20

TWELFTH NATIONAL ORGANIC CHEMISTRY SYMPOSIUM

of the

AMERICAN CHEMICAL SOCIETY

Auspices of the Division of Organic Chemistry
and the Colorado Section

☆

June 12-15, 1951 — 69
Denver, Colorado

ELFTH NATIONAL ORGAN

CHEMISTRY SYMPOSIUM

of the

IERICAN CHEMICAL SOCIETY

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eadquarters—Shirley-Savoy Hotel, Denver, Colorado.

eetings—Lincoln Room, Shirley-Savoy Hotel.

egistration—Lincoln Room Lobby, Shirley-Savoy Hotel.

Monday, June 11, 2:00 p.m. to 8:00 p.m.

Tuesday, June 12, 8:00 a.m. to 8:00 p.m.

Wednesday, June 13, 8:00 a.m. to 8:00 p.m.

Thursday, June 14, 9:00 a.m. to 8:00 p.m.

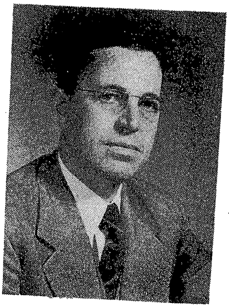
Friday, June 15, 9:00 a.m. to 12:00 noon.

Speakers at the Twelfth National Organic Chemistry Symposi

P. D. Bartlett

H. C. Brown

M. Carmack



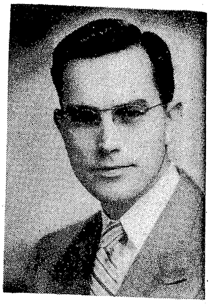
A. C. Cope

V. du Vigneaud

R. C. Elderfield

L. F. Fieser

C. D. Hurd



N. J. Leonard

J. D. Roberts

W. H. Urry

W. G. Young

R.B. [illegible] Bequest. F.B.S. [illegible] mposiu

armack

lderfield

eonard

Young

Program

Tuesday Afternoon

1:30 P.M. Welcome. REX E. LIDOV, Chairman, Colorado Section.
Response. WILLIAM S. JOHNSON, Chairman, Organic Division.
2:00 P.M. 1. PAUL D. BARTLETT. Recent Developments in Carbonium Ion Theory.
3:00 P.M. Discussion of paper 1.
3:30 P.M. 2. HERBERT C. BROWN. Steric Stains.
4:30 P.M. Discussion of paper 2.

Tuesday Evening

8:00 P.M. 3. WILLIAM G. YOUNG. Displacement Reactions in Allylic Systems.
9:00 P.M. Discussion of paper 3.

Wednesday Morning

9:00 A.M. 4. WILBERT H. URRY. Structural Influences in the Reactions of Free Radicals in Solution.
10:00 A.M. Discussion of paper 4.
10:30 A.M. 5. JOHN D. ROBERTS. Properties and Reactions of Some Cyclopropyl and Cyclobutyl Derivatives.
11:30 A.M. Discussion of paper 5.

Wednesday Afternoon

4:00 P.M. Social Hour. Empire Room, Shirley-Savoy Hotel.

Wednesday Evening

8:00 P.M. 6. LOUIS F. FIESER. Oxidation of Steroids.
9:00 P.M. Discussion of paper 6.

Thursday Morning

9:00 A.M. 7. MARVIN CARMACK. The Organic Chemistry of Some Compounds Containing Multi-Sulfur Functions.
10:00 A.M. Discussion of paper 7.
10:30 A.M. 8. NELSON J. LEONARD. Clemmensen Reduction-Rearrangement.
11:30 A.M. Discussion of paper 8.

Thursday Evening

8:00 P.M. 9. ARTHUR C. COPE. Substituted Cycloöctatretraenes.
9:00 P.M. Discussion of paper 9.

Friday Morning

9:00 A.M. 10. ROBERT C. ELDERFIELD. Reaction of *o*-Phenylenediamine Derivatives with Carbonyl Compounds, and Related Reactions.
10:00 A.M. Discussion of paper 10.
10:30 A.M. 11. VINCENT DU VIGNEAUD. Studies on the Pressor and Oxytocic Hormones of the Posterior Pituitary.
11:30 A.M. Discussion of paper 11.

Friday Afternoon

2:00 P.M. 12. CHARLES D. HURD. High Temperature Syntheses of Polycyclic Hydrocarbons.
3:00 P.M. Discussion of paper 12.

Adjournment

Denver Committees

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The Colorado Section of the American Chemical Society is acting as host section.

