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

AUSPICES OF THE DIVISION OF ORGANIC CHEMISTRY
FLORIDA STATE UNIVERSITY

June 17–21, 1973
Tallahassee, Florida

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

Tallahassee, Florida
June 17–21, 1973

Auspices of the

Division of Organic Chemistry

and the

Florida State University
Department of Chemistry

In cooperation with

The Florida State University
Division of Continuing Education

Speakers at the Twenty-Third National Organic Chemistry Symposium

P.D. Bartlett

O.L. Chapman

M.J.S. Dewar

W.S. Johnson

J. Kochi

J.C. Martin

G. Stork

E.C. Taylor

B. Trost

G.M. Whitesides

PROGRAM

SUNDAY, JUNE 17

Registration:	At your place of residence or at Longmire Lounge 2:00 P.M. to 10:00 P.M.

MONDAY, JUNE 18

Registration:	Longmire Lounge
Meetings:	Ruby Diamond Auditorium
9:00 A.M.	Welcome Address
	Response. ANDREW STREITWIESER, Chairman Division of Organic Chemistry, ACS
9:30 A.M.	W.S. JOHNSON, "Some Recent Developments in Non-Enzymic Biogenetic-like Olefin Cyclizations"
10:30 A.M.	Discussion of Paper 1: ERNEST ELIEL presiding
11:00 A.M.	M.J.S. DEWAR, "Molecular Orbital Theory as a Chemical Tool"
12:00 Noon	Discussion of Paper 2: ERNEST ELIEL presiding
8:00 P.M.	O.L. CHAPMAN, "Photochemical Studies at Low Temperature"
9:00 P.M.	Discussion of Paper 3: ANTHONY M. TROZZOLO presiding

TUESDAY, JUNE 19

Registration:	Longmire Lounge
Meetings:	Ruby Diamond Auditorium
9:00 A.M.	E.C. TAYLOR, "Thallium in Organic Synthesis"
10:00 A.M.	Discussion of Paper 4: STANLEY CRISTOL presiding
10:30 A.M.	G.M. WHITESIDES, "Studies in Organometallic Chemistry"
11:30 A.M.	Discussion of Paper 5: STANLEY CRISTOL presiding
8:00 P.M.	GEORG WITTIG, Roger Adams Award Address "From Diyls over Ylids to my Idyll"
	ANDREW STREITWIESER presiding
9:30 P.M.	Social Hour

WEDNESDAY, JUNE 20

Registration:	Longmire Lounge
Meetings:	Ruby Diamond Auditorium
9:00 A.M.	B. TROST, "Innovations in Organic Syntheses"
10:00 A.M.	Discussion of Paper 6: WILLIAM SHEPPARD presiding
10:30 A.M.	J. KOCHI, "Organocopper, Silver and Gold Species in Catalytic, Oxidation and Reduction Processes"
11:30 A.M.	Discussion of Paper 7: WILLIAM SHEPPARD presiding
8:00 P.M.	J.C. MARTIN, "The Organic Chemistry of Sulfuranes, Sulfurane Oxides and Related Hypervalent Species"
9:00 P.M.	Discussion of Paper 8: EDWARD M. BURGESS presiding

THURSDAY, JUNE 21

Registration:	Longmire Lounge
Meetings:	Ruby Diamond Auditorium
9:00 A.M.	G. STORK, "New Organic Synthetic Methods"
10:00 A.M.	Discussion of Paper 9: JEREMIAH P. FREEMAN presiding
10:30 A.M.	P.D. BARTLETT, "The Resolution of Mechanisms in Cycloaddition"
11:30 A.M.	Discussion of Paper 10: JEREMIAH P. FREEMAN presiding

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 Georg Wittig of the Institut für Organische Chemie der Universität Heidelberg. His award address is entitled, "From Diyls over Ylids to my Idyll."

