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A

THESIS

PRESENTED TO THE FACULTY

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FOR

THE DEGREE OF

DOCTOR OF PHILOSOPHY

BY

GEORGE HOLMES RICHTER

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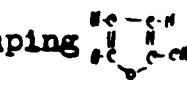
# HISTORICAL PART

## HISTORICAL INTRODUCTION

Only those compounds that may be considered as direct derivatives, or homologues, of α methyl furane will be considered. In this discussion the name furfur- is used to denote the grouping  , the position of any side chain will be denoted by the Greek letters α, α′, β, β′.

The parent substance α methyl furane was prepared in 1880 by A. Atterberg (Ber. 13, 880) and named "Sylvane", for it was isolated from the tar of "Pinus Sylvestis". The αα′ dimethyl furane is the only known member of the possible di substituted compounds (Ber. 20, 1085. 1887). The αα′β tri methyl furane (Amer. Chem. Jour. 25, 44. 1901) as well as the αββ′ isomer (Ber. 47, 294. 1914) and (C. 1918 2, 528) are known. The tetramethyl compound (Ber. 47, 292, 307. 1914) has also been prepared. The di, tri and tetramethyl derivatives can be prepared by distillation of cellulose in the presence of Zn under ordinary pressure (C. 1918 2, 528).

There are no ethyl or butyl furane compounds known at the present time. The α propyl furane was prepared by the catalytic reduction of furo ethyl carbinol (C. 1913 2, 2046).

In the series of compounds in which the furane nucleus is substituted by unsaturated side chains, the

α vinyl furane (Ber. 27,287. 1894) is known. This compound was prepared by heating furo acrylic acid, a molecule of $CO_2$ easily splits out, forming the above compound. Both the α vinyl dihydro furane and α ethyl tetrahydro furane were prepared by Romburgh and coworkers (C.A. 17,1214. 1923) the former by heating mannitol hexaformate and the latter by further reduction of the dihydro compound. The allyl furanes are unknown. Furo butylene is known and its reactions with $N_2O_3$ have been studied: the gas adds on the double bond. On reduction an hydroxy amine was produced(Ber.11,1511.1878)(Ber.10,1365.1877). Furo butylene oxide was prepared by oxidation of the unsaturated hydrocarbon with nitric acid(Ber.17,854.1884). The sym. difuro ethylene was prepared by a vacuum distillation of polythiofurfuraldehyde in 18% yield(Jour. Amer. Chem. Soc. 51,1270.1929). Furo acetylene is known, it was prepared by the elimination of HBr from the dibromide of furoethylene (Ann. Chim:7,14-42. 1927).

Furane may be reduced to give tetrahydro furane or synthesized directly from tetramethylene chlorohydrin by heating. Furane was described first in the Jour. of Russian Phys. Chem. Soc. 14,371.1882. The α methyl derivative was prepared by A. Lipp(Ber.22,2571.1889)by the dehydration of the corresponding glycol. The αα′dimethyl tetrahydro furane(Jahresber.d.Chem.1864 515) has been prepared. The β/β′isomer is also known (C. 1913 1,2027). Other di substituted members are unknown. Ethyl tetrahydro furane is

described in Comp.rendus 159,82.1914. Trimethyl tetra hydro furane(C.1911 2,1118) and α methyl α'ethyl tetra hydro furane are known. β n-propyl tetrahydro furane has been prepared(C. 1915 1,982) but other isomeric compounds and homologues are unknown at the present time. The only known tetramethyl derivative is the αα'αα' compound(C.1899 1,773) The isomeric αα diethyl and α methyl α iso-propyl compounds (C. 1916 1,5) are known. All of these compounds were made by the dehydration of the glycols. The α methly α iso-propyl tetrahydro furane was prepared by the electrolytic reduction of methyl heptenecne (Jour. of Chem. Soc. 101,1028. 1912). The butyl furanes are unknown. Also the di-furfur compound has not been prepared. The vinyl and allyl tetrahydro furanes are unknown.

ALCOHOLS . These may be divided into four classes:

(a)Alcohols with saturated side chains attached to furane nucleus.

(b)Alcohols with unsaturated side chains attached to furane nucleus.

(c)Alcohols with saturated side chains attached to tetrahydro furane nucleus.

(d)Alcohols with unsaturated side chains attached to tetrahydro furane nucleus.

(a) Furfuryl alcohol,the first member,has been known for a long time(Jahresber. d. Chem.1860 269). The furo ethyl alcohol is not known. However,both the 1furo propanol-1

and furo-n-propyl alcohol are known. The first compound was prepared by the action of $Zn(C_2H_5)_2$ on furfuraldehyde (Ber.27,1969.1884). It is interesting to note that an acetate of this alcohol could not be prepared. The saturated alcohol behaves in a normal manner (C.1913 2,2046). Adams prepared the furo propyl alcohol by the catalytic reduction of furo-acrolein (Jour. Amer. Chem. Soc. 49,2101 1927). An acetate and α naphthyl urethane were prepared by Adams. The next higher member,furo-propyl carbinol,was prepared by the action of propyl magnesium bromide on furfural(C.1910 1,450),the alcohol was then converted into the corresponding chloride and acetate. A general consideration of the 2°and 3° alcohols of this series is given in Amer. Chem. Jour. 35,68 (1906).

(b). The only known member of this series is the α furo allyl alcohol. It was prepared by the catalytic reduction of furo-acrolein(Jour. Amer. Chem. Soc. 49,2101.1927). The α naphthyl urethane was prepared and an attempt was made to make the acetate,by treatment with acetic anhydride, but was not successful.

(c). There are two compounds in this series that have been made. The tetrahydro furfuryl alcohol (Ber. 53,1656. 1920)and tetrahydro furo propyl alcohol(Jour. Amer. Chem. Soc. 49,2101.1927). The 3-5 dinitro benzoate,acetate and α naphthyl urethane were prepared from the latter.

(d). Thereis only one known member in this group,it is the

tetrahydro furo acrylic alcohol. It was prepared by reducing furo acrolein with a specific catalyst. An acetate was prepared (Jour. Amer. Chem. Soc. 49,2101.1927).

DERIVATIVES OF THE ALCOHOLS: The compounds that were considered were only those that could be regarded as direct derivatives of furfuryl alcohol. No xanthogenates,even of the first member,are known. The halogen compounds are of great interest from the synthetic point of view. The iodide and bromide have been prepared in an ethereal solution(Jour. Amer. Chem. Soc. 49,1061.1927). Kirner has isolated the chloride by using the Darzens reaction (Jour. Amer. Chem. Soc. 50,1955. 1928). In the same manner Kirner has isolated the tetrahydro furfuryl chloride in goodyield. The corresponding bromide has been prepared by Dox (Jour. Amer. Chem. Soc. 50,2033.1928),at the present time the iodide is unknown.

All attempts in this laboratory to prepare the Grignard reagent have failed. The halogen compounds can easily be converted into ethers by treating the ethereal solution of the halide with the desired alcohol and solid KOH,the reactions go in the cold and the yields are good(Jour. Amer. Chem. Soc. 49,1067. 1927). In this manner the methyl,ethyl, n-propyl,n-butyl,allyl,benzyl,furfuryl and cinnamyl ethers have been made(Jour. Amer. Chem. Soc.50,1958. 1928).

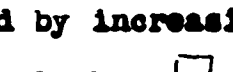
Furfuryl amine is known(Ann.214,228. 1882,Ber.14,725, 1059,1475. 1881. Ber.20,399,730. 1887) a hydrochloride,

platinic chloride, di-oxalate and picrate have been prepared. A furo vinyl nitrite (Ber. 18, 1362. 1885) and nitrite of 2-oxy-methyl furane (Gazz. 24, (2) 21. 1894) are known. At present there are no nitro, nitrite, iso-cyanate, mercaptan or sulfides known. Furo ethyl amine and the corresponding tetrahydro amine have been described by Windaus (Ber. 53, 2304. 1920). There is an excellent bibliography on the aliphatic amines in the bulletin "Furfural and its Derivatives" by the Miner Laboratories. The corresponding tetrahydro furfuryl compounds and higher homologues are not known.

ALDEHYDES: There is a vast amount of literature on the first member of this series-furfural. A good bibliography is given in the bulletin "Furfural and its Derivatives." The next higher homologue, furo acetaldehyde, has been prepared by I.J. Rinkes (Rec. 39, 204. 1920), the reaction is interesting. The amide of furo acrylic acid is treated with NaOCl (Hoffman reaction) to give the amine (not isolated). The amine was hydrolized to give the furo vinyl alcohol which immediately rearranges into the stable furo acetaldehyde. A semicarbazone was prepared. The higher members of this series have not been made.

The corresponding tetrahydro furo acetaldehyde and higher homologues are not known. The tetrahydro furfural is a commercial product (Ber. 57, 1443. 1924). The method used for the preparation was the reduction of the acetal followed by a hydrolysis.

KETONES: There are two cases of isomerism that have to be

considered here. In one case the higher homologues are formed by increasing the value of x in . The other case is essentially the same except the higher members are formed by increasing the number of methylene groups in the type linkage  . Both types are well known and described.

Furyl-methyl,ethyl,propyl,iso-butyl,iso-amyl and phenyl ketones are described in Arch.der Pharm. 252,437, 445(1914)also (C.1914 2,1196). They were all prepared by the action of the corresponding alkyl Grignard reagent on furo nitrile(from the dehydration of the amide of furoic acid),semicarbazones were prepared for each member. Acetyl furane has been known a long time,it is described in Ber. 33,493(1900),Ber.34,1072(1901) and C.1898 1,327. The homologues,with methyl groups in the furane nucleus,are also known(Ber. 27,405.1894 and Gazz.24,(1) 435.1894).

