

THE REACTIONS OF SOME OF THE PRIMARY AMINES

WITH CARBONYL DIURETHANE.

by

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INTRODUCTION .

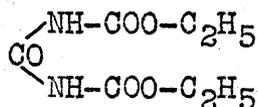
The research on the reactions of the primary amines with carbonyl diurethane which I have undertaken and which is described in this thesis , is a continuation and extension of a part of the work done on carbonyl diurethane by F. B. Dains* at the University of Chicago. A part of this work is being carried on at the present time at the University of Kansas by C. H. Kidwell and by me , under the direction of Dr. Dains. The results obtained by Mr. Kidwell will be presented by him in another paper.

In order to make a satisfactory presentation of the work done it is necessary to preface the description of the experimental work by a discussion of the theory involved. Accordingly this paper is divided into four parts. The first consists of an outline of the reactions of carbonyl diurethane as far as they have been reported . The second part is a discussion of the reactions which may take place between carbonyl diurethane and the primary amines, and an indication of the way in which the reactions may be expected to take place, with equations showing the products which would be formed in these reactions.

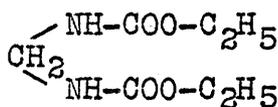
The third part is devoted to a description of the experimental work done and of the results attained. A summary of these results and a discussion of the facts brought out in the course of the experiments completes the paper.

* Jour. Am. Chem. Soc., XXI , 1899 , pp.185-192 .

In addition to the work on carbonyl diurethane a part of the experimental work was devoted to the related compounds, methylene diurethane, phenyl methylene diurethane, and o-nitro-phenyl methylene diurethane. These compounds are similar in their constitution to carbonyl diurethane and for this reason their reactions will be of interest in a study of the reaction of that compound.

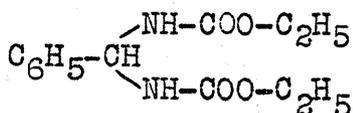


Carbonyl Diurethane

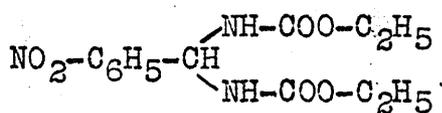


Methylene Diurethane.

The above formulae show the difference between carbonyl diurethane and methylene diurethane. In the latter the urethane groups are attached to a methylene carbon, while in carbonyl diurethane they are attached to a keto carbon. Phenyl methylene diurethane and o-nitro-phenyl methylene diurethane are derived from methylene diurethane by the substitution of a phenyl group and a nitro-phenyl group, respectively, in place of one of the hydrogens of the methylene group. The constitution of these two compounds is illustrated by the formulae below:



Phenyl methylene diurethane



O-nitro-phenyl methylene Diurethane.

The results obtained in the work on these compounds will therefore be described and discussed in connection with the work on carbonyl diurethane.

REACTIONS OF CARBONYL DIURETHANE .

The first mention of carbonyl diurethane was by Loeb^{**} who suggested it as a possible intermediate product in the reaction between urethane and phosgene. Loeb carried out this reaction in a benzene solution and obtained as the sole product, allophanic ethyl ester and his idea was that carbonyl diurethane might be formed and then be decomposed by recrystallization from alcohol or chloroform, losing alcohol and carbon dioxide and giving allophanic ethyl ester .

Folin^{*} showed that the carbonyl diurethane which Loeb had suggested as a possible intermediate product was in reality a very stable compound and could be obtained with about a 40% yield by heating a mixture of one mole of phosgene and two moles of urethane in a sealed tube, to a temperature of 85° C. for half an hour. Pyridine was used to combine with the hydrochloric acid liberated.

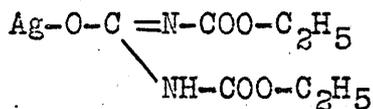
Carbonyl diurethane is a white crystalline solid which is nearly insoluble in cold water and readily soluble in hot. It is also soluble in alkalies and in most of the organic solvents. It shows no decomposition on recrystallization from any organic solvent or from water, neither does heating in a sealed tube with a benzene solution of hydrochloric acid produce any decomposition.

Folin^{*} prepared the silver salt by dissolving the carbonyl diurethane in an alkali and then adding silver nitrate to the solution. He was unable to obtain the di-silver salt and found that the solution of carbonyl diureth-

^{**} Ber. d. Chem. Ges., XIX, pp. 2344.

^{*} Am. Chem. Jour., XIX, pp. 342-352 .

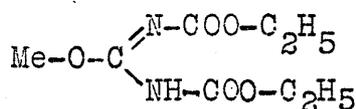
ane in ammonia gave no precipitate with silver nitrate solution. He stated that the constitution of the silver salt is represented by the formula :



He found that the silver salt is not only somewhat soluble in hot water, but is also decomposed by it to some extent.

Dains^{*} improved and simplified the method for the preparation of carbonyl diurethane, this method being outlined in this paper under the preparation of that substance. Dains prepared the mono-sodium salt of carbonyl diurethane by dissolving carbonyl diurethane in absolute alcohol and adding to the solution a concentrated solution of sodium ethylate. He was unable to obtain the di-sodium salt. With copper sulphate he found that copper carbonyl diurethane was not obtained but hydrated copper hydroxide instead, showing that the sodium salt is hydrolyzed in solution.

Dains was able to show by experimental evidence that the silver salt and the other metallic derivatives of carbonyl diurethane must have the constitution represented by :

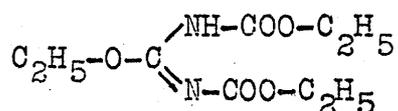


This proof resulted from his investigation of the action of alkyl iodide upon the silver salt. He suspended the silver salt in dry ether and added ethyl

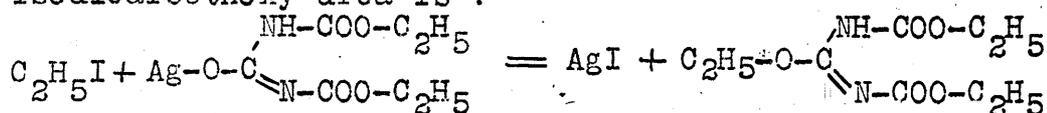
* Jour. Am. Ch. Soc., XXI, pp. 186-190 .

iodide, the product being the ethoxy ether of carbonyl diurethane, or ethyl isodicarbethoxy urea. This product is a colorless oil, insoluble in water and in dilute alkalies but soluble in most organic solvents. It decomposes upon distillation at ordinary pressures.

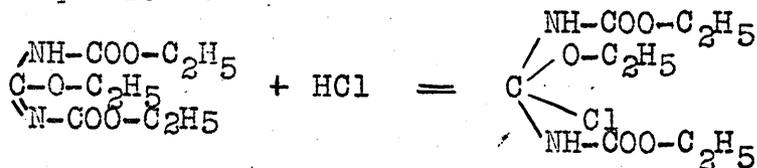
He showed further that this substance split off ethyl chloride with dry hydrogen chloride and that with alcoholic ammonia it gave guanidine dicarboxylate. From these two reactions he proved that the third ethoxy group in ethyl isodicarbethoxy urea is attached to the central carbon atom and that the constitution of the compound must therefore be :



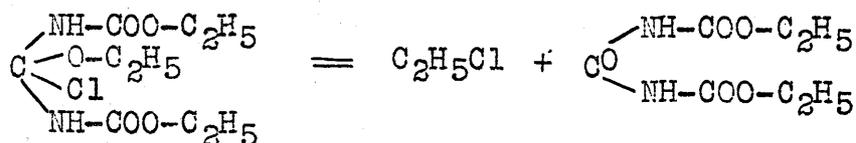
The equation representing the formation of the ethyl isodicarbethoxy urea is :



The reaction between dry hydrogen chloride and the ethoxy ether of carbonyl diurethane is represented by the equation :

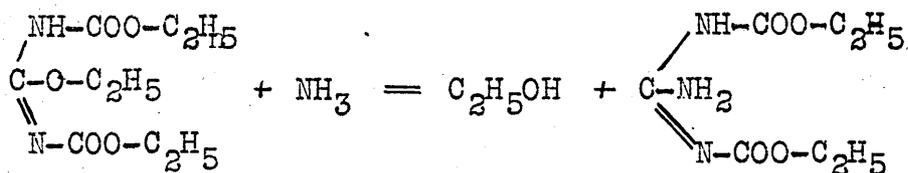


This product decomposes immediately to form ethyl chloride and carbonyl diurethane :



The reaction between ethyl isodicarbethoxy urea and

ammonia is represented by the equation :



The products are ethyl alcohol and dicarbethoxy guanidine.

This summarizes as far as they have been reported the reactions of carbonyl diurethane.

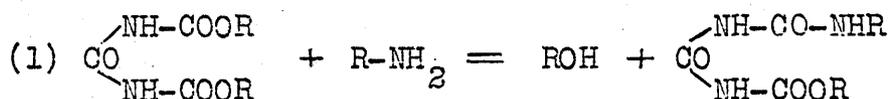
With respect to the related compounds; methylene diurethane, phenyl methylene diurethane and o-nitro-phenyl methylene diurethane, a search thru the literature seems to show that no reactions have been reported except that Conrad and Hock*, who first prepared methylene diurethane by the method of condensing formaldehyde with urethane; report that that substance is decomposed by heating with dilute sulphuric acid, giving formaldehyd, carbon dioxid, ethyl alcohol and ammonia. The compound o-nitro-phenyl methylene diurethane is not listed in the literature of organic compounds.

* Ber. d. Chem. Ges., XXXVI, pp. 2206.

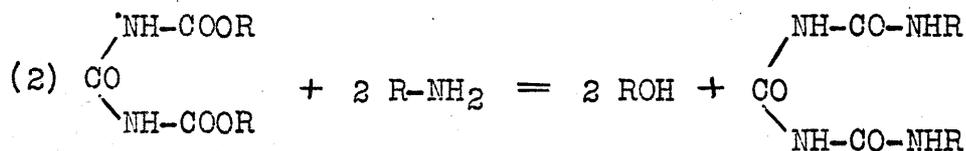
POSSIBLE REACTIONS BETWEEN CARBONYL DIURETHANE
AND THE PRIMARY AMINES .

An outline of the ways in which carbonyl diurethane and the primary amines may react and the products which are to be expected when these reactions take place, is desirable as a preliminary to the discussion of the reactions actually observed in the experimental work.

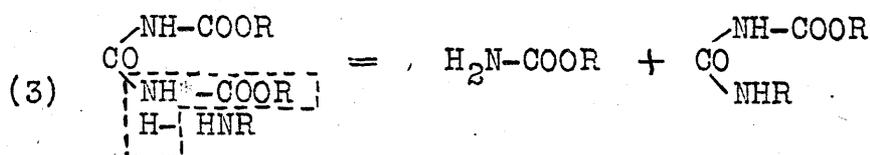
The first reaction which would be expected in a mixture of an amine with carbonyl diurethane would be one in which one mole of the amine reacts with a mole of carbonyl diurethane to give as products alcohol and a substituted carbethoxy biuret:



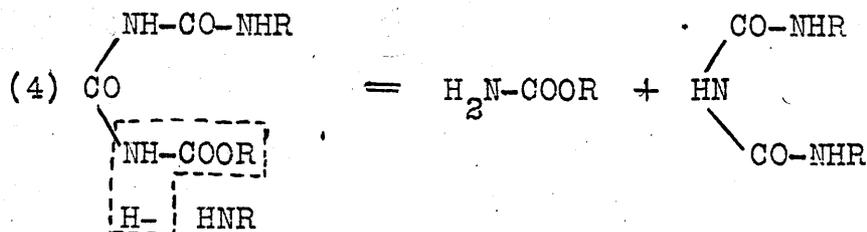
The second way would be for two moles of the amine to react as before; carbonyl di-substituted diurea would be the product :



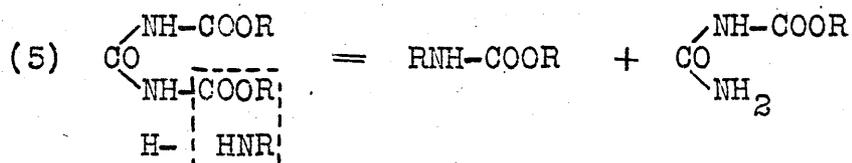
If one mole of the amine reacted with one of carbonyl diurethane so as to split off urethane, the product resulting would be a substituted allophanic ester, thus :



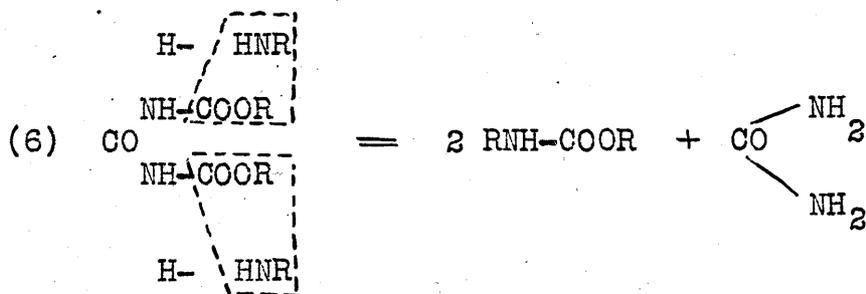
The carbethoxy biuret obtained in equation (1) may also react with a mole of the amine to split off urethane and give as the other product a substituted biuret :



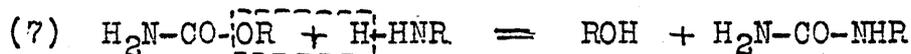
One mole of the amine may react with the carbonyl diurethane so that a substituted urethane is split off, the other product being allophanic ester :