General Chairman	E. W. D. Huffman
Assistant General Chairman	Stanley J. Cristol
Chairman of Registration Committee	Daniel E. Richardson
Chairman of Rooms and Reservations Committee	L. C. Atchison

Division of Organic Chemistry

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

	1949-1950	1950-1951
Chairman	Ralph W. Bost	William S. Johnson
Secretary	Nelson J. Leonard	Nelson J. Leonard
Chairman-elect	William S. Johnson	Robert C. Elderfield
	Karl Folkers	Thomas P. Carney
	Byron Riegel	John C. Sheehan
	Harold R. Snyder	Byron Riegel
	William G. Young	William G. Young

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:

NELSON J. LEONARD, *Secretary*
Organic Division, A.C.S.
Department of Chemistry
University of Illinois
Urbana, Illinois

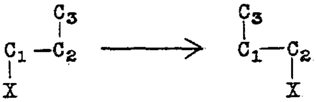
Extra copies of this Symposium Abstract Booklet can be obtained at $1.00 each from the Secretary.

RECENT DEVELOPMENTS IN CARBONIUM ION THEORY

Paul D. Bartlett

Five Stages in Development of Carbonium Ion Theory

1. Existence of tertiary and certain secondary carbonium ions established by conductivity studies in liquid sulfur dioxide (Walden, 1902).
    - Correlation with halochromism of triarylmethyl compounds.
2. Ionization postulated as a mechanism of those organic reactions favored by ionizing conditions
    - Molecular rearrangements (Meerwein, 1922; Whitmore, 1932)
    - Solvolysis (Hughes, 1935)
    - Polymerization by acids (Whitmore, 1934)
    - Hydride transfer and paraffin alkylation (Bartlett, Condon, and Schneider, 1944)
3. Stereochemistry of carbonium ions and carbonium ion reactions
    - sp^2 hybridization (Pauling, 1928) and near coplanarity of the triphenylcarbonium ion
    - Isomerism in the crystal violet cation (Lewis, Magel, and Lipkin, 1942)
    - Configuration in a molecular rearrangement:



$$\underset{X}{C_1}-\overset{C_3}{C_2} \longrightarrow \overset{C_3}{C_1}-\underset{X}{C_2}$$

        - Inversion at C_1 (Bernstein and Whitmore, 1939)
        - Inversion at C_2 (Bartlett and Pöckel, 1937)
        - Retention at C_3 (Lane and Wallis, 1941)
    - Racemization and partial inversion in solvolysis (Hughes, Ingold, et al., 1937)
4. Demonstration of bridged ions
    - In the i-sterol rearrangement (Winstein and Adams, 1948)
    - In phenylbutanols and phenylpentanols (Cram, 1949)
    - In nor-isobornyl sulfonates (Winstein and Trifan, 1950)
    - Driving forces in homoallyl and homobenzyl systems (Winstein)
    - Formulation of bridged ions as π-complexes (Dewar)
5. Bound nature of the carbonium ion
    - Specific role of solvents in solvolysis (Swain)
    - Rapid exchange of halogen in trityl halides (Swain)

STERIC STRAINS

Herbert C. Brown

I. Introduction.

A program for the systematic study of steric effects was initiated in 1940. At that time the place of steric effects in chemical theory had fallen to a particularly low point and theorists went to extreme lengths to avoid attributing any significant chemical effects to the size and bulk of atoms or groups of atoms. Early efforts were devoted to a number of qualitative studies designed to indicate whether steric effects were an important factor in chemical phenomena. These studies definitely indicated the importance of steric effects. With this confirmation in hand, the program was extended to include quantitative studies which might serve to establish a quantitative theory of steric effects.

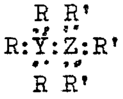
Considerable data have now been accumulated. Although a truly quantitative theory is still a matter for the future, it has proven possible to attain a clearer understanding of the importance of steric effects in chemical equilibria and reactions. In particular, these studies have led to the concept that steric effects may operate to facilitate as well as to hinder chemical reactions and have thereby afforded a clearer understanding of the effects of structure on chemical behavior.