Georg Wittig

FLORIDA STATE UNIVERSITY COMMITTEES

Executive	J. Saltiel
Auditorium and Facilities	D. DeTar
Registration	J. Leffler
Housing and Meals	M. Schwartz
Transportation	H. Walborsky
Recreation and Entertainment	R. Dougherty W. Herz

DIVISION OF ORGANIC CHEMISTRY

The plans and program of the Twenty-third 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.

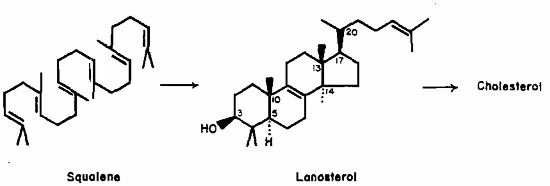
	1971-1972	1972-1973
Chairman	J.A. Berson	A.J. Streitwieser
Chairman-elect	A.J. Streitwieser	E.L. Eliel
Secretary-Treasurer	J.P. Freeman	J.P. Freeman
Secretary-Treasurer-Elect		E.M. Burgess
National Symposium Executive Officer	N.J. Turro	N.J. Turro
Executive Committee	M. Caserio J.C. Martin R. Petit A.M. Trozzolo	C.J. Collins W.A. Sheppard M.C. Caserio J.C. Martin
Councilors	S.J. Cristol N.A. LeBel	S.J. Cristol N.A. LeBel
Alternate Councilors	F.G. Bordwell H. Goering	F.G. Bordwell H. Goering

CONTENTS

SOME RECENT DEVELOPMENTS IN NON-ENZYMIC BIOGENETIC-LIKE OLEFIN CYCLIZATIONS

W.S. Johnson

One of the most important and exciting achievements of modern chemistry has been the elucidation, in extraordinary detail, of the elaborate pathway by which cholesterol is biologically synthesized from acetate.[1] This accomplishment is without parallel, in view of the magnitude of the structural as well as stereochemical complexities that are implicated.



Of all the stages involved in the biogenesis of cholesterol, there is one transformation which is of outstanding interest, particularly to the organic chemist: namely that in which the open-chain polyolefin, squalene, undergoes (enzyme-catalyzed) polycyclization to produce the tetracyclic substance, lanosterol. Particularly impressive about this process is the fact that this substrate, which has no centers of asymmetry, is thus converted into a product with no less than seven asymmetric centers (at C-3, -5, -10, -13, -14, -17, and -20), and although this product is theoretically capable of existing in 128 different stereochemical forms, only a single isomer is produced in the biosynthesis. This is a truly impressive example of a completely stereoselective process.

MOLECULAR ORBITAL THEORY AS A CHEMICAL TOOL

Michael J.S. Dewar

MOLECULAR ORBITAL THEORY AS A CHEMICAL TOOL

Michael J.S. Dewar

While the present theory of structure and reactivity in organic chemistry rests on the results of simple MO theory, it is only quite recently that any real prospects have opened for more quantitative applications. If the results of quantum mechanical calculations were sufficiently accurate and reliable, they would be of major practical value in two main connections. First, prediction of the properties of transient intermediates (e.g. carbonium ions) whose structures often cannot be determined by available experimental techniques. Secondly, the prediction of reaction paths and the properties of transition states, these again not being directly observable.

To be useful in these connections, the calculations must be applicable to molecules of all kinds and must be of "chemical" accuracy; i.e. the errors in heats of atomization, bond lengths, and bond angles should be at most of the order of 1 kcal/mole, 0.01 Å, and 1° respectively and force constants should be reproduced to a few percent.(1)

(1) For detailed arguments see M.J.S. Dewar and E. Haselbach, J.Amer.Chem.Soc., 92, 590 (1970); M.J.S. Dewar, Fortsch.der chem. Forsch., 23, 1 (1971).

The calculations must also be feasible at reasonable cost, this including the computer time needed to optimize the entire geometry, for molecules of reasonable size, i.e. at least a dozen atoms other than hydrogen. (2)

(2) The optimization of geometries is essential Our studies have shown that even the most innocuous-seeming assumptions, e.g. that all C(sp^3)-H bond lengths (not angles) are equal, is sufficient to produce errors that are intolerable in a chemical sense.

