CHEMISTRY

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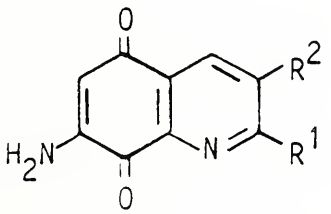
ABSTRACTS

Synthesis of 2-Amino-2-methyl and 2-Amino-3-methylquinoline-5,8-diones (1 and 2). Macklin B. Arnold, Mark A. Horn and Mohammad Behforouz, Department of Chemistry, Ball State University, Muncie, Indiana 47306.——As part of our research toward the total synthesis of antibiotic antitumor agent lavendamycin methyl ester, we prepared aminoquinones 1 and 2. 1 was prepared from 8-hydroxy-2-methylquinoline through a series of transformations. 2 was prepared by the Diels-Alder condensation of 2-acetamido-6-bromo-quinone with 1-(dimethylamino)-1-aza-1,3-diene followed by base hydrolysis.

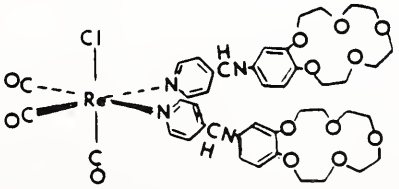


1; $R^1 = CH_3$, $R^2 = H$

2; $R^1 = H$, $R^2 = CH_3$

Rhenium(I) Complexes of Pyridine-functionalized Benzo-15-Crown-5. John D. Bain, P. Elaine Parsons and Bruce N. Storhoff, Department of Chemistry, Ball State University, Muncie, Indiana 47306.——A new ligand with three types of metal binding sites has been synthesized by condensing 4-pyridinecarboxaldehyde with NH_2-derivatized benzo-15-crown-5 (NH_2 group meta and para to the catechol-type oxygens). A Re(I) derivative was obtained by reacting this functionalized crown ether with $Re(CO)_3(CH_3CN)_2Cl$ in a 2:1 ratio. Spectroscopic data (^1H and ^{13}C NMR, IR) indicate that this ligand is bound to the cis positions on rhenium (see I) *via* the less-hindered pyridine nitrogens, thereby providing a bis crown with two additional imine-nitrogen and crown ether sites available to bind other metals.

I



Infrared Studies of Charge-transfer Complexes of Metalloporphyrins and Biologically Active Quinones. James W. Brown and J.L. Kirsch, Butler University, Indianapolis, Indiana 46208.——Charge-transfer complexes are formed between various metalloporphyrins and biologically active quinones, namely Vitamin K and 2,6 Dimethylbenzo-

quinone, a plastoquinone isomer. These quinones have a characteristic carbonyl stretching frequency in the infrared region around 1650-1700 cm^{-1}. Electronic charge is transferred from the large, conjugated porphyrin ring to the quinone. If the quinone acts as an acceptor of electronic charge then this charge is donated to the antibonding orbitals of the carbonyl bond. This donation lowers the bond order of the carbonyl bond and shifts the stretching frequency to a lower wavenumber. Such shifts were observed using FT-IR spectroscopy with the sample in a KBr matrix. The relative shifts were used to determine the relative strengths of the complexes.

The Sometime Peripatetic Carbonyl Function. MARVIN CARMACK, Department of Chemistry, Indiana University, Bloomington, Indiana 47405; MOHAMMAD BEHFOROUZ, Department of Chemistry, Ball State University, Muncie, Indiana 47306; GLENN A. BERCHTOLD, Department of Chemistry, M.I.T., Cambridge, Massachusetts; SAMUEL M. BERKOWITZ, Arizona Chemical, Bay Point, Florida 32407; RALPH P. BARONE, New Jersey; DONALD WIESLER, Department of Chemistry, Indiana University, Bloomington, Indiana 47405.——The action of elemental sulfur (S_8) in hot secondary amine (*e.g.*, morpholine) can cause the stepwise migration of the ketone or aldehyde function along a chain of methylene groups, or around a ring of mostly methylene groups. Thus, under surprisingly mild conditions, 4-heptanone generates a mixture of 4-, 3-, 2-heptanones and heptanal. The active sulfur-nitrogen catalyst is a dithio-*bis*-sulfenamide, and the reactive intermediates from the carbonyl groups are enamines. We discuss a proposal that the central highly reactive intermediates in these complex oxidation-reduction reactions may be thiirenium and/or thiiranium sulfilamines.

