

CHEMISTRY

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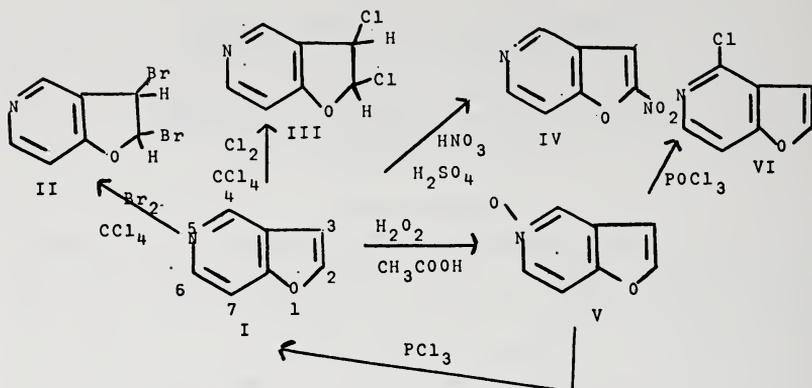
ABSTRACTS

Using an On-Line Minicomputer in the Undergraduate Chemistry Laboratory. STANLEY L. BURDEN, Chemistry Department, Taylor University, Upland, Indiana 46989.—Applications are described which use a minimal configuration, on-line minicomputer system to collect, reduce and display data in undergraduate chemistry laboratory experiments. Students interested in gaining experience with implementing on-line minicomputer systems designed and wired the interfacing and wrote the necessary software for various applications. Other students then used the configured system in conjunction with experiments in gas chromatography, kinetics and electrochemistry. Results from selected student experiments are presented and compared to other methods commonly used to collect and/or reduce similar data. Advantages, limitations and potential applications of the on-line system are discussed.

Further Studies on the Physical and Chemical Evaluation of Used Motor Oil. ROSS C. KOILE and ROBERT E. VAN ATTA, Ball State University, Muncie, Indiana 47306.—A previous report described the results of chemical and physical tests for the evaluation of the condition of automobile crankcase oil while it was in use in a particular vehicle. The present report describes extension of the earlier work to several different types of vehicles and drivers, including different types of driving, highway, and weather conditions and engine stress. Viscosity, acidity, colorimetric, and gas chromatographic data are reported for the same commercial oil, resulting from measurements taken at intervals from the crankcases of the test vehicles. Problems due to sampling procedures, availability of supplies and equipment, effect of engine design, and vehicle and engine conditions are discussed. A summary of the two-year project and potential future prospects are presented.

The Chemistry of the Furopyridines. JOHN W. MCFARLAND, WILLIAM ESSARY, LALE CILENTI, WILLIAM COZART, ALAN KAYLO, and PHILIP MCFARLAND, Department of Chemistry, DePauw University, Greencastle, Indiana 46135.—Furo[3,2-c]pyridine (I) was prepared and its reactions studied. The bicyclic compound behaves both like a diene and an aromatic compound. Halogenation with bromine and chlorine gave 2,3-dibromo-2,3-dihydrofuro[3,2-c]pyridine (II) and 2,3-dichloro-2,3-dihydrofuro[3,2-c]pyridine (III), respectively. Nitration of I afforded 2-nitrofuro[3,2-c]pyridine (IV), while treatment with hydrogen peroxide gave the N-oxide (V). The N-oxide (V) was deoxygenated and chlorinated to 4-chlorofuro[3,2-c]pyridine (VI) by phosphorus oxychloride and

deoxygenated to I by phosphorus trichloride. Attempts at acylating and sulfonating I have thus far been unsuccessful.



Determination of the Formation Constants of HF , HF_2^- , and AgF in Aqueous Solution Using the Fluoride Electrode. DWAIN SPARKS and EUGENE SCHWARTZ, Chemistry Department, DePauw University, Greencastle, Indiana.—The complexing of hydrogen ion by fluoride ion in aqueous solution at 25.0°C at an ionic strength of unity with sodium perchlorate as the supporting electrolyte was studied using the fluoride-ion specific membrane electrode. In contrast to similar work with this system reported in the literature, here the fluoride electrode was the only ion probe employed. Such a technique necessitated the use of a successive approximation approach because of change of the ionic strength due to the formation of the complexes themselves. The formation constants of HF and of HF_2^- as calculated in several ways from the values of \bar{n} , the average number of fluoride ions bound by each hydrogen ion, were 8.45×10^2 and 5.05 , respectively.