If two moles of the amine should react in the same way as in equation (5) two moles of the substituted urethane would be obtained together with one mole of urea :

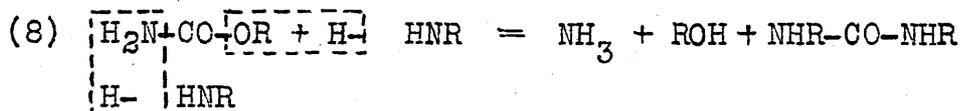


The urethane which results from reaction (4) may then react with one mole of an amine to give a mono-substituted urea, thus :



In the same way the urethane may react with two

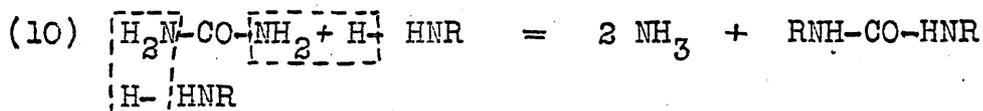
moles of the amine to give a di-substituted urea :



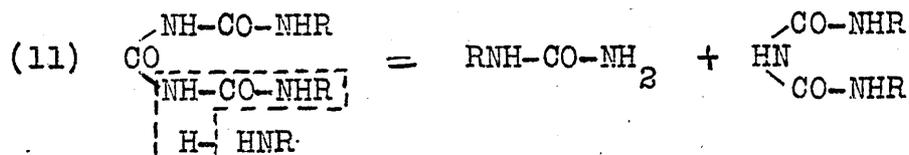
The urea which results from reaction (6) may also react with one mole of an amine, thus :



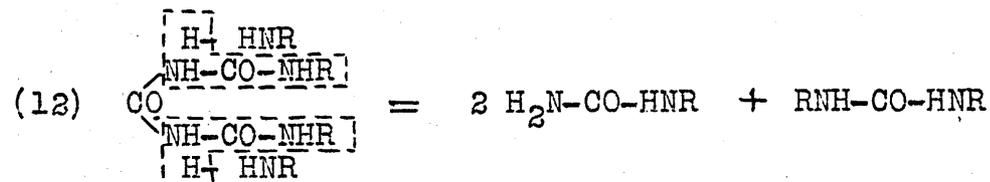
or two moles may react in the same way :



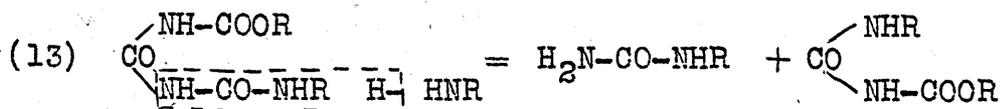
A further possibility for reaction lies in the fact that the carbonyl di-substituted diurea formed in reaction (2) may react further with one mole of an amine to give a mono-substituted urea and a di-substituted biuret, thus :



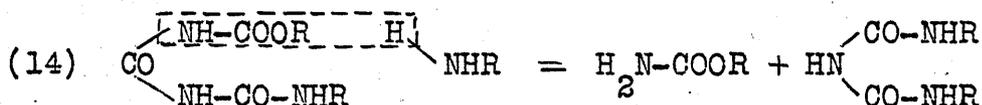
This carbonyl di-substituted diurea may also react with two moles of the amine in the same way and give as products two moles of a mono-substituted urea and one mole of a di-substituted urea .



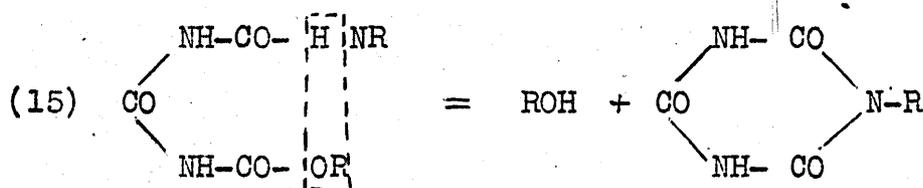
The substituted carbethoxy biuret formed in reaction (1) may react with one mole of an amine to give as products a mono-substituted urea and a mono-substituted carbethoxy urea :



A reaction might also take place between one mole of an amine and the carbethoxy biuret to give urethane and a di-substituted biuret :



The substituted carbethoxy biuret may also lose water under the conditions in some of these experiments and give a substituted cyanuric acid, according to the following equation :



There is evidently a close relationship in constitution between carbonyl diurethane, phenyl methylene diurethane and methylene diurethane. In the reactions just outlined for carbonyl diurethane the reacting substances generally split off alcohol, ammonia or urethane and there seems to be no reason as far as the structure of the moles of the other compounds is concerned why they should not react in the same way to give analogous products.

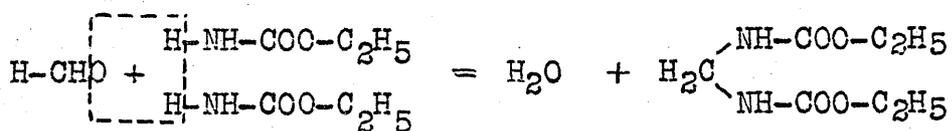
In methylene diurethane two positive hydrogen atoms replace the negative oxygen atom of the carbonyl group of carbonyl diurethane; this may be found to exert an influence on the reactivity of the rest of the molecule, especially upon the reactivity of the carbethoxy group. In phenyl methylene diurethane one of these positive hydrogens is replaced by a negative phenyl group which would be expected to make this compound resemble carbonyl diurethane in its reactivity. The same thing is true of o-nitro-phenyl methylene diurethane in which one of the hydrogens is replaced by the still more negative nitro-phenyl group.

These compounds will probably require an extended investigation of their reactions before a satisfactory explanation can be offered for the fact that they do not show the reactivity which would be expected when they are subjected to the same conditions of reaction as carbonyl diurethane

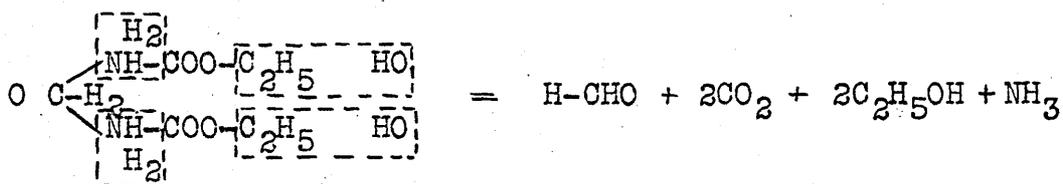
The experiments upon methylene diurethane, phenyl methylene diurethane, and o-nitro-phenyl methylene diurethane are described and discussed in advance of those upon carbonyl diurethane because they are simpler and because they were carried out with the purpose of throwing light upon the reactions of the latter compound.

METHYLENE DIURETHANE .

Methylene diurethane is a white crystalline substance which may be most readily prepared by the condensation of formaldehyde with urethane. M. Conrad and K. Hock* were the first to show that it can be prepared in this way by using hydrochloric acid as a catalyst. The reaction by which it is formed is represented by the following equation, using one mole of the aldehyde for two moles of urethane :



Methylene diurethane is insoluble in water and is readily soluble in alcohol, ether and other organic solvents. When it is heated with dilute sulphuric acid it is decomposed into carbon dioxide, ethyl alcohol, ammonia and formaldehyde as shown by the following equation.



The melting point of pure methylene diurethane is 131° C. Owing to the fact that there was a considerable quantity of the pure substance available which gave the above melting point it was not necessary to prepare any of the material for use in these experiments.

* Ber. d. Chem. Ges., XXXVI, pp. 2206.

METHYLENE DIURETHANE WITH ANILINE .

In order to produce a reaction between methylene diurethane and aniline 10 grams of the material was heated with 11.5 grams of aniline for $2\frac{1}{2}$ hours at 120° C. The solid material crystallized from the solution gave M. P. 130° C. and since the M.P. of pure methylene diurethane is 131° C. it is evident that no reaction took place. A faint odor of ammonia was noticeable and the vapors turned red limus blue.

The heating was continued at a temperature of 160° C for two hours longer. A moderately strong odor of ammonia was produced but as before there was no change in the M.P. of the solid material.

The mixture was then heated at a temperature of $195-200^{\circ}$ C. for two hours longer. The odor of the ammonia evolved was very strong. The M.P. of the solid residue washed with gasoline was $125-129^{\circ}$ C.

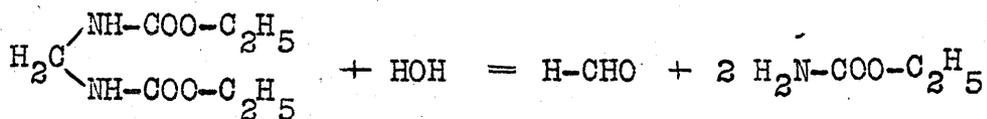
The dried residue obtained from this reaction was re-crystallized from alcohol three times and then dried. The product obtained was a white flaky crystalline substance which gave M.P. 235° C. but began to char and show signs of decomposing at 230° C. When some of this product was mixed with pure diphenyl urea the M.P. of the mixture was 235° C.

On allowing the alcohol solution to stand for several weeks a white crystalline substance separated and was found to be the same as the diphenyl urea obtain-

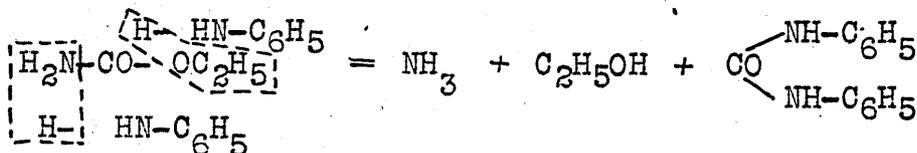
ed previously. On adding hydrochloric acid and water a further amount of a white crystalline precipitate was formed which after recrystallization gave the same M.P. The total yield of the diphenyl urea obtained in this reaction was a very small one .

DI-PHENYL UREA .

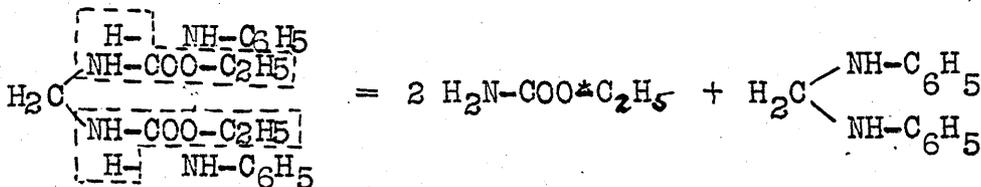
The formation of the diphenyl urea when aniline and methylene diurethane are heated together may take place in more than one way but the more probable explanation is that the presence of a small quantity of water, at the high temperature used results in the hydrolysis of the methylene diurethane according to the following equation :



The products of this reaction are formaldehyde and urethane. The excess of aniline present then acts upon the urethane according to the following equation :



The other possibility for the formation of diphenyl urea under these conditions is that the aniline should react with the methylene diurethane for the formation of urethane, thus :



The urethane could then react with an excess of aniline as in equation (2) above for the formation of diphenyl urea. The compound, $C_6H_5-NH-CH_2-NH-C_6H_5$, symmetrical diphenyl di-amino methane is known, but its formation under the conditions of this experiment seems unlikely. The formation of the product obtained in this reaction apparently depends more upon the high temperature used than on the reactivity of the substances in the reaction mixture. Even at the high temperature used $200^\circ C.$, the amount of diphenyl urea obtained was small, less than one gram from twenty one grams of the original materials used, hence the conclusion that the formation of the urethane is due to hydrolysis and not to the action of the aniline, for otherwise a much larger yield would be expected.

The following analyses confirm the fact that the product of the above reaction is diphenyl urea. The theoretical per cent of nitrogen in diphenyl urea is 13.3 % The analyses show : (1) 13.20% (2) 13.26 % .

Analyses :

(1) Watch glass sample = 5.3191 gm.

" " = $\frac{5.0161}{0.3030}$ "

0.15 N acid in receiver = 25.00 cc.

0.1785 N base to titrate excess = 5.00 cc.

5.00 cc times 1.19 = 5.95 cc.

Ammonia evolved = 19.05 cc. 0.15 N acid.

Weight nitrogen in sample = 0.0400 gm.

Per cent " " " = 13.20% .

(2) Watch glass sample = 5.2252 gm.

" " " = $\frac{5.0161}{0.2091}$ "

N/2 acid in receiver = 10.00 cc.

N/2 base to titrate excess = 5.98 cc.

5.98 cc. times 1.008 = 6.03 cc.

Ammonia evolved = 3.97 cc. N/2 acid.

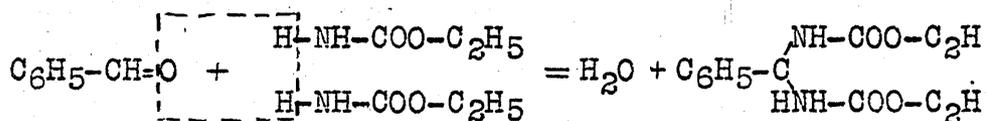
Weight nitrogen in sample = 0.02765 gm.

Per cent " " " = 13.26 % .

PREPARATION OF PHENYL METHYLENE DIURETHANE .

The preparation of phenyl methylene diurethane was carried out as follows : 20 grams of urethane was added to water and after it had dissolved 15 grams of benzaldehyde was added to the solution, the urethane and benzaldehyde being in the proportion of one mole of the aldehyde to two moles of urethane. After the addition of a few cc. of concentrated hydrochloric acid and a few minutes standing a large quantity of a white crystalline substance separated and formed a semi-solid mass in the beaker. This crystalline solid was filtered off, recrystallized from dilute alcohol, washed and dried. The M.P. was 178° C.

