TWENTY-FIRST NATIONAL ORGANIC CHEMISTRY SYMPOSIUM

of the

AMERICAN CHEMICAL SOCIETY

AUSPICES OF THE DIVISION OF ORGANIC CHEMISTRY
THE UNIVERSITY OF UTAH
and the
SALT LAKE SECTION OF THE ACS

June 15-19, 1969
Salt Lake City, Utah

TWENTY-FIRST NATIONAL
ORGANIC CHEMISTRY
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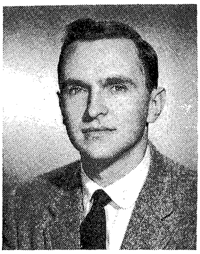
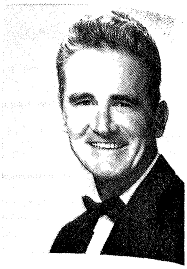
AMERICAN CHEMICAL SOCIETY

Speakers at the Twenty-first National Organic Chemistry Symposium

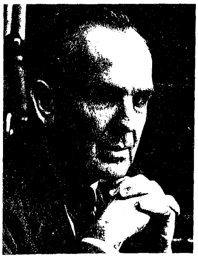


R. Breslow

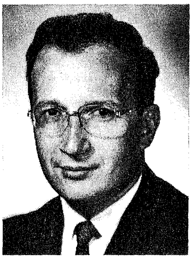
H. C. Brown



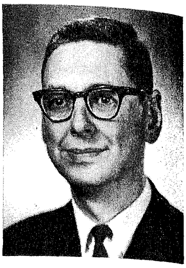
D. J. Cram



W. von E. Doering

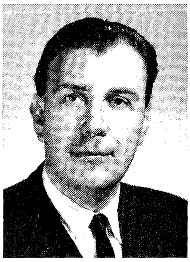


R. Hoffmann

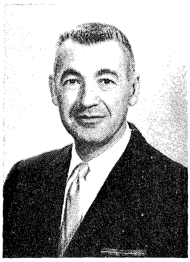


J. Meinwald

G. A. Olah



A. I. Scott



S. Winstein

P. S. Skell

PROGRAM

SUNDAY, JUNE 15

Registration: Kingsbury Hall, 2:00–11:00 P.M.

MONDAY, JUNE 16

Registration and Meetings: Kingsbury Hall

9:00 A.M.	Welcome. HENRY EYRING, Distinguished Professor of Chemistry, University of Utah Response. JERROLD MEINWALD, Chairman, Division of Organic Chemistry, ACS.
9:30 A.M.	DONALD J. CRAM, "Invisible and Revealed Reactions."
11:00 A.M.	P. S. SKELL, "Low Temperature Chemistry of High Temperature Intermediates."
8:00 P.M.	H. C. BROWN, "The Versatile Organoboranes."

TUESDAY, JUNE 17

9:00 A.M.	A. I. SCOTT, "Synthesis and Biosynthesis of Indole Alkaloids."
10:30 A.M.	JERROLD MEINWALD "Some Recent Studies on Intramolecular Photochemical Reactions."
8:00 P.M.	V. PRELOG, Roger Adams Award Address, "Problems in Chemical Topology."

WEDNESDAY, JUNE 18

9:00 A.M.	W. von E. DOERING, "Stereochemistry of the 1,3-Sigmatropic Rearrangement of Methylenecyclobutane."
10:30 A.M.	GEORGE A. OLAH, "Study of Carbonium Ions and New Aspects of Ionic Organic Chemistry in the Superacidity Range."
8:00 P.M.	ROALD HOFFMANN, "Stereochemistry of Cycloadditions."

THURSDAY, JUNE 19

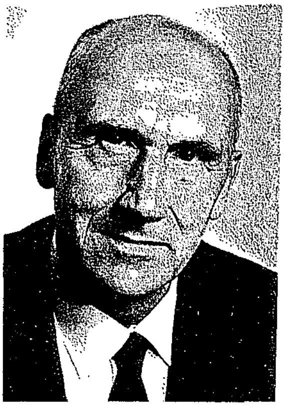
9:00 A.M.	RONALD BRESLOW, "Recent Studies on Conjugated Systems."
10:30 A.M.	S. WINSTEIN, "Neighboring Groups and Nonclassical Ions."

