SEVENTH NATIONAL ORGANIC CHEMISTRY SYMPOSIUM
of the
AMERICAN CHEMICAL SOCIETY

AUSPICES OF THE VIRGINIA SECTION AND THE DIVISION
OF ORGANIC CHEMISTRY

December 28-30, 1937
Richmond, Va.

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December 28-30, 1937 *Richmond, Va.*

Program

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Registration and Meetings: The John Marshall Hotel.

Tuesday Morning, December 28, 1937

10:30 A.M. Address of Welcome. I. A. Updike, Chairman, Virginia Section.

10:45 A.M. Response. Frank C. Whitmore, President-Elect, American Chemical Society.

11:00 A.M. Chemistry of Thiamin. R. R. Williams.

Tuesday Afternoon

2:00 P.M. Chemistry of the Saponins. C. R. Noller.

3:00 P.M. The Structure of Gossypol. Roger Adams.

4:00 P.M. Natural Tannins. Alfred Russell.

Tuesday Evening

7:30 P.M. A Symposium on the Application of Micro and Semimicro Methods to Organic Research.
Alsoph H. Corwin, Chairman; Lyman C. Craig; Walter R. Kirner.

(1) "The Teaching of Small Scale Technique to Freshmen." David Harker and D. V. Sickman.

(2) "Micro Qualitative Elementary Analysis." H. K. Alber.

(3) "Micro Analytical Technique as an Aid to the Organic Chemist." W. R. Kirner.

(4) "The Micro Determination of Carbon and Hydrogen." Alsoph H. Corwin.

(5) "Micro Distillation Apparatus and Technique." Lyman C. Craig.

(6) "Chromatographic Methods in the Small Scale Purification of Organic Compounds." Nathan L. Drake.

During the Symposium an exhibit of micro and semi-micro apparatus will be on display.

Wednesday Morning, December 29, 1937

9:00 A.M. Pentaarylethanes. W. E. Bachmann.

10:00 A.M. Organosodium Reagents in the Wurtz Reaction. A. A. Morton.

11:00 A.M. Pyrolysis of Ethers and Esters. C. D. Hurd.

Wednesday Afternoon

2:00 P.M. Novel Reactions of Certain Types of Esters with Sodium Alkoxides. S. M. McElvain.

3:00 P.M. The Michael Condensation. Ralph Connor.

4:00 P.M. The Reactions between Metallic Enolates and Substituted Quinones. L. I. Smith.

Wednesday Evening

6:30 P.M. Dinner—Informal—Included in Registration Fee. Admission by ticket.

8:00 P.M. Protein Structure in Relation to Biological Problems. Max Bergmann.

Thursday Morning, December 30, 1937

9:00 A.M. Studies in the Synthesis of Compounds with Narcotic and Analgesic Action. Erich Mosettig.

10:00 A.M. The Wagner-Meerwein Rearrangement. Paul D. Bartlett.

11:00 A.M. Aliphatic Fluorides. A. L. Henne.

Thursday Afternoon

2:00 P.M. Syntheses from Natural Gas Hydrocarbons. H. B. Haas.

3:00 P.M. The Behavior of Carbohydrates in Alkaline Solution. Wm. L. Evans.

4:00 P.M. Adjournment.

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Richmond Committees

* * *

The Virginia Section of the American Chemical Society is acting as host for the Symposium.

General Committee—W. Catesby Jones, Chairman; Dr. Sidney S. Negus; Dr. Lyndon F. Small.

Registration—Rodney C. Berry.

Information—James W. Schofield.

Hotel—L. W. Himmler.

Meeting Facilities—A. I. Whitenfish.

Micro-Chemical Exhibit—Thomas Garber.

Dinner—Page Hudson.

Photographic—Foley F. Smith.

Division of Organic Chemistry

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

	1935-36	1936-37	1937-38
Chairman	Henry Gilman	L. C. Raiford	Lyndon F. Small
Secretary	R. L. Shriner	R. L. Shriner	R. L. Shriner
	C. E. Boord	Homer Adkins	Homer Adkins
	A. J. Hill	C. E. Boord	L. F. Fieser
	J. R. Johnson	Henry Gilman	L. C. Raiford

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 $1.00. 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. Furthering and promoting policies which make for the advancement of organic chemistry.

I hope that you, as an organic chemist, are interested in these activities and will join the division by signing the form below and mailing it to me.

Cordially yours,

R. L. SHRINER, *Secretary-Treasurer.*
Department of Chemistry
University of Illinois
Urbana, Illinois

CEHMISTRY OF THIAMIN.