The reaction by which the phenyl methylene diurethane is formed is a condensation between the aldehyde group of the benzaldehyde and the amino groups of two moles of urethane as shown by the equation :



The hydrochloric acid added to the reaction mixture acts as a catalyst for the above reaction. The reaction may be made to take place in the same way using sodium ethylate as the catalyst* . F. Lehmann** has also showed that if benzaldehyde cyanhydrin is heated on a water bath for three hours with two moles of urethane 50% of the theoretical per cent yield of

* Ber. d. Chem. Ges., XXVII, pp. 1250

** Ber. d. Chem. Ges., XXXIV, pp. 370

phenyl methylene diurethane can be obtained, hydrocyanic acid being liberated.

The phenyl methylene diurethane was obtained with about a 90% yield using HCl as the catalyst. The product is a very fine white silky crystalline substance which is readily soluble in hot alcohol and slightly soluble in cold, but is nearly insoluble in water.

No analysis was made on this material because it is shown to be very pure by the fact that its M.P. is 178° C. while the highest M.P. given for it in the Beilstein is 178-179° C.

PHENYL METHYLENE DIURETHANE WITH ANILINE.

Phenyl methylene diurethane and aniline were heated together in a flask attached to a reflux condenser at a temperature of 125-130° C. for three hours. The solid product which was separated was recrystallized from water and gave M.P. 176° C. which was practically identical with that of the original material. When this product was mixed with pure phenyl methylene diurethane the M.P. was not lowered, hence the mixture of phenyl methylene diurethane and aniline does not react to give any new product under the conditions of the above experiment.

The same mixture was then heated to a temperature of 150-160° C. for three hours. The solid material separated and recrystallized gave M.P. 176° C. showing in this case also there is no reaction.

The reaction was tried again under the same conditions at 190-195° C. but as before the material was recovered unaltered. An odor of ammonia was noticeable in the flask at this temperature. A final attempt to produce a reaction was made by sealing up three grams of phenyl methylene diurethane with an excess of aniline in a bomb tube and heating in a bomb furnace for four hours at 230° C. The product resulting was a dark brown oily liquid. When this liquid was boiled with water it gave a large lump of resinous black material and from the water solution a small amount of a white crystalline substance separated on standing. This melted at 173-175° C. showing that no new compound which could be identified was formed and that the only reaction which took place was the decomposition of the materials at the high temperature used. A strong odor of ammonia was given off when the tube was opened showing that ammonia is one of the products of this decomposition. The black resinous substance was not identified.

WITH BENZOYL CHLORIDE .

An attempt was made to prepare the benzoyl derivative of phenyl methylene diurethane by the following method. Seven grams of the material was dissolved in a small amount of benzene and an equimolecular quantity of pyridine was added. The flask was attached to a reflux condenser and heated to the B.P. for two hours with slow addition of benzoyl chloride thru

the condenser tube. From the benzene solution the only product which could be separated and identified was benzoic acid which was obtained in quantity almost equivalent to the benzoyl chloride added. The benzoic acid was identified by its M.P. and by a determination of the M.P. of the mixture of this product with pure benzoic acid.

M. P. pure benzoic acid 121.2° C.

" (observed) 120° C.

WITH ACETYL CHLORIDE .

On account of the fact that the phenyl methylene diurethane was found so unreactive it was thought desirable to prepare the acetyl derivative, if possible. This was first attempted by heating seven grams of the material dissolved in a small amount of benzene with slow addition of acetyl chloride. After heating for several hours the benzene was allowed to evaporate spontaneously and the solid residue was recrystallized from ether. This solid gave M.P. 176-177° C, and when mixed with pure phenyl methylene diurethane no lowering of the M.P. was observed, showing this product to be the original material.

This reaction was tried again in the same way except for the addition of a mole of pyridine for each mole of the phenyl methylene diurethane, but the result was the same; the material was recovered unchanged.

A third attempt to prepare the acetyl derivative was made by dissolving five grams of the material in glacial acetic acid and adding an excess of fused sodium acetate and then an excess of acetic anhydride. This mixture was then heated for five hours in a flask attached to a reflux condenser, the temperature being allowed to go to 180° C. The material left in the flask was found to be extremely soluble in water and in organic solvents and it was not possible to obtain from the mixture resulting any organic compound or crystalline substance except sodium acetate.

WITH AMMONIA SOLUTION.

To produce a reaction between phenyl methylene diurethane and ammonia three grams of the material was treated with an excess of a 28% solution of ammonia and allowed to stand in a stoppered flask for several days. The M.P. of the crystalline material was 176° C, and when it was mixed with pure phenyl methylene diurethane there was no appreciable lowering of the M.P. hence there is no reaction under these conditions.

A further attempt to produce a reaction was made by heating three grams of the material with an excess of 28% ammonia solution to the temperature of the water bath in a sealed bottle for 1½ hours. The M.P. of the product was 174° C. and produced no M.P. lowering when mixed with the pure material, indicating no reaction in this case.

WITH LIQUID AMMONIA .

Altho phenyl methylene diurethane does not react with ammonia solution it seemed possible that it might react with liquid ammonia due to the fact that no water would be present to disturb the reaction and further, the concentration of the ammonia in the reaction mixture would be much higher than in a solution of ammonia in water.

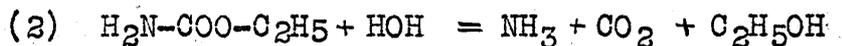
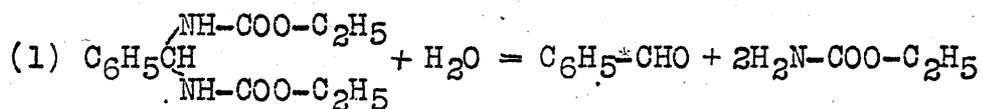
Accordingly, four grams of phenyl methylene diurethane was placed in a Dewar bulb and a large excess of liquid ammonia was added to it. The mixture was stirred thoroly and was then allowed to stand for ten hours in order to allow the excess of ammonia to evaporate. Alcohol was then added to the solid residue and it was dissolved by warming. On adding a small amount of water and cooling in an ice mixture a white flocculent crystalline precipitate was formed. On drying this gave M.P. 179° C. This was the original material, hence the necessary conclusion that under these conditions also the material is unreactive.

HYDROLYSIS OF PHENYL METHYLENE DIURETHANE.

Two grams of phenyl methylene diurethane was mixed with a strong solution of sodium hydroxide in 50% alcohol and the mixture was distilled from a small distilling flask. The odor of benzaldehyde was noticeable from the start and after most of the liquid

had been distilled over there was evolved a very strong odor of ammonia. When some of the gas evolved was passed into a solution of calcium chloride a white precipitate was produced, showing that CO_2 gas was being evolved by the reaction. On standing the distillate separated into two layers, the lower one of which was benzaldehyde, identified by its odor.

The reactions representing the hydrolysis are ;



The first reaction produces benzaldehyde and urethane and the second hydrolyzes the urethane to form ammonia, carbon dioxide and ethyl alcohol. These reactions resemble to a certain extent those in which sodium ethylate acts upon phenyl methylene diurethane except that in this case the reaction is carried out at a higher temperature and hence results in a more complete decomposition of the material.

SODIUM SALT OF PHENYL METHYLENE DIURETHANE

NOT OBTAINED.

An attempt to prepare the sodium-salt of phenyl methylene diurethane was made as follows : 5 grams of the substance was dissolved in absolute alcohol to make a saturated solution. Sodium ethylate was prepared by treating cold alcohol cautiously with small pieces of sodium until no further action took place. The sodium ethylate was then added to the alcohol solution in excess of the amount theoretically necessary to form the di-sodium salt. After a half hour a gelatinous precipitate began to form and was completely precipitated in twenty four hours. On standing for some time this precipitate changed to the pulverulent form. The addition of ether threw down a further amount of the precipitate. This substance was filtered off, washed with absolute alcohol and ether and dried for 48 hours in a vacuum desiccator.

This substance was analyzed for sodium by weighing accurately a small sample into a weighed crucible and then treating with concentrated sulphuric acid one drop at a time until completely decomposed, finally igniting the crucible and the resulting sodium sulfate to constant weight over a Meker burner. The crucible was then reweighed and the weight of sodium sulfate determined. From this the weight of sodium and the per cent of sodium in the sample were readily calculated.

Analyses ;

(1) Weight of sample = 0.2566 gm.
" " sodium sulphate = 0.2143 gm.
" " Na in sample = 0.07038 "
Per cent " " " = 27.43 %

(2) Weight of sample = 0.1279 gm.
" " sodium sulfate = 0.1098 gm.
" " Na in sample = 0.03565 "
Per cent " " " = 27.87 %

(3) Weight of sample = 0.1153 gm.
" " sodium sulfate = 0.09790 gm.
" " Na in sample = 0.03169 "
Per cent " " " = 27.49 %

In order to confirm the constitution of this sodium salt the silver salt was prepared from it as follows : 2 grams of the sodium salt was dissolved in water and an aqueous solution of silver nitrate was added to this solution until precipitation was complete . The precipitate obtained was white and flocculent. After stirring thoroughly the precipitate was filtered off, washed with water and dried in the dark in a desiccator for 12 hours. The analysis for silver was made by weighing accurately a sample of the salt into a weighed crucible and then to ignite for several hours over a Meker burner. Reweighing the crucible then gave the weight of silver in the weighed sample and from this data the per cent silver was calculated.

Analyses :

- (1) Weight of sample = 0.4280 gm.
" " Ag in sample = 0.3005 gm.
Per cent " " " = 70.21 %
- (2) Weight of sample = 0.4251 gm.
" " Ag in sample = 0.2981 gm.
Per cent " " " = 70.13 %
- (3) Weight of sample = 0.6687 gm.
" " Ag in sample = 0.47778 gm.
Per cent " " " = 71.45 %

The sodium salt obtained in the above experiment was sodium acid carbonate which was proved by the above analyses and by the fact that it effervesced on the addition of acid liberating CO_2 gas. The theoretical percent of sodium in sodium acid carbonate is 27.45 % while the analyses obtained are : (1) 27.43 % (2) 27.87 % (3) 27.49 %.

If the silver salt prepared above were the normal silver carbonate the per cent of silver in it would be theoretically 78.4 %. The fact that the results obtained in the analysis of the silver salt fall below this figure may be explained by the occlusion of silver nitrate by the precipitate, by the fact that the precipitate formed may not have been pure silver carbonate but may have contained some basic silver carbonate as well

as the normal salt or by the presence of impurities in the sodium salt from which the silver salt was prepared. The sodium salt used in the preparation of the silver salt was not pure but contained some organic compounds resulting from the decomposition of the sodium ethylate used in its preparation so that the silver salt may have contained some of these compounds or their silver salts.

Further proof of the constitution of the sodium salt was obtained by the titration of a weighed quantity of the salt, which was done as follows: a sample of the salt was weighed out and dissolved in 100 cc. of water. To this solution an excess of half-normal hydrochloric acid was added and the solution was then titrated with half-normal sodium hydroxide solution using phenolphthalein indicator. The result obtained by this method showed that the sodium salt contained 28.18 % sodium as compared with the theoretical per cent 27.45 % for NaHCO_3 . The results obtained by this method could not be expected to be as accurate as those obtained by the gravimetric method for the reason that the indicator is affected by the CO_2 in the solution and so will not show accurately the correct end point for the titration.

Analysis :

Weight of sample = 0.2618 gm.

N/2 acid added = 10.00 cc.

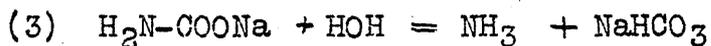
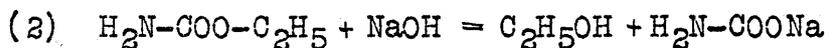
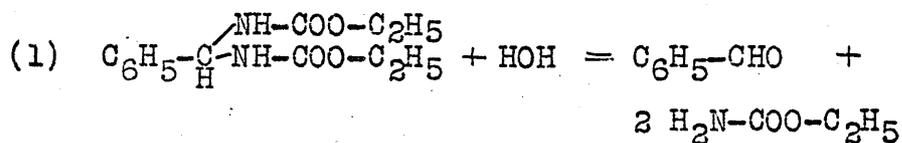
N/2 base to titrate excess = 3.58 cc.

One cc. acid = 0.0115 gm. Na.

Weight Na in sample = 0.0738 gm.

Per cent Na " = 28.18 % .

The reactions by which the sodium acid carbonate is formed are given by the following equations :



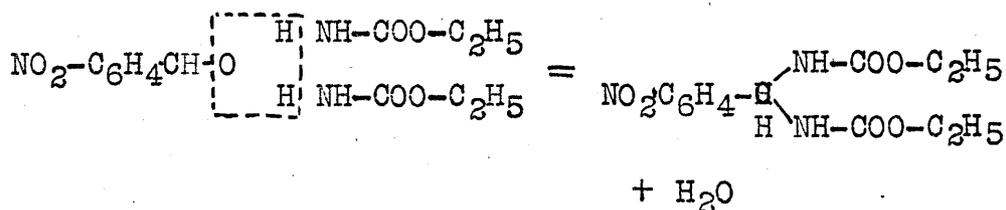
The first equation represents the hydrolysis of the phenyl methylene diurethane to form benzaldehyde and urethane. The second shows the hydrolysis of the urethane to form ethyl alcohol and sodium carbamate and the last one shows the final hydrolysis of the sodium carbamate to give ammonia and sodium acid carbonate .

