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Preparation of Methyl Ethyl Sulfate

PREPARATION OF METHYL ETHYL SULFATE AND ITS USE AS AN ALKYLATION AGENT

BY

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Floyd Kinyon Thayer.

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PART I.

PREPARATION OF METHYL ETHYL SULFATE
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INTRODUCTION

The secondary or neutral esters of sulfuric acid have long been known to possess the power of alkylation. Because of difficulties met in preparation dimethyl sulfate $(CH_3)_2SO_4$ has been the only one used to any extent as an alkylating agent.

An interesting problem presented itself in the study of mixed esters of sulfuric acid as regards their alkylating properties. This work was undertaken primarily to ascertain the action of methyl ethyl sulfate when used to alkylate.

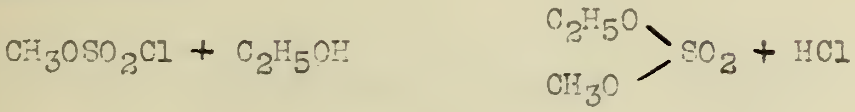
The preparation of mixed sulfates, although attempted by several, did not meet with success until the early part of this century.

HISTORICAL

Behrend[1] claimed to have prepared methyl ethyl sulfate in two ways. By the action of methyl alcohol upon the ethyl ester of chloro-sulfonic acid

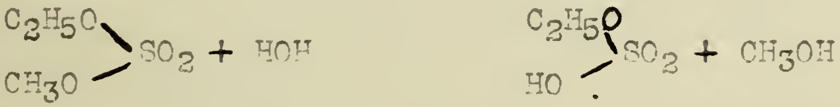
$$C_2H_5O\ SO_2Cl + CH_3OH \qquad \begin{matrix} C_2H_5O \\ CH_3O \end{matrix} > SO_2 + HCl$$

and the reverse process of ethyl alcohol upon the methyl ester of chlorosulfonic acid.



$$CH_3OSO_2Cl + C_2H_5OH \qquad \begin{matrix} C_2H_5O \\ CH_3O \end{matrix} > SO_2 + HCl$$

Behrend stated that when this methyl ethyl sulfate was treated with water that the methyl group was hydrolyzed off according to the equation



$$\begin{matrix} C_2H_5O \\ CH_3O \end{matrix} > SO_2 + HOH \qquad \begin{matrix} C_2H_5O \\ HO \end{matrix} > SO_2 + CH_3OH$$

Thus it could be concluded from his work that the methyl group was most active and therefore would be the one with the most pronounced alkylative property.

But Claesson[2] has shown Behrend's work to be unreliable. Bushong[3] and the writer have both repeated part of Behrend's work with the same conclusion. Bushong[3] thus was really the first to prepare mixed alkyl sulfates. He, however, did not make methyl ethyl sulfate but confined his work to the preparation of ethyl isoamyl, ethyl isobutyl and ethyl isopropyl sulfates. In no case did he test any of his secondary sulfates as alkylating agents.

THEORETICAL PART

I. Preparation of the Ethyl Ester of Chloro-Sulfonic Acid

Every method for the preparation of mixed alkyl sulfates necessitated the use of esters of chloro-sulfonic acid ($ROSO_2Cl$).

Müller[4] made ethyl chloro-sulfonic acid by passing ethylene through chloro-sulfonic acid. The writer did not find this a convenient nor satisfactory method for the preparation of large quantities of the ester.

Behrend[1] found that by the addition of 1 mol of ethyl alcohol to sulfuryl chloride (SO_2Cl_2) he could obtain the ester in fair amounts. Bushong[3] and later Willcox[5] improved the method until it was very reliable and good yields obtained.

II. Preparation of the Methyl Ester of Chloro-Sulfonic Acid.

The methyl ester was prepared by following the same procedure given for the ethyl ester.

This ester, as all the others of chloro-sulfonic acid, was found to have a very disagreeable action upon the eyes.

III. Preparation of Butyl Ester of Chloro-Sulfonic Acid.

In practically identical manner was the butyl ester prepared. It was somewhat more unstable than either the methyl or ethyl esters and on standing turned pink and finally changed into an oily substance.