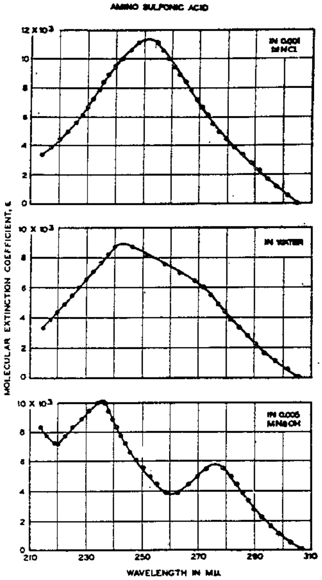
R.R.Williams

$$\underset{\text{VITAMIN}}{C_{12}H_{18}N_4OSCl_2} + Na_2SO_3 \longrightarrow \underset{\text{I}}{C_6H_9N_3SO_3} + \underset{\text{II}}{C_6H_9NSO} + 2NaCl$$

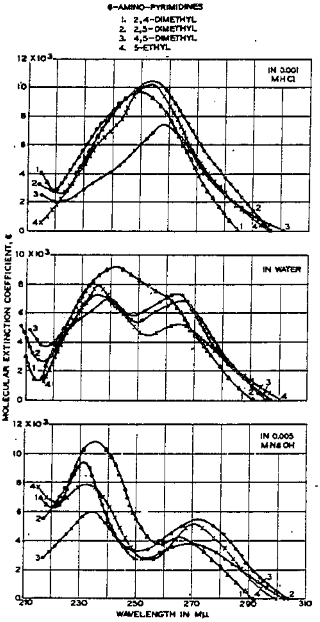
$$\underset{\text{I}}{C_6H_9N_3SO_3} \xrightarrow[\text{IN } H_2O]{HCl} \underset{\text{V}}{C_6H_8N_2SO_4} + NH_3 \text{ (i.e.}-OH \text{ REPLACES} -NH_2\text{)}$$

$$\left.\begin{array}{l} \underset{\text{I}}{C_6H_9N_3SO_3} \xrightarrow{H_2O} H_2SO_4 \\ \underset{\text{I}}{C_6H_9N_3SO_3} \xrightarrow{NaOH} H_2SO_3 \end{array}\right\} \begin{array}{l}\text{A SULFONIC GROUP IS PRESENT} \\ \text{MARKING ORIGINAL POINT OF} \\ \text{ATTACHMENT TO THIAZOLE}\end{array}$$

1. Sulfite cleavage and resulting sulfonic acids.



2. Ultraviolet absorption of amino sulfonic acid.



3. Ultraviolet absorption of alkylated 6 amino pyrimidines.

CHEMISTRY OF THE SAPONINS

C.R.NOLLER

Crystalline Saponins of Known Composition

Name	Source	Hydrolytic Products	
		Aglycone	Sugars
Tigonin	Digitalis lanata	Tigogenin	2 Glucose 2 Galactose Xylose
Digitonin	Digitalis purpurea	Digitogenin	2 Glucose 2 Galactose Xylose
Parillin	Smilax medica	Sarsasapogenin (Parigenin)	2 Glucose Rhamnose
Amolonin	Chlorogalum pomeridianum	Tigogenin	3 Glucose Galactose 2 Rhamnose
α-Hederin	Hedera helix	Hederagenin	Arabinose Rhamnose
Cyclamin	Cyclamen europaeum	Cyclamiretin	3 Glucose 2 Arabinose
Solanin-t	Solanum tuberosum	Solanidin-t	Glucose Galactose Rhamnose

Steroid Sapogenins

Name	Sources	Empirical Formula	Functional Groups		
			Hydroxyl	Oxidic Oxygen	Double Bonds
Tigogenin	D. purpurea (Foxglove) C. pomeridianum (Amole)	$C_{27}H_{44}O_3$	1	2	0
Gitogenin	D. purpurea D. germanicum	$C_{27}H_{44}O_4$	2	2	0
Digitogenin	D. purpurea	$C_{27}H_{44}O_5$	3	2	0
Chlorogenin	C. pomeridianum	$C_{27}H_{44}O_4$	2	2	0
Sarsasapogenin (Parigenin)	Smilax (several species) (Sarsaparilla Root)	$C_{27}H_{44}O_3$	1	2	0
Smilagenin	Smilax officinalis (Jamaica sarsaparilla)	$C_{27}H_{44}O_3$	1	2	0
Solanidin-t	Solanum tuberosum (Potato)	$C_{27}H_{43}ON$	1	1 N (Heterocyclic)	1

STRUCTURE OF GOSSYPOL

Roger Adams

$$\begin{tikzcd}
& \text{Cotton Seed} \arrow[dl, "\text{Ether}"'] \arrow[dr, "\text{CHCl}_3"] & \\
\text{Yellow Gossypol} & & \text{Red Gossypol} \arrow[ll, "\text{Ether}"']
\end{tikzcd}$$

Yellow Gossypol

$C_{30}H_{30}O_8$

m.p. 184°
m.p. 199°
m.p. 214°

$\xrightarrow{\text{HAc}}$ Gossypol - Acetic Ac.
$C_{30}H_{30}O_8 \cdot CH_3CO_2H$

$\xrightarrow{-2H_2O}$ Anhydrogossypol
$\xleftarrow{+2H_2O}$ $C_{30}H_{26}O_6$

$\xrightarrow{40\%\ \text{NaOH}}$ Apogossypol
$C_{28}H_{30}O_6$

$\xrightarrow{Ac_2O + \text{NaAc}}$ Hexaacetylgossypol
$\xleftarrow{H_2SO_4}$ $C_{30}H_{24}O_2(OCOCH_3)_6$

$\xrightarrow{(CH_3)_2SO_4(CH_3OH)}$ Gossypol tetramethyl ether
$C_{30}H_{26}O_4(OCH_3)_4$