Compounds of the second type are known. The first member,acetonyl furane,is described in Comp. rend. 142,215 1906 (C.1906 1, 669),the next higher homologue is known and described in Ber.32,1320 (1899). The first compound was made through the condensation of α chloro propionic ester on furfural to give . This substance on hydrolysis loses $CO_2$ and rearranges to give the ketone . A semicarbazone and oxime were prepared. The α(furo)γketo butanone(1-furo-butanone-3) was made by the reduction of furfural acetone(Ber. 32, 1320. 1899). Ketones with unsaturated side chains are possible,the first

member, furfural acetone, is described in Ber. 32, 1320 (1899).

The studies of the ketones of furane are the most complete of any series of furane compounds. This is due to the fact that they occur extensively in nature. In determining the constitution of these the synthetic method was used in most every case. This often necessitated the synthesis of a complete series of homologues, such an example is found in Arch. der Pharm. 252, 437 (1914), other cases are too numerous to mention.

The corresponding ketones with the furane nucleus reduced are almost unknown. There is one member 1-furobutanone-3, prepared by Adams (Jour. Amer. Chem. Soc. 45, 3029. 1923) by the catalytic reduction of furfural acetone.

ACIDS: (a). Acids with unsaturated side chains linked to furane nucleus: these, in general, can be produced by the condensation of furfural with fatty acids (Perkin reaction). It is probable that many of the structures of this group, as given in the literature, are wrong. At the time that most of these reactions were carried out it was not well known that the condensation in the Perkin reaction takes place on the $\alpha$ carbon atom of the acid. The first member, furyl acrylic acid, has been known a long time Ber. 10, 357 (1877) 20, 2812 (1887) 21, 1083 (1888) 31, 1122 (1898) 24, 143 (1891) and 27, 283 (1894). The next higher homologue is also known Ber. 14, 575 (1881). The furyl angelic acid is also known (Ber. 10, 1364. 1877 and 12, 1200. 1879).

(b). Acids with saturated side chains attached to furane nucleus: these were made by reducing the above acids, the references are the same in each case. The first member, furo acetic acid, was made in this laboratory and is described in another part of this paper.

(c). Acids with unsaturated side chains attached to a reduced furane nucleus: members of this class are unknown.

(d) Acids with saturated side chains linked to a reduced furane nucleus: two members are known, tetrahydro furane carboxylic acid and β tetrahydro furane propionic acid, these are described by Adams in Jour. Amer. Chem. Soc. 45, 3029 (1923).

AMIDES: The amide of furoic acid is well known (Ber. 19, 1277. 1886) also the amide of furo acrylic acid (loc.cit.).

CHLORIDES: The chloride of furoic acid is known and used in the Schotten-Baumen reaction for the identification of amines and alcohols (Ber 37, 2949. 1904)

HYDRAZIDE: Azide, etc. of furoic acid are described in C. 1897 1, 1024.

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# INTRODUCTION

## Part One

The chemistry of furane derivatives is unusual in that the simplest possible compounds are unknown. Many higher members and a host of complex compounds are described in the literature. The reason for this anomaly seems to lie in the fact that a large number of the known compounds are not synthetic but were isolated from natural sources. Synthesis in the furane series is complicated by the fact the compounds are unstable and the starting material for all common compounds, furfuryl chloride, was unknown up to 1928.

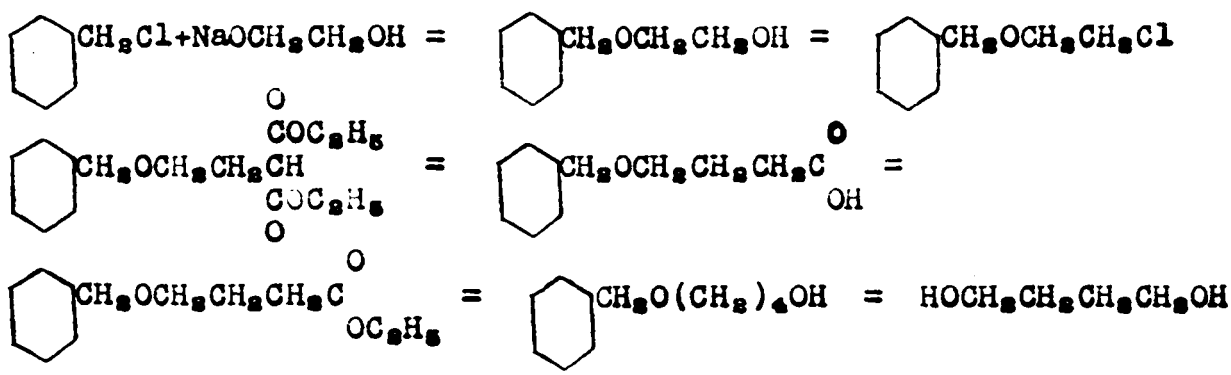
Kirners synthesis of this compound (J.Am.Chem.Soc. 50, 1955 1928) opened up the field for the preparation of numerous interesting compounds. By means of this chloride, the cyanide, mercaptan, sulfide, thio cyanate, furo acetic acid, furfuryl malonic ester, furfuryl ethyl malonic ester, and the two barbituric acids derived from these compounds and furfuryl acetoacetic ester were prepared. The hydrolysis of furfuryl acetoacetic ester was carried out, both the acidic and ketonic products were isolated. With the exception of the last two products the compounds mentioned above are new.

Hjort investigated the physiological action of the two barbituric acid derivatives and found that they compared favorably with other drugs of this type. In spite of the strong hypnotic action of furfuryl ethyl barbituric acid the duration of its effect is very short (2 hrs.). This is explained, perhaps, by the fact that the furane nucleus is very susceppible to attack. The corresponding tetrahydro furfuryl compounds do not show this effect.

## Part Two

The simple glycols and their corresponding chlorohydrins have found extensive use in organic synthesis. The fact that these compounds, which once were only of theoretical interest, are now available in large quanities indicates the extensive use and practical interest that has centered around them. In spite of the development of these compounds the higher homologues are unknown(tetramethylene chlorohydrin) or have been prepared in an impure state(tetramethylene glycol).

It seemed to be of interest then, to investigate these compounds and devise methods for their synthesis that would make these substances common enough for research at least. Several investigations have been rather tedious due to the fact that sufficient amounts of the glycol could not be obtained(Ber.46,2620.1914 and J.Am.Chem.Soc. 45,3115.1923). The synthesis of the glycol is indicated by the following equations:



It is suprising that such a simple compound as tetramethylene chlorohydrin had never been prepared. The preparation in this laboratory was accomplished by means of the Darzens reaction. This compound offers greater synthetic possibilities than the glycol for it is unsymmetrical and both groups are reactive.

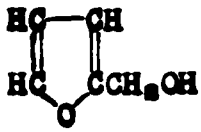
This substance offers the possibility of stepping up the series four carbon atoms at a time, eg. through the Grignard reaction.

While this work was in progress A. Muller in Vienna attacked the same problem and succeded in preparing the glycol by the reduction of ethyl succinate. Previous work (Rec. Trav. chim. 34, 101. 1915) indicated that this was not a very satisfactory method. Also Bennett, in England, made the chlorohydrin but was unable to isolate it.

# EXPERIMENTAL PART

# SYNTHESIS IN FURANE SERIES

## SYNTHESIS OF FURFURYL CHLORIDE




+ $SOCl_2$ +


= PRODUCT

| | | | |
|---|---|---|---|
| 54 gms | 74.4 | 52.2 | theory=63.8 |
| 98.0 | 119 | 79.0 | 116 |
| .55 mols | .60 | .66 | .55 |

The method of procedure is essentially the same as that outlined by Kirner in Jour. Amer. Chem. Soc. 50, 1955 (1928). The furfuryl alcohol and pyridine were dissolved in 50 cc of ether and placed in a three necked Pyrex flask fitted with stirrer, dropping funnel and thermometer. The temperature of the contents was brought down to 6-8° and a solution of the thionyl chloride in 50 cc of ether started in. It was found that less charring took place and slightly better yields were obtained if the thionyl chloride was added as rapidly as possible, eg. about 5-8 minutes for each 10 cc portion. After the addition of the thionyl chloride, it is necessary to remove the ice bath and permit the contents to warm up to room temperature for 20-30 minutes.

The material is then cooled until the salts crystallize and the supernatent liquid is then siphoned off, the residue is broken up and extracted twice with ether. The ether solutions were washed with cold KOH, water and then dried over anhydrous $Na_2CO_3$.

Kirner obtained the chloride in 63% yield. In most of the experiments it was assumed that the crude solution was about 63% of the theory and the solution, or aliquot portion, was used without isolating the furfuryl chloride.

The above directions are typical and in each experiment in which furfuryl chloride was used the preparation was the same.

