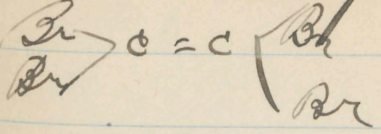
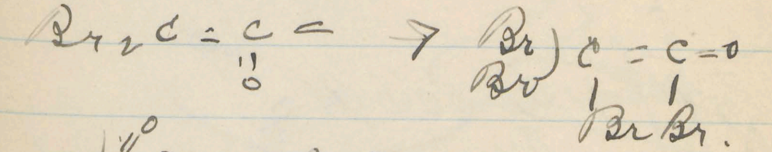
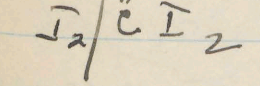
Wednesday Nov. 24, 1909



$Br_2C=CBr_2$



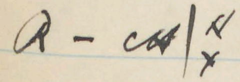
$Br_2C=C=O \rightarrow Br_2C(Br)=C(Br)=O$



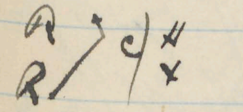
$I_2C(=O)I_2$ Red in color due to diss. iodine.

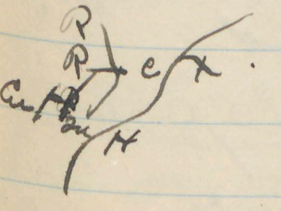
C_2H_5I 72° Boils. 1.944 Sp. Gr.
CH_3I 2.3 Sp. Gr.

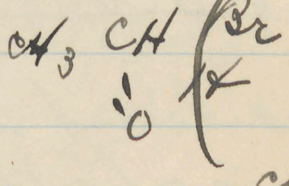
To detect subs halogen, destroy comp. by burning.



$R-CH(H)(X)$

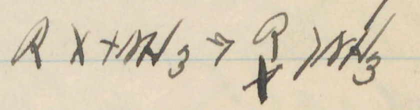




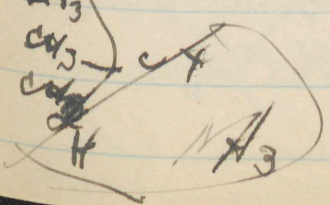


Oxidized by air.

ethylidene diss

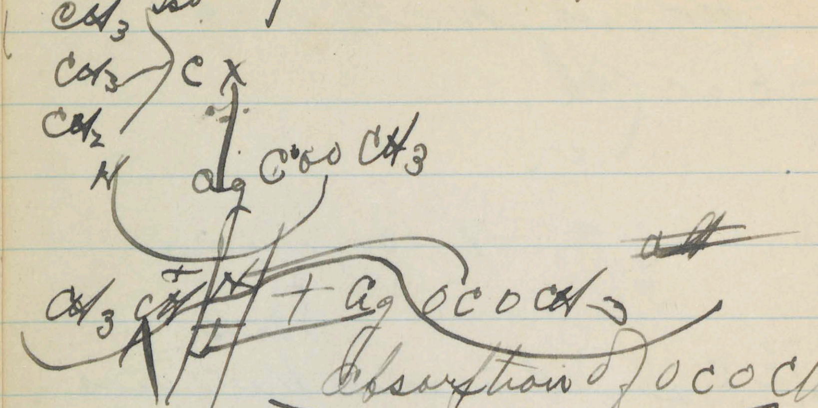


$RX + NH_3 \rightarrow R(X)NH_3$



Get NH_4X + rest [illegible]

Iso butylene = quant by NH_3 + $AgOCOCH_3$.



$(CH_3)_2C{=}CH_2$ + H, X, $AgCOOCH_3$

$CH_3CH^{I}_{H}$ + $AgOCOCH_3$

~~CH~~

Absorption of $OCOCH_3$.

$CH_3CH^{I}_{H} \rightleftarrows CH_3CH$ ~~+ HI~~

$AgOCOCH_3$

$AgNO_3$. Result same.

x HOC_2H_5

CH_3CH_2I + $AgOCOCH_3$

HOC_2H_5.

with ~~$AgOCOCH_3$~~. → 40%

$CH_3CH^{H}_{OC_2H_5}$

Acetic acid is not touched + alc. is absorbed. 95% Ether formation

with $AgNO_3$ get 95%

$CH_3CH_2ONO_2$ → $CH_3CH^{H}_{OC_2H_5}$

5% 95%

Experimental proof of ethylidene diss + not olefine diss.

Not olefine diss in ~~$CH_2 \; CH_2$~~

~~H I~~

KOH

Very small amt olefine. It comes by rearrang

$CH_3CH^{H}_{I}$ + KOH.

Rearrangement

$CH_3CH^{H}_{I}$ Na ~~OHH~~ OC_2H_5

C_2H_5I

Ethylidene takes up Na OC_2H_5, Et. Prod.

1/4 [illegible] Finely divided.

$\frac{Na}{I}$ OC_2H_5

C_2H_5.

No olefine No ether formation

HgOH is taken up quant.

Hence this proves ~~that we~~ have ethylidene diss as an intermediate prod. It must be active olefine.

Halogens in benzol derivs the X is not much diss

Not enough diss into HX is the reason.

$Cl-C \equiv N$

$AgOCOCH_3$ } Can't get $AgCl$.

Monday Apr 29, 1909.

$AlCl_3$ in alcs. has tendency to increase activity diss

C_nH_{2n+2}

$C_nH_{2n+1} \rightarrow$ X X H, 1st addition prod

~~C_2H_5~~ $CH_3 \; CH_2Cl + Cl_2 \rightarrow CH_3CHCl_2 + HCl.$

Those H having to C atoms containing Cl are most active & we get $CH_3CCl_3 + HCl$.

$AlCl_3$ (Fe Cr Al Finely divided) or $AlBr_3$.

Contact agents

$AlBr_3 + C_nH_{2n+2} \rightarrow CH_2Br_2 + CH_2Br$. aethylen bromide

or finely divided Fe + Al.

$CH_3CH_2-CH_2Br = Br\,AlBr_2$

at 100° we get

$CH_3\underset{Br}{CH}-CH_3$ we shift Br.

Al(Cl=Cl, Cl=Cl, Cl=Cl) Al.

(Na-Cl=Cl-Na) X

From C_6H_{14} [illegible] we get [illegible]

C_2Cl_4	CH_2Cl_2	CH_2I_2
C_2Cl_6	$CHCl_3$ 68	CHI_3
CCl_4	CCl_4 74.	CI_4.

$C_2I_2 = C_2I_2$

$CI_2 = CI_2$

$CH_3CH_2OH + CaOCl_2$ Scarcely known.

$(CH_3)CHO + Cl_2$

$CCl_3CHO + 3HCl.$ chloral.

$NaOH \rightarrow CCl_3$

KOC

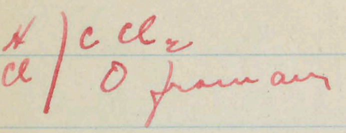
OH.

From wood $\rightarrow CH_3OH$, $\frac{CH_3}{CH_3}$ > CO + CH_3COOH,

$\frac{CH_3}{CH_3}$ > CO + $Cl_2 \rightarrow CCl_3$ / CCl_3 { –C OK, OK

CH_3COOCa by lime & we get acetone.

$CHCl_3$

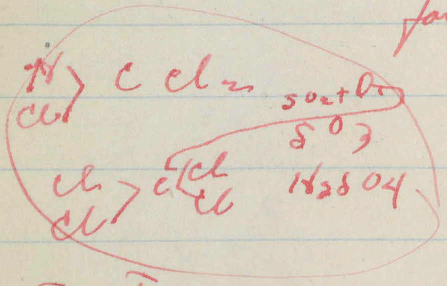


$\left.\begin{matrix}H\\Cl\end{matrix}\right) CCl_2$

O from air

C_2H_5-OH.

$\left.\begin{matrix}Cl\\Cl\end{matrix}\right> C = O$ gives ethyl carbonate + HCl which decreases mass action & prevents formation of $COCl_2$.



$\left.\begin{matrix}H\\Cl\end{matrix}\right> CCl_2$ SO_2+Cl_2

SO_3

$\left.\begin{matrix}Cl\\Cl\end{matrix}\right> C\begin{matrix}Cl\\Cl\end{matrix}$ H_2SO_4

$OCCl_2$

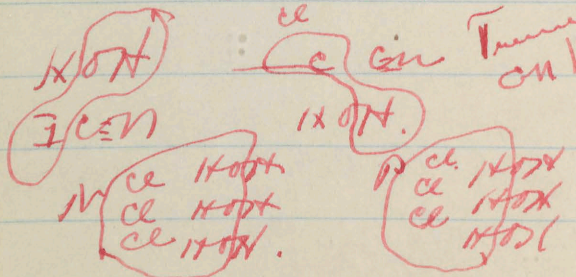
SO_2

$+HCl$

$\left.\begin{matrix}I\\I\end{matrix}\right> C\begin{matrix}I\\I\end{matrix}$ HIO

$\left.\begin{matrix}Cl\\Cl\end{matrix}\right> C\begin{matrix}Cl\\Cl\end{matrix}$ $CHCl_3 + NOCl$.

$HC\begin{matrix}Cl\\Cl\end{matrix}$ HOH.



$\overset{Cl}{C}$ CN

HOH

$I\,C\equiv N$

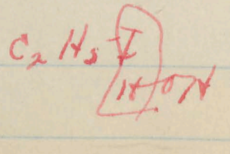
HOH.

$N\begin{matrix}Cl & HOH\\Cl & HOH\\Cl & HOH.\end{matrix}$

$P\begin{matrix}Cl & HOH\\Cl & HOH\\Cl & HOCl\end{matrix}$

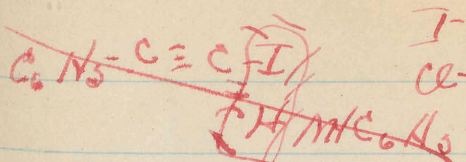
Tremendous diff between

on holding Cl or I.



