FIFTEENTH NATIONAL ORGANIC

CHEMISTRY SYMPOSIUM

of the

AMERICAN CHEMICAL SOCIETY

AUSPICES OF THE DIVISION OF ORGANIC CHEMISTRY OF THE A.C.S.,

THE UNIVERSITY OF ROCHESTER

AND THE ROCHESTER SECTION OF THE A.C.S.

★

June 17-20, 1957

Rochester, New York

FIFTEENTH NATIONAL ORGANIC

CHEMISTRY SYMPOSIUM

of the

AMERICAN CHEMICAL SOCIETY

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Headquarters and Registration—Men's Dining Hall, University of Rochester.

Sunday, June 16, Noon to Midnight

Monday, June 17, 7:00 A.M. to Midnight

Tuesday, June 18, 7:00 A.M. to Midnight

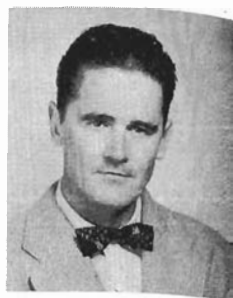Wednesday, June 19, 8:00 A.M. to 3:00 P.M.

Meetings—Strong Auditorium

Speakers at the Fifteenth National Organic Chemistry Symposium

H. C. Brown	D. Y. Curtin	D. J. Cram
W. G. Dauben	C. Djerassi	C. R. Hauser
W. E. Parham	C. C. Price	R. W. Taft, Jr.
E. E. Van Tamelen	S. Winstein	R. B. Woodward

Program

Monday, June 17

10:00 a.m.   Welcome. Cornelis W. deKiewiet, President, The University of Rochester.
Response. John D. Roberts, Chairman, Division of Organic Chemistry, A.S.C.

10:30 a.m.   CHARLES R. HAUSER. The Ortho Substitution Rearrangement and Related Reactions.

11:30 a.m.   Discussion of Paper 1.

2:00 p.m.   CARL DJERASSI. Application of Optical Rotatory Dispersion Studies to Structural and Stereochemical Problems in Organic Chemistry.

3:00 p.m.   Discussion of Paper 2.

3:30 p.m.   E. E. VAN TAMELEN. Recent Work in the Field of Natural Products.

4:30 p.m.   Discussion of Paper 3.

8:00 p.m.   ROBERT B. WOODWARD. Recent Advances in the Chemistry of Natural Products.

9:00 p.m.   Discussion of Paper 4.

Tuesday, June 18

9:00 a.m.   SAUL WINSTEIN. Neighboring Carbon and Hydrogen in Some Carbonium Ion Reactions.

10:00 a.m.   Discussion of Paper 5.

10:30 a.m.   ROBERT W. TAFT, JR. Polar Substituent Constants and Some Application.

11:30 a.m.   Discussion of Paper 6.

2:00 p.m.   HERBERT C. BROWN. A Quantitative Approach to Aromatic Substitution.

3:00 p.m.   Discussion of Paper 7.

3:30 p.m.   DAVID Y. CURTIN. Certain Aspects of the Chemistry of Cyclohexadienones.

4:30 p.m.   Discussion of Paper 8.

8:15 p.m.   Concert. The Curtis String Quartet.

9:30 p.m.   Social Hour.

Wednesday, June 19

Thursday, June 20

Rochester Committee

★

The University of Rochester and the Rochester
Section of the American Chemical Society are acting as hosts

Committees in Charge

General.. A. Weissberger
Registration, Mail, and Finance....................................J. R. Thirtle
Registration..R. W. Helmkamp
Transportation..R. E. Wing
Housing.. V. Boekelheide
Meals..D. S. Tarbell
Lecture Facilities...W. H. Saunders
Publicity..E. M. Crane
Plant Visits...D. D. Reynolds
Recreation..J. W. Gates, Jr.

Chairman of the Rochester Section— M.Gates (1956),

P. W. Vittum (1957)

Division of Organic Chemistry

The plans and program of the Fifteenth 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.

