[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KANSAS.]

THE ACTION OF AMMONIA AND AMINES ON THE SUBSTITUTED UREAS AND URETHANES. I. CARBONYL-DIURETHANE.

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Various investigators have studied the action of substituted amines upon urethane[1] and phenyl-urethane[2] and have found that the corresponding substituted ureas were formed in every instance. A similar reaction occurs in the case of allophanic ester (carbethoxy-urea) which, when heated with aniline gave diphenyl biuret and finally diphenylurea.[3] None of the possible intermediate products however, were isolated.

The study of the action of ammonia and amines on carbonyl-diurethane, $CO(NHCOOC_2H_5)_2$, dicarbethoxy-urea, was undertaken, since it contains both urea and urethane groupings, and its progressive decomposition presents some interesting possibilities, offering in addition an opportunity for the isolation of the intermediate products. Thus the experimental work has shown that carbonyl-diurethane with ammonia, if water is present, yields carbethoxy-biuret, allophanic ester, biuret and cyanuric acid. The reactions thus involve both amide formation and the loss of carbethoxy groups by hydrolysis.

When aniline and carbonyl-diurethane are heated, the nature of the reactions is conditioned by the temperature, diphenyl-urea being the main product at the boiling point of aniline. At lower temperatures there were isolated intermediate compounds, such as phenyl-carbethoxy-biuret, carbonyldiphenyl-diurea, phenyl-allophanic ester, diphenyl-biuret, and monophenyl-urea. The series is an interesting one as it throws much light on the progressive nature of the reaction. The details will be given more fully, however, in connection with the experimental work.

Experimental Work.

Preparation of Carbonyl-diurethane.—This can be made easily and in quantity by adding a mixture of two molecules, each, of urethane and pyridine to a 10% solution of phosgene in benzene.[4] It crystallizes from hot water in silky needles, melting at 108° and forms both sodium and silver salts.

Action of Liquid Ammonia.—The carbonyl-diurethane dissolves with the greatest ease in liquid ammonia and can be recovered unchanged on evaporation of the solvent, even when it has been in the solution for several days.

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[1] *Monats.*, 11, 199 (1890); *Gazz. chim. ital.*, 29, 1, 121 (1899).

[2] *Gazz. chim. ital.*, 29, II, 136 (1899); *J. Chem. Soc.*, 53, 552 (1888).

[3] Hofmann, *Ber.*, 4, 262 (1871).

[4] *Am. Chem. J.*, 19, 348 (1897); THIS JOURNAL, 21, 186 (1899).

Carbethoxy-biuret, $NH_2CONHCONHCOOC_2H_5$. — The presence of water, even in small amounts, brings about the expected interaction.

Carbonyl-diurethane was dissolved in a large excess of liquid ammonia containing between 1 and 2% of water in a Dewar flask. The residue left after evaporation of the ammonia, was crystallized from hot water, in which it is easily soluble. The main product separated in fine leaves or as a white powder, depending upon concentration. It is readily soluble in alcohol, less so in chloroform, and melts with decomposition at 162–163°.

It dissolves, also, in dil. sodium hydroxide or ammonia solution, but on acidifying only cyanuric acid and not the original material is obtained, while the solution gives a test for ethyl alcohol.

Calc. for $C_5H_9O_4N_3$: N, 24.01. Found: N, 23.93, 24.21.

The compound is evidently carbethoxy-biuret, formed by replacing one ethoxy group of the diurethane with NH_2. It very readily loses alcohol with consequent ring closure and the formation of cyanuric acid.

This may explain the formation of cyanuric acid in the decomposition of urethane in many reactions. With one mol. of cyanic acid the urethane yields the stable allophanic ester. With two mols. of acid the more reactive carbethoxy-biuret would be formed, which readily breaks down into cyanuric acid and alcohol.

As evidence for this addition of cyanic acid, as will be pointed out later, is the fact that one of the products formed by the action of phenyl isocyanate on urethane is phenylcarbethoxy-biuret, $C_6H_5NHCONHCONHCOOC_2H_5$ which by the further loss of alcohol goes over to phenylisocyanuric acid.