Gossypol hexamethyl ether
$C_{30}H_{24}O_2(OCH_3)_6$

$\xrightarrow{\text{Liquid } NH_3}$ Diaminogossypol
$C_{30}H_{28}O_6(NH_2)_2$

$\xrightarrow{C_6H_5NH_2}$ Dianilinogossypol
$C_{30}H_{30}O_6(=N-C_6H_5)_2$

$\xrightarrow{NH_2OH}$ Dioxime of Gossypol
$C_{30}H_{30}O_6(=N-OH)_2$

$\xrightarrow{\text{Cold } KMnO_4}$ $H-CO_2H$; CH_3CO_2H;
$(CH_3)_2CHCO_2H$

$\xrightarrow{\text{Dimethyl-butadiene}}$ Addition compound $-2H_2O$
$C_{42}H_{46}O_8$

$\xrightarrow{O_3 \text{ in HAc}}$ Gossypolic Acid
$\left[C_{12}H_{14}O_4\right]_x$

$\xrightarrow{H_2 \text{ and Pd}}$ Hydrogossypol
$C_{30}H_{38}O_8$

THE CHEMISTRY OF THE NATURAL TANNINS

Alfred Russell

The amorphous tannins occur to a greater or less extent in practically all forms of plant life. The tannin content is usually much greater than that of any other single plant product and it may therefore be supposed that they represent reserve, discarded or defensive material of some sort.

Chemically the tannins may be divided into three groups according to the effect obtained by boiling with dilute mineral acids.

1. Depside group.
2. Diphenyl methylolid group.
3. Phlobatannin group.

Only a single member is known definitely to belong to the Depside group. Gallotannin, occurring chiefly in oak galls, by acid treatment hydrolyses to give approximately ten molecular equivalents of gallic acid and one molecular equivalent of glucose. To explain the fission products Emil Fischer decided that pure gallotannin was a penta ester of digallic acid and glucose. Finally he was able to synthesise penta m-digalloylglucose (Fig. 1) through the steps shown. This product bore a close resemblance to natural gallotannin; indeed so far as comparison of amorphous products could be made the two were identical.

One member only is known to belong to the second group. Ellagitannin, occurring chiefly in certain nuts and pods, by acid treatment converts to ellagic acid and glucose only. It may therefore be supposed that the tannin is a glucoside of ellagic acid (Fig. 2) although this is noc definitely established.

Excepting gallotannin and ellagitannin it seems likely that all other tannins are phlobatannins. By treatment with boiling dilute mineral acids no fission products can be isolated, but the tannins convert completely to amorphous water insoluble materials, red or brown in color. By treatment with fused alkali each phlobatannin gives a polyhydric phenol (resorcinol, pyrogallol or phloroglucinol) and a phenolic acid (protocatechuic or gallic). Taken with the fact that a phlobatannin often occurs side by side with a coloring matter of the benzopyran type giving, with alkali, the same fission products as the tannin, it is probable that phlobatannins are built on the benzopyran model (Fig. 3). Phlobatannins are not coloring matters so that, if of the benzopyran type, they are most likely derived either from flavans or from flavanones, and it is the opinion of K. Freudenberg that each phlobatannin is a polymer of a corresponding polyhydroxy flavan; in one case such a flavan (catechin - 3:5:7:3′:4′-pentahydroxy flavan) occurs along with a tannin (catechu tannin) (Fig. 4).

PENTAARYLETHANES

Werner E. Bachmann

Preparation of Pentaarylethanes:

(a) $$2(C_6H_5)_3CBr + Mg \rightarrow 2(C_6H_5)_3C + MgBr_2$$

$$2(C_6H_5)_3C + Mg + MgBr_2 \rightarrow 2(C_6H_5)_3CMgBr$$

$$(C_6H_5)_3CMgBr + (C_6H_5)_2CHBr \rightarrow (C_6H_5)_3C-CH(C_6H_5)_2 + MgBr_2$$

(b) $$(C_6H_5)_3COCH_3 + 2Na \rightarrow (C_6H_5)_3CNa + NaOCH_3$$

$$(C_6H_5)_3CNa + (C_6H_5)_2CHBr \rightarrow (C_6H_5)_3C-CH(C_6H_5)_2 + NaBr$$

Properties of Pentaarylethanes:

(a) $$R_3C-CHR_2 + 2HI \rightarrow R_3CH + R_2CH_2 + I_2$$
(In hot AcOH)

(b) $$R_3C-CHR_2 + Br_2 \xrightarrow[(70-100^\circ)]{} R_3CBr + R_2CHBr$$

(c) $$R_3C-CHR_2 + I_2 \xrightarrow[(70-100^\circ)]{} R_3CI + R_2CHI$$

(d) $$R_3C-CHR_2 + O_2 \xrightarrow[(70-100^\circ)]{} R_3C-O-O-CHR_2 \ (90-95\%) \text{ and } R_3C-O-O-CR_3 \ (5-10\%)$$

(e) $$R_3C-CHR_2 \rightarrow R_2CH-CHR_2 + \text{dec. products of } R_3C$$
(In ethyl benzoate, 213°)

(f) $$R_3C-CHR_2 \rightleftarrows R_3C- + -CHR_2$$

Temperature at Which Color Develops
(Solvent: Ethyl benzoate)