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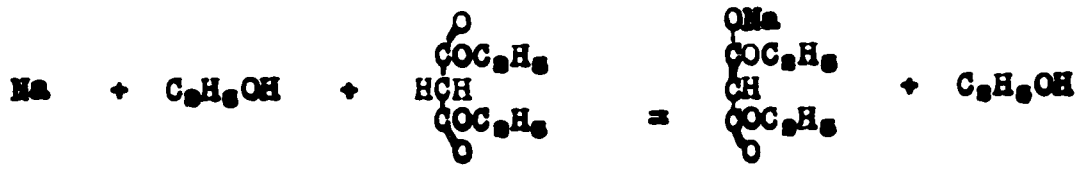
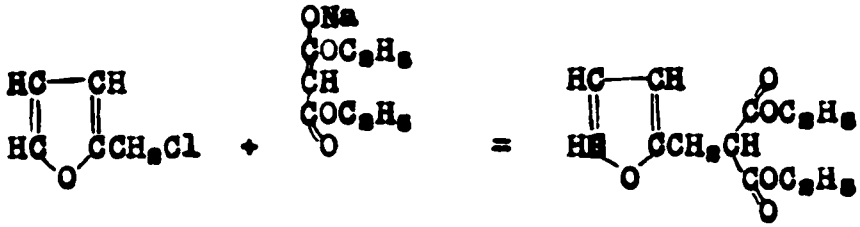
## FURFURYL MALONIC ESTER



| | | | | |
|---|---|---|---|---|
| 23 | 46 | 160 | | |
| 3.9gms | 80gms | 136gms | | |
| .17 M | 1.7 M | .85 M | | |



| | |
|---|---|
| 116 | 240 |
| 19.6gms | 40.5 gms theory |
| .169 M | .169 M |

80 grams of absolute ethyl alcohol(J.C.S. 1288,1927) were placed in a three neck 500cc Pyrex flask fitted with reflux condenser,stirrer and dropping funnel. 3.9 gms of sodium were added through one of the necks and then closed, after solution of the sodium was complete 136 gms of malonic ester were run into the flask through the dropping funnel. The condenser was turned down and the flask heated on the water bath,about 60cc of alcohol were removed in 45 Minutes. This is the maximum amount that could be removed by the water bath. The condenser was then turned up as a reflux condenser.

19.6 grams of furfuryl chloride in 40 cc of Grignard ether were placed in the dropping funnel and run into the warm solution, the temperature was about 80°, the solution of the chloride was added over a period of 40 minutes. At the end of this addition the water bath was replaced and the material stirred and heated at the temperature of the water bath for two and one half hours. The material was worked up the following day.

The colored solution was poured into a separatory funnel and extracted with water. The water layer was then removed and extracted with ether. The ester and the ether extract were combined and dried over anhydrous $Na_2SO_4$.

The material was placed in a suitable distillation flask and the ether removed. The excess malonic ester was collected up to 105° under 20 m/m. The pressure was then lowered to 4 m/m and the product distilled.

| | | |
|---|---|---|
| First drop<br>119.5° | bath | press.<br>4m/m |
| Last drop<br>127.1° | | press.<br>4m/m |

This fore run weighed 3.7gms, the fraction was cut.

| | | |
|---|---|---|
| First drop<br>125.5° | bath<br>149° | press.<br>4 m/m |
| Last drop<br>125.8° | bath<br>156° | press.<br>3 m/m |

Note that the pressure went down 1 m/m during the distillation.

The product is a colorless oil, the odor resembling that of malonic ester.

Weight of product = 27.2 gms (67.3%)

Weight of fore run = 3.7 gms (76.3%)

Another experiment carried in the same manner as above except that during the addition of the chloride the reflux condenser was turned down so that the ether distilled off as fast as the chloride was added. The crude yield in this experiment was 93%.

Analysis:

.2033 gms gave .1283 gms $H_2O$ and .4457 gms $CO_2$.

% Carbon found = 59.79 % Hydrogen found = 7.06

% Carbon calc. = 59.97 % Hydrogen calc. = 6.70

$D_{20}^{20} = 1.11196$

$D_4^{20} = 1.10999$

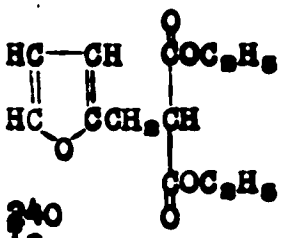
$N_D^{20} = 1.4591$

$M_D$(calc.) = 59.433

$M_D$(found) = 59.152

++++++

## ETHYLATION OF FURFURYL MALONIC ESTER



+ Na + $C_2H_5OH$ + $IC_2H_5$ = PRODUCT

| | | | | |
|---|---|---|---|---|
| 240 | 23 | 46 | 156 | 268 |
| 48 gms | 5.3gms | 101gms | 156 gms | 53.6gms(theory) |
| .2 M | .22M | 2.2M | 1.0 M | .2M |

5.3 grams of clean sodium were dissolved in 101 grams of absolute ethyl alcohol(loc. cit.) which was contained in a three necked Pyrex flask fitted with a reflux condenser,stirrer and dropping funnel. The furfuryl malonic ester was run into the solution and the condenser arranged for downward distillation. The flask was surrounded by a water bath and as much alcohol as possible removed by distillation. 95 cc were obtained in this manner.

The ethyl iodide was then added at the rate of 100 drops per minute. The reaction was apparently complete after three fourths of the iodide had been added. However, all of the iodide was added and the mixture refluxed for 2.5 hours.

The solution was then poured into a separatory funnel and treated with an equal volume of water. The lower layer was removed and the upper water layer washed with ether. The ether washings were added to the product and the solu-

tion dried over anhydrous $Na_2SO_4$.

On attempting a distillation it was found that Iodine distilled over also. The material was washed with a concentrated solution of thiosulfate and redistilled. The original boiling point was 125.6° after the first treatment the boiling point was 128° and after the second the boiling point went to 135°

| First drop | bath | press. |
|---|---|---|
| 135.4° | 148° | 5 m/m |

The temperature went rapidly to 136.8°; the bulk of the material distills at this temperature.

| Last drop | bath | press. |
|---|---|---|
| 136.8° | 153° | 5 m/m |

Weight of fraction = 36 grams (68.2%)

This was again treated with thiosulfate and distilled, the fore run was taken up to 130° at 3 m/m.

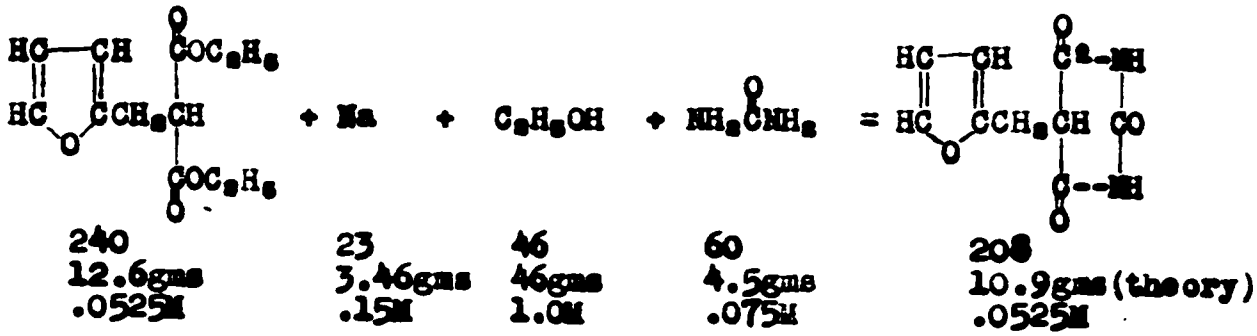
| First drop | bath | press. |
|---|---|---|
| 128.3° | 140° | 3 m/m |

The boiling point went up to 129.0° then

| Last drop | bath | press. |
|---|---|---|
| 128.5° | 160° | 3 m/m |

++++++++++

## SYNTHESIS OF FURFURYL BARBITURIC ACID[1]




The absolute alcohol was of special preparation (loc. cit.) one mol. was measured out and poured into a Pyrex combustion tube, one end of which was sealed off. The sodium was then added and the open end of the tube fitted with a $CaCl_2$ tube. The contents soon began to boil so that it was necessary to cool the tube with tap water. To get the last pieces of sodium in solution it was necessary to warm the tube with a luminous flame. After the contents had cooled, the ester was added and then the required amount of urea (dried over $H_2SO_4$ in Vac.) was placed in the tube and the end sealed off.

The sealed tube was placed in a section of pipe and steam passed in over night. The next day the tube was opened and the contents filtered off on a Buchner funnel and washed with a small amount of ethyl alcohol. The material was then dissolved in 100cc of water and dilute HCl added until the solution was just acid. The crystals were filtered off. The mother liquors were worked over,

[1] Dox and Yoder- Jour. Amer. Chem. Soc. 41, 1141 (1919)

the total amount of material obtained was 7.4 grams. This material was not pure, on ignition there was a residue of $Na_2CO_3$. Also, it was later found that the compound decomposed rather rapidly in acid solution and in this experiment the material was in an acid solution for 20 or 30 minutes.

REPEAT: The above quanities were used and the experiment carried out in the same manner. However, in this experiment the contents solidified at the beginning and remained solid throughout the entire time of heating. Doubtless, the yield could be improved by adding enough alcohol to bring all of the material in solution.

