

TWENTIETH NATIONAL ORGANIC
CHEMISTRY SYMPOSIUM
of the
AMERICAN CHEMICAL SOCIETY

AUSPICES OF THE DIVISION OF ORGANIC CHEMISTRY
THE UNIVERSITY OF VERMONT
and the
WESTERN VERMONT SECTION OF THE ACS



June 18-22, 1967
Burlington, Vermont

TWENTIETH NATIONAL ORGANIC
CHEMISTRY SYMPOSIUM
of the
AMERICAN CHEMICAL SOCIETY

Speakers at the Twentieth National Organic Symposium



F. A. L. Anet



O. L. Chapman



G. L. Closs



G. S. Hammond



H. O. House



R. Pettit



R. B. Woodward



P. R. Schleyer



H. E. Simmons

Pettit
1967

PROGRAM

SUNDAY, JUNE 18

Registration: Patrick Gymnasium, 2:00-11:00 P.M.

MONDAY, JUNE 19

Registration and Meetings: Patrick Gymnasium

- 9:00 A.M. Welcome. CLINTON D. COOK, Vice President, University of Vermont Response. GILBERT STORK, Chairman, Division of Organic Chemistry, ACS
- 9:30 A.M. PAUL von R. SCHLEYER, "Structure and Reactivity in Carbonium Ion Reactions"
- 11:00 A.M. R. PETTIT, "The Chemistry of Cyclobutadiene-Iron Carbonyl Complexes"
- 8:00 P.M. "Chemical Approaches to Enzyme Mechanisms"
WILLIAM P. JENCKS, "Acetoacetyl-CoA: Succinate Coenzyme A Transferase"
E. T. KAISER, "Enzyme Chemistry of Highly Reactive Cyclic Esters"

TUESDAY, JUNE 20

- 9:00 A.M. HOWARD E. SIMMONS, "Macrocyclic Amines"
- 10:30 A.M. G. L. CLOSS, "Mechanisms of Carbenoid Reactions"
- 8:00 P.M. JOHN D. ROBERTS, Roger Adams Award Address, "Some Problems Relating to the Calculation of Steric Effects in Simple Molecules"
- 9:30 P.M. Social Hour

WEDNESDAY, JUNE 21

- 9:00 A.M. F. A. L. ANET, "Conformational and Valency Isomerism in Eight-Membered Rings"
- 10:30 A.M. HERBERT O. HOUSE, "A Study of Some Reactions of Organomagnesium Compounds"
- 8:00 P.M. R. B. WOODWARD, "Recent Advances in the Chemistry of Natural Products"

THURSDAY, JUNE 22

- 9:00 A.M. O. L. CHAPMAN, "Photocycloaddition Processes"
- 10:30 A.M. GEORGE S. HAMMOND, "The Life and Times of an Excited Molecule"

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 Synthesis, 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 John D. Roberts of the California Institute of Technology. His award address is entitled "Some Problems Relating to the Calculation of Steric Effects in Simple Molecules."



J. D. Roberts

VERMONT COMMITTEES

Executive	W. N. White, Chairman A. P. Krapcho, M. E. Kuehne	
Registration.	W. N. White, A. P. Krapcho	
Housing	J. H. Waters	
Auditorium	G. C. Crooks, T. B. Flanagan	
Transportation.	C. A. Wulff, M. E. Kuehne	
Recreation and Entertainment.	R. C. Woodworth, D. C. Gregg, M. H. Gianni	
Chairman of the Western Vermont Section	W. N. White	

Division of Organic Chemistry

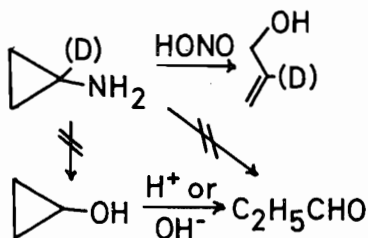
The plans and program of the Twentieth National Organic Chemistry Symposium have been developed by the members of the Executive Committee of the Division of Organic Chemistry who have served during the past two years.