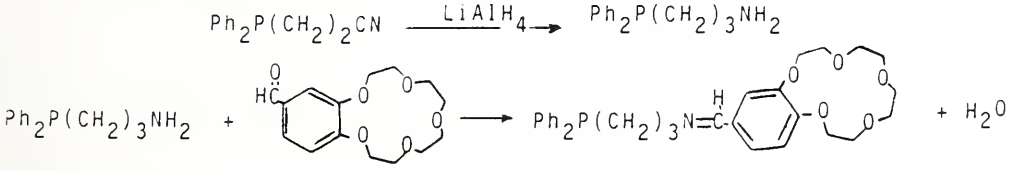
The Reductive Isomerization of αBromoketones. MARVIN CARMACK, Department of Chemistry, Indiana University, Bloomington, Indiana 47405; and JOHN M. CHIGAS, Amoco Oil Research Laboratory, Naperville, Illinois.——Some years ago, R. L. Clarke reported (J. Org. Chem., 1963, 28, 2626) that α-bromoketones, when heated with a thiol (*e.g.*, 1-propane-thiol) and HBr in chloroform, generate a mixture of isomeric enethio ethers, which, upon hydrolysis, yield a mixture of the original ketone without the bromo group and its isomeric ketone with the carbonyl in the position of the original bromo function. We report on studies of this mechanism, which embodies proposed reactive intermediates as S-halothiiranium derivatives. There is a certain parallelism of this acid-catalyzed reaction and the base-catalyzed isomerization discussed in the preceding paper.

Corrosion Potentials of Some Metals and Alloys in the Presence of Sulfur Oxyanions. SHRIKRISHNA W. DHAWALE, Indiana University East, Richmond, Indiana 47374.——Metals and alloys undergo corrosion in sulfur environment. In the present investigation I have studied open circuit potentials of few metals and alloys in the presence of thiosulfate and tetrathionate ions. The open circuit potentials are measured against saturated calomel reference electrode. The potential of corroding surface in an electrolyte measured under open circuit conditions are also known as corrosion potentials. Few studies on the effect of concentration and pH of electrolyte on corrosion potentials are reported here. Under fixed temperature corrosion potential of a metal or an alloy varies with time in a given electrolyte. In some cases it varies in cycles of more anodic and less anodic values with respect to reference electrode. This variation is explained using the passivity model. When passive film is formed there is no contact of metal and its environment. The potential becomes less anodic. Breaking of passive films exposes the metal to the surrounding electrolyte and therefore the potential becomes more anodic making the metal mroe susceptible to dissolution or corrosion. These investigations are helpful in mechanistic studies of corrosion.

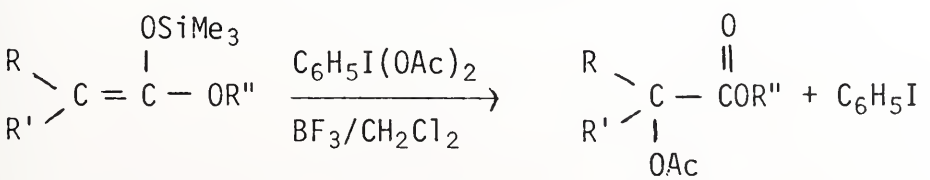
An Easy Way to Draw Enantiomers. HOWARD E. DUNN, University of Southern Indiana, Evansville, Indiana 47712.——An observation of mine is that most people have a great deal of difficulty drawing mirror image isomers of chiral molecules, particularly of the more complex bicyclic systems. I have discovered that most if not all individuals have an unrecognized innate ability to draw mirror image isomers (enantiomers). When one claps his hands or imitates a director of an orchestra his hands and arms move in a synchronous mirror image fashion. By placing a piece of chalk in both hands it is a simple matter to use this natural phenomenon to simultaneously produce mirror image drawings of complex molecules on a chalk board.

