CHEMISTRY

Chair: Dennis G. Peters
Department of Chemistry
Indiana University, Bloomington, Indiana 47405 (812) 335-9671

Chair-Elect: Stanley L. Burden
Science Center
Taylor University, Upland, Indiana 46989 (317) 998-5127

ABSTRACTS

Regiospecific Addition of Organocuprate Reagents to α, β-Unsaturated Esters. M. Behforouz, J.L. Bolan and T.T. Curran, Department of Chemistry, Ball State University, Muncie, Indiana 47306.——A series of organocuprate complexes were made *in situ* by the reactions of Grignard reagents with cuprous thiophenoxides, and the reactions of these complexes with α, β-unsaturated esters were studied.

$$\underset{|\quad|}{R-C=C-CO_2Me} + \underset{MgX}{R'CuSAr} \rightarrow \underset{R'\quad H}{\overset{|\quad|}{R-C-C-CO_2Me}}$$

Ar = C_6H_5-, o $-MeOC_6H_4-$, R = Aryl and Alkyl, R′ = CH_3,I°, II° and III°.

Excellent yields of saturated esters were obtained when R was an aryl group. No detectable amounts of 1,2-adducts were obtained even with a hindered alkyl group. High yields of 1,4-addition products on methyl crotonate were also obtained for a number of Grignard reagents when cuprous 2-methoxythiophenoxide was used as the catalyst.

β-Carbolines and Their Tetrahydro Compounds Derived from the Amino Acid β-Methyltryptophan. M. Behforouz, M.E. Ogle and H. Zarrinmayeh, Department of Chemistry, Ball State University, Muncie, Indiana 47306.——In our research toward the total synthesis of antitumor and antibiotic agent, *Lavendamycin*, a number of β-carbolines and their tetrahydro derivatives were prepared. These compounds have been shown to possess a number of psychological and neurochemical activities. β-Methyltryptophan or its ester were condensed with aldehydes to give the corresponding tetrahydro-β-carboline acids or esters. Esterification of the acids gave the corresponding esters which upon aromatization afforded β-carbolines.

Computerized Electronic Weighing. Stanley L. Burden, A. Griffin, K. Hartmen, G. Passon, D. Baxter, A. Pedersen, T. Ferris, P. VanVleet, B. Zimmerman, P. Clark and R. Phillips, Department of Chemistry and Computer Science, Taylor University, Upland, Indiana 46989.——A Cahn electronic balance has been interfaced to an Apple II Plus microcomputer using an ADALAB card. Software has been written to permit a user, among other options, to make up a standard solution and then prepare a series of dilutions from it without using any volumetric glassware. Typically only plastic bottles, a beaker and medicine dropper or graduated cylinder is all that are required to make a series of standards suitable for calibrating spectrophotometers, ion selective electrodes, etc. The system eliminates the need for tedious pipettings or the use of microburets to accurately deliver small volumes of solution. The software also has provisions for calibrating pipets and doing statistics such as average, range,

standard deviation and confidence limits on series of replicate measurements. Both hardware and software will be discussed.

Effects of Alkali Metal Cation and Crown Ether Ring Size and Rigidity on Binding Constants and Carbon-13 NMR Chemical Shifts in Napthalene-containing Crown Ethers. CHRISTOPHER COLBURN, MARK R. JOHNSON, JOHN A. MOSBO AND LYNN R. SOUSA, Department of Chemistry, Ball State University, Muncie, Indiana 47306.——Carbon-13 NMR spectra from six naphthalene-containing crown ethers ranging from a 22-crown-6 to a 14-crown-4 have been obtained in the presence of varying concentrations of alkali metal ions (Na^+, K^+, Rb^+ and Cs^+). Through use of a non-linear least squares computer program, the carbon-13 chemical shift data provided equilibrium constants for each combination of crown ether and cation. The values were dependent upon the sizes of the crown ether and cation, and upon the conformational rigidity of the ether ring. The least squares fitting also provided crown-cation complex limiting chemical shifts for essentially all carbon atoms. These ranged from no change upon complexation to shift differences of 4.6 ppm. Although not all chemical shift assignments could be made to specific carbons of the ether ring, assignments were made for the naphthalene carbons. In many cases, the chemical shift changes upon complexation could be rationalized in terms of charge density changes and changes in ether ring conformations.