The tube was opened and the solid material removed by filtration on a Buchner funnel. The compound was dissolved in 125 cc of water and made strongly acid with conc. HCl. The solution was cooled in an ice bath during this addition. The product was immediatly filtered off and washed. The weight of the crude material was 4gms(38%). The melting point of the crude product was 187°-188.7°. After one recrystallization from water the melting point was 186°-187.5°

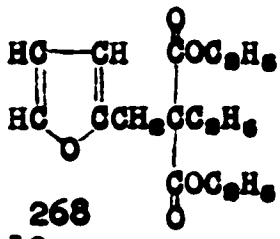
ANALYSIS:

.2511 gm sample gave 30.00 cc $N_2$ at 762.3 m/m. T= 26.0°

% Nitrogen calc. = 13.46

% Nitrogen found = 13.22

## FURFURYL ETHYL BARBITURIC ACID



| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | + | Na | + | $C_2H_5OH$ | + | $H_2N-\overset{O}{\overset{\|}{C}}-NH_2$ | = | PRODUCT |
| 268 | | | 23 | | 46 | | 60 | | 236 |
| 10gms | | | 3.8 | | 46gms | | 3.42gms | | 8.8 |
| .037M | | | .165M | | 1.M | | .057M | | .037M |

This condensation was carried out exactly as the previous one. The time of heating was ten hours. The contents of the tube were filtered off and concentrated to a small volume on the hot plate. This was treated with an excess of concentrated HCl and cooled. The crystalline precipitate was filtered off at once, washed and recrystallized from water. Weight of product = 4.5gms (51%). The melting point was 144.5°-145.0°

ANALYSIS:

.1168 gm sample gave 13.15cc $N_2$ at 23.6° and 760.1 m/m

% Nitrogen found = 12.41

% Nitrogen calc. = 11.86

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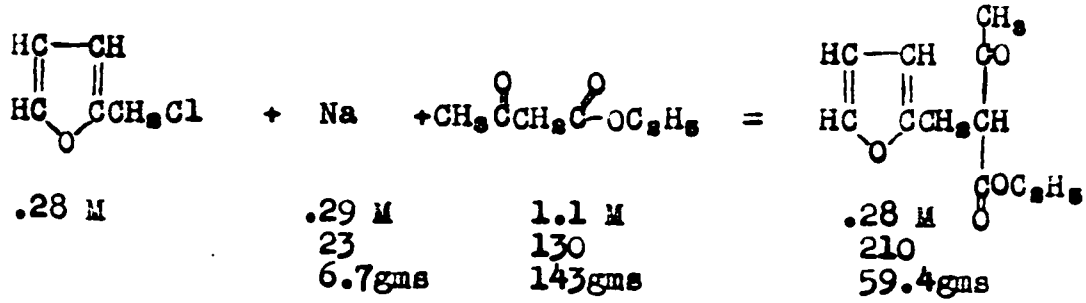
FURFURYL ACETOACETIC ESTER




6.7 grams of clean sodium were dissolved in 100cc of absolute ethyl alcohol(loc.cit.) in a three neck Pyrex flask fitted with dropping funnel, stirrer and reflux condenser. The freshly distilled acetoacetic ester was added through the dropping funnel. The condenser was then turned down and the alcohol removed by distillation. 100cc of distillate were obtained. The contents of the flask were then cooled to room temperature and the chloride in 150cc of ether was added over a period of 25-30 minutes. There was no heat evolved so a water bath was placed around the flask and the ether removed by distillation, the contents were then heated and stirred at the temperature of the water bath for five hours and then allowed to stand over night.

The mixture was then poured into a separatory funnel and washed with water, the water layer was removed and extracted with ether. The ester and ether washings were combined and dried over anhydrous $Na_2SO_4$.

After standing over night the ether was removed by

distillation and the residue fractionated. Acetoacetic ester was taken off up to 96° under water pump. The crude material boiled at 107°-114° at 4m/m. The weight of the fraction was 36.3grams(61%). This material was then re-fractionated

| | | |
|---|---|---|
| First drop 111.2° | bath 130° | pressure 4 m/m |
| Last drop 111.5° | bath 130° | pressure 4 m/m |

There was very little loss in weight.

ANALYSIS:

.1993 gm gave .1193gm $H_2O$ and .4556gm $CO_2$

% Carbon calc. = 62.82 % Hydrogen calc. = 6.71

% Carbon found =62.35 % Hydrogen found = 6.70

$D_{20}^{20} = 1.10562$

$D_4^{20} = 1.10366$

$N_D^{20} = 1.4718$

$M_D$(calc.) = 53.172

$M_D$(found) = 53.290

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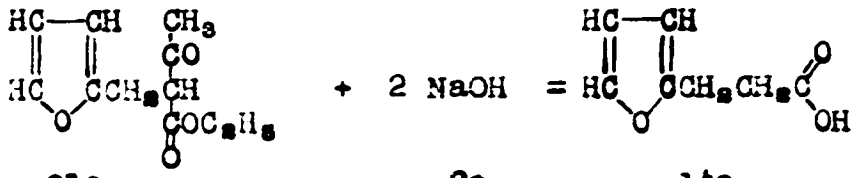
ACID SPLITTING OF FURFURYL ACETOACETIC ESTER[1]



| | | |
|---|---|---|
| 210 | 80 | 140 |
| 27.6gms | 21.2gms | 18.3gms (theory) |
| .131 M | .265 M | .131 M |

21.2 grams of NaOH were placed in a graduate and the volume made up to 42 cc with water. 27.6 grams of the ester were poured into a 150cc Erlenmeyer flask and shaken with the alkali. The contents solidified in 1-2 minutes,2-3 minutes later the material started to liquify and it was necessary to cool the flask as heat was evolved. The flask was allowed to stand,with frequent shaking,for four days. 75cc of water were then added and the flask shaken until solution was complete. The aqueous solution was then extracted with ether(to remove any ketone,this was worked up later).

The water solution was then treated with concentrated HCl,it was necessary to cool the flask during the neutralization,the temperature being kept below 20°by means of an ice bath. At the neutral point there was no separation but after there was an excess of HCl the material separated as an oil which soon crystallized on further cooling. This was immediatly filtered off and washed with cold water.

[1] Z.Anorg. Chem. 147,304(1925)

The crude material weighed 13 grams (72%).

The aqueous mother liquors may be extracted with ether to remove a further quanity of the acid. About three fourth to one gram were recovered . The crude material was recrystallized twice from water, the melting point of the final product was 56.5°-58°. The literature gives two values for the substance, 51° and 58.5° (Ber. 10, 357. 31, 1122)

The ether extract containing the ketone was evaporated. The ketone is a very pleasent smelling liquid, it weighed 2.1gms (14.3%). This was mixed with 2.2gms of semicarbazine hydrochloride and 2gms of potassium acetate and dissolved in the smallest amount of alcohol-water mixture. After standing over night the crystalls were filtered off and recrystallized from 95% alcohol, they melted sharply at 140°- 141°. The literature gives the melting point as 143° (Ber. 32, 1320).

.....

## SYNTHESIS OF FURFURYL CYANIDE

| | | |
|---|---|---|
| 116. | 49 | 107 |
| 35gms | 18.1gms | 32gms theory |
| .301 M | .37 M | .301 M |

The ethereal solution of the chloride was used (in about 200cc of ether). A 500cc round bottom flask was fitted with a two hole stopper, in one side was placed a dropping funnel and the other was fitted with a goose neck attached to a condenser.

18 gms of NaCN were dissolved in the smallest amount of water. The solution was then warmed to 60°-80° and the ethereal solution slowly dropped into the solution. During the addition the flask was shaken and rotated to insure good mixing. The ether distilled off at approximately the same rate as the addition of the chloride. The time of addition was one hour. At the end of this time the material was heated until it just began to boil, the heating was then discontinued and the flask allowed to cool. There was a separation into two layers.

After cooling, the oily layer was separated off and the aqueous layer extracted twice with ether. The product and ether washings were combined and dried over anhydrous sodium sulfate over night. The weight of the crude oil was 29 grams (92%)

The ether was removed by distillation and the product fractionated. The material boiled over a range of 75°-91° at 27 m/m. A systematic fractionation was carried out, the material being cut into four fractions: 74°-76°, 76°-77°, 80°-88° and the residue (furfuryl alcohol) boiled at 88°-93°. The pressure during the fractionation remained at 27m/m. After four fractionations a product boiling from 74°-74.5° at 27m/m was obtained. The material is a colorless oil that smells like parched pecans.

ANALYSIS:

.1528 gm gave 16.82cc of $N_2$ at 25° and 765.3 m/m.

% Nitrogen calc. = 13.08

% Nitrogen found = 12.45

$D_{20}^{20}$ = 1.04813

$D_4^{20}$ =1.04627

$N_D^{20}$ = 1.4833

$M_D$ (calc.) = 30.571

$M_D$ (found.)= 29.236

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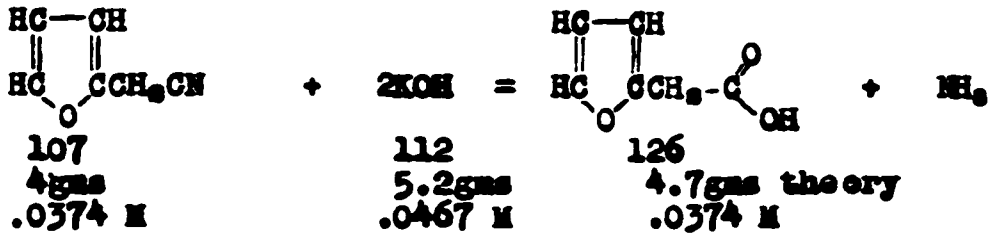
## HYDROLYSIS OF FURFURYL CYANIDE




A 25% solution of KOH was made by dissolving 5.2 gms of KOH in 21cc of water. This was placed in a small flask fitted with a reflux condenser, four grams of the nitrile were then added to the flask and the material heated on the hot plate for one hour. At the end of 4-5 minutes there was a vigorous evolution of $NH_3$ and the oily layer went into solution.

