TWENTY - SECOND NATIONAL
ORGANIC CHEMISTRY
SYMPOSIUM

of the

AMERICAN CHEMICAL SOCIETY

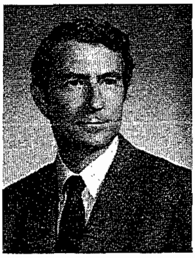
PICES OF THE DIVISION OF ORGANIC CHEMISTRY
UNIVERSITY OF MICHIGAN SECTION OF THE ACS
IN COOPERATION WITH
UNIVERSITY OF MICHIGAN EXTENSION SERVICE

June 13-17, 1971
Ann Arbor, Michigan

TWENTY-SECOND NATIONAL
ORGANIC CHEMISTRY
SYMPOSIUM
of the
AMERICAN CHEMICAL SOCIETY

Speakers at the Twenty-second National Organic Chemistry Symposium


D. Arigoni


J.A. Berson


P.G. Gassman


N.J. Leonard


J.A. Marshall


K. Mislow


K. Nakanishi


L.A. Paquette


R. West


P.R. Story

PROGRAM

SUNDAY, JUNE 13

Registration, Mary Markley Residence Hall, 6:00-9:00 P.M.

MONDAY, JUNE 14

Registration and Meetings: Rackham Building

9:00 A.M. Welcome. MARVIN L. ESCH, United States Congress

Response. RONALD BRESLOW, Chairman, Division of Organic Chemistry, ACS

9:30 A.M. PAUL R. STORY, "The Synthesis of Macrocyclic Compounds."

11:00 A.M. JAMES A. MARSHALL, "Carbocyclic Synthesis."

8:00 P.M. JEROME A. BERSON, "Stereochemical and Mechanistic Studies of Molecular Rearrangements."

TUESDAY, JUNE 15

9:00 A.M. LEO A. PAQUETTE, "Catalysis of Strained σ Bond Rearrangements by Silver (I) Ion."

10:30 A.M. ROBERT WEST, "Cyclic Conjugated Chlorocarbons and Their Quinoid Derivatives."

8:00 P.M. HERBERT C. BROWN, Roger Adams Award Address, "Boranes in Organic Chemistry."

WEDNESDAY, JUNE 16

9:00 A.M. PAUL G. GASSMAN, "The Nitrenium Ion - A New Reactive Intermediate."

10:30 A.M. NELSON J. LEONARD, "The Chemistry of Cytokinins."

8:00 P.M. D. ARIGONI, "Biosynthesis."

THURSDAY, JUNE 17

9:00 A.M. KOJI NAKANISHI, "Structural and Synthetic Studies on a Few Y Bases from Phenylalanine t-RNA."

10:30 A.M. KURT MISLOW, "Pyramidal Inversion."

THE ROGER ADAMS AWARD IN ORGANIC CHEMISTRY

The Roger Adams Award in Organic Chemistry has been established with joint sponsorship by the American Chemical Society, Organic Reactions, Inc. and Organic Syntheses, Inc. The award is made biennially to an individual, without regard to nationality, for outstanding contributions to research in organic chemistry. The award consists of a medal and an honorarium of ten thousand dollars. The presentation of the award is made at the biennial National Organic Chemistry Symposium of the Division of Organic Chemistry of the American Chemical Society and the recipient delivers a lecture as part of the program of the Symposium.

The award recognizes the distinguished career of Roger Adams. He has played a vital role in each of the three organizations sponsoring the award, having been both Chairman of the Board of Directors and President of the American Chemical Society and a co-founder of both Organic Syntheses and Organic Reactions.

The recipient of the award this year is Professor Herbert C. Brown of Purdue University. His award address is entitled "Boranes in Organic Chemistry."

H. C. Brown

MICHIGAN COMMITTEES

Executive	P.A.S. Smith
Auditorium and Facilities	M.M. Green and R.C. Elderfield
Registration	P.W. LeQuesne and J. Groves
Housing	J.R. Wiseman and J. Groves
Transportation	A. Ashe and J.P. Marino
Recreation and Entertainment	S.N. Ege and M.M. Martin

DIVISION OF ORGANIC CHEMISTRY

The plans and program of the Twenty-second National Organic Chemistry Symposium have been developed by the members of the Executive Committee of the Division of Organic Chemistry who have served during the past two years.