$C_2H_5\,I$

HOH

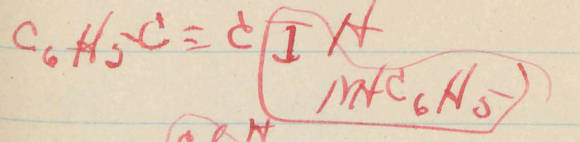


~~$C_6H_5-C\equiv C-I$~~

~~H NHC_6H_5~~

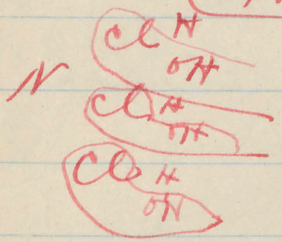
$I-C\equiv N$ Large mass I makes inert &

$Cl-C\equiv N$. Cl makes active



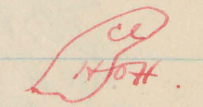
$C_6H_5-C\equiv C\ I\ H$

NHC_6H_5



$N\begin{matrix}Cl\begin{matrix}H\\OH\end{matrix}\\Cl\begin{matrix}H\\OH\end{matrix}\\Cl\begin{matrix}H\\OH\end{matrix}\end{matrix}$

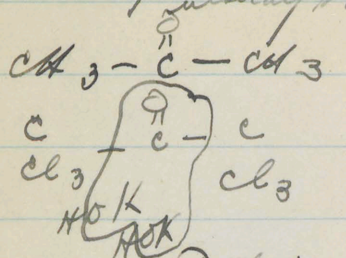
PCl_2



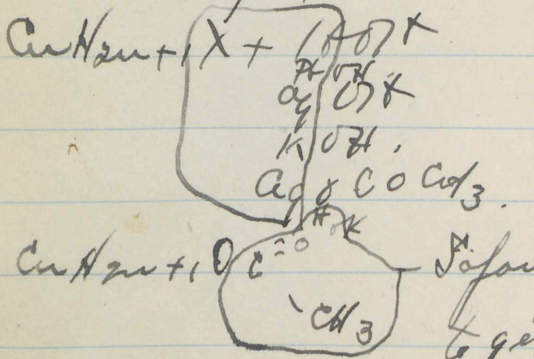
Cl

HOH.

Tuesday Nov. 30, 1909.



Prep Monatomic Alcohols



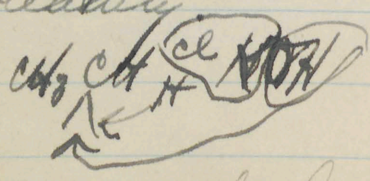
Saponification of ester to get alcohol.

All alcohols by additions by K_2CO_3 separate out of H_2O sol.

C_2H_5-OH + CH_3OH - fractionate.

$C_nH_{2n}\overset{H}{X}$ + HOH Sealed tubes 200 to 300

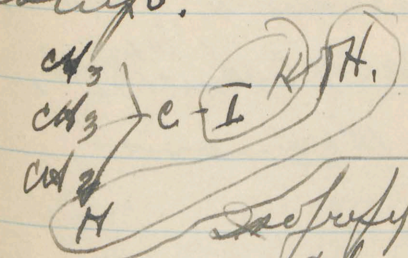
Salts of H_2O like AgOH + PbOH act more readily



Tertiary alkyl halides with OH comps

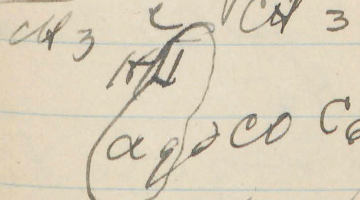
give olefines exclusively

Limited to I + II alcohols with OH comps.



Olefine is only product.

Isopropyl iodide



Propane when exchanges fast.

Dilute with ether and we control action. Above is exception to rule unless we are careful

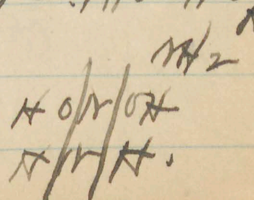
$C_nH_{2n+1}NH_2 + HONO \rightarrow C_nH_{2n+1}OH$
$+ N_2$
$+ H_2O$

$NH_3 + HONO$.

$NH_4ONO \rightarrow NH_3 + HONO \rightarrow HONO$

NO group is unsaturated

K or Na NO_2 Lab Method.
+ NH_4Cl & we get NH_3



$NH_{3\,ONO_2}^{\;H} \rightarrow NH_3 + HONO \rightarrow \overset{HNH}{\underset{O}{H\,N\,OH}}$

Laughing gas.

Analogous to above reaction with HOH O.

$C_nH_{2n+1}NH\,H. + HONO \rightarrow C_nH_{2n+1}OH + N_2 + H_2O$

$HONOH$ Non-ionic

$N\,NR$

HON Isolate, Aromatic.

NC_6H_5

Diazo benzol.

$N\,C_nH_{2n+1}$

$N\,OH.$

Fatty diazo comps.

$\overset{N}{\underset{N}{\|}}{>}C_nH_{2n} + 2H_2O$

$CH_2{<}\overset{N}{\underset{N}{\|}} + HOH \rightarrow CH_3OH + N_2$

$HOC_2H_5 \rightarrow CH_3OC_2H_5 + N_2$

X_2

$HX + CH_3X + N_2$

$CH_2X_2 + N_2$

Fatty diazo comps have N bound to same Carbon.

$CH_3CH_2CH{<}\overset{N}{\underset{N}{\|}}$ HOH.

$CH_3\,\underset{N}{CH}\,\underset{N}{CH_2}$

$CH_3CH_2CH_2NH_2 + HONO$ $\frac{2}{3}$ n Propyl alc.

$\frac{1}{3}$ Iso " "

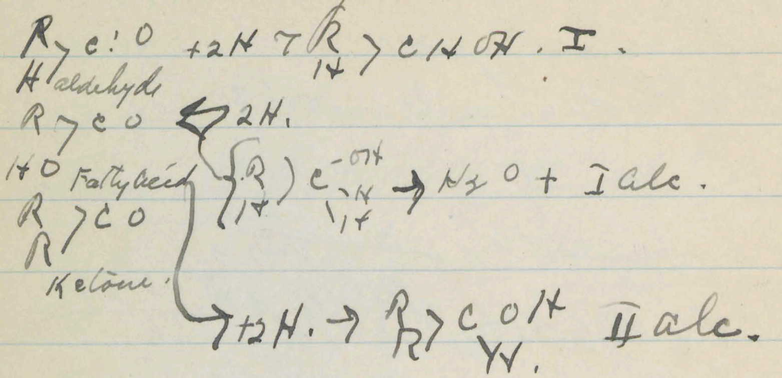
$\overset{CH_3\;\;CH_3}{\underset{CH_2NH_2}{\vee_C}} + HONO$

25% ~~III~~ butyl alcohol.

25% III butyl alcohol.

50% isobutylene

Wednesday Dec. 1st 1909.



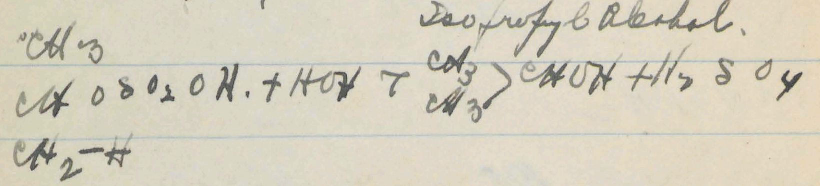
$\genfrac{}{}{0pt}{}{R}{H}{>}C{:}O + 2H \rightarrow \genfrac{}{}{0pt}{}{R}{H}{>}CHOH$. I.

aldehyde

$\genfrac{}{}{0pt}{}{R}{HO}{>}CO \leftarrow 2H$ Fatty acid $\genfrac{}{}{0pt}{}{R}{H}{>}C{\substack{-OH\\-H\\-H}} \rightarrow H_2O +$ I alc.

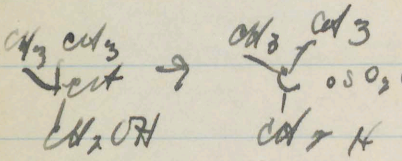
$\genfrac{}{}{0pt}{}{R}{R}{>}CO$ Ketone. $+2H \rightarrow \genfrac{}{}{0pt}{}{R}{R}{>}C\genfrac{}{}{0pt}{}{OH}{H}$. II alc.

$C_nH_{2n} + H_2SO_4$



Isopropyl alcohol.

$\begin{matrix}CH_3\\ CH\,OSO_2OH\\ CH_2-H\end{matrix} + HOH \rightarrow \genfrac{}{}{0pt}{}{CH_3}{CH_3}{>}CHOH + H_2SO_4$



$\begin{matrix}CH_3\ CH_3\\ CH\\ CH_2OH\end{matrix} \rightarrow \begin{matrix}CH_3\ CH_3\\ C\ OSO_2OH\\ CH_2H\end{matrix}$

Pour into H_2O & make alkaline & liquid separates out Tertiary butyl alcohol.

$\begin{matrix}CH_3\\ CH_3-\\ CH_3\end{matrix}{>}COH.$

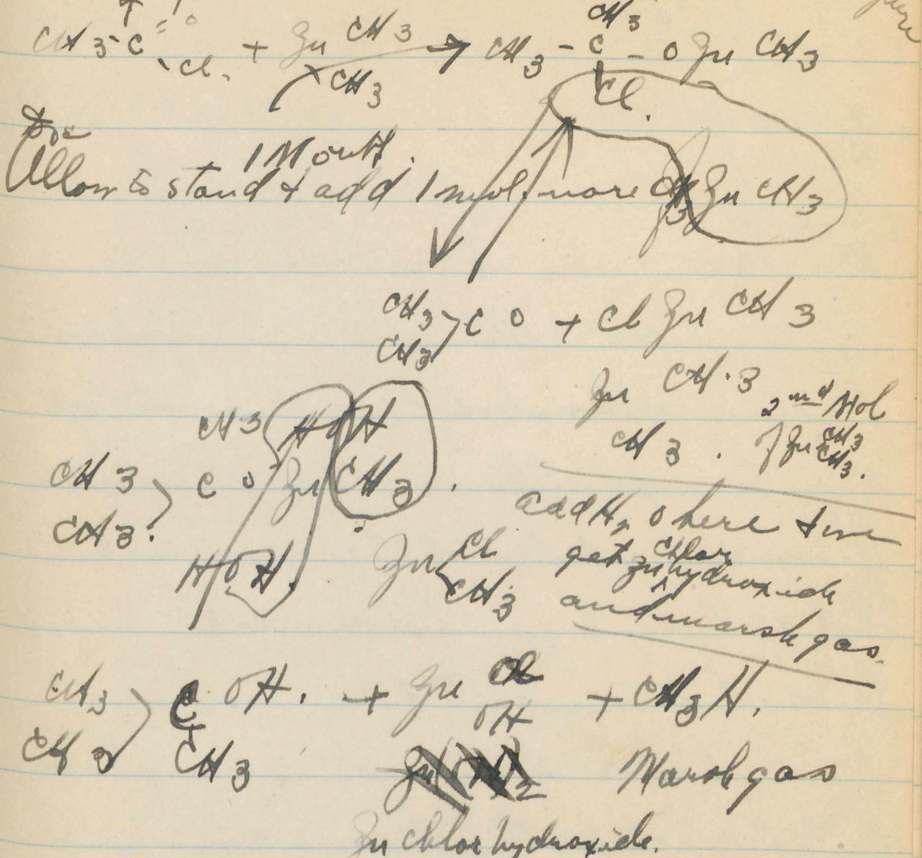
$\begin{matrix}CH_3\\ CH_3\\ C_2H_5\end{matrix}{>}COH$

Lose H_2O on boiling with dil Acid

Act as if only olefine + H_2O.