	1955-1956	1956-1957
Chairman	N. J. Leonard	J. D. Roberts
Chairman-elect	J. D. Roberts	M. S. Newman
Secretary	W. E. Parham	W. E. Parham
	T. L. Jacobs	T. L. Jacobs
	C. C. Price	C. C. Price
	T. Cairns	D. J. Cram
	J. Cason	D. Y. Curtin

An Invitation to Organic Chemists who are not members of the Division of Organic Chemistry

The Executive Committee of the Division of Organic Chemistry extends to you a cordial invitation to become a regular member of the division.

Each of the divisions of the American Chemical Society serves a field of specialization and the Organic Division endeavors to serve organic chemists by furthering organic chemistry. To that end, it wishes to have associated with it as many organic chemists as possible.

The requirements for divisional membership are: (1) membership in the American Chemical Society, (2) active interest in organic chemistry, and (3) payment of annual dues of $1.50. These dues are used to pay the expenses involved in the activities of the division which are:

1. Mailing of notices and forms for the presentation of papers at the Spring and Fall Meetings of the A.C.S.

2. Lithoprinting and distributing to members abstracts of the papers to be presented, in advance of the national meetings.

3. Arranging for National Symposia on organic chemistry. These are held every two years and the speakers and program are determined by the members of the Organic Division.

4. Establishing and promoting policies vital to the advancement of organic chemistry.

If you wish to become a regular member of the Organic Division, all that is necessary is to give or send your name, mail address, and $1.50 to:

> WILLIAM E. PARHAM, *Secretary*
> Organic Division, A.C.S.
> Department of Chemistry
> University of Minnesota
> Minneapolis 14, Minnesota

Extra copies of this Symposium Abstract Booklet can be obtained at $1.00 each from the Secretary. Abstracts of the 11th, 12th, 13th, but not the 14th, Symposia are also available at the same price.

THE ORTHO SUBSTITUTION REARRANGEMENT
## AND RELATED REACTIONS

Charles R. Hauser

This type of rearrangement was observed by Somme-
let in 1937 with benzhydryltrimethylammonium hydroxide,
and developed by Wittig and by the author and cowork-
ers. Our results will be discussed.

Part I

Sodium amide in liquid ammonia was shown to be
particularly suitable for effecting the rearrangement,
and evidence was presented for the mechanism represe-
nted below with the intermediate carbanion from benzy-
ltrimethylammonium ion (with S.W. Kantor, J. Am. Chem.
Soc., 73, 4122 (1951)).

95% yield
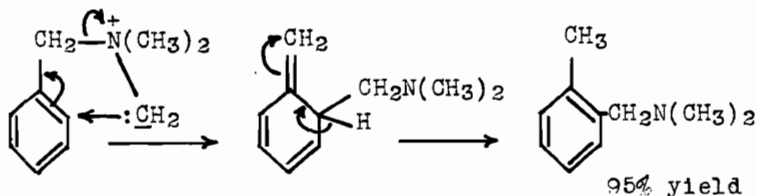
The analogous reaction of 2,4,6-trimethylbenzyl-
trimethylammonium ion with sodium amide in liquid am-
monia gave exo-methylenecyclohexadieneamine I which
cannot undergo the prototropic change; this product
was isolated in 70% yield by rapid steam distillation
of the alkaline reaction mixture (with D.N. Van Eenam,
J. Am. Chem. Soc., 78, 5698 (1956)).

I   (70%)

Calc'd. λ_{max} 313 mμ.
Found λ_{max} 313 mμ. (3.8)
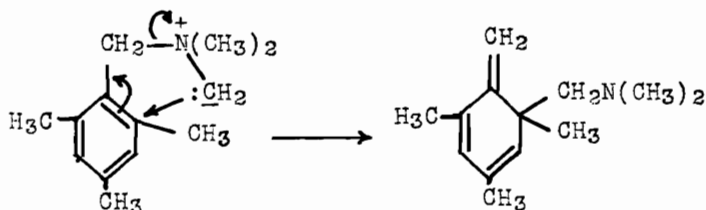
Exo-methyleneamine I underwent thermal isomeri-
zation to regenerate the aromatic ring; this 1,3-shift
appears to be dependent on solvent as well as temper-