	1965-1966	1966-1967
Chairman	H. O. House	Gilbert Stork
Chairman- Elect	Gilbert Stork	Harry H. Wasserman
Secretary	Norman A. LeBel	Norman A. LeBel
National Symposium Officer	F. G. Bordwell	F. G. Bordwell
Executive Committee	Ronald Breslow Andrew Streitwieser Cheves Walling Harry H. Wasserman	Ronald Breslow Ernest L. Eliel William D. Emmons Andrew Streitwieser

STRUCTURE AND REACTIVITY IN CARBONIUM
ION REACTIONS

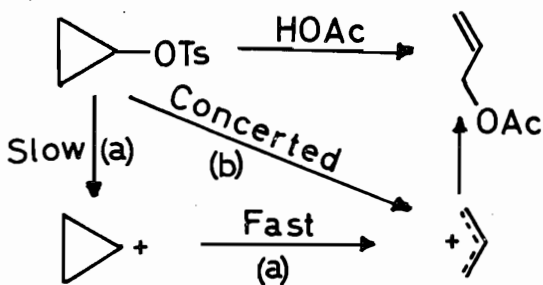
Paul von R. Schleyer

THE CYCLOPROPYL CATION-OLD PROBLEM!



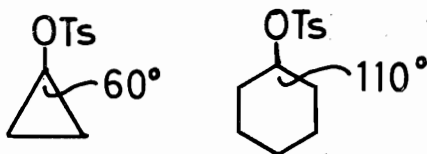
Kischner -1905
 P. Lipp, et al -1932
 Corey, Atkinson-
 (with D) 1964

POSSIBLE ACETOLYSIS MECHANISMS



Roberts, Chambers (1951) chose (a)

CYCLOPROPYL ACETOLYSIS RATE



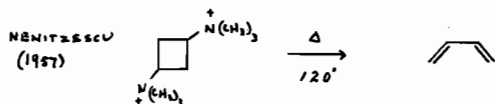
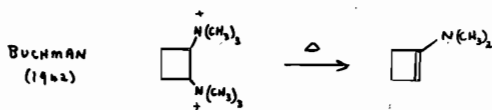
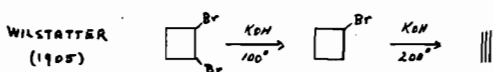
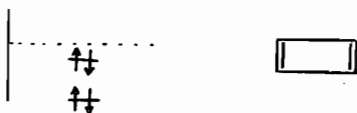
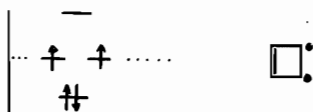
rel. rates 10^{-5}

1

Slow rate - stepwise mechanism?

THE CHEMISTRY OF CYCLOBUTADIENE-IRON
CARBONYL COMPLEXES

R. Pettit



LONGUET-HIGGINS & ORGEL (1956)

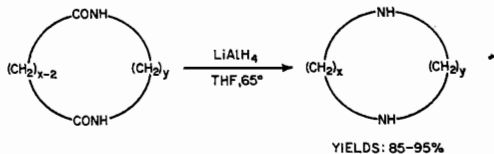
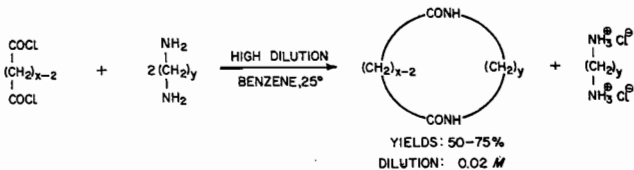


c.f.



