Summary

All attempts at the formation of a hexamethoxy indigo by means of the synthesis employed in these communications were unsuccessful; many interesting derivatives of gallic acid, however, were obtained.

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[CONTRIBUTION FROM THE FIXED NITROGEN RESEARCH LABORATORY]

SOME NEW REACTIONS OF THE MIXED AQUO-AMMONOCARBONIC ACIDS

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RECEIVED NOVEMBER 3, 1926 PUBLISHED FEBRUARY 5, 1927

In a recent paper[1] defining the term "mixed aquo-ammonocarbonic acid," it was shown that there is a large discrepancy between the number of known compounds of this type and the number which may be formulated. Furthermore, there are several reactions, rather simple in nature, which would be expected to characterize these compounds as mixed aquo-ammonocarbonic acids, but which have not as yet received experimental verification. In this paper are presented the results of some work bearing upon this problem, which has been carried out at various times in this Laboratory.

Many investigators have demonstrated the conditions under which ammonia may act to synthesize one compound of this type from another by ammonation or partial ammonalysis; for example, the ammonalysis of urea to guanidine. A few such reactions are also described in the present paper. The reverse type of reaction, namely, the hydration or partial hydrolysis of one compound to another, is considerably more difficult to control. The action of water ordinarily leads to disruption of substances containing two or more carbon atoms per molecule to form aquocarbonic acid or other simple carbonic acids, such as urea or guanidine which, while thermodynamically unstable in water solution, are only slowly hydrolyzed. However, when anhydrous alcohol is substituted for water, the solvolysis is less extensive and the esters of the more complex acids may be isolated. This may be illustrated by the experiments described below.

Action of Alcohol on Guanylurea

Guanylurea, a mixed aquo-ammonocarbonic acid containing two carbon atoms, was found to react with anhydrous ethyl alcohol to form a carbethoxy-guanidine identical with that obtained by Nencki[2] by the action of ethyl chlorocarbonate on guanidine. The reaction may be expressed by

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[1] Blair, THIS JOURNAL, **48**, 87 (1926).

[2] Nencki, *Ber.*, **7**, 1594 (1874).

the equation $H_2NC(NH)NHCONH_2 + C_2H_5OH = H_2NC(NH)NHCOOC_2H_5 + NH_3$. This reaction is to be contrasted with that of guanylurea with water, which yields two simple carbonic acids, $H_2NC(NH)NHCONH_2 \xrightarrow{H_2O} (H_2NC(NH)NHCOOH+NH_3) \xrightarrow{H_2O} H_2NC(NH)NH_2 + HOCOOH + NH_3$.

Ten g. of guanylurea hydrochloride was dissolved in 100 cc. of an approximately 1 *N* solution of hydrogen chloride (to act as catalyst) in anhydrous alcohol. The solution was heated in a small laboratory autoclave at 140° for two hours. On opening the autoclave, the solution was filtered from a very small quantity of white, insoluble material and the filtrate concentrated to a volume of 10 cc. When filtered from the ammonium chloride which was deposited during the evaporation, the solution was a viscous, clear, brown liquid which did not deposit crystals when chilled. To identify carbethoxyguanidine in this solution, advantage was taken of the low solubility of carbethoxyguanidine nitrate. At this point 30 cc. of a 50% solution of ammonium nitrate in water was added to the solution forming a white, crystalline precipitate weighing 2.1 g. This, when recrystallized from alcohol, melted at 182–183°, and when mixed with carbethoxyguanidine nitrate made by Nencki's method, the temperature of melting was not changed. The nitrogen content of the substance was found, in two determinations, by the Devarda modification of the Kjeldahl method, to be 28.55 and 28.65%; calcd. for $C_4H_{10}O_5N_4$: N, 28.86%.

Action of Alcohol on Biuret

Many investigators[3] have prepared not only biuret itself, but also nitrogen esters of biuret by the action of ammonia and amines on various esters of allophanic acid. Therefore, it was surprising to find that the reverse alcoholysis of biuret to an allophanic ester has apparently not yet been demonstrated.

Biuret was heated in solution in anhydrous ethyl alcohol containing hydrogen chloride, and esterification was found to take place as expressed by the equation $H_2NCONHCONH_2 + C_2H_5OH = H_2NCONHCOOC_2H_5 + NH_3$.

Two g. of biuret and 50 cc. of an anhydrous alcoholic solution 1.68 *N*, with respect to hydrogen chloride, was heated at 140–145° for two hours. The solution was filtered from 0.72 g. of material which consisted almost entirely of ammonium chloride. The filtrate was concentrated and chilled, causing the crystallization of 0.32 g. of material which, when recrystallized from alcohol, melted at 190°.

Anal. Calcd. for $C_4H_8O_3N_2$: N, 21.20. Found: 21.32.

Action of Alcohol on Ethyl Allophanate

It might be expected that the action of ethyl alcohol on ethyl allophanate would result in further alcoholysis to form carbethoxy-urethan: $H_2NCONHCOOC_2H_5 + C_2H_5OH = HN(COOC_2H_5)_2 + NH_3$.

This, however, was not the case, for the product of the reaction was found to be urethan, showing that the reaction takes the course repre-

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[3] Hofmann, *Ber.*, **4**, 262 (1871). Dains and Wertheim, THIS JOURNAL, **42**, 2303 (1920).

sented by the equation $H_2NCONHCOOC_2H_5 + C_2H_5OH = 2H_2NCOOC_2H_5$.

Five g. of ethyl allophanate and 100 cc. of anhydrous alcoholic hydrochloric acid (1.15 *N*) were autoclaved at 156–157° for four hours. The cooled solution was filtered from about 1 g. of ammonium chloride, then concentrated to a viscous, oily residue from which urethan was recovered by distillation. The residue consisted largely of ammonium chloride.

The melting point of the distillate was 49°, which would not serve to distinguish between urethan, m. p. 51–52°, and carbethoxy-urethan; m. p., 49–50°. However, its nitrogen content was found to be 14.97% which, when compared with the 15.73% calculated for urethan and the 8.70% calculated for carbethoxy-urethan, was sufficient for identification as the former substance.

The source of the ammonium chloride in this experiment is, then, to be attributed, probably, to the complete alcoholysis of a portion of the mixed aquo-ammonocarbonic esters, ethyl allophanate and ethyl carbamate, to ethyl carbonate: $H_2NCOOC_2H_5 + C_2H_5OH + HCl = CO(OC_2H_5)_2 + NH_4Cl$. Ethyl carbonate, however, was not isolated from the reaction mixture.

Action of Ammonia on Carbethoxy-cyanamide and on Dicarbethoxy-cyanamide

When sodium cyanamide in suspension or free cyanamide in solution in ether is treated with ethyl chlorocarbonate, both carbethoxy-cyanamide and dicarbethoxy-cyanamide are formed.[4] We have found that fair yields are also obtainable with crude calcium cyanamide in ether suspension.

It was shown by Diels and Gollmann[5] that dicarbethoxy-cyanamide reacts with aqueous ammonia to form a product which they designated as an ammonium salt of carbethoxy-cyanamide, together with urethan: $NCN(COOC_2H_5)_2 + 2NH_3 = NCN(NH_4)COOC_2H_5 + H_2NCOOC_2H_5$. This product melted at 107–108°. It seemed possible that the substance might in reality be the isomeric carbethoxy-guanidine; m. p., 114–115°. However, in repeating their work, a sample of the ammonium salt was obtained (calcd. for $C_4H_9O_2N_3$: N, 32.05%; found: 32.01%), which melted at 106–106.5°, and when mixed with a known sample of carbethoxy-guanidine melted at 96–100°, showing the non-identity of the two substances.

Furthermore, all attempts to bring about the ammonation of carbethoxy-cyanamide to carbethoxy-guanidine failed to give this result, the products in all cases being cyanamide and urethan according to the equation $NCNHCOOC_2H_5 + NH_3 = H_2NCN + H_2NCOOC_2H_5$, or products such

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[4] Bässler, *J. prakt. Chem.*, [2] **16**, 125 (1877).

[5] Diels and Gollmann, *Ber.*, **44**, 3158 (1911).

as dicyanodiamide, urea or ammelide, formed by further reaction of these two. The four experiments which were carried out may be briefly described as follows.

1. Two cc. of carbethoxy-cyanamide and 1 g. of ammonium chloride were dissolved in 50 cc. of absolute alcohol and heated at 100° for five hours. The only products isolated were cyanamide, dicyanodiamide and urea.

2. Ammonium nitrate was substituted for ammonium chloride in an experiment similar to that just described, giving, however, identical results. The relatively insoluble carbethoxy-guanidine nitrate was not formed.

3. One g. of the ammonium salt of carbethoxy-cyanamide, dissolved in 50 cc. of a concentrated, anhydrous solution of ammonia in alcohol, was heated at 110° for five hours. Cyanamide and urethan were identified as products of the reaction.

4. The ammonium salt of carbethoxy-cyanamide was heated alone at 105–110° for two hours. Initial fusion was followed by evolution of ammonia and gradual solidification. The product was impure ammelide, as identified by its solubility properties and an analysis.

Anal. Calcd. for $C_3H_4O_2N_4$: N, 43.8. Found: 45.2, 45.3.

These results may be well explained by the assumption that in the reversible reaction expressed by the equation $H_2NC(NH)NHCOOC_2H_5 = H_2NCOOC_2H_5 + H_2NCN$, equilibrium lies far to the right. In accordance with this, it was found to be impossible to synthesize carbethoxy-guanidine by the action of cyanamide on urethan. This was attempted in three experiments, with results as follows.

1. Five g. of urethan and 2.43 g. of cyanamide dissolved in 70 cc. of water were heated in a laboratory autoclave at 150° for two hours. The products of the reaction were dicyanodiamide, urea and guanidine carbonate, while carbethoxy-guanidine was absent.

2. A carefully dried sample of cyanamide weighing 7.22 g., and 14.85 g. of urethan were heated with 100 cc. of anhydrous alcohol in an autoclave for an hour, at 170°. Under these conditions, the urethan was largely unchanged and the other products were dicyanodiamide, ammelide and ammonia.

3. Ten g. of dry cyanamide and 20.5 g. of dry urethan were mixed. The two solid substances dissolved in each other with absorption of heat, so that the temperature fell to about 10° and gave a liquid mixture which was, however, not entirely homogeneous until again heated up to about 20°. This solution was then heated (precautions being taken to avoid access of atmospheric moisture) to 80° for about two hours, then to 105° for two hours. At the higher temperature, the melt gradually deposited crystals which were found to be pure dicyanodiamide, while the urethan remained practically entirely unaffected.

Although it thus appears to be impossible to bring about the ammonation of carbethoxy-cyanamide to the corresponding guanidine derivative, and although dicarbethoxy-cyanamide also, apparently, may not be ammonated to a dicarbethoxy-guanidine by the action of aqueous ammonia, it was found possible to bring about the latter reaction by the use of ammonium nitrate suspended in absolute alcohol. Even under these conditions, the principal reaction which takes place is the same as when aqueous ammonia is used, namely, ammonation to carbethoxy-cyanamide and urethan.

The dicarbethoxy-guanidine which is obtained in this reaction is not the same as that of Nencki, which was shown by Dains[6] to be symmetrical. The new compound, therefore, is the unsymmetrical carbethoxy-guanidine, formed as expressed by the equation $NCN(COOC_2H_5)_2 + NH_3 = H_2NC(NH)N(COOC_2H_5)_2$.

A solution of 8.0 g. of dicarbethoxy-cyanamide in 50 cc. of absolute alcohol was heated with 3.5 g. of ammonium nitrate in a laboratory autoclave at 100° for five hours. At the end of this time, 1.1 g. of unchanged ammonium nitrate was filtered off and the filtrate evaporated to dryness. From the residue, both carbethoxy-cyanamide and urethan were extracted by means of ether. The ether-insoluble residue was recrystallized from alcohol and found to be the unsymmetrical dicarbethoxy-guanidine. The substance is moderately soluble in alcohol and acetone, very slightly soluble in cold water and insoluble in ether and chloroform; m. p., 184° (uncorr.).

Anal. Calcd. for $C_7H_{13}O_4N_3$: N, 20.7. Found: 20.9, 20.8.

The fact that this compound is unsymmetrical indicates that the dicarbethoxy-cyanamide first prepared by Bässler is also unsymmetrical; that is to say, it is a true cyanamide and not a carbo-di-imide derivative. Dicarbethoxycarbo-di-imide, $C(NCOOC_2H_5)_2$, remains undiscovered.

Action of Ethyl Chlorocarbonate on Dicyanodiamide

In view of the fact that ethyl chlorocarbonate reacts so smoothly with free guanidine, it was of interest to investigate its reaction with cyanoguanidine, or dicyanodiamide.

Equal weights of sodium dicyanodiamide (prepared by the action of sodium ethylate on dicyanodiamide in ethyl alcohol solution) and ethyl chlorocarbonate in an ether solution were heated in an autoclave at 90–100° for two days. The filtrate, concentrated to a small volume, deposited, on standing, fine white crystals of carbethoxy-dicyanodiamide (carbethoxy-cyanoguanidine). These were filtered off, recrystallized from ether and dried.

The substance does not melt, but decomposes at a high temperature, as do ammeline, cyanuric acid, etc. The crystals are monoclinic, and usually twinned on the carbon axis, with refractive indices as follows: $\alpha = 1.432$; $\gamma = 1.618$.

Anal. Calcd. for $C_5H_8O_2N_4$: N, 35.9. Found: 35.2, 35.6.

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[6] Dains, THIS JOURNAL, **21**, 186 (1899).

Summary

The work described in this paper has resulted in adding two new mixed aquo-ammonocarbonic acids, namely, unsymmetrical dicarbethoxy-guanidine and carbethoxy-cyanoguanidine, to the list of those already known. The manner in which one compound of this type may be synthesized from another by partial solvolysis has been illustrated by several typical reactions.

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THE STRUCTURE OF FURAZAN OXIDES

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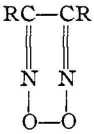
RECEIVED NOVEMBER 8, 1926 PUBLISHED FEBRUARY 5, 1927

The structure of furazan oxides, other than fused aromatic derivatives, has never been conclusively proved. At various times four structures have been proposed. The first, an internal peroxide (I), does not correctly represent the properties of these substances. This was first pointed out by Wieland and Semper[1] who favored either Formula II or III. Structure II, however, was first suggested by Werner.[2] These two formulas were based largely on the reactions by which furazan oxides were formed. A few years later Green and Rowe,[3] as well as Forster and Fierz,[4] showed that the aromatic fused ring oxides have a symmetrical structure (IV). They suggested further, on the basis of this work, that all furazan ozides have a similar structure (V). Angeli[5] and later Bigiavi,[6] studying the behavior of furazan oxides with the Grignard reagent, also favored Structure V.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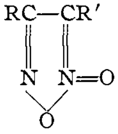
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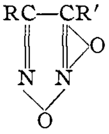
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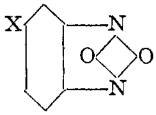
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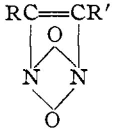
V

Wieland, in defense of his contention that these substances have an unsymmetrical structure, next offered evidence of two isomeric monophenyl furazan oxides[7] (VIa and VIb). This evidence has been largely vitiated by the work of Ponzio,[8] who showed that probably the two sub-

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[1] Wieland and Semper, *Ann.*, **358**, 36 (1908).

[2] Werner, "Lehrbuch der Stereochemie," Gustav Fischer, Jena, **1904**, p. 260.

[3] Green and Rowe, *J. Chem. Soc.*, **103**, 897 (1913).

[4] Forster and Fierz, *ibid.*, **103**, 1918 (1913).

[5] Angeli, *Gazz. chim. ital.*, **46**, 300 (1916); *Atti. accad. Lincei*, [V] **25** (2), 7 (1916).

[6] Bigiavi, *Gazz. chim. ital.*, [2] **51**, 324 (1921).

[7] Wieland, *Ann.*, **424**, 107 (1921).

[8] Ponzio, *Gazz. chim. ital.*, [1] **53**, 379 (1923).