APPLICATION OF OPTICAL ROTATORY DISPERSION

STUDIES TO STRUCTURAL AND STEREOCHEMICAL

PROBLEMS IN ORGANIC CHEMISTRY

Carl Djerassi

Rotatory dispersion represents simply the measurement of optical rotation at different wave lengths. Such measurements have been carried out since the time of Biot in the early nineteenth century but virtually all of the work in this field has been carried out by physical chemists -- concerned with the theory of this phenomenon -- rather than by organic chemists who might be interested in this method as an aid in the solution of organic problems. All of the important results up to 1935 have been summarized by one of the pioneers in this field, T. M. Lowry in his book "Optical Rotatory Power" (Longmans, Green and Co., London, 1935).

During the past three years nearly one thousand dispersion curves have been measured at Wayne State University and the results have demonstrated clearly that rotatory dispersion can be a powerful adjunct to organic chemical research. The lecture will be concerned with a survey of the scope of this method and its direct application to: (a) location of carbonyl groups in polycyclic systems; (b) analytical and kinetic problems; (c) detection of subtle conformational and stereochemical changes; (d) determination of absolute configuration.

For reasons outlined elsewhere (C. Djerassi and W. Klyne, Proc. Chem. Soc., 55 (1957)) it is preferable to employ a nomenclature system somewhat different from that used by physical chemists (see T. M. Lowry, loc. cit.). As shown in Fig 1., a plain curve is one lacking maxima, minima or inflections and is exhibited by substances which have no optically active absorption band within the spectral region examined. Such curves are of no particular utility for our purposes other than demonstrating that rotations are always larger in the ultraviolet than in the visible region (cf. conventional sodium D line at 589 mμ) and that rotations of substances with small $[\alpha]_D$ are best measured in the ultraviolet.
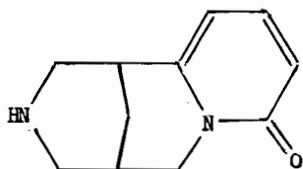
TOTAL SYNTHESIS OF LUPIN ALKALOIDS

E. E. van Tamelen
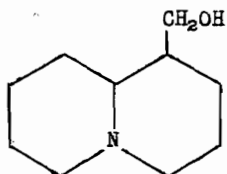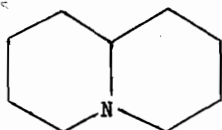
Synthesis: G. R. Clemo, W. McG.
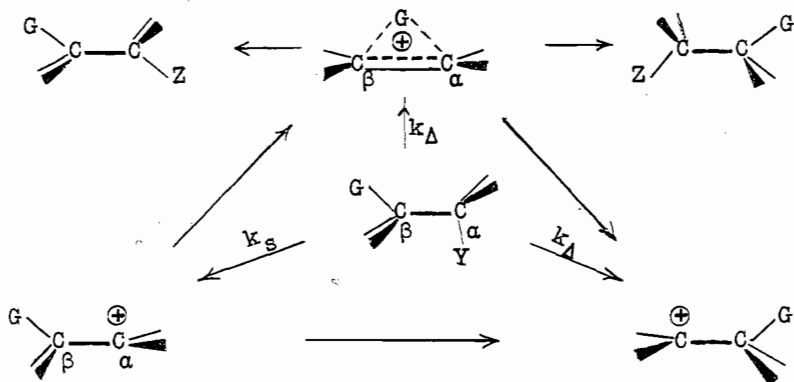Morgan, and R. Raper,
J. Chem. Soc., 965 (1937)

LUPININE

CAULOPHYLLINE
(N-methylcytisine)

RHOMBIFOLINE
(N-butenylcytisine)

CYTISINE

NEIGHBORING CARBON AND HYDROGEN IN SOME CARBONIUM ION REACTIONS

Saul Winstein

Neighboring Carbon or Hydrogen Participation in Solvolytic Substitution and Rearrangement

k_Δ

k_s

k_Δ

Competition Between Anchimerically Assisted and Unassisted Processes

| | | Assistance | |
		Anchimeric	Nuc. Solvent Partic.
	k_Δ	+	−
	k_s	−	+
	k_c	−	−

$$\frac{k_\Delta}{k_s} = \frac{(k_\Delta/k_c)}{(k_s/k_c)}$$

β-CH$_3$ increases
p-Anisyl $> C_6H_5$

EtOH $>$ AcOH $>$ HCOOH

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Polar Substituent Constants and Some Applications

Robert W. Taft, Jr.