Butlerow.

Butlerow Method. abs. ether as solvent CO_2 atmosphere



$CH_3-C\genfrac{}{}{0pt}{}{=O}{-Cl} + Zn\genfrac{}{}{0pt}{}{CH_3}{CH_3} \rightarrow CH_3-\overset{CH_3}{\underset{Cl}{C}}-OZnCH_3$

~~for~~ Allow to stand 1 Month & add 1 mol. more $ZnCH_3$

$\genfrac{}{}{0pt}{}{CH_3}{CH_3}{>}CO + ClZnCH_3$

$Zn\genfrac{}{}{0pt}{}{CH_3}{CH_3}$ 2nd Mol $Zn\genfrac{}{}{0pt}{}{CH_3}{CH_3}$.

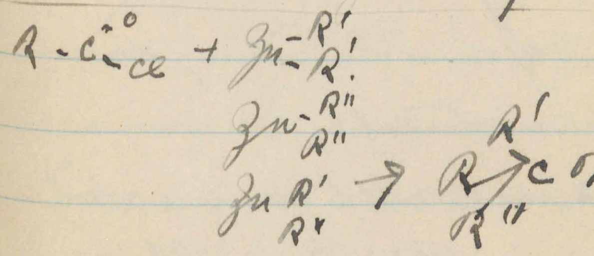
$\genfrac{}{}{0pt}{}{CH_3}{CH_3}{>}C\begin{matrix}CH_3\ HOH\\ O\,Zn\,CH_3\\ HOH\end{matrix}$

$Zn\genfrac{}{}{0pt}{}{Cl}{CH_3}$ add H_2O here & we get zinc chlor hydroxide and marsh gas.

$\genfrac{}{}{0pt}{}{CH_3}{CH_3}{>}\underset{CH_3}{C}OH. + Zn\genfrac{}{}{0pt}{}{Cl}{OH} + CH_3H.$

~~$Zn(OH)_2$~~ Marsh gas

Zn chlor hydroxide.



$R-C\genfrac{}{}{0pt}{}{=O}{-Cl} + Zn\genfrac{}{}{0pt}{}{-R'}{-R'}$.

$Zn\genfrac{}{}{0pt}{}{-R''}{R''}$

$Zn\genfrac{}{}{0pt}{}{R'}{R''} \rightarrow \begin{matrix}R'\\ R\\ R''\end{matrix}{>}COH$. General method whereby we can make many of the alcohols but method is very expensive.

Slightly ionizable Very small.
Slightly acid Less than H_2O.

I $R\ CH_2\ OH$
II $R, R' > CH\ OH$ KOH.
III $R, R', R'' > C\ OH$.
Na.

These alcohols are obtainable from vegetable kingdom. Other alcohols are made by subjects grape sugar to alc. fermentation yeast & we get alcohol & CO_2. yeast plant does not do this but zymase an albumenoid subs which is secreted.

Fusel oil contains butyl alcoh & amyl alcohol. Amyl alcohol is injurious in cheap liquors. Fusel oil comes from breaking down of proteinaceous material.

Pyridine & CH_3OH are used to denature alcohol.

HOH 100
CH_3OH 66 Sp. Gr. 0.817
C_2H_5-OH. 78 0.806
C_3H_7OH. 98
nao 81

CH_3OCH_3 23°.6
C_2H_5-OC_2H_5- 36°

$H\ SH$ gas. not diss liquids.

C_2H_5-SH B.pt. 36.

Alcohols before they boil must be in bi, tri molecular form otherwise they would boil very low & be a gas.

CH_3 lowers Sp. Gr. & makes less than H_2O.

CH_3 makes diff of about 20° in boiling point if structure is the same. Forked chain lowers B.Pt.

CH_3
$CH_3 > C$-$CH_2\ OH$. Melts 53.
CH_3 Recently discovered alcohol.

Being close to HOH. CH_3OH & C_2H_5·OH. mix with H_2O in all proportions. As soon as mass becomes larger sol. decreases C_3H_7OH. etc.

$CH_3CH_2OH + KOH$. Deep brown color is $CH_3CH_2OK + HOH$. due to salt of alcohol.

Putting in Metal in alc increases dissociation of ethylidene. $RCH^{H}OM$.

Test for H_2O_2 & aldehyde in ether due to slow burning.

$CH_3CHO + KOH \rightarrow$ Resin & this is what causes color in Alc KOH. because aldehyde is formed & aldehyde resin is formed.

To determine I II III alcohols use oxidizing agent.

$KMnO_4$, CrO_3

$\begin{matrix}R\\H\end{matrix}>C\begin{matrix}H\\OH\end{matrix} \rightleftarrows \begin{matrix}R\\H\end{matrix}>C\begin{matrix}-\\ \backslash\end{matrix} + H_2O$.

$CH_3\underset{\wedge}{CH}\overset{H}{}OH \rightarrow$ Get no trace of glycol hence we get ethylidene.

80% to CH_3CHO

$CH_2-CH_2 + H_2O$

$\begin{matrix}CH_2 & - & CH_2\\ \downarrow & & \downarrow\\ OH & & OH\end{matrix}$.

Glycol.

Monday Dec. 6, 1909.

With Pt. sponge on watch glass and pour on alcohol temp. rises & we get alcohols oxidized. Sponge does not affect dissociation of alcohol, but increases the activity of the oxygen.

$\begin{matrix}R\\H\end{matrix}>C=\left|\begin{matrix}H\\OH\end{matrix}\right.$

$\begin{matrix}R\\R\end{matrix}>C/\begin{matrix}H\\OH\end{matrix}$. Methylene diss & not olefine in this case: can't be isolated.

$\underset{\text{aldehyde}}{RCHO} + H_2O \rightarrow \begin{matrix}R\\H\end{matrix}>C\begin{matrix}OH\\OH\end{matrix} \rightarrow \boxed{R\underset{\overset{\|}{O}}{C}OH} + H_2O$.

$\begin{matrix}R\\R\end{matrix}>C=O$ Can't be oxidized further

Ketone

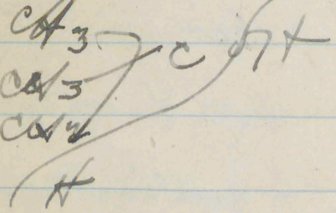
$\begin{matrix}R\\R\end{matrix}>\underset{\overset{\|}{O}}{C}\left|\begin{matrix}ONa\\H\end{matrix}\right.$

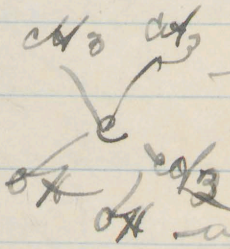
$\begin{matrix}R\\R\end{matrix}>\underset{\overset{\|}{O}}{C}\left|\begin{matrix}ONa\\H\end{matrix}\right.$

} spontaneously combustible hence much more diss are the salts than the original substance

$\begin{matrix}R\\CH_2\\H\end{matrix}>C\begin{matrix}H\\OH\end{matrix}$ Enolmol is formed.

formic acid must consist of $CO + H_2O$ to $\frac{1}{10}$ 1 % at ord temp. & with AgOH we get silver mirror ~~oxide~~ & CO_2. Hence formic acid is physiologically almost as bad as CO.



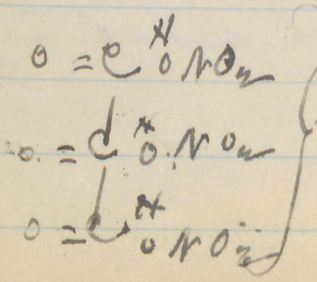


Glycol should be the result but we are not yet positive. Glycol is very easily oxidized further.

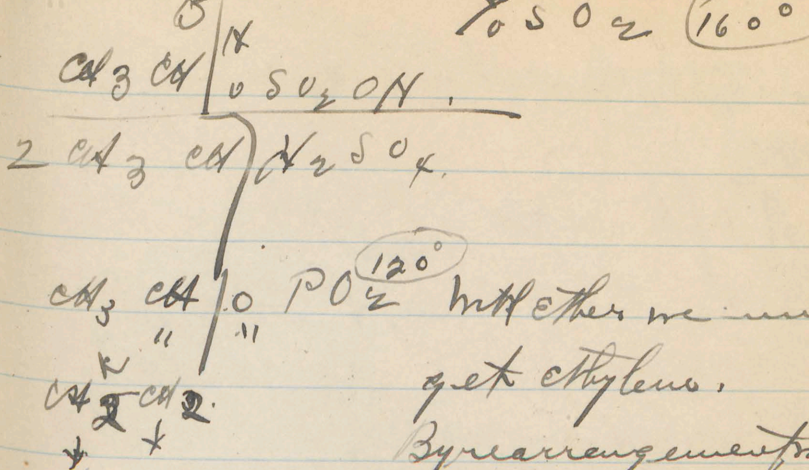
$CH_3\,CH\overset{H}{\underset{ONa}{|}}$ $HON\overset{=O}{\underset{=O}{}}$

Intra molecular oxidation.