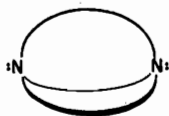
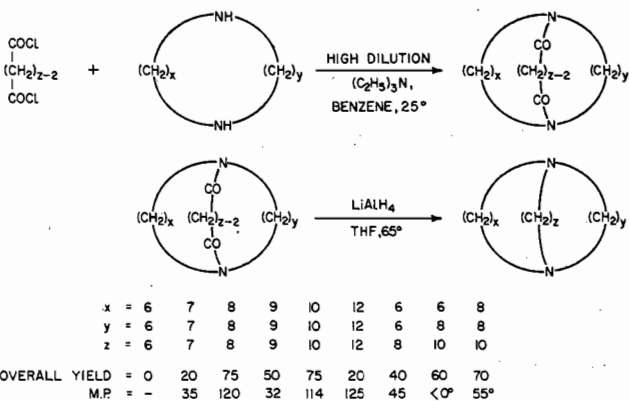
MACROBICYCLIC AMINES

Howard E. Simmons

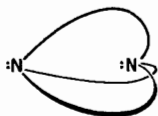


x = 6 7 8 9 10 12 6
y = 6 7 8 9 10 12 10

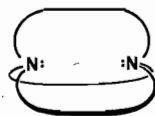
Method of Stetter



S₀₀



S_{0i}



S_{ij}

$$\text{SHAPE}_n = \sum_a C_n^{(a)}$$

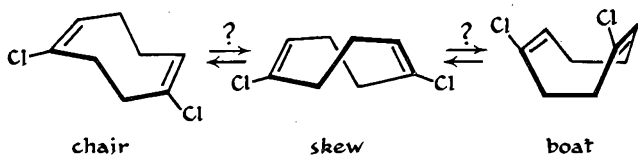
MECHANISMS OF CARBENOID REACTIONS

G. L. Closs

SOME PROBLEMS RELATING TO
THE CALCULATION OF STERIC EFFECTS
IN SIMPLE MOLECULES

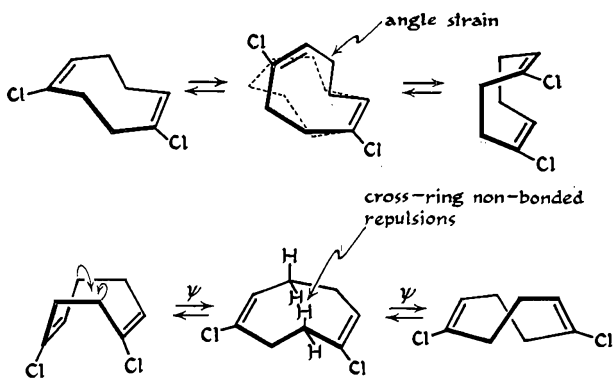
John D. Roberts

1,6-Dichloro-1,5-cyclooctadiene



$\mu = 2.60 \text{ D}$, indicates boat-like form

(Roberts, 1950)

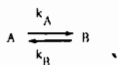


Estimated $E_a(\text{max})$ $\left\{ \begin{array}{l} \text{chair} \rightleftharpoons \text{boat} \quad \sim 9 \text{ kcal} \\ \text{boat} \rightleftharpoons \text{skew} \quad 3-14 \text{ kcal} \end{array} \right.$

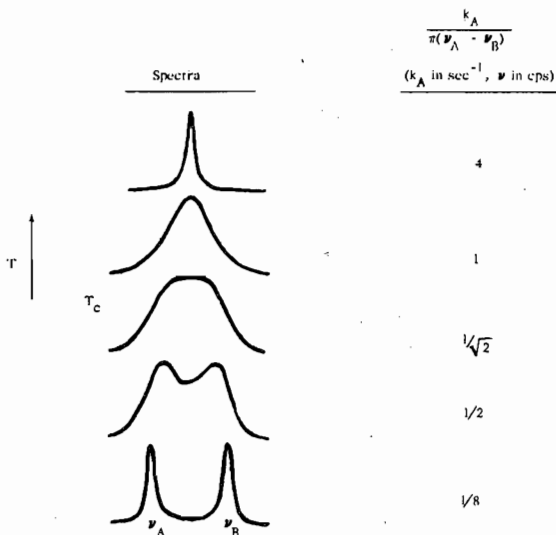
CONFORMATIONAL AND VALENCY ISOMERISM
IN EIGHT-MEMBERED RINGS

F. A. L. Anet

EFFECT OF RATES ON NMR SPECTRA



For equal populations: $k_A = k_B$



For more complex systems see:

C. S. Johnson Jr., *Advan. Magnetic Resonance*, 1, 33 (1965);

L. W. Reeves, *Advan. Phys. Org. Chem.*, 3, 187 (1965).

T_c C	ΔF^\ddagger (kcal / mole) at T_c	
	$\nu_A - \nu_B = 20$ cps	$\nu_A - \nu_B = 1,000$ cps
0	13.9	11.8
-90	9.2	7.8
-120	7.7	6.5
-140	6.6	5.6
-160	5.6	4.7
-180	4.6	3.8

A STUDY OF SOME REACTIONS OF
ORGANOMAGNESIUM COMPOUNDS

Herbert O. House

ETHER SOLUTIONS OF ORGANOMAGNESIUM REAGENTS

REAGENT	NMR (cps above TMS)	APPARENT DEGREE OF ASSOCIATION
$\text{Br-CH}_2\text{CH}_2\text{-Br} \longrightarrow \text{MgBr}_2$	---	1.09-1.62 (0.002-0.13M) ^{a,b}
$\text{CH}_3\text{Br} \longrightarrow \text{CH}_3\text{MgBr}$	92.5 cps ($J_{13\text{C-H}}$ 107 cps)	---
$\text{CH}_3\text{I} \longrightarrow \text{CH}_3\text{MgI}$	92 cps	---
$(\text{CH}_3)_2\text{Hg} \longrightarrow (\text{CH}_3)_2\text{Mg}$	83-90 cps ($J_{13\text{C-H}}$ 105.5 cps) (0.8-0.03M, 33 to -54°)	1.20-1.28 (0.13M)
$\text{CH}_3\text{Br} \longrightarrow \text{CH}_3\text{Li}$	111-114 cps ($J_{13\text{C-H}}$ 97 cps)	4.0°
$\text{CH}_3\text{CH}_2\text{Br} \longrightarrow \text{CH}_3\text{CH}_2\text{MgBr}$	41 cps	1.04-1.96 (0.004-0.5M) ^{a,b,d}
$(\text{CH}_3\text{CH}_2)_2\text{Hg} \longrightarrow (\text{CH}_3\text{CH}_2)_2\text{Mg}$	37-42.5 cps (35 to -34°)	1.00-1.18 (0.002-0.3M) ^{a,b}

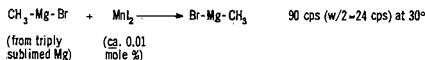
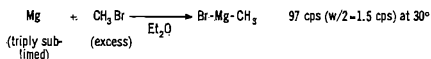
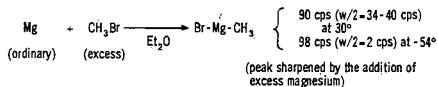
^aM. B. Smith and W. E. Becker, *Tetrahedron*, **22**, 3027 (1966).

^bA. D. Vreugdenhil and C. Blomberg, *Rec. Trav. Chim.*, **82**, 453 (1963).

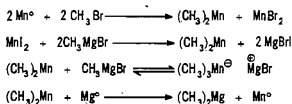
^cL. M. Seitz and T. L. Brown, *J. Am. Chem. Soc.*, **88**, 4140 (1966);
K. C. Williams and T. L. Brown, *ibid.*, **88**, 4134 (1966).

^dE. C. Ashby and M. B. Smith, *J. Am. Chem. Soc.*, **86**, 4363 (1964).