Because of the very weak complexing of silver ion by fluoride ion, measurements of the bound fluoride ion in this system had to be made in one molar silver perchlorate solution. This approach required the estimation of combined activity and liquid junction effects between the test solution and that used to calibrate the fluoride electrode. An estimation of the formation constant of AgF is reported.

Inexpensive Instruments for Constant-Current Coulometric Titrations. ROBERT E. VAN ATTA, Ball State University, Muncie, Indiana 47306.—The techniques of constant-current coulometric titration permit rapid, convenient, and accurate measurement of microgram quantities of acids, bases, metals, and various other ionic chemical species capable of electrochemical generation and/or reaction at properly designed electrodes. Two instruments capable of performing such titrations are described. These devices (one manual and the other automatic-recording), which may be constructed by students, are inexpensive, convenient, and accurate. The fundamental circuit includes a control circuit so designed that manual or voltage-regulator control maintain the generator current

constant to within 0.1% with ease. Titration results to within 1 to 2 parts per thousand are readily attainable from measurements requiring less than 10 minutes for completion. Circuit diagrams, test solution cells and typical student results for acid-base and redox coulometric titrations are presented. These instruments are particularly adaptable to instructional use in first-year quantitative analysis or instrumental methods courses.

Analyzing Environmental Samples in the Undergraduate Science Laboratory by X-Ray Fluorescence Spectroscopy. DANIEL P. FADAL and STANLEY L. BURDEN, Physics and Chemistry Departments, Taylor University, Upland, Indiana 46989.—Because of its relative ease of sample preparation and its capability for multi-element analysis, x-ray fluorescence spectroscopy is receiving increased use for analyzing a wide variety of samples in environmental studies. Procedures and equipment are described which are currently being used to make this technique available to undergraduate science students. A unique student-designed and constructed chamber which permits a conventional x-ray diffraction unit to be used as a continuously variable x-ray energy source is described. Results from student analyses of several environmental samples are presented.

Effect of Sampling Parameters and Other Physical and Chemical Conditions on the Chemical Analysis of White River Waters. MICHAEL A. SAILOR and ROBERT E. VAN ATTA, Ball State University, Muncie, Indiana 47306.—Results of a 25-day analytical study of the White River at Muncie, Indiana, are reported. Several inorganic chemical species were monitored at appropriate time intervals; these species included alkalinity, chloride, iron, free ammonia, nitrite, nitrate, dissolved oxygen, ortho-, meta-, total inorganic and organic phosphates, and sulfate. Also monitored were color, calcium-, magnesium-, and total hardness, pH and specific conductance, turbidity, and water temperature. All analyses were completed with the aid of a Hach DR/EL-2 water analyzer. The variance and importance of sampling parameters and other physical and chemical conditions related to the analyses are presented and discussed.

Spectrophotometric Determination of Stability Constants: A Study of the Complex Ions Formed from Di-n-Butyloxamine and Ni^{+2} , Co^{+2} and Cu^{+2} Ions. JOHN M. GARDLIK and WARREN E. HOFFMAN, Indiana Institute of Technology, Fort Wayne, Indiana 46803.—In previous work reported to this academy (Proc. Ind. Acad. Sci., Vol. 79, pp. 129-133, 1969), the use of Job's Method of Continuous Variation showed di-n-butyloxamine to form 2:1 complexes with Ni^{+2} , Cu^{+2} , and Co^{+2} ions. It seemed desirable to our group to get a quantitative measure of the stability of these complexes. Using the same set of data obtained for Job's Method, one can determine the stability constants following the method of Newman and Hume. The stability constants for the complex ions, $Ni(di-n-butyloxamine)_2^{+2}$, $Co(di-n-butyloxamine)_2^{+2}$, and $Cu(di-n-butyloxamine)_2^{+2}$ in methanol were determined spectrophotometrically to be 7.91×10^3 , 3.12×10^5 , and 1.65×10^3 ,

respectively. This paper deals only with systems in which only one complex ion is formed.

