CHEMISTRY

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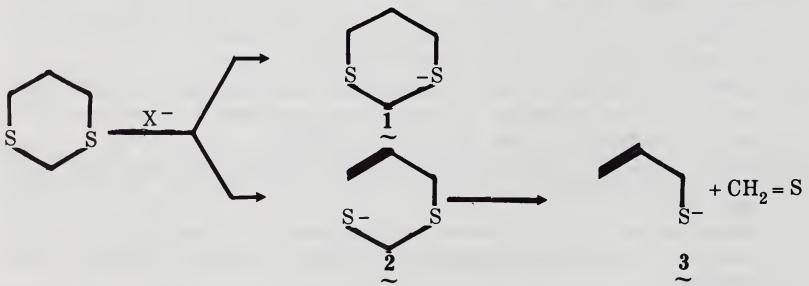
ABSTRACTS

Comparisons of the Semi-empirical Molecular Orbital Treatments MINDO/3 and MNDO with Some Simple Phosphines. RANDALL K. ATKINS, PAUL L. BOCK, JOHN A. MOSBO, and BRUCE N. STORHOFF, Department of Chemistry, Ball State University, Muncie, Indiana 47306.——The semi-empirical molecular orbital computer programs MINDO/3 and MNDO were used to obtain heats of formation data and optimized geometries for all unique conformations of fourteen phosphines: PH_2R (R = H, Me, Et, i-Pr, t-Bu, Ph), PHR_2 (R = Me, Et, i-Pr), and PRR_2' (R = R' = Me, Et; R = Me, R' = Et; R = Et, Ph, R' = Me). The bond lengths, bond angles, twist angles and heats of formation predicated by the two treatments were compared, and the effect of differences discussed in terms of effective phosphine sizes and conformational populations. Computed phosphorus-carbon rotational barrier heights were compared to experimental data.

Gas Phase Chemistry of 1,3-Dithiane. JOHN E. BARTMESS, ROBERT L. HAYS, and STEPHEN R. WILSON, Department of Chemistry, Indiana University, Bloomington, Indiana 47405.——In a negative ion modified (ICR) mass spectrometer, we have examined the gas phase bimolecular chemistry of the acyl anion equivalent 1,3-dithiane. Unlike solution where only deprotonation to give **1** occurs, in the gas



phase successive eliminations are also seen. As X^- is varied, the three ionic products are seen to occur or not occur consistent with their thermochemistry. Similar chemistry is seen for the five membered ring. The difference between gas phase and solution is attributed to ion-pairing of the metal ion of the base with the sulfur in solution, thus not allowing the base access to the hydrogen leading to elimination. The lack of a counter ion in the gas phase lets the base access either site.

Laboratory Interfacing with the Apple II Plus Microcomputer: A Computer Controlled Titrator with High Resolution Color Graphics Display. STANLEY L. BURDEN, DAVID WOODALL, KATHLEEN DONICA, RICK THOMPSON, JON CONDIT, STEVEN BEESON, and DOUGLAS TAYLOR, Department of Chemistry and Information Science, Taylor University, Upland, Indiana 46989.——An Apple II Plus microcomputer has been

interfaced to an Orion 701 pH meter and a Sargent constant rate buret and software has been written to configure a computer controlled titrator. The high resolution graphics capability of the Apple is used to provide a real time, color plot of the titration data as it is being collected. One of the user selectable options includes specifying a pH or millivolt reading at which the continuous titrant delivery is automatically changed to a dropwise addition as the endpoint is approached. Milliliters of titrant used and normality of titrate are computed and displayed on the television screen at the completion of the titration.

Test of Nonisothermal Apparatus Suitable for the Study of Energy and Mass Transport Coefficients. MARSHALL P. CADY, JR., Department of Natural Sciences, Indiana University Southeast, New Albany, Indiana 47150.——A new nonisothermal apparatus capable of measuring energy and mass transport coefficients of clear liquid mixtures has been designed and assembled. The apparatus consists of a newly designed thermal cell and a dual Savart plate Bryngdahl interferometer. Preliminary tests prove that nonisothermal techniques can be used to directly measure system properties with a high degree of accuracy and without corrections for complex energy transport phenomena associated with wall effects.