EFFECT OF MANGANESE ON THE NMR SIGNAL OF
METHYLMAGNESIUM DERIVATIVES

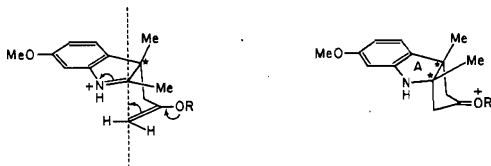
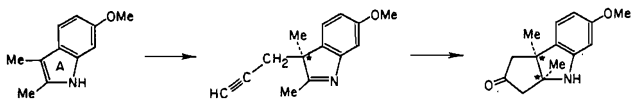
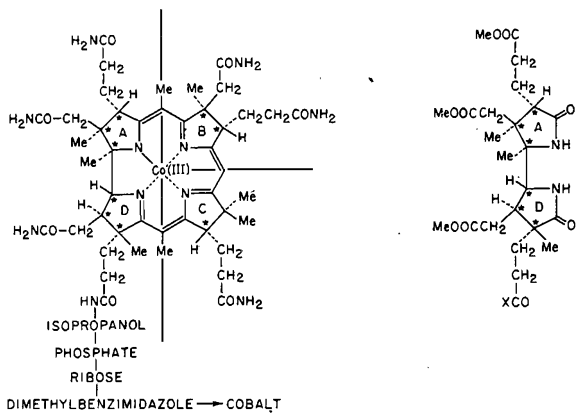


POSSIBLE INTERPRETATION



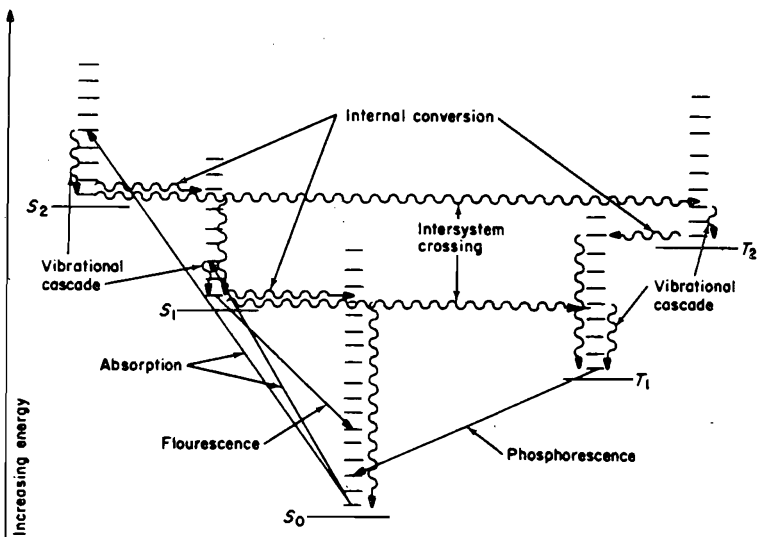
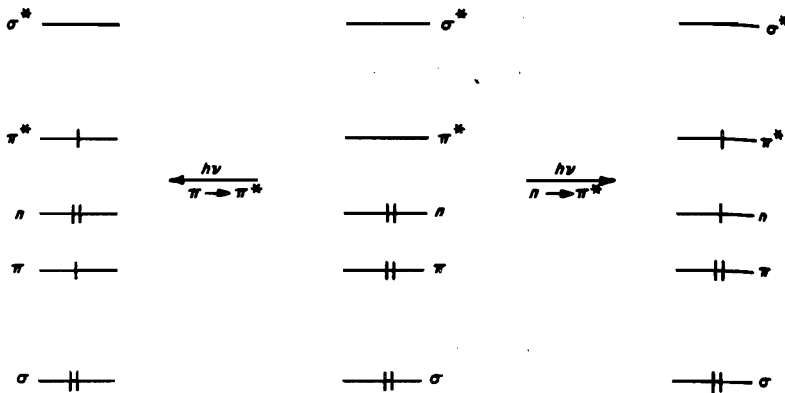
RECENT ADVANCES IN THE CHEMISTRY OF
NATURAL PRODUCTS

R. B. Woodward



PHOTOCYCLOADDITION PROCESSES

O. L. Chapman



THE LIFE AND TIMES OF AN
EXCITED MOLECULE

George S. Hammond

A Mechanism for Photosensitized Reactions