$CH_3\,CH\overset{H}{\underset{ONa}{|}}$ $HON\overset{=O}{\underset{=O}{}}$



nitroglycerine. Smokeless powder acts same way.



$CH_3\;CH\,|\,O\;PO_2$ 120° with ether we must get ethylene.

$CH_2\;CH_2$

By rearrangement we get by mol. reversible process ethylene. With Al_2O_3 we get ~~ethylene~~.

$ROH + \underline{H_2SO_4}$ HCl

$HONO_2$

R|OH. PCl_5

HCl. Impossible

$\overset{R}{H} \rangle \overset{C}{\wedge} \Big| \overset{H}{OSO_2OH} \rightarrow \overset{R}{H} \rangle \overset{C}{\wedge} + H_2SO_4$.

$HONO_2$

HCl

Dissociation must be above a certain limit before HCl or $HONO_2$ is added on. Methyl nitrate separates out in streams at 0° when we

have H_2SO_4 present with CH_3CH_2OH and
$HONO_2$.

$3.\ RO|H\ \begin{matrix}Cl\\Cl\\Cl\end{matrix}{>}P$ $(RO)_3P + HCl$

$3\ C_nH_{2n} + (RO)_3P$

$CH_3CH^{H}_{Cl}$.

Do get $R(OH)_3$ + $3RCl$.

$ROH + H_2SO_4 \rightarrow R|OSO_2OH + HOH$

$R|OH$ starts at 95° & at 140° is complete

Williamson's method,

C_2H_5-OSO_2OH

C_2H_5-$OSO_2OC_2H_5$.

C_2H_5-OH.

$\underset{H}{C_2H_4)}OSO_2O\underset{H.}{(C_2H_4}$ Ethylidene

Ethylidene then simply adds on the C_2H_5OH.

Must have at least % dis at 90° before ether formation starts to take place

Ether. $CH_3CH^{H}|OC_2H_5$ Must be reversible

Dumas Stass Reaction.

$RCH_2OH + KOH \rightarrow RC^{O}_{OK} + 2H_2$

CaO. Fatty Acid.

at 250°.

Can be ~~determined~~ used to determine R quantitatively.

$\overset{R}{R}{>}CHOH + KOH \rightarrow \overset{R}{R}{>}CO + H_2$

Really an oxidation of primary alc at 250°

$CH_3OH\ KOH$

$HOC^{O} + 3H_2$
KO

alc in acid.

R-$CH_2OH + KOH$,

$\rightarrow RCHOK + H_2O$

H Salt. no air present.

$RCH \rightarrow HOK$

$R\,CH_2OH$ HOK: metallic K here
$+H_2$

$CH_2{}^{ONa}_{H.}$ to 400° we get $CH_2{}^{OH\ Na}_{OH.\ Na.}$

$CH\ OH.$
$H\ OH.$

$C-Na$
‖
$C-Na$ Sodium carbide.

$CH_2{}^{OH}_{OH}$
↓
$H\ OH.$
↓
CH_3OH
↓
$HCOOH$

Bivalent carbon alone take up hydroxyl ions & these set free H and then by loss of H_2O we can get metallic carbide —

Na methylate in solder bath to 400° we get:

$C-Na$
‖
$C-Na$

formalin & formaldehyde + $NaOH$ gives methyl alcohol & formic acid in equal quantities

Tuesday Dec. 7, 1909.

$2\ CH_3CH_HOH \rightarrow CH_3CH\ 12H - OH.$

$CH_3CH{}^{OH}_{OH}$ H H

$\rightarrow \left.\begin{matrix}CH_3\\CH_3\end{matrix}\right]CO =$

$\left(\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right]C{}^{OH}_{|}\right)_2$ Pinacone.

Glycerine & sugar goes much more energetically but alone H can be proved to be proved.

Sulphates & phosphates of tertiary butyl alcohol cannot be isolated. Gives iso butylene & H_2O & like NH_4OH gives $NH_3 + HOH$. & $NH_4Cl \rightarrow NH_3 + HCl$ 350°

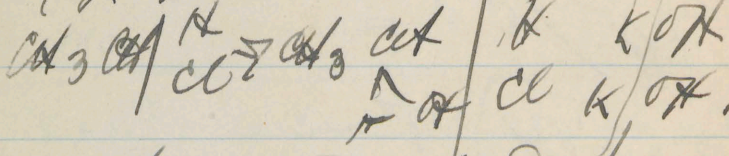
Ethyl alcohol burnt with [illegible] we get acetic acid.

aldehyde
Ethyl alcohol + heat $\rightarrow CH_3CH\ O|{}^{H}_{H}$ 80%
20% to $CH_3CH_2 \rightarrow CH_2-CH_2 + H_2O$ Hot tube
ethylene + water.

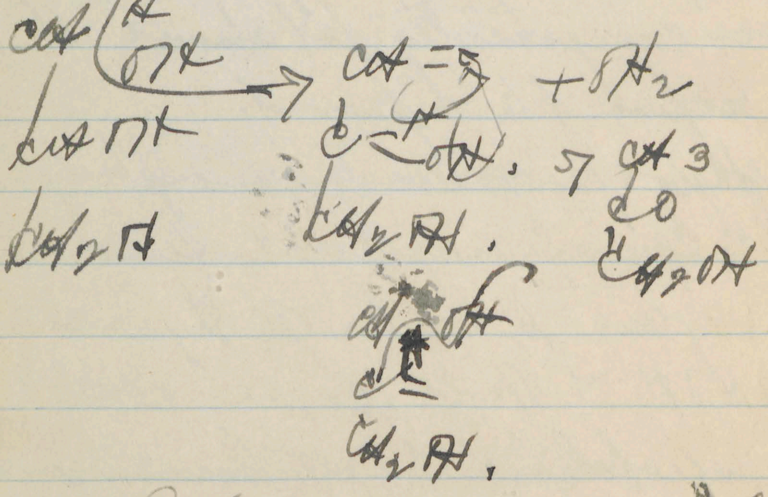
Pass C_2H_5OH over P_2O_5 & we get ethylene + H_2O quant. This is due to rearrangement.

C_2H_5Cl hot tube 650° & through H_2O we get CH_2–CH_2 quant.

Add KOH

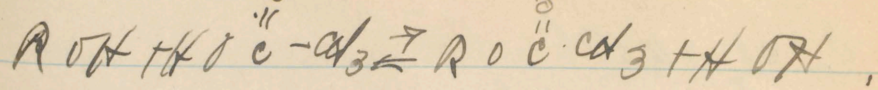


We get acetic acid in harmony with Dumas Stas reaction.



5-8% of glycerine goes each as given above

Shifting of hydroxyl groups in organic molecules

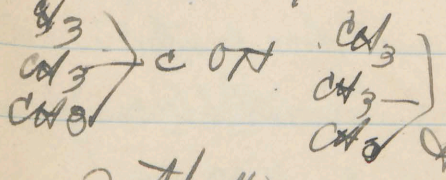


$ROH + HO\overset{O}{\overset{\|}{C}}-CH_3 \rightleftarrows RO\overset{O}{\overset{\|}{C}}CH_3 + HOH$.

I 46% to 50%

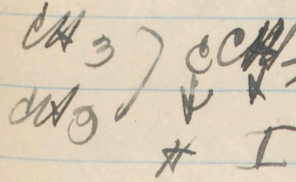
II 17-26%

III 1-2%



$+ H_2O$ don't go this way.

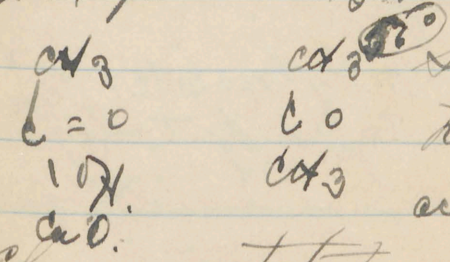
with HX



$+ HOH$.

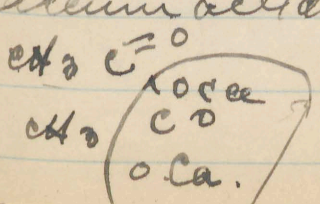
This don't have anything in regard to basic character of alcohols.

Wood spirit. CH_3OH 66°



Shiftings must take place to give acetone & acetic acid.

Calcium acetate to make chloroform.



$CaCl_2\ 2KOH$

$CaCl_2\ 4\ HOCH_3$.

Separate out crystals distil.

Wednesday Dec. 8, 1909.

Fused $CaCl_2 + CH_3OH$ can be heated to 100° without loss of alcohol. Form stable compounds like hydrates.

$CaCl_2$	– $CaCl_2\ 4\,CH_3OH$ =
NH_3	K_2CO_3 causes methyl alcohol
H_2NR.	to separate out as layer in
HNR_2	H_2O sol.

Call BaO + $CuSO_4$ anhydrous.

Distil with small quantity of sodium.

$$\begin{matrix} COO\boxed{H\ HO}CH_3 \\ COO\boxed{H\ HO}CH_3 \end{matrix}$$

Methyl oxalate 185°

Saponify + we $\overset{KOH}{}$ get.

pure methyl alcohol

acetone free The acetone goes over before 185°.

CH_3OH alcohol.

$\overset{H}{C}H_2O$. aldehyde.

$\downarrow$

$\left.\begin{matrix}H\\HO\end{matrix}\right\rangle CO$. formic acid.

CO_2

CH_3CH_2OH. CH_2O aldose hexoses.

CH_2OH	× $CHOH$	
CO	× $CHOH$	
$CHOH$		
$CHOH$	× $CHOH$	$\rightarrow$ $2\,CO_2$ $2\,CH_3CH_2OH$.
$CHOH$	× $CHOH$	
CH_2OH	CH_2OH	

d fructose.

laevulose. dextrose, d Gluc~~ose~~ Honey.

fruit sugar.

$\downarrow$ $2\ CH_3\ CHOH\ COOH + \left(\begin{matrix}3\,CH_4\\CO_2\end{matrix}\right)$

by Yeast.