The solution was cooled and extracted twice with ether, the extracts being discarded. The aqueous solution was cooled to 10° and treated with Norite and filtered. The filtrate was treated with concentrated HCl until there was a definate excess of mineral acid. Crystallization starts as soon as the solution is cooled. The product is almost pure white and weighs 2 gms (42.5%) the melting point of the crude material was 108.5°-109.5°. After one recrystallization the melting point was 108.5°-109.5° This sample was analyzed:

.1813 gm gave .0776 gm $H_2O$ and .3802gm $CO_2$

% Carbon calc. = 57.14 % Hydrogen calc. = 4.79

% Carbon found = 57.19 % Hydrogen found = 4.79

## FURFURYL THIOCYANATE

| | | |
|---|---|---|
| 116. | 81 | 139 |
| 9.gms | 8.gms | 10.7gms (theory) |
| .0771M | .0987M | .0771M |

The reaction was carried out in acetone solution. The acetone was prepared by treating one liter of acetone with 75gms $KMnO_4$ and 150gms CaO, the material was refluxed for one hour then distilled. The distillate was treated with 50gms of $KMnO_4$ and 100gms of CaO and distilled through a Clark column, the fraction boiling from 56.6°-56.8° was collected.

The NaSCN was dissolved in 65cc of the acetone. The chloride was added to the solution in the three neck Pyrex flask and refluxed for two and a half hours. There was an immediate precipitate of NaCl on addition, cooling was not necessary. The solution was allowed to stand over night. The material was filtered and the acetone removed by distillation, the residue in the flask solidified and it was necessary to treat it with water and extract with ether. The ether solution was dried over anhydrous $Na_2SO_4$ and distilled the following day.

The distillation was carried out in a modified Claisen flask with a condenser on the side arm.

| First drop | bath | press. |
|---|---|---|
| 111.5° | 162° | 27 m/m |

The boiling point went up to 114.6° then falls to

| Last drop | bath | press. |
|---|---|---|
| 112.2° | 170° | 27 m/m |

%Yield = 74%

The compound was then redistilled under 2m/m pressure the fraction boiling from 66°-67° was collected, it was a colorless oil that had a slight oder.

ANALYSIS:

.1998gm sample gave .3350gm $BaSO_4$

% Sulfur calc. = 23.05

% Sulfur found = 23.03

$D_{20}^{20}$ =1.18919

$D_4^{20}$ =1.18709

$N_D^{20}$ = 1.5614

$M_D$ (calc. as RSCN) = 36.083

$M_D$ (found) = 37.971

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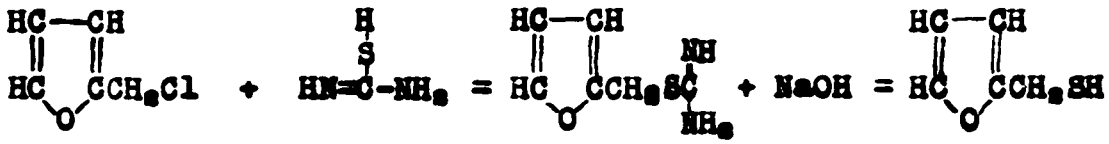
## FURFURYL MERCAPTAN



| | | | |
|---|---|---|---|
| 116 | 76.1 | | 114. |
| .29 M | .58 M | | .29 M |
| | 44.gms | | 33.gms |

An attempt was made to synthesize this compound by the action of the chloride on NaSH but the yields were low and the product was very impure.

44 grams of the thio urea were powdered and placed in a 500cc Pyrex flask fitted with a reflux condenser. The chloride, in 200cc of ether, was added through the top of the condenser. The mixture was heated on the hot plate for 41 hours. After the first 18 hours 75cc of acetone were added to the mixture. There was no odor of the chloride at the end of this period of refluxing. The acetone was removed by distillation and 72gms of NaOH in 300cc of water were added and the solution again refluxed for ten hours.

The cooled material was then cleared with Norite and filtered into a 500cc separatory funnel and extracted with $CCl_4$. Other extractants can be used but they form very stable emulsions or even gels. The solution was dried over anhydrous $Na_2SO_4$.

The $CCl_4$ was removed by distillation and the product distilled.

| First drop | bath | pressure |
|---|---|---|
| 84.1° | 110° | 65 m/m |

The boiling point was constant at this temperature. The weight of the fraction was 11 grams(33%). The product is a colorless oil that possesses a typical mercaptan odor.

ANALYSIS:

.2045 gm gave .4203 gm $BaSO_4$

% Sulfur calc. = 28.10

% Sulfur found = 28.17

$D_{20}^{20} = 1.13386$

$D_4^{20} = 1.13186$

$N_D^{20} = 1.5329$

$M_D$(calc.) = 31.489

$M_D$(found) = 31.302

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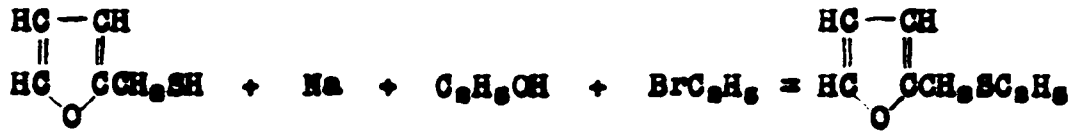
# FURFURY ETHYL SULFIDE




| | | | | |
|---|---|---|---|---|
| 5.7gms | 1.15gms | 15cc | 10.9gms | 7.11(theory) |
| 114 | 23 | | 109 | 142 |
| .05 M | .05 M | | .1 M | .05 M |

The sodium was dissolved in 30cc of 95% ethyl alcohol. The mercaptan was added to this solution and the flask washed with an additional 5cc of alcohol. The solution was placed in a 200cc Pyrex round bottom flask fitted with a reflux condenser. The bromide was added to the solution through the top of the condenser in 3-4 gram portions, there was a vigorous evolution of heat but as soon as the ebullition stopped another small portion of the bromide was added. There was an almost immediate precipitate of sodium bromide. After addition was complete the flask was placed on the steam bath and refluxed for an hour.

On cooling the material the crystalline sodium bromide readily separated out and the clear supernatant liquid was easily decanted. The precipitate of sodium bromide was then washed with a small amount of ether. The ether washings and the supernatant liquid were combined and the material distilled without drying.

The solvent, ie. ether and alcohol, was removed by distillation and the residue fractionated.

| | | |
|---|---|---|
| First drop<br>90.5° | bath<br>118° | pressure<br>28 m/m |
| Last drop<br>90.8° | bath<br>130° | pressure<br>28 m/m |

The weight of the fraction was 5.7 gms (80%).

ANALYSIS:

.1983 gm gave .3379 gm of $BaSO_4$.

% sulfur calc. = 22.56

% sulfur found = 22.40

$D_{20}^{20}$ = 1.05144

$D_4^{20}$ = 1.04958

$N_D^{20}$ = 1.5140

$M_D$(calc.) = 41.005

$M_D$(found) = 40.773

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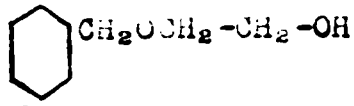
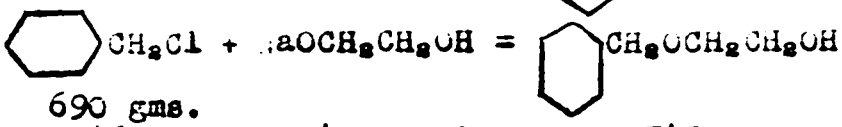
# PART TWO

# SYNTHESIS OF TETRAMETHYLENE GLYCOL

# AND

# TETRAMETHYLENE CHLOROHYDRIN

**Preparation of** 



690 gms.
5.46 Mols  4.92 Mols.  745gms.

$CH_3OH$ + Na = $CH_3ONa$
32  23
625gms  113gms
19.5Mols  4.92Mols  4.92Mols

800cc of absolute methyl alcohol were placed in a 3L. Pyrex flask. The 113 gms. of sodium were added, the flask being well cooled throughout this step, then 900gms of ethylene glycol were added and the excess $CH_3OH$ removed by distillation. The last traces being removed under reduced pressure at a temperature of 165°. While this viscous solution was still warm the addition of the benzyl chloride was started, the reaction was a little slow at first but soon cooling was necessary. The contents of the flask were not allowed to go above 150°. The mixture was allowed to stand over night. The following day the NaCl was filtered off with a Buchner. The NaCl was washed with 150cc of ether. The filtrate was fractionated to remove the benzyl chloride and glycol. The fraction was cut at 120° under 6m press. (bath- 131°)

At this stage it was thought best to recover the glycol. The distillate, from the step above, was extracted with 3-100cc portions of toluene and 2-75cc portions of ether. This was to recover the benzyl chloride.

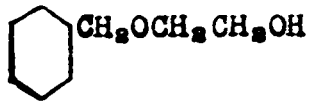
The crude glycol was then fractionated, the high boiling fraction was added to the product. 500gms of pure ethylene glycol were recovered.