ORTHO-NITROPHENYL METHYLENE DIURETHANE .

This substance was prepared as follows : 5 grams of o-nitro benzaldehyde and 6 grams of urethane were in 20 cc. of 95 % alcohol and allowed to stand for ten hours after adding a few cc. of concentrated HCl. A large quantity of a white crystalline substance separated and formed a solid mass in the beaker; this substance was filtered off, recrystallized from dilute alcohol and dried. M.P. 180° C.

The product is a very fine white crystalline substance which is readily soluble in hot alcohol and slightly soluble in cold and which is nearly insoluble in water. The M.P. of o-nitro-phenyl methylene diurethane differs from that of phenyl methylene diurethane (179° C.) by only one degree.

The reaction is a condensation between the aldehyde group of o-nitro benzaldehyde and two moles of urethane and is represented by the equation :



The hydrochloric acid used acts as a catalyst for the above reaction. From the 11 grams of material used the theoretical yield would be 10.4 grams; the yield obtained was 9.3 grams which is 90 % of the theoretical.

O-nitro-phenyl methylene diurethane is not listed in the literature of organic compounds so it was analyzed to confirm its constitution, since its formation is analogous to that of phenyl methylene diurethane. The theoretical per cent of nitrogen is 13.50 %. The analyses show (1) 13.66 % (2) 13.41 %.

Analyses :

(1) Watch glass + sample = 5.3224 gm.

" " " = $\frac{5.0161}{0.3064}$ "

N/2 acid in receiver = 10.00 cc.

N/2 base to titrate excess = 3.99 cc.

3.99 cc. times 1.008 = 4.02 cc.

Ammonia evolved = 5.98 cc. N/2 acid.

Weight nitrogen in sample = 0.04186 gm.

Per cent " " " = 13.66 %.

(2) Watch glass + sample = 5.3173 gm.

" " " = $\frac{5.0160}{0.3013}$ "

N/2 acid in receiver = 10.00 cc.

N/2 base to titrate excess = 4.20 cc.

4.20 cc. times 1.008 = 4.23 cc.

Ammonia evolved = 5.77 cc. N/2 acid.

Weight nitrogen sample = 0.04039 gm.

Per cent " " " = 13.41 %.

O-NITRO-PHENYL METHYLENE DIURETHANE WITH ANILINE.

Six grams of nitro-phenyl methylene diurethane was heated with an excess of aniline on a water bath at 160-170° C. for three hours. The product was an oily dark brown liquid which solidified partly on cooling. This was dissolved in alcohol and then recrystallized. A strong odor of ammonia was evolved.

To the alcohol solution water was added and the solution was boiled and filtered. On cooling this filtrate a small amount of a white crystalline substance separated which after recrystallization and drying gave M.P. 173° C. showing that it was the original material. The residue left on the filter was a dark brown semi-solid mass which was dissolved in alcohol and then reprecipitated by the addition of a large excess of water.

This solid was then redissolved in alcohol and treated with an excess of water in the same way, boiled and filtered. From the filtrate a larger amount of a white crystalline substance separated which after drying gave the same M.P. as the original material. The recovery of the original material and the failure to obtain any other product from the reaction mixture shows that there is no reaction except a partial decomposition of the materials due to the high temperature used.

The same mixture was heated again for three hours at 200° C. and the solid left in the flask was dissolved in alcohol. The addition of water caused the precipitation of a moderate amount of a flocculent white substance which on recrystallization gave M. P. 173° C. In this case also the larger part of the material was recovered unchanged and no new crystalline product could be separated from the reaction mixture.

WITH AMMONIA SOLUTION.

Five grams of nitro-phenyl methylene diurethane was boiled with an alcoholic solution of 28 % ammonia for an hour in a flask attached to a reflux condenser. The ammonia was in considerable excess. When the solution cooled a white flocculent precipitate separated which after washing and drying gave M. P. 180° C. This material was the original substance hence under these conditions o-nitro-phenyl methylene diurethane does not react with ammonia.

AMINO-PHENYL METHYLENE DIURETHANE .

Since o-nitro-phenyl methylene diurethane has a nitro group attached to a phenyl group it should be possible to reduce this nitro group to an amino group giving o-amino-phenyl methylene diurethane.

This reduction was carried out as follows : Nine grams of the material was added to 50 cc of very dilute alcohol in a flask attached to a long air condenser. About 30 grams of tin was added to the mixture and then concentrated hydrochloric acid was added from time to time, keeping the flask cool by immersing it in cold water. The flask was shaken continually during the addition of the acid. The nitro-phenyl methylene diurethane was reduced and the hydrochloride was formed by the excess of hydrochloric acid present. After all the solid had dissolved the liquid was filtered off from the tin and the acid was neutralized with sodium hydroxide. A white precipitate was formed and was filtered off, and was placed in a beaker with an excess of alcohol and boiled for several minutes. A part of the precipitate dissolved and the liquid was filtered off from the insoluble portion.

The alcoholic filtrate was diluted with water and cooled in a freezing mixture. A small quantity of a white flocculent precipitate was formed but it could not be obtained pure altho two attempts to prepare it were made. The M.P. was not sharp but seemed to be about 160° C.

PREPARATION OF CARBONYL DIURETHANE .

Carbonyl diurethane was prepared according to the method used by Dains*. A mixture of pyridine and urethane was made in equimolecular proportions and a small amount of benzene was added to complete the solution. A ten per cent solution of phosgene in benzene was prepared and placed in a flask connected to a condenser and surrounded by a freezing mixture. The phosgene used was just in excess of that required to react completely with two moles of the urethane. The urethane solution was added slowly thru the top of the condenser.

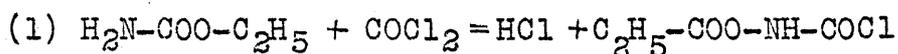
A reaction took place immediately and a reddish colored solid separated on the sides of the flask. After all of the urethane had been added the freezing mixture was replaced by a water bath and the mixture was heated slowly to the temperature of the boiling point and maintained at that temperature for one hour. The liquid in the flask separated on cooling into two layers, the upper one being benzene and the lower one a red oil which later became semi-solid and crystalline. The upper layer was separated and on standing crystallized out a small quantity of carbonyl diurethane.

The red oil was treated with water and warmed to drive off the benzene and cooled in a freezing mixture. The carbonyl diurethane crystallized out and was separated. On concentrating the filtrate and

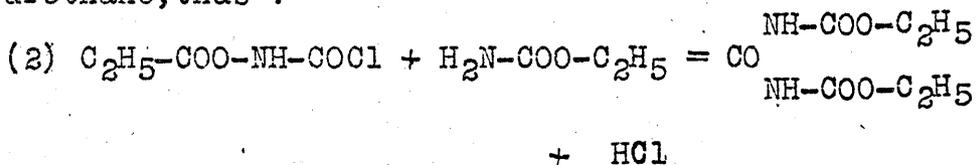
* Jour. Am. Chem. Soc., XXI, 1899, pp. 186.

and cooling a second crop of crystals was obtained. Extraction with ether gave no further crystals. The product was purified by crystallizing from water. The yield was just slightly over 70% of the theoretical. The M.P. of the crystals was 104° C. while that of pure carbonyl diurethane is 107° C.

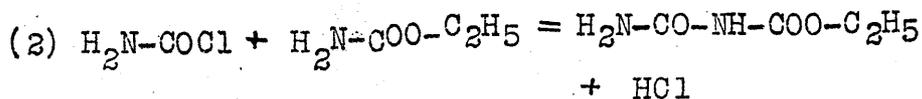
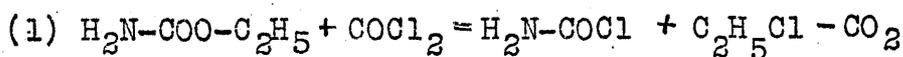
Polin* showed that the reaction for the formation of carbonyl diurethane takes place in two stages which may be represented by the equations given below :



The chloride which is formed in this reaction is itself quite reactive and acts upon a second mole of urethane, thus :



In addition to these two reactions there is another which takes place whenever phosgene is allowed to react with urethane and which yields allophanic ethyl ester as its product; taking place in two stages, thus :



* Am. Chem. Jour., XIX, 1897, pp. 349.

CARBONYL DIURETHANE WITH ORTHO-TOLUIDINE.

Forty grams of carbonyl diurethane was mixed with o-toluidine in the proportion of one mole of the carbonyl diurethane to two of the toluidine and was heated on an oil bath at a temperature of 110-115° C for two hours. The product was separated by cooling the flask in ice. A portion of the material gave M.P. 96° C. The material was found to be unchanged carbonyl diurethane, hence there is no reaction at this temperature.

The same mixture was heated again at 130° C. The product was washed with warm dilute hydrochloric acid and recrystallized three times from hot alcohol. It gave M.P. 149-150° C. A portion of this product was dissolved in hot dilute sodium hydroxide solution and reprecipitated with hydrochloric acid. This product when dried was a fine white crystalline powder which did not melt below 300° C.

The alcohol filtrate from the 149° product formed another white crystalline precipitate after standing 24 hours which after recrystallization and drying gave M.P. 188° C. After standing four days this filtrate yielded a further amount of a white crystalline precipitate which gave on drying MP. 150-170°C.

When water was added to the alcohol filtrate with small amounts of hydrochloric acid a considerable amount of a reddish white precipitate was formed. This

substance was insoluble in sodium hydroxide, moderately soluble in hot alcohol and practically insoluble in cold alcohol and in water. This product was recrystallized five times from dilute alcohol and warmed with a dilute sodium hydroxide solution. It gave M.P. 195°C. It still retained a part of its pink color. The amount obtained was less than one gram.

The 149° product after recrystallization gave M.P. 156°C. It is a fine white powder completely soluble in sodium hydroxide solution.

The 188 product and the 150-170° product were combined and warmed with dilute NaOH solution. A portion dissolved probably due to the presence of a small amount of the 156° product. The part which was insoluble in NaOH was recrystallized several times from alcohol, washed and dried. The product was a white fibrous crystalline material which melts at 200°C. with charring. This product is identical with the 195° product obtained above.

On cooling the solution left after the treatment with water and HCl a small amount of white crystalline substance melting at 126°C. was obtained.

In order to determine what the products would be if the reaction were carried out at a higher temperature 40 grams of carbonyl diurethane was heated for two hours at 130-140°C. with two moles of o-toluidine. The solid product was separated by recrystallization

from alcohol and cooling in an ice mixture. This gave white flocculent crystals melting at 148°C . A part of this material was found to be soluble in sodium hydroxide solution. When the alcohol solution was allowed to stand for some time a further product separated in white flocculent crystals which gave M.P. 166°C . A part of this material was also found to be soluble in sodium hydroxide solution. On evaporating the alcohol solution a white precipitate was obtained which gave after washing and drying M.P. 183°C .

When another quantity of carbonyl diurethane was heated with o-toluidine under approximately the same conditions as those just described the first products obtained did not give quite the same melting points as those enumerated above but the final purified products were the same except for the fact that the amounts of each differed considerably and the melting points of the pure substances obtained did not always agree more closely than one or two degrees.

By recrystallization of the crystalline products described above the following white crystalline substances were obtained; (1) M.P. $183-184^{\circ}\text{C}$. (2) M.P. $193-195^{\circ}\text{C}$. (3) M.P. $244-245^{\circ}\text{C}$. (4) M.P. 200°C . (5) M.P. 116°C . (6) M.P. above 300°C . Product (6) was obtained by acidifying the solution of sodium hydroxide in which a portion of the crystalline material had dissolved on treating with warm dilute sodium hy-

dioxide solution. The white substance which was then precipitated was recrystallized, dried and analyzed.

The reaction of carbonyl diurethane was tried at 170-180°C. by heating a mixture of 20 grams of the material with two moles of the toluidine for two hours. The product was separated by recrystallizing from alcohol and was recrystallized also from benzene. A portion of the material was moderately soluble in alcohol but a considerable part was soluble with difficulty even in hot alcohol. The product after the first crystallization gave M.P. 178°C. On allowing the solution to stand a white flocculent precipitate separated which after washing and drying gave M.P. 181°C. On adding water to the solution a further amount of the precipitate was obtained.

The different fractions of crystalline material obtained from this reaction were separated and gave the following products; (1) M.P. 248°C. (2) M.P. 193°C. (3) M.P. 196°C. (4) M.P. 200°C. (5) M.P. 188°C. (6) M.P. 186°C.

From the reaction carried out at 130°C. the products are (1) o-tolyl carbethoxy biuret (2) di-o-tolyl biuret (3) not identified. When the reaction took place at 130-140 C. the products were (1) o-tolyl carbethoxy biuret (2) di-o-tolyl biuret (3) carbonyl di-o-tolyl diurea (4) di-o-tolyl urea (5) o-tolyl cyanuric acid (6) M.P. 116°C. not identified. (7) M.P. 126°C. not identified.

The products when the reaction was carried out at 170-180°C. were (1) di-o-tolyl urea (2) di-o-tolyl biuret (3) mono-o-tolyl urea (4) carbonyl di-o-tolyl urea. When the reaction was allowed to take place at a high temperature for a long time the sole product was di-o-tolyl urea .

The identification of the products named above and the proof of their constitution is given on the following pages.

(1) TOLYL CARBETHOXY BIURET .