The effect of structure on reactivity is analyzed for some systems which may be discussed in terms of the effect of a substituent on the reactivity of an adjoining reaction center.

Basic Assumption:

$$\log(k/k_0) = \text{polar effect} + \text{steric effect} + \text{resonance effect}$$

For rate of hydrolysis of esters, $RCO_2C_2H_5$,

polar substituent constant for group R relative to CH_3,

$$\sigma^* \equiv 1/2.48 \left[\log(k/k_0)_{OH^-} - \log(k/k_0)_{H^+} \right]$$

Assuming further that:

a.) $(\text{steric effect})_{OH^-} \cong (\text{steric effect})_{H^+}$

b.) $(\text{resonance effect})_{OH^-} \cong (\text{resonance effect})_{H^+}$

Additive Relationship of σ^* Values to Structure

R	σ^*	R	σ^*	R	σ^*
CH_3	0.00	CH_3	0.000	CH_3	0.000
CH_2Cl	+1.05	CH_3CH_2	-0.100	CH_2OH	+0.555
$CHCl_2$	+1.94	$(CH_3)_2CH$	-0.190	$CH_2C_6H_5$	+0.215
CCl_3	+2.65	$(CH_3)_3C$	-0.300	$CH(OH)C_6H_5$	+0.765

Methylene Reduction Factor

R	σ^*	R	σ^*	R	σ^*
CF_3	+2.78	$ClCH_2$	+1.050	C_6H_5	+0.600
CF_3CH_2	+0.92	$Cl(CH_2)_2$	+0.385	$C_6H_5CH_2$	+0.215
$CF_3(CH_2)_2$	+0.32	$CH_3CH=CH$	+0.360	$C_6H_5(CH_2)_2$	+0.080
$CF_3(CH_2)_3$	+0.12	$CH_3CH=CHCH_2$	+0.13	$C_6H_5(CH_2)_3$	+0.02

Steric Substituent Constant, $E_s \equiv \log(k/k_0) - \text{polar effect}$

(for unconjugated subst.) E_s Values and Structure

Ortho Substituted Benzoates
Van der Waals Radius

Subst.	$E_s - E_{s(F)}$	$R - R_F$	$\sigma^* - \sigma^*_{(F)}$
F	(0.00)	(0.00)	(0.00)
Cl	-0.31	0.45	-0.04
Br	-0.49	0.60	-0.03
CH_3	-0.49	0.65	-0.41
I	-0.69	0.80	-0.04

Aliphatic Series, $RCO_2C_2H_5$

R	E_s	σ^*	R	E_s
H	+1.24	+0.490	CH_3	0.00
CH_3	0.00	0.00	C_2H_5	-0.07
CF_3	-1.16	+2.78	$i-C_3H_7$	-0.47
$C(CH_3)_3$	-1.54	-0.30	$t-C_4H_9$	-1.54
CCl_3	-2.06	+2.65	$BrCH_2$	-0.27
CBr_3	-2.43	+2.65	Br_2CH	-1.85
$C(C_2H_5)_3$	-3.8	-0.36	Br_3C	-2.43

A QUANTITATIVE APPROACH TO
AROMATIC SUBSTITUTION

Herbert C. Brown

Directive effects in aromatic substitution have long been of interest to the organic chemist. The topic has been actively investigated since the early days of the structural theory. Moreover, the phenomena of aromatic substitution provided a proving ground for the electronic theory of organic chemistry in its days of infancy.

In view of the considerable effort which has been devoted to this subject in the past, it might not appear that the phenomena of directive effects should offer a particularly fruitful area for additional study. However, we became interested in the problem in the course of investigations dealing with the mechanism of Friedel-Crafts reactions.

Such reactions involving the further alkylation of mono-alkylaromatics, such as toluene, exhibit two anomalies.

1. In the presence of molar amounts of the Friedel-Crafts catalyst, the entering alkyl groups assumes a position almost exclusively meta with respect to the first alkyl substituent.