The quality of temperature control and measurement has been verified and the instrument has been tested by measurement of the temperature dependence of the refractive index of water. The refractive index, n, is related to the Bryngdahl interferometric fringe number, N, by the equation:

$$-dn/dT = CN/\Delta T$$

where ΔT is the difference in temperature between the upper and lower cell boundaries and C is an instrument constant which is evaluated from isothermal interferometric images. We find that for water at 632.8 nm and atmospheric pressure

$$-(dn/dT)10^4 = 0.313 + 0.02806T$$

where T is in °C and can vary between 23°C and 38°C. Values of -(dn/dT) computed from this equation are 2-3% lower than the standard established by Tilton and Taylor. However, this deviation is comparable to the standard deviation between all isothermal studies on water. In the absence of corrections for wall effects, previous nonisothermal determinations have yielded considerably lower values. Bryngdahl found values from 5% higher at 15°C to 12% lower at 26°C; Olson and Horne found a value 5% lower at 25°C.

Thermal cell construction is based upon the cell design pioneered by Krishnamurti but it only weighs approximately 20 pounds. It utilizes a parallel plate configuration in which aluminum blocks form the upper and lower cell boundaries. The blocks are separated by precision nylon spacers and the block surfaces have been machined flat to within 0.001 inch. Front and back boundaries consist of optically flat plate glass held in place by nylon frames. The temperature of the aluminum blocks is controlled with a combination electronic heat pump and water heat bath. Furthermore, the vertical temperature distribution is precisely determined with an internal thermocouple system. Temperatures are controlled to within approximately 0.005°C. Distinctive cell features include a relatively heavy weight, large distances (approximately 2 inches) between the internal heat bath and the cell-liquid surface, and the absence of highly polished silver mirror boundaries. These features are designed to eliminate vibrations, fluid convection, external heat flux problems, and infrared reflection problems at boundaries.

Ultimately, we hope to simultaneously measure thermal diffusivities diffusion

coefficients, and thermal diffusion factors of associating solutes in nonassociating solvents with this new thermal cell—Bryngdahl interferometer arrangement. The effort described in this paper proves the accuracy of the instrument under steady — state temperature conditions. To reach our goal, we must now prove that the time evolution of (N,T) data can be analyzed numerically for the thermal diffusivity coefficient of a pure liquid. These tests will be published in a future paper.

The Schmidt Reaction of 3a,4,5,6,-Tetrahydrosuccinimido[3,4-b]acenaphthen-10-one and Its Alkylated Derivatives. E. CAMPAIGNE and R. YODICE, Department of Chemistry, Indiana University, Bloomington, Indiana 47405.——The rearrangement of 3a,4,5,6-tetrahydrosuccinimido[3,4,-b]acenaphthen-10-one and two methylated derivatives using Schmidt conditions is described. The ratio of the major product, 2,3,8,9-tetrahydro-3-oxo-1*H*-benz[*de*]isoquinoline-1,9a(7*H*)-dicarboximide(**1**), to the minor product, 2,3,6,7-tetrahydro-3-oxo-4*H*-benz-[*ij*]isoquinoline-4,4a(5*H*)-dicarboximide, under different acidic conditions is given. The ratios of analogous products from the methylated derivatives are similar under similar conditions. Alkylations and thionations of **1** produced a variety of heterocycles, of interest as potential anticonvulsants.

The Identification of Synthetic Fibers of Forensic Interest by a Combination of Differential Thermal Analysis and Infrared Spectrophotometry. R. J. COFFEY, D. J. REULAND and W. A. TRINLER, Department of Chemistry, Indiana State University, Terre Haute, Indiana 47809.——A method of differentiating between fibers of forensic interest by differential thermal analysis and infrared spectrophotometry is described. Thermograms of the first melt were used. Sample size varied from 0.1 to 20 milligrams. In most cases fibers of different composition or from different manufacturers could be identified by the morphological features of the thermograms and the melting temperatures. In some cases infrared spectra also were required for identification. Obtaining a thermogram of the first melt enhances the evidential value of the analysis by recording the effect of the previous thermal history of the fiber on the thermogram. In some cases this allowed for the differentiation of similar fibers from different manufacturers. Care was taken to ensure that the sample and the comparator were run under as similar experimental conditions as possible. Where comparisons could be made the various endotherms and exotherms of the first melt were consistent with those reported by other investigators.

