

## CHEMISTRY

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### ABSTRACTS

**Thallium (I) Cyclopentadienide: A Useful Reagent for the Preparation of Thallium Derivatives.** B. N. STORHOFF, Ball State University, Muncie, Indiana 47306, and H. C. LEWIS, Jr., University of Wisconsin, Fox Valley Campus, Menasha, Wisconsin 54952.—Thallium reagents have recently proved to be useful in synthetic organic and organometallic chemistry. A convenient starting material for the preparation of certain thallium reagents is thallium (I) cyclopentadienide. Thus organothallium derivatives result from the reaction of thallium cyclopentadienide with organic molecules containing an acidic hydrogen. The synthetic method is particularly useful for the preparation of Tl(I)  $\beta$ -diketonates.

**The Li-NH<sub>3</sub> Reduction of Trans-4-t-butylcyclohexyl Methanesulfonate and of 1-Deutero-trans-4-t-butylcyclohexyl Methanesulfonate.** P. A. WISEMAN and C. L. RENNER, Department of Chemistry, Ball State University, Muncie, Indiana 47306.—Trans-4-t-butylcyclohexyl methanesulfonate was reacted with lithium in liquid ammonia to give a mixture of t-butylcyclohexane and trans-4-t-butylcyclohexanol. The nature of the product was dependent on the Li concentration. Low Li concentrations favored hydrocarbon production; high Li concentrations gave predominantly alcohol.

1-Deutero-trans-4-t-butylcyclohexyl methanesulfonate was reduced with Li-NH<sub>3</sub> and the resulting hydrocarbon examined using a Varian nuclear magnetic resonance spectrometer with deuterium probe. The nuclear magnetic resonance spectrum was compared to those of *cis* and *trans*-4-deutero-t-butylcyclohexane. The deuterium n.m.r. spectra indicate that the hydrocarbon from the Li-NH<sub>3</sub> reduction consists of a 20-80 mixture of *cis* and *trans*-4-deutero-t-butylcyclohexane.

**Synthesis of -Ene Nitriles as a First Step in the Synthesis of Bicyclo Alkanes with a Bridgehead Nitrile.** STANLEY WEST, WILLIAM NESBITT, and TERRY L. KRUGER, Department of Chemistry, Ball State University, Muncie, Indiana 47306.—Cope eliminations from bridgehead positions were examined by a series of reactions leading up to synthesis of a bridgehead nitrile. Synthesis of an -ene nitrile followed by a Diels-Alder reaction was used to prepare the bridgehead nitrile. The -ene nitrile was prepared by making a cyano-hydrin followed by reaction with dimethylamine to give an amino nitrile. The amine function was then oxidized so that the compound will Cope eliminate to the -ene nitrile. This series of reactions was carried out in a yield of over 90 per cent and was very convenient. The -ene

nitrile was then reacted with cyclopentadiene in a Diels-Alder reaction which produced the desired bridgehead nitrile.

**The Mechanism of the Cope Elimination.** JAMES W. KRESS, GLENN SHERWOOD and TERRY L. KRUGER, Department of Chemistry, Ball State University, Muncie, Indiana 47306.—The mechanism of the Cope elimination has been established as involving a concerted, five-membered, cyclic transition state. New data from kinetic studies of substituted N, N-diethyl-aniline oxides and from CNDO/INDO calculations of possible configurations of the transition state contribute to a further understanding of the extent of carbon-nitrogen bond cleavage and extent of proton transfer at the transition state. Present data suggest that transfer of proton precedes carbon-nitrogen bond cleavage; that is, the transition state occurs before much disruption of the carbon-nitrogen bond. Interpretations of substituent effects, isotope effects, and molecular orbital results were presented along with suggestions of practical synthetic tests of the fine details of the mechanism.