2. In the presence of catalytic quantities of the Friedel-Crafts catalyst, the entering alkyl group occupies all available positions, with little selectivity between meta and para orientation.

Thus Norris showed that the reaction of 1 mole of aluminum chloride and 1 mole of ethyl chloride with m-xylene gives 1,3-dimethyl-5-ethylbenzene almost exclusively. Condon demonstrated that the isopropylation of toluene in the presence of catalytic quantities of aluminum chloride in nitromethane yielded 37.5% o-, 29.8% m- and 32.7% p- isopropyltoluene.

The first of these orientation problems was resolved by McCaulay and Lien. They demonstrated that in the presence of molar quantities of catalyst, isomerization occurs to give the most stable (meta - orientated) σ-complex. However, Condon demonstrated that the high yields of the m-isopropyltoluene

CERTAIN ASPECTS OF THE CHEMISTRY OF CYCLOHEXADIENONES

David Y. Curtin

Cyclohexadienones in the p Claisen Rearrangement
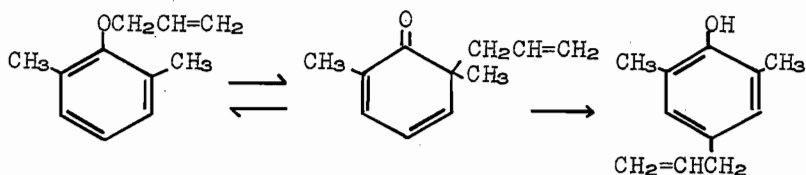
Hurd and Pollack, J. Org. Chem., 3, 550 (1939).

Mumm and Diedericksen, Ber., 72, 1523 (1939).

Dewar, "The Electron Theory of Organic Chemistry," Oxford University Press, London, 1949, p. 229.

Ryan and O'Connor, J. Am. Chem. Soc., 74, 5866 (1952).

Schmid, Haegele and Schmid, Experientia, 9, 414(1953; Helv. Chim. Acta, 37, 1080 (1954). Kalberer and Schmid, ibid., 40, 13 (1957).

Conroy and Firestone, J. Am. Chem. Soc., 75, 2530 (1953); ibid., 78, 2290 (1956).

Rhoads, Raulins and Reynolds, ibid., 75, 2531 (1953); 76, 3456 (1954).

Curtin and Johnson, ibid., 76, 2276 (1954); 78, 2611 (1956).

Marvell and Teranishi, ibid., 6165 (1954).

THE CONFORMATION AND CONFIGURATION OF POLYMER CHAINS

Charles C. Price

The geometry of polymer chains is one vital factor affecting the physical and chemical properties of polymers. The plastic, rubbery or fibre-forming properties of synthetic polymers and the important biological properties of such natural polymers as proteins and nucleic acids are in part due to the detailed conformation and configuration of the chains.

The preferred conformation of crystalline polymers has been worked out in some detail by X-ray analysis.

$$CH_2=C\overset{x}{\underset{y}{\diagup}} \longrightarrow \left(CH_2\overset{x}{\underset{y}{C}}\right)_n$$
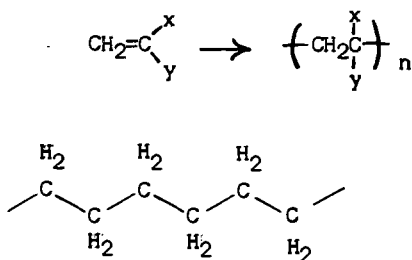
For crystalline polyethylene, the predicted repeat distance for a simple _trans_ zig-zag chain is 2.52 Å, precisely as observed.

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ULTRAVIOLET LIGHT INDUCED TRANSFORMATIONS IN ALICYCLIC SYSTEMS
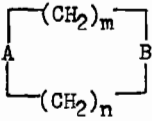
WILLIAM G. DAUBEN

1.