	1969-1970	1970-1971
Chairman	F.G. Bordwell	R. Breslow
Chairman-elect	R. Breslow	J.A. Berson
Secretary	J.P. Freeman	J.P. Freeman
National Symposium Executive Officer	W.M. Jones	W. M. Jones
Executive Committee	M. Stiles K.L. Rinehart H. Hart M.P. Cava S.J. Cristol N.A. LaBel H.L. Goering J. Meinwald	M.P. Cava H. Hart A.M. Trozzolo R. Pettit F.G. Bordwell S.J. Cristol N.A. LaBel H.L. Goering

CONTENTS

THE SYNTHESIS
OF
MACROCYCLIC COMPOUNDS

P. R. Story

THE SYNTHESIS OF MACROCYCLIC COMPOUNDS

Paul R. Story

We shall consider a macrocyclic compound to contain as an essential component a large ring of 9 atoms or more. The chemistry of such systems is relatively unknown, primarily because of the considerable difficulties attendant to their synthesis.

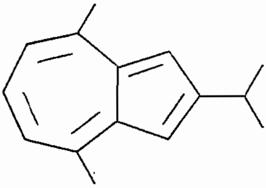
In this lecture, several new synthetic methods will be discussed and placed in historical perspective. These new methods, which serve to reduce entry to macrocyclic systems to the ordinary, include Sondheimer's acetylene cyclopolymerization, Corey's allylic dibromide cyclization, the cyclic olefin metathesis reaction of Calderon and of Wasserman, our own ketone peroxide fragmentation synthesis, and several special syntheses. The new synthetic methods have succeeded in overcoming one or both of the principal disadvantages inherent in earlier syntheses; that is, the twin problems of working at high dilution and the necessity of obtaining a long-chain difunctional precursor have been solved.

The synthesis of macrocyclic compounds by peroxide decomposition provides the first method to offer true generality. At this time

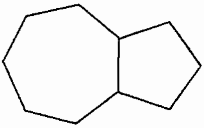
CARBOCYCLIC SYNTHESIS

J.A. Marshall

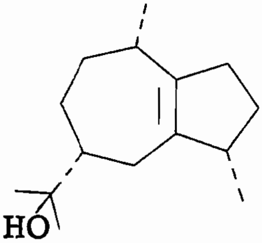
Azulenes and hydroazulenes have challenged the ingenuity of synthetic organic chemists since 1939 when the correct structure for vetivazulene, a dehydrogenation product of the sesquiterpene β-vetivone, was first surmised by Pfau and Plattner.[1] Shortly thereafter other sesquiterpenes which gave rise to azulenes upon dehydrogenation were recognized as derivatives of hydroazulene (bicyclo-[5.3.0]decane). In the ensuing thirty-two years numerous natural products containing this ring system have been discovered. A few examples are shown below.



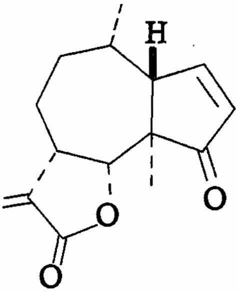
VETIVAZULENE[1]



HYDROAZULENE



GUAIOL[2]



AMBROSIN[3]

Early syntheses of hydroazulenes were mainly concerned with efficient construction of the bicyclo[5.3.0]decane framework such that dehydrogenation reactions leading to

STEREOCHEMICAL
AND
MECHANISTIC STUDIES OF
MOLECULAR REARRANGEMENTS

J.A. Berson

Stereochemical and Mechanistic Studies of Molecular Rearrangements

or

Thermal Reactions and Diradicals - Pseudo, Virtual, and Actual

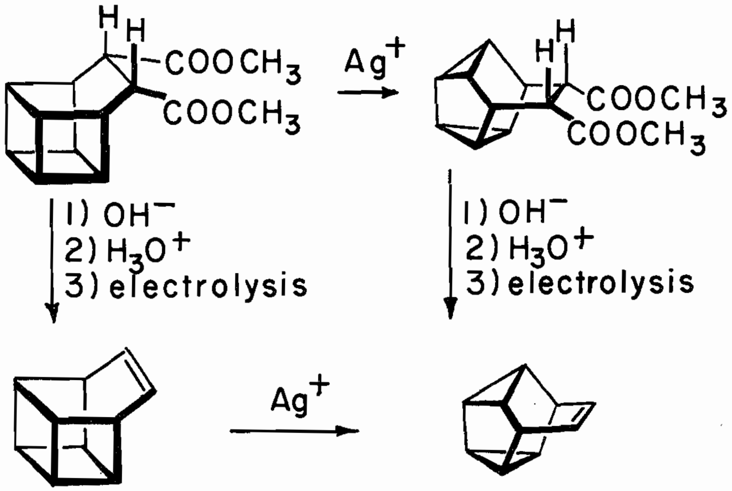
Although it is sometimes possible to identify concerted thermal reactions by special stereochemistry and low activation energy, there is a large group of processes for which the kinetic criterion of mechanism is too insensitive a probe. In these reactions both concerted and diradical pathways seem to be in competition. Examples are available in some [1,3] sigmatropic rearrangements and in the pyrolysis of bicyclo[2.1.0]pentanes. It is characteristic of these processes that there is some lack of definition of the mechanistic details because one does not know exactly what behavior to expect of the diradicals.