Molecular Mechanics (MM2) Calculations and Cone Angles of Phosphine Ligands. GREG L. DURST, MIAN CHIN, PAUL L. BOCK AND JOHN A. MOSBO, Departments of Chemistry, Ball State University, Muncie, Indiana 47306 and James Madison University, Harrisonburg, Virginia 22807.——Molecular mechanics (MM2) calculations were performed on all 54 potentially low energy conformations of 16 phosphines (Ph_3; $PH_{3-n}R_n$ where n = 1 to 3 and R = Me and Et, n = 1 or 2 and R = i-Pr, and n = 1 and R = t-Bu; PMe_2Ph; and $PRPh_2$ where R = Me, Et, i-Pr, t-Bu, and Ph). The results are compared to those previously obtained from MINDO/3 and MNDO calculations, and to experimental data. Single conformer cone angles and weighted average cone angles were calculated from MM2 optimized geometries employing Tolman's general definition, and are compared to Tolman's values, MINDO/3 results and experimental data. The weighted average cone angles are suggested as the best single representation of phosphine ligand sizes.

The Preparation and Study of Phosphine-functinalized Benzo-15-Crown-5. VIDA FARAZI AND BRUCE N. STORHOFF, Department of Chemistry, Ball State University, Muncie, Indiana 47306.——The reaction sequence summarized below has been used to obtain a phosphine derivative of benzo-15-crown-5. The reaction of I with $(PhCN)_2PdCl_2$ provides several complexes as evinced by spectroscopic data. In particular, ^{31}P NMR data are consistent with the formation of both *cis* and *trans* $(I)_2PdCl_2$ in which I is bonded to Pd via the P(III) centers. Spectroscopic evidence also suggests that I can chelate to Pd through the P(III) and imine-nitrogen lone pairs and yield a complex of the stoichiometry $IPdCl_2$.



Hypervalent Idone Oxidation: α-Acetoxylation of Esters Using Iodobenzenediacetate. JEFF M. GARGAS, ATILLA TUNCAY AND ROBERT M. MORIARTY, Department of Chemistry, Indiana University Northwest, Gary, Indiana 46408 and University of Illinois at Chicago, Chicago, Illinois 60607.——Silyl enol ethers react with $C_6H_5I(OAc)_2$ in the presence of a Lewis acid catalyst to yield α-acetoxyesters in good yields with reversal of polarity at α-position. The mechanism of α-functionalization will also be discussed.



R = alkyl or aryl R' = CH_3 or H R" = CH_3 or C_2H_5

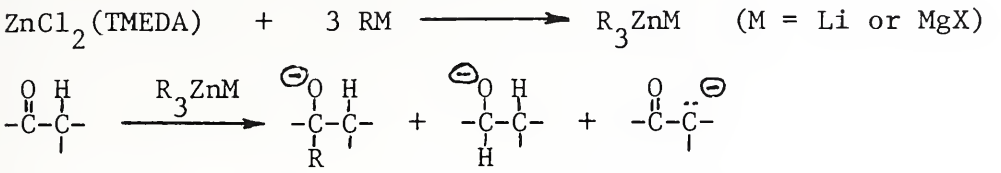
Effect of Temperature on Protein Titration Curves: Theory and Experiment. G.I.H. Hanania and R. F. Sultan, Departments of Chemistry, American University of Beirut, Lebanon, and Indiana University, Bloomington, Indiana 47405.——We have extended application of the discrete-charge model of intramolecular electrostatic interaction in globular proteins to enable computation and interpretation of H^+ titration curves at different temperatures. For this purpose, ferrimyoglobin was titrated with acid and with base, over the range of protein stability, pH 4.0 to 11.0, at four temperatures between 10° and 50°C, and a constant protein concentration and zero salt ionic strength. The experimental results were then compared with theoretical calculations, the latter involving the computation of acid-dissociation constant and effective charge for each of the 60 ionizing groups on the protein; as well as the net protein charge, as a function of pH, ionic strength and temperature. There was good agreement between the calculated and the experimentally determined titration curves, even at 50°C. It may be concluded that any thermally induced perturbations in conformation, or changes in heat capacity of the native protein structure that may occur, will probably have compensating effects, such that the observed net pH and temperature variations are adequately accounted for in thermodynamic terms.

