

CHEMISTRY

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ABSTRACTS

A Quantum Chemical Study of the Formation of Formaldimine from HCN Via a Radical Mechanism. JOHN A. RICKETTS, Department of Chemistry, DePauw University, Greencastle, Indiana 46135, and NOEL J. FITZPATRICK, Department of Chemistry, University College Dublin, Belfield, Dublin, 4, Ireland.—Geometry optimized ab initio LCAO-SCF-MO calculations using a minimal STO-3G basis set are discussed for the reaction involving HCN and a hydrogen atom. Of the three isomeric species, cis HCNH, trans HCNH, and H_2CN , the calculations predict that the H_2CN radical is thermodynamically preferred. Consequently, H_2CN can serve as a possible precursor of formaldimine, H_2CNH in a prebiotic atmosphere. In addition pertinent kinetic comparisons of the reaction of HCN with a hydrogen atom to form either trans HCNH or H_2CN are made using a simulated reaction pathway.

Reaction of Phenyl Isocyanate with Active Methylene Compounds. LEROY A. MCGREW, Department of Chemistry, Ball State University, Muncie, Indiana 47306.—Phenyl isocyanate undergoes addition of active methylene compounds such as ethyl acetoacetate and 2,4-pentanedione under mild conditions in the presence of a small amount of a tertiary amine. Addition occurs across the nitrogen-carbon double bond of the isocyanate such that the products are 2-(phenylcarbonyl) derivatives of the active methylene compounds. Seven such monoadducts have been prepared, but all attempts to produce diadducts by addition of the remaining acidic hydrogen to a second molecule of isocyanate have failed. Spectral studies suggest that those monoadducts containing at least one acetyl group prefer to be completely enolized with the formation of two intramolecular hydrogen bonds. Methods of preparation, structures and spectra of the monoadducts were discussed.

The Separation and Identification of the Two Forms of Human Adenosine Deaminase. GARY L. DUNNINGTON and PANG F. MA, Department of Chemistry, Ball State University, Muncie, Indiana 47306.—Two different forms of adenosine deaminase have been observed in human tissues: the high molecular weight enzyme (A form) and the low molecular weight enzyme (C form). These two forms of the enzyme are present in various proportions in different tissues. The separation and identification of the two enzyme forms in previous studies were achieved by gel filtration column chromatography, followed by measurements of enzyme activity in the elution fractions. A rapid and efficient method is needed to perform routine analysis of the enzyme form dis-

tribution and to study the inter-relationship of the two enzyme forms. This study shows the applicability of thin-layer gel filtration technique for the separation and identification of the two forms of adenosine deaminase in human tissue extracts.

Syntheses of β -diamines and β -amino alcohols. MARILYN GEHLHAUSEN and J. A. MOSBO, Department of Chemistry, Ball State University, Muncie, Indiana 47306.—New synthetic routes to the preparations of β -diamines and β -amino alcohols have been realized. Excess methylamine combined with an α,β -unsaturated ketone or aldehyde followed by reductive amination employing NaBH_3CN gave β -diamines in up to 40% yield. Thus, from crotonaldehyde N^1,N^3 -dimethyl-1,3-butanediamine was obtained. Similarly, methylamine combined with an α,β -unsaturated ketone or aldehyde followed by reduction with NaBH_4 resulted in the preparation of β -amino alcohols. This reaction with crotonaldehyde produced 3-methylamino-1-butanol. The likelihood of the reaction sequence consisting of initial addition of amine across the double bond followed by reduction of the carbonyl group was investigated.

Determination of the Concentrations of Selected Substances in the Waters of Otter Creek and the Wabash River, Vigo County, Indiana. JOSEPH R. SIEFKER and LARRY D. BROWN, Department of Chemistry, Indiana State University, Terre Haute, Indiana 47809.—The surface waters of Otter Creek and the Wabash River were sampled February-May 1974. The pH of each sample was measured. The concentrations of ammonia, hydrazine, surfactants; and fluoride, chloride, phosphate, nitrate, nitrite, aluminum, copper, iron, manganese, and nickel ions were determined. Maximum, minimum, and average concentrations were calculated.