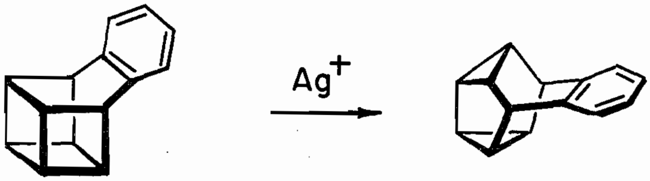
The chemistry of a large group of true diradicals now becomes available for examination in the reactions of

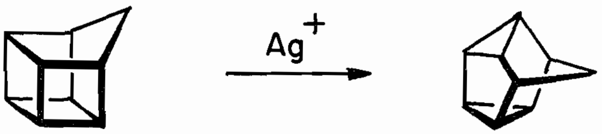
CATALYSIS OF STRAINED σ BOND REARRANGEMENTS BY SILVER (I) ION

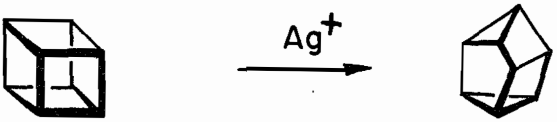
Leo A. Paquette

The Formal $[_\sigma 2_a + _\sigma 2_a]$ Skeletal Isomerization of Caged Molecules









CYCLIC CONJUGATED CHLOROCARBONS AND THEIR QUINOID DERIVATIVES

R. West

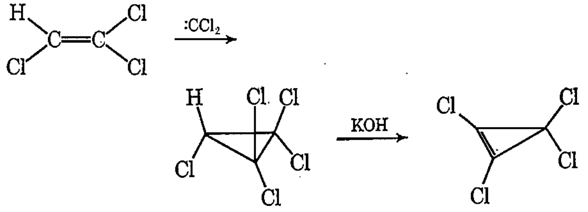
CONJUGATED CYCLIC CHLOROCARBONS AND THEIR QUINONOID DERIVATIVES

Robert West

Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706

Many of the interesting recent findings in chlorocarbon chemistry center about the conjugated cyclic chlorocarbons. Of the monocyclic members of this series, only hexachlorobenzene was known before 1964. Since that time $C_3Cl_3^+$, $C_5Cl_5^-$, $C_7Cl_7^+$ and C_8Cl_8 have been prepared as stable species and evidence has been presented for the transient existence of C_4Cl_4 and $C_5Cl_5^+$ (1). This lecture will deal with some of the chemistry of two of these species, $C_3Cl_3^+$ and $C_7Cl_7^+$, as well as two bicyclic conjugated chlorocarbons, dodecachloroheptafulvalene and octachlorofulvalene.

<u>Trichlorocyclopropenium Ion</u>. The starting material tetrachlorocyclopropene, now commercially available, is synthesized by dichlorocarbene addition to trichloroethylene followed by elimination of HCl:



BORANES
IN
ORGANIC CHEMISTRY

H.C. Brown

BORANES IN ORGANIC CHEMISTRY

Herbert C. Brown

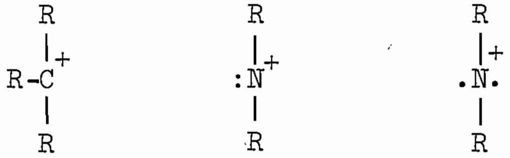
In the past, it has been customary for recipients of the Roger Adams Award to discuss in the Award Address recent developments in research programs under current study in their laboratories. I started to do the same. However, certain recent experiences persuaded me to break with tradition and to try a new approach.