Pentaarylethane	Temp., °C
$(C_6H_5C_6H_4)_3C-CH(C_6H_4C_6H_5)_2$	71
$(C_6H_5C_6H_4)_3C-CH(C_6H_5)(C_6H_4C_6H_5)$	78
$(C_6H_5C_6H_4)_3C-CH(C_6H_5)_2$	81
$(C_6H_5C_6H_4)_2(C_6H_5)C-CH(C_6H_5)_2$	83
$(C_6H_5)_3C-CH(C_6H_5)(C_{10}H_7)$	85
$(C_6H_5C_6H_4)(C_6H_5)_2C-CH(C_6H_5)_2$	88
$(C_6H_5)_3C-CH(C_6H_5)(C_6H_4C_6H_5)$	92

ORGANOSODIUM REAGENTS IN THE WURTZ REACTION

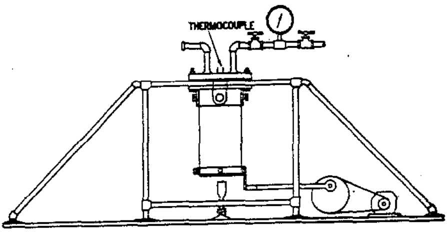
A. A. Morton

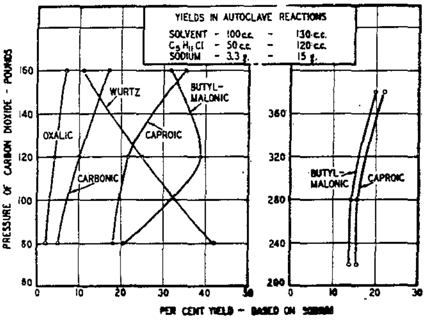
Reaction in the autoclave.

$$\left.\begin{array}{l} C_5H_{11}Cl \\ Na \\ CO_2 \end{array}\right\} \xrightarrow[\text{or benzene}]{\text{Pet. ether}} \begin{array}{l} C_5H_{11}COONa,\ C_4H_{10}(COONa)_2, \\ (COONa)_2,\ Na_2CO_3,\ C,\ C_5H_{10}, \\ C_5H_{12},\ C_{10}H_{22},\ NaCl. \end{array}$$

Under high pressure of carbon dioxide the yields of oxalic and carbonic acids increase.
At low pressures the Wurtz reaction may predominate.

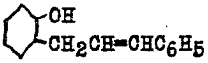
AUTOCLAVE FOR REACTIONS IN PRESENCE OF CARBON DIOXIDE



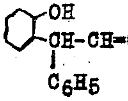


THE PYROLYSIS OF ETHERS AND ESTERS

Charles D. Hurd



(A)

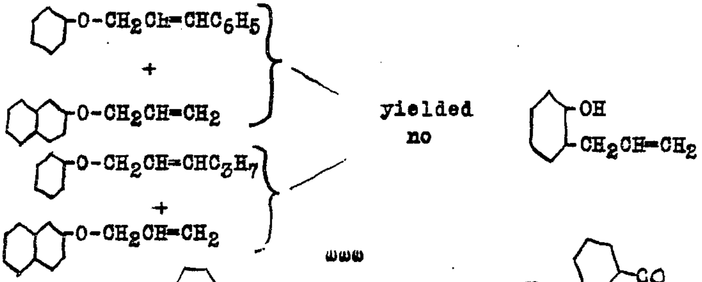


(B)

A, prepared directly
B, prepared by rearrangement

Ozonolysis, J.A.C.S., 59, 107 (1937)
A ⟶ C_6H_5CHO, only.
B ⟶ HCHO, only

ωωω



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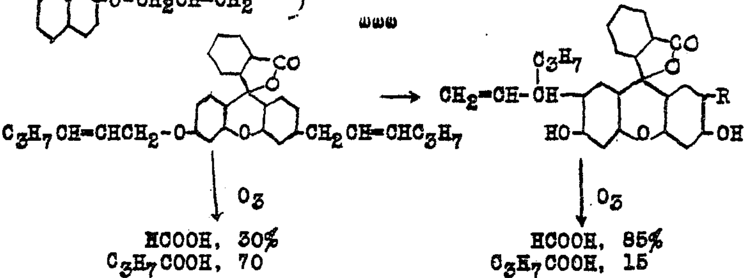

J.A.C.S., 59, 112 (1937)

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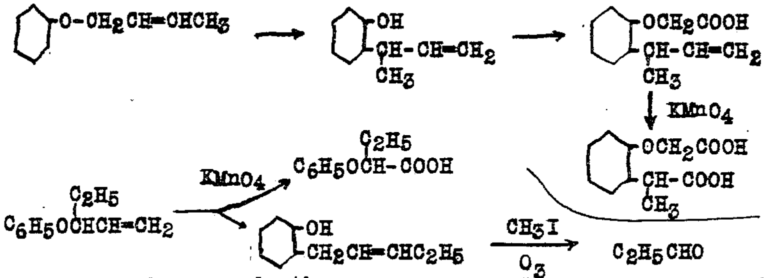
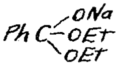


Lauer and others, J.A.C.S., 58, 1388, 1392 (36)

Novel Reactions of Certain Types of Esters with Sodium Alkoxides.

S.M. McElvain.

