The Reaction of Nitriles and Dicyandiamide

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Guanamine formations from dicyandiamide and nitriles[1-5] and their application to the preparation of various compounds[6,7] have been investigated by many workers, but the systematic investigation of the reaction of dinitriles with dicyandiamide has not yet been reported. This paper will, therefore, describe the formation of mono and diguanamines from dinitriles and dicyandiamide, the reaction of cyano groups in polymer molecules with dicyandiamide, and the chemical behavior of the cyano group of β-cyanopropioguanamine.

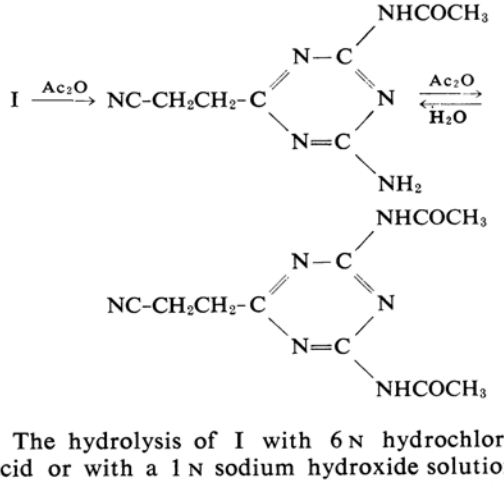
The reaction of one mole of succinonitrile and two moles of dicyandiamide with sodium methoxide as a catalyst in methanol gave an addition compound consisting of one molecule of each starting material instead of the expected succinoguanamine. The structure of the addition compound (I) was determined to be β-cyanopropioguanamine by identifying it with an authentic sample prepared from ethyl β-cyanopropionate and biguanide.

Succinoguanamine (II) was obtained by the reaction of I with dicyandiamide at 130—140°C in either dimethylformamide or methyl cellosolve in the presence of either sodium methoxide or potasium hydroxide. It was also identified with the authentic sample prepared from dimethyl succinate and biguanide. The reaction of one mole of succinonitrile and two moles of dicyandiamide at 130—140°C in methyl cellosolve in the presence of potassium hydroxide also gave succinoguanamine.

When the reaction of succinonitrile with dicyandiamide was carried out in methanol, I was precipitated from the reaction mixture in an almost pure state as a result of its insolubility to methanol, even if an excess dicyandiamide was employed. On the other hand, in methyl cellosolve, diguanamine was obtained with two moles of dicyandiamide and one mole of succinonitrile, or with one mole each of I and dicyandiamide. The reaction of each mole of succinonitrile and dicyandiamide in methyl cellosolve gave I, together with a trace amount of II.

The results suggest that mono and diguanamine selectively can be obtained from the dicyano compound and dicyandiamide, depending on the reaction temperature and solvent employed. Similar reactions of dicyandiamide with various nitriles were carried out under various reaction conditions; the results are summarized in Tables I and II. The yields of mono and diguanamines from dinitriles with odd numbers of methylene groups were comparatively low.

The acetylation of I with acetic anhydride gave mono and diacetyl derivatives. The diacetyl derivative was easily hydrolyzed to form the monoacetyl derivative by heating it in glacial acetic acid or water. This behavior is similar to that of acetoguanamine.[8]



The hydrolysis of I with 6 N hydrochloric acid or with a 1 N sodium hydroxide solution, followed by the neutralization of the reaction

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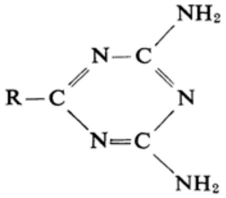
[1] A. Ostrogovich and Gh. Gheorghiu, *Gazz. chim. ital.*, **60**, 648 (1930).
[2] U. S. Pat. 2302162 (1942); *Chem. Abstr.*, **37**, 2016 (1943).
[3] Brit. Pat. 642409 (1950); ibid., **46**, 146 (1952).
[4] U. S. Pat. 2532519 (1950); ibid., **45**, 3429 (1951).
[5] Brit. Pat. 758601 (1956); ibid., **51**, 10594 (1957).
[6] H. J. Sims, H. B. Parseghian and P. L. de Benneville, *J. Org. Chem.*, **23**, 724 (1958).
[7] L. S. Luskin, P. L. de Benneville and S. Meland, ibid., **23**, 1082 (1958).
[8] A. A. Ryabinin, *Zhur. Obschchei Khim.*, **22**, 541 (1952).