Corrosion of Some Copper Alloys and Metals in Thiosulfate and Tetrathionate Solutions. SHRIKRISHNA W. DHAWALE AND LINDA J. ALEXANDER, Department of Chemistry, Indiana University East, Richmond, Indiana 47374.——The corrosion of copper and some copper base alloys was investigated in thiosulfate solutions and tetrathionate solutions. The work has shown that the copper and the alloys used corrode quite rapidly in such solutions.

It was also observed that the metal copper or the copper base alloys destabilized the thiosulfate ions. The interaction of thiosulfate ions and the alloys was studied by the standard iodometric titrimetric procedures. It was found that there was faster change in the titer values in the presence of copper compared to that of copper alloys. It was also observed that the rate of change of titer values was much greater in the dilute thiosulfate solutions compared to the relatively concentrated ones. Some filtered solutions showed the presence of copper ions.

In the tetrathionate solutions, the formation of thiosulfate ions was investigated by iodometric titrations. Copper and some of its alloys showed no conversion of tetrathionate to thiosulfate ions. However, iron and nickel showed such conversion appreciably. Further experiments on this conversion are in progress in our laboratory.

Pilot Studies Directed Toward the Synthesis of Cucurbitanes-II Conversion of Hecogenine to 9,11-Dehydro-12-deoxyhecogenine. JEFFREY S. DUFFY AND BEN NASSIM, Department of Chemistry, Indiana University Southeast, New Albany, Indiana 47150.——A hecogenine derivative having the requisite functionalities to be utilized as a key intermediate in studies relating to Cucurbitane analogs has been synthesized.

Hecogenine was dibrominated at the 11 and 23 positions in chloroform using bromine and catalytic amount of borontriflouride etherate. This dibrominated product was dehydrobrominated at the 11-position in hot collidine. The 23-position was debrominated by treatment with zinc powder in refluxing ethanol. Then the 12-keto functional group was reduced by ketalization with 1,2-ethanedithiol followed by desulfurization with raney nickel to afford the desired product 9,11-dehydro-12-deoxyhecogenine. The synthesis along with spectral properties of the products will be discussed.

Pilot Studies Directed Toward the Synthesis of Cucurbitanes-I Generation of a Diosphenol System in the A-ring of Hecogenine. DEKE T. GUNDERSEN AND BEN NASSIM, Department of Chemistry, Indiana University Southeast, New Albany, Indiana, 47150.——Two methods for generation of an α -diketone (diosphenol) system in the A-ring of steroids were examined. One procedure involved the use of $CuCl_2$/HOAc in aqueous media and the other, molecular oxygen under basic condition. The latter process resulted in a cleaner product and higher yield and was selected as the method of choice. Thus, hecogenine was transformed into a 2,3-diketo (diosphenol) derivative with an approximate over all yield of 55%. This transformation included an initial oxidation of the 3-hydroxy group of the hecogenine using Sarett reagent (CrO_3/Pyridine) followed by treatment of a *tert*-butanol solution of the resulting 3-oxo product with potassium *t*-butoxide and oxygen gas. The Δ 1,2-2-acetoxy-3-keto derivative was obtained by the acetylation of the diosphenolic product with acetic anhydride and pyridine.

Palladium Catalyzed β-Arylation of Methyl Vinyl Ketone with Thallated Aromatics. RICHARD A. KJONAAS, Department of Chemistry, Indiana State University, Terre Haute, Indiana 47809.——It is well known that the reaction of aryl halides with olefins in the presence of a palladium catalyst to give arylated olefins (the Heck Reaction) is useless when the olefin is a vinyl ketone. This is due to polymerization and other side reactions of the vinyl ketones under the harsh reaction conditions required. A variation of the Heck Reaction involving milder conditions and the use of arylthallium compounds instead of aryl halides has been reported for a variety of olefins. A thorough search of the literature, however, showed that the only known example of this reaction in which the olefin is a vinyl ketone involves heating at 120°C in dimethylformamide (a very inconvenient solvent). We have investigated the reaction at ISU using a variety of solvents, reaction conditions, and thallated aromatics. The reaction can be carried out at room temperature in ether or tetrahydrofuran to give good yields of benzalacetone derivatives.