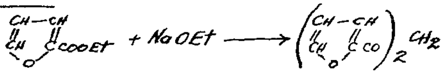
$RCOONa$ $\qquad RCOCH_2COR$



$$PhC\begin{cases}ONa\\OEt\\OEt\end{cases}$$

Scheibler (1932):

$$PhCOOC_2H_5 + C_2H_5\text{-}ONa \longrightarrow PhCOONa + C_2H_4 + C_2H_5OH$$



Adickes (1933):

$$PhCOOEt + NaOEt \longrightarrow (PhCO)_2CH_2$$

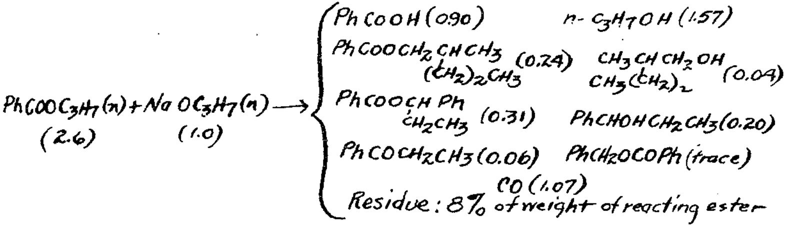
$$PhCOOCH_2CH_3 \longrightarrow PhCOCH_3 + CH_2O$$

$$PhCOCH_3 + PhCOOEt \longrightarrow (PhCO)_2CH_2 + EtOH$$

$$\underset{(2.1)}{PhCOOC_2H_5} + \underset{(1.0)}{NaOC_2H_5} \xrightarrow{175\text{-}180^\circ} \begin{cases} PhCOOH\ (0.55) & C_2H_5OH\ (1.8) \\ (PhCO)_2CH_2\ (0.40) & PhCH_2OCOPh\ (0.15) \\ PhCOCH_3\ (\text{traces}) & CO\ (0.58) \\ \text{Residue: 4\% of weight of reacting ester} \end{cases}$$

$$\underset{0.81}{PhCOOCH_3} + \underset{(1.0)}{NaOCH_3} \xrightarrow{175\text{-}180^\circ} \begin{cases} PhCOOH\ (0.70) & CH_3OH\ (0.18) \\ CH_3OCH_3\ (0.55) & PhCH_2OCOPh\ (0.012) \\ \text{No residue} & \text{No gas} \end{cases}$$

$$PhCOOCH_3 + CH_3ONa \longrightarrow PhCOONa + CH_3OCH_3$$



$$\underset{(2.6)}{PhCOOC_3H_7(n)} + \underset{(1.0)}{NaOC_3H_7(n)} \longrightarrow \begin{cases} PhCOOH\ (0.90) & n\text{-}C_3H_7OH\ (1.57) \\ PhCOOCH_2\underset{(CH_2)_2CH_3}{CH}CH_3\ (0.24) & \underset{CH_3(CH_2)_2}{CH_3CH}CH_2OH\ (0.04) \\ PhCOO\underset{CH_2CH_3}{CH}Ph\ (0.31) & PhCHOHCH_2CH_3\ (0.20) \\ PhCOCH_2CH_3\ (0.06) & PhCH_2OCOPh\ (\text{trace}) \\ & CO\ (1.07) \\ \text{Residue: 8\% of weight of reacting ester} \end{cases}$$

Guerbet reaction:

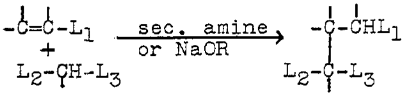
$$CH_3CH_2CH_2OH + CH_3CH_2CH_2ONa \longrightarrow NaOH + CH_3CH_2CH_2CH(CH_3)CH_2OH$$

Tischtschenko reactions (forward and reverse):

$$\begin{tikzcd} PhCOOCH_2R \arrow[r, shift left] & RCHO \arrow[l, shift left] \arrow[d, shift left] & + & PhCHO \arrow[r, shift left] \arrow[d, shift left] & RCOOCH_2Ph \arrow[l, shift left] \\ & RCOOCH_2R \arrow[u, shift left] & & PhCH_2OCOPh \arrow[u, shift left] & \end{tikzcd}$$

THE MICHAEL CONDENSATION

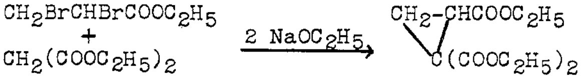
by Ralph Connor

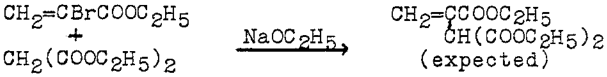


$$\begin{array}{c} -\overset{|}{C}=\overset{|}{C}-L_1 \\ + \\ L_2-\underset{|}{C}H-L_3 \end{array} \xrightarrow[\text{or NaOR}]{\text{sec. amine}} \begin{array}{c} -\overset{|}{C}-CHL_1 \\ | \\ L_2-\underset{|}{C}-L_3 \end{array}$$

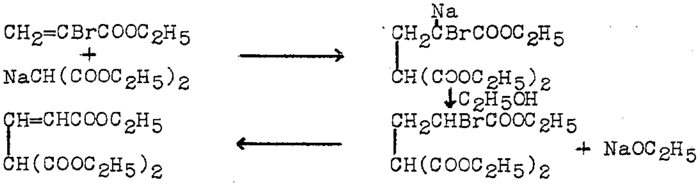
L_1 = $-COR$, $-COOR$, $-NO_2$, $-SO_2R$, $-CN$, $-CONH_2$
L_2 and L_3 = same groups as L_1 and $-CHO$. One may be C_6H_5-.
If one is $-COR$ or $-NO_2$ sometimes other may be H or R.