IV. Preparation of Methyl Ethyl Sulfate.

At the time Bushong did his work[3] on the secondary esters of sulfuric acid only the following were known: methyl, ethyl, normal propyl and isoamyl. Bushong in his work prepared by a new method not only di-isoamyl, di-isobutyl and di-isopropyl sulfates but sulfates in which there were two different radicals as ethyl-isopropyl,

ethyl isobutyl and ethyl-isoamyl sulfates. He, however, recorded no sulfates with a methyl group nor did he mention any attempt at their synthesis.

Bushong's method for the preparation of mixed alkyl sulfates consisted in the addition of 1 mol of the ethyl ester of chlorosulfonic acid to 1.5 or 2 mols of the sodium alcoholate suspended in ligroin or ether. He states that "When absolute ether and only 1.5 molecules of the alcoholate are used an almost clear solution results after some standing". The writer has been unable in any of his different experiments to obtain a clear solution. Furthermore, the preparation of methyl ethyl sulfate by this method necessitated refluxing for 24 hours.

Bushong in his work isolated 5 different reaction products namely (1) alkyl ethyl sulfate, $ROSO_2-OC_2H_5$; (2) alkyl sodium sulfate, $RO-SO_2-ONa$; (3) a mixed ether $R-O-C_2H_5$; (4) sodium sulfate; (5) alcohol. Necessarily then the yield of secondary ester must be low.

An attempt to prepare this compound with ethyl chlorosulfonic acid and absolute alcohol, as described by Behrend[1], resulted unsuccessfully; only higher and lower boiling substances could be isolated.

V. Preparation of Methyl Butyl Sulfate.

When sodium methylate and the butyl ester of chloro-sulfonic were refluxed together methyl butyl sulfate $\left(\begin{matrix}C_4H_9O\\CH_3O\end{matrix} > SO_4\right)$ was obtained.

VI. Preparation of Ethyl Butyl Sulfate.

On very small quantities of ethyl butyl sulfate were obtained from sodium ethylate and butyl chloro-sulfonic acid.

VII. The Use of Methyl Ethyl Sulfate as an Alkylating Agent.

In the determination of the comparative alkylative properties possessed by the methyl and ethyl groups standard conditions were necessary.

A 10% NaOH solution of phenol (C_6H_5OH), in which the molar strength of the NaOH was .1 mol greater than that of the phenol, was treated with di-methyl sulfate $(CH_3)_2SO_4$ of same quantity as the phenol. The percentage of anisole, $C_6H_5OCH_3$, obtained by this method in two different runs of varying quantities was found to check within nine-tenths of a percent, being 73.8% and 74.7%.

The same method was followed when the methyl ethyl sulfate was used. The yield of anisole was found to be 56.7% of the theory, i.e. 56.7% of the amount of $C_6H_5OCH_3$ was formed that should be formed if all of the methyl group reacted. The yield of phenetole, $C_6H_5OC_2H_5$, was 13.4% of the theoretical. Which means that of the total amount of alkylation done the methyl group was responsible for 80.2% and the ethyl group for 19.8%.

EXPERIMENTAL PART

I. Preparation of the Ethyl Ester of Chloro-Sulfonic Acid.

Two hundred and twenty-six grams (1 mol) of SO_2Cl_2 was placed in a distilling flask fitted with a two hole rubber stopper through which were inserted the stem of a dropping funnel and a glass tube drawn to a fine capillary and extending below the surface of the acid chloride. The delivery stem of the distilling bulb was attached to the vacuum line through a wash bottle containing water. The air drawn in through the capillary tube was first well dried by bubbling through concentrated sulfuric acid. The distilling flask was immersed in a freezing mixture of ice and salt, and absolute alcohol, 84 grams, (a little in excess of 1 mol) was slowly dropped through the separatory funnel.

When all the alcohol had been added, the freezing mixture was removed but the air current was continued for half an hour. The reaction mixture was now removed, washed once with ice water and allowed to dry over anhydrous copper sulfate.