NMR Studies of 2-Hydroxy-2,5-diphenyl-3,4-dichlorofuran in $CDCl_3$. Marie G. Hankins, Warren Hankins, Jeff Klingler and Diana Julian, University of Southern Indiana, Evansville, Indiana 47712.——In 1964, P. S. Anderson reported the NMR spectrum of 2-Hydroxy-2,5-diphenyl-3,4-dichlorofuran in $CDCl_3$. She indicated the appearance of two one-proton singlets for the 5-benzylic and 2-hydroxyl protons, each of which, separated into two peaks on addition of DMSO-D_6. Subsequent studies using solvent effects contradicted Ms. Anderson's original assignment of peaks to the isomers of this compound. Continuing studies on higher resolution instruments indicate that addition of DMSO-D_6 is not necessary to separate the peaks. In fact, an NMR spectrum of the compound run with a 200 MHz Fourier Transform NMR shows two peaks for each of the protons and the C-13 spectrum indicates two peaks for one of the carbons. Two isomers must be present in the original $CDCl_3$ solution.

Evidence for the Enzyme System Responsible for L-Ascorbic Acid Entrapment in Human Erythrocytes. John Henley and Eugene S. Wagner, Center For Medical Education, Ball State Universsity, Muncie, Indiana 47306.——Radioactive labelled ascorbic and dehydroascorbic acids when incubated with human blood migrate irreversibly into red blood cells. Isolation and characterization of the moieties trapped within the cells via IR established both their identities as L-ascorbic acid. Evidence in the form of the degree of *in vitro* entrapment of ascorbic acid as a function of times of incubation and the effect of incubation temperature, an anion recognition site inhibitor, N-ethylmaleimide, on the rate of entrapment will be presented to support the following hypothesis. Ascorbic acid is oxidized on or near the surface of the red blood cell to dehydroascorbic acid which migrates through the lipid portion of the cell wall and is reduced back to ascorbic acid within cell by an enzyme complex such as glutathione reductase. The resulting L-ascorbic acid can not pass through the cell wall and is therefore entrapped.

The Reaction of Triorganozincate Reagants with Carbonyl Compounds: Addition versus Reduction and Enolization. Richard A. Kjonaas and Kimberly K. Clingerman, Department of Chemistry, Indiana State University, Terre Haute, Indiana 47809.——A variety of carbonyl compounds treated with triorganozincate reagents in an attempt to compare these reagents with other carbanion type organometallic reagents in their ability to transfer an R group without giving the usual side reactions—deprotonation and transfer of an

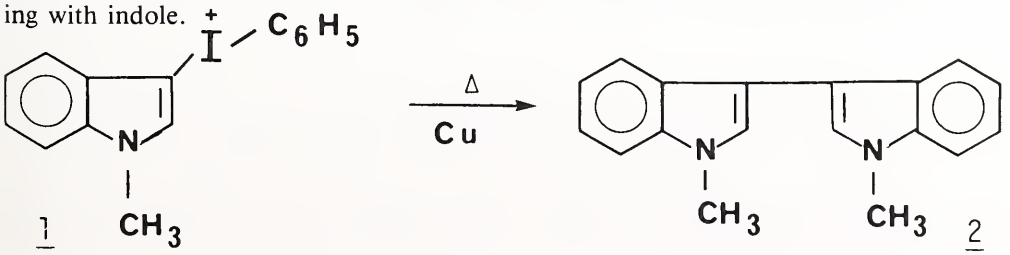
electron followed by a hydrogen atom. The zincate reagents appear to surpass Grignard reagents in their ability to resist these two alternative reaction paths.