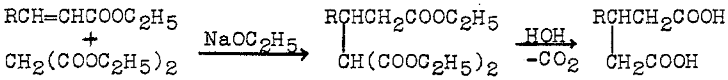
$$\begin{array}{c} CH_3CH=C(COOC_2H_5)_2 \\ + \\ CH_2(COOC_2H_5)_2 \end{array} \longrightarrow \begin{array}{l} CH_3CHCH(COOC_2H_5)_2 \\ \quad | \\ \quad CH(COOC_2H_5)_2 \end{array}$$



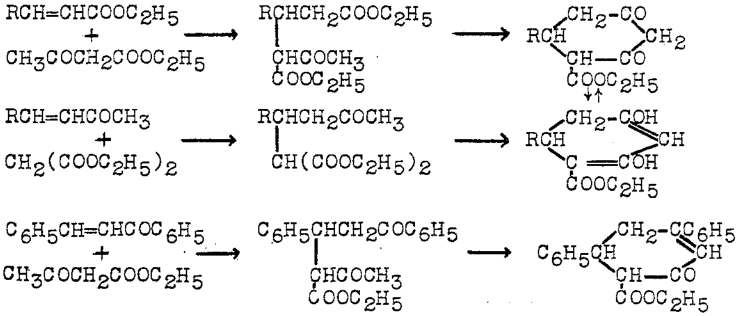


$$\begin{array}{c} CH_2=CBrCOOC_2H_5 \\ + \\ CH_2(COOC_2H_5)_2 \end{array} \xrightarrow{NaOC_2H_5} \begin{array}{l} CH_2=CCOOC_2H_5 \\ \quad\; CH(COOC_2H_5)_2 \\ \text{(expected)} \end{array}$$



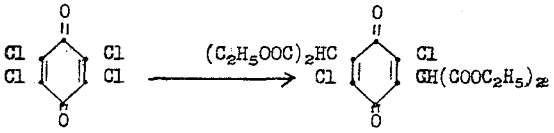


$$\begin{array}{c} RCH=CHCOOC_2H_5 \\ + \\ CH_2(COOC_2H_5)_2 \end{array} \xrightarrow{NaOC_2H_5} \begin{array}{l} RCHCH_2COOC_2H_5 \\ \quad | \\ \quad CH(COOC_2H_5)_2 \end{array} \xrightarrow[-CO_2]{HOH} \begin{array}{l} RCHCH_2COOH \\ \quad | \\ \quad CH_2COOH \end{array}$$

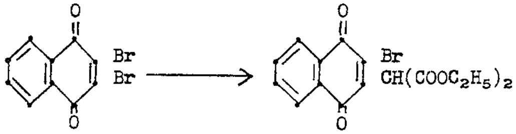


REACTIONS BETWEEN METALLIC ENOLATES AND SUBSTITUTED QUINONES

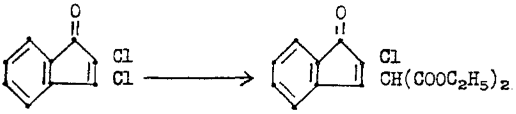
LEE IRVIN SMITH

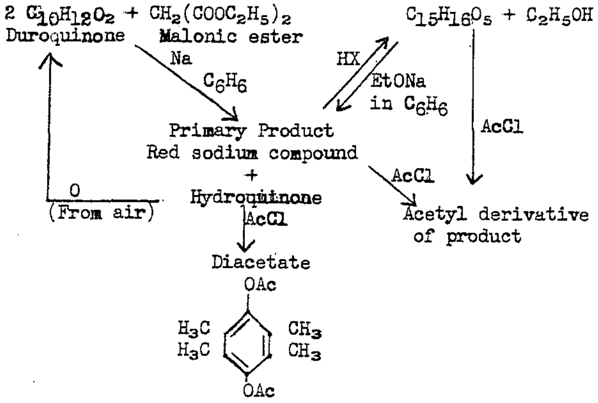


Stieglitz, Am. Chem. J. 13, 38 (1891)



Liebermann, Ber. 32, 262 (1897)



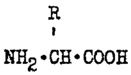


When ethanol is used as the solvent, much of the quinone is polymerized to a dimer which is very difficult to separate from the malonic ester addition product.

PROTEIN STRUCTURE IN RELATION TO BIOLOGICAL PROBLEMS

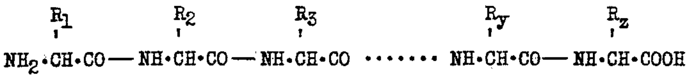
Max Bergmann

General Formula of Amino Acids



$$NH_2\cdot\overset{R}{\overset{|}{C}}H\cdot COOH$$

General Formula of Proteins (E. Fischer)



$$NH_2\cdot\overset{R_1}{\overset{|}{C}}H\cdot CO - NH\cdot\overset{R_2}{\overset{|}{C}}H\cdot CO - NH\cdot\overset{R_3}{\overset{|}{C}}H\cdot CO \cdots\cdots\cdots NH\cdot\overset{R_y}{\overset{|}{C}}H\cdot CO - NH\cdot\overset{R_z}{\overset{|}{C}}H\cdot COOH$$

(R_1, R_2, R_3, etc. = Side chains)

A protein consisting of 30 amino acid residues (among them 18 of different nature) can give rise to the existence of <u>1.28×10^{27}</u> different proteins (E. Fischer).