II. Molecular Addition Compounds.

Study of the stability of molecular addition compounds has proven a particularly valuable tool in these investigations of steric strains. The stability of a typical addition compound, such as trimethylamine-trimethylboron, can be readily established by studies of its dissociation in the gas phase or by calorimetric measurements.

$$Me_3N_{(g)} + BMe_{3(g)} = Me_3N{:}BMe_{3(g)} + 17.6 \text{ kcal.}$$

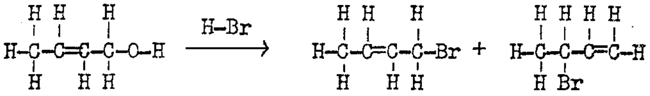
In typical addition compound of this kind,



$$\begin{array}{c} R\ \ R' \\ \ddot{}\ \ \ddot{} \\ R{:}Y{:}Z{:}R' \\ \ddot{}\ \ \ddot{} \\ R\ \ R' \end{array}$$

DISPLACEMENT REACTIONS IN ALLYLIC SYSTEMS

William G. Young

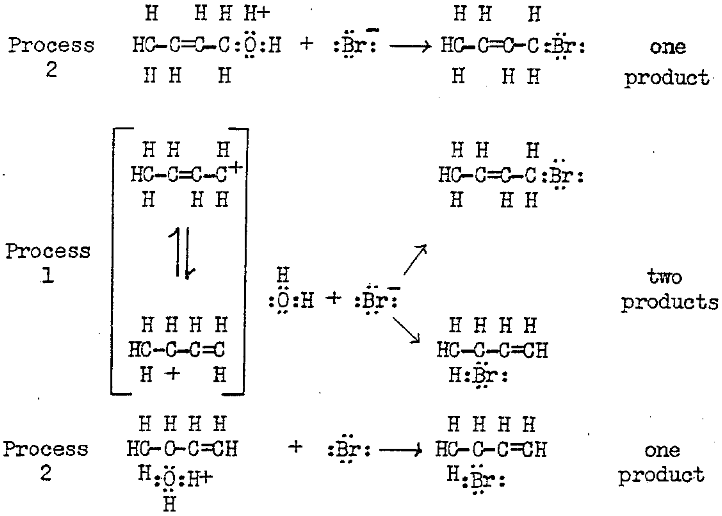


Primary Secondary

Allylic Bromides

Controlled conditions to avoid rearrangement of starting materials and final products.

Reaction of Butenols with Hydrogen Bromide



85-95% by Process 1

STRUCTURAL INFLUENCES IN THE REACTIONS OF FREE RADICALS IN SOLUTION

W. H. Urry

The influence of structure upon the relative reactivities of free radicals and of substances attacked by free radicals has been determined by deuterium tracing techniques. Differences in the reactions of free chlorine atoms, free bromine atoms and free radicals produced in peroxide decompositions may be partially attributed to differences in their reactivities.

$$CH_3CH_2COOH + SO_2Cl_2 \xrightarrow[\text{peroxide}]{} \underset{(60\%)}{ClCH_2CH_2COOH} + \underset{(40\%)}{CH_3CHClCOOH}$$

$$CH_3CH_2COOH + Br_2 \xrightarrow[\text{light}]{} CH_3CHBrCOOH + HBr$$

$$CH_3CH_2COOH + (CH_3COO-)_2 \longrightarrow CH_4 + CO_2 + \begin{array}{l} CH_3CHCOOH \\ \vert \\ CH_3CHCOOH \end{array}$$

The relative reactivities of atoms and free radicals have been determined from the ratio of the rates of their attack upon hydrogen or deuterium attached to carbon. Results indicate that the free chlorine atom is the most reactive studied (the least able to distinguish between hydrogen and deuterium). This is the probable reason for its attack at all available positions.

Determination of Relative Attack upon Hydrogen or Deuterium by Free Radicals from Diacetyl Peroxide

$$(CH_3COO-)_2 + \underset{17.61\text{ mole }\%}{CH_3CHDCOOH} \longrightarrow CH_4 + CH_3D \quad 1.40\text{ mole }\%\ CH_3D$$

Determined by flotation-temperature analysis of water obtained by combustion of the methane.

$$CH_4 + CH_3D + O_2 \longrightarrow H_2O + D_2O$$

1st liter .35 mole % D_2O
2nd liter .35 mole % D_2O

Calculation of k_H/k_D

f = mole fraction of α-deuteroethylbenzene
m = mole fraction of deuterium oxide in the water of methane combustion
k_H = specific rate constant for the attack by free radical upon α-hydrogen

PROPERTIES and REACTIONS of SOME CYCLOBUTYL and CYCLOPROPYL DERIVATIVES

John D. Roberts

Early Work on Properties of Small-Ring Hydrocarbons

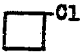
(Freund, Gustavson, Willstätter, Zelinsky, etc.)