Ergosterol   Lumisterol

Calciferol   Tachysterol

2.

$$\text{Ergosterol} \xrightarrow[40°]{h\nu} \text{Calciferol}$$

$$\xrightarrow[0°]{h\nu} \text{Precalciferol} \xrightarrow[40°]{\triangle}$$
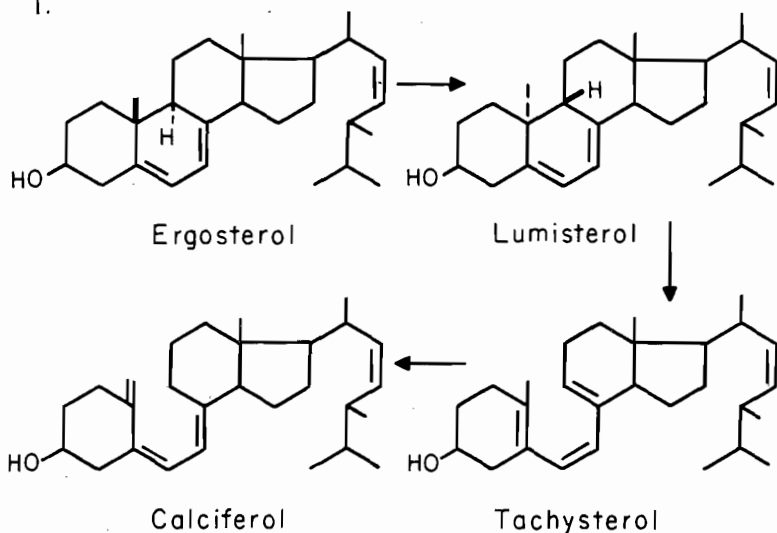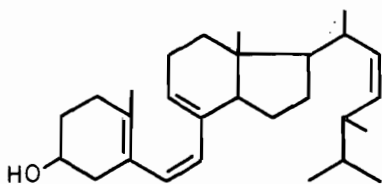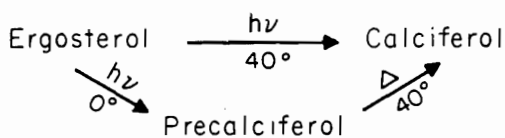
D. J. Cram

Transannular Effects Observed By Others

A	B	Effect	Author
$C=O$	$CH_2C=O$	Facile condensation	Plattner
$C=O$	NH	$\ominus O\text{-}C\text{-}\overset{\oplus}{N}H$	Leonard
CH_2	CH—CH $\underset{H}{\overset{}{\diagdown O \diagup}} \oplus$	Wagner-Meerwein	Cope, Prelog
CHOH	CHOH	Pinacol	Prelog
CH=CH	CHOTs	Ring Formation	Cope, Goering
CH=CH	$CH=CHCOCH_3$	Abnormal $\mu.v.$	Braude
	CH_2	Resolvable	Luttringhaus

$$\begin{array}{c} \text{—}(CH_2)_m\text{—} \\ A \quad\quad\quad\quad B \\ \text{—}(CH_2)_n\text{—} \end{array}$$

Transannular Effects Studied in Present Investigation

A	B	Effect of values of m and n on
		Spectral properties Relative rates electrophilic substitution
	X	Resolvability Inter-ring activating and deactivating influence of X
	$-C\equiv C-$ $-COCH=CH-$	Spectral properties
	$>$CHOTs	Rate and stereochemistry of solvolysis
$-C\equiv C-$	$-C\equiv C-$	Possible cyclobutadiene character

$$\begin{array}{c} \text{—}(CH_2)_m\text{—} \\ A \quad\quad\quad\quad B \\ \text{—}(CH_2)_n\text{—} \end{array}$$
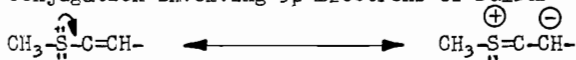
HETEROCYCLIC COMPOUNDS OF SULFUR

WILLIAM E PARHAM

Resonance Interactions of Sulfur

1. Conjugation Involving 3d Orbitals of Sulfur
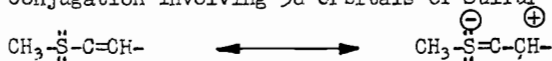
2. Conjugation Involving 3p Electrons of Sulfur

Resonance in the 1,4-Dithiadiene System

I

II

Ia
(four structures)

Ib
(four structures)

Ic
(two structures)

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