The Syntheses and Reactions of Some Tetrahydrofuran Complexes of Rhenium(I). BRUCE N. STORHOFF and CHRISTOPHER L. SCANLON, Department of Chemistry, Ball State University, Muncie, Indiana 47306.—Tetrahydrofuran complexes of rhenium(I) have been obtained from the direct reaction of halopentacarbonylrhenium(I) species with tetrahydrofuran (THF). The THF complexes have been assigned dimeric structures with bridging halogen groups from spectroscopic and molecular weight data. These THF complexes have proved to be useful synthetic intermediates yielding complexes of the stoichiometries $\text{Re}(\text{CO})_5\text{L}_2\text{X}$ and $\text{Re}_2(\text{CO})_8\text{L}_2\text{X}_2$ upon reaction with a variety of ligands (L).

The Stereochemistry of Insertion Reactions Involving Carbon-Iron σ -Bonds. P. L. BOCK, Department of Chemistry, Ball State University, Muncie, Indiana 47306, and G. M. WHITESIDES, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.—The stereospecifically 1,2-dideuterated 3,3-dimethylbutyl grouping has been used to follow the stereochemical course of insertion reactions involving the carbon-iron σ -bond of an alkyliron compound. Carbonyl insertion reactions take place with >90% retention of configuration at carbon; sulfur dioxide insertion proceeds with >95% inversion of configuration at carbon; the insertion of dimethyl acetylenedicarboxylate takes place with >80% retention of configuration at carbon.

The Heat Pump and Its Role in the "Energy Crisis." JAMES D. COPP and JOHN H. MEISER, Department of Chemistry, Ball State University, Muncie, Indiana 47306.—Due to the recent energy crisis, it appears à propos to reexamine the heat pump as a possible means to conserve fossil fuels normally used for home space heating purposes. In this paper, both the theoretical efficiency and the performance coefficient vs. temperature of some commercially available heat pumps are discussed. In addition, a graph of BTU/hr. vs. cost is shown in the comparison of heat pumps versus fuel oil, natural gas, and electric resistance heating. From the data presented, the tentative conclusion can be made that heat pumps in combination with resistance heating for low temperature use can provide a viable alternative to continual consumption of oil and gas for space heating purposes.

Effects of Phosphorus Stereochemistry on Pmr Coupling Constants in Cyclic Organophosphorus Compounds. JOHN A. MOSBO, Department of Chemistry, Ball State University, Muncie, Indiana 47306.—Intra-ring proton and 31-phosphorus coupling constants were determined by computer simulation of 220 MHz pmr spectra obtained for isomeric 2-methoxy- and 2-methyl-2-oxo-4-methyl-1,3,2-dioxaphosphorinanes in benzene and chloroform. Whereas a methoxy group in the two position has been previously shown to have a marked preference for axial orientation, a 2-substituted methyl group shows no great preference. This behavior is reflected in the different values for the coupling constants

of the isomeric pairs. Furthermore, the different coupling constant values observed in chloroform and benzene indicate preference for equatorial phosphoryl orientation in the more polar solvent.

Comparison of the Irreversible Binding of Penicillin to Human Serum and Plasma. LEWIS TRUEX and EUGENE WAGNER, Ball State University, Muncie, Indiana 47306.—Immunological responses to low molecular weight compounds are believed to be mediated by irreversible binding of such compounds with body protein resulting in the formation of antigens. The *in vitro* incubation of recrystallized human serum with radioactively labeled benzylpenicillin, followed by exhaustive dialysis, electrophoretic separation into its constituent fractions, and scintillation counting of these fractions indicated a distribution of covalently bound penicillin in each fraction in proportions related to their distribution in blood. The implementation of the preceding procedure on the plasma of twelve students and two penicillin-sensitive patients resulted in a comparison of the distribution of covalently bound penicillin in the constituent protein fractions of the subjects' plasma and recrystallized human serum.

The Mechanisms of the Willgerodt-Kindler Reactions. MARVIN CARMACK, GLENN A. BERCHTOLD, SAMUEL BERKOWITZ and MOHAMMAD BEHFOROZ.—The original Willgerodt and Kindler Reactions, dating from approximately 1890 and 1920, respectively, were conversions of aryl *n*-alkyl ketones into ω -arylcaboxamides and thiocaboxamides by action of ammonium polysulfide or secondary amines with sulfur. In a long-continued study of these reactions we have elucidated some of the more surprising aspects of these reactions, in particular the ability of ketonic functions to isomerize along a chain of methylene groups in a series of complex and reversible reactions involving the addition of basic nitrogen to the ketonic function, dehydration, addition of elemental sulfur, formation of labile heterocyclic sulfur intermediates which can reversibly read basic nitrogen in two possible ways. We have been able to apply the reaction of isomerization without necessarily pushing the reaction to the stage of irreversible terminal oxidation to a carboxamide derivative, and by this means cause the isomerization of both open-chain and cyclic ketones into families of isomeric carbonyl compounds. Such a reaction is in some cases useful for the preparation of uncommon carbonyl compounds from more readily available ones.