	Br_2 addition	H_2, Ni	HBr addition	ΔH of combustion per CH_2 group, kcal.
$CH_2=CH_2$	++, 25°	++, 25°	++	170
	±, 25°	+, 80°	+	168.5
	-	+, 120°	-	165.5
	-	+, 300°	-	159
	-	-	-	157

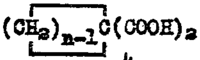
Important Work on Relative Reactivities of Small-Ring Derivatives (up to 1944)

$CH_3CH=CHCl$

comparable reactivity toward alcoholic KOH (Gustavson, 1891)

"  "

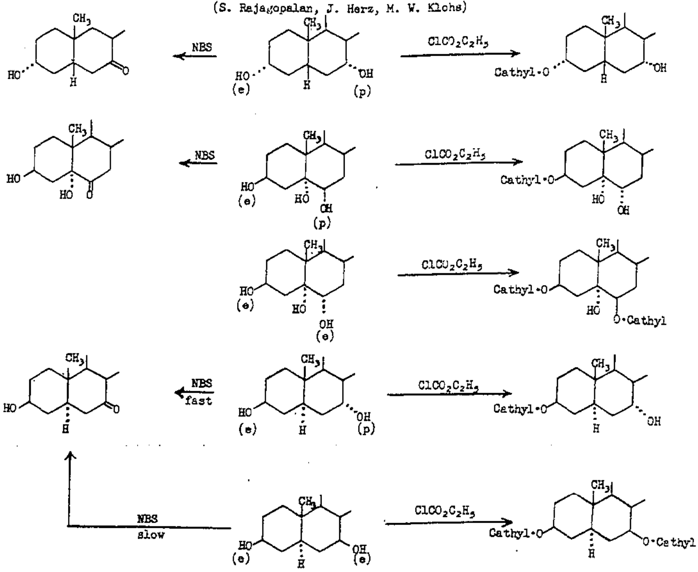
unusually unreactive toward KI in acetone (Perkin, 1894)

Ring size, n	 $(CH_2)_{n-1}CHCOOH$ $K_A \times 10^3$	 $(CH_2)_{n-1}C(COOH)_2$ $K_A \times 10^4$
3	1.5	140
4	1.8	7.0
5	1.2	5.5
6	1.3	3.1
	(Zelinsky and Isgaryschew, 1908)	(Vogel, 1929)

OXIDATION OF STEROIDS

Louis F. Fieser

Selective Oxidation and Cathylation (Carbethoxylation)
(S. Rajagopalan, J. Herz, M. W. Klohs)

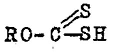


THE ORGANIC CHEMISTRY OF SOME COMPOUNDS CONTAINING MULTI-SULFUR FUNCTIONS

Marvin Carmack

Introduction. The sulfur atom has a pronounced tendency to combine with itself to form multi-sulfur groupings behaving as functional units. Some other combinations of sulfur and carbon or sulfur and nitrogen also show functional unity. Some of the types of compounds falling within the scope of "multi-sulfur functions" include:

Polysulfides $R-S_n-R'$

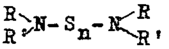
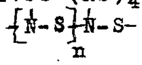
Xanthic acid derivatives  $RO-C(=S)-SH$ and $RO-CS-S_n-CS-OR$

Thioacids $RCSSH$

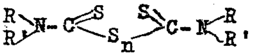
Thiocarbonic acid and derivatives H_2CS_3 R_2CS_3

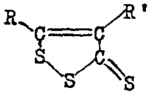
Perthiocarbonic acid derivatives H_2CS_4

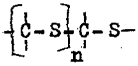
Orthothiocarbonic acid derivatives $(RS)_4C$

Amine sulfides  $R_2N-S_n-NR'_2$  $-[N-S]_n-N-S-$

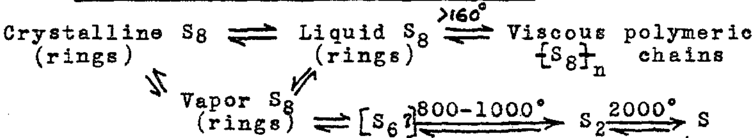
Dithiocarbamates  $R_2N-CS_2^{\ominus}\ M^{\oplus}$

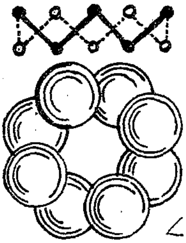
Thiurampolysulfides  $R_2N-C(=S)-S_n-C(=S)-NR'_2$