The Irreversible Binding of Benzylpenicillin to Human Erythrocytes. MADONNA L. TALBERT and EUGENE S. WAGNER, Department of Chemistry, Ball State University, Muncie, Indiana 47306.—Recent studies using a Beckman LS-100C liquid scintillation system have shown that the *in vitro* 9-hour incubation of benzylpenicillin- C^{14} with human blood followed by exhaustive dialysis results in 4.5% irreversible binding of the antibiotic to components of the blood. This finding prompted experiments which measured the relative irreversible binding of benzylpenicillin- C^{14} to the plasma and erythrocyte portions of blood. The distribution of covalently bonded benzylpenicillin- C^{14} was 1.9% (plasma) and 2.6% (erythrocytes). Further studies indicated that of the benzylpenicillin- C^{14} bound to erythrocytes, one half is bound to the cell membrane and one half is bound to the hemoglobin within the erythrocyte. The effect of the covalent bonding of this antibiotic to hemoglobin on the oxygen carrying capacity of hemoglobin has been investigated.

Using Time-Shared Computer Drill and Testing in General Chemistry. STANLEY L. BURDEN and RONALD J. LOSURE, Chemistry Department, Taylor University, Upland, Indiana 46989.—Software has been developed which permits students to drill and take tests specified by the instructor on various types of questions drawn at random from data in the computer. No supervision is required at any point in the drill or testing procedure. A student immediately receives correct answers

for any questions missed, as well as his final score, expressed as a per cent, for all questions attempted during the drill or testing session. The student may specify the number and type of questions in a drill session and drill as he wishes before taking a test for a grade. When the student is ready to take a test for a grade, he specifies this to the computer and then receives a test in which the total number of questions, the number of each type of question, weighting factors, the time limit for the test, and date by which the test must be taken has been previously specified by the instructor. The computer keeps a record of the student's score and his total accumulated connect and CPU time. Since the questions on each student's test are different, a record can also be kept of both the questions and responses for each student's most recent test. Improvement in student test scores has been achieved in addition to highly favorable student evaluations of their experiences.

Chemical Oxygen Demand and Biochemical Oxygen Demand Problems.

ROBERT H. L. HOWE, Tippecanoe Laboratories, Eli Lilly and Co., Lafayette, Indiana 47902.—The problems constantly involved in testing the C.O.D. or B.O.D. of water and waste water samples are explained. The correction of these problems is suggested.

Chemistry and the Revolution. DONALD J. COOK, DePauw University, Greencastle, Indiana 46135.—The development of modern chemistry and the growth of the United States of America take place in almost the same time span of history. Beginning with the Industrial Revolution in England and the Scientific Revolution in men's thinking in Europe, one can find an interplay with the spirit of political independence in America. Benjamin Franklin, Joseph Priestly, Benjamin Rush and Benjamin Thompson (who became Count Rumford) lived, studied, made scientific discoveries and participated fully in the political revolutions of the late 1700's.

Byproducts of the Darzens Condensation. CHARLES J. KELLEY, OSMUND T. O. CHAN, LINDA M. ETTSTAD, HAZEL H. SZETO, PACO A. PARATORE, STEPHEN B. STACKHOUSE, and MARVIN CARMACK, Department of Chemistry, Indiana University, Bloomington, Indiana 47401.—In connection with the synthesis of some natural products, we have undertaken an extensive study of the Darzens condensation of 3,4-dioxygenated benzaldehydes with alkyl chloroacetate esters. In addition to the desired 3-aryl glycidic esters, we isolated several byproducts from the condensation under a variety of reaction conditions. The merits of alternative sets of reaction conditions will be discussed in light of the yields of glycidic esters obtained and the quantities of byproducts encountered. While the heretofore reported byproducts in the Darzens condensation result from the reaction of one mole of aldehyde with one mole of chloroacetate, we have obtained a novel byproduct resulting from the combination of the aldehyde with two moles of chloracetate. Physical and chemical data will be presented which establish the structure of the new byproduct as a substituted tetric acid. Additionally the mechanism of its formation will be discussed in light of the quite specific reaction conditions required for its production.