The rapid pace of chemical developments in the past two decades has resulted in major changes in the nature of graduate education in chemistry. There are few courses and very little, if any, time is devoted to acquainting the student with the historical development of concepts or research programs. Instead, the emphasis is placed on self-education of the student through reading the current literature. Consequently, many of our younger colleagues may be lacking the kind of historical perspective that was an accepted part of the education of chemists of earlier generations. I decided to devote the first half of my lecture to tracing my activities over the past 35 years in exploring the role of boranes in organic chemistry. The last half of this lecture I plan to devote in a more conventional manner to two recent developments in the organoborane area.

THE NITRENIUM ION-A NEW REACTIVE INTERMEDIATE

P. G. Gassman

Divalent positive nitrogen (the nitrenium ion) constitutes a new type of reactive intermediate which possesses properties of interest to both the synthetic and the physical organic chemist. In principle, the nitrenium ion is nothing more than the nitrogen analogue of the carbonium ion. In practice the nitrenium ion possesses most of the properties of carbonium ions, in addition to certain characteristics which are unique to this divalent electron-deficient nitrogen species. Foremost among these special properties is the ability of the nitrenium ion to exist in either singlet or triplet form.



$$\mathrm{R{-}\overset{R}{\underset{R}{C}}{}^{+}} \qquad \mathrm{:\overset{R}{\underset{R}{N}}{}^{+}} \qquad \mathrm{.\overset{R}{\underset{R}{N}}{}^{+}.}$$

singlet triplet

Nitrenium ions are synthetically useful in a variety of different types of reactions. Of particular importance from a synthetic viewpoint are molecular rearrangements involving alkyl migrations to divalent positive nitrogen centers, π-routes to azabicyclic molecules, and the special uses of phenylnitrenium ions (anilenium ions).

THE CHEMISTRY OF CYTOKININS

N. J. Leonard

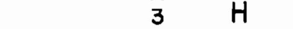
THE CHEMISTRY OF CYTOKININS

Nelson J. Leonard

Cytokinins

Cytokinin is the generic name for substances that promote cell division in plant tissue, such as excised pith or callus, under certain conditions of bioassay and that bring about growth and morphogenesis.[1] It is recognized that cytokinins play a regulatory role in many phases of plant development including cell enlargement, formation of roots and buds, germination of seeds, development of flowers and fruit, and resistance to aging and various adverse environmental conditions. Presumably most if not all of these effects are a consequence of a primary function of cytokinins in regulating protein biosynthesis.

Whereas the existence of a specific cell division factor was postulated as early as 1892, the modern era of research on the cytokinins began in 1955 with the isolation of kinetin, 6-furfurylaminopurine, from old preparations of yeast DNA or from autoclaved, freshly prepared DNA.[2] The structure of the artifact was confirmed by synthesis, and this was quickly followed by the synthesis of active analogs, such as 6-benzylaminopurine (BAP).



KINETIN

BAP

STRUCTURAL AND SYNTHETIC STUDIES ON A FEW Y BASES FROM PHENYLALANINE t-RNA

K. Nakanishi

Structural and Synthetic Studies of Y bases from some phenylalanine transfer ribonucleic acids

Koji Nakanishi, Columbia University

The tRNA's from different organisms contain numerous modified odd bases.[1-3] Of especial interest are the so-called Y bases contained in most of the phenylalanine tRNA's adjacent to the 3′-terminal of their anticodons. Ever since the first isolation of the Y base from $tRNA^{Phe}_{yeast}$ in 1967,[4] it has attracted great interest because of its important biochemical role and intense fluorescence.

Although it was found that mild acid treatment of $tRNA^{Phe}_{yeast}$ could excise the Y base, leaving the rest of tRNA intact,[5] its structure has remained unsolved because of the tediousness and difficulty in securing enough material, its unstable nature (stable only between pH 3-9), and structural complexity comprising probably a new

PYRAMIDAL INVERSION

K. Mislow

PYRAMIDAL INVERSION

Kurt Mislow

Pyramidal molecules R_3M are interconverted by transposition of the tricoordinate atom M from one side of a plane, defined by the three ligands, to the other. In this process (pyramidal inversion) the invertomers may be isometric (automerization, enantiomerization) or anisometric (diastereomerization), corresponding to symmetrical and nonsymmetrical double-well potentials, and to planar and nonplanar transition states, respectively. The processes of interest are purely conformational changes in the electronic ground state; chemically catalyzed processes, intramolecular rearrangements and photochemical processes will be disregarded.

An experimental program has been undertaken to shed light on the question: What are the major structural features which determine the magnitude of inversion barriers?