On distillation under diminished pressure, practically all boiled over from 92-95° at 100 mm. The yield was 165 grams or 71% of the theory.

II. Preparation of the Methyl Ester of Chloro-Sulfonic Acid.

Following the same procedure, 435 grams of SO_2Cl_2 and 160 grams of absolute CH_3OH gave 219 grams of CH_3OSO_2Cl which was a 53% yield. Boiling point found to be 73-75° at 100 mm.

III. Preparation of the Butyl Ester of Chloro-Sulfonic Acid.

Similarly, 150 grams of SO_2Cl_2 and 83 grams of absolute normal butyl alcohol resulted in 105 grams of butyl chloro-sulfonic acid which was approximately 55% of the theory.

This ester boils at 64° under 4 mm.

IV. Preparation of Methyl Ethyl Sulfate.

In a dry ether suspension of 26 grams of sodium methylate (free from alcohol) there was added slowly 90 grams (1.3 mols) of ethyl chloro-sulfonic acid and the mixture stirred. After all the ester has been added, the reaction mixture was refluxed on the water bath for 24 hours, filtered from the salt and the ether distilled off under diminished pressure. The remaining liquid boiled at 73° at 6 mm. Yield 13.2 grams or 19.7% of the theory.

Analysis for sulfur by Carius.

0.4323 gram sample gave 0.7129 grams $BaSO_4$.

	Calculated for $\left.\begin{matrix}C_2H_5O\\CH_3O\end{matrix}\right> SO_2$	Found
% Sulfur	22.85	22.60

V. Preparation of Methyl Butyl Sulfate.

Twenty-five grams (3 mols) of $NaOCH_3$ when added to 25 grams (1 mol) of But. SO_2Cl in 200 cc. of petroleum ether and refluxed gently for 24 hours gave a little less than 6 grams of product having a b.p. of 100° at 8 mm. Yield approximately 24% of the theory.

Analysis for sulfur by Carius.

0.4273 gram sample gave 0.6096 grams $BaSO_4$.

	Calculated for $\left.\begin{matrix}C_4H_9O\\CH_3O\end{matrix}\right> SO_2$	Found
% Sulfur	19.05	19.55

VI. Preparation of Ethyl Butyl Sulfate.

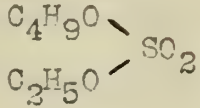
In 125 cc. of dry ether, 25 grams (2 mols) of $NaOC_2H_5$ and 30 grams (1 mol) of But OSO_2Cl were reacted. Only 1.3 grams of product, b.p. 106° at 6 mm. were isolated which corresponded to

about 4% yield.

Analysis for sulfur by Carius.

0.3364 gram sample gave 0.3239 grams $BaSO_4$

0.4028 gram sample gave 0.3474 grams $BaSO_4$

	Calculated for	Found
	 $\begin{matrix}C_4H_9O\\C_2H_5O\end{matrix}\!>\!SO_2$	
% Sulfur	17.48	12.00 11.82

VII. The Use of Methyl Ethyl Sulfate as an Alkylating Agent.

(a) Alkylation with Di-methyl Sulfate.

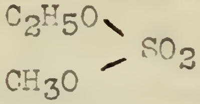
In a 1/2 liter round bottom flask were placed 36.6 grams (1 mol) of C_6H_5OH, 19.6 grams (1.1 mol) of NaOH and 176.4 grams of H_2O. This mixture was cooled with ice and stirred while 50 grams (1 mol) of $(CH_3)_2SO_4$ was added drop by drop. The stirring was continued for 5 minutes after all the $(CH_3)_2SO_4$ had been added. The flask was now fitted with a reflux condenser and refluxed for 15 minutes;at the end of this time the reaction mixture had separated into definite layers of anisole and aqueous solution. After being cooled the anisole was separated and dried over a little $CaCl_2$. It was now distilled under diminished pressure, using a very efficient fractionating column.

The product boiling from 45° to 55° at 11 mm. was weighed and found to be 31 grams or 73.8% of the theory.