The constitution of the product melting at 156 C. is proved to be that of o-tolyl carbethoxy biuret by the following analyses. The theoretical per cent of nitrogen in tolyl carbethoxy biuret is 15.86 % . The analyses show : (1) 15.70% (2) 15.93 % (3) 16.17 % (4) 16.06 % (5) 16.03 % .

Analyses :

(1) Watch glass + sample = 5.0137 gm.

" " = $\frac{4.7150}{0.2987}$ "

N/2 acid in receiver = 10.00 cc.

N/2 base to titrate excess = 3.30 cc.

Ammonia evolved = 6.7 cc. N/2 acid.

Weight Nitrogen = 0.0469 gm.

Per cent " = 15.70 %

(2) Watch glass + sample = 5.0132 gm.

" " = $\frac{4.7144}{0.2988}$ "

N/2 acid in receiver = 10.00 cc.
N/2 base to titrate excess = 3.20 cc.
Ammonia evolved = 6.8 cc. N/2 acid .
Weight nitrogen in sample = 0.0476 gm.
Per cent " " " = 15.93 %.

(3) Watch glass + sample = 5.0165 gm.
" " " = 4.7149 "
" " " = 0.3016 "

N/2 acid in receiver = 10.00 cc.
N/2 base to titrate excess = 3.03 cc. .
Ammonia evolved = 6.97 cc. N/2 acid.
Weight nitrogen in sample = 0.04879 gm.
Per cent " " " = 16.17 % .

(4) Watch glass + sample = 5.5568 gm.
" " " = 5.2548 "
" " " = 0.3020 "

0.15 N acid in receiver = 25.00 cc.
0.1785 N base to titrate excess = 160 cc.
Ammonia evolved = 23.10 cc. 0.15N acid.
Weight Nitrogen in sample = 0.0485 gm.
1.6 cc. times 1.19 = 190 cc.
Per cent Nitrogen in sample = 16.06 % .

(5) Watch glass + sample = 5.5546 gm.
" " " = 5.2545 "
" " " = 0.3001 "

0.15 N acid in receiver = 50.00 cc.
0.1785N base to titrate excess = 22.45 cc.

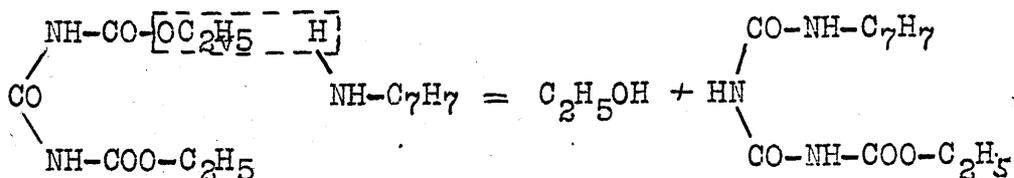
22.45 cc. times 1.19 = 26.71 cc.

Ammonia evolved = 23.29 cc. 0.15N acid.

Weight Nitrogen in sample = 0.0489 gm.

Per cent " " " = 16.03 %.

The reaction by which the tolyl carbethoxy biuret is formed is represented by the following equation :



It was found that the product identified as o-tolyl carbethoxy biuret is soluble in dilute alkalies.

(2) O-TOLYL CYANURIC ACID .

Proof of the fact that the product obtained by treating o-tolyl carbethoxy biuret with sodium hydroxide and then reprecipitating with with acid, is tolyl cyanuric acid, is given by the following analyses. The theoretical per cent of niytrogen in o-tolyl cyanuric acid, $\text{C}_{10}\text{H}_9\text{N}_3\text{O}_3$, is 19.18 %. The analyses show: (1) 19.34 % (2) 18.76 % (3) 18.59 % (4) 19.27%.

Analyses :

(1) Watch glass - sample = 5.5570 gm.

" " " = 5.2548 "

" " " = 0.3022 "

0.15 N acid in receiver = 35.00 cc.

0.1785N base to titrate = 6.02 cc.

6.02 cc. times 1.19 = 7.16 cc.

Ammonia evlved = 27.84 cc. 0.15N acid.

Weight nitrogen in sample = 0.05846 gm.

Per cent " " " = 19.34 % .

(2) Watch glass + sample = 5.0144 gm.

" " " = 4.7144 "
" " " = 0.3000 "

0.15 N acid in receiver = 45.00 cc.

0.1785 N base to titrate = 15.3 cc.

15.3 cc. times 1.19 = 19.20 cc.

Ammonia evolved = 26.80 cc. 0.15 N acid.

Weight nitrogen in sample = 0.05628 gm.

Per cent " " " = 18.76 % .

(3) Watch glass sample = 5.3240 gm.

" " " = 5.0161 "
" " " = 0.3079 "

0.15 N acid in receiver = 50.00 cc.

0.1785 N base to titrate = 19.10 cc.

19.9 cc. times 1.19 = 23.73 cc.

Ammonia evolved = 27.28 cc. 0.15 N acid .

Weight nitrogen in sample = 0.05726 gm.

Per cent " " " = 18.59 % .

(4) Watch glass + sample = 5.2728 gm.

" " " = 5.0161 "
" " " = 0.2568 "

N/2 acid in receiver = 10.00 cc.

N/2 base to titrate excess = 2.93cc:

0.505 N base " " = 2.90 cc.

Ammonia evolved = 7.07 cc. N/2 acid.

Weight nitrogen in sample = 0.04949 gm.

Per cent " " " = 19.27 % .

Tolyl cyanuric acid was prepared as follows :

Twelve grams of the tolyl carbethoxy biuret was warmed with a dilute solution of sodium hydroxide. This solution was allowed to cool and was then acidified with hydrochloric acid. A heavy white pulverulent precipitate was thrown down; this was filtered off, washed and recrystallized. It was found that it did not melt below 300°C. The conversion of the tolyl carbethoxy biuret into the cyanuric acid was nearly quantitative.

SILVER SALT OF O-TOLYL CYANURIC ACID.

In order to obtain further confirmation of the constitution of the product identified as o-tolyl cyanuric acid it was thought desirable to prepare the sodium and silver salts. Accordingly an attempt was made to prepare the sodium salt as follows: Sodium ethylate was prepared by dissolving small pieces of sodium in cold absolute alcohol. The tolyl cyanuric acid was dissolved in absolute alcohol and this solution was added to the sodium ethylate and the mixture was allowed to stand for several days. No precipitate was produced nor was there any other evidence of the formation of a sodium salt.

The addition of water to a small portion of the solution did not cause any precipitate to form but when water was added to the solution of the mixture in gasoline and the gasoline was allowed to evaporate a white precipitate was left in the solution.

This white precipitate was found to be tolyl cyanuric acid and so no sodium salt was obtained by this method. If it were formed it would probably be easily hydrolyzed by the addition of water.

The silver salt was prepared by two different methods. The first was to dissolve some of the tolyl cyanuric acid in dilute ammonia. The excess ammonia was neutralized by the addition of a few drops of nitric acid. Silver nitrate solution was then added to the solution in considerable excess. The silver salt was precipitated in the gelatinous form which changed over very slowly to a more pulverulent form. This was then filtered off and dried in the dark.

The other method used was to dissolve some of the tolyl cyanuric acid in dilute sodium hydroxide solution. The excess of sodium hydroxide was neutralized by adding a few drops of nitric acid. Silver nitrate solution was then added in excess. The precipitate of the silver salt formed a very thick jelly which slowly changed over to a gelatinous precipitate and finally became almost pulverulent. This precipitate was filtered off and dried. It was analyzed for silver by igniting a weighed sample in a weighed crucible to constant weight and determining the weight of silver obtained.

The analysis for silver shows that the mono-silver salt is the product. The theoretical per cent of silver in $C_{10}H_8O_3N_3Ag$ is 34.61 %. Analysis shows (1) 34.99 %.

Analysis :

Crucible sample 14.8053 gm.

" " $\frac{13.3650}{1.4403}$ "

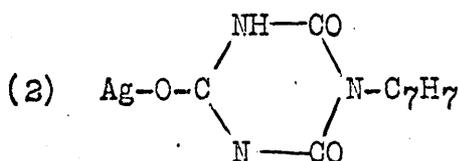
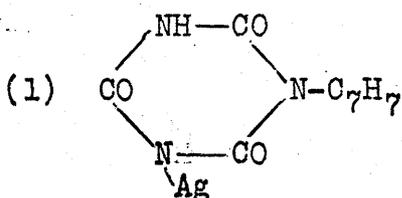
Crucible silver 13.8700 gm.

" " $\frac{13.3650}{0.5050}$ "

Per cent silver 34.99 % .

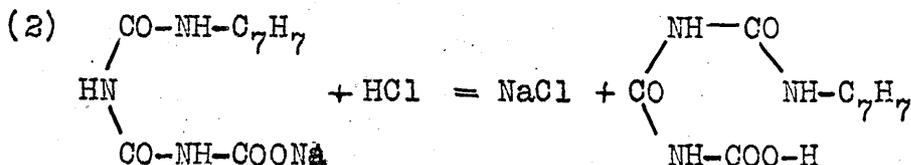
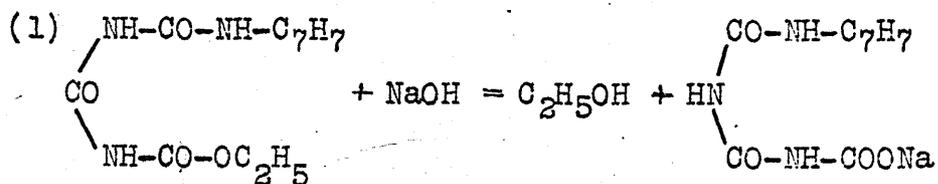
The di-silver salt could not be obtained altho a considerable excess of the silver nitrate was used in the precipitation. The cause of the error in the analysis probably lies in the fact that the precipitation of the silver salt in the gelatinous form caused the occlusion of some of the silver nitrate used in the precipitation.

The structure of the silver salt is not definitely known but may be represented by one of the two formulae given below.

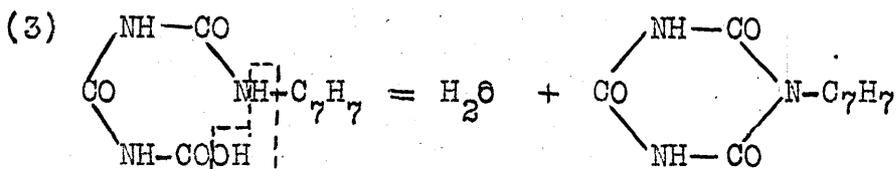


The reactions by which the tolyl cyanuric acid is formed when tolyl carbethoxy biuret is dissolv-

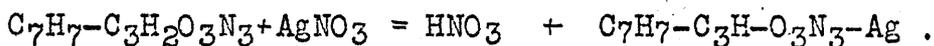
ed in sodium hydroxide and reprecipitated by acid may be represented by the following equations :



The first equation represents the formation of the sodium salt due to the hydrolysis of the ethoxy group of the tolyl carbethoxy biuret. The second equation represents the formation of the free acid from the sodium salt. Equation (3) below shows the formation of the tolyl cyanuric acid by the splitting out of water from the mole of the free acid formed in (2)



The equation representing the formation of the silver salt is :



(3) DI-O-TOLYL BIURET .

The constitution of the 200° product is confirmed as that of di-o-tolyl biuret by the analyses given below. The theoretical per cent of nitrogen in di-o-tolyl biuret, $C_{16}H_{17}O_2N_3$, is 14.84 %. The analyses show : (1) 14.97 % (2) 15.03 % .

Analyses :

(1) Watch glass + sample = 5.2379 gm.

" " = $\frac{5.0161}{0.2218}$ "

0.15 N acid in receiver = 25.00 cc.

0.18 N base to titrate = 7.65 cc.

7.65 cc. times 1.2 = 9.18 cc.

Ammonia evolved = 15.82 cc. 0.15N acid.

Weight nitrogen = 0.03322 gm.

Per cent " = 14.97 % .

(2) Watch glass + sample = 5.2676 gm.

" " = $\frac{5.0160}{0.2516}$ "

N/2 acid in receiver = 10.00 cc.

N/2 base to titrate = 4.55 cc.

4.55 cc. times 1.01 = 4.60 cc.

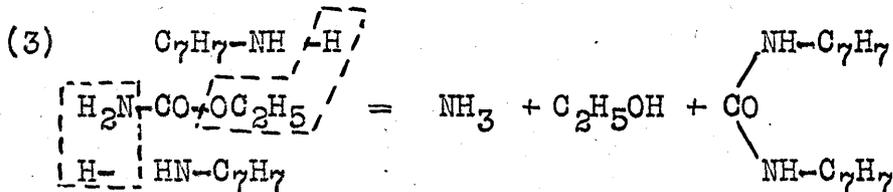
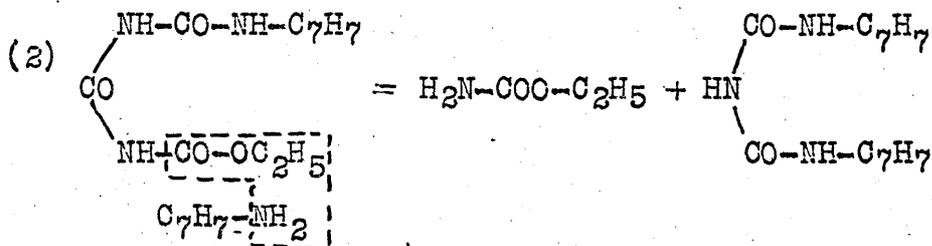
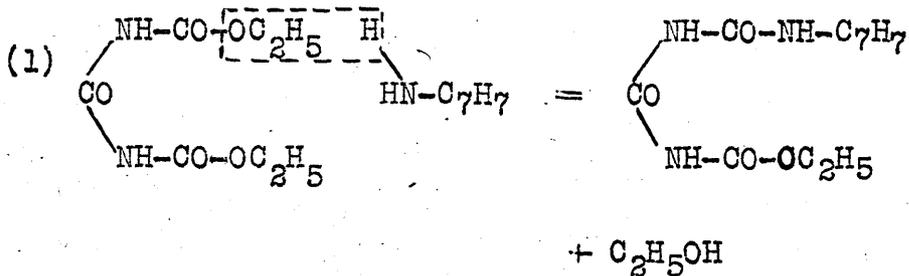
Ammonia evolved = 5.40 cc. N/2 acid.