Besides the carbethoxy-biuret, biuret in traces, and cyanuric acid were identified as the other products of the reaction between ammonia and the diurethane.

Action of Alcoholic Ammonia.—Carbonyl-diurethane was dissolved in absolute alcohol, saturated with ammonia, and allowed to stand for several days. The urethane was recovered practically unchanged, though in some instances a little allophanic ester was obtained.

Action of Aqueous Ammonia.—Carbonyl-diurethane dissolves readily in the cold in 28% ammonium hydroxide, forming a clear solution, but on standing an abundant white precipitate is deposited. This latter can be crystallized from hot water, alcohol, or chloroform. In each case fine, white needles of ethyl allophanate ester, melting at 192°, were obtained.

Calc. for $C_4H_8O_3N_2$: N, 21.21. Found: 21.23, 21.09.

Di-Silver Salt of Ethyl Allophanate.—Some of the allophanate ester was dissolved in hot water and to this solution was added one drop of conc. ammonium hydroxide. Silver nitrate solution produced no effect, but when a few crystals of solid silver nitrate were added a very gelatinous precipitate was formed. Vigorous stirring converted this into a white crystalline precipitate.

In the absence of strong light, this was filtered off, washed with cold water, and finally with a little ether. The dry silver salt seems to be fairly stable in the light and when care is used remains uncolored.

Calc. for $C_4H_6O_3N_2Ag_2$: Ag, 62.40. Found: 62.03.

Biuret.—The filtrate from the allophanic ester which gave tests for ethyl alcohol was evaporated to dryness. A portion of the white residue was shown to contain biuret by the color test with copper sulfate and potassium hydroxide, but not enough was formed to isolate. This agrees with the observations of Hofmann,[1] who found that biuret was produced when allophanic ester was heated with ammonia solution at 100°.

Cyanuric Acid.—The residue was now dissolved in hot water and treated with a solution of mercuric sulfate in dil. sulfuric acid. Treatment of the mercury salt with hydrogen sulfide and concentration of the filtrate gave a white solid, which crystallized from hot water in small, glassy prisms which effloresce rapidly in the air. These were dried for analysis.

Calc. for $C_3H_3O_3N_3$: N, 32.55. Found: 32.71.

A molecular-weight determination made by titration of the acid with sodium hydroxide solution, using thymolphthalein as an indicator, gave the figure 128.5 instead of 129 (calc.).

The acid also yielded the characteristic copper salt, while in ammonia solution conc. silver nitrate precipitated a di-silver salt.

Calc. for $C_3HO_3N_3Ag_2.2NH_3$: Ag, 57.2. Found: 56.36.

In a previous paper[2] a silver salt was obtained from the product formed by the action of ammonia on carbonyl-diurethane, containing 60.31 and 60.36% of silver. This corresponds closely to that required for the di-silver salt of carbonyldiurea.

Calc. for $C_3H_4O_3N_4Ag_2$: Ag, 60.00. Found: 60.31; 60.36.

It was assumed therefore that the original product contained carbonyl-diurea. Lack of time prevented proper confirmation and the present re-investigation shows that the diurea which might be expected is not formed under these conditions, but that the silver salt obtained was a mixture.

Results of the Action with Ammonia.—The foregoing experiments indicate then that ammonia reacts with carbonyl-diurethane in two ways: (1) In the presence of small amounts of water, amide formation occurs with one of the ethoxy groups with the formation of carbethoxy-biuret and this in part by the loss of alcohol goes over into the cyanuric acid. (2) With larger amounts of water, the main reaction is hydrolysis of one

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[1] *Ber.*, 4, 264 (1871).

[2] THIS JOURNAL, 21, 192 (1899).

of the carbethoxy groups with the resulting production of allophanic ester: at the same time, carbethoxy-biuret is formed, but being unstable in the ammonia solution appears only as its decomposition product: biuret is formed only to a very limited extent.

Action of Ethylamine.—Carbonyl-diurethane dissolves easily in a 35% solution of ethylamine. On standing allophanic ester is produced in 80% yield, due evidently to a simple hydrolysis of the urethane molecule. It was identified by its melting point (192°) and analysis.

