6. Chloro-allyl chloride has been utilized as an alkylating agent in the preparation of some new derivatives of diethyl malonate.

New Haven, Connecticut

[Contribution from the Massachusetts Institute of Technology, Laboratory of Organic Chemistry]

THE UREA DEARRANGEMENT

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Ammonia and cyanic (or isocyanic) acid combine in two ways, to form ammonium cyanate or to form urea. Each of these products is readily converted into the other, or better, each in solution is in equilibrium with a certain amount of the other. An aqueous solution of ammonium cyanate yields urea[1] on evaporation, and an aqueous solution of urea after boiling gives a precipitate of silver cyanate[2] if silver nitrate is added. When a solution of urea is treated with nitrous acid in the cold, ammonium nitrite is formed and cyanic acid[3] is liberated, and the recent work of Werner[4] has brought to light still other facts in support of the opinion that urea is an addition compound of ammonia and *isocyanic* acid. When urea is heated, it yields, in addition to biuret, precisely the compounds[5] which would be formed by the dry heating of ammonium cyanate. As ammonia and isocyanic acid combine with each other to form ammonium cyanate and urea, or better, a mixture of the two, so these two substances under suitable conditions break down into ammonia and isocyanic acid. There are reversible changes as follows:[6] $NH_4NCO \rightleftarrows NH_3 + HNCO \rightleftarrows NH_2{-}CO{-}NH_2$. As the conversion of ammonium cyanate into urea is generally known as an instance of the "urea rearrangement," so for the purpose of the present paper it will be convenient to denominate the reverse of this change as the "urea dearrangement." The urea dearrangement provides a simple means for interpreting and correlating a considerable number of reactions in the urea and guanidine series. It provides a ready means for the synthesis of certain substituted ureas and thio-ureas. The present paper brings forward evidence to show

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[1] Wöhler, *Pogg. Ann. Physik*, **12**, 253 (1828).

[2] Wöhler and Liebig, *Ann.*, **26**, 301 (1838). Walker and Hambly, *J. Chem. Soc.*, **67**, 747, 751 (1895).

[3] Wöhler and Liebig, *Ann.*, **26**, 261 (1838).

[4] Werner, many papers on carbamides. *J. Chem. Soc.*, **117**, 1356 (1920), etc.

[5] Wöhler, *Pogg. Ann. Physik*, **15**, 622 (1829). *Ann. chim. phys.*, [2] **43**, 67 (1830). Weidemann, *J. prakt. Chem.*, [1] **43**, 277 (1848). *Pogg. Ann. Physik*, **74**, 78 (1849). *Ann.*, **68**, 325 (1848). Hofmann, *Ber.*, **4**, 262 (1871). Schiff, *Ann.*, **299**, 236 (1898).

[6] We use the familiar formula for urea. Werner's formula, whatever may be said for it in the case of urea, is not well adapted to the interpretation of our reactions in the case of the substituted ureas.

that it takes place when urea, thio-urea, substituted ureas and thio-ureas, and guanidine are heated. These substances dearrange into substituted ammonias and substituted isocyanic acids.

When urea and aniline are heated together at 160°, the urea dearranges into ammonia and isocyanic acid. The ammonia escapes, and the isocyanic acid combines with the aniline to form phenylurea.[7] Phenylurea at 160° dearranges in two senses, the two modes of dearrangement corresponding to two well-known methods for the preparation of that substance.

$$C_6H_5NH_2 + HNCO \rightleftarrows C_6H_5NH{-}CO{-}NH_2 \rightleftarrows C_6H_5NCO + NH_3$$

The products of both modes of dearrangement may be detected as such or may be inferred from the material which remains. Ammonia and aniline may be detected by their odor. Isocyanic acid may be detected by silver nitrate. The aniline which is formed by one mode of dearrangement combines with the phenylisocyanate formed by the other to produce *sym*-diphenylurea.

$$C_6H_5NH_2 + C_6H_5NCO \rightleftarrows C_6H_5NH{-}CO{-}NHC_6H_5$$

Phenylurea, therefore, heated alone or with aniline yields *sym*-diphenylurea;[8] and diphenylurea can be prepared in excellent yields, without isolating the intermediate phenylurea, by heating urea with an excess of aniline or of aniline hydrochloride at 160°.[9]

The heating of urea with an excess of a primary aromatic amine appears to be a general method[10] for the preparation of *sym*-di-substituted ureas, and we have prepared a number of substances by this process. In the aliphatic series the reaction works, but the products are more difficult to isolate—and a further study of the matter is now under way in this Laboratory. In the case of volatile amines we find that the use of the hydrochloride gives satisfactory results.