Weight nitrogen in sample = 0.0378 gm.

Per cent " " " = 15.03 % .

When this product was mixed with pure di-o-tolyl biuret the M.P. of the mixture was not lowered.

The reactions by which the di-o-tolyl biuret is produced on heating carbonyl diurethane with o-toluidine may be represented by the following equations:



(4) CARBONYL DI-O-TOLYL DIUREA.

The two products, one melting at 183° and the other at 186°C. were found to be identical since when they were mixed the M.P. of the mixture was not lowered. When mixed with any of the other products of the reaction the M.P. was lowered several degrees and the difference in analysis also shows that this substance is a distinct product. The analysis of the 183° material is: (1) 17.27 % (2) 17.03 %. that of the 186° material is; (3) 17.06 %.

Analyses :

(1) Watch glass+ sample = 5.2486 gm.

" " " = 5.0160 "
" " " = 0.2326 "

N/2 acid in receiver = 10.00 cc.

N/2 base to titrate = 4.22 cc.

4.22 cc. times 1.01 = 4.26 cc.

Ammonia evolved = 5.74 cc. N/2 acid.

Weight nitrogen in sample = 0.04018 gm.

Per cent " " = 17.27 % .

(2) Watch glass+ sample = 5.2478 gm.

" " " = 5.0161 "
" " " = 0.2317 "

N/2 acid in receiver = 10.35 cc.

N/2 base to titrate = 4.68 cc.

4.68 cc. times 1.008 = 4.71 cc.

Ammonia evolved = 5.64 cc. N/2 acid.

Weight nitrogen in sample = 0.03946 gm.

Per cent " " " = 17.03 % .

(3) Watch glass - sample = 5.2606 gm.

" " = $\frac{5.0161}{0.2446}$ "

N/2 acid in receiver = 10.00 cc.

N/2 base to titrate = 4.00 cc.

4.00 cc. times 1.01 = 4.04 cc.

Ammonia evolved = 5.96 cc. N/2 acid.

Weight nitrogen in sample = 0.04172 gm.

Per cent " " " = 17.06 % .

In order to obtain further light on the constitution of this material determinations of the molar weight of the substance in solution were made. The substance was not sufficiently soluble in benzene so that that solvent could be used; it was necessary therefore to use alcohol as the solvent. If the substance were carbonyl di-o-tolyl diurea, $C_{17}H_{18}O_3N_4$, it should have a molar weight of 326 and the results obtained in these determinations come within ten per cent of that value. The determinations were made by the boiling point method. The difficulty in making the determination lay in the fact that that the molar boiling point raising for alcohol as the solvent is small and further since the substance to be determined has a high molar weight the rise in temperature produced by dissolving a moderately large sample will be small. There was not available a large amount of material for this determination and even if there had been the limit of solubility of the

substance would have prevented a large rise in temperature being obtained. The values obtained are :

(1) 359 (2) 362.5 . The reason for the ten per cent difference from the theoretical value may lie in the polymerization of the dissolved substance due to the use of alcohol as the solvent.

Molar weight determination :

(1) Tube + alcohol = 79.6236 gm.

" " = $\frac{52.1225}{27.5011}$ "

Allowance for vapor in condenser = 0.2 gm.

Boiling point of alcohol = 77.12° C.

Watch glass + sample = 5.3170 gm.

" " = $\frac{5.0160}{0.3010}$ "

Boiling point rise = 0.035° C.

Formula: $M.W. = 1150 \frac{W}{E \cdot W}$

where w is the weight of the sample and W is the weight of the solvent and E is the degrees rise in the boiling point of the solution.

$M.W. = 1150 \frac{0.301}{0.035 \cdot 27.3011} = \underline{362.5}$.

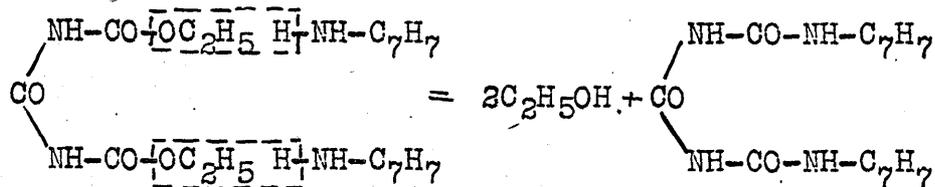
(2) Watch glass + sample = 5.5274 gm.

" " = $\frac{5.0160}{0.5114}$ "

Boiling point rise = 0.06° C.

$M.W. = 1150 \frac{0.5114}{0.06 \cdot 27.3011} = \underline{359}$.

The reaction by which the carbonyl di-o-tolyl diurea is formed is represented by the following equation :



The evidence offered that carbonyl di-o-tolyl diurea is one of the products of the reaction between carbonyl diurethane and o-toluidine may be considered as practically conclusive. There are only two slight objections to its acceptance. The first is that even after a number of recrystallizations the M.P. of the material does not agree exactly with that given by Pickard and Carter* who reported that they prepared and identified this substance from o-tolyl hydroxy oxamide, $\text{C}_7\text{H}_7\text{-NH-CO-CO-NH-OH}$, and that it melted at 190°C ., whereas the highest M.P. obtained for the substance resulting from the reaction between carbonyl diurethane and o-toluidine is 186°C .

The second reason is that none of the carbonyl di-o-tolyl diurea was obtained in the attempt to prepare it by the condensation of mono-o-tolyl urea with phosgene and hence the 186° product could not be compared with any material known to be the diurea.

It was not found possible to obtain any reaction between mono-phenyl urea and phosgene so that no sy-

* Chem. Soc. London., 81, pp.1571 .

mmetrical carbonyl diphenyl diurea could be obtained. Bruce* prepared it by heating some of the diureid, $C_6H_5-NH-CO-NH-COCH_3-N-CO-NH-C_6H_5$, with dry hydrogen chloride in a sample tube, ethyl chloride being evolved. The product he found to melt at $211^{\circ}C$.

Pickard and Carter**, however prepared what they identified as carbonyl diphenyl diurea, by warming an aqueous solution of the sodium salt of phenyl acetyl hydroxy oxamide. They found the M.P. of the substance to be $140^{\circ}C$. This discrepancy could be easily explained and the correctness of the melting points settled if either the carbonyl diphenyl diurea or the carbonyl di-tolyl diurea could be prepared by some independent method.

MONO-TOLYL UREA WITH CARBONYL CHLORIDE .

In an attempt to prepare symmetrical carbonyl di-o-tolyl diurea a ten per cent solution of phosgene in benzene was added to a mixture of mono-o-tolyl urea and pyridine in the ratio of one mole of the phosgene to two moles of the urea. The addition was made at the temperature of a freezing mixture and on warming on a water bath an oily reddish layer separated at the bottom of the solution. This layer was separated from the solution and warmed with alcohol. The alcohol solution was cooled and water was added to make the product crystallize.

* Jour. Am. Chem. Soc., XXVI, pp. 450.

** Chem. Soc. London, 81, pp. 841.

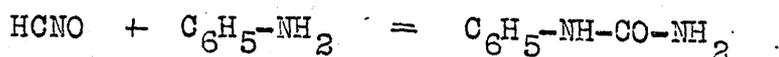
The crystals which were white and glistening and when recrystallized they gave M.P. 188°C. When they were mixed with the original material there was no lowering of the M.P. showing that there was no reaction since the mono-o-tolyl urea was recovered unchanged. In the attempt to obtain this product the same method was used three different times with slight changes in the procedure and in the manner of separating the product but in no case was any other product than the original material obtained from the reaction mixture.

PREPARATION OF MONO-PHENYL UREA .

Mono-phenyl urea was prepared by the action of aniline upon potassium cyanate in an acetic acid solution. Thirty two grams of the cyanate was dissolved in about 200 cc. of water and thirty seven grams of aniline was added. A few cc. of acetic acid was added and the mixture was stirred continuously until a white precipitate began to form in the solution. A few drops of hydrochloric acid was added to catalyze the reaction. The addition of more cyanate caused a further amount of the precipitate to be formed. The crystals were filtered off, washed, recrystallized and dried.

The crystals gave M.P. 147°C. while that of pure mono-phenyl urea is 147°C.

The yield obtained was 33 grams and since the theoretical yield would be 69 grams this is a 47.8 % yield. The product is soluble in hot water and only slightly soluble in cold; it is readily soluble in alcohol and ether. The reaction for its formation is given by :



MONO-PHENYL UREA WITH CARBONYL CHLORIDE.

An attempt to prepare symmetrical carbonyl diphenyl diurea was made by adding a ten per cent solution of phosgene to a mixture of mono-phenyl urea and pyridine in the ratio of one mole of phosgene to two of the urea. The mixture was kept at the temperature of a freezing mixture during the addition and was then heated on a water bath. An oily brown layer separated at the bottom of the solution. The liquid above was decanted off and the oil was dissolved in alcohol. water was added to this alcohol solution and it was then cooled after filtering. A considerable quantity of fine needle like white crystals separated from this solution and were filtered off and dried. Their M.P. was 146°C. and when mixed with pure mono-phenyl ure the M.P. was not lowered showing that no reaction had taken place.

This method was tried a second time under slightly different conditions but without results.

(5) MONO-O-TOLYL UREA .

The product obtained from the reaction of carbonyl diurethane with o-toluidine which gives M.P. 188° C. is mono-o-tolyl urea which is shown by the fact that on mixing it with pure mono-o-tolyl urea there is no lowering of the M.P. The analyses below give confirmatory evidence of its constitution. The theoretical per cent of nitrogen for $C_8H_{10}ON_2$ is 18.66 %. The analyses are; (1) 18.89 % (2) 18.45 % .

Analyses :

(1) Watch glass + sample = 5.2705 gm.

" " " = 5.0160 "

" " " = 0.2545 "

N/2 acid in receiver = 10.00 cc.

N/2 base to titrate = 3.10 cc.

3.10 cc. times 1.01 = 3.13 cc.

Ammonia evolved = 6.87 cc. N/2 acid.

Weight Nitrogen in sample = 0.04809 gm.

Per cent " " " = 18.89 % .

(2) Watch glass + sample = 5.2237 gm.

" " " = 5.0161 "

" " " = 0.2076 "

N/2 acid in receiver = 10.00 cc.

N/2 base to titrate = 4.50 cc.

4.50 cc. times 1.008 = 4.53 cc.

Ammonia evolved = 5.47 cc. N/2 acid.

Weight Nitrogen = 0.03829 gm.

Per cent " " = 18.45 % .

PREPARATION OF MONO-O-TOLYL UREA .

A solution of potassium cyanate acidified with acetic and hydrochloric acids was allowed to react with an equimolecular quantity of o-toluidine. After stirring thoroly a large amount of a flocculent precipitate was formed in the solution. This was filtered off recrystallized and dried. It is soluble in alcohol and practically insoluble in cold water.

The reaction by which it is formed is :



The M.P. of pure mono-o-tolyl urea is 188°C . This product melted at 188°C . The theoretical per cent of nitrogen in mono-tolyl urea is 18.66 % . Analysis shows : (1) 18.80 % (2) 18.43 % .

Analyses :

(1) Weight of sample = 0.2519 gm.

Ammonia evolved = 6.77 cc. N/2 acid.

One cc. N/2 acid = 0.007 gm. Nitrogen.

Weight Nitrogen = 0.04739 gm.

Per cent " = 18.80 % .

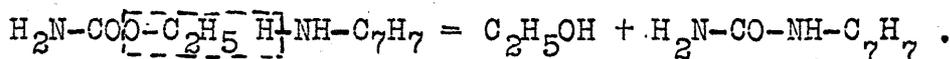
(2) Weight of sample = 0.2545 gm.

Ammonia evolved = 6.70 cc. N/2 acid .

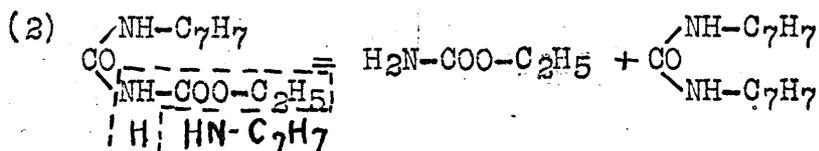
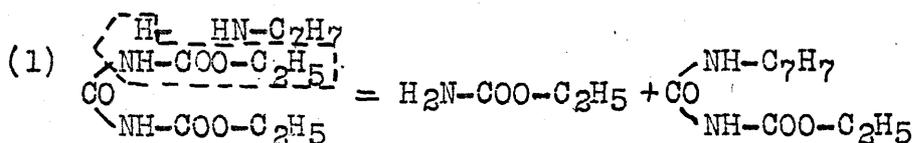
Weight Nitrogen = 0.04690 gm.

Per cent " = 18.43 % .