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 V. Prelog of the Swiss Federal Institute of Technology. His award address is entitled "Problems in Chemical Topology."



V. Prelog

UTAH COMMITTEES

Executive	P. D. Gardner
Registration, Housing, and Auditorium	E. L. Allred and W. G. Bentrude
Transportation, Recreation and Entertainment	W. W. Epstein

DIVISION OF ORGANIC CHEMISTRY

The plans and program of the Twenty-first 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.

	1967–1968	1968–1969
Chairman	H. H. Wasserman	J. Meinwald
Chairman-elect	J. Meinwald	F. G. Bordwell
Secretary	N. A. LeBel	N. A. LeBel
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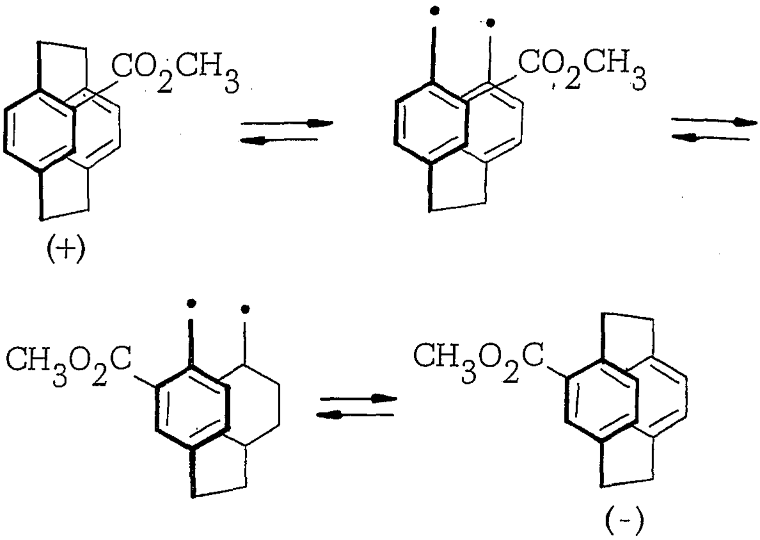
INVISIBLE AND REVEALED REACTIONS

D. J. Cram

Examples of how four types of invisible reactions are turned into revealed reactions are given. In each case the strategy involved manipulation of the symmetry properties of the starting material, and comparison of the symmetry properties of starting materials and products. In some systems, invisible reactions were detected by trapping intermediates, which in the absence of the trapping agents gave back only starting material.

1) When heated to 200°, the [2.2]paracyclophane system cleaves reversibly to give a biradical, which was detected stereochemically.



LOW TEMPERATURE CHEMISTRY OF HIGH TEMPERATURE INTERMEDIATES

Philip S. Skell

The technique of employing high temperature reagents in reactions with low-temperature-stable materials (Wescott) has made it possible to develop a sophisticated chemistry employing high temperature species. The high temperature zone is physically separated from the low temperature zone by high vacuum which serves for thermal insulation and also precludes gas phase reactions; substrate and high temperature species react on the low temperature wall. Reactions in condensed phase are not accompanied by the secondary decompositions characteristic of exothermic gas phase reaction.

THE VERSATILE ORGANOBORANES

Herbert C. Brown

THE VERSATILE ORGANOBORANES

Herbert C. Brown

Hydroboration involves the addition of the hydrogen-boron bond to a carbon-carbon double or triple bond.

$$\mathrm{C{=}C} + \mathrm{H{-}B}\!< \;\longrightarrow\; \mathrm{H{-}C{-}C{-}B}$$

The decade following the initial discovery of a simple means for achieving hydroboration was largely devoted to a systematic study of the scope and characteristics of the reaction. These studies established that hydroboration is essentially quantitative, involves a cis anti-Markovnikov addition from the less hindered side of the double bond, and can tolerate almost all functional groups.

This development made the organoboranes readily available for organic synthesis. Unfortunately, little was known about the synthetic possibilities for these intermediates. Consequently, the second phase of the investigation involved a systematic exploration of the chemistry of organoboranes, with emphasis on reactions of synthetic utility. This program is now in its initial phases.

Considerable progress has been made. This lecture will review the high points of the research at Purdue in this area.