Energy Surfaces of Sigmatropic Shifts. JOSEPH J. GAJEWSKI and KEVIN E. GILBERT, Department of Chemistry, Indiana University, Bloomington, Indiana 47405.—— Transition state structure variation in the 2,3-sigmatropic shift has been revealed by secondardy deuterium kinetic isotope effects at the α and γ carbons of various 3° -allyl amine oxides. Both extensions of Hammond's Postulate and Thornton's perpendicular effect are reasonable predictors of the variation observed. Secondly, mathematical models for sigmatropic shift energy surfaces have been developed to allow correlation of rate data as a function of the stabilities of product and the transition states for non-concerted bond breaking and bond making.

The Chemistry of Cyanogen Compounds Degradation. ROBERT H. L. HOWE, West Lafayette, Indiana 47906.——The degradation of a number of cyanogen compounds by respective chemical, biological and physical methods is presented. Some experience of the author is discussed.

Parameterization of the Empirical Molecular Conformation Approach CAMSEQ for Phosphines. MARK D. MCINTIRE, PAUL L. BOCK, JOHN A. MOSBO and BRUCE N.

STORHOFF, Department of Chemistry, Ball State University, Muncie, Indiana 47306. ——The empirical computational technique CAMSEQ is based on three types of energy functions: (1) Lennard-Jones 6-12 potential functions represent steric, nonbonded interactions, (2) Coulomb's law functions approximate electrostatic interactions, and (3) truncated fourier series are used to modify the torsional barriers. The latter has not been previously parameterized for P-C and C-C bonds in phosphines, a necessity for optimal use of the program. This paper described the process for parameterization based on the available experimental data of some simple phosphines and substituted ethanes. Use of fully parameterized CAMSEQ with larger phosphines was discussed and the results compared to other computational techniques..

A Study of Adenosine Deaminase in Human Serum. THOMAS W. MYERS and PANG F. MA, Department of Chemistry, Ball State University, Muncie, Indiana 47306.——Adenosine deaminase (adenosine aminohydrolase, EC 3.5.4.4) catalyzes the hydrolytic deamination of adenosine to produce inosine and ammonia. Clinical and experimental investigations have shown that adenosine deaminase is critical in developing and maintaining immunological competence. The clinical and chemical aspects of adenosine deaminase have become quite numerous. Because of the current interest, the monitoring of adenosine deaminase activity is a very important problem. Little information has been reported concerning the activity of the different molecular weight forms of adenosine deaminase in disease states or of the stability of the different forms during storage. Most studies determining the activity of the individual forms of adenosine deaminase have utilized one of the following techniques in order to separate the different molecular forms of the enzyme: sucrose density gradient sedimentation, gel electrophoresis, isoelectric focusing, or thin-layer chromatography. These methods all present various problems when used in clinical studies. The difficulty and time required to perform these separations have made duplication of results difficult in previous studies. Gel filtration was used in order to provide a rapid, quantitative, and reproducible separation of the different forms of adenosine deaminase. The gel filtration method and the determination of the stability of the different molecular forms of adenosine deaminase during storage are presented. Potential applications toward clinical studies also are discussed.

Equilibria Between Diols and the NMR Shift Reagent Eu(fod)$_3$. LOIS M. OUNAPU, JOHN A. MOSBO, PAUL L. BOCK and TERRY L. KRUGER, Department of Chemistry, Ball State University, Muncie, Indiana 47306.——The solution equilibria between a difunctional molecule, S, and the lanthanide shift reagent Eu(fod)$_3$, L, can include three product forms: LS and LS_2 where the substrate functions as a monodentate ligand, and LS_b where a single substrate functions as a bidentate ligand. An iterative computer program was used to fit experimental and calculated proton NMR chemical shifts while optimizing the parameters of equilibrium constants and limiting chemical shifts. Results were compared from fits of (1) LS_2 parameters only, (2) LS and LS_b parameters only, and (3) LS, LS_2 and LS_b parameters for strongly chelating diols (e.g., *d,l*-2,4-pentanediol), the more weakly chelating *cis*-1,3-cyclohexanediol, and the non-chelating *trans*-1,3-cyclohexandiol. The viability of single and double equilibrium constant fits for each type of diol were discussed.

