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# Vibrational Predissociation in Linear Hydrogen-Bonded Complexes

Shannon Lieb

Butler University, [slieb@butler.edu](mailto:slieb@butler.edu)

J. W. Bevan

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**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  $\alpha$ -diketone (diosphenol) system in the A-ring of steroids were examined. One procedure involved the use of  $\text{CuCl}_2/\text{HOAc}$  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 ( $\text{CrO}_3/\text{Pyridine}$ ) followed by treatment of a *tert*-butanol solution of the resulting 3-oxo product with potassium *t*-butoxide and oxygen gas. The  $\Delta$  1,2-acetoxy-3-keto derivative was obtained by the acetylation of the diosphenolic product with acetic anhydride and pyridine.

**Palladium Catalyzed  $\beta$ -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  $\text{HCN}\cdots\text{HF}$ ,  $\text{HCN}\cdots\text{HCN}$  and  $\text{OC}\cdots\text{HF}$  has previously been attributed to the lifetime of the vibrationally excited complex. The energy of vibrational excitation  $\text{H}-\text{X}$  in the model complex  $\text{A}-\text{B}\cdots\text{H}-\text{X}$  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 consistent with the linewidths of the rovibrational spectra of these complexes. The model proposed here is that a large portion of the  $\text{H}-\text{X}$  vibrational energy (in excess of the hydrogen bond dissociation energy) goes into the  $\text{A}-\text{B}$  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)	
$\text{HCN}\cdots\text{HF}$	$4.7 \times 10^{-11}$	$1.8 \times 10^{-11}$	$1.7(5) \times 10^{-10}$

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

(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  $\text{HN}(\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH})_2$  with  $\text{O} - \text{C}_6\text{H}_4(\text{CH}_2\text{Br})_2$ . 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:

