of 2-chloro-1-methoxyethene are produced as well as minor amounts of at least eleven by-products. A few of these by-products, acetaldehyde, methyl acetate, 1,1-dimethoxyethane, 1,1-dimethoxy-2-chloroethane and 3-chloropropanal have been identified tentatively by GC-MS analysis. Mechanisms by which these minor by-products form remain to be elucidated; they should prove interesting.

A Study of an Oscillating Chemical Reaction. PHILIP L. BURKHOLDER, 143 Littleton St., West Lafayette, Indiana and JAMES T. STREATOR, Department of Chemistry, Manchester College.—An acidic solution of potassium iodate, malonic acid, hydrogen peroxide, and manganese II sulfate will oscillate at 25° as the system approaches an equilibrium state. The period of the oscillations can be varied over a considerable range by varying the concentrations of the reactants. The presence of an iodine intermediate can be made quite visible by the addition of starch. A study of this reaction was made to devise procedures for measuring temperature and spectral changes that occur during the oscillations. These procedures were used in an attempt to unravel some of the kinetic and thermodynamic properties of the system.

The Photolytic Rearrangement of 1-Adamantyl Azide. GRANT KRAFT and A. GILBERT COOK, Department of Chemistry, Valparaiso University, Valparaiso, Indiana 46383.—The photolytic rearrangement of 1-adamantyl azide has been studied in several solvent systems. The photolysis of the azide in methanol, ethanol and isopropanol produced 1-methoxy-2-azahomoadamantane, 1-ethoxy-2-azahomoadamantane and 1-isopropoxy-2-azahomoadamantane, respectively, in yields of 90-95%. Photolysis of the azide in cyclohexane and *n*-heptane gave a dimeric compound, and photolysis in furan solvent yielded primarily the dimer with some furan adduct. Several possible mechanisms for the rearrangements are discussed.