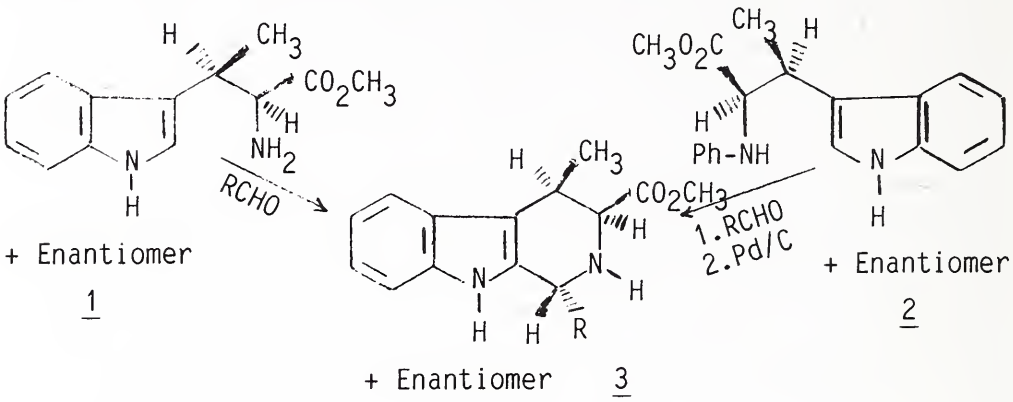
Total Synthesis of a 6-Methyl-A-seco-A,19-dinorsteriod, MIKE MUNCHHOF AND BEN NASSIM, Department of Chemistry, Indiana University Southeast, New Albany, Indiana 47150.——"Dinordrin" a previously synthesized A,19-dinor steroid has shown strong contraceptive properties. In other studies, it has been found that, in general, addition of a methyl group to the 6-position of steroid skeletones increases their antifertility properties. Thus, a total synthesis of a 6-Methyldinordrin analog was undertaken. Optically active (7aS)-Methyl-4-(phenylsulfonylmethyl) perhydroindan-1,5-dione was treated with methyl-3,6-dioxoheptanote-6-ethyleneketal under basic condition to produce a substitution product which after saponification, decarboxylation and cyclization yielded 4-nor-3,5-secoester-9-ene-2,5, 17-Trione 2-ethyleneketal. The 17-ketone was then selectively ketalized and the product was methylated at the 6-position using LDA followed by methyl iodide. The ketals were removed under an acidic condition and the resulting A-seco product is to be annulated to produce the steroid skeletone.

The Effect of Guanidinium Chloride on the Extent of Glutamoyl Peptide Bond Cleavage by *Staphylococcus aureus* Protease V8. MICHAEL D. OBER AND ERIC R. JOHNSON, Department of Chemistry, Ball State University, Muncie, Indiana 47306.——The effect of guanidinium chloride, a common protein denaturant, on the proteolytic activity of *Staphylococcus aureus* Protease V8 (SPV8) was examined. The cleavage extent of glutamoyl peptide bonds by SPV8 was found to decrease with increasing guanidinium chloride concentrations. At 5.0 *M* guanidinium chloride and 37 °C, over 80% of this activity was lost, presumably due to denaturation of the protease. However, a small amount of proteolytic activity persisted at guanidinium chloride concentrations up to 6.0 *M*. SPV8 also appears to be less sensitive to guanidinium chloride denaturation at temperatures below 37 °C. Thus SPV8 appears to retain some proteolytic activity under denaturing conditions, albeit at substantially reduced levels at temperatures above 25 °C. This paper was supported by the Graduate Student Research Fund and the Faculty Research Program of Ball State University.