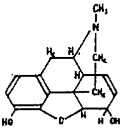
SLIDE II

Proteolytic Enzymes

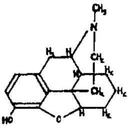
Enzyme		Substrate
Proteinases	Pepsin Trypsin Chymotrypsin Cathepsin Papain Bromelin	High molecular proteins
Polypeptidases	Carboxy-polypeptidase	$-CO \mid NH\cdot CHR\cdot COOH$
	Amino-polypeptidase	$NH_2\cdot CHR\cdot CO \mid NH-$
Dipeptidase		$NH_2\cdot CHR\cdot CO \mid NH\cdot CHR'\cdot COOH$

STUDIES IN THE SYNTHESIS OF COMPOUNDS WITH NARCOTIC AND ANALGESIC ACTION

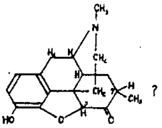
Erich Mosettig



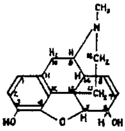
Morphine

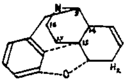


Dihydrodesoxymorphine-D
(Desomorphine)



Methyldihydromorphine
(Methyldilaudid)



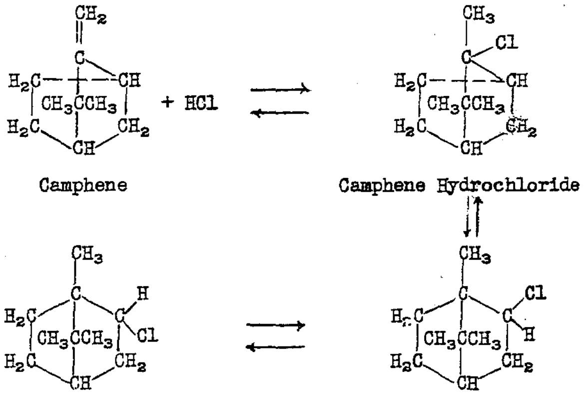


cis and trans asym. Octahydrophenanthrene

THE WAGNER-MEERWEIN REARRANGEMENT

By Paul D. Bartlett and Irving Pöckel

The most studied case of this rearrangement (Meerwein and van Emster, Ber., <u>55</u>, 2506 (1922)):



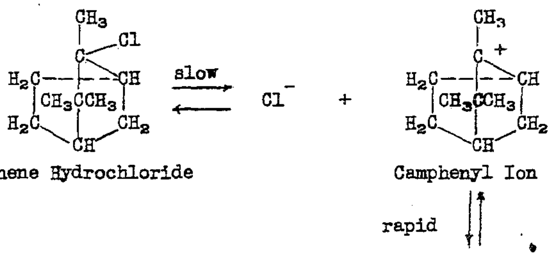
Camphene — Camphene Hydrochloride

Bornyl Chloride — Isobornyl Chloride

Meerwein and van Emster established that:

1. It is the chloride which rearranges, and the rearrangement is strictly reversible.
2. The rearrangement is favored by ionizing solvents, and is extremely slow in ether or pyridine.
3. The rearrangement is catalyzed by hydrogen chloride and by the chlorides of iron, mercury, tin, and antimony.
4. Isobornyl chloride comes easily into equilibrium with camphene hydrochloride, but only drastic conditions will bring it into equilibrium with its geometrical isomer, bornyl chloride.

Ionic mechanism proposed by Meerwein and van Emster:



Camphene Hydrochloride — Camphenyl Ion

FLUORINATION METHODS

Albert L. Henne

I. DIRECT ACTION OF FLUORINE ON
  - A. CARBON
  - B. HYDROCARBONS
  - C. ORGANIC SUBSTANCES

II. ADDITION OF HF TO
  - A. ETHYLENIC SUBSTANCES
  - B. ACETYLENIC SUBSTANCES

III. ESTERIFICATION OF AN ALCOHOL WITH HF

IV. INTERACTION OF AN ORGANIC HALIDE OR SULFATE WITH AN INORGANIC FLUORIDE

FLUORINATION BY SUBSTITUTION

$$\left.\begin{matrix} Me_2SO_4 \\ \text{OR} \\ AcCl \end{matrix}\right\} + KF \longrightarrow \left\{\begin{matrix} MeF + K_2SO_4 \\ \text{OR} \\ AcF + KCl \end{matrix}\right.$$

$$RBr + \left\{\begin{matrix} AgF \\ HgF \\ HgF_2 \end{matrix}\right. \longrightarrow RF + \left\{\begin{matrix} AgBr \\ HgBr \\ HgBr_2 \end{matrix}\right.$$

$$\begin{matrix} R \\ R' \end{matrix}\!\!>CCl_2 + SbF_3 \longrightarrow \begin{matrix} R \\ R' \end{matrix}\!\!>CClF \longrightarrow \begin{matrix} R \\ R' \end{matrix}\!\!>CF_2$$