Zymase, sol in H_2O. C H O N.

Related to albumenoids

$C_6H_{12}O_6$

$2CH_3CH_2OH$

$2CO_2$

1 CH_2O

2 × CHOH $\boxed{HO}$ Enz

3 × CHOH

4 × CHOH

5 × CHOH

6. CH_2OH

$(C_6H_{10}O_5)_x + xH_2O$

$+ H_2SO_4.$

Barley Heat paste

$CH\ O$

$CH\ OH$

$CH\ OH$

$CH\ OH$

$CH\ OH$

$CH_2\ OH.\ x.$

Diastase

Maltose $C_{12}H_{22}O_{11}$

Maltase Enzyme.

Starch to superheated steam 120–140

Mechanical Chemical to maltose

& then dextrose & glucose.

Diastase, H O Eng, splits starch

80% Maltose 20% Maltose dextrine

Goes over ultimately to maltose.

Cool sol to 15° & put in yeast of

special kind 25 to 30% varieties

Nitrogenous material & phosphorous

acid. Must be plenty of H_2O present

& strong alc. over 8% kills enzyme

Separate Alc from H_2O by frac distillations

Fusel Oil $CH_3\ CH_2\ CH_2\ OH$ 98°

$CH_3 > CH - CH\ OH$, 107°

CH_3

Iso amyl

optical active amylate.

Glycerine $CH_2\ CH_2\ CH\ OH\ CH_2\ OH.$

Succinic $CH_2 - CH_2 - COOH.$

COOH

100 pts sugar

2.5 – 3.7 pts glycerine

$\frac{1}{800}$ vol part. fusel oil.

0.4 – 0.7 pts Succinic.

Monday Dec. 13, 1909.

Unsaturated Alcohols.

		X	Y
CH_2	CH_2	$CH\,OH$	CH_2
$\Vert$	$\Vert$	$\Vert$	$\Vert$
CH	CH	CH	$C\,OH$
$\vert$	$\vert$	$\vert$	$\vert$
CH_3.	$CH_2\,OH$	CH_2	CH_3
	γ	α known as	β

enols aldehydes + ketones.

allyl alcohol.

Glycerine + oxalic acid → allyl alcohol

Ought to show behavior of olefine

add Halogens + HX also H_2SO_4.

" " " " " I alcohols.

unsaturated aldehyde $\begin{matrix} CH_2 \\ \Vert \\ CH \\ \vert \\ CHO \end{matrix} \rightarrow \begin{matrix} CH_2 \\ \Vert \\ CH \\ \vert \\ C - OH. \\ \Vert \\ O \end{matrix}$

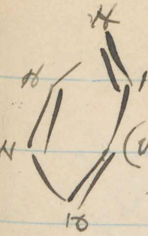
$CH\,Br$

$CH\,Br$ Propylargyl alcohol.

$\begin{matrix} \vert \\ C\,OH \\ H_2 \end{matrix}$, alcohol of acetylene series.

Two pts of attack { double bond (1)

in unsaturated alcs. { alcohol group (2)



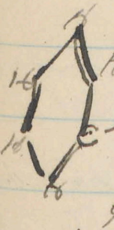
(OH) not an alcohol.

an acid
{ Carbolic acid
{ Phenols.

Comparable to III alcohols.

$CH_3\,C \overset{=O}{-OH}$. Influence of unsaturation

$CH_3\,C \overset{H_2}{-OH}$. C group unsat O on same C as OH group.



$\hat{O} / \hat{H}$ Influence of double bond to make acid

$CH\ \hat{O} / \hat{H}$

^ are known only

$C_6H_5\,\underset{\Vert}{C}\ / OH$ Enols, of aldehydes can't be isolated

→ X → $\begin{matrix} CH_2O \\ \vert \\ CH_2 \\ \vert \\ CH_3 \end{matrix}$ Y = $\begin{matrix} CH_3 \\ \vert \\ CO \\ \vert \\ CH_3 \end{matrix}$

CH_3	$CH\,OH$
CHO	$\Vert$
	CH_2
acetaldehyde	vinyl alcohol can't be isolated.

Formaldehyde

CH_2O small amount present

$\boxed{CH\,\hat{O}\hat{H}}$ Lead hydroxide in H_2O sol with formaldehyde gives enol molecules & hence silver reduction depends on this & also sugar formation.

CHO

CH_2OH with alkalies to gives dextrose & levulose

$\to CHOH$

$\to CHOH$

Aldol condensation is most important condensation in organic chemistry

Acetaldehyde CH_2 with alkali

$CHOH$. gives Hg salt

$Hg\boxed{OH}$ Mercury alcohol

White salt.

Alcohols to ethers.

$\boxed{C_2H_5 \cdot OH + H_2SO_4}$

$\left.\begin{array}{l}C_2H_5\\C_2H_5\end{array}\right\rangle O$ $\left.\begin{array}{l}CH_3\\C_2H_5\end{array}\right\rangle O$ Mixed ether. ROR'

$\left.\begin{array}{l}H\\H\end{array}\right\rangle O$ $\left.\begin{array}{l}CH_3\\CH_3\end{array}\right\rangle O$ Simple ether ROR.

Williamson can't be correct. $\boxed{1862}$?

$C_2H_5\boxed{I + Na}OCH_2CH_3 \to$ Ether

$CH_3\boxed{I + Na}OC_2H_3 \to$

$C_2H_5\boxed{I + Na}OCH_3 \to$

$\left.\begin{array}{l}Ag\\Ag\end{array}\right\rangle O + 2IR.$

$\left.\begin{array}{l}R\boxed{I\ Ag}\\R'\boxed{I\ Ag}\end{array}\right\rangle O$

$C_2H_5{-}OH + HOSO_2OH.$

$C_2H_5{-}OSO_2OH + H_2O.$

$(C_2H_5)OSO_2O + H_2O$ 0.25% −20°C. below zero.

$C_2H_5{-}OSO_2OH + C_5H_{11} \cdot OH.$

$C_2H_5{-}OC_5H_{11} + H_2O.$

140°

$C_5H_{11}OC_5H_{11}$

$C_5H_{11}OSO_2OH + C_2H_5OH.$

$C_5H_{11}OC_2H_5 + H_2SO_4.$

$C_2H_5OH + H-OSO_2OH.$ } I 0° + -20°

$C_2H_5-OSO_2OH + H_2O$

140° II { $C_2H_5-OSO_2OH + C_2H_5-O-H \rightarrow$

$C_2H_5-OC_2H_5 + H_2SO_4$

If ionization takes place we should have ether formation at ordinary T's. Before 94° we have no ether formed. 94°-140° the amt of ether formed increases.

Benzol sulphonic acid is cheaper $H.OSO_2C_6H_5$ and hence is used in making of ether commercially.

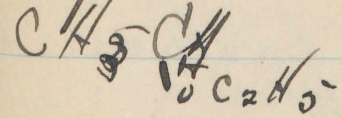
Colby + Liebig and the theories Williamson

$RCH\begin{smallmatrix}H\\ \end{smallmatrix}OH.$ When H is replaced the R CH is formed.

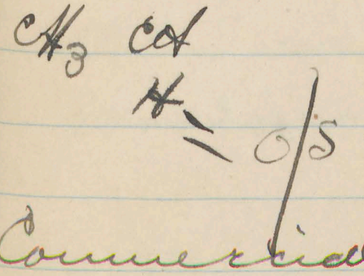
$CH_3CH_2 + H_2SO_4$ (50-70%) Ethylidene at 140°

10% Ethylidene at 95%

Ethylidene absorbs HOC_2H_5.



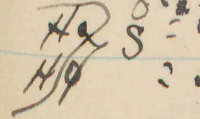
$CH_3-CH\begin{smallmatrix}H\\OC_2H_5\end{smallmatrix}$



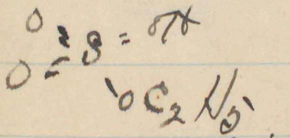
$CH_3CH\begin{smallmatrix}H\\O\end{smallmatrix}|SO_2$

80% SO_3 at 160°

Commercial ether always has SO_2 in it.



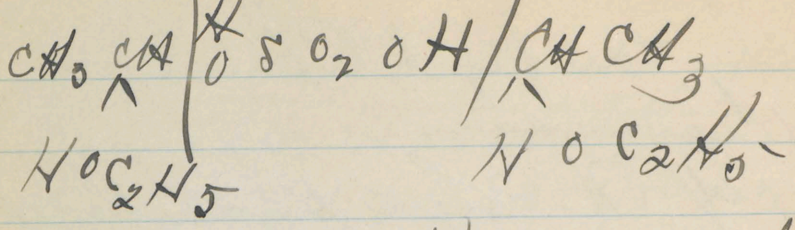
$\begin{smallmatrix}H\\H\end{smallmatrix}S\begin{smallmatrix}OC_2H_5\\=OH\\=O\end{smallmatrix}$



$\begin{smallmatrix}O\\O\end{smallmatrix}=S\begin{smallmatrix}=OH\\OC_2H_5\end{smallmatrix}$

There may be enough SO_3 present in H_2SO_4 to give ether we don't know. Di ethyl sulphate speed of reaction is

important thing Primary don't play much role in reaction



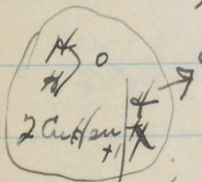
$CH_3CH \,\Big|\, \overset{H}{O}SO_2OH \,/\, CH\,CH_3$

$HOC_2H_5 \qquad HOC_2H_5$

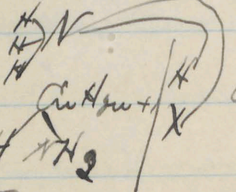
action must be reversible we get $CH_3CH \,\Big|\, \overset{H}{O}C_2H_5$.

It forms spontaneously at ord temperatures. Get acetic acid even at ord temps

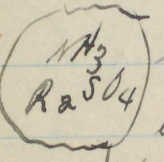
Tuesday Dec. 14, 1909.



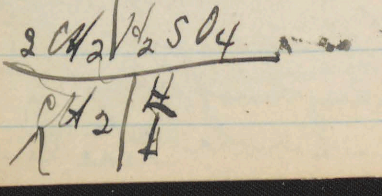
Ether But Ag_2O works better.



amine formation.