While mono-substituted ureas dearrange in two senses, the symmetrical di-substituted compounds in which the two substituent groups are alike can dearrange in only one. A secondary amine, heated with urea, ought to give only the *unsym*-di-substituted compound, not the tetra derivative, for the reason that the dearrangement products of the *unsym*-di-substituted compound cannot recombine to form anything except the original

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[7] Fleischer, [*Ber.*, **9**, 995 (1876)] prepared phenylurea by heating equimolecular amounts of aniline and urea at 150–170°.

[8] Weith [*Ber.*, **9**, 821 (1876)] prepared *sym*-diphenylurea by heating phenylurea with aniline at 180–190°.

[9] Baeyer [*Ann.*, **131**, 252 (1864)] prepared diphenylurea by heating 1 part of urea with 3 of aniline at 180–190°, and Claus [*Ann.*, **179**, 126 (1875)] by heating cyanuric acid with an excess of aniline at 180°—the cyanuric acid evidently depolymerizing to isocyanic acid under these conditions.

[10] Girard [*Ber.*, **6**, 444 (1873)] used this method long ago for the preparation of di-*o*-tolyurea.

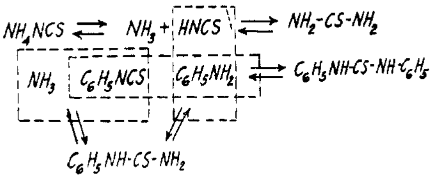
substance from which they came in the first place.

$$R_2NH + HNCO \rightleftarrows R_2N—CO—NH_2$$

We have heated urea with diphenylamine and with ethylaniline, but have found no evidence that any reaction took place—a fact which may perhaps be due to the inactivity of the hydrogen atoms in these substances or perhaps to the circumstance that they are not miscible with melted urea. We have heated urea with dibutyl and di-amyl amines and with their hydrochlorides; the formation of ammonium chloride gave evidence that a reaction had taken place, but the products were exceedingly difficult to separate, and the matter of the aliphatic amines will be the subject of a later investigation.

Just as urea in many of its reactions acts like nascent isocyanic acid, so phenylurea acts like nascent phenylisocyanate. Hofmann[11] found that it yielded phenylurethane when heated with alcohol in a sealed tube at 150°. Since the formation of urethane from isocyanate and alcohol is a reversible reaction, it is to be expected that the urethane heated with an amine would yield a *sym*-di-substituted urea—as actually happened in the case where Dixon[12] prepared *sym*-dibutylurea by heating butylurethane with butylamine for 3 hours at 210–240°. We have heated phenol with phenylurea and with *sym*-diphenylurea, but have obtained no phenyl-phenylurethane in our experiments.

In the case of thio-urea we have examined the reversible reactions which are indicated below.



Nearly all of these reactions have been known for a long time, but the fact that they are reversible has not been emphasized. When thio-urea or ammonium thiocyanate is heated at 160° with aniline or with aniline hydrochloride, phenyl-thio-urea and *sym*-diphenyl-thio-urea are formed. The reaction with thio-urea has apparently not been noted heretofore.[13] During the course of these reactions, considerable hydrogen sulfide was given off. We are not able to account for this and are studying the matter further. Guanidine was found in the reaction product, and it may be that the hydrogen sulfide came from a reaction which led to the forma-

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[11] Hofmann, *Ber.*, **18**, 3228 (1885).

[12] Dixon, *J. Chem. Soc.*, **67**, 556 (1895).