TABLE I. SYNTHESIS OF MONOGUANAMINES



R-	Reaction time, hr.	Yield %	M. p. °C	Recryst. solvent	N, anal.	
					Found	Calcd.
CH_3-	a)	—				
C_2H_5-	a)	—				
$C_{13}H_{27}$-	4[a]	—[1]				
$C_{17}H_{35}$-	5[a]	Trace	Wax			
NC-CH_2-	a)	—[2]				
NC-$(CH_2)_2$-	1/4—1/2[a]	60—70	241.5—242.0	Water	51.47	51.19
NC-$(CH_2)_3$-	5[a]	10	163—167	Water	47.0	47.17
NC-$(CH_2)_4$-	6[a]	50	253—255 (d.)	50% MCS*	43.5	43.72
NC-$(CH_2)_7$-	2.5[b]	30[3]	195—199	85% methanol	36.8	35.87
C_6H_5-	7[a]	25	221—222			
o-NC-C_6H_4-	1/4—1/2[a]	60—85	230.5—231.5	Water	39.85	39.61
	2[b]	85				
m-NC-C_6H_4-	1[a]	65	265—273	50% MCS	39.6	39.61
	1[b]	80				
p-NC-C_6H_4-	1[a]	50	329.5—330.5	80% MCS	39.1	39.61
	1[b]	90				

a) Methanol and sodium methoxide were used as the reaction solvent and catalyst respectively.

b) Methyl cellosolve and potassium hydroxide were used as the reaction solvent and catalyst respectively.

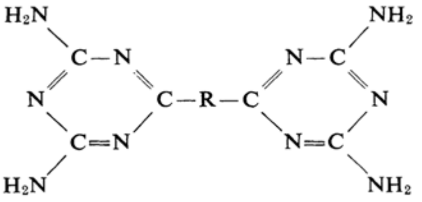
1) Not characterized adduct was obtained; m. p. >330°C. When it was heated in water, mirystonitrile was separated on the surface.

2) Tar-like substance was obtained.

3) When methanol was used as the reaction solvent, guanamine was not obtained.

* MCS indicates methyl cellosolve (ethyleneglycol monomethyl ether).

TABLE II. SYNTHESIS OF DIGUANAMINES



-R-	Reaction time hr.	Yield %	M. p. °C	N, anal.	
				Found	Calcd.
-$(CH_2)_2$-	1	70	>360	*1	
-$(CH_2)_3$-	2	25*2	265—270	*1	
-$(CH_2)_4$-	3	90	285 (d.)	50.57	50.70
-$(CH_2)_7$-	4	50*2		*1	
-C_6H_4-(*o*-)	7	60	343—345	44.9	44.57*3
(*m*-)	1	90	>360	47.4	47.26
(*p*-)	6	90	>360	*1	

*1 Elemental analyses of these compounds were done several times but the analytical values varied each time. Identification of these compounds was done by their infrared spectra.

*2 One mole of nitriles were treated with four moles of dicyandiamide.

*3 Calcd. as monohydrate of isophthaloguanamine. The result of carbon and hydrogen analyses also coincided with the value of the monohydrate.

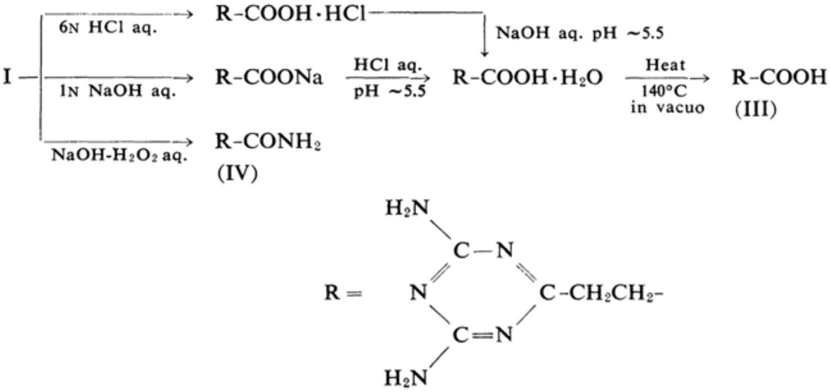
TABLE III. THE REACTION OF AS RESINS AND DICYANDIAMIDE

Exp. No.	AS resin	g.	Dicy. g.	KOH g.	MCS ml.	DMF ml.	React. time hr.	N[*1] anal. %	Conv.[*2] %
1	AS1	2	3	0.2	20	20	7.5	10.30	9
2		2	3	0.2	20	20	5	9.90	8
3		2	2.2	0.2	20	20	5	10.84	10
4	AS2	2	2	0.2	20	25	5	7.87	3
5	AS3	1.5	2.6	0.2	35	25	5.5	—	1[*3]
6		1	0.8	0.1	50	10	2	—	1[*3]

[*1] The nitrogen content of starting AS resins were 8.30% (AS1), 7.30% (AS2) and 5.39% (AS3).