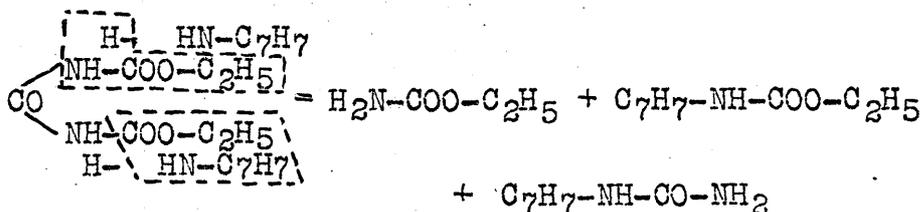
The formation of the mono-o-tolyl urea when carbonyl diurethane is heated with o-toluidine may be accounted for in more than one way. It is possible that urethane is first formed and that this then reacts according to the following equation :



The formation of the urethane may result either from partial or complete interaction between carbonyl diurethane and o-toluidine according to the following equations :



The other possibility and the less likely one is that an excess of toluidine should react with the carbonyl diurethane to give as products: mono-tolyl urea, tolyl urethane and urethane according to the following equation :



No evidence was obtained of the presence of tolyl

CARBONYL DIURETHANE WITH O-TOLUIDINE AT
HIGH TEMPERATURES.

In order to determine what the reaction product would be if carbonyl diurethane and o-toluidine were allowed to react at a high temperature for a longer time, ten grams of the material was heated with an excess of o-toluidine for 12 hours at 200°C. The product resulting was very difficultly soluble in 95 % alcohol and after recrystallization gave M.P. 248°C. and began to boil at a temperature only two degrees above that.

When it was mixed with pure di-o-tolyl urea the M.P. was 248°C. showing that the product is di-o-tolyl urea. Its constitution is also confirmed by the following analyses. Theoretical per cent N in di-o-tolyl urea is 11.60 %. Analysis shows :

(1) 11.58 % (2) 11.60 %.

Analyses :

(1) Watch glass + sample = 5.7256 gm.

" " " = $\frac{5.0161}{0.7095}$ "

0.15 N acid in receiver = 50.00 cc.

0.1785 N base to titrate = 9.12 cc.

9.12 cc. times 1.19 = 10.85 cc.

Ammonia evolved = 39.15 cc. 0.15N acid.

One cc. acid = 0.0021 gm. Nitrogen .

Weight Nitrogen = 0.08272 gm.

Per cent " = 11.58 % .

(2) Watch glass + sample = 5.2846 gm.

" " " = ~~5.0160~~ "

" " " = 0.2685 "

N/2 acid in receiver = 10.00 cc.

N/2 base to titrate = 5.50 cc.

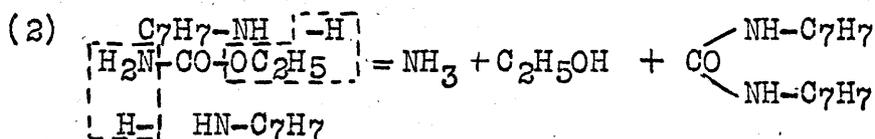
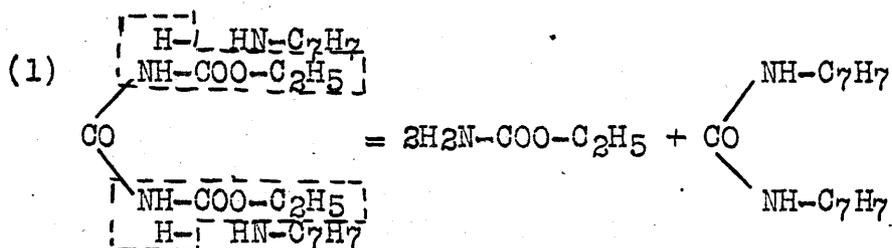
5.50 cc. times 1.01 = 5.55 cc.

Ammonia evolved = 4.45 cc. N/2 acid .

Weight Nitrogen = 0.03115 gm.

Per cent " = 11.60 % .

The reactions by which the di-o-tolyl urea is formed are represented by the following equations :



Di-o-tolyl urea is also obtained as one of the products when the reaction is carried out at 130-140° C. but only in very small amount. When the reaction is carried out at 170-180°C. the yield is moderately large but when the reaction is allowed to take place below 130°C. none is obtained .

MONO-O-TOLYL UREA WITH CHLOR-CARBONIC ESTER.

Since it was thought that one of the unidentified products of the reaction might be tolyl allophanic ester it was thought desirable to prepare this substance in order to identify the product. Pickard and Garter* prepared o-tolyl allophanic ester and reported that it melts at 137°C.

In order to prepare it ten grams of the urea was mixed with a few cc. of benzene and pyridine was added in excess of the amount theoretically necessary to combine with the hydrochloric acid liberated in the reaction. The chlorcarbonic ester was added a few drops at a time during a period of about an hour.

From the solution there separated a quantity of a brownish white crystalline substance which when recrystallized from alcohol gave M.P. 135°C. When the solution was allowed to evaporate a small amount of solid material was left which after recrystallization gave M.P. 136°C. The total yield of the two products was about two grams.

In order to obtain a larger amount of this substance for analysis this reaction was carried out a second time in the same way except that no benzene was added and the mixture was heated in order to insure that the reaction should go to completion. From this reaction the yield of the tolyl allophanic ester was slightly

* Chem. Soc. London., 81, pp. 1571.

more than four grams. The product was obtained sufficiently pure that it melted at 137°C. In addition to these two products a small amount of a white crystalline substance was obtained which after recrystallization gave M.P. 186°C. and was found to be a part of the original material recovered unchanged since when it was mixed with pure mono-o-tolyl urea the M.P. of the mixture was not lowered.

The product which one would expect to obtain from this reaction is o-tolyl allophanic ester which should contain theoretically 12.61 % nitrogen. The analyses show : (1) 12.88 % (2) 12.72 % .

Analyses :

(1) Watch glass + sample = 5.2687 gm.

" " " = 5.0160 "

" " " = 0.2527 "

N/2 acid in receiver = 10.00 cc.

N/2 base to titrate excess = 5.30 cc.

5.30 cc. times 1.01 = 5.35 cc.

Ammonia evolved = 4.65 cc. N/2 acid.

Weight Nitrogen = 0.03255 gm.

Per cent " = 12.88 % .

(2) Watch glass + sample = 5.2163 gm.

" " " = 5.0160 "

" " " = 0.2002 "

N/2 acid in receiver = 10.00 cc.

N/2 base to titrate excess = 6.30 cc.

6.30 cc. times 1.01 = 6.36 cc.

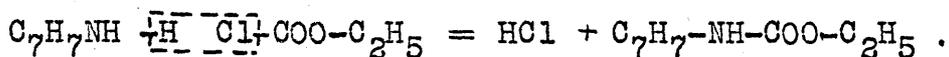
Ammonia evolved = 3.64 cc. N/2 acid.

Weight Nitrogen = 0.02548 gm.

Per cent Nitrogen = 12.72 % .

O-tolyl-allophanic ester , the product of this reaction is readily soluble in alcohol and in acetic acid and is moderately soluble in water. It was found that tolyl allophanic ester is soluble in warm dilute sodium hydroxide solution and that when hydrochloric acid is added to this solution and it is allowed to stand the larger part of the tolyl allophanic ester is reprecipitated.

The reaction for the formation of tolyl allophanic ester is given by the following equation :



I was unable to find o-tolyl allophanic ester among the products of the reaction between carbonyl diurethane and o-toluidine.

CARBONYL DIURETHANE WITH α NAPHTHYLAMINE.

Six grams of α naphthylamine was heated with an excess of carbonyl diurethane in a flask attached to a reflux condenser for three hours at 130°C. The solid which was left in the flask was warmed with alcohol. Part of the product was readily soluble in alcohol while the rest was very difficultly soluble. The soluble portion was recrystallized and gave M.P. 198°C.

This product was analyzed for nitrogen with this result : (1) 13.92 % .

Analysis :

(1) Watch glass + sample = 5.2178 gm.
" " " = 5.0161 "
" " " = 0.2017 "
N/2 acid in receiver = 10.00 cc.
N/2 base to titrate excess = 5.95 cc.
5.95 cc. times 1.008 = 5.99 cc.
Weight Nitrogen = 0.02807 gm.
Per cent " = 13.92 % .

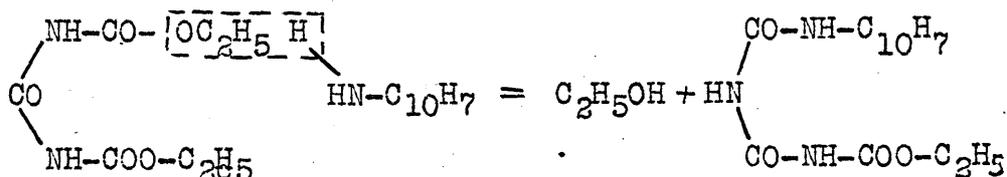
The quantity of the 198°C product available was not sufficient for a second analysis and on account of insufficient time and the fact that the results as far as they were obtained seem to be entirely analogous to those obtained with β naphthylamine the investigation of the reaction between carbonyl diurethane and α -naphthylamine was not carried any further.

(1) α NAPHTHYL CARBETHOXY BIURET .

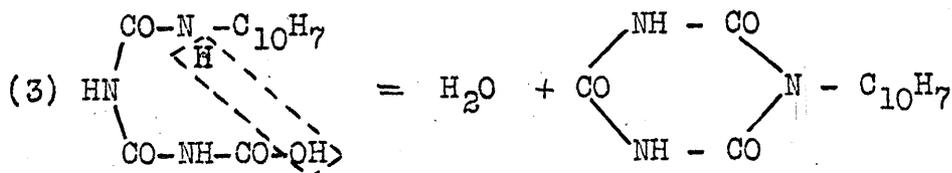
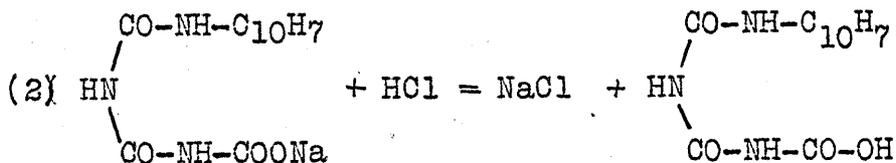
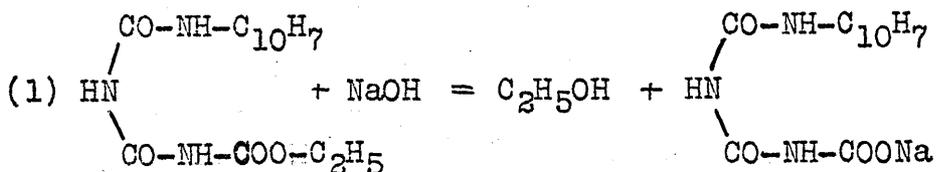
It was found that the 198^o product is soluble in solutions of alkalies and when the alkaline solution is acidified a white pulverulent precipitate is produced which after washing and drying is found not to melt below 290^o C. This behaviour is analogous to that observed with the 196^o product from the reaction of β naphthylamine and carbonyl diurethane and shows that the 198^o product is α naphthyl carbethoxy biuret and that the product obtained by dissolving it in alkali and reprecipitating with the addition of acid, is α naphthyl cyanuric acid. The theoretical per cent of nitrogen in naphthyl carbethoxy biuret, $C_{15}H_{15}O_4N_3$, is 13.95 % while the percentage found on analysis is 13.92 % .

Some question might arise as to whether this product might not perhaps be di- α -carbonyl diurea, due to the fact that the per cent of nitrogen in that substance is 14.07 % , very close to that of the carbethoxy biuret and within the limits of error of the method used in the analysis; that question is disposed of by the fact that the substance dissolves in alkali and gives a high melting derivative, a substituted cyanuric acid, when this solution is acidified. The diurea would probably not be appreciably soluble in alkali and if it were would not be reprecipitated by the addition of acid as the 198^o product was .

The equation representing the formation of the α naphthyl carbethoxy biuret from the reaction of carbonyl diurethane and α naphthylamine is :



The equations representing the reactions by which the α naphthyl cyanuric acid is formed are :



(2) DI- α -NAPHTHYL UREA .

The product melting at 280°C was analyzed for nitrogen by the Kjeldahl method with the following results:

(1) 9.28 % (2) 9.36 % .

Analyses :

(1) Watch glass + sample = 5.4103 gm.

" " " = 5.0160 "

" = 0.3943 "

N/2 acid in receiver = 10.00 cc.

N/2 base to titrate excess = 4.73 cc.

4.73 cc. times 1.008 = 4.77 cc.

Ammonia evolved = 5.23 cc. N/2 acid.

Weight Nitrogen = 0.03661 gm.

Per cent " = 9.28 % .

(2) Watch glass + sample = 5.3938 gm.

" " " = 5.0160 "

" = 0.3778 "

N/2 acid in receiver = 10.00 cc.

N/2 base to titrate excess = 4.91 cc.

4.91 cc. times 1.008 = 4.95 cc.