Vibrational Predissociation of Linear Hydrogen Bonded Complexes. SHANNON G. LIEB, Department of Chemistry, Butler University, Indianapolis, Indiana 46208, and J.W. BEVAN, Department of Chemistry, Texas A&M University, College Station, Texas 77840.——This investigation involves a preliminary study of the application of semiclassical collision theory to the determination of predissociative lifetimes of hydrogen-bonded complexes. Linebroadening found in the rovibration spectra of the linear hydrogen-bonded complexes HCN···HF, HCN···HCN and OC···HF has previously been attributed to the lifetime of the vibrationally excited complex. The energy of vibrational excitation H – X in the model complex A – B···H – X is in large excess of the hydrogen bond dissociation energy. The lifetime of the complex is thereby attributed to energy migration to the hydrogen bond and disposition of the remaining energy into vibrational, rotational and translational channels of the dissociated fragments. Several attempts at elucidation of the mechanism for *linear* complexes have not produced lifetimes consistant with the linewidths of the rovibrational spectra of these complexes. The model proposed here is that a large portion of the H – X vibrational energy (in excess of the hydrogen bond dissociation energy) goes into the A – B fundamental stretch leaving only a small portion of energy for rotational and translational energy of the fragments. The mechanism proposed is dominated by a vibration-to-vibration energy transfer and assumes that this energy transfer can be calculated via semiclassical collision theory. A summary of the results is shown on the following table:

Complex	Calculated Lifetimes		Experimental Lifetimes
	(a)	(b)	
HCN···HF	4.7×10^{-9}	1.8×10^{-9}	$1.7(5)\times10^{-10}$

HCN···HCN	1.3×10^{-9}	6.0×10^{-9}	$1.9(4) \times 10^{-9}$
OC···HF	2.2×10^{-6}	1.9×10^{-9}	$8(5) \times 10^{-10}$

(a) based on treatment due to H.K. Shin, *J. Chem. Phys.* 60, 1064 (1974).
(b) based on treatment due to L. Sentman, *Chem. Phys. Lett.* 18, 493 (1973).

The Syntheses of Functionalized Aza Crown Ethers. ROBERT J. MORRIS, MARK M. MCDONALD, JOHN A. MOSBO AND BRUCE N. STORHOFF, Department of Chemistry, Ball State University, Muncie, Indiana 47306.——An aza 17-crown-5 has been prepared from the reaction of $HN(CH_2CH_2OCH_2CH_2OH)_2$ with o $-C_6H_4(CH_2Br)_2$. The purification and subsequent identification of this new compound was accomplished by alumina column chromatography and spectroscopic measurements. Two additional crown ethers were synthesized from this aza compound. The N-allyl species has been obtained by reacting to the aza crown with allyl bromide in refluxing acetonitrile which contained sodium carbonate. A phosphine was obtained from the reaction of the crown with diphenylphosphine and aqueous formaldehyde in benzene. These compounds have also been characterized spectroscopically.

A Quest for Flashy Crowns: Crown Ethers with Cation-enhanced Fluorescence. LYNN R. SOUSA, BETH E. BEESON, BYUNGKI SON, STASIA A. BARNELL AND THOMAS E. MABRY, Department of Chemistry, Ball State University, Muncie, Indiana 47306.——Several crown ether compounds containing both a fluorescent chromophore and a fluorescence quencher have been synthesized. These compounds have been designed to signal the presence of alkali and/or alkaline earth cations by an increase in fluorescence intensity. The synthesis of this new type of crown ether will be discussed, and the response of the fluorescence spectra of several chromophore-bearing crown ethers to cations will be described. Cation enhancements of fluorescence of 300 percent or more have been observed for several simple crown ether compounds.

The Construction of Space-filling Models from Crystallographic Data. ALAN SPOTT* AND J.C. HUFFMAN, Molecular Structure Center, Department of Chemistry, Indiana University, Bloomington, Indiana 47405.——A specialized drill has been constructed to allow the construction of space-filling molecular models. Seamless methacrylate (or similar material) spheres of various diameters and colors are precisely drilled and cut to yield a molecular model in which the diameters of the intersecting spheres are proportional to the van der Waals radii of the corresponding element. A computer program (FORTRAN77) calculates the angles and the required depth of cut for each intersection. After the balls are drilled using a molecular model drill, a specialized milling machine cuts the faces to the proper depth.