**Determination of Dose-Related Excretion of Ascorbic Acid.** EUGENE S. WAGNER, Department of Chemistry, Ball State University, Muncie, Indiana 47306.—The proposal that, when properly used, ascorbic acid (Vitamin C) is effective in both the prevention and alleviation of the common cold suggested a pedagogically significant and theoretically interesting experiment for a Medical Biochemistry laboratory. The reported optimum daily intake of vitamin C varies somewhere between 250 mg and 10 g. Ten medical students measured the excretion of L-ascorbic acid in the urine as a function of increased dosage of the vitamin. No attempt was made to correlate increased dosage to prevention or alleviation of cold symptoms. In addition to demonstrating to the students the difficulty in determining optimum dosage of pharmaceutical agents because of individual variabilities, the experiment showed an unusual dose-related correlation of excreted ascorbic acid.

**The Effect of Hydrogen Ion Concentration on the Kinetic Parameters of Thyroid Monoamine Oxidase.** CLEO L. HUANG and ARTHUR R. SCHULZ, Department of Biochemistry, Indiana University School of Medicine, Indianapolis, Indiana 46202.—A reaction sequence was proposed for the reaction catalyzed by thyroid monamine oxidase based on analysis of initial velocity measurements, product inhibition studies, substrate inhibition studies, and studies of inhibition of the reaction by 3-iodotyramine. These studies suggest that iodotyramine interacts with a regulatory site on the enzyme which is distinct from the active site. An investigation was conducted on the effect of hydrogen ion on the kinetic parameters to obtain additional information concerning the interaction of substrate with the active site and the interaction of iodotyramine with the regulatory site of the enzyme. The data from this investigation suggest that the substrate for thyroid monamine oxidase is the protonated amine, and the ammonium ion is one of the products of the reaction. The ionic species of iodotyramine which interacts with the enzyme is the zwitterion, *i.e.*, the phenoxy ion with a protonated amine. The free enzyme contains an acidic group with a pKa of 8.4 which is not detectable in the enzyme-substrate complex while

the enzyme-substrate complex contains an acidic group with a  $pK_a$  of 7.7. A reaction mechanism was presented which is consistent with the experimental evidence.

**Synthesis of Oxygen-18 from Enriched Water for Use in Isotopic Analysis by Mass Spectrometry.** KENNETH L. BRIDGES, Department of Chemistry, Ball State University, Muncie, Indiana 47306.—In the course of research on the rate of vanadium(VI) yl-oxygen exchange with water, it was necessary to analyze the oxygen-18 content of reaction water. Except in cases where the mass spectrometer has been especially designed for such use, water, because of its considerable memory effect, cannot be analyzed directly. Therefore, the oxygen isotopic composition of water is determined indirectly after conversion into molecular oxygen which is more suitable for mass spectroscopic analysis. A method for preparing oxygen-18 enriched molecular oxygen from water of low enrichment was given. An electric discharge tube was used which provided molecular oxygen with the same isotopic composition as that of the starting water.

**Techniques for Preparing Video Tapes for the Chemistry Classroom.** FREDERICK K. AULT and BRUCE N. STORHOFF, Department of Chemistry, Ball State University, Muncie, Indiana 47306.—One of the problems associated with video tape projection in chemistry classes has been the display of scientific equations and written materials. Overhead projection techniques and certain studio techniques were used to solve the problem and improve the quality of presentations.

**Oxaziranes: Synthesis and Chemistry.** M. L. DRUELINGER, Department of Chemistry, Indiana State University, Terre Haute, Indiana 47809.—In continued studies on the synthesis and chemistry of oxaziranes and similar small polyheterocycles, I prepared several new nitrones and examined their behavior when exposed to ultraviolet light. The nitrones were prepared by the condensation of hydroxylamines with carbonyl compounds or by the addition of diazo compounds to nitroso compounds. All new compounds were fully characterized by spectral analysis. The resulting nitrones were photochemically closed to oxaziranes. These highly strained compounds were themselves photolabile and underwent rearrangement and/or fragmentation. These latter processes were dependent on both wave-length and substituents.