SYNTHESIS AND BIOSYNTHESIS OF INDOLE ALKALOIDS

A. I. Scott

SYNTHESIS AND BIOSYNTHESIS OF INDOLE ALKALOIDS

Amongst the alkaloids of known structure some 800 members (e.g. strychnine, yohimbine, reserpine) can in principle be derived biosynthetically from the condensation of tryptophan with a set of 9 or 10 carbon atoms - the "C_9-C_{10}" unit. Although the tryptophan or tryptamine segment has been clearly shown to be incorporated into several classes of alkaloid by ^{14}C labelling experiments it is only within the last four years that the origin of the "C_9 - C_{10} unit" has been unequivocally demonstrated as mevalonoid.[1] A great majority of the indole alkaloids can be recognised structurally by three distinct arrangements of the "C_9 - C_{10}" unit viz. the Corynanthe (A), Aspidosperma (B) and Iboga (C) families.

A typical example of each class is shown without stereochemical implication in Fig. 1. The apparently more complex alkaloids such as strychnine and quinine can be satisfactorily formulated on a Corynanthe— template (but as "C_9") and in support of this, the incorporation of ^{14}C-geraniol into quinine has been demonstrated in Cinchona species. Much of the earlier biosynthetic work on these alkaloids concerned the incorporation of specifically and differently labelled mevalonates. All of our earlier experiments were confirmed independently and often simultaneously by the work of A. R. Battersby and D. Arigoni and their colleagues.[2] As suggested in 1962 by Wenkert[3] and Thomas[4] the indole alkaloids are derived from the pathway mevalonate (IV) ⟶ geraniol (V) ⟶ "cyclopentanoid monoterpene"(VI) and thence by scission (VII) and condensation with tryptamine to give the alkaloid (Fig. 2).

SOME RECENT STUDIES ON INTRAMOLECULAR PHOTOCHEMICAL REACTIONS

Jerrold Meinwald

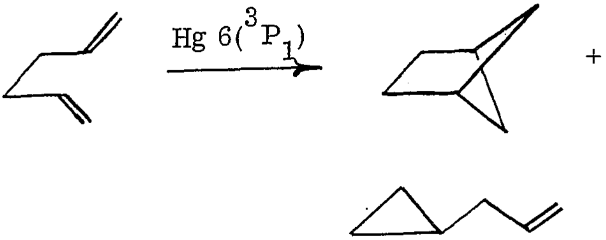
SOME RECENT STUDIES ON INTRAMOLECULAR PHOTOCHEMICAL REACTIONS

Jerrold Meinwald

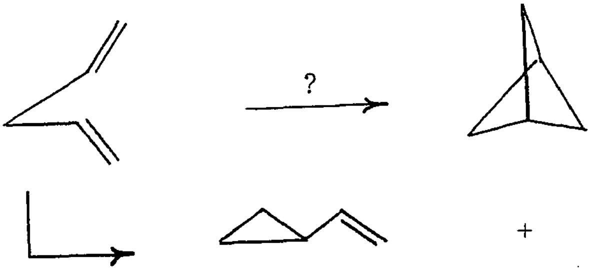
A special feature of photochemical reactions is their potential for the synthesis of highly strained products from unstrained starting materials. Our interest in the preparation of a variety of small-ring compounds provided the original motivation for the studies on photochemical isomerizations described here.

I. MERCURY SENSITIZED REACTIONS OF 1, 4-PENTADIENES.

$$\mathrm{Hg}\ 6(^1S_0) \xrightarrow{2537\,\mathrm{\mathring{A}}} \mathrm{Hg}\ 6(^3P_1)$$



(Srinivasan 1963)



PROBLEMS IN CHEMICAL TOPOLOGY

V. Prelog

PROBLEMS IN CHEMICAL TOPOLOGY

V. Prelog

Chemical Topology vs. mathematical topology

Mathematical topology deals with topological properties of geometrical figures i. e. such properties that are invariant towards topological transformations (e. g. stretching, twisting, turning inside out etc.).

Chemical topology deals with properties of geometrical figures that are either isomorphous or homomorphous with momentary or time average topography of chemical particles.

"When I use a word" Humpty Dumpty said in rather a scornful tone "it means just what I choose it to mean - neither more nor less". Lewis Carroll, Through the Looking-Glass.