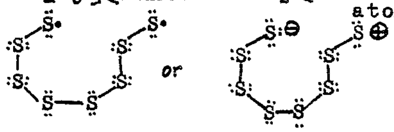
Trithiones 

Polymercaptals  $-[C-S]_n-C-S-$

Properties of elementary sulfur







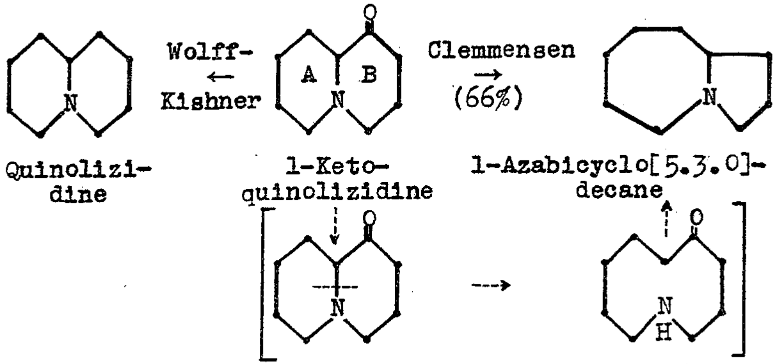
Bacon and Fanelli - 1944
Powell and Eyring - 1944

S-S 2.07 Å
∠S-S-S 105±2° Li and Donohue - 1944

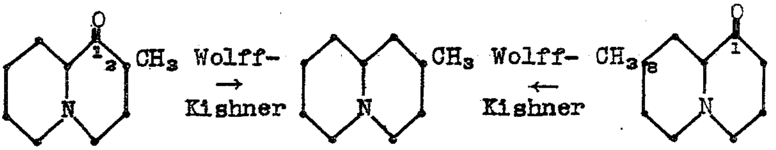
CLEMMENSEN REDUCTION-REARRANGEMENT

Nelson J. Leonard

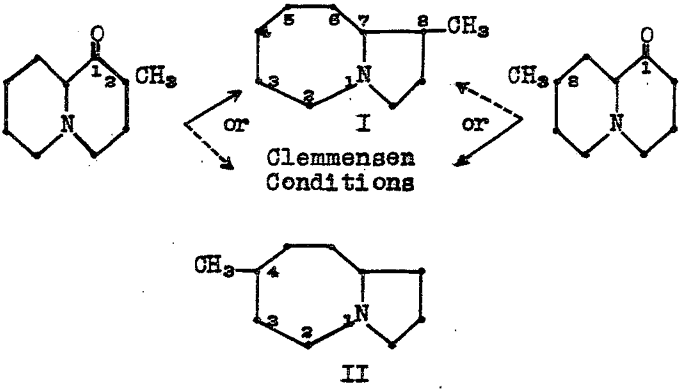
<u>Bicyclic α-Aminoketones</u>.-



Clemo, Ramage, and Raper, J. Chem. Soc., 2959 (1932);
Clemo, Metcalfe, and Raper, <u>ibid</u>., 1429 (1936);
Prelog and Seiwerth, Ber., <u>72</u>, 1638 (1939).



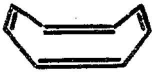
Clemo and Metcalfe, J. Chem. Soc., 1518 (1937);
Clemo, Cook, and Raper, <u>ibid</u>., 1183 (1938).



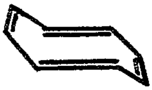
SUBSTITUTED CYCLOÖCTATETRAENES

Arthur C. Cope

Substituted cycloöctatetraenes are of interest as derivatives of a hydrocarbon that has unusual chemical reactivity. Their properties may aid in determining the geometric configuration of the cycloöctatetraene ring, which is believed to have either a non-planar "boat" or "crown" structure.



Boat



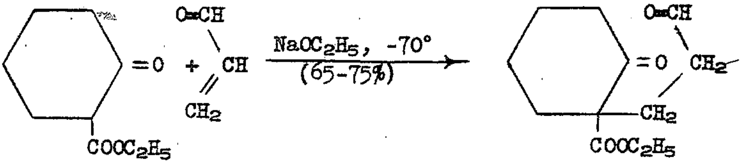
Chair

Crown

Indirect Syntheses of Eight-Membered Cyclic Polyolefins

(a) From carbonyl-bridged compounds
(F. S. Fawcett, G. Munn, E. C. Hermann)
J. Am. Chem. Soc., 72, 3399, 3405 (1950).