Synthesis of 3,3'-Biindolyls Using Mixed Iodonium Salts. JULIUS PAWLOWSKI, ATILLA TUNCAY AND ROBERT M. MORIARTY, Departments of Chemistry, Indiana University Northwest, Gary, Indiana 46408 and University of Illinois at Chicago, Chicago, Illinois 60607.——Biindoles have been isolated very recently from marine organisms. Very few synthetic routes to these compounds are available in the literature. We report here the synthesis of N,N'-dimethyl-3,3'-biindolyl 2 using hypervalent iodine methodology starting with indole.



Tetrahydro-β-carbolines Derived from β-Methyltryptophan. David A. Rusk and Mohammad Behforouz, Department of Chemistry, Ball State University, Muncie, Indiana 47306.——1,2,3,4,-Tetrahydro-β-Carbolines of type 3 were prepared by either condensation of the amino acid 1 or its benzyl derivative 2 with aldehydes.



Magnetic Susceptibilities of Acetylacetone and Dipivaloyl-methane Complexes. Briand T. Sanderson and Eugene P. Schwartz, Department of Chemistry, DePauw University, Greencastle, Indiana 46135.——A Johnson Matthey magnetic susceptibility balance constructed on the Evans principle was used to measure the magnetic susceptibilities of solid neutral acetylacetonate complexes of the elements scandium through gallium (excluding titanium) and of the dipivaloylmethanato complexes of vanadium through zinc (excluding titanium). The susceptibilities of certain other second and third row transition elements also were determined. Ring contributions were estimated from the corresponding beryllium and aluminum complexes. The magnetic susceptibility of an ion was found not to depend on the nature of the complex within experimental uncertainty. Mn(III) and Fe(III) complexes were high spin, whereas Ru(III) was low spin. Co(III) was low spin with a high ion magnetic contribution. This ion contribution decreased from Co(III) to Ir(III) and from Co(II) to Zn(II).

Unusual Dielectric Behavior of *bis*-dipivaloylmethanato Complexes of Nickel, Copper and Zinc. Eugene P. Schwartz, Department of Chemistry, DePauw University, Greencastle, Indiana 46135.——Benzene solutions of *bis*-dipivaloylmethanato complexes of copper, nickel, and zinc exhibit non-linear dielectric behavior. Atomic polarizations of the copper and zinc complexes (planar and tetrahedral, respectively) undergo at low concentration a marked decrease with increasing concentration. In contrast, the atomic polarization of the planar nickel complex remains almost constant despite the change in dielectric slope which occurs at high concentrations.

4-Hydroxynonynal in Batten's Disease. A. Sideeq and A.N. Siakotos, Indiana University School of Medicine, Department of Pathology, Indianapolis, Indiana 46223.

A Study of the Adenosine Deaminase Conversion Factor in Pathological Human Blood Serum. Rebecca Smith and Pang F. Ma, Center for Medical Education, Ball State University, Muncie, Indiana 47306.——Previous studies have shown that advanced mammals, including man, exhibit both the large and small molecular forms of the purine catabolic enzyme adenosine deaminase. Through gel filtration column chromotography, an estimation of molecular weights was determined as 200,000 for the large enzyme form and 35,000 for the small enzyme form which can be reversibly converted into the large form when in the presence of a conversion factor. This conversion factor is composed

of a high molecular weight glycoprotein that is aggregated during the conversion process. Previous studies have also shown a tissue specific distribution of the two molecular forms, which would suggest that the conversion factor would be present in higher levels within those tissues where the large form predominates. Knowing that the enzyme follows specific distribution patterns for its two forms, an attempt is made to study the conversion factor levels under various pathological conditions in human blood serum using established gel filtration procedures and simple enzyme assay.