PHOTOCHEMICAL STUDIES AT LOW TEMPERATURE

O.L. Chapman

PHOTOCHEMICAL STUDIES AT LOW TEMPERATURE

O. L. Chapman

Department of Chemistry, Iowa State University, Ames, Iowa

Three goals have been set for our low temperature photochemistry studies.

1. Identification of primary photoproducts.
2. Synthesis of highly reactive molecules of theoretical interest.
3. Utilization of highly reactive molecules in the synthesis of structurally complex molecules.

In achieving these goals, the major difficulty lies in determination of product structure. This difficulty becomes acute in rare gas matrix experiments (5-20° K). The methods we have used are listed below.

1. Spectroscopic observation
2. Mass spectra of volatile products
3. Chemical behavior of reactive molecules on warming

THALLIUM IN ORGANIC SYNTHESIS

E.C. Taylor

Thallium in Organic Synthesis

Edward C. Taylor
Princeton University

The discovery of thallium in 1861 did not, unlike the discovery of many elements, represent a milestone in the development of modern chemistry. Investigations of thallium and its compounds proceeded rather slowly and, during the first half of the present century, led to relatively unspectacular results. The organic chemist regarded thallium as an obscure toxic metal, organothallium chemistry as dull and predictable, and the utility of organothallium compounds in organic chemistry as virtually non-existent. However, these attitudes are now no longer tenable, largely as a result of an intensive collaborative study of thallium chemistry initiated some five years ago at Princeton University and at the University of East Anglia. More than 70 specific and often unique synthetic transformations based on the use of thallium reagents have now been discovered.*

This lecture will discuss recent developments in Tl^{+3}-mediated aromatic substitution reactions and oxidations of olefins, enols, and pyrazolones.

All of the work described in this lecture was carried out in collaboration with DR. ALEXANDER MCKILLOP of the University of East Anglia.

---

* See A. McKillop and E. C. Taylor, Chemistry in Britain, 9, 4 (1973).

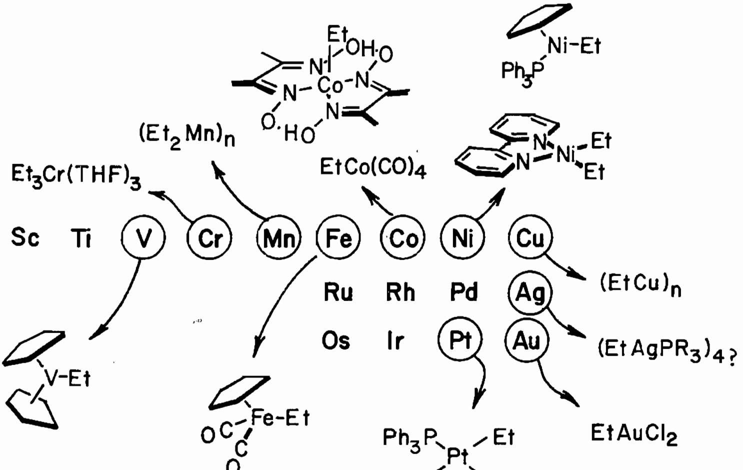
STUDIES IN ORGANOMETALLIC CHEMISTRY

G.M. Whitesides

Among the present concerns of organometallic chemistry is the development of new methods for catalytic and stoichiometric organic synthesis. This lecture will touch on several subjects that are pertinent to rational development of these methods, particularly factors determining the stability of transition metal organometallic compounds, and the influence of aggregation on certain reactions of organometallic reagents.

Thermal Decomposition of Transition Metal Organometallic Compounds.