Calc. for $C_4H_8O_3N_2$: N, 21.21. Found: 21.34, 21.38.

Carbonyl-diurethane and Substituted Amines.—In contradiction to the preceding work it will be noted that reaction occurs only at relatively elevated temperatures (110° or above) and in the absence of water no opportunity for hydrolysis occurs. One experiment will be described in some detail; with the others the results will be recorded more briefly.

The Action with Aniline at 110–15°.—Aniline (two mols.) and carbonyl-diurethane (one mol.) were heated for one hour in an oil bath in a flask fitted with a condenser. Alcohol and ammonia were both given off and identified. The semi-solid contents of the flask, which still contained aniline, were separated by fractional crystallization, from alcohol into two products: A, melting at 210°, and B, at 174°.

Diphenyl-biuret.—Diphenyl-biuret, the 210° compound A, is difficultly soluble in alcohol and insoluble in sodium hydroxide solution. Its analysis, melting point and comparison with a known sample of α-diphenyl-biuret, $C_6H_5NHCONHCONHC_6H_5$, proved it to be this substance.

Calc. for $C_{14}H_{13}O_2N_3$: N, 16.47. Found: 16.68, 16.70.

Heated with aniline it gave diphenyl-urea, and with acetic anhydride, acetanilide.

Phenyl-carbethoxy-biuret, $C_6H_5NHCONHCONHCOOC_2H_5$.—The 174° compound B is readily soluble in hot alcohol from which it separates in small, glistening plates. It is insoluble in hot water but dissolves in dil. alkali, even ammonium hydroxide.

Calc. for $C_{11}H_{13}O_4N_3$: N, 16.76. Found: 16.65, 16.71.

This corresponds to phenyl-carbethoxy-biuret, a fact confirmed by its behavior.

Di-sodium Salt.—The biuret was dissolved in as small an amount of cold absolute alcohol as possible and to it was added a solution of sodium ethylate. The white, gelatinous precipitate, which became granular on standing, was filtered off, dried and analyzed.

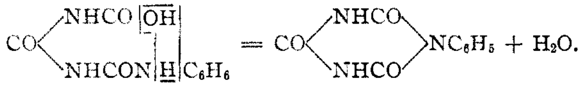
Calc. for $C_{11}H_{11}O_4N_3Na_2$: Na, 15.59. Found: 15.66.

Di-silver Salt.—When silver nitrate is added to a solution of the di-sodium salt in water, a thick, gelatinous precipitate of the silver salt was obtained. This was washed as thoroughly as possible and dried.

Calc. for $C_{11}H_{11}O_4N_3Ag_2$: Ag, 46.37. Found: 47.99, 47.93.

The excess of silver is doubtless due to inability to wash out all of the occluded silver nitrate.

Phenyl-isocyanuric Acid.—When the phenyl-carbethoxy-biuret is dissolved in sodium hydroxide solution, alcohol splits off very readily and can be detected in the solution. Acids precipitate then, not the original compound, but instead, phenyl-isocyanuric acid. It would seem probable that with the aqueous alkali a very soluble sodium salt of the type C_6H_5-NHCONHCONHCOONa is formed. The free acid is unstable, the ring closing with loss of water.



$$\mathrm{CO}\left\langle\begin{matrix}\mathrm{NHCO}\,\boxed{\mathrm{OH}}\\ \mathrm{NHCON}\boxed{\mathrm{H}}\mathrm{C_6H_6}\end{matrix}\right. = \mathrm{CO}\left\langle\begin{matrix}\mathrm{NHCO}\\ \mathrm{NHCO}\end{matrix}\right\rangle\mathrm{NC_6H_5} + \mathrm{H_2O}.$$

The phenyl-isocyanuric acid was purified by recrystallization from hot water, from which it separated in fine needles, showing a melting point of from 290–300° in different preparations.

Calc. for $C_9H_7O_3N_3$: N, 20.48. Found: 20.11, 21.00, 20.88.

It forms a silver and a copper salt. The same acid has been obtained previously by heating triphenyl-ammelin[1] or phenyl-ammelin[2] in a sealed tube at 150° with hydrochloric acid.

Phenylisocyanate and Urethane.—The phenyl-carbethoxy-biuret and phenylisocyanuric acid were obtained by another interesting method, the details of which will be published later. A mixture of phenyl-isocyanate (one mol.) and urethane (two mols.) failed to react at a water bath temperature, but when heated at 130° for several hours the following progressive series of compounds were formed: phenyl-urethane, phenyl-allophanic ester,[3] phenyl-carbethoxy-biuret, and phenyl-isocyanuric acid.[4]

The Action of Aniline at 130–50°.—A number of experiments were made at the above temperatures with the resulting formation of phenyl-carbethoxybiuret, diphenyl-biuret in a larger yield than before, and a new product, melting at 211°, which was separated by fractional crystallization from the biuret. It is insoluble in water, difficultly soluble in alcohol, from which it crystallizes in white leaflets, insoluble in alkalies and gave figures on analysis corresponding to carbonyl-diphenyl-diurea.

$$\mathrm{CO(NHCOOC_2H_5)_2 + 2C_5H_5NH_2 = CO(NHCONHC_6H_5)_2 + 2C_2H_5OH.}$$

Calc. for $C_{15}H_{14}O_3N_4$: N, 18.79. Found: 18.77, 19.00.

It is evidently identical with the diurea melting at 211° obtained by Bruce[5] by the action of dry hydrogen chloride on *o*-methyl-diphenyl-diureido-isourea, $C_6H_5NHCONHC(OCH_3)NCONHC_6H_5$.

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[1] *Ber.*, **20**, 1070 (1886); **21**, 868 (1887).

[2] *Monats.*, **11**, 8 (1890).

[3] *Ber.*, **22**, 1573 (1889).

[4] *Am. Chem. J.*, **19**, 346 (1897).

[5] THIS JOURNAL, 26, 450 (1904).

Pickard and Carter[1] state that they obtained this same diurea by the rearrangement of phenyl-acetyl-hydroxamic oxamide, but they describe it as crystallizing from alcohol in prisms and melting at 140°. This may be an error in recording the melting point, or it is possible that they actually obtained here impure monophenyl-urea, since in another experiment[2] they found that the above oxamide boiled with pyridine actually yields monophenyl-urea.

The Reaction with Aniline at 170°.—Besides varying quantities of the products previously described there was isolated a little monophenyl-urea (m. p. 147°) and diphenylurea (m. p. 235°). At higher temperatures diphenyl-urea is the main product. The formation of the mono- and diphenyl-urea can be readily explained by the action of aniline on carbonyl-diphenyl-diurea or on the biuret.

$$CO(NHCONHC_6H_5)_2 + C_6H_5NH_2 = C_6H_5NHCONH_2 + HN(CONHC_6H_5)_2. \quad (I).$$

$$HN(CONHC_6H_5)_2 + C_6H_5NH_2 = C_6H_5NHCONH_2 + CO(NHC_6H_5)_2. \quad (II).$$

The validity of the second equation was shown by actual experiment.

Phenyl-diurethane and *o*-Toluidine.—Carbonyl-diurethane (one mol.) and *o*-toluidine (two mols.) react when heated at 130° with loss of ammonia and alcohol. The main product forms fine, white crystals, moderately soluble in alcohol and melting at 155–6°. Its analysis and reactions show that it is *o*-tolyl-carbethoxy-biuret, $o\text{-}C_7H_7NHCONHCONHCOOC_2H_5$.

Calc. for $C_{12}H_{15}O_4N_3$: N, 15.86. Found: 16.06, 15.93.

***o*-Tolyl-isocyanuric Acid.**—The carbethoxy derivative is completely soluble in dil. sodium hydroxide solution but the original compound is not precipitated on acidifying, but instead there is a quantitative yield of *o*-tolyl-isocyanuric acid. This crystallizes from alcohol in white needles which do not melt at 300°.

Calc. for $C_{10}H_9O_3N_3$: N, 19.18. Found: 19.34, 19.27.

Mono-silver Salt.—When this substance is dissolved either in dil. ammonia solution or in sodium hydroxide solution, silver nitrate gives a gelatinous precipitate which slowly changes to pulverulent crystals.

Calc. for $C_{10}H_8O_3N_3Ag$: Ag, 34.61. Found: 34.99.

No di-silver salt could be obtained even when a large excess of silver nitrate was used.

This is in agreement with the observations of Rathke,[3] who isolated only the mono-silver salt in the case of phenyl-isocyanuric acid.

Di-*o*-Tolyl-biuret, $NH(CONHC_7H_7)_2$.—A second product obtained

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[1] *J. Chem. Soc.*, 79, 843 (1901).

[2] *Ibid.*, 81, 1567 (1902).

[3] *Ber.*, 21, 868 (1888).

from the reaction between the urethane and *o*-toluidine was insoluble in alkali and was purified by repeated crystallization from hot alcohol from which it separates in needle-like crystals melting at 202–3°.

Calc. for $C_{16}H_{17}O_2N_3$: N, 14.84. Found: 14.97, 15.03.

The same biuret was prepared by heating a mixture of *o*-toluidine and allophanic ester.

Ethyl-*o*-tolyl-allophanate.—In addition to the two biurets just described, there was isolated a small amount of product melting at 126°, but not enough for adequate identification. This is possibly impure *o-tolyl-allophanic ester* which melts at 137° and which has been obtained by Pickard[1] from *o*-tolyl-hydroxy-oxamide. For comparison the ester (m. p. 137°) was prepared by adding chloro-carbonic ester to the mono-*o*-tolyl-urea in a little benzene and pyridine (one mol.) This yield is poor. The *o*-tolyl-allophanic ester is readily soluble in alcohol, acetic acid, hot water, and dil. alkali solution.

Calc. for $C_{10}H_{13}O_2N$: N, 12.61. Found: 12.88, 12.72.

Action of *o*-Toluidine at 140°.—The products here were: *o*-tolyl-carbethoxy-biuret, a little di-*o*-tolyl-urea, and in addition, carbonyl-di-*o*-tolyl-diurea, $CO(NHCONHC_7H_7)_2$. This is difficultly soluble in alcohol and insoluble in alkali solution. It melts at 186°.

Calc. for $C_{17}H_{18}O_3N_4$: N, 17.19. Found: 17.27, 17.06.

A molecular-weight determination by the boiling-point method using alcohol as a solvent gave 359 and 363 instead of the calculated 326. The error is due to the fact that it is only slightly soluble in boiling alcohol. Pickard describes this same diurea (m. p. 190°) as having been obtained from the sodium salt of *o*-tolyl-acetyl-hydroxy-oxamide on warming with water.

Action of *o*-Toluidine at 170–180°.—After a tedious fractional crystallization, there were isolated di-*o*-tolyl-biuret, carbonyl-di-*o*-tolyl-diurea and di-*o*-tolyl-urea. This latter melted at 248°, was identified by comparison with a known sample of the urea and by analysis.

Calc. for $C_{15}H_{16}ON_2$: N, 11.60. Found: 11.58, 11.60.

In addition there was found among the reaction products a compound melting at 188° which proved to be mono-*o*-tolyl-urea, $C_7H_7NHCONH_2$. The melting point was unchanged when mixed with pure urea.

Calc. for $C_8H_{10}ON_2$: N, 18.66. Found: 18.89, 18.45.

Action of *o*-Toluidine at 200°.—At this temperature di-*o*-tolyl-urea was the only substance identified.

Carbonyl-diurethane and β-Naphthylamine.—β-Naphthyl-carbethoxy-biuret, $\beta\text{-}C_{10}H_7NHCONHCONHCOOC_2H_5$, is the main product when the above compounds are heated at 130–140° for 3 hours. It crystallizes from

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[1] *J. Chem. Soc.*, 81, 1571 (1902).

alcohol, in which it is readily soluble, in fine, white needles melting at 196°.

Calc. for $C_{15}H_{15}O_4N_3$: N, 13.95. Found: 13.97, 14.00.

It dissolves completely in dil. sodium hydroxide solution, from which acid throws down a powdery precipitate of β-naphthyl-isocyanuric acid, melting at 290–1°, which is almost insoluble in the various organic solvents.

Calc. for $C_{13}H_9O_3N_3$: N, 16.50. Found: 16.31, 16.47.

Carbonyl-di-β-naphthyl-diurea, $CO(NHCONHC_7H_{10})_2$.—The original reaction mass also contained a small quantity of a compound which was insoluble in alcohol and after recrystallization from glacial acetic acid melted at 293°. It contains 13.75% nitrogen (Calc. 14.08) and would seem to be identical with the same diurea obtained by Pickard,[1] although his compound was recrystallized from dilute alcohol, softened at 213° and decomposed about 290°.

Carbonyl-diurethane and α-Naphthylamine.—The α-naphthylamine seems to react more completely at 130° than do the other amines since only a small yield of the α-naphthyl-carbethoxy-biuret, α-$C_{10}H_7NHCONHCONHCOOC_2H_5$, was obtained. This is easily soluble in alcohol from which it crystallizes in fine, white needles melting at 198°.

Calc. for $C_{15}H_{15}O_4N_3$: N, 13.95. Found: 13.92.

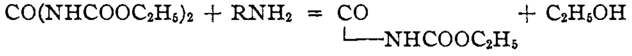
It is soluble in alkalies, acids precipitating a compound melting above 290°, which from analogy is doubtless the α-naphthyl-isocyanuric acid. The main product of the reaction and the normal end product was di-α-naphthyl-urea, melting at 280°.

Calc. for $C_{21}H_{16}ON_2$: N, 9.00. Found: 9.28, 9.36.

Di-α-naphthyl-biuret, $NH(CONHC_{10}H_7,\alpha)$. — In addition a little biuret was found. This forms white crystals difficultly soluble in the usual organic solvents, and melts at 278–9°.

Calc. for $C_{22}H_{17}O_2N_3$: N, 11.83. Found: 12.06, 12.20.

The Action of Substituted Amines.—The results with aniline and *o*-toluidine indicate plainly the following general reactions in the decomposition of carbonyl-diurethane:



$$CO(NHCOOC_2H_5)_2 + RNH_2 = CO\left[\begin{array}{l} NHCONHR \\ NHCOOC_2H_5 \end{array}\right. + C_2H_5OH \qquad (I)$$

The R-carbethoxy-biurets which result afford a simple method for the synthesis of R-isocyanuric acids.

$$CO(NHCOOC_2H_5)_2 + 2RNH_2. = CO(NHCONHR)_2 + 2C_2H_5OH, \text{ carbonyl-diurea.} \qquad (II)$$

The other products isolated can be readily accounted for by the action

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[1] *J. Chem. Soc.*, **79**, 896 (1901).

of RNH_2 on the biuret or diurea or by the decomposition of the diurea with loss of cyanic acid.

There is some evidence to show that the urethane can react with the aniline yielding a substituted allophanic ester and urethane $(CONHCOOC_2H_5)_2 + RNH_2 = RNHCONHCOOC_2H_5 + NH_2COOC_2H_5$, but the proof as yet is not absolutely conclusive.

The General Reactivity of Carbonyl-diurethane and Its Derivatives.

The study of carbonyl-diurethane has shown that it presents two general points of attack. First: The ethoxy groups can be readily replaced by an amino or substituted amino grouping. Second: It forms metallic salts, as do also the carbethoxy-biurets, but not the ordinary biuret or diureas where the carbethoxy groups are replaced by the CONHR complex: this reactivity is evidently directly dependent upon the carbonyl grouping, since neither methylene-diurethane nor the substituted methylene-diurethanes form metallic salts or react with amines.

Methylene-diurethane and Amines.—Methylene-diurethane, $CH_2(NHCOOC_2H_5)_2$, which is readily formed by the condensation of formaldehyde with urethane[1] is sensitive to both dil. acids and alkalies, breaking down into formaldehyde, ammonia, carbon dioxide, and alcohol. Heated with aniline, no reaction occurs at 130°, at 160° traces of ammonia were evolved, but the residue consisted of unchanged diurethane. At 200° the odor of ammonia is more pronounced and the mass darkens, but the only product isolated besides unchanged diurethane was a little diphenyl-urea.

Calc. for $C_{13}H_{12}ON_2$: N, 13.2. Found: 13.30, 13.26.

This could be accounted for by a slight dissociation of the methylene-diurethane into formaldehyde and urethane which latter then reacts with the aniline, giving ammonia and diphenyl-urea.

Phenyl-methylene-diurethane, $C_6H_5CH(NHCOOC_2H_5)_2$. — This was prepared in order to ascertain whether the more negative phenyl group would facilitate the amide reaction. It fails, however, to react either with liquid ammonia, or with conc. aqueous ammonium hydroxide. Heated with aniline at 200° no action was observed; at 230° only resinous decomposition products and unchanged phenyl-methylene-diurethane were obtained.

Phenyl-methylene-diurethane and Sodium Alcoholate.—The diurethane was dissolved in absolute alcohol and a solution of sodium alcoholate added. On standing a precipitate gradually formed, but investigation showed that this was not a salt of the diurethane but practically pure sodium hydrogen carbonate formed by hydrolysis.

***o*-Nitro-phenyl-methylene-diurethane,** $o\text{-}NO_2C_6H_4CH(NHCOOC_2H_5)_2$. —*o*-Nitro-benzaldehyde (one mol.) and urethane (two mols.) were dis-

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[1] *Ber.*, 36, 2206 (1903).

solved in 95% alcohol and to this mixture was added $^1/_{10}$ of its volume of conc. hydrochloric acid. On standing the diurethane separated in 90% yield. It forms fine, white crystals from alcohol, is nearly insoluble in hot water and melts at 190°.

Calc. for $C_{13}H_{17}O_6N_3$: N, 13.50. Found: 13.66, 13.41.

The introduction of the negative nitro group was found to have no effect, the urethane does not give an amide either with ammonia or with aniline, at temperatures up to 200°.

It is interesting to note in this connection that substituted urethanes, $R_2NCOOC_2H_5$, exhibit the same stability towards aniline on heating. For instance, phenyl-methyl-urethane[1] and diphenyl-urethane[2] failed to react with this amine when heated at 180–200°.

Summary.

(1) Carbonyl-diurethane and ammonia yield carbethoxy-biuret, allophanic ester, biuret and cyanuric acid.

(2) Aniline and substituted amines at varying temperatures give substituted carbethoxy-biurets, diureas, biurets and mono- and diureas.

(3) Carbethoxy-biurets or substituted carbethoxy-biurets are soluble in alkalies, but on acidifying, ring closure occurs with the formation of cyanuric acid or of mono-substituted-isocyanuric acids.

(4) Methylene-diurethane, phenyl and *o*-nitro-phenyl-methylene-diurethane show no tendency to react with ammonia or aniline, even when heated.

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[CONTRIBUTION FROM THE EXPLOSIVES CHEMICAL LABORATORY OF THE PITTSBURGH EXPERIMENT STATION, BUREAU OF MINES.]

THE PREPARATION OF HEXANITRO-DIPHENYLAMINE FROM CHLOROBENZENE.[3]

BY E. J. HOFFMAN AND PERRY A. DAME.

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The investigation of hexanitro-diphenylamine was undertaken by the Bureau of Mines at the suggestion of Dr. C. E. Munroe, Chairman, Committee on Explosives Investigations, because of interest in the subject on the part of the Army and Navy Ordnance Departments. The experimental part of this paper is confined to the presentation of experiments made by the authors on the preparation of this explosive substance, in 4 successive steps, from chlorobenzene.

Among the earlier investigators of hexanitro-diphenylamine were

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[1] *Ber.*, 17, 3043 (1884).

[2] *Ibid.*, 5, 284 (1872).

[3] Published by permission of the Director, U. S. Bureau of Mines.