

# ABSTRACTS OF DOCTORAL DISSERTATIONS

1954

## ORGANIC OXIDATION WITH DITERTIARBUTYL CHROMATE AND RELATED REACTIONS

Lewis W. Bowman, Chemistry

A modified method for the safe preparation of relatively large amounts of the new oxidant, di-*t*-butyl chromate, has been developed. In various oxidations employing this oxidant three solvents, *n*-pentane, benzene, and toluene, were used. Benzene was found to be superior to the other two.

Using both di-*t*-butyl chromate and di-*t*-amyl chromate, neopentyl alcohol has been oxidized to trimethylacetaldehyde in fair yields.

Various secondary alcohols have been oxidized with di-*t*-butyl chromate in benzene to the corresponding ketones in nearly quantitative yields. Oxidation of highly branched secondary alcohols has significantly depressed the cleavage reaction they have been previously shown to undergo on oxidation with chromic acid. When excess pyridine is added the cleavage reaction is further reduced to 0-1% and the yield of the ketone raised to 90-97%.

Several classes of compounds not containing a hydroxyl group were not attacked by di-*t*-butyl chromate. Propionaldehyde and isovaleraldehyde were oxidized to the *t*-butyl ester of the corresponding acid in poor yield.

A novel reaction of silver chromate with several organic bromides was briefly investigated. Using *sec*-butyl bromide, methyl ethyl ketone was obtained in 35% yield, while *n*-butyl bromide afforded only a small yield of *n*-butyraldehyde.

## VAT DYES FROM PHENANTHRAQUINONE

Chung Cheng Chen, Chemistry

A systematic exploratory study was made on the phenanthraquinoid vat dyes. Four phenanthraquinoid vat dyes were made from phenanthraquinone: green, black, light-red and wine-red.

Phenanthrene is the only starting material available commercially. Phenanthraquinone is available but expensive. All the derivatives of phenanthraquinone used in this research were made from phenanthrene, and the procedures for the preparation of these derivatives are described. Five new derivatives of phenanthraquinone were prepared.

The general structures of dyes substantive to cellulosic fibers are discussed briefly. Structures for the light-red and wine-red vat dyes made in this research are suggested. Schemes for the proof of the structures of these two dyes are proposed. A critical survey of the literature concerning the vat dyes derived from phenanthraquinone is given.

## THE STUDY OF TERPENE DIMERIZATION

William D. Coder, Jr., Chemistry

The dimers produced by the action of 85% phosphoric acid on dipentene,  $\alpha$ - and  $\beta$ -pinene appear to have the same basic structure, while the dimers produced from camphene-tricyclene mixtures are somewhat different. In all cases, the dimers appears as complex mixtures of cis-trans, and other isomers containing rearranged double bonds. The dipentene dimer appears to have the basic structure of a 1,3,3,6-tetramethyl-1-(4-methylcyclohexenyl)-tetrahydroindan and is most likely 2,2,4,7-tetramethyl-4-(4-methyl-3-cyclohexenyl)bicyclo[4.3.0]-6-nonene. The mechanism proposed for the dimerization with 85% phosphoric acid involves a carbonium ion attack followed by a ring closure reaction in which the anion plays an important role.

## GAS ABSORPTION ACCOMPANIED BY CHEMICAL REACTION

Richard E. Emmert, Chemical Engineering

Experiments were conducted on the absorption of carbon dioxide in aqueous solutions of monethanolamine in a very short wetted-wall column.

When the absorption was effected from pure carbon dioxide streams, the results conformed to a theoretical relation for absorption combined with very-fast second-order reaction. This is in accordance with expectations based on the probable mechanism and rate of the reaction. The data indicate that there is no appreciable effect of non-equilibrium at the interface for this particular reaction system.

When mixed gas streams were used, it was necessary to resort to empiricism to correlate the data, although the correlating expression arose from theoretical considerations.

A secondary reaction which occurs too slowly to affect the absorption rate was detected. Its rate was determined by a conductivity method and was found to check closely the rate predicted from a rate expression for the decomposition of carbamate to form carbonate. The reaction believed to occur during an absorption process is the very rapid formation of carbamate.

Existing theory for simultaneous absorption and chemical reaction is reviewed, and new results are presented for three cases when interfacial resistance is present; namely, (1) physical absorption, (2) absorption combined with first-order irreversible reaction, and (3) absorption accompanied by very-fast second-order reaction.



## STUDIES ON TERTIARY PINENE HYDROCHLORIDE

Leonard Louis Gelb, Chemistry

Tertiary pinene hydrochloride was permitted to rearrange at room temperature in the presence of a large excess of various nucleophilic and electrophilic reagents. In comparable cases, products obtained by fractionation differed quantitatively rather than qualitatively. No fenchyl derivatives and no bornyl esters, alcohols, or ether were obtained in acid, water, or alcohol solvents, respectively. A comparison of products from the Wagner-Meerwein rearrangement in water, aqueous sodium iodide, and alcohol of *t*-pinene hydrochloride made from pure  $\alpha$ -pinene and pure  $\beta$ -pinene shows a predominance of monocyclic over bicyclic terpenes, a larger amount of bornyl chloride with  $\alpha$ -pinene than with  $\beta$ -pinene, a larger amount of monocyclics with alcohol than with water, and  $\alpha$ -pinene returned from both starting materials with water only. In a slight excess of hydrogen chloride, the proportion of monocyclics to bicyclic terpenes was reversed.