Chirality

I call any geometrical figure or group of points chiral, and say it has chirality if its image in a plane mirror ideally realized, cannot be brought to coincide with itself. Lord Kelvin 1904

STEREOCHEMISTRY OF THE 1,3-SIGMATROPIC REARRANGEMENT OF METHYLENECYCLOBUTANE

W. von E. Doering

Stereochemistry of the 1,3-Sigmatropic Rearrangement of Methylenecyclobutane

W. von E. Doering

The current question of mechanism in thermal reorganizations involving the opening and closing of small rings in unrestricted systems concerns rotational requirements.

In the methylenecyclobutane rearrangement, rotations of 90° at C_2 and C_5, 180° at C_4, and either 0° or 180° at C_3 (or their equivalent) are required. These rotations are clearly not free since optically active starting materials give products retaining large amounts of activity. The rotations are therefore partial and may occur in an R or an S sense and may be coupled or uncoupled. The details of the problem will be outlined and the results so far obtained in the solution of the problem will be presented.

STUDY OF CARBONIUM IONS AND NEW ASPECTS OF IONIC ORGANIC CHEMISTRY IN THE SUPERACIDITY RANGE

George A. Olah

In our continuous study of stable, long-lived carbonium ions in strongly acidic solvent systems like SbF_5, HF-SbF_5, FSO_3H-SbF_5 (SO_2, SO_2ClF, SO_2F_2) we worked out, in past years, many of the techniques for observing practically every type of carbonium ions and demonstrated their application on a considerable number of examples. It became increasingly obvious to us that the remaining problems of interest center around ions, the structure of which could be effected by rapid processes of equilibration or neighboring π-, n-, or σ-participation. We concentrated our efforts, therefore, to the study of these ions.

As successful as proton magnetic resonance spectroscopy is in the study of carbonium ions where no question of static versus dynamic equilibrating ions is involved, in such latter cases the slow nmr method clearly is insufficient to provide conclusive answers to structural problems.

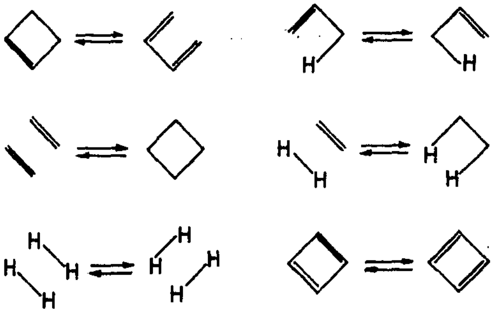
Of the available techniques for such studies, we found Carbon-13 nmr spectroscopy and laser based Raman spectroscopy to be of the greatest value.

^{13}C STUDY OF CARBONIUM IONS OF KNOWN STRUCTURE

Alkylcarbonium Ions. The ^{13}C shift of the t-butyl cation, in SO_2ClF-SbF_5 solution at -20° is -135.4 ppm (from $^{13}CS_2$), with a long-range coupling to the methyl protons of 3.6 Hz. From the methyl ^{13}C satellites in the proton spectrum of the ion, the long-range proton-proton coupling constant was found to be 3.5 Hz. The ^{13}C shift of the isopropyl cation, under identical conditions, was found to be -125.0 ppm with a long-range coupling to the methyl protons of 6.0 Hz. The direct ^{13}C-H coupling was found to be 169 Hz in agreement with the value previously determined in SbF_5 solution. From the ^{13}C satellite spectrum of the ion, the long-range proton-proton coupling constant was found to be 6.0 Hz. The effect of substituting the methyl group in the t-butyl