The above run was repeated, using one-half quantities. The anisole thus obtained amounted to 15.7 grams of 74.7% of the theory.

The anisole from both of the above runs was found to have a b.p. of 152° at 748 mm. which conformed to that given in the literature.

(b) Alkylation with Methyl Ethyl Sulfate.

The same procedure was followed as described under preceding part. The quantity of  $\begin{matrix} C_2H_5O \\ CH_3O \end{matrix} > SO_2$ was 27.3 grams.

The yield of anisole was 11.4 grams.

The yield of phenetole was 3.2 grams.

SUMMARY

Methyl ethyl, methyl butyl and ethyl butyl sulfates were prepared from the esters of chloro-sulfonic acid and the sodium alcoholates.

The total alkylation which took place when methyl ethyl sulfate was used as an alkylating agent showed that the methyl group was responsible for 80.2% and the ethyl group for 19.8%.

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PART II.

ATTEMPTED SYNTHESIS OF THE β-ETHYL GLYCOCOLL ESTER OF THE ETHYL ESTER OF PARA NITRO BENZOIC ACID.

INTRODUCTION

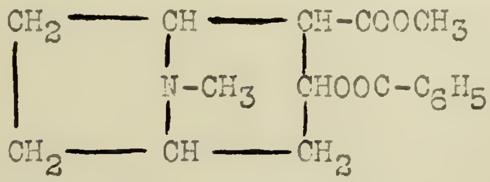
Much interest has been evidenced of late in the relation of physiological action to chemical constitution. Particularly have investigators been attracted to the field of anesthetics.

Novacaine (procaine) which has the formula (para)-NH_2-⬡-$COOCH_2CH_2$-$N(C_2H_5)_2.HCl$ has been found to be a powerful anesthetic and much less toxic than cocaine. But as novacaine failed to possess some other properties of cocaine, the synthesis of related compounds and their action offered a problem of interest.

Cocaine has not been found to be an ideal local anesthetic. It was not only discovered to be toxic if improperly handled but habit forming properties were noted. Yet cocaine was found to be about sixteen times as effective as novacaine when used on the mucous membrane.

The question arose, what particular group or groups and their arrangement might be responsible for these properties of cocaine. If this knowledge was ascertained, then there was hope of synthesizing a compound having the desirable qualities of both cocaine and novacaine.

It has been pointed out[1] that cocaine



may owe to some extent its pharmacological action to the presence of an acylated hydroxyl group in the γ position with regard to the nitrogen atom.

The tri-methylene homologue of novacaine has been synthesized and its anesthetic action found to be about the same, although

it is more toxic than procaine.

In addition to the acylated hydroxyl group, cocaine was seen to differ also in the fact that it had a carboxy ester group.

With these observations on the structure of cocaine in mind this work was undertaken with the object of synthesizing a compound which was to be different from novacaine only in the substitution of an acetic ester group for one of the ethyl groups

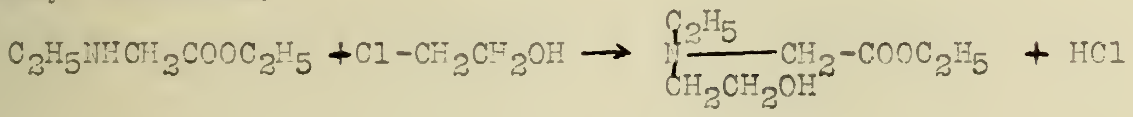
(P)NH_2$COOCH_2CH_2$-$N(C_2H_5)CH_2COOC_2H_5$ and also the synthesis of its homologue (P)NH_2$COOCH_2CH_2CH_2$-$N(C_2H_5)CH_2COOC_2H_5$.

Another observation was that while being strongly anesthetic novacaine had none of the mydriatic properties of cocaine. With the addition of the acetic ester group, it was to some measure expected that these new compounds might possess mydriatic action.