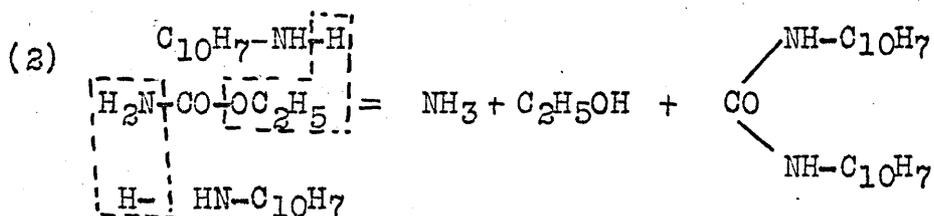
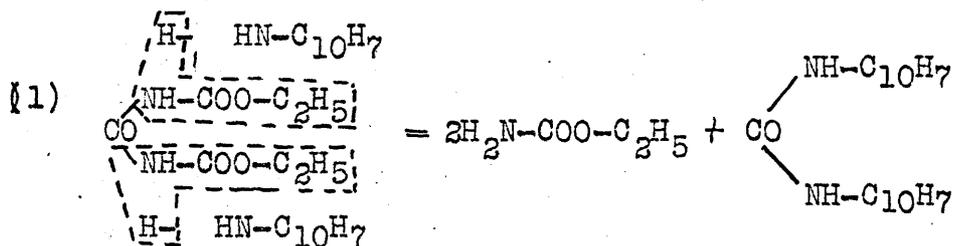
Ammonia evolved = 5.05 cc. N/2 acid.

Weight Nitrogen = 0.03521 gm.

Per cent " = 9.36 % .

The above analyses confirm the constitution of this product as that of di- α -naphthyl urea which has a theoretical per cent nitrogen for $C_{21}H_{16}ON_2$ of 9.00 %.

The equations which represent the formation of di- α naphthyl urea from heating carbonyl diurethane with α naphthylamine are :



CARBONYL DIURETHANE WITH β NAPHTHYLAMINE .

Seven grams of carbonyl diurethane was mixed with a slight excess of β naphthylamine, placed in a flask attached to a reflux air condenser and heated to 130°C . for three hours on an oil bath. Upon cooling the material in the flask solidified. After treating this material with hot alcohol and filtering a white powdery residue remained which was very difficultly soluble in alcohol. It was recrystallized twice from glacial acetic acid and gave M.P. 289°C . The yield was not large.

On cooling the alcoholic filtrate a white flocculent crystalline precipitate was formed. This precipitate retained a pinkish color even after several recrystallizations. The yield was about three grams.

This reaction was carried out a second time using double quantity of each of the materials and heating the mixture to 140°C . The products obtained in this case were the same as in the other reaction except that recrystallization gave both products with greater purity as shown by the fact that one melted at 291°C and the other at 196°C . The 196°C product was proved to be identical with the product obtained from the first reaction which melted at 194°C . In addition to these two products it was found that the addition of water to the alcoholic filtrate gave a precipitate whose M.P. was about 140°C . and which was found to be largely naphthylamine mixed with small amounts of

the two products of the reaction.

This reaction was tried twice more at temperatures of 120° and 150°, respectively, and it was found that in every case the products were the same with the exception that at the higher temperatures the proportion of the 291° product obtained was greater while when the reaction was run at low temperatures the 196° product was in the greater proportion and there was a larger amount of the β naphthylamine recovered unchanged from the reaction mixture.

(1) β NAPHTHYL CARBETHOXY BIURET .

The product obtained from this reaction which melted at 196°C. is naphthyl carbethoxy biuret, which is confirmed by the following nitrogen analyses: (1)

13.97 % (2) 14.00 % (3) 13.90 % . The theoretical per cent of nitrogen in naphthyl carbethoxy biuret, $C_{15}H_{15}O_4N_3$, is 13.95 % .

Analyses :

(1) Watch glass + sample = 5.2265 gm.

" " " = $\frac{5.0161}{0.2104}$ "

N/2 acid in receiver = 10.00 cc.

N/2 base to titrate excess = 5.75 cc.

5.75 cc. times 1.008 = 5.79 cc.

Ammonia evolved = 4.21 cc. N/2 acid .

Weight Nitrogen = 0.02943 gm .

Per cent " " = 13.97 % .

(3) Watch glass + sample = 5.2428 gm.

" " " = $\frac{5.0160}{0.2267}$ "

N/2 acid in receiver = 10.00 cc.

N/2 base to titrate excess = 5.42 cc.

5.42 cc. times 1.008 = 5.47 cc.

Ammonia evolved = 4.53 cc. N/2 acid .

Weight Nitrogen = 0.03171 gm.

Per cent " = 14.00 % .

(2) Watch glass + sample = 5.2331 gm.

" " " = $\frac{5.0161}{0.2070}$ "

N/2 acid in receiver = 10.00 cc.

N/2 base to titrate excess = 5.85 cc.

5.85 cc. times 1.008 = 5.89 cc.

Ammonia evolved = 4.11 cc. N/2 acid.

Weight Nitrogen = 0.02877 gm.

Per cent " = 13.90 % .

Further confirmation of its constitution is obtained from the fact that it is soluble in water solutions of alkalies on warming and is not reprecipitated on cooling but when the solution is acidified a pulverulent precipitate is immediately thrown down. This precipitate is naphthyl cyanuric acid which is confirmed by the nitrogen analyses: (1) 16.09 % (2) 16.21 %. The theoretical per cent of nitrogen of naphthyl cyanuric acid is 16.46 % .

β NAPHTHYL CYANURIC ACID.

The naphthyl cyanuric acid was prepared from the naphthyl carbethoxy biuret by warming three grams of this material with a moderately concentrated solution of sodium hydroxide. This alkaline solution was then filtered and cooled and acidified with dilute sulfuric acid. A heavy white precipitate was immediately thrown down; this was filtered off, washed and dried and was then analyzed for nitrogen. This product did not melt below 290°C .

The reactions by which the β naphthyl carbethoxy biuret is formed and the reactions by which it is converted into β naphthyl cyanuric acid are identical with those given for the formation of the corresponding α naphthyl compounds under the description of the reactions of α naphthylamine.

The theoretical per cent of nitrogen in naphthyl cyanuric acid is 16.46 %. The analyses follow :

Analyses :

(1) Watch glass + sample = 5.2718 gm.

" " = 5.0160 "

" = 0.2558 "

N/2 acid in receiver = 10.00 cc.

N/2 base to titrate excess = 4.04 cc.

4.04 cc. times 1.008 = 4.07 cc.

Ammonia evolved = 5.93 cc. N/2 acid.

Weight Nitrogen = 0.04153 gm.

Per cent " = 16.21 % .

(2) Watch glass + sample = 5.2722 gm.

" " " = $\frac{5.0160}{0.2562}$ "

N/2 acid in receiver = 10.00 cc.

N/2 base to titrate excess = 4.09 cc.

4.09 cc. times 1.008 = 4.12 cc.

Ammonia evolved = 5.88 cc. N/2 acid.

Weight Nitrogen = 0.04116 gm.

Per cent " = 16.09 % .

(2) PRODUCT M.P. 291°C. NOT IDENTIFIED.

No definite report on the constitution of the product melting at 291°C. can be made at this time on account of the failure to obtain satisfactory analyses. By analogy with the α naphthylamine reaction this product would seem to be di- β naphthyl urea but the results on analysis show the percentage of nitrogen to far too great. Its M.P., 291°C. agrees well with that reported for di- β naphthyl urea in Beilstein --293°C.

The analyses obtained are: (1) 13.44 % (2) 13.36 %
(3) 13.75 % (4) 13.12 % .

Analyses :

(1) Watch glass + sample = 5.3175 gm.

" " " = $\frac{5.0160}{0.3015}$ "

N/2 acid in receiver = 10.00 cc.

N/2 base to titrate excess = 4.18 cc.

4.18 cc. times 1.008 = 4.21 cc.

Ammonia evolved = 5.79 cc. N/2 acid .

Weight Nitrogen = 0.04053 gm.

Per cent " = 13.44 % .

(2) Watch glass + sample = 5.3273 gm.

" " " = 5.0160 "
" " " = 0.3113 "

N/2 acid in receiver = 10.00 cc.

N/2 base to titrate excess = 4.03 cc.

4.03 cc. times 1.008 = 4.06 cc.

Ammonia evolved = 5.94 cc. N/2 acid .

Weight Nitrogen = 0.04158 gm.

Per cent " = 13.36 % .

(3) Watch glass + sample = 5.2712 gm.

" " " = 5.0161 "
" " " = 0.2551 "

N/2 acid in receiver = 10.00 cc.

N/2 base to titrate excess = 5.18 cc.

5.18 cc. times 1.008 = 5.22 cc.

Ammonia evolved = 4.78 cc. N/2 acid .

Weight Nitrogen = 0.03346 gm.

Per cent " = 13.12 % .

SUMMARY AND CONCLUSIONS .

As a summary and discussion of the results accomplished in this investigation it will be particularly interesting to compare the products actually obtained with those which the preliminary discussion showed might be obtained. With o-toluidine according to that outline it might be possible to find among the products the following :

- (1) O-tolyl carbethoxy biuret
- (2) Carbonyl di-o-tolyl diurea
- (3) Di-o-tolyl biuret
- (4) Mono-o-tolyl urea
- (5) D-o-tolyl urea
- (6) O-tolyl cyanuric acid
- (7) Tolyl allophanic ester
- (8) Urethane
- (9) Allophanic ester
- (10) Urea
- (11) Tolyl urethane
- (12) Mono-o-tolyl carbethoxy urea

Of the products named above the first six named were obtained and identified; the last six were not. If urea, urethane or tolyl urethane were formed they would probably react further to give some of the other products named above, which accounts for the fact that they do not appear among the reaction products. The same thing

may possibly be true in the cases of the tolyl allophanic ester, allophanic ester and the mono-o-tolyl carbethoxy urea or it may be that a change in the conditions of the reaction would cause these products to appear.

The tolyl cyanuric acid does not appear as a primary product of the reaction but is prepared from the o-tolyl carbethoxy biuret.

The second point of interest brought out in this work is the influence of the temperature upon the course of the reaction and upon the products which are obtained. The tendency evidenced is that at the lower temperatures the greater part of the product is o-tolyl carbethoxy biuret and the di-o-tolyl biuret, while at somewhat higher temperatures mono-o-tolyl urea and di-o-tolyl urea began to appear, and as the temperature was raised their proportion increased until at the highest temperature used the sole product is di-o-tolyl urea. At the intermediate temperatures another product, carbonyl di-o-tolyl diurea, is also obtained but it does not appear at either the higher or the lower temperatures. A summary of this temperature effect in the reaction with o-toluidine is given on the following page.

Of the possible products from the reaction between α naphthylamine and carbonyl diurethane only two, α naphthyl carbethoxy biuret and di- α naphthyl urea

were obtained. The tendency for the formation of the other products is apparently not very great or else they react further under the conditions of these experiments.

In the same way the only products from the reaction of β naphthylamine and carbonyl diurethane are β naphthyl carbethoxy biuret and di- β naphthyl urea (?). In both cases the naphthyl cyanuric acid was obtained as a secondary product.

The experiments with methylene diurethane, phenyl methylene diurethane and o-nitro-phenyl methylene diurethane were rather disappointing as the only reaction apparently possible to obtain was the one between methylene diurethane and aniline in which the sole product is diphenyl urea. Small amounts of other products may have been formed but the difficulty of separating any crystalline substance from the reaction mixture made it impossible to obtain any of these substances for identification. An opportunity for further investigation is offered by the compounds diphenyl methylene diurethane and phenyl methyl methylene diurethane to see if they show the same unreactivity.

With regard to the reactions of carbonyl diurethane it is desirable that experiments should be tried using a series of the amines including ethylamine, aniline, ortho and meta toluidines, phenyl hydrazine, and

SUMMARY OF REACTION BETWEEN CARBONYL DIURETHANE
AND ORTHO-TOLUIDINE .

Reaction Product	Quantity of each product obtained.			
	130°C.	140°C.	180°C.	200°C.
(1) $\begin{array}{l} \text{NH-C}_7\text{H}_7 \\ \diagdown \text{CO} \\ \diagup \text{NH}_2 \end{array}$	None	None	Several grams	None
<u>Mono-o-tolyl urea</u>				
(2) $\begin{array}{l} \text{NH-C}_7\text{H}_7 \\ \diagdown \text{CO} \\ \diagup \text{NH-C}_7\text{H}_7 \end{array}$	None	Very little	Several grams	Sole product.
<u>Di-o-tolyl urea</u>				
(3) $\begin{array}{l} \text{CO-NH-C}_7\text{H}_7 \\ \diagdown \text{HN} \\ \diagup \text{CO-NH-C}_7\text{H}_7 \end{array}$	Small amount	Several grams	Several grams	None
<u>Di-o-tolyl biuret</u>				
(4) $\begin{array}{l} \text{CO-NH-C}_7\text{H}_7 \\ \diagdown \text{HN} \\ \diagup \text{CO-NH-COO-C}_2\text{H}_5 \end{array}$	Principal product	Several grams	None	None
<u>O-tolyl carbethoxy biuret</u>				
(5) $\begin{array}{l} \text{NH-CO-NH-C}_7\text{H}_7 \\ \diagdown \text{CO} \\ \diagup \text{NH-CO-NH-C}_7\text{H}_7 \end{array}$	None	Several grams	Several grams	None .
<u>Carbonyl di-o-tolyl diurea</u>				
(6) $\begin{array}{l} \text{NH} = \text{CO} \\ \diagdown \text{CO} \quad \diagup \text{N-C}_7\text{H}_7 \\ \diagup \text{NH} - \text{CO} \end{array}$	Several grams	Several grams	None	None.
<u>O-tolyl cyanuric acid</u> (secondary product)				

naphthylamines, etc., together with a correlation of the results so that more definite conclusions as to the course of the reaction between an amine and carbonyl diurethane may be drawn.

In conclusion, I wish especially to thank Dr. Dains for his continued kindness in directing the work and for the many valuable suggestions he has offered to aid in its prosecution .