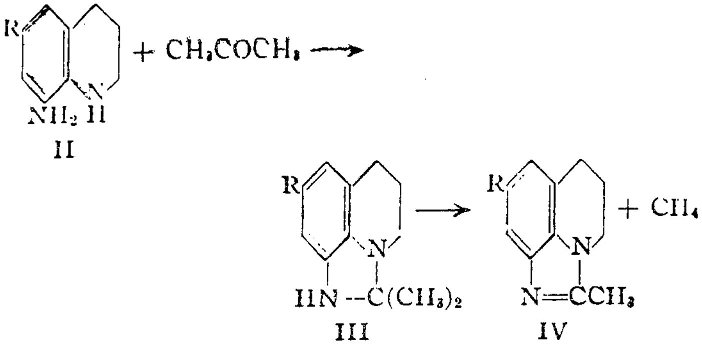
(b) From a β-ketoester with a carbonyl bridge
(M. E. Synerholm, E. S. Graham and D. J. Marshall).



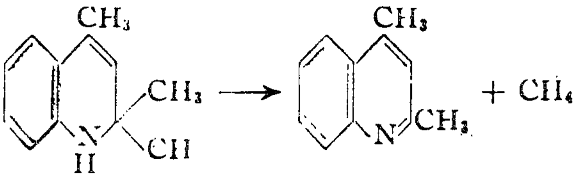
REACTION OF o-PHENYLENEDIAMINE DERIVATIVES WITH CARBONYL COMPOUNDS, AND RELATED REACTIONS.

Robert C. Elderfield

8-Amino-1,2,3,4-tetrahydroquinolines react with acetone to give imidazoles with loss of methane.



The Riehm quinoline synthesis also involves formation of an azomethine linkage by loss of hydrocarbon.



STUDIES ON THE PRESSOR AND OXYTOCIC HORMONES OF THE POSTERIOR PITUITARY

Vincent du Vigneaud

Slide

I. 53 Transfer distribution of oxytocic material of 250 units per mg. between sec-butyl alcohol and 0.05% acetic acid: -o-, weight in mg., -●-, total units of activity.

II. (a) 53 Transfer distribution of oxytocic material of 550 units per mg. showing experimental values for weights (-o-) and the theoretical curve for a single substance (-●-).

(b) 53 Transfer distribution of material of 550 units per mg. showing experimental values for activity (-o-) and the theoretical curve for a single substance (-●-).

III. Amino acid pattern obtained from beef oxytocic material (a) compared with one obtained from an artificial mixture of amino acids (b).

IV. The amino acid composition of a high potency beef oxytocin preparation.

V. The molar ratios between constituents of oxytocin preparations from beef and hog pituitaries.

VI. The amino acid composition of a high potency oxytocin preparation which had been subjected to counter-current distribution between dilute ammonia and sec-butyl alcohol (110 transfers).

VII. The amino acid pattern obtained from a high potency oxytocin preparation after oxidation with performic acid, counter-current distribution (280 transfers), and hydrolysis.

VIII. The amino acid pattern obtained from a high potency oxytocin preparation desulfurized with Raney nickel.

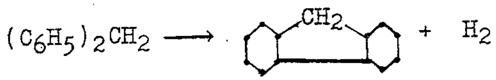
HIGH TEMPERATURE SYNTHESES OF POLYCYCLIC HYDROCARBONS

Charles D. Hurd

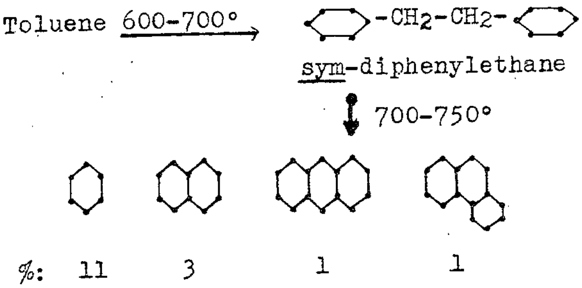
Cyclizations at Red Heat

1. Acetylene at 500-700° into
   (a) benzene, naphthalene, polycyclics
   (b) C, H_2, C_2H_4, CH_4

2. Benzene (700°) into biphenyl (no naphthalene or anthracene). Similarly,

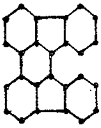


3.



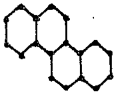
o,o'-Bitolyl ⟶ phenanthrene

Fluorene ⟶ difluorenylene,



Indene,

⟶ Chrysene



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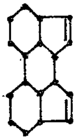

or