THEORETICAL PART

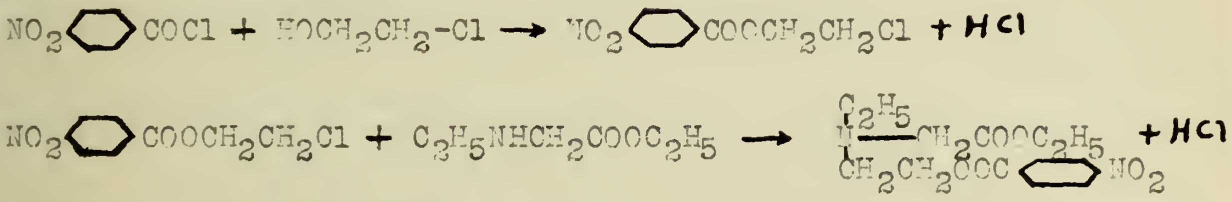
Discussion of Methods.

Three methods presented themselves for the synthesis of the β-ethyl glycocoll ester of the ethyl ester of p-nitro benzoic acid: (1) The preparation of ethyl glycocoll ester and then its condensation first with ethylene chlorohydrin and finally with p-nitro benzoyl chloride.

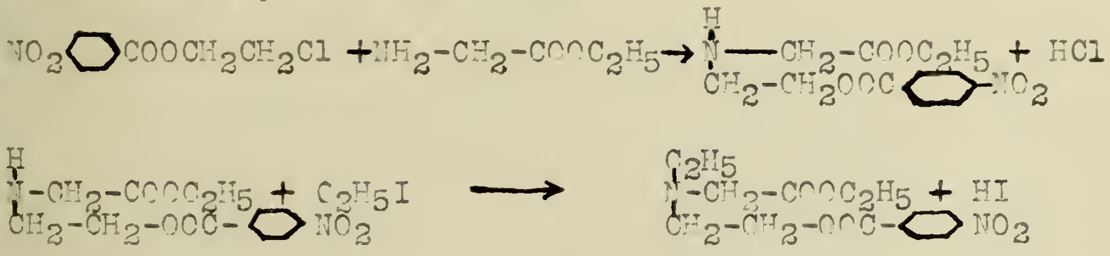


$$C_2H_5NHCH_2COOC_2H_5 + Cl-CH_2CH_2OH \rightarrow \overset{C_2H_5}{\underset{CH_2CH_2OH}{N}}-CH_2-COOC_2H_5 + HCl$$

(2) Condensation of p-nitro benzoyl chloride first with ethylene chlorohydrin and this β chlor ethyl ester of p-nitro benzoic acid with ethyl glycocoll ester.



(3) By the condensation of β chlor ethyl ester of p-nitro benzoic acid with glycocoll ester and then treatment with ethyl iodide to give the tertiary amine desires.



These methods were tried and not found successful. (1)This synthesis failed for the reason that in the condensation of the chlorhydrin and ethyl glycocoll ester no constant boiling product could be isolated in sufficient quantities to even analyze. (2)Here

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$$[illegible]$$

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a reaction between the β chlor ethyl ester of p-nitro benzoic acid and ethyl glycocoll ester took place only at high temperatures and gave no product that could be isolated. (3) The β chlor ethyl ester of p-nitro benzoic acid gave no condensation product with glycocoll ester.

I. Preparation of Methylene Amino Aceto Nitrile.

The method used was that of Klages[2]. Although the directions called for KCn, the yields were found to be just as good when an equivalent amount of NaCN was used.

II. Preparation of Glycocoll Ester Hydrochloride.

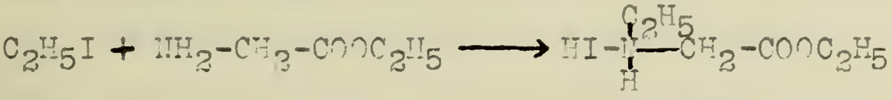
Again following Kalges directions[2] excellent results were obtained.

III. Preparation of Glycocoll Ester.

Glycocoll ester was obtained from its hydrochloride as described by E. Fischer[3]. It was found to be very unstable and on standing for a few hours readily changed into a white crystalline mass[4].