[*2] Conversion means the ratio of the number of cyano groups converted to diamino-*sym*-triazine to those of the starting polymers.

[*3] Determined from infrared spectra.



mixture up to pH 5.5, gave β-carboxypropioguanamine (III). The hydrolysis of I with an alkaline aqueous solution of hydrogen peroxide gave β-(4, 6-diamino-*sym*-triazin-2-yl) propionamide (IV). Each compound, III and IV, combines with one molecule of water, and the dehydration of the hydrates can be conducted by heating them at a temperature above 140°C under reduced pressure.

The reaction of dicyandiamide with cyano groups in polymer molecules was studied in order to modify the properties of the polymers. Polyacrylonitrile and acrylonitrile-styrene copolymers (AS resins) were used as the polymers. Copolymers containing 4, 6-diamino-*sym*-triazine were obtained from the AS resins, but not from polyacrylonitrile. The reaction mixture with polyacrylonitrile gelled and colored in the presence of potassium hydroxide. The mixture of dimethylformamide and methyl cellosolve was suitable for the reaction solvent. The infrared spectra of the modified AS resins obtained here showed new peaks at 3025—3060 (two peaks), 1630, 1545 and $824\,\mathrm{cm}^{-1}$, the locations of the characteristic bands of guanamines.9) The ratio of the number of cyano groups converted to diamino-*sym*-triazine to that of the starting polymer was determined by nitrogen analysis. The acrylonitrile contents of the starting copolymers were 47.3 mol.% (AS1), 42.8 mol.% (AS2) and 33.3 mol.% (AS3). The results obtained are summarized in Table III. It can be concluded that no degradation of the polymer main chain occurred in the course of the reaction; only a small change in reduced specific viscosity was observed (0.84 before to 0.78 after the reaction for the sample of Exp. No. 2).

The modified AS resins gave insoluble and infusible substances when treated with an aqueous solution of formaldehyde. However, the reaction, as well as the properties of the products, has not yet been investigated in detail.

Experimental

β-Cyanopropioguanamine (I).—To a mixture of 30 g. of succinonitrile and 31 g. of dicyandiamide in 230 ml. of absolute methanol, 50 ml. of methanol containing 3 g. of sodium was added. The reaction mixture was then heated and stirred under reflux for 30 min. After the mixture had then cooled, the resulting precipitate was filtered, washed twice with 30 ml. of methanol, and dried. It was recrystallized from water; m. p. 241.5—242°C (colorless needles); yield, 40 g. (66%); IR, 3505, 3440,

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9) W. M. Padgett, II, and W. F. Hamner, *J. Am. Chem. Soc.*, **80**, 803 (1958).

3370 (N-H), 2270 (C≡N), 1672, 1645, 1543, 1425 and 818; UV, 258 mμ ($\varepsilon_{max}=3800$).

Found: C, 44.35; H, 5.05; N, 51.47. Calcd. for $C_6H_8N_6$: C, 43.89; H, 4.90; N, 51.19%.

Succinoguanamine (II). — Into a solution of 1.8 g. of I and 0.9 g. of dicyandiamide in 20 ml. of dimethylformamide there was added 5 ml. of a methanolic solution of sodium methoxide which had been freshly prepared from 0.1 g. of sodium; the mixture was then heated at 130—140°C for 3 hr. After the mixture had then been cooled, a white precipitate formed was filtered and washed with hot water. It did not melt at 360°C. The infrared spectrum showed the absorption bands characteristic to guanamines, but not around the 2250 cm^{-1} of C≡N. When methyl cellosolve was used as the reaction solvent, potassium hydroxide was used as the catalyst.

Guanamines. — *o-Cyanobenzoguanamine.* — a) (In methanol) To a solution of 6.2 g. of phthalonitrile and 4.2 g. of dicyandiamide in 40 ml. of methanol, there was added a sodium methoxide solution which had been made by dissolving 0.5 g. of sodium in 10 ml. of methanol. The mixture was refluxed for 30 min. The white precipitate thus formed was filtered and recrystallized from water; yield, 8.8 g. (85%); m. p. 230.5—231.5°C.