[13] Schiff [*Ann.*, **148**, 338 (1868)] prepared phenyl-thio-urea by heating ammonium thiocyanate with aniline, and Clermont [*Ber.*, **9**, 446 (1876); **10**, 494 (1877)] by heating ammonium thiocyanate with aniline hydrochloride. Dixon, Ref. 12, prepared *iso*-amyl-thio-urea from the amine hydrochloride and potassium thiocyanate.

tion of this material. The separation and purification of the phenyl- and diphenyl-thio-urea involved a tedious fractional crystallization, made more difficult by the circumstance that thiocarbanilide, while apparently insoluble in water, dissolves to a considerable extent in water which contains phenyl-thio-urea in solution. During the manipulation of the substances the hot solutions smelled strongly of phenyl mustard oil, evidence that they dearrange to some extent even in solution, and probably one of the causes for poor yields.

Phenyl-thio-urea dearranges in two modes and, therefore, gives thiocarbanilide on heating. The odors of aniline, ammonia, and phenyl mustard oil are given from the product, and thiocyanic acid may be detected by ferric chloride. Thiocarbanilide dearranges in only one manner, to form phenyl mustard oil and aniline. These combine again, and, when thiocarbanilide is distilled, the distillate consists of thiocarbanilide contaminated with phenyl mustard oil enough to smell but not enough to isolate. The preparation of phenyl mustard oil by the distillation of thiocarbanilide with strong hydrochloric acid probably does not depend upon the fact that the acid attacks the thiocarbanilide, but depends rather upon the fact that the acid combines with the aniline which is formed by the spontaneous dearrangement of the thiocarbanilide and leaves the phenyl mustard oil free to escape.

Guanidine differs from urea in having an imino group in place of the oxygen, and may be prepared from ammonia and cyanamide,[14] by a method entirely analagous to the preparation of urea from ammonia and isocyanic acid. Of the formulas for tautomeric cyanamide, one corresponds to *cyan-ammonia*, NH_2CN, and the other to *isocyanimic* acid, HNCNH. Cyanamide is a derivative of the "cyanic" acid which combines with ammonia to form urea, a fact which we take to be excellent evidence that the isocyanic acid formula, HNCO, is probably correct for the "cyanic" acid which is involved in urea formation. "Cyanic" acid is undoubtedly a mixture of tautomers: isocyanic acid is the tautomer of interest for the present discussion.

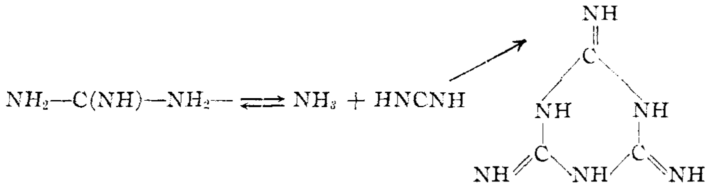
The similarity between guanidine and urea is further indicated by the fact that nitrous acid in cold solution removes ammonia from guanidine and leaves cyanamide.[15] If nitrosoguanidine, which may be regarded as guanidine nitrite minus water, is dissolved in water and warmed, nitrogen escapes and cyanamide remains in solution.

We find that guanidine undergoes the urea dearrangement. Since guanidine itself is deliquescent and difficult to prepare in a state of purity, we have worked with the carbonate. When this substance is heated strongly in a test-tube, ammonia is given off and cyanamide may be de-

[14] Erlenmeyer, *Ann.*, **146,** 259 (1868). Volhard, *J. prakt. Chem.*, [2] **9,** 21 (1874).

[15] Pellizari, *Atti. accad. Lincei.*, **30,** I, 171 (1921).

tected in the residue by testing with ammoniacal silver nitrate. When it is heated in a sublimation apparatus, the first portions of the sublimate contain considerable guanidine carbonate while the latter portions consist almost entirely of melamine, the tri-mer of cyanamide.

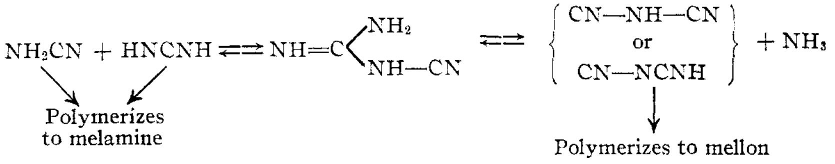


$$NH_2—C(NH)—NH_2 \rightleftharpoons NH_3 + HNCNH$$

We have not been able to prepare phenylated guanidines by heating guanidine and aniline. Melamine was found in the reaction mass, and the aniline was recovered quantitatively. The use of the dearrangement of guanidine as a means of synthesis will be studied further.