The product was then fractionated.

| | | |
|---|---|---|
| First drop | bath | pressure |
| 104° | | 7m/m |
| Last drop | bath | pressure |
| 117° | | 7m/m |

The bulk of the material distilled at 117°

| | |
|---|---|
| The distillate weighs | 485gms(65%) |
| The residue weighs | 143gms.(12%) .59 Mols. |

SYNTHESIS OF 

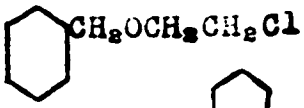
(ALTERNATIVE METHOD)

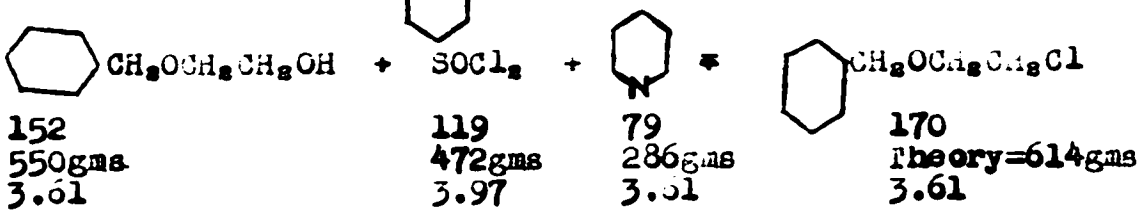
23 Grams of clean sodium were added to 160cc of pure anhydrous methyl alcohol in a 500 cc round bottom Pyrex flask. After solution was complete one mol of benzyl alcohol was added. The methyl alcohol was then removed by distillation under reduced pressure. One mol of ethylene chlorohydrin was then slowly added to the sodium benzylate. Considerable heat was evolved at this stage. The contents of the flask were kept below 50° by means of an ice bath. After addition was complete the mixture was heated on the steam bath for thirty minutes.

After cooling the mixture 200 cc of water were added to dissolve the sodium chloride. The oily layer was separated off and the mother liquors extracted with ether several times. The ethereal solution was dried over anhydrous sodium sulfate then fractionated.

A systematic fractionation was necessary to isolate a semi-pure product. The material boiled at 115°-116° under 4 m/m pressure.

The yield by this method is very poor, in this case it was 18-20%.

SYNTHESIS OF 




550 gms of the alcohol were placed in a 3 necked flask (2 L) fitted with an electric stirrer, dropping funnel and reflux condenser. The pyridine was added and the stirrer started. Thionyl chloride was added over a period of three hours. The arrangement was such that the large flask could be cooled, the temperature was not allowed to go above 45-55°, and for the greatest portion of the time it remained at room temperature. The first portion of thionyl chloride was added at the rate of one drop per second, the last half was added much faster. The characteristic white precipitate formed after the first half of the thionyl chloride had been added. This disappeared on further addition. The solution began to crystallize as soon as the reaction was finished. Plates about 1cm long and 2-3cm wide crystallized out on standing over night.

300cc of water were added and the material stirred until solution was complete. 100cc of ether were then added and the emulsion stirred for an additional five minutes. The oily layer was then separated off and the water layer extracted several times with ether (3-100cc portions) (note 1) The oily layer and ether extract were united and washed with water. If an emulsion forms it can be easily broken by

the addition of more ether.

The ethereal solution was dried over $CaCl_2$ for two days and fractionated:

| First drop | bath | pressure |
|---|---|---|
| 99° | 116° | 7m/m |

The bulk of the material comes over at 99°-100°

| Last drop | bath | pressure |
|---|---|---|
| 108° | 132° | 7m/m |

The weight of the distillate =528 gms.(86% yield)

Note(1). The aqueous layer was worked up to recover the pyridine as follows: a stream of air from a drying tower was blown through the solution until most of the ether and $SO_2$ were removed. Sticks of solid KOH were added until there was a separation into two layers. The pyridine layer was removed with ether and dried over KOH then distilled.

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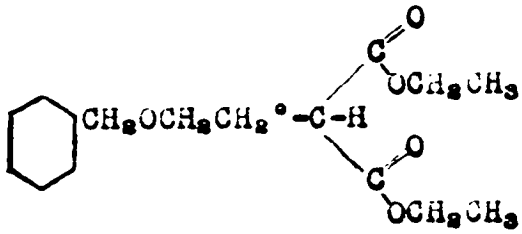
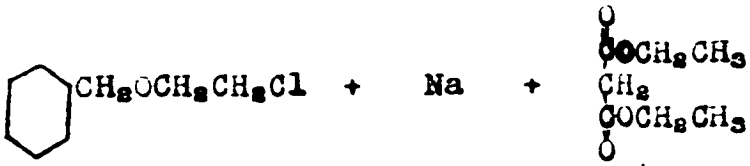
SYNTHESIS OF 



| | | | | |
|---|---|---|---|---|
| gms | 525 | 73.5 | 545 | Theory=819gms |
| Mol. wt. | 170 | 23. | 160 | |
| Mols. | 3.09 | 3.20 | 3.40 | |

The reaction was carried out in absolute ethyl alcohol made by the directions of Smith(J.C. S. 1288. 1927) with sodium and ethyl acetate. The pure dry alcohol was distilled directly into the apparatus which consisted of the 3 necked 2L Pyrex flask fitted with stirrer,reflux and dropping funnel.

The 73.5gms of Na were cut in large cubes and added as quickly as possible,the flask being cooled between additions. After solution was complete the malonic ester was added as rapidly as possible. The solution was stirred until transparent. The chloride was added as fast as it could flow through the funnel. About 45 seconds later the turbidity due to the NaCl became evident.

The apparatus was fitted with an oil bath and hot plate and the solution stirred and refluxed for a period of five days. At the end of this period the ethyl alcohol was removed by distillation.

The contents of the flask were then poured on a Buchner

funnel and the NaCl separated off. This was washed several times with ether. The ether washings and filtrate were combined and fractionated.

50 gms of the unchanged chloride were recovered, as well as the excess of malonic ester. The product was collected from 145°-175°. The bulk of the product boiling sharply at 162°-163° under 3m/m pressure.

There was a slight decomposition on distillation, this could likely be avoided if the fractionation was faster. In this case the time of distillation was well above eight hours. The yield was 75.4%

In another experiment on the synthesis of this compound the alcohol used was dried over lime. The yield in this case dropped off to 59%.

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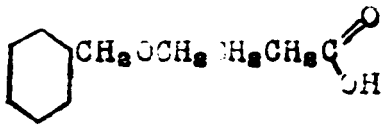
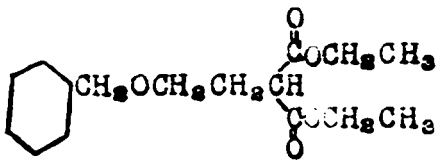
SYNTHESIS OF 



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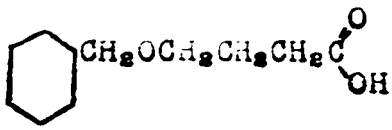

| | | |
|---|---|---|
| Mol. wt. | 294 | 194 |
| Gms. | 616 | 406-theory |
| Mols. | 2.098 | 2.098 |

616gms of the ester were poured into alcoholic NaOH, made by dissolving 4.6 Mols(184gms) of NaOH in least possible amount of water then diluting this solution with 2 L of 95% alcohol. A white precipitate formed. Heat is evolved in this reaction so the necessary steps had to be taken to cool the flask. The reaction was apparently over after five minutes, but was allowed to stand at room temperature for several days. The ethyl alcohol was removed by distillation, the flask being heated on the steam bath. The residue is a fluffy yellow colored substance.

The material was dissolved in 500cc of water, this was added directly to the original flask. The flask was fitted with a condenser and the rest of the alcohol removed, this is essential for the best extraction.

The solution was then extracted twice with ether to remove any unhydrolized material. 130 cc of $H_2SO_4$(98%) were then carefully added. The solution nearly boiled over due to the low boiling ether that remained in solution after the extraction. The solution itself did not rise above 45-

50% On standing a few minutes there was a separation into two layers. The upper oily brown layer was removed, the aqueous layer was extracted with 4-75cc portions of ether. The oil was then added to the washings and the volumn made to 1.5L. This solution was treated with annydrous $Na_2SO_4$, after a few hours there is again a separation into two layers the ethereal layer was removed and treated with more $Na_2SO_4$. After drying over night the ether was distilled off in a 1L flask(in portions)so that all of the material in the end was in this flask. The temperature of the flask was raised by means of an oil bath until $CO_2$ began to be evolved. This was at 110°. The time required to complete this reaction was six and one half hours. The temperature was finally raised to 157°.

Yield=397gms(97.7%).

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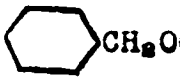
SYNTHESIS OF

A trial run was made to determine if any difficulties would be encountered. 25gms of 98% $H_2SO_4$ were added to 225 gms of freshly prepared anhydrous ethyl alcohol(Smith-loc. cit.),,then 25gms of the acid were added. This slightly turbid solution was refluxed for 7 hours. t the end of this time 42gms of $NaHCO_3$ were added. The $Na_2SO_4$ was removed by filtration on a Buchner and thoroughly washed with ethyl alcohol. The alcohol solution was placed in a pyrex flask and the alcohol removed by distillation. The residue is treated with water and extracted with ether three times. The ether solution was washed $Na_2CO_3$ then distilled water and finally dried over $CaCl_2$. On evaporation of the ether the residue weighed 28.5 gms. Theory= 28.6
Boiling point of the ester=131°-138° under 3m/m pressure.
Yield = 99.6%.

In an earlier experiment of ours on esterification in which 30gms of the acid were dissolved in 300cc of absolute alcohol and refluxed for eleven hours with concentrated $H_2SO_4$( composed of 20cc $H_2SO_4$ + 10cc of 20% fuming sulfuric). This was worked up for the ester in the usual manner but no ester was obtained. The product(8-10gms) on analysis was found to be  $CH_2OCH_2CH_3$. The formation of this compound was explained by assuming that the acid split the ether to benzyl alcohol which in turn was alkyl-

ated by ethyl sulfuric acid.