A Comparative Study of the Interaction Between the Conversion Factors from Human Tissues with the Small Forms of Adenosine Deaminase from Various Organisms. SHASHI PUTTASWAMY, PANG F. MA, Department of Chemistry, Ball

State University, Muncie Indiana 47306.——Two molecular forms of adenosine deaminase have been reported from bovine livers. These two forms were found to differ in their size, and they have also been found to be interconvertible. Adenosine deaminases extracted from human tissues exhibited similar properties as well. Previous studies have shown the presence of a conversion factor which formed an aggregate with the small form (the C-form) of the enzyme, and the resulting enzyme complex was identified to be the large form (the A-form) of adenosine deaminase. Studies have been made with rat tissues in the past, and the C-form of the adenosine deaminase has been found to be present. On the other hand, the large form of this enzyme was absent in these rat tissues which were examined. Thus, it has been concluded that the enzyme-form distribution in rat differs from that of human and bovine tissues since the latter two have both the C-form and the A-form present in them. In this study, the conversion factor isolated from human liver will be tested for its universality in transforming the small form of adenosine deaminase from other species into the large form of the enzyme. By so doing, we might be able to veryify any differences that might exist between the small form of the enzyme present in the different species.

The Hydrolysis of Bovine Glucagon by a Denaturant-stable Protease. BRENDA L. SCHUFFMAN and ERIC R. JOHNSON, Department of Chemistry, Ball State University, Muncie, Indiana 47306.——A denaturant-stable serine protease isolated from Pronase, a commercially available proteolytic enzyme mixture, catalyzes the hydrolysis of bovine glucagon in the presence of 6.0 *M* guanidinium chloride. With the use of this denaturant, an average of two peptide bonds per glucagon molecule were catalytically hydrolyzed by the stable protease. Utilizing dansylation techniques, one of the new N-terminal amino acids produced by protease action on glucagon has been identified as valine. Since bovine glucagon contains only one valine residue, the specificity of action of this stable protease in the presence of denaturant includes the Phe(22)-Val(23) peptide bond of bovine glucagon.

Dielectric and Electronic Polarizations of Substituted Metal-Acetylacetone Complexes. EUGENE SCHWARTZ, MARK BRADLEY, and TIMOTHY NEUFELD, Department of Chemistry, DePauw University, Greencastle, Indiana, 46135.——The total dielectric polarizations and the electronic polarizations of a number of substituted symmetrical metal-acetylacetone (2,4-pentanedione) complexes were measured in benzene at 25.0°C. A heterodyne beat method was used to measure the dielectric constants at 13 KHz for the total polarizations and a differential refractometer for the refractive indices for the electronic polarizations. Polarizations were calculated by the method of Halverstadt and Kumler. Metals used were aluminum, beryllium, chromium (III), and iron (III). The ligands used included those with hydrogen (chromium only), phenyl, and *t*-butyl groups substituted for methyl at the 2- and 4-positions and with phenyl, chlorine, and bromine substituted for hydrogen at the 3-position of the parent 2,4-pentanedionates. Electronic polarization changes caused by substitution were found not to depend on the nature of the central metal. In contrast, the corresponding changes in atomic polarization (the difference between the total and electronic polarization) upon substitution were found to depend on the metal. Substitution of phenyl for hydrogen at the 3-position produces a smaller increment of electronic polarization than does such substitution at the 2,4-positions. The opposite effect was found for the atomic polarizations upon such substitution. Electronic polarization increments upon substitution of chlorine and bromine for hydrogen at the 3-position indicate that these halogens in the complexes have the character of being bonded to an aromatic ring, especially, so for bromine.

The Isolation of a New Denaturant-stable Protease from a Commercial Protease Preparation, Pronase. WANDA J. WILLS and ERIC R. JOHNSON, Department of Chemistry, Ball State University, Muncie, Indiana 47306.——Pronase, a commercially available mixture of proteolytic enzymes, has been shown to contain two protease components that are stable and active in 6.0 *M* guanidinium chloride (W. M. Awad, Jr., *et al.* (1972) *Proc. Nat. Acad. Sci. (USA) 69* 2561-2565). During the purification of these two stable proteases from Pronase, a third component was isolated that survived incubation with the other two stable proteases for one week in 6.0 *M* guanidinium chloride. This newly isolated protease was found to possess esterase activity againt N-α-acetyl-L-tyrosine ethyl ester both in the absence and presence of 6.0 *M* guanidinium chloride, suggesting that this protease is also stable and active in the presence of denaturant. This new stable protease demonstrated chromatographic behavior on carboxymethylcellulose which was significantly different from that exhibited by previously isolated stable proteases. Polyacrylamide gel electrophoresis at pH 4.3 of the newly isolated stable protease resulted in a single band of substantially different electrophoretic mobility than the other stable Pronase components.