Since cyanamide is at once a derivative of ammonia and a derivative of isocyanic acid, since it is both cyan-ammonia and isocyanimic acid, it is natural that it should combine with itself, in the same way that ammonia combines with isocyanic acid, to form a derivative of urea in which the cyan group of the cyan-ammonia and the imino group of the isocyanimic acid will be found each in its proper place. It has long been known that cyanamide "polymerizes"[16] when its aqueous solution is evaporated, to form dicyanodiamide or cyanoguanidine. We believe that this polymerization is a case of the urea rearrangement.

Dicyanodiamide dearranges in two modes. When it is heated,[17] ammonia comes off, melamine sublimes, a golden yellow residue of mellon, $C_6H_3N_9$, evidently the tri-mer of dicyanimide (C_2HN_3) remains, and cyanamide may be detected in it by testing with ammoniacal silver nitrate.



$$NH_2CN + HNCNH \rightleftharpoons NH=C\begin{cases}NH_2\\NH—CN\end{cases} \rightleftharpoons \left\{\begin{matrix}CN—NH—CN\\ \text{or}\\ CN—NCNH\end{matrix}\right\} + NH_3$$

Dicyanodiamide, heated with guanidine carbonate, yields melamine,[18] a result which we suppose to be due to the combination of the dicyanodiamide with cyanamide from the dearrangement of the guanidine. The explanation of the formation of melamine when ammonia water and dicyanodiamide are heated together which was given in an earlier paper[19]

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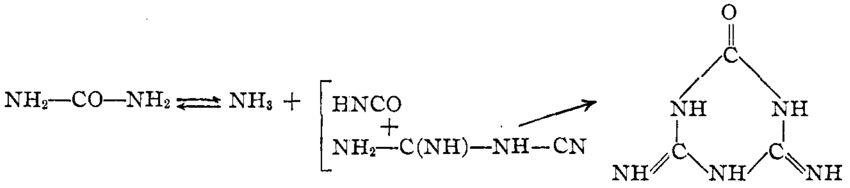
[16] Beilstein and Geuther, *Ann.*, **108**, 99 (1858); **123**, 241 (1862). Ulpiani, *Gazz. chim. ital.*, **38**, II, 381, 398 (1908).

[17] Drechsel, *J. prakt. Chem.*, [2] **13**, 331 (1876). For a different interpretation of these changes compare Franklin, THIS JOURNAL, **44**, 486 (1922).

[18] Smolka and Friedreich, *Monatsh.*, **10**, 93 (1889).

[19] Davis, THIS JOURNAL, **43**, 2230 (1921).

is, therefore, probably wrong. A portion of the dicyanodiamide is hydrolyzed by the action of the ammonia to yield first guanylurea and later guanidine, the guanidine dearranges to form cyanamide which combines with the unaltered dicyanodiamide to yield melamine. We have tested this explanation by heating dicyanodiamide with urea, with thio-urea, and with ammonium thiocyanate. Isocyanic acid is produced by the dearrangement of urea; and, since it is chemically similar to cyanamide, it was expected that it would combine with dicyanodiamide in the same manner that cyanamide does, to yield a substance which differs from melamine by having an oxygen in place of one of the imino groups. We find that this is the case: dicyanodiamide heated at 160° with urea yields ammeline.



Similarly, dicyanodiamide heated with thio-urea or with ammonium thiocyanate[20] yields thio-ammeline.

Discussion of Experiments

Aniline and Urea.—Ninety-three g. of aniline and 60 g. of urea were heated under a reflux air-condenser in the oil-bath for 1 hour at 160°. The urea first melted and formed a heavy layer beneath the aniline, but this layer soon disappeared, the mass bubbled up, and ammonia was given off in abundance. At the end of an hour of heating the evolution of ammonia had practically ceased except when the mixture was shaken. The mass solidified on cooling. It was broken up under warm water, and filtered. The aqueous filtrate contained some aniline, and was distilled with steam. As the aniline passed off, crystals precipitated in the liquid. These, filtered off and recrystallized from alcohol, yielded 2.1 g. of pure *sym*-diphenylurea, m. p. 235°, identified by a mixed melting point with a sample prepared synthetically from phosgene and aniline. The steam distillate, shaken out with ether, etc., yielded 18.2 g. of aniline, b. p. 179–182°. The crystals from the treatment with warm water were boiled with 200 cc. of 50% alcohol and filtered hot. The undissolved portion consisted of practically pure *sym*-diphenylurea, and yielded, after recrystallization from alcohol, 18.5 g. of the pure material. The 50%-alcohol liquors by systematic fractionation yielded an additional 5.0 g. of *sym*-diphenylurea and 21.8 g. of phenylurea, stout needles from water, m. p. 147°, identified by a mixed melting point with a sample of material on hand. In this experiment 19.9% of the aniline was recovered unchanged and 40.2% of it appeared in the form of phenylated urea.

Six g. of urea and 20 g. of aniline (more than 2 equivalents) were heated together similarly for 1 hour at 160°. The hot liquid, poured into 200 cc. of alcohol, gave an immediate crystalline precipitate of *sym*-diphenylurea. This, recrystallized from alcohol, yielded 6.1 g. of the pure material. The alcohol filtrates, distilled with steam for the removal of aniline and alcohol, yielded an additional 1.4 g. of diphenylurea, and, by

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[20] The reaction with urea has been noted [Smolka and Friedreich, *Monatsh.*, **11**, 42 (1890)] and that with thiocyanic acid [Rathke, *Ber.*, **18**, 3106 (1885); **20**, 1059 (1887)].

evaporation, 2.3 g. of phenylurea. The yield of phenylated ureas here corresponds to 52.3% of the urea which was used.

Six g. of urea and 30 g. of aniline (more than 3 equivalents) were heated together for 5 hours at 160°. The mass deposited crystals during the heating, and at the end of 5 hours ammonia was still coming off slowly. With the help of alcohol the cold material was broken up and transferred to a large flask where it was distilled with steam for the removal of aniline and alcohol. When the crystals were filtered off, rinsed, and dried, they amounted to 17.3 g. of slightly brownish but practically pure *sym*-diphenylurea, m. p. 234–235°. The aqueous liquors yielded 1.2 g. of phenylurea. The yield of phenylated ureas in this experiment corresponds to 81.0% of the urea which was used.

Effect of Heat on Phenylurea.—One and a half g. of phenylurea was heated in a test-tube in an oil-bath at 160°. The material melted, but the hot liquid began to deposit crystals within half an hour. A piece of red litmus paper in the condenser was turned blue. After 2 hours' heating the mass was almost solid, and the hot material had an odor of ammonia and of aniline. Taken up in hot 50% alcohol, it yielded 0.9 g. of *sym*-diphenylurea (77%).

When a small quantity of phenylurea was heated over a free flame, it melted and the colorless liquid presently began to effervesce violently with the liberation of ammonia. When the residue was extracted with cold water, the water gave a white precipitate of silver cyanate when silver nitrate was added.

***sym*-Di-β-naphthylurea.**—When 15 g. of β-naphthylamine and 3 g. of urea were heated at 160°, the molten material did not mix but remained in 2 phases. The mass effervesced with the liberation of ammonia, and at the end of half an hour it was swollen with gas bubbles and had practically solidified. The heating was continued for half an hour longer. The reaction product, broken up with water, digested with dil. hydrochloric acid, filtered off, washed, and dried, still contained naphthylamine and was, therefore, washed thoroughly with warm alcohol; it yielded 7.1 g. of *sym*-di-β-naphthylurea, m. p. 296° with decomposition (45.5%). Beilstein reports m. p. 293°. The substance is sparingly soluble in the usual organic solvents, including acetone, amyl acetate, and ethyl acetate. From these three it is deposited in the form of fine white needles.

***sym*-Di-α-naphthylurea.**[21]—When 10 g. of urea and 72 g. of α-naphthylamine (3 mols) were heated at 160° for 3 hours, and the material was washed thoroughly with alcohol, the product consisted of 39 g. (75% yield) of *sym*-di-α-naphthylurea, a white powder melting at 286°. Recrystallization of the product from ethyl acetate caused no change in the melting point..

Analysis. Calc.: N, 8.97. Found: 9.12.

***sym*-Di-*p*-tolylurea.**[21]—Five g. of *p*-toluidine and 1.4 g. of urea were heated at 160° for 2 hours. At the end of that time ammonia was still coming off. The mixture, recrystallized from alcohol, yielded 2.96 g. (53% yield) of *sym*-di-*p*-tolylurea as glistening flakes, m. p. 264°, identified by a mixed melting point with a sample prepared from phosgene and *p*-toluidine.

***sym*-Di-*o*-tolylurea.**[21]—Ten and four-tenths g. of *o*-toluidine and 2.8 g. of urea were heated at 160° for 7 hours. The evolved ammonia was collected in standard hydrochloric acid, and was found to correspond to 80% of the theoretical amount. The 8.68 g. of di-*o*-tolylurea corresponded to a 77.5% yield; m. p. 248°.

Reaction of Urea with Secondary Amines.—Diphenylamine and urea were heated together, first at 160°, then at 180°; ammonia was given off very slowly, and the materials remained liquid in separate phases. The diphenylamine was removed by distillation with steam. The residue, which showed a faint purplish fluorescence, contained an ***unsym***-diphenylurea, and no biuret. Cyanuric acid was evidently present in small amount.

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[21] These experiments were carried out by W. M. Perry.

Urea and mono-ethylaniline do not mix when heated together at 160°. From such an experiment the ethylaniline was recovered almost completely.

Both primary and secondary aliphatic amines will be discussed, it is hoped, in a later paper.

Aniline and Thio-urea.—Seventy-six g. of thio-urea and 93 g. of aniline (1 mol of each) were heated in an oil-bath at 160–165° for 4 hours. Hydrogen sulfide came off in abundance, and large orange-brown crystals[22] collected in the condenser. After 4 hours' heating the mixture was still effervescing actively. The heating was continued for an hour longer at 170–175°. The reaction product was broken up under alcohol and fractionally crystallized from alcohol, from alcohol and water, and from water. There were obtained 3.4 g. of *sym*-diphenyl-thio-urea, or thiocarbanilide, as pearly leaflets from alcohol, m. p. 153.0–153.5° (identified by a mixed melting point with a sample prepared by the usual method from carbon disulfide and aniline), and 17.4 g. of phenyl-thio-urea as needles from water, m. p. 153°. For the identification of the phenyl-thio-urea, 1 g. of the substance was dissolved in 10 cc. of strong hydrochloric acid, and the solution was distilled slowly. The distillate gave the odor of phenyl mustard oil and contained a few oily droplets. The residue in the distillation flask, treated with water and filtered yielded material from which 0.6 g. of phenyl-thio-urea was recovered, and the filtrate, made alkaline with caustic soda, liberated a gas which had the odor of ammonia and turned litmus paper blue. The yield of phenylated thio-ureas in this experiment corresponds to 12.9% of the thio-urea which was used.

Thirty-eight g. of thio-urea and 64.7 g. of aniline *hydrochloride* (half a mol. of each) were heated for $2^1/_2$ hours at 160°. The material melted at first, but solidified again during the heating. There were obtained 2.7 g. of phenyl-thio-urea and 7.0 g. of thiocarbanilide, corresponding to 9.7% of the thio-urea which was used.

Aniline and Ammonium Thiocyanate.—Seventy-six g. of ammonium thiocyanate and 96 g. of aniline were heated together for 2 hours at 160°; 19.3 g. of aniline (20.8%) was recovered from the reaction mixture. Fractional crystallization yielded 2.0 g. of thiocarbanilide and 24.1 g. of phenyl-thio-urea, corresponding to 16.8% of the ammonium thiocyanate which was used.

Effect of Heat on Phenyl-thio-urea.—Three g. of phenyl-thio-urea was heated for 2 hours at 160°. Gas bubbles came off, and hydrogen sulfide was detected by means of lead acetate paper. The product was a yellowish oil which had the odor of hydrogen sulfide, of aniline, and of phenyl mustard oil. Worked up from 50% alcohol, it yielded 0.8 g. of thiocarbanilide.

Three g. of phenyl-thio-urea and 3 cc. of aniline heated similarly for 2 hours at 160° gave no gas bubbles, and the reaction product, when cold, was a solid which had the odor of ammonia, of hydrogen sulfide, and of phenyl mustard oil. From dil. alcohol it yielded 1.0 g. of thiocarbanilide.

A small quantity of phenyl-thio-urea, heated in a test-tube, melted and effervesced. The odors of ammonia, of aniline, and of phenyl mustard oil could be detected. The residue treated with water gave the characteristic thiocyanate red with ferric chloride. Thiocarbanilide, after the same treatment, did not give the red color.

Distillation of Thiocarbanilide.—Two lots of 50 g. each of thiocarbanilide were distilled, one alone and one in a current of hydrogen chloride. Offensive odors were produced. The distillate in each case consisted of a white crystalline solid which

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[22] These were crystals of *ammonium sulfide* and phenyl-thio-urea. They were deliquescent. Their water solution dissolved sulfur, gave hydrogen sulfide on treatment with acid, and yielded phenyl-thio-urea when allowed to evaporate spontaneously. Whether they were mixed crystals or crystals of an addition compound we have not determined.

smelled strongly of phenyl mustard oil. They were distilled separately with steam. The turbid distillates gave a strong odor of phenyl mustard oil, but none of this material could actually be isolated. The solid material which remained after the steam distillation was found to be practically pure thiocarbanilide. A small portion of the material from the distillation in hydrogen chloride was found to be soluble in water: this was identified as aniline hydrochloride.

Phenol and Phenylated Urea.—When 2.76 g. of phenol and 2 g. of phenylurea were heated together for 6 hours at 170–180°, ammonia was evolved during the heating. The reaction product, distilled with steam for the removal of phenol, yielded 0.96 g. of *sym*-diphenylurea. There was no evidence of phenyl-phenylurethane.

Ten g. of *sym*-diphenylurea and 15 g. of phenol were boiled together for an hour in an all-glass reflux apparatus, and yielded, after the phenol had been removed by distillation with steam, 9.1 g. of the original diphenylurea. There was no evidence of phenyl-phenylurethane.

Effect of Heat on Guanidine.—Guanidine carbonate was prepared by mixing in equimolecular quantities an alcoholic solution of guanidine nitrate with an alcoholic solution of sodium ethylate. Sodium nitrate precipitated, and guanidine remained in the alcohol solution. After filtration, the alcohol was saturated with carbon dioxide until precipitation was complete. The white finely crystalline precipitate of guanidine carbonate, filtered off and washed with alcohol, gave only a faint test for nitrate with the diphenylamine reagent. By recrystallization from water, large, transparent, colorless crystals of guanidine carbonate were obtained which gave no test for nitrate.

When guanidine carbonate was heated carefully in a test-tube, it decrepitated, gave off ammonia without melting, and yielded a white sublimate. Heated more strongly, it gave ammonia and the same sublimate and left a golden-yellow residue which melted on stronger heating and decomposed giving off gas and leaving a buff-colored solid. After the strong heating, the test-tube was rinsed with a few cubic centimeters of cold water. This gave a yellow precipitate of silver cyanamide with ammoniacal silver nitrate. It gave no test for biguanide.

A sublimation apparatus was constructed from a wide-necked flat-bottomed flask, the stopper of which carried a test-tube through which water was circulated. Guanidine carbonate was spread out on the bottom of the flask, and heat was applied by means of a sand-bath. The heating was continued for several days at such a rate that slow sublimation took place. At first ammonia fumes were produced and a liquid condensate which crystallized on cooling. These crystals were readily soluble in water; they effervesced with hydrochloric acid, and gave with ammonium picrate a yellow crystalline precipitate, m. p. 318° with blackening: hence they were guanidine carbonate. After a few hours no more of this material was condensed, but a white pulverulent sublimate was collected, readily soluble in hot water, sparingly in cold. A cold water extract of this sublimate gave a test for cyanamide with ammoniacal silver nitrate. The sublimate recrystallized from water gave transparent rhomb-shaped plates. These sublimed without melting, but on strong heating melted to yield a white sublimate and a yellow residue. Their water solution gave a blue precipitate with copper sulfate, and with silver nitrate a white precipitate soluble in hot water from which it crystallized as a white, finely granular mass. This granular mass, boiled with conc. silver nitrate solution, dissolved, and the solution on cooling deposited needles which were converted by ammonia water into an amorphous powder soluble in an excess of ammonia water. The sublimate, therefore, was melamine along with a little cyanamide.

The formation of cyanamide by the dearrangement of dicyanodiamide may be demonstrated nicely by heating a small quantity of that material in a test-tube until violent decomposition sets in at a temperature slightly above the melting point. If the tube is rinsed out with water, the solution with ammoniacal silver nitrate gives a yellow precipitate of silver cyanamide.

Aniline and Guanidine.—Two g. of guanidine carbonate and 4.18 g. of aniline were heated at 170° to 180° for 5 hours. Ammonia was evolved. By distillation with steam 3.9 g. or 95% of the original aniline was recovered. There remained 0.7 g. of a sparingly soluble material which was identified as melamine by the tests which have been described above.

Reaction of Dicyanodiamide with Urea, Thio-urea, and Ammonium Thiocyanate.[23]—Twenty g. of dicyanodiamide and 14.5 g. of urea were heated together for 2 hours at 150°. The material sintered but did not melt completely; ammonia was given off and the mass solidified during the heating. The cake, broken up under boiling water, yielded 8 g. of ammeline, a white powder insoluble in hot water, soluble in cold caustic soda solution, soluble in hot sodium carbonate solution and deposited again when the solution cools. The aqueous filtrate, evaporated to a small volume and treated with ammonium picrate, yielded 0.5 g. of guanidine picrate, m. p. 315°.

A higher temperature gave better yields. Three g. of dicyanodiamide and 4.3 g. of urea, when heated at 160° for 2 hours, melted completely but solidified again during the heating, and yielded 2.1 g. of ammeline and no detectable guanidine. Three g. of dicyanodiamide and 2.15 g. of urea gave 2.3 g. of ammeline.

When 10 g. of dicyanodiamide and 9.5 g. of thio-urea were heated at 160° for 2 hours, ammonia and hydrogen sulfide were given off slowly. The cake, broken up under boiling water, yielded 1.5 g. of thio-ammeline, a white powder insoluble in hot water, soluble in cold caustic soda solution, and soluble in hot sodium carbonate solution from which it is deposited again when the solution cools. The aqueous filtrate gave only a faint precipitate with ammonium picrate.

Ten g. of dicyanodiamide and 9.5 g. of ammonium thiocyanate were heated at 160° for 15 minutes. The mass melted promptly, a vigorous reaction set in, ammonia and hydrogen sulfide came off in abundance, and the material quickly solidified. Two and a half g. of thio-ammeline was obtained, and the filtrates with ammonium picrate gave 0.5 g. of a precipitate which was evidently not pure guanidine picrate. Its melting point could not be observed as it began to darken at 230° and was apparently completely charred at 260°.

Summary

Urea, thio-urea and guanidine, and derivatives of these substances, undergo the "urea dearrangement." Just as urea yields ammonia and isocyanic acid, so these compounds yield derivatives of ammonia and derivatives of isocyanic acid. A recognition of this fact leads to the understanding and correlation of a large number of otherwise diverse reactions. It is the basis of a number of syntheses.

The heating of urea with primary aromatic amines is a convenient method for the preparation of symmetrical di-substituted aromatic ureas. The application of the reaction in the aliphatic series is now being studied.

The similarity between guanidine and urea, and between cyanamide and isocyanic acid, has been pointed out in a number of reactions. The polymerization of cyanamide to dicyanodiamide has been interpreted.

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[23] These experiments were carried out by William S. Johnson.