The program, which runs on an IBM personal computer, and the specialized drills used to construct the models will be described, and the resulting models compared with those constructed using CPK models and those drawn by computer.

* *Participant, 1985 Indiana University High School Science Student Institute.*

Equilibria and Spectra of Iodo Complexes of Copper (I) in Aqueous Solution. KENNETH L. STEVENSON, JANET L. BRAUN, REBECCA A. SPARKS AND MELINDA A. STEVENSON, Department of Chemistry, Indiana University-Purdue University at Fort Wayne, Fort Wayne, Indiana 46809.——Copper(I) iodide dissolves in aqueous solutions of sodium iodide, forming several complexes as shown by the reaction scheme:

$$CuI(s) + 2I^- = CuI_2^-$$
$$CuI_2^- + I^- = CuI_3^{2-}$$
$$CuI_3^{2-} + I^- = CuI_4^{3-}$$

$$2CuI_3^{2-} = Cu_2I_6^{4-}.$$

A method has been developed for determining the ultraviolet spectra of several of these individual species by analyzing the spectra of equilibrated solutions at a variety of iodide and copper concentrations. The results of this analysis indicate that iodo complexes of copper(I) exhibit some striking similarities and some interesting differences from the spectra of bromo and chloro complexes of copper (I). Some of these properties will be explained in terms of charge-transfer-to-solvent transitions and hard and soft acid-base theory.

15-Crown-5 Systems with Sidearms Containing Additional Funtionalities. KIMBERLY K. STROUSE, NEIL ANTHONY, JOHN M. BRUMFIELD, LEROY A. KROLL, JOHN A. MOSBO AND BRUCE N. STORHOFF, Department of Chemistry, Ball State University, Muncie, Indiana 47306 and Taylor University, Upland, Indiana 46989.——The reaction of 15-crown-5-$CH_2OCH_2CH=CH_2$ with 9-borabicyclo-[3.3.1]nonane (9 – BBN) followed by oxidation and hydrolysis provided the primary alcohol, 15-crown-5-$CH_2OCH_2CH_2CH_2OH$. The tosyl derivative of the latter provided the nitrile upon reaction with sodium cyanide. Although coordinating solvents such as DMSO are usually used for these types of reactions, this reaction proceeded clearly, smoothly, and in high yield in benzene at room temperature. Presumably, the crown ether promotes this facile reaction by serving as an efficient phase-transfer agent. A phosphine derivative has also been synthesized by reacting the tosylate with lithium diphenylphosphide. Spectroscopic data from the primary alcohol and derivatives were compared to those from the corresponding secondary alcohol products.

Variable Temperature NMR Studies of the Association of Aliphatic Alcohols in Dilute Carbon Tetrachloride Solutions. BERT THOMAS AND JOE KIRSCH, Department of Chemistry, Butler University, Indianapolis, Indiana 46208.——Temperature dependent nmr spectroscopy is used to study the hydrogen bonding in a series of aliphatic alcohols with differing steric hindrance at the hydroxyl site. The Saunders and Hyne method was used to determine both the extent of the polymerization (n – mer) and the values of the equilibrium constants for the association process as a function of temperature. The enthalpy and entropy changes for the association process are calculated from the temperature dependent equilibrium constants. The extent of polymerization and the values of enthalpy and entropy changes are related to the steric hindrance at the hydroxyl site for the series of alcohols.

The Effects of Retinoids on Phospholipid Model Membrane Phase Behavior. STEPHEN R. WASSALL, WILLIAM STILLWELL AND MARTEL ZELDIN, Departments of Physics, Biology and Chemistry, Indiana University-Purdue University at Indianapolis, Indianapolis, Indiana 46223.——Retinoids (vitamin A and derivatives) are lipid soluble and are known to modify cell membrane properties, e.g. increase permeability. We are employing DSC (differential scanning calorimetry) to investigate the effects of retinol (vitamin A), retinoic acid (vitamin A acid) and retinal (vitamin A aldehyde) on the phase behavior of DPPC (dipalmitoylphosphatidylcholine) model membranes. All three retinoids eliminate the pretransition at <5 mol% incorporation, and the main gel-liquid crystalline transition is broadened and its onset temperature lowered with increasing retinoid concentration. The results are compared with the effects produced by introduction of other lipid soluble membrane components. Comparison with the influence of α-tocopherol (vitamin E) and fatty acids, in particular, is made.