Alkyl derivatives of a large number of the transition metal ions have been prepared. In general, additional ligands are required to lend thermal stability to these substances, and the nature and number of these ligands leading to maximum thermal stability is not clearly understood. Representative examples of stable metal alkyls are the following:



FROM DIYLS OVER YLIDS TO MY IDYLL

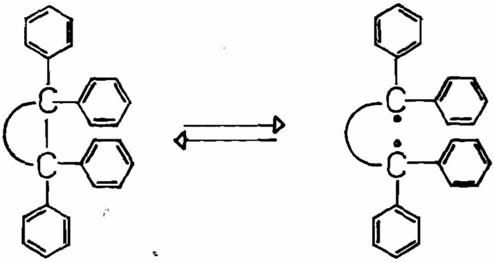
Georg Wittig

From Diyls over Ylids to My Idyll

Georg Wittig

Today I have the pleasant task of sketching for you the course over which my research has traversed during the past fifty years. In brief, I might describe the pathway taken as "from diyls, over ylids and ate complexes, to my idyll". In the description that now follows, I shall choose to emphasize those particular facets of my work which arose from the interaction of chance with intention.

The starting point of my presentation will be those diradicals (diyls, for short) which we synthesized in an effort to assess the influence of ring strain on intramolecular coupling.



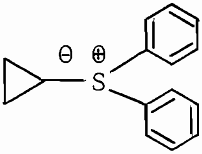
INNOVATIONS IN ORGANIC SYNTHESES

B. Trost

Innovations in Organic Synthesis

Barry M. Trost

The synthesis of complex organic molecules requires the continuing development of new approaches and new reactions. In the latter case, new synthetic reagents offer the possibility of a novel chemical transformation allowing fresh approaches to the design of chemical synthesis. Diphenylsulfoniumcyclopropylides appear to be such versatile reagents. These reagents have generated new oxaspiropentane and cyclobutanone syntheses from which have evolved the processes of cyclopentane annelation, lactone annelation, secoalkylation, and geminal alkylation.



ORGANOCOPPER, SILVER AND GOLD SPECIES
IN
CATALYTIC, OXIDATION AND REDUCTION PROCESSES

J. Kochi

The coinage metals and their complexes, particularly copper, are involved in a variety of catalytic reactions of organic substrates. The catalysis may involve the metal: (i) as a σ-Lewis acid in Friedel-Crafts and related reactions,[1] (ii) in a π-coordinative capacity particularly in reactions of alkenes, e. g., cyclopropanation with diazo compounds,[2] or (iii) as a redox couple in which the metal fluctuates between several discrete oxidation states.[3]

Oxidation and reduction proceeding via these mechanistic categories may be classified essentially as heterolytic or homolytic processes. However, the differentiation between them may be somewhat arbitrary, since the actual timing involved in making and breaking bonds can be difficult to assess. Reactive intermediates are not always readily detected, since stereospecific reactions can result from within the coordination sphere of the metal catalyst and it will be difficult to follow the changes in oxidation states of the metal nucleus.

To probe such processes, we have focussed our attention primarily on the alkyl-metal intermediates and examined their chemical properties. As a group, the coinage metals commonly exist in three oxidation states: M^{I} (d^{10}), M^{II} (d^{9}) and M^{III} (d^{8}), the redox potentials (eV in aqueous solution) of which are listed below:

M^{o}	M^{I}	M^{II}	M^{III}
Cu($3d^{10}$, 4s)	0.52	0.15	4×10^{4} sec^{-1}
Ag($4d^{10}$, 5s)	0.80	1.98	> 2.2
Au($5d^{10}$, 6s)	1.7	[unstable]	1.5 (3e)

The following disproportionation equilibria are established in the absence of stabilizing ligands:

THE ORGANIC CHEMISTRY OF SULFURANES, SULFURANE OXIDES AND RELATED HYPERVALENT SPECIES

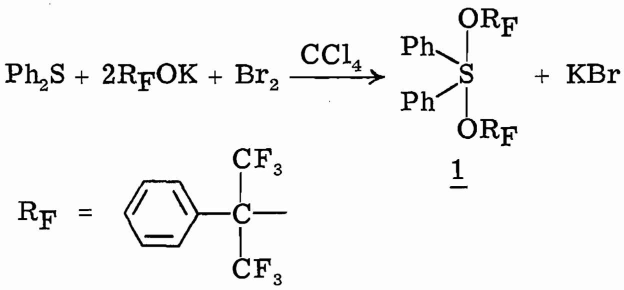
J.C. Martin

THE ORGANIC CHEMISTRY OF SULFURANES AND RELATED HYPERVALENT SPECIES

J. C. Martin

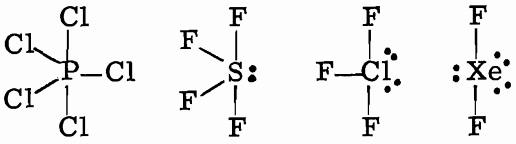
Department of Chemistry, University of Illinois
Urbana, Illinois 61801

We have isolated and studied a number of organic tetracoordinate sulfur (IV) species which can be considered ketal analogs of sulfoxides. Most extensive study has been accorded dialkoxydiphenylsulfurane <u>1</u>.[1] Removal of KBr by filtration of the reaction mixture from the above reaction leaves a solution from which the sulfurane can be isolated in high yield as a colorless crystalline material, stable indefinitely at room temperature in the absence of moisture.



1

Hypervalent species such as 1, in which the valence shell of some atom has been expanded beyond the usual closed shell configuration, have been known for many years.



NEW ORGANIC SYNTHETIC METHODS

G. Stork

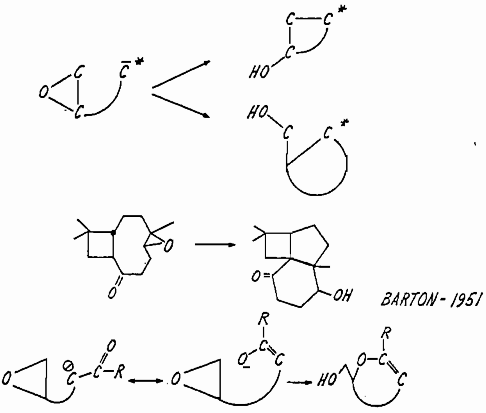
NEW ORGANIC SYNTHETIC METHODS

Gilbert Stork

Department of Chemistry, Columbia University
New York, New York 10027

The lecture will focus on four new synthetic methods which have been under study in the author's laboratory.

The first involves the cyclization of epoxynitriles, a method which turns out to be of some generality. A particularly interesting feature is that the method provides a non photochemical synthesis of four-membered rings.



THE RESOLUTION OF MECHANISMS IN CYCLOADDITION

P.D. Bartlett

The Resolution of Mechanisms in Cycloaddition

Paul D. Bartlett

The establishment of clear examples of pure concerted, dipolar ionic, and biradical reaction mechanisms has been followed by a stage in which the frequent occurrence of plural reaction paths has become evident, and it becomes important to understand the factors that predispose a particular pair of reactants to react by one or another of these mechanisms.

When a direct concerted reaction mechanism is forbidden, the result may be (1) failure to react, (2) reaction with the configurational result of the easiest allowed concerted pathway, or (3) reaction in part or entirely by a stepwise sequence. In cycloaddition, perhaps unlike sigmatropy, the third is the most common occurrence.

A theoretically possible way of accounting for partial configuration loss in cycloaddition might be to postulate the allowed (2_s+2_a) mechanism, with the antarafacial role divided between the reactant whose configuration is observed and the other reactant. Such a hypothesis is subject to test where both reactants have known configuration, as in the addition of 1,2-dichloro-1,2-difluoroethylene (1212) to trans-cyclooctene (R. Wheland, next two pages). It is evident that the high retention of configuration by the trans-cyclooctene is not coupled to corresponding inversion in the 1212.

A more subtle question arises in the 1,4-addition of reagents noted for their ability to initiate biradical mechanisms leading to (2+2) cycloaddition.