The evidence suggests a bridged ion type of structure for pinene hydrochloride, a concerted elimination mechanism for the rearrangement by solvolysis, and a catalytic rearrangement with strong Lewis acids.

## SYNTHESIS OF 1,6-DIAMINOMANNITOL

Loran Andrew Henderson, Chemistry

The purpose of this investigation was the synthesis of 1,6-diaminomannitol by a method which did not involve the blocking of the secondary hydroxyl groups of mannitol.

The preferential attack of the primary hydroxyl groups of mannitol was accomplished by slowly adding benzenesulfonyl chloride to a stirred pyridine suspension of mannitol cooled to 0°. The crystalline mannitol-1,6-dibenzenesulfonate thus obtained is a new compound, m.p. 122-3°. The dibenzenesulfonate ester was ammonolyzed to the dibenzenesulfonate salt of 1,6-diaminomannitol.

The ammonolysis was carried out in an inert anhydrous medium at room temperature. The new compound (1,6-diaminomannitol dibenzenesulfonate) was obtained in the form of white crystals: m.p. 238-40°.

The success of this new synthesis was proved by conversion of the 1,6-diaminomannitol dibenzenesulfonate to 1,6-diaminomannitol dihydrochloride which has been prepared by an independent method.

## KINETIC STUDIES OF KETONE-FORMALDEHYDE REACTIONS

Leo Raymond Kangas, Chemistry

A study was made of the reaction of acetone, diethyl ketone, diisopropyl ketone, methyl ethyl ketone, methyl isopropyl ketone, and methyl *t*-butyl ketone with formaldehyde. The reactions were carried out at three different temperatures, namely, 15°, 25°, and 35°C. Three ratios of ketone to formaldehyde were used, namely, 45:1, 30:1, and 20:1. The catalyst was 0.05 *N* LiOH, and solutions were 50% in methanol in order to facilitate solubility. The reactions were followed by polarographic measurement of the unreacted formaldehyde.

The data obtained indicated the following:

(1) Methyl *t*-butyl ketone showed no reaction with formaldehyde under the conditions.

(2) Acetone and diisopropyl ketone reacted at approximately the same rate. Methyl ethyl ketone and methyl isopropyl ketone showed the fastest reaction rates and their velocities were approximately the same. Diethyl ketone was intermediate in rate of reaction.

(3) The energy of activation,  $E_a$ , ranged from 11,000 to 16,000.

(4) The reaction rate was proportional to the hydroxide concentration.

(5) The reaction was found to be first order in respect to formaldehyde concentration.

(6) A neutral salt like LiCl had no effect on the reaction rate, indicating that the product of the ionic charges on the reactants was zero.



## CHROMATOGRAPHIC ADSORPTION STUDIES OF VARIOUS ORGANIC COMPOUNDS, PARTICULARLY HYDROXY-SUBSTITUTED COMPOUNDS

Samuel C. T. McDowell, Chemistry

An investigation has been made of the chromatographic adsorption properties of hydroxy-substituted benzene compounds and organic acids. The temperature-solubility effect on adsorption was studied for the isomers of nitroaniline. In addition, a large number of compounds were evaluated as chromatographic adsorbents.

A greater adsorption affinity was shown for phenolic substituted OH groups than for alcoholic OH groups on similar molecules. A less pronounced increase in adsorption of the para isomer versus the ortho was noted for the hydroxy phenols than that which occurs for the nitrophenols, amino-phenols or nitroanilines.

It was shown that adsorption of the nitroaniline isomers on alumina or silica gel decreased with increase in adsorption temperature. A relationship between solubility, temperature, and adsorption is indicated.

Adsorption affinities for all these compounds mentioned have been determined for several different adsorbent and solvent systems. These values will enable chromatographic separations of many of these compounds to be made, even though they may be components of complex mixtures that cannot be separated by other physical or chemical methods.

## EXPERIMENTAL NEAR INFRARED SPECTROMETER

Pat Richard Pondy, Chemistry

An experimental spectrometer for operation in the 0.8 to 2.2 micron range has been designed and constructed.

This instrument has been applied to the study of B-H, C-H, N-H, and O-H linkages in polyatomic molecules. From observed frequencies, the dissociation energies, force constants, and bond lengths have been calculated by approximative reduction of the polyatomic system to a diatomic molecule.

The molecules diborane, pentaborane, and decaborane have been subjected to detailed spectral study in the range of this instrument. Spectra of ammonia and dimethylamine have been recorded in both liquid and vapor phases. The spectral structures of diborane, ethylene, and ethane have been compared.