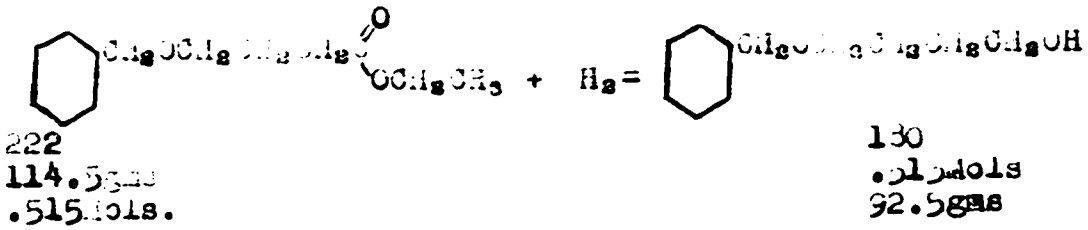
The esterification was then carried out on a large scale. 395gms of the acid(2.03 Mols.) were dissolved in 3,350 cc of absolute alcohol(57.4 Mols) and 270 gms of sulfuric acid added. This slightly turbid solution was refluxed for eight hours. After cooling,445 gms of $NaHCO_3$ in enough water to make a paste were added. The precipitate of $Na_2SO_4$ was filtered off on a Buchner. If the filtration becomes difficult,it will be found that the addition of more water will increase the size of the $Na_2SO_4$ crystals thus making the filtration a great deal faster.

The alcoholic solution was then run into a large Pyrex flask and the alcohol removed by distillation. As soon as the temperature of the vapors went to 85°the distillation was interrupted and the contents cooled and poured into a separatory funnel. The oily layer was removed,the mother liquors extracted three times with large volumes of ether. The extracts and oily layer were combined and washed with dilute alkali(5% $Na_2CO_3$) followed by water and then dried over anhydrous $CaCl_2$.

The ether was fractionated off and the low boiling impurities removed up to 130° under the vacuo of the water pump. Weight of ester =382.5 gms = 85.1% yield.

The ester was later fractionated from 131°-138° under 3m/m pressure. It was found that the above crude product was only 92.% pure.

## REDUCTION OF THE ESTER



222
114.5gms
.515 mols.

180
.51 mols
92.5gms

115 grams of sodium were placed in a 3L 3necked Pyrex flask fitted with a stirrer, condenser and dropping funnel. 250 cc of dry toluene were added and the flask heated until the sodium became molten. The stirrer was started and the flask allowed to cool with the stirrer going at high speed. When the temperature reached 60° a solution of 114 gms of the ester in 150 cc of the special alcohol (Smith, loc.cit.) were added over a period of three minutes. Ice water was poured over the apparatus. After the reaction had slowed down 500cc more of the alcohol were run in over a period of ten minutes. The contents were stirred until all of the sodium had reacted, then 300 cc of water carefully added, This required about five minutes. The solution was then refluxed for thirty minutes and the alcohol-toluene mixture removed by distillation.

The contents of the flask were placed in a separatory funnel and the oily layer removed. The water solution was twice extracted with 150 cc portions of ether.

200 cc of water were added to the oily layer then this

mixture was extracted with 200cc of ether(note1) all the other extracts were then combined and washed with water. The ether was removed by distillation and the residue fractionated:

Boiling point = 135° under 2m/m pressure. Weight of the distillate = 45.7 grams. (62.%)

Note 1. It was thought that the benzyl ether might be split by the sodium. P. Schorigins study indicated that this was possible(Ber.56,176 andBer.57,1627). The aqueous solution mentioned above was saturated with $K_2CO_3$ and extracted with ethyl alcohol. After the alcohol was removed by distillation the residue was fractionated:

| First drop | bath | pressure |
|---|---|---|
| 134° | 195° | 25m/m |
| Last drop | bath | pressure |
| 135° | 240° | 25m/m |

weight of the distillate = 4.4 grams.

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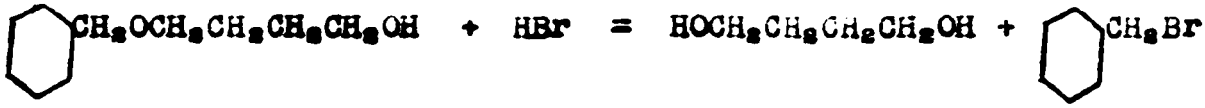
## NOTES ON THE REDUCTION

Three reductions in all were carried out ,the yields in order were 62%,46.5% and 47.7%. With the exception of the third reduction the others were carried out as far as possible according to the procedure as outlined above. The special alcohol used in these reductions doubtless contained much more water than was best for the reaction. This was due to the long period of standing,some three months before the last two reductions were carried out and to repeated opening of the bottle in order to obtain samples for the experiments on esterification.

It was found that the reaction would go smoothly if the sodium was allowed to cool to room temperature before the addition of the solution of the ester. This will produce a pronounced difference in the violence of the reaction and is highly recommended.

All of the water solutions,the original mother solution and separately the washings of the oily layer were worked up for the recovery of tetramethylene glycol. In each about six grams total were obtained. Four grams being recovered from the water washings of the oily layer and two grams from the mother solution after the reduction. Extraction of the saturated $K_2CO_3$ solution with ethyl alcohol is recommended over the extraction with amyl alcohol. The amyl alcohol unravels other substances than the glycol which later interfere with the purification of the glycol.

## SPLITTING OF THE BENZYL ETHER




| | |
|---|---|
| mol wt=180 | 40.0 |
| mols =.253 | .208 |
| mols recovered=.045 | 18.1gms theory |

45.7 grams of the benzyl ether were placed in a 250cc flat bottom flask and 75cc of concentrated HBr poured over it. The solution was cooled in an ice bath and saturated with dry HBr gas. The flask was stoppered and left over night.

Solid $K_2CO_3$ was added until neutral(an excess is to be avoided). The solution was then extracted four times with small volumes of benzene. The benzene extracts were then washed with water. The water washings were returned to the original solution. The solution can now be extracted with ethyl alcohol after being saturated with $K_2CO_3$: The alcohol was removed by distillation and the residue fractionated.

| | | |
|---|---|---|
| First drop | bath | pressure |
| 131.0° | 148° | 17m/m |
| Last drop | bath | pressure |
| 131.5° | 166° | 17m/m |

Weight of glycol = 11 grams (61% yield)

PHYSICAL CONSTANTS OF TETRAMETHYLENE GLYCOL

Boiling point =131.0°- 131.5° under 17 m/m

$D_{20}^{20} = 1.0189$

$D_4^{20} = 1.0171$

$N_D^{20} = 1.4467$

$M_D$(calc.)=23.722

$M_D$(fd.) =23.651

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NOTES ON SPLITTING OF BENZYL ETHER

In all there were two such reactions carried out, the foregoing was according to the directions of Bennett (J.C. S. 481. 1927). The isolation of the product from the acid solution is based on a method worked out in this laboratory. The second splitting was carried out by our own method. 66 grams of the ether were mixed with 175 cc of concentrated HBr. This solution was allowed to stand 68 hours then worked up as above except that amyl alcohol was used in place of the ethyl. This makes the extracted glycol not as pure as that isolated by extraction with ethyl alcohol for the b.p. is 118.5°-124°under 8 m/m. also the product smells slightly of amyl alcohol. Taking into consideration the recovered ether the yield by our method was found to be 70%

The latter method in my estimation is the best, for dry HBr gas is not easy to prepare, futhermore the yields are not as high as those of our own method.

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## NOTES ON TETRAMETHLYENE GLYCOL

Without doubt it is best to use ethyl alcohol for the extraction of the saturated $K_2CO_3$ solution. The amyl alcohol imparts a smell to the glycol that cannot be removed by fractionation.

The literature reports the melting point of the glycol to be 0-16°( Beilstein ) and 16° ( Meyer und Jacobsen ). With the product isolated by us the melting point was found to be 19.2°-19.4°. The boiling point was found to be 131.0° -131.5° under 17m/m pressure. The glycol when pure has no odor at all. The literature is unanimous in reporting the smell as like that of leeks.

The di-phenyl urethane was made, following the directions of J. Hamonet (Bull.Soc.Chim. 33,525. 1905). The melting point of the product was found to be 179.5°. The value given by Hamonet is 180-181°.

| Solubility: | $H_2O$ | ETHER | $CCl_4$ | $C_5H_{11}OH$ | $C_2H_5OH$ | $C_6H_6$ |
|---|---|---|---|---|---|---|
| | + | - | - | + | + | - |

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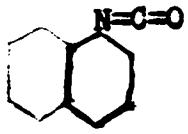
DI- α NAPHTHYL URETHANE OF TETRAMETHYLENE GLYCOL

2  + $HOCH_2CH_2CH_2CH_2OH$ = PRODUCT

3.76 gms 1.0 gm.

The above quanities were mixed in a large Pyrex test tube and heated for a few seconds, the solution turned a faint blue then solidified.

The material was removed from the test tube and washed with petroleum ether then water. The product was then washed once with alcohol and recrystallized from Xylene.

The melting point of the purified material was found to be constant at 198.5°-199.0°.

Analysis:

Sample
.8866 gm

Acid
76.41 cc

Alkali (back titration)
33.99 cc = 34.57 cc acid

Nitrogen calculated = 6.55%

Nitrogen found = 6.49%

++++++++++++++++++++

TETRAMETHYLENE CHLOROHYDRIN

| | | | |
|---|---|---|---|
| 90 | 119 | 79 | 108.5 |
| 20gms | 26.4 | 17.6 | 24.(theory) |
| .222M | .222M | .222M | .222M |

Preliminary experiments showed that it was possible to convert glycols to the chlorohydrins with $SOCl_2$ in a yield of about 50%. This was found to be the case with trimethylene glycol but little or no success was obtained with ethylene glycol.

The glycol and pyridine were placed in a 3 necked 200cc Pyrex flask fitted with stirrer,reflux condenser and dropping funnel. A water bath at 56° was placed around the flask and kept at this temperature during the entire reaction. The $SOCl_2$ was added over a period of one hour. The temperature of the bath was then raised to 80°and held there for one hour. The material was then worked up in the usual way and distilled.

| | | |
|---|---|---|
| First drop 84.1° | bath 115° | pressure 16m/m |
| Last drop 85.0° | bath 126° | pressure 16m/m |

All except the first few drops came over at 85.0°

Yield = 50%

In this experiment an attempt was made to raise the boiling point by increasing the pressure,so that the condensation would be more efficient. The boiling point did

not go up but the compound decomposed into tetrahydro furane and HCl.

Analysis of chlorohydrin:

Sample: .3175 gms

AgCl: .4176 gms

Chlorine found = 32.53%

Chlorine calc. = 32.67%

$D_{20}^{20} = 1.0902$ $D_4^{20} = 1.0883$ $N_D^{20} = 1.4518$

$M_D$(calc.) = 27.064

$M_D$(fd.) = 26.893

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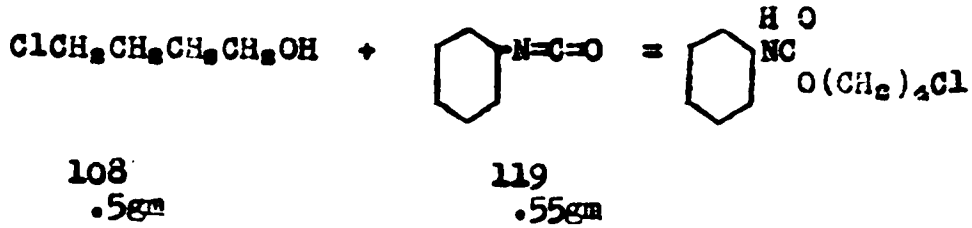
PHENYL URETHANE OF TETRAMETHYLENE CHLOROHYDRIN




.5 gram chlorohydrin were placed in a 125cc flat bottom flask and 100cc of petroleum ether added(60°-70°). .55grams of phenyl iso-cyanate were then added and the solution allowed to stand for two days. The solution was brought to a small volume by heating on the hot plate and slowly cooled, if the cooling is too rapid the substance separates as an oil. The crystals are collected and washed with petroleum ether and recrystallized from the same solvent. The melting point of the product was 54°.

Analysis:

Sample = .0608gms
Ag Cl = .0381gms

Chlorine found = 15.50
chlorine calc. = 15.58

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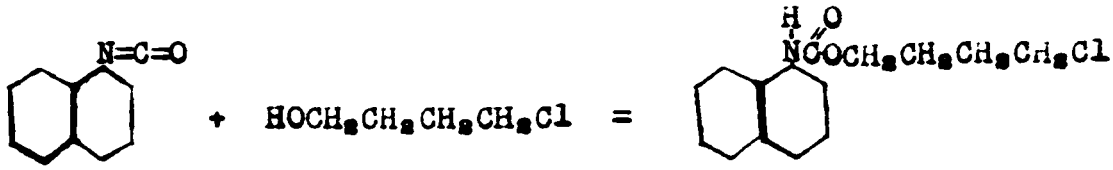
## α NAPHTHYL URETHANE OF TETRAMETHYLENE CHLOROHYDRIN




1.57gms 1.0gms

The above quantities were mixed in a 150cc flat bottom flask and diluted with 90cc of petroleum ether(low boiling). The solution was allowed to stand for two weeks.

At the end of this period the mass of crystalline material which had collected on the bottom of the flask was filtered off and recrystallized from petroleum ether.

The melting point of the product was found to be 69°-70°. This was found to be constant and the material was analyzed.

Analysis:

Sample = .3401 gms

Ag Cl = .1768 gms

Chlorine calculated = 12.78%

Chlorine found = 12.85%

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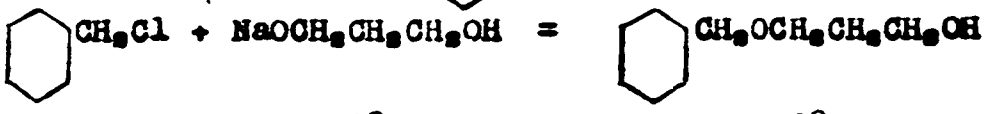
SYNTHESIS OF



| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | $CH_2Cl$ | + | $NaOCH_2CH_2CH_2OH$ | = | | $CH_2OCH_2CH_2CH_2OH$ | | |
| | .3mol 37.8gms | | .28mols | | | .28 46.5gms theory | | |
| $CH_3OH$ | + | Na | + | $HOCH_2CH_2CH_2OH$ | = | $NaOCH_2CH_2CH_2OH$ | | |
| 45. | | 6.45 | | 64. | | | | |
| 1.4 mols | | .28m | | .84m | | .28m | | |

The sodium was dissolved in the methyl alcohol and the glycol added. The reaction flask was fitted with a stirrer,condenser and dropping funnel. After solution was complete the excess alcohol was removed by heating the flask to 180° for an hour. The benzyl chloride was run into the hot solution. Time of addition was ten minutes. Heat was evolved but the contents were not permitted to boil. The mixture was then allowed to stand until it had cooled to room temperature. The sodium chloride was removed on a Buchner and the filtrate fractionated.

The benzyl chloride came over first,88°-95° under 21m/m,glycol from 95°-130° under 30m/m. The product was so contaminated with NaCl that it had to be washed before distillation. The compound boils sharply at 107.5° under 2 m/m pressure.

The yield was 65%,which was about the same as the next lower homologue.

PHYSICAL CONSTANTS OF $CH_2OCH_2CH_2CH_2OH$

$D_4^{20} = 1.0483$

$N_D^{20} = 1.5153$

$M_D$(calc.)= 47.947

$M_D$(fd.) = 47.808

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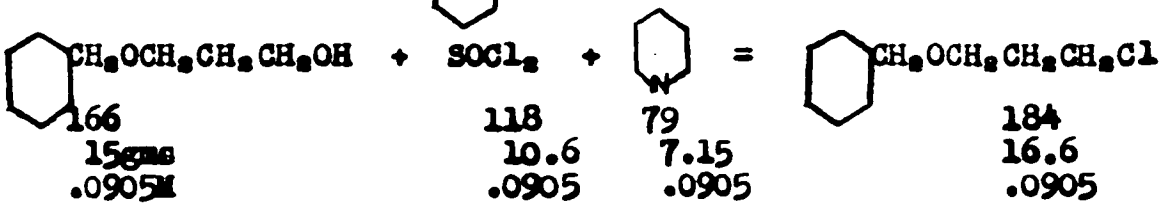
SYNTHESIS OF



| | | | | |
|---|---|---|---|---|
| 166 | 118 | 79 | | 184 |
| 15gms | 10.6 | 7.15 | | 16.6 |
| .0905M | .0905 | .0905 | | .0905 |

The thionyl chloride was added to the pyridine solution of the alcohol. The time of addition was seven minutes. The typical intermediate white precipitate appeared after the first half of the thionyl chloride had been added and redissolved on further addition. At the end of the reaction the solution separated into two layers.

The material was placed in a separatory funnel and an equal volume of water added. The oily layer was then extracted with ether and washed with dilute hydrochloric acid(2%),sodium carbonate(2%) and distilled water. The ethereal solution was dried over anhydrous sodium sulfate for one day.

The ether was removed by distillation and the residue fractionated:

| | | |
|---|---|---|
| First drop 128.5° | bath 147° | pressure 15 m/m |
| Last drop 132° | bath 147° | pressure 15 m/m |

Weight of the fraction = 13.3 gms(80% yield)

$D_{20}^{20}$=1.0842 $D_4^{20}$=1.0822 $N_D^{20}$= 1.5131

$M_D$(calc.)=51.289 $M_D$(fd.)=51.266

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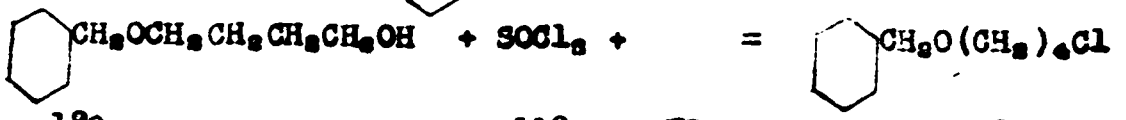
SYNTHESIS OF



| | | | | |
|---|---|---|---|---|
| 180 | 118 | 79 | | 198 |
| 10gms | 6.55 | 4.4 | | 11-theory |
| .055mols | .055 | .055 | | .055 |

The alcohol was dissolved in the pyridine and the thionyl chloride added slowly enough that the solution did not go above 40°-50°. The time of addition was about five minutes. The typical white precipitate appeared after the first third of the thionyl chloride had been added.

After the reaction was complete there was a separation into two layers. The mixture was mixed with twice its volume of water and extracted with ether. The solution(ether) was washed with dilute acid, alkali and distilled water then dried over anhydrous sodium sulfate for two days.

The ether was removed by distillation and the residue fractionated:

| | | |
|---|---|---|
| First drop 122° | bath 147° | pressure 5 m/m |
| Last drop 123° | bath 159° | pressure 5 m/m |

Weight of fraction = 4.3 grams.