Get a mixture at 0° of mono di and tri subs NH_3.

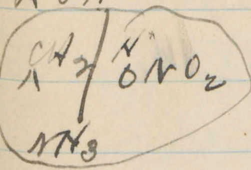


$2CH_2\,H_2SO_4$

$CH_2 \,\Big|\, \overset{H}{H}$

R_3PO_4

$RONO_2$



$CH_3 \,\Big|\, \overset{H}{O}NO_2$, NH_3

Gives methylated ammonia.

CH_3ONO } Don't give above prods

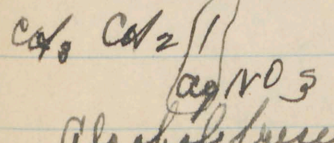
CH_3OCCH_3 } Higher T required

methyl nitrate + alc KOH gives ether.

Sulphate phosphates

Diss. material acts and not the molecules.

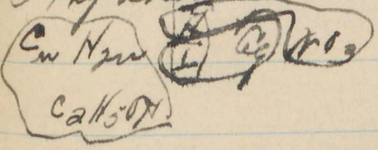
Friedel-Krafts reaction makes it possible to replace H atoms of C_6H_6. CH_3Cl $AlCl_3$ etc etc.



$CH_3CH_2 \,\Big|\, I$ $AgNO_3$

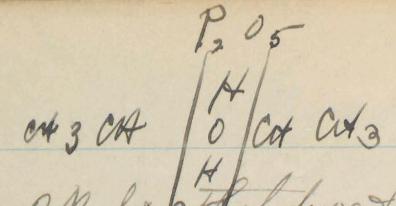
Alcohol present gives ether 9.5%

Ethylene must be present.



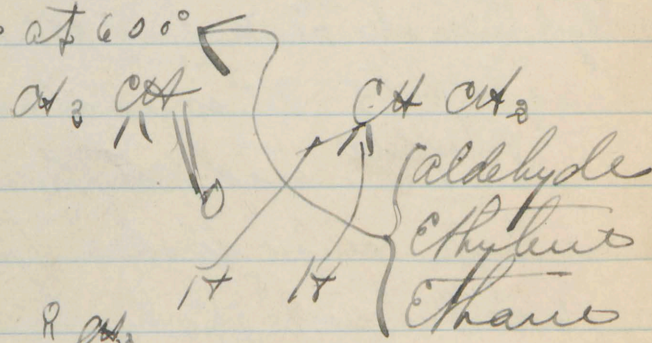
$C_nH_{2n}\,\overset{H}{I}\,Ag\,NO_3$ C_2H_5OH

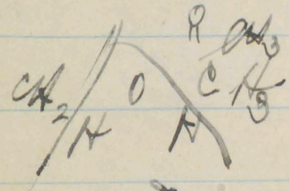
Properties of Ethers Look up.



2 Mols ethylidene + H_2O at ord T, burns in air Gives same oxidation products as alcohols. P_2O_5 slowly pulls off H_2O at ord. T's alkyl phosphates form. Ethylene + H_2O over P_2O_5 at 200° Ether

Hot tube at 600°





$R\rangle O + HI \xrightarrow{Dry}$ RI + HOC_2H_5.
R

HBr slowly at low T's.

HCl acts like H_2SO_4

$R\rangle O + Br_2 \rightarrow R_2OBr_2$
R

HCl
HBr
H_2SO_4 With H_2O we get tacking subs.
Due to unsaturated oxygen atoms

Wednesday Dec 16, 1909.

$(CH_3O)_2SO_2$

NH_3

CH_3NHH.
$(CH_3)_2NH$.
$(CH_3)_3N$
$(CH_3)_2SO_4$

RCH_2SH Thio alcohols (acids) I + II Only
Se Mercaptans. No III.
Te

$R\rangle S$ Thio ethers.
R Se
Te

CH_3CH_2SH. Boils 36 Made in Saxony.

~~$CH_3CH_2Cl + K$~~ ~~SH~~ Sealed tubes.

$CH_3CH\,H\,Cl\,K\,SH$.

$RSNa - I\ {}^{H}CHR$.
HSR.

Towards oxidizing agents.

$RCH_2SH \rightarrow RCH + H_2S$

$R-CH_2$ ~~OH~~

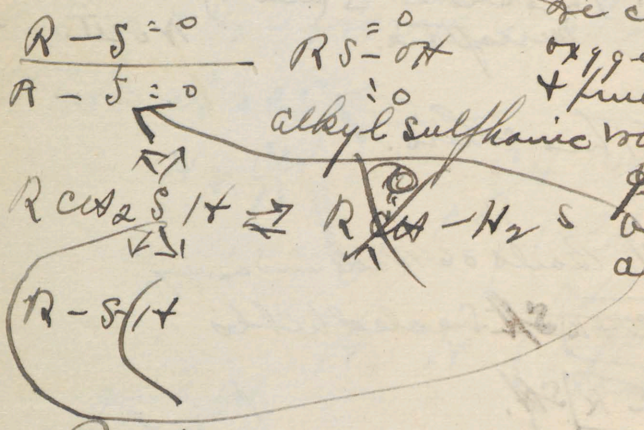
$R\rangle S\ HOH. \rightarrow H_2S + 2C_nH_{2n}$.
R

$R\rangle S$
R

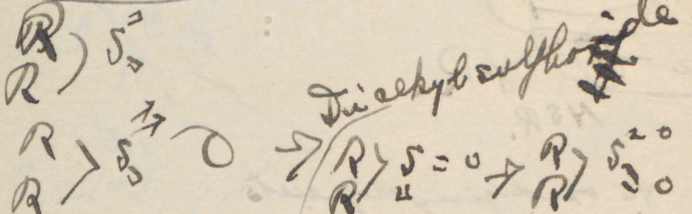
$$\begin{matrix}R\,S & NaI\\ R\,S & NaI\end{matrix}$$

$$\begin{matrix}R\,SH-O\\ R\,SH-O\end{matrix}$$

Sulphur atom is unsaturated in thio alcohols + ethers hence are quite poisonous.



We can replace oxygen with Cl + pull this off with H and get back our thio alcohol.



Have lower Mpt than sulphones.

Dialkyl sulphone 238° Boils 139 Melts.

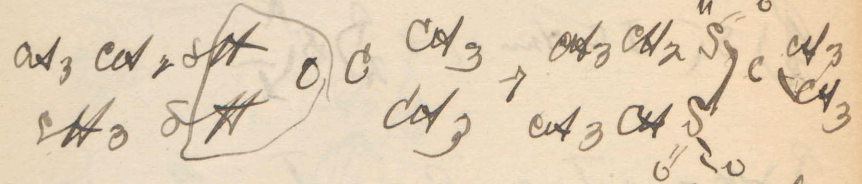
Treat with H and get thioethers back.

$$\begin{matrix}R\,SH\\ R\,SH\end{matrix}\ O\ C\begin{matrix}R\\ R\end{matrix}$$

Mercaptols

$$\begin{matrix}R\,SH\\ R\,SH\end{matrix}\times O\ \begin{matrix}CH\\ R\end{matrix}$$

Mercaptals.



Sulphonal.

$\begin{smallmatrix}R\\R\end{smallmatrix}\rangle S + X_2$ Take up Halogens like olefines

$\begin{smallmatrix}R\\R\end{smallmatrix}\rangle S\begin{smallmatrix}X\\X\end{smallmatrix}$ Can pull off Halogens. Take up HX. — Problem

$\begin{smallmatrix}R\\R\end{smallmatrix}\rangle S + IR \to \begin{smallmatrix}R\\R\end{smallmatrix}\rangle S\begin{smallmatrix}R\\I\end{smallmatrix}$

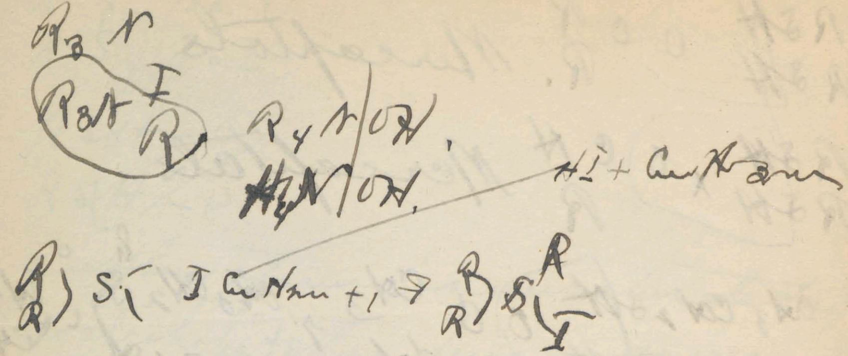
Trialkyl sulph~~ide~~onium - iodide.

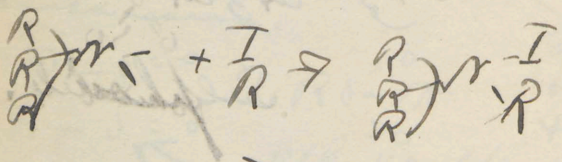
$R_3S \to$.

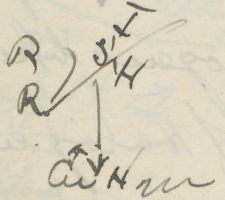
$I + AgOH$.

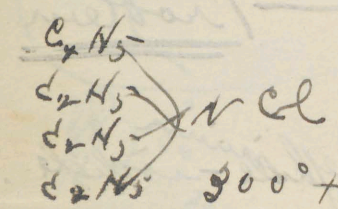
$\begin{smallmatrix}R\\R\end{smallmatrix}\rangle S\begin{smallmatrix}R\\OH\end{smallmatrix}$ Trialkyl sulphonium hydroxide.

$\begin{smallmatrix}R\\R\end{smallmatrix}\rangle S\begin{smallmatrix}H\\OH\end{smallmatrix}$ not yet.

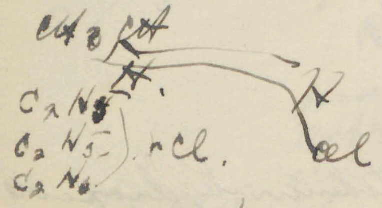


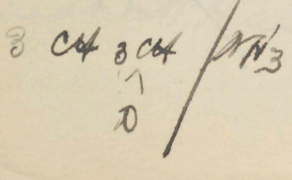




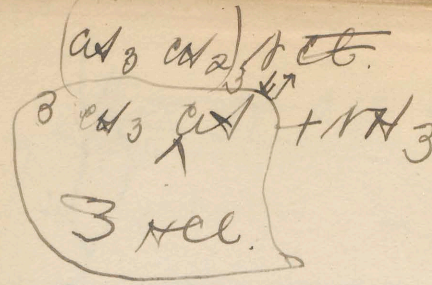


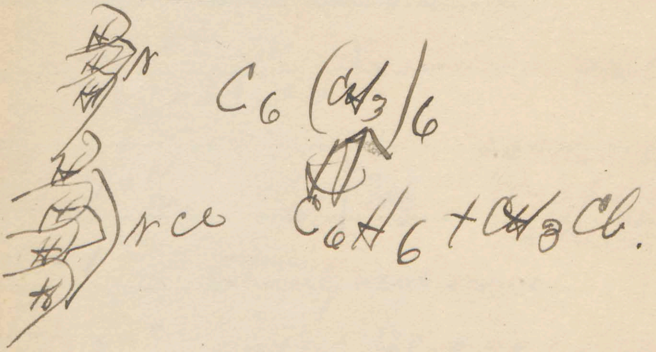
$300° + HCl \rightarrow NH_4Cl + C_2H_5Cl$

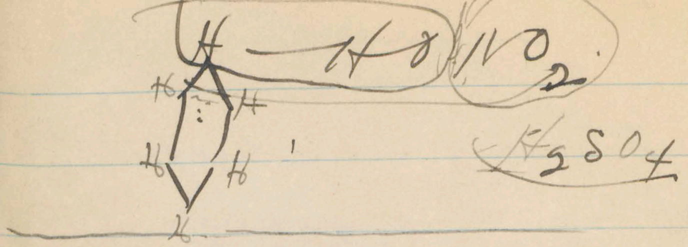




Oxidized by $KMnO_4$ at 0°
and we get CH_3COOH.



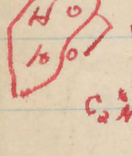




$\begin{matrix}R\\R\end{matrix}\!>O\!<\!\begin{matrix}H\\Cl\end{matrix}\quad\begin{matrix}H\\OSO_2OH.\end{matrix}$ Oxonium salts.

$\begin{matrix}CH_3\\CH_3\end{matrix}\!>O\!<\!\begin{matrix}H\\Cl.\end{matrix}$ $-1°$ $\left.\begin{matrix}H\\Cl\end{matrix}\right|NH_3$ add H_2O & HCl drops off & comp. is decomposed.

Extremely weak bases.



adding of C_2H_5-OH to H_2SO_4 & dropping off of H_2O.

·Ethers

Oxidation. Formation of oxonium comps.

Prods. formed by burning of ether.

$CH_3CH^{H}_{\searrow O}$

$CH_3\ CH{-}H$

SO_2
H_2O
HOC_2H_5.
H_2O_2
CH_3CHO
vinyl ether

Impurities in ether for which we can get test! NaOH removes all but H_2O.

Baker's Exp. on dehydrating the last trace of H_2O.

P_2O_5 is much better than Na wire to dry out last trace but must work rapidly.

$CH_3\,CHO$

Vinyl Ether.

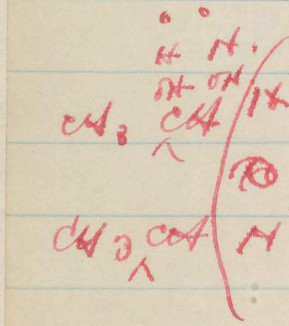
$HgCl_2 + KHCO_3$ Gives with vinyl ether in ether a ppt. Aldehyde gives no such ppt. Meyer says alc. but not so

$CH_2=CH\diagdown$ O vinyl ether

$CH_2=CH\diagup$ Divinyl oxide.

To get distil off CrO_3

Bpt about 39°

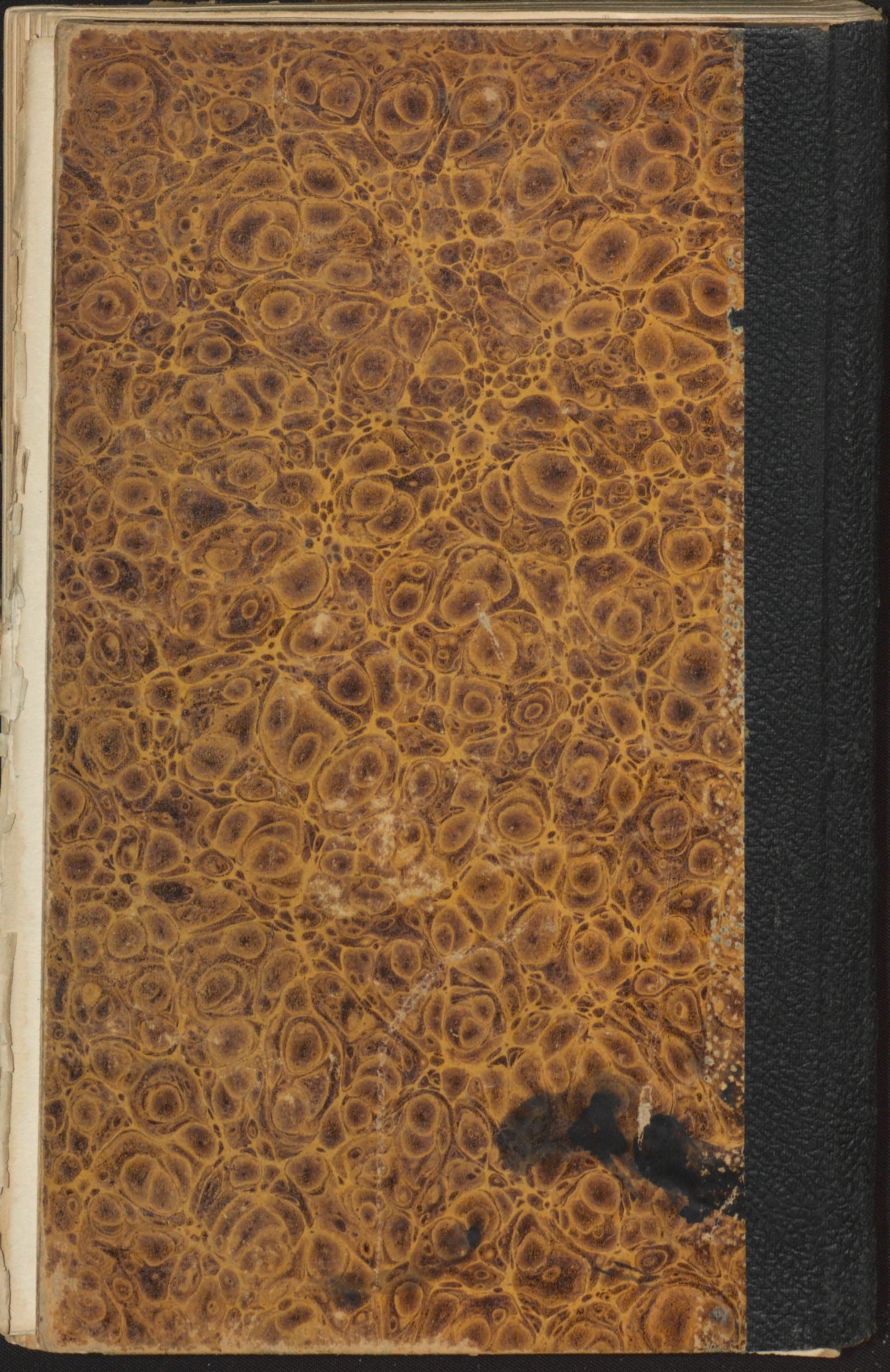


$$CH_3\,\overset{\overset{H}{OH}}{CH}\;\Big(\;H$$

$$CH_3\,\overset{\overset{H}{OH}}{CH}\;\Big(\;H$$

Traube interpretation

H_2O is necessary to combustion!



Please give to Mr Rosenthal for review perhaps and tell him I am eager to see him when I am next in Chicago* J.U.N.

IMPORTANT FACTORS IN THE DEVELOPMENT OF A RESEARCH LABORATORY

An address by Professor John U. Nef, Sr.
on the occasion of the exercises in connection with the
opening of the Kent Chemical Laboratory, Jan. 1, 1894.

*Perhaps he & Mr. Strauss might like to lunch with me & talk about this next time I'm in Chicago?

There can be no doubt that the great energy and ability of the American people have thus far been devoted almost exclusively, and with remarkable success, to the material development of the country. This, as Professor Hale showed very clearly in his convocation address last June, was a necessity of the situation; the intensity with which this work has been done and the marvelous achievements in a material respect, have been alike the wonder and the envy of the old world. At the same time, however, the criticism is made that America has comparitively little to show in the way of actual achievements in arts, literature, or science - which must be regarded as very important factors in the history of a country. So vigorous~~ly~~ has been the work of developing the material interests of the country, and so alluring the opportunities in this direction to men of enterprise, that it is no wonder, and indeed quite natural, that other things should, for the time being, be apparently lost sight of. Americans have been accused of being worshippers of gold to the exclusion of every ideal thing except religion. Certain it is that when Louis Agassiz told people that he had to devote himself to science, and had consequently no time to make money from his discoveries, he was regarded as an interesting curiosity.

As a consequence of this state of affairs it was natural that education, including the study of the sciences, was regarded solely as a means to a practical end. The majority of the ablest men were anxious to get through with their general school work as soon as possible and thus be able to devote their entire strength to the great material opportunities at hand on every side.

Within the last fifteen years a most remarkable change has taken place in respect to higher education in this country. This has been in the realization that a university has a two-fold function: the first, being to teach or

to impart known facts; the second function, which had before been overlooked or much neglected, being to enlarge the boundary of knowledge in arts, literature, and science. It has become perfectly clear that the standing of a university in the world depends chiefly on the ideal achievements of the men connected with it, <u>i</u>.<u>e</u>., on the work done by them in enlarging the boundary of human knowledge. Although this point may now be generally recognized, more is required than this. The men in the new movement are pioneers, and the difficulties in the way are enormous; it is absolutely necessary that a portion of the energy and ability which have hitherto been applied almost exclusively to the material advancement of the country, be diverted into university or into ideal channels. That the tendency of late is in this direction, is a most interesting and cheering fact, The pioneer work in developing the material resources of the country has been practically accomplished, and in a most wonderful manner, and it is this latter fact that has long ago led some of the keenest minds of Europe, among others the great chemist Liebig, to predict great things of this country when once it has recognized the importance of ideal as well as material achievements. That the country has been awakening to its possibilities in the former respect, is apparent on all sides.

The foundation of Johns Hopkins University, of Clark University, of the Leland Stanford, Junior, University, of the University of Chicago, and the establishment of graduate schools at Harvard and Columbia, are evidences of this. The foundation of the Art Institute, of the Thomas Orchestra, and of the Columbian Museum in this city, are local evidences of this tendency. The chief pride of everyone in the World's Columbian Exposition has been its great artistic success, and the resultant educational effect.

When a magnificent building, such as the one we are formally dedicating

this evening, is erected and equipped by a citizen of Chicago, Mr. Sidney A. Kent, to be devoted to the cause of chemical science, this is a matter in which not only Chicago, Illinois, the United States, but the whole scientific world has reason to rejoice. Here is what Du Bois Reymond, has justly called another temple to be devoted to the cause of science, which is international in its interests and not limited to any age or country. Much will therefore be expected from those whose privilege it will be to work in this building for the cause of chemical science.

There is one lesson which the past has taught and which is of vital importance, namely: "The spirit of pure scientific research must be fostered with the utmost care."

A chemical laboratory is judged by the scientific world chiefly by the quality of its scientific publications, and by this is meant the results of original work, carried out in the laboratory, which positively advance the science or open new fields therein. While it is true, to a great extent, that the power of scientific investigation is inborn and not acquired, it is also certain that a proper atmosphere must exist for its development. It requires inspiration and example to kindle into flame the spark which may exist in men beginning their life-work. That the inspiration and example must come from their instructors is evident. We have abundant proof that the men who have been great scientific discoverers have been those who have devoted themselves to the science for its own sake, never considering for a moment the material benefits that might result to them therefrom. They have been men who,,like Agassiz, had no time to make money, or to patent or take advantage of their discoveries, which belong to the world. They have loved and worked for their science with the same fervor and enthusiasm that men fight for a country's cause. There is no one thing which, in the estimation

of many, is at present exerting a more pernicious influence over chemical science in Germany than the fact that so many discoveries made by university instructors have been patented. The result is obvious; it tends to make men work, not for the cause of science, but for material objects, and the consequence must be, if persisted in, the loss of prestige that Germany has so long held in chemical science. The state, owing chiefly to the pioneer work of Liebig, has done much to foster the cause of chemical science by erecting and equipping magnificent laboratories for instruction and research. The men whose privilege it is to be connected with such laboratories, who hold life positions, and whose families, in case of death, are provided for by government pensions, surely have most ideal possibilities before them, and they can devote themselves, unhampered by cares, to the cause of science; and it is but just that the state, which has done so much for them, receive the benefit of any discoveries that may, by chance, turn out to be of practical value.

If the question were asked what factors are of importance in order that this country may in time do its share in advancing the cause of chemical science, or even, in time, take the lead over other nations in this subject, the answer would be that we must have, first of all, men whose heart and soul are in their work, and whose whole life and strength are devoted to the science purely for its own sake. The obstacles and difficulties to be overcome are tremendous, but no greater than those which the pioneers in the development of the material resources of the country have had to overcome. And who ever accomplished anything in the world without intense effort? The road to fame or fortune is alike beset with great difficulties, and that man who is afraid of or appalled by difficulties is a weakling and does not see his opportunity.

It is very generally admitted that the one factor which has made the German university what it is today is its docent system. This system, briefly stated, is the following: A man, in order to become an instructor in the university, must, after he has taken the degree of doctor of philosophy, devote one or more years to independent investigation. The result of his work is presented in the form of a thesis, called "Habilitations-Schrift," which, if accepted, gives him the title of docent, and the right to offer lectures in the university. During the period in which the instructor remains docent, he receives no compensation from the university except such as he may draw from the attendance at his lectures, which is generally merely nominal; many of the docents lecture <u>publice</u> or gratis. A man may remain docent for many years, very often from four to eight years. His promotion depends chiefly on the quality and quantity of his investigations.

There are two universities in this country which have adopted the docent system, namely, Clark University and the University of Chicago. These require, however, of a candidate merely that he shall have the degree of doctor of philosophy, and not that he shall present a "Habilitations-Schrift." This is due simply to the exigency of the situation. Fifteen years ago it was exceedingly rare that men worked on in a university in this country, after receiving a bachelor's degree, except in the professional schools: law, medicine and theology.

Today this is changed, but it is now very unusual for men with the degree of doctor of philosophy to work on independently. In order to encourage this, the University of Chicago has wisely adopted the docent system. The appointments are open to men having the above qualifications, and are annual appointments. The appointee has the opportunity to offer lectures in his chosen department, but his chief work is that of self development and investi-

gation. There is no one factor which compares with this docent system in importance, in the development of the future American university, and of great men who by their work will make Americans proud of their country. A man who presents a thesis for the degree of doctor of philosophy, whether here or in Germany, has his subject suggested to him by the instructor, and carries out the work generally under his guidance and instruction. He is not therefore entirely independent in his work, and has not yet developed a field of research work strictly his own. He is perhaps enthusiastic in his work, and sees possibilities before him. He is, in consequence, at the most critical and important period of his life; and if an opportunity can be open to him to devote his main strength and energy, for some years to come, to scientific research and to self-development, it is a godsend to him who is really anxious and capable of doing something for science and his country.

During the last thirty years any number of young men have gone to Germany to study chemistry, and have come back with their doctor of philosophy degree. Why is it that so few of them have done anything for science since their return? The chief reason is, that they have gone into the work of teaching immediately. To be sure, if they cared to, many might have found time and opportunity for research; but, first of all, they found absolutely no sympathy, appreciation, or expectation for this kind of work, and were forced to stand entirely alone, and the difficulties in the way were enormous. And as their chief strength was devoted to teaching, and above all, because they had not developed any field of research strictly their own before beginning their life work of instruction, they have lost their interest in the important matter of doing something for science.

What is the reason that many men have been and are still going to Germany to study chemistry? Simply in order to come in contact with and to receive instruction from men who have made the science of chemistry what it is today.

To come in contact with a great man is a privilege never to be forgotten; he inspires both as a teacher and as an investigator. If we ever expect to check this exodus to Germany we must have our universities filled with men who are doing important work in advancing their subject. Men will go where there is ~~xixexi~~ life, activity, and enthusiasm; and nowhere is this more marked than in a productive chemical laboratory.

Supposing, for an instant, that these possibilities existed in this country, there are many reasons why incalculably more good can be done than by having our young men go abroad. The men in the universities here understand the conditions of education in the country more fully, and also, as a consequence, could appreciate and help those who come to them for instruction and research more fully than any other country can; and the most important point of all is that they could exert a stronger and much more direct influence by improving and inspiring the more elementary work in the high schools and colleges.

Finally, a word may be said as to the possibilities in science in the future, and the desirability of young men of energy and ability taking up work in it. No man need fear, as did Alexander the Great in his youth, that there will be no worlds left to conquer. The possibilities in science and the resultant good to the world are beyond all imagination. This matter cannot be presented more forcibly and remarkably than has been done by Joseph Priestley, the father of the chemistry of gases, in 1774, in the following words:

"If extensive and lasting fame be at all an object, literary, and especially scientific, pursuits are preferable to political ones in a variety of respects. The former are as much more favorable to the display of the human faculties than the latter, as the system of nature is superior to any political system upon earth.

[A perfect work of God]

"If extensive usefulness be the object, science has the same advantage

over politics. The greatest success in the latter seldom extends farther than one country and one particular age; whereas , a successful pursuit of science makes the man a benefactor of all mankind and of every age. How trifling is the fame of any statesman that this country has ever produced, to that of Lord Bacon, of Newton, or of Boyle; and how much greater are our obligations to such men as these, than to any other in the whole Biographia Britannica; and every country in which science has flourished can furnish instances for similar observations."

He then quotes a passage from the letter of the not too enthusiastic philosopher, Beccaria, of Turin, who writes: "I am sorry that the <u>political world</u>, which is so very transitory, should take the great Franklin from the <u>World of nature</u>, which can never change nor fail."

"I own," says Priestley, "it is with peculiar pleasure that I quote this passage respecting this truly great man, at a time when some of the infatuated politicians of this country are vainly thinking to build their wretched and destructive projects on the ruins of his established reputation; a reputation as extensive as the spread of science itself, and of which it is saying very little indeed to pronounce that it will last and flourish when the names of all his enemies shall be forgotten."

That these predictions have proved true has long ago been evident. America honored and remembered one of its great men, Benjamin Franklin, at the Columbian Exposition, by placing his statue before the Electricity Building, chiefly because of his achievements in physical science.

Term Exam 1910 (Autumn)

1 - Schommer J.J.	B' ~~!!~~ A	~~C~~ finals A'
2 - Hattfeld absent	(~~!!~~	B'
3 - Webb A.A.	— ~~C~~ ~~D~~ → D	absent —
4 - Zuradsky	— B	C
5 - Schweitzer H.E.	C'	C
6 - Allee W.C.	C'	~~C~~ B'
7 - West F.L.	— B'	B
8 - Potterf L.O.	B'	~~C~~ B'
9 - Potter P.D.	B'	
10 - Carter A.B.	— C	C
11 - Reddick, G.A.	— C	C
12 - Smith, L.F.	— D	C
13 - Koch, F.C.	C'	C
14 - Cookins, F.D.	B' →	B
15 - Haessler, P.C.	— B	C'
16 Leach absent	(~~!!~~ B →	C
(17) Currie — absent — a visitor		absent

$\frac{1}{8}$

a
a'
B
B'
C
C'
D
E
F

analyze