IV. Preparation of Ethyl Glycocoll Ester.

Ethyl iodide (1 mol) reacts with freshly prepared glycocoll ester to give the hydroiodide of the mono ethyl derivative



$$C_2H_5I + NH_2-CH_2-COOC_2H_5 \longrightarrow HI-\overset{C_2H_5}{\underset{H}{N}}-CH_2-COOC_2H_5$$

The free ethyl glycocoll ester was obtained from this in almost identical manner as glycocoll ester was obtained from its hydrochloride.

V. Attempted Condensation of Ethyl Glycoll Ester with (1) Ethylene Chlorohydrin; (2) Trimethylene Chlorohydrin.

(1) Ethylene chlorohydrin was caused to react with ethyl glycocoll ester by heating on an air bath. On standing 10 hours, white crystals were formed. But an attempt to obtain the desired condensation product by treating with NaOH resulted only in an oily liquid that could not be obtained in large enough quantities to fractionally distil.

(2) When tri-methylene chlorohydrin was used, a viscous liquid was obtained after treatment with NaOH and extraction with ether. However, on distillation, this liquid gave no constant boiling product and much remained behind even though at a temperature of 215° at 5 mm.

VI. Preparation of β Chloro Ethyl Ester of Para Nitro Benzoic Acid.

The only available literature that could be found were German patents[4]. In working with small amounts, it was found best to use an excess of ethylene chlorohydrin rather than equivalent molar quantities.

VII. Attempted Condensation of β Chloro Ethyl Ester of Para Nitro Benzoic Acid with (1) Ethyl Glycocoll Ester; (2) Glycocoll Ester.

(1) The mixture of the two substances was heated on a water bath for 4 hours and also refluxed. No product could be crystallized out except the β Chlor Ester.

(2) Glycocoll ester gives no better results. After trying to effect the condensation not only by heating on water bath and refluxing but even in xylene solution, the only product isolated was again found to be the β chlor ester of p-nitro benzoic acid.

EXPERIMENTAL PART

I. Preparation of Methylene Amino Aceto Nitrile $(CH_2=N-CH_2-CN)_2$

In a 5 l. round bottom flask were placed 1 kilogram of HCHO (40% Formalin) and 360 grams of finely divided NH_4Cl. This mixture was stirred and at the same time cooled by an ice-salt bath to +5°. Then with vigorous agitation during a period of 3 hours, there was added a solution of 440 grams of KCN (or 332 grams of NaCN) in 600 cc. of water. After one-half of the cyanide solution had been added, 250 cc. of glacial acetic acid was run in through a second dropping funnel. The rate of addition was such that all of the acid was added within 1 1/2 hours.

The NH_4Cl dissolved completely during the operation and gradually methylene amino aceto nitrile separated in white crystals. The mixture was stirred 2 hours more. The crystalline mass was filtered off and washed a few times with water. Care was taken to keep the temperature less than 15° during the whole of the stirring.

Yield 250-300 grams. Average 60% of theory.

M.P. found to be 127-129°. Literature gave 128-129°.

II. Preparation of Glycocoll Ester Hydrohydrochloride.

68 grams of $(CH_2=N-CH_2-CN)_2$ were placed in a 3 l. round bottom flask. First 870 cc. of 95% C_2H_5OH was added, then 500 cc. of absolute C_2H_5OH which had been saturated with dry HCl gas. This mixture was refluxed on water bath for 1 hour and then filtered hot from separated NH_4Cl and allowed to crystallize. M.P. found 138-141°. Given in literature 144°. Yield 130 grams, 90% of theory.

III. Preparation of Glycocoll Ester.

50 grams $HClNH_2.CH_2-COOC_2H_5$ was covered with 25 cc. of H_2O. (only partially dissolved) and a layer of 100 cc. of ether was added.

With strong cooling 40 cc. of 33% NaOH was poured in slowly after which enough K_2CO_3 was added that the aqueous layer became a thick paste. The ether extract was dried over anhydrous K_2CO_3 first, then over BaO. After the ether was driven off, the residue was distilled under diminished pressure.