STEREOCHEMISTRY OF CYCLOADDITIONS

Roald Hoffman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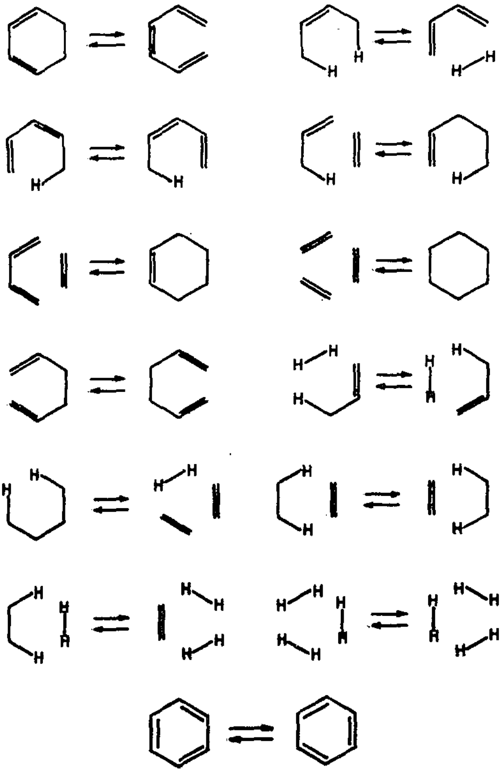
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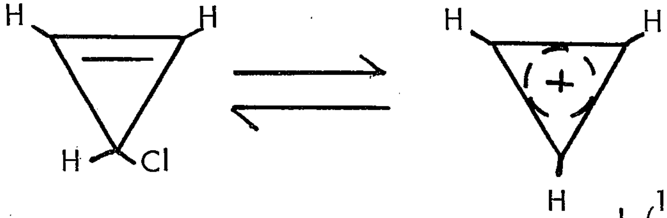
RECENT STUDIES OF CONJUGATED SYSTEMS

Ronald Breslow

Tetrachlorocyclopropene + tri-n-butyltin hydride ⟶

trichlorocyclopropenes → dichlorocyclopropenes → monochlorocyclopropenes

1,3 $\rightleftharpoons$ 3,3-dichlorocyclopropenes $\xrightarrow{H_2O}$ cyclopropenone



J (^{13}C-H) = 265 Hz

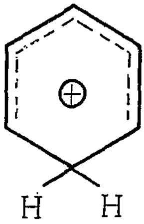
R. Breslow and G. Ryan, JACS, 89, 3073 (1967).

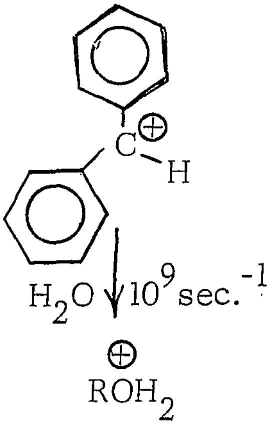
R. Breslow, J. Groves and G. Ryan, JACS, 89, 5048 (1967).

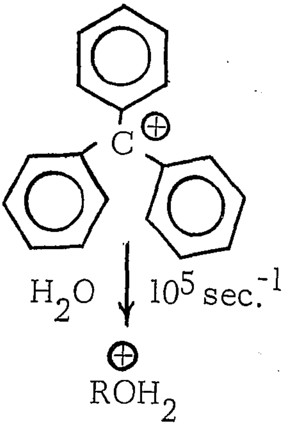
NEIGHBORING GROUPS
AND
NONCLASSICAL IONS

S. Winstein

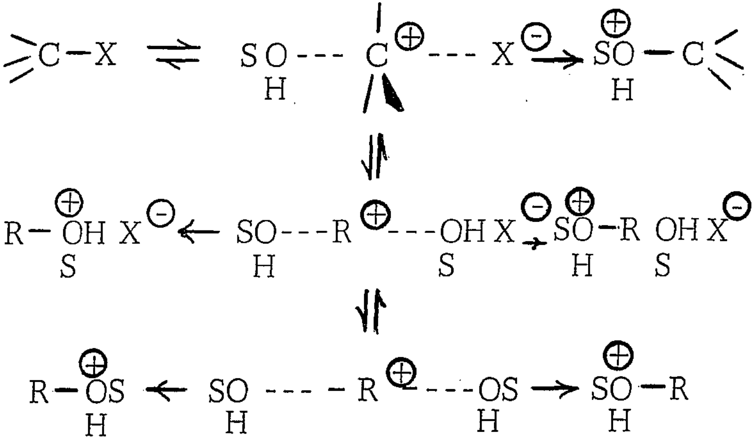
Examples of classical cations:







In solvolysis of simple primary and secondary derivatives, it is especially important to recognize that the intermediates are encumbered.



Such derivatives solvolyze with ca. 100% inversion in the more common solvolyzing solvents. Examples are: