[Contribution from the Research Division, Stamford Research
Laboratories, American Cyanamid Company]

CHEMISTRY OF DICYANDIAMIDE. I. CARBALKOXY-CYANAMIDES AND -DICYANDIAMIDES

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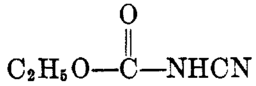
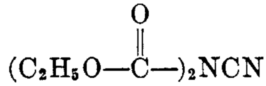
A new field of cyanamide derivatives resulted from investigation of a spontaneous reaction which occurred during a study of the chemistry of cyanamide. This paper deals with this preliminary work from which grew the successful reactions of dicyandiamide with acyl halides and anhydrides (1), sulfonyl halides (2), carbon disulfide (3), and cyanogen chloride (4). It is planned to discuss the interesting chemistry of the above derivatives in future papers.

The particular reaction which initiated this research was the spontaneous decomposition of carbethoxycyanamide (I). Examination of the literature revealed that a rather thorough study of both carbethoxy- and dicarbethoxy-cyanamide (II) had been made in 1877 by Bässler (5). In his study of the properties and reactions of carbethoxycyanamide, Bässler stressed the instability of the compound and the fact that freshly prepared samples rapidly deposited an amorphous or crystalline solid. Bässler unfortunately was not able to purify satisfactorily and/or analyze this unknown solid. Analytical difficulties for this compound were also encountered in this laboratory. For some unknown reason subsequent workers (6, 7) failed to comment on the instability of carbethoxycyanamide. A German patent (6) did, however, simplify the method of preparation.



$$C_2H_5O\text{—}\overset{\overset{O}{\|}}{C}\text{—}NHCN$$

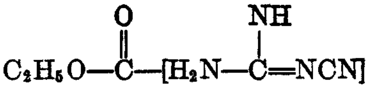
I



$$(C_2H_5O\text{—}\overset{\overset{O}{\|}}{C}\text{—})_2NCN$$

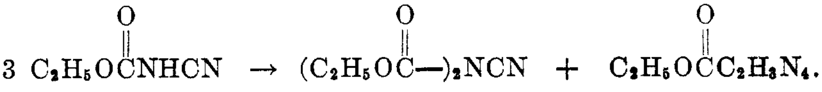
II

In the present work carbethoxycyanamide was isolated as a light yellow liquid which deposited solid by the following day. Deposition of solid continued to occur but ceased within a month. Crystallization from hot water gave slender needles which were identified as carbethoxydicyandiamide (III), subsequently prepared from dicyandiamide and ethyl chlorocarbonate. Examination of the residual liquid revealed that it was now dicarbethoxycyanamide. The over-all reaction could be represented as shown:



$$C_2H_5O\text{—}\overset{\overset{O}{\|}}{C}\text{—}[H_2N\text{—}\overset{\overset{NH}{|}}{C}{=}NCN]$$

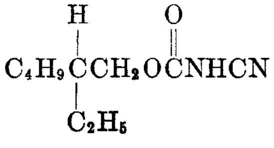
III



$$3\ C_2H_5O\overset{\overset{O}{\|}}{C}NHCN \rightarrow (C_2H_5O\overset{\overset{O}{\|}}{C}\text{—})_2NCN + C_2H_5O\overset{\overset{O}{\|}}{C}C_2H_3N_4.$$

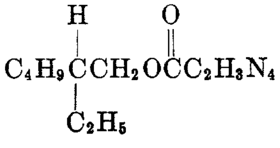
To learn whether the mechanism involved the intermediate formation of cyanamide, freshly prepared carbethoxycyanamide was heated with cyanamide in alcohol. Carbethoxydicyandiamide was not obtained and the product appeared to be a cyanamide-carbethoxycyanamide salt.

It was not ascertained whether the decomposition of carbalkoxycyanamides was a general reaction, although carbo-2-ethylhexoxycyanamide (IV) was found also to yield the dicyandiamide derivative V.



$C_4H_9\underset{C_2H_5}{\overset{H}{C}}CH_2O\overset{O}{\overset{\|}{C}}NHCN$

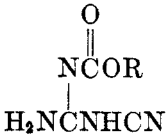
IV



$C_4H_9\underset{C_2H_5}{\overset{H}{C}}CH_2O\overset{O}{\overset{\|}{C}}C_2H_3N_4$

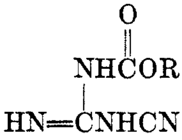
V

A somewhat questionable preparation of carbethoxydicyandiamide has been described by Pinck and Blair (7). The yield was not stated but must have been low and the only identification was a nitrogen analysis plus determination of refractive indices. In the present work the procedure of Pinck and Blair was repeated and a minute quantity of product was obtained whose refractive indices were consistent with those described (7). The refractive indices of carbethoxydi-



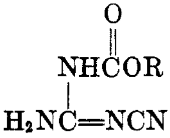
$H_2N\overset{N\overset{O}{\overset{\|}{C}}OR}{\overset{|}{C}}NHCN$

VI



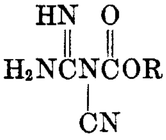
$HN{=}\overset{NH\overset{O}{\overset{\|}{C}}OR}{\overset{|}{C}}NHCN$

VII



$H_2N\overset{NH\overset{O}{\overset{\|}{C}}OR}{\overset{|}{C}}{=}NCN$

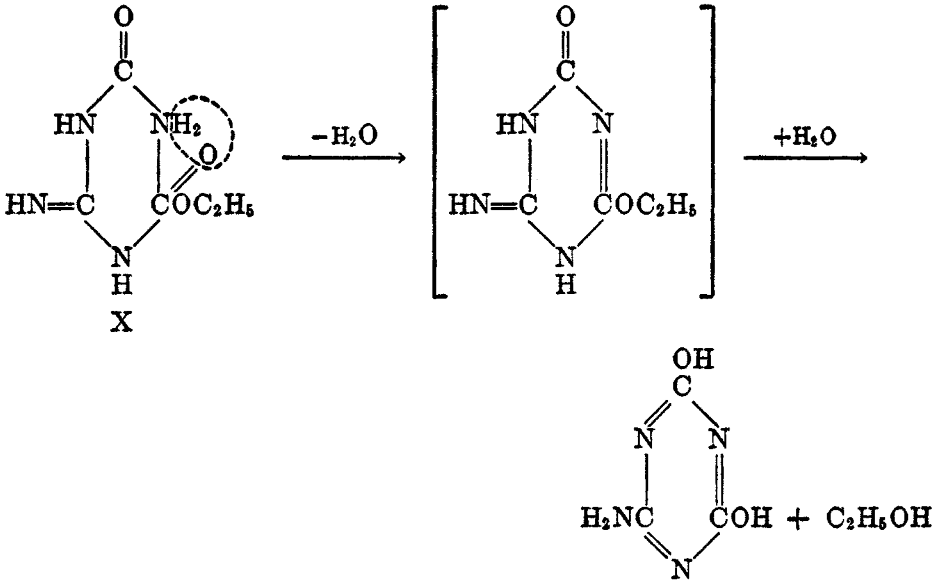
VIII



$H_2N\underset{CN}{\overset{HN}{\overset{\|}{C}}}N\overset{O}{\overset{\|}{C}}OR$

IX

R = alkyl

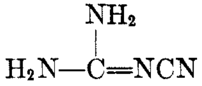


X

XI

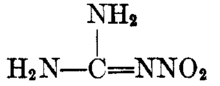
cyandiamide prepared in the present work were different from those described by Pinck and Blair. These data indicated but did not conclusively prove that the above authors did not isolate carbethoxydicyandiamide.

The problem of assigning a structure to carbalkoxydicyandiamides is complex since structures VI–IX are all theoretically possible. Structure IX, however, was immediately eliminated since carbethoxyguanylurea (X), prepared by acid hydrolysis of carbethoxydicyandiamide, could be cyclized to ammelide (XI). This reaction is only possible with structures VI–VIII, barring migration of the carbethoxy group. Of these three remaining tautomeric forms, VIII is preferred and will be employed to represent carbalkoxydicyandiamides. This formula is in agreement for a derivative prepared from the non-ionic structure of dicyandiamide (XII) as discussed by Hughes (8). In substantiation of Hughes' structure for dicyandiamide (2-cyanoguanidine) similar conclusions, based on different evidence, regarding an analogous-type structure of another negatively substituted guanidine [2-nitroguanidine (XIII)] have recently been presented (9). Form VIII probably predominates but hydrogen atoms undoubtedly shift with formation of derivatives, such as the guanylureas.



$$H_2N-\overset{\overset{NH_2}{|}}{C}=NCN$$

XII



$$H_2N-\overset{\overset{NH_2}{|}}{C}=NNO_2$$

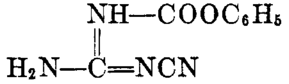
XIII

In addition to carbethoxydicyandiamide, a number of carbalkoxydicyandiamides were prepared from dicyandiamide and chlorocarbonates. It was found that successful acylation of dicyandiamide was dependent upon the presence of an organic solvent such as acetone.

Reaction of dicyandiamide with an acid chloride can be likened to acylation of an amino acid. Two equivalents of base are required. One destroys the zwitterion by forming a salt, which although highly hydrolyzed (10) brings out the basicity of the guanyl group. The second equivalent acts as the acid acceptor. After reaction, the dicyandiamide molecule, now containing an additional negative substituent, has become a stronger acid and is obtained as a salt.

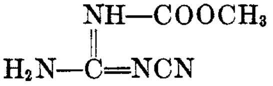
Not all of the carbalkoxydicyandiamides could be converted to the corresponding guanylureas since hydrolysis of the carbalkoxy group occurred.

One interesting phenomenon was observed in that carbophenoxydicyandiamide (XIII) could not be recrystallized. It was hydrolyzed by water, insoluble in most organic solvents, and attempted recrystallization from aqueous methanol gave carbomethoxydicyandiamide (XIV) plus some diphenyl carbonate which may have been formed during reaction.



$$H_2N-\overset{\overset{NH-COOC_6H_5}{\|}}{C}=NCN$$

XIII



$$H_2N-\overset{\overset{NH-COOCH_3}{\|}}{C}=NCN$$

XIV

Acknowledgment. The authors wish to thank Dr. J. A. Kuck under whose direction analyses were conducted, Dr. A. F. Kirkpatrick for crystallography data, Miss D. Holm-Hansen for helpful assistance with certain of the prepara-

tive work, Mr. N. B. Colthup for infrared spectra, and Mr. W. H. Montgomery for conducting the pressure reaction.

EXPERIMENTAL[1]

I. REACTIONS OF CHLOROCARBONATES

A. With cyanamide. Carbethoxycyanamide (I), *carbethoxydicyandiamide* (III), *and dicarbethoxycyanamide* (II). A modified procedure of a German patent (6) was employed. One mole (108.5 g.) of ethyl chlorocarbonate was gradually added with stirring to 44.6 g. (1.0 mole) of 94% cyanamide and 84 g. (2.0 moles) of 95% sodium hydroxide in 750 ml. of water. The temperature was maintained below 20°. Stirring was continued for 30 minutes, chloroform was then added, the mixture cooled, and acidified with 100 g. of concentrated hydrochloric acid. The chloroform layer was separated and dried over sodium sulfate. Removal of the solvent under reduced pressure gave 101 g. (88.5%) of carbethoxycyanamide as a light yellow oil of ethereal odor which gave a strongly acidic reaction when dissolved in water. The following day it was observed that solid had separated, which after filtering, washing with acetone, and drying weighed 15 g. The filtrate was allowed to stand further. Another run, employing 2.4 times the quantities used above, was made at this time, giving an 88% yield of carbethoxycyanamide. Within a day 16 g. of solid had formed. The preparations were then combined and after a month a total of 120 g. (77%) of carbethoxydicyandiamide was collected. Crystallization from hot water gave fine colorless needles. On gradual heating melting did not occur up to 360°, but decomposition occurred when a sample was immersed at 225°. Solubility in ether was negligible and the compound gave an acidic reaction to litmus paper in water solution. The material was readily dissolved by alkali or ammonia and reprecipitated by acids, and formed a colorless, insoluble silver salt in the presence of ammonia.

Anal. Calc'd for $C_5H_8N_4O_2$: C, 38.46; H, 5.12; N, 35.89.
Found: C, 38.79;[2] H, 5.21; N, 35.83.

A portion of the residual liquid, after removal of all of the carbethoxydicyandiamide, was poured into water, giving a heavy oil. According to Bässler (5), dicarbethoxycyanamide is water-insoluble and melts at 32.8°. Solid sodium bicarbonate was added, liberating a small amount of carbon dioxide, and the oil was extracted with ether. The ethereal solution was thoroughly washed with water and allowed to evaporate in a vacuum desiccator. The next day a mixture of oil and solid was present (room temp. 30°). On slight cooling the entire mass solidified to a colorless solid.

For better identification, 5 g. of the dicarbethoxycyanamide was hydrolyzed according to the procedure of Diels and Gollmann (11). Recrystallization of the crude *unsym*-dicarbethoxyurea from methanol gave colorless crystals, m.p. 86–87°, in agreement with the literature value (11).

Carbo-2-ethylhexoxycyanamide (IV) *and carbo-2-ethylhexoxydicyandiamide* (V). 2-Ethylhexyl chlorocarbonate was isolated in 87% yield as a colorless liquid, b.p. 106–107°/30 mm. by following the procedure of Bergmann and Zervas (12) for the preparation of benzyl chlorocarbonate. The procedure as given in a German patent (6) for the preparation of carbethoxycyanamide was followed. To 22.4 g. (0.50 mole) of 94% cyanamide in 200 ml. of water was added 96.3 g. (0.50 mole) of 2-ethylhexyl chlorocarbonate. A few drops of phenolphthalein solution were added, the stirred mixture cooled to 10°, and 42 g. (1.0 mole) of 95% sodium hydroxide in 50 ml. of water added drop by drop. When a few ml. of alkali had been added, it was observed that the mixture remained alkaline. After addition of 100 ml. of acetone, reaction proceeded satisfactorily and the temperature was maintained at 10°. Acidification with a slight excess of hydrochloric acid liberated the carbo-2-ethylhexoxycyanamide as an oil which was extracted with chloroform. Removal of the solvent

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[1] All melting points are uncorrected.

[2] Best value of eight determinations.

gave a quantitative yield (99 g.) of colorless oil. Solid gradually deposited and at the end of 19 days, the pasty mixture was dissolved in a small volume of hot acetate. On cooling crystals separated (18 g.) and the filtrate, after removal of solvent, was again set aside. Two weeks later an additional 10 g. of solid was isolated. The now quite viscous liquid, presumed to be bis(carbo-2-ethylhexoxy)cyanamide, was not examined further. The total yield of carbo-2-ethylhexoxydicyandiamide (28 g.) represented a 77% conversion from the cyanamide. Another recrystallization from ethyl acetate gave colorless plates which decomposed at 139–140° in a preheated bath. On slow heating decomposition occurred at 131°.

Anal. Calc'd for $C_{11}H_{20}N_4O_2$: C, 55.00; H, 8.33; N, 23.33.
Found: C, 55.00; H, 8.45; N, 23.18.

B. With dicyandiamide. Carbethoxydicyandiamide (III). A slurry of 168 g. (2.0 moles) of dicyandiamide in one liter of acetone was stirred and cooled to 10°. After addition of 198 g. (3.0 moles) of 85% potassium hydroxide pellets, the mixture was vigorously stirred for an hour at 3°. The temperature was then kept below 10° while 162.8 g. (1.5 moles) of ethyl chlorocarbonate was slowly added. Stirring was continued an hour after removal of the ice-bath. The slurry was drowned in ice-water, the resulting solution acidified with excess acetic acid, the colorless solid filtered, washed with water, and air-dried. The crude yield was 163 g. (73%) and recrystallization from hot water gave slender, colorless needles, identical in appearance with the previously isolated sample of carbethoxydicyandiamide. Decomposition occurred at 225° on immersion at that temperature. The infrared spectra of both samples, run as a Nujol mull, were identical throughout the rock salt region. The refractive indices were: $\alpha = 1.395 \pm 0.003$; $\beta = 1.633 \pm 0.003$.

Carbo-2-ethylhexoxydicyandiamide (V). To a mixture of 8.4 g. (0.10 mole) of dicyandiamide and 19.3 g. (0.10 mole) of 2-ethylhexyl chlorocarbonate in 75 ml. of 66% acetone was added, with vigorous stirring at 30°, a solution of 8.4 g. (0.20 mole) of 95% sodium hydroxide in 25 ml. of water. The solution was acidified with acetic acid, and the solid filtered, washed with water, and dried. The crude yield was 14 g. (58%) and recrystallization from ethanol gave colorless plates identical in appearance to the purified product isolated from carbo-2-ethylhexoxycyanamide. Decomposition occurred at 139–140° in a preheated oil-bath and at 131° when gradually heated. Fusion with the previously described sample behaved in a similar manner. Infrared spectra of both samples run as a Nujol mull were identical throughout the rock salt region.

Carbobenzyloxydicyandiamide. A mixture of 132 g. (2.0 moles) of 85% potassium hydroxide, 126 g. (1.50 moles) of dicyandiamide, and 600 ml. of 50% acetone was placed in a flask equipped with a stirrer, thermometer, and addition funnel. The temperature was maintained at 0–5° while 170.5 g. (1.0 mole) of benzyl chlorocarbonate (12), in 50 ml. of acetone was slowly added. Dilution with water and acidification of the resulting solution with acetic acid gave 154 g. (70.5%) of colorless solid. Recrystallization from methanol produced broad plates, decomposing at 184–185°.

Anal. Calc'd for $C_{10}H_{10}N_4O_2$: C, 55.05; H, 4.59; N, 25.69.
Found: C, 55.00; H, 4.65; N, 25.77.

Carbocyclohexoxydicyandiamide. The chlorocarbonate was prepared from cyclohexanol by employing the procedure of Bergmann and Zervas (12) for benzyl chlorocarbonate. The compound was isolated in 89% yield as a colorless oil which was not distilled. A procedure similar to that used for carbobenzyloxydicyandiamide was employed and gave a quantitative crude yield of oily product. Recrystallization from methanol which contained about 15% of Cellosolve gave a 47% recovery of large plates which decomposed at 229–230°.

Anal. Calc'd for $C_9H_{14}N_4O_2$: C, 51.43; H, 6.67; N, 26.67.
Found: C, 51.30; H, 6.88; N, 26.69.

Carbophenoxydicyandiamide (XIII) *and carbomethoxydicyandiamide* (XIV). To a stirred mixture of 132 g. (2.0 moles) of 85% potassium hydroxide, 126 g. (1.50 moles) of dicyandiamide, and 600 ml. of 50% aqueous acetone was added 156.5 g. (1.0 mole) of phenyl chlorocarbonate in 50 ml. of acetone at 4–6°. After addition, water was added giving a milky solution which was slowly acidified with acetic acid. Solid began precipitating immediately but when almost all of the acid was added, carbon dioxide was evolved. The pasty solid was filtered, washed with water, and allowed to air-dry overnight. On the following day the damp material was dissolved in hot methanol which contained about 10% Cellosolve.

After treatment with decolorizing charcoal, the warm filtrate was diluted with a small quantity of water. The first crop of solid, consisting of a mixture of needles and chalky solid, weighed 48 g. and decomposed at 206°, with softening below this temperature. Dilution of this filtrate with additional water gave 4 g. of colorless needles which melted at 79–80°. A sodium fusion of this latter material gave negative results for the presence of nitrogen. When a portion was boiled with alkali and acidified, carbon dioxide was evolved and an oil smelling of phenol separated. This compound was undoubtedly diphenyl carbonate whose m.p. is 80° (13). Recrystallization of the first crop of solid from methanol gave 16 g. of colorless plates. Dilution of this filtrate precipitated an additional 15 g. of diphenyl carbonate. The 16 g. of material, after another recrystallization, did not possess a sharp decomposition point on gradual heating; however, when immersed in an oil bath at 230° rapid decomposition occurred. Analysis gave values in agreement for carbomethoxydicyandiamide.

Anal. Calc'd for $C_4H_6N_4O_2$: C, 33.80; H, 4.26; N, 39.42.
Found: C, 33.98; H, 4.40; N, 39.39.

For further identification, 5 g. of the solid was added to 15 ml. of concentrated hydrochloric acid. A vigorous exothermic reaction occurred and an amorphous solid separated. Solution occurred on addition of 20 ml. of water and heating. On cooling colorless plates separated which after recrystallization from ethanol decomposed at 180–181°. A positive guanylurea type color test was obtained with copper sulfate and base (14). Analysis gave values in agreement for carbomethoxyguanylurea hydrochloride.

Anal. Calc'd for $C_4H_8N_4O_3 \cdot HCl$: C, 24.44; H, 4.61; N, 28.58.
Found: C, 24.46; H, 4.68; N, 28.67.

Another attempt to prepare pure carbophenoxydicyandiamide was made, using the conditions described above. The crude yield of dry solid was 96.5% and the material decomposed to an infusible solid at 155°. As had been found, alcohols were unsuitable for crystallization and the compound was insoluble in anhydrous non-hydroxylated solvents. An attempt to employ 50% aqueous acetone was unsuccessful. The solid dissolved but carbon dioxide was evolved, free phenol was detected in the solution, and product did not separate on cooling.

II. HYDROLYSIS OF CARBALKOXYDICYANDIAMIDES

Carbethoxyguanylurea hydrochloride. Addition of 39 g. (0.25 mole) of carbethoxydicyandiamide to 60 g. (0.30 mole) of 18.5% hydrochloric acid produced an exothermic reaction. Complete solution occurred and the mixture refluxed. Heating was continued several minutes and the solution allowed to cool. Such a thick paste resulted that acetone was added to give a filterable slurry. Filtration and air-drying gave 45 g. (85.5%) of solid decomposing at 165°. Recrystallization from a small volume of hot water gave small, colorless crystals which decomposed at 171°.

Anal. Calc'd for $C_5H_{10}N_4O_3 \cdot HCl$: C, 28.50; H, 5.23; N, 26.60.
Found: C, 28.56; H, 5.33; N, 26.61.

Carbethoxyguanylurea (X). An equivalent of ammonium hydroxide was added to a slurry of 35.5 g. (0.17 mole) of carbethoxyguanylurea hydrochloride in 100 ml. of water. The mixture was stirred for a short time and the precipitated solid filtered, giving 29 g. or a quantitative yield of the base. Recrystallization from methanol gave fine needles which decomposed at 165°.

Anal. Calc'd for $C_5H_{10}N_4O_3$: C, 34.48; H, 5.75; N, 32.18.
Found: C, 34.37; H, 5.80; N, 32.29.

Ammelide (X). A slurry of 229 g. (1.31 moles) of carbethoxyguanylurea in 1300 ml. of water and 670 ml. of concentrated ammonium hydroxide was heated to boiling, giving a clear solution. On continued heating water and ammonia were allowed to escape and a solid separated which after filtering and drying gave 168 g. (85%) of infusible product. For purification a portion of the material was redissolved in hot ammonia solution, treated with decolorizing charcoal, filtered, and the filtrate concentrated. The finely divided product obtained in this manner was easily filtered. Use of sodium hydroxide in the cold as the cyclizing agent, followed by acidification with acetic acid, precipitated the ammelide in a form exceedingly difficult to filter, although the yield was 94%.

Anal. Calc'd for $C_3H_4N_4O_2$: C, 28.13; H, 3.13; N, 43.75.

Found: C, 28.21; H, 3.17; N, 43.91.

Attempted preparation of carbocyclohexoxyguanylurea. (a). A solution of 21 g. (0.10 mole) of carbocyclohexoxydicyandiamide in a mixture of 500 ml. of methanol and 100 ml. of Cellosolve was cooled to 10° and 10 g. (0.10 mole) of concentrated hydrochloric acid was added. The temperature rose to 15° and within a short time colorless plates began to separate. These were identified as starting material, probably precipitated by the water in the acid. The mixture was then heated on a steam-bath for five minutes and the solution poured onto ice. An oil separated which smelled similar to cyclohexanol. Diatomaceous earth was added and the mixture filtered to remove the oil. The clear filtrate gave a positive guanylurea test with copper sulfate and alkali (14) and treatment with ammonia did not precipitate ammelide. These facts indicated that the carbocyclohexoxy group had been removed and guanylurea hydrochloride had been formed.

(b). Complete solution occurred after refluxing a mixture of 10.5 g. (0.05 mole) of carbocyclohexoxydicyandiamide and 9.5 g. (0.05 mole) of *p*-toluenesulfonic acid monohydrate in 150 ml. of 2B-alcohol.[3] A short time later it appeared that a gas was being evolved and a small quantity of solid separated from solution. Refluxing was continued for 15 minutes and after standing overnight the solid was filtered from the solution which smelled of cyclohexanol. The solid weighed 2 g. and gave a positive guanylurea test (14). Unlike carbalkoxyguanylurea salts it could not be converted to ammelide and was probably guanylurea *p*-toluenesulfonate.

III. MISCELLANEOUS ATTEMPTS TO PREPARE CARBETHOXYDICYANDIAMIDE

A. From cyanamide. A solution containing 22.8 g. (0.20 mole) of freshly prepared carbethoxycyanamide and 8.9 g. (0.20 mole) of 94% cyanamide in 50 ml. of ethanol was refluxed for four hours during which time solid separated. The material was filtered, washed with acetone, and air-dried. The filtrate and acetone washings were combined and refluxed two hours longer without further deposition of solid. Concentration of the solution gave a residue of solid and oil which was triturated with acetone. The solid was filtered and washed with acetone. Both crops of solid decomposed at 187–191° and the total weight was 12.4 g. Mixture melting points with dicyandiamide [205° with decomposition (14)] and carbethoxydicyandiamide gave marked depressions. The substance was easily soluble in hot water but on cooling only a small portion separated. Treatment with ammoniacal silver nitrate solution gave a heavy, yellow precipitate of silver cyanamide. Since carbethoxydicyandiamide formed a colorless silver salt, the material was not examined further. The compound probably was a salt, $H_2NCN \cdot 2C_2H_5O\text{-}CO\text{-}NHCN$, similar to cyanamide dihydrochloride (15).

B. From dicyandiamide. Sodium dicyandiamide was prepared in 95.5% yield, following the general procedure of Bamberger (16) from dicyandiamide and sodium ethoxide. In this experiment the procedure of Pinck and Blair (7) was followed. A mixture of 15 g. of sodium dicyandiamide and 15 g. of ethyl chlorocarbonate in 150 ml. of anhydrous ether was heated at 90–100° for 48 hours in an autoclave. When removed from the autoclave, the mixture consisted of nearly colorless solid and liquid. The solid was filtered and washed well with ether. The combined filtrate and washings were evaporated, leaving an amorphous solid

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[3] Denatured ethyl alcohol.

and an oil smelling of diethyl carbonate. The less than a gram of solid was filtered and digested with a pound of ether. About half of the material dissolved and after filtration the clear filtrate was concentrated to a small volume, giving a nearly colorless, somewhat amorphous-appearing solid. The amount of material was very small, but sufficient to determine the refractive indices by the immersion method: $\alpha = 1.430 \pm 0.003$; $\beta = 1.543 \pm 0.003$; γ = not obtainable. Pinck and Blair recorded the following values: $\alpha = 1.432$; $\gamma = 1.618$. Although γ was not determined on carbethoxydicyandiamide prepared in this laboratory, the β value (1.633) was greater than the γ (1.618) recorded by Pinck and Blair. Since γ is always greater than β, γ for our material must be much greater than the γ reported by the above authors. The data, although incomplete, indicated that the product prepared by the Pinck and Blair procedure and their product were the same physical species, while carbethoxydicyandiamide, prepared in this laboratory was a different physicochemical phase.

SUMMARY

1. Carbethoxycyanamide has been found to decompose spontaneously into dicarbethoxycyanamide and carbethoxydicyandiamide.

2. Carbethoxydicyandiamide and several other carbalkoxydicyandiamides have been prepared from dicyandiamide and alkyl chlorocarbonates.

3. In aqueous methanol carbophenoxydicyandiamide formed carbomethoxydicyandiamide.

4. The structure and mode of formation of carbethoxydicyandiamide have been discussed.

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