Some Observations on the Use of an Open-ended Multioption Laboratory for Organic Chemistry. TERRY L. KRUGER, Department of Chemistry, Ball State University, Muncie, Indiana 47306.—The experiences and conclusions drawn for operation of an open-ended (the results are not known beforehand), multioption (each student has a different task) organic laboratory for chemistry majors will be presented.

The equipment, time, and staff necessary are prime considerations in undertaking a course such as this. The types of experiments found suitable so far, the cost, the time and scheduling, the advantages and disadvantages to both student and department will receive comment.

The experiments that have proven most successful have procedures that must be adjusted by the student according to variations in reactivity

that are covered in the lecture portion of the course. Nitration or bromination of substituted benzenes and ester formation are traditional experiments that can easily be designed so that each student has a different task. These two experiments have been used with good results in our regular track Organic Chemistry course. Unusual experiments that have realized various degrees of success are: (1) alkylation of an aryl amine followed by Hofmann Elimination, oxidation, and Cope Elimination; (2) Nitrosation of Amines; and (3) Analysis of Rit Dyes. Attempts with this approach for photochemistry, condensation reactions, and reactions of aldehydes and ketones gave uneven results.

Extensive use of instrumentation has seemed desirable and is taken in stride by the students. Perhaps the greatest benefit to the student from this type of experience is the time spent in the library becoming familiar with various primary and secondary source materials.

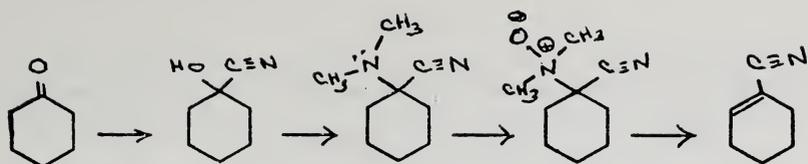
The chemistry department profits from the enhanced interest in and capacity for chemical research and by the greater contact of the students with each other and with the departmental faculty and staff. Student enthusiasm, my own stimulation, and the students' continued interest are other nonquantifiable benefits of this experience.

A Study of Adenosine Deaminase in Normal and Cancerous Human Tissues.¹ MARK J. NIEBAUER and PANG F. MA, Department of Chemistry, Ball State University, Muncie, Indiana 47306.—Two molecular forms of adenosine deaminase (the A form and the C form of molecular sizes 200,000 and 35,000 respectively) were found in various proportions in different human tissues. There seems to be an indication of an increase of the C form enzyme activity in cancerous tissues than in the corresponding normal tissues. A conversion factor which is capable of converting the C form into the A form enzyme has been reported. This study was made to examine the relative amount of the two enzyme forms in normal lymph nodes and tumor of the lymph nodes from a cancer patient.

Studies of the γ -Pyrone Nucleus. GERALDINE M. HUITINK, Indiana University, South Bend, Indiana 46615.—The effect of selected substitutes on the relative fluorescence and stability of the γ -pyrone nucleus is reported.

The Synthesis of Some Cycloalkene Carbonitriles. JANICE L. STROHM and TERRY L. KRUGER, Department of Chemistry, Ball State University, Muncie, Indiana 47306.—Beginning with cyclohexanone and cyclopentanone, synthesis of their corresponding cycloalkene-1-carbonitriles is performed by a reaction sequence starting with the formation of the cyanohydrin and continuing through the α -dimethylaminonitrile which provides the title compounds when oxidized and thermolysed as shown in the following reaction sequence.

¹ Supported in part by a grant from the Delaware County "Little Red Door" Cancer Society, and by a Student-Faculty Research Grant from Ball State University to MJN.



The effects of substituents on the reaction sequence and particularly on the elimination mechanism for a variety of alkyl cyclopentanones and cyclohexanones will be discussed, particularly the "locked" ring of 4-(*t*-butyl)-cyclohexanone. The equatorial hydroxy on the 4-(*t*-butyl)-cyclohexanone cyanohydrin has proven difficult to replace by secondary amines.