$$AcCl + SbF_3 \longrightarrow AcF + SbCl_3$$

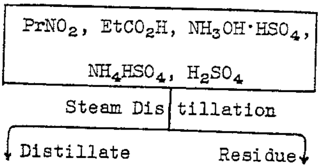
CONVERSION OF NITROPARAFFINS TO ALKANOIC ACIDS AND NITROALKANOLS

H. B. Hass

1. Prior Work

Authors	Nitroparaffin	Acids	Products
Victor Meyer and students	$EtNO_2$	H_2SO_4	$MeCO_2H + (NH_3OH)_2SO_4$
Preibish	$MeNO_2$	H_2SO_4	$CO + (NH_3OH)_2SO_4$
Mel'nikov	$MeNO_2$	H_2SO_4	CO, CO_2, $(NH_3OH)_2SO_4$ $(NH_4)_2SO_4$
Meyer & Locher	$MeNO_2$	HCl	HCO_2H NH_3OHCl
	$EtNO_2$	HCl	$MeCO_2H$ NH_3OHCl
	$PrNO_2$	HCl	$EtCO_2H$ NH_3OHCl
Geuther	$EtNO_2$	H_3PO_3	$MeCO_2H$ $NH_4H_2PO_4$
Werner	$EtNO_2$	H_3PO_3	$MeCO_2H$ NH_2OH salt
	$EtNO_2$	H_2SO_4	$MeCO_2H$ NH_2OH salt
	$EtNO_2$	HCl	$MeCO_2H$ NH_2OH salt
	$EtNO_2$	H_2SO_3	$MeCO_2H$ NH_2OH salt
Demole	$isoPr\cdot C(NOH)\cdot NO_2$	H_2SO_4	$CH_3\cdot CH(CH_3)\cdot CO_2H + N_2O$
Zublin	$BuNO_2$	HCl	$PrCO_2H$
Henry	$O_2N\cdot(CH_2)_3\cdot CN$	HCl	Succinic acid
Gabriel & Koppe	$C_6H_5\cdot CH_2NO_2$	HCl	$C_6H_5\cdot CO_2H$
Worstall	$nC_5H_{11}\cdot CH_2NO_2$	HCl	$nC_5H_{11}\cdot CO_2H$
	$nC_6H_{13}\cdot CH_2NO_2$	HCl, H_2SO_4	$nC_6H_{13}\cdot CO_2H + NH_2OH$ salts
	$nC_7H_{15}\cdot CH_2NO_2$	HCl	$nC_7H_{15}\cdot CO_2H + NH_2OH$ salts
	$nC_8H_{17}\cdot CH_2NO_2$	HCl	$nC_8H_{17}\cdot CO_2H + NH_2OH$ salts

2. Method of Analysis of Reaction Mixtures, e.g., from $PrNO_2$



$\underline{EtCO_2H}$ titrated using neutral red.
$\underline{PrNO_2}$ treated with excess NaOH and back-titrated with thymolpthalein.

$\underline{\overset{+}{NH_3}OH}$ determined by oxidation to N_2O with Fe^{+++} and titrating with $KMnO_4$ the Fe^{++} thus produced.
$\underline{\overset{+}{NH_4}}$ determined by distilling from basic solution into standard acid after destroying $\overset{+}{NH_3}OH$ by means of H_2O_2.
$\underline{H_2SO_4}$ determined by titration.

3. Reaction Mechanism

1.) $R\cdot C(NOH)OH + \overset{+}{H} + H_2O \rightarrow RCO_2H + \overset{+}{NH_3}OH$ as suggested by Bamberger and Rust is definitely the last step. A 44% yield of hydroxamic acid has been obtained in the present study.

THE BEHAVIOR OF CARBOHYDRATES IN ALKALINE SOLUTIONS

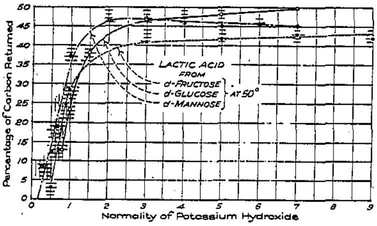
by Wm. Lloyd Evans

The Behavior of Carbohydrates in Alkaline Solutions

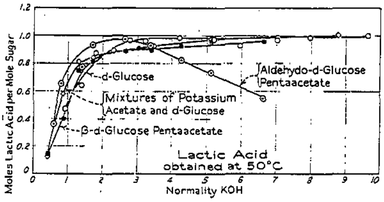
I. Rearrangements
   1a. Mutarotation.
   2a. Formation of other carbohydrates.
   3a. Formation of hypothetical sugar enediols.
   4a. Formation of saccharinic acids.

II. Polymerization to other Carbohydrates
   1a. Glycol aldehyde ⟶ Tetroses
   2a. Glyceric aldehyde ⟶ Fructose

III. Degradation
   1a. Fragmentation of carbon chain.
   2a. Formation of acids.



The effect of an increasing alkali normality on the yields of lactic acid from d-fructose, d-glucose, and d-mannose at 50°. (A 50% conversion of carbon to lactic acid is equivalent to one mole of lactic acid per mole of hexose used.)



The action of aldehydo-d-glucose (0.5 mole) in potassium hydroxide solutions of increasing normality. The mechanism of hexose degradation in alkaline solutions with the consequent formation of lactic acid postulates the opening of the pyranose ring to form the aldehydo-hexose, which in turn yields lactic acid through the intermediate formation of glyceric aldehyde.