The yields were not as high as claimed, 13% of low boiling was isolated in addition to a 31% theoretical yield boiling at 50-51° and 10 mm.

E. Fischer gave the yield as 70% and the b.p. 43-44° at 11 mm.

IV. Preparation of Ethyl Glycocoll Ester.

To 33 grams (1 mol) of freshly distilled glycocoll ester was added 50.8 grams (1 mol) of C_2H_5I. The flask was shaken and within a few minutes much heat was liberated which necessitated cooling the flask from time to time. On standing for a period of 12 to 15 hours, the liquid turned to a solid mass of yellowish crystals.

To free ethyl glycocoll ester from its hydroiodide, the crystals were mixed with 30 cc. of water and a layer of 150 cc. of ether added. Now with simultaneous strong cooling, there was added 50 cc. of 33% NaOH after which enough K_2CO_3 to form a thick paste. The ether was poured off after vigorous shaking. The contents of the flask were extracted 2 or 3 times more and the ether in every case dried over anhydrous K_2CO_3 for 5 minutes, then over BaO for seval hours. The ether extract was filtered and ether distilled off. The remaining liquid boiled 70-75° at 18 mm.

There was only a trace of low-boiling. Yield 12 grams. Approximately 30% of theory.

Analysis by Kjeldahl method with a 0.4091 gram sample gave 10.10% N. Calculated for $C_2H_5NH-CH_3-COOC_2H_5$ 10.68% N.

V. Attempted Condensation of Ethyl Glycocoll Ester with (1) Ethylene Chlorohydrin, (2) Trimethylene Chlorohydrin.

(1) To 8.8 grams (1 mol) of $C_2H_5NH-CH_2-COOC_2H_5$ there was added 4 grams (1 mol) of $HO-CH_2CH_2-Cl$. A very slight amount of heat was generated and the mixture was now refluxed for 2 hours. White crystals formed on standing. These crystals were treated with NaOH and extracted with ether. After the ether was driven off, only a few drops of oily substance remained, most of which boiled 110-115° at 12 mm.

(2) 11.6 grams (1 mol) of $C_2H_5NH-CH_2-COOC_2H_5$ was slowly added to 8.2 grams (1 mol) of $ClCH_2CH_2CH_2OH$ as the latter was being refluxed. After heating for 3 hours, the contents of the flask yielded upon addition of NaOH and extraction with ether, 9 grams of a red brown transparent liquid. Upon attempting to distil this liquid, it was found to boil from 40° to 215° at 5 mm. with much remaining behind undistilled even at that temperature.

VI. Preparation of β Chloro Ester of Para Nitro Benzoic Acid.

A mixture of 13 grams of $P-NO_2-C_6H_4COCl$ and 50 grams of $ClCH_2CH_2OH$ was refluxed for 4 hours. After distilling off the excess chlorohydrin, the remaining oil was crystallized from petroleum ether which gave pale yellow crystals. M.P. 52-54°, literature records 56°. The yield was 11 grams or 78% of theory.

VII. Attempted Condensation of β Chloro Ester of Para Nitro Benzoic Acid with (1) Ethyl Glycocoll Ester; (2) Glycocoll Ester.

(1) 1 gram (1 mol) of $P-NO_2-C_6H_4COOCH_2CH_2Cl$ and 5 grams

(1 mol) of $C_2H_5NH-CH_2-COOC_2H_5$ were heated on water bath for 4 hours. No reaction took place. These two compounds were refluxed but no condensation was effected.

(2) 4 grams (1 mol) of $P-NO_2-C_6H_4-COOCH_2CH_2Cl$ was added to 2 grams (1 mol) of $NH_2CH_2-COOC_2H_5$. Only after strong heating did any reaction take place and then the mixture turned purple. No product could be obtained either from this purple solution or after refluxing the two in a xylene solution.

SUMMARY

An attempt to prepare the β ethyl glycocoll ester of the ethyl ester of p-nitro benzoic acid by three different methods resulted unsuccessfully.

A search through the literature revealed very good methods for the preparation of methylene amino aceto nitrile and glycocoll ester hydrochloride.

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