Found: C, 56.19; H, 4.19; N, 39.85. Calcd. for $C_{10}H_8N_6$: C, 56.59; H, 3.80; N, 39.61%.

b) (In methyl cellosolve) A mixture of 1.1 g. of phthalonitrile, 0.8 g. of dicyandiamide and 0.1 g. of potassium hydroxide in 15 ml. of methyl cellosolve was heated at 130—140°C for 2 hr. The reaction mixture was then poured into cold water. A white precipitate was collected by filtration and recrystallized from water; yield, 1.6 g. (80%); m. p. 230—231°C.

Phthaloguanamine.—a) (From *o*-cyanobenzoguanamine) A mixture of 1.1 g. of *o*-cyanobenzoguanamine, 0.5 g. of dicyandiamide, 0.1 g. of potassium hydroxide and 20 ml. of methyl cellosolve was heated at 130—140°C for 8 hr. The white powder which was thus precipitated was filtered and washed with methanol. M. p. 340—343°C.

b) (From phthalonitrile) A mixture of 1.3 g. of phthalonitrile, 1.7 g. of dicyandiamide, 0.2 g. of potassium hydroxide and 30 ml. of methyl cellosolve was heated at 130—140°C for 7 hr. The white powder which was thus precipitated was filtered and washed with methanol. M. p. 340-343°C.

Other mono and diguanamines were synthesized by similar procedures. The results are summarized in Tables I and II.

2-Acetamino-4-amino-6-β-cyanoethyl-1, 3, 5-triazine.—A solution of 6 g. of I in 30 ml. of acetic anhydride was heated under reflux for several minutes, thus precipitating a white solid. This was collected by filtration and recrystallized from water; m. p. 230—231°C.

Found: N, 41.02. Calcd. for $C_8H_{10}N_6O$: N, 40.76%.

2, 4-Diacetamino-6-β-cyanoethyl-1, 3, 5-triazine.—When the above reaction was continued without the isolation of the monoacetate, the precipitate disappeared once, thus forming a clear solution. After another hour of reflux, however, a grayish precipitate was deposited. This was collected by filtration and recrystallized from acetic anhydride; m. p. 213—215°C.

Found: N, 33.7. Calcd. for $C_{10}H_{12}N_6O_2$: N, 33.86%.

The Monohydrochloride of I.—A solution of 1 g. of I in 10 ml. of cold 6 N hydrochloric acid was allowed to stand overnight in ice box. The white precipitate which was thus formed was filtered and washed with methanol; m. p. 208—209°C (decomp.); IR, 2280 (C≡N).

Found: N, 41.61; HCl, 18.5 (from the neutralization value with 0.1 N NaOH aq.). Calcd. for $C_6H_8N_6\cdot HCl$: N, 41.90; HCl, 18.2%.

The Acidic Hydrolysis of I.—*β-(4,6-Diamino-sym-triazin-2-yl)propionic Acid (III).*—A mixture of 3 g. of I in 60 ml. of 6 N hydrochloric acid was heated to reflux for 5 hr. The white precipitate which was thus formed was filtered and recrystallized from water, giving colorless needles of a monohydrochloride of III. They did not melt, but they did decomposed at a temperature above 250°C, forming a black mass.

Found: N, 31.72 (Kjeldahl method). Calcd. for $C_6H_9N_5O_2\cdot HCl$: 31.89%.

A solution of 2 g. of the monohydrochloride in 100 ml. of water was neutralized with a 1 N sodium hydroxide aqueous solution to a pH value of 5.5. The white precipitate which was thus formed was collected and recrystallized from water, giving a monohydrate of III; m. p. 262°C (decomp.). The infrared spectrum of this compound showed absorption bands at 3350 (broad), 2800—2500 cm^{-1} (COOH) and other regions characteristic of guanamines.

Found: N, 35.03 (Kjeldahl method). Calcd. for $C_6H_9N_5O_2\cdot H_2O$: N, 34.81%.

The monohydrate was dehydrated by heating it at 140°C in vacuo for 5 hr., thus forming III; m. p. 262°C (decomp.); IR, 3450, 3300 (N-H), 2800—2500 cm^{-1} (COOH).

Found: N, 38.00 (Kjeldahl method). Calcd. for $C_6H_9N_5O_2$: N, 38.24%.

The Alkaline Hydrolysis of I.—A mixture of 2 g. of I and 1 g. of sodium hydroxide in 25 ml. of water was refluxed for 30 min. The evolution of ammonia was observed. After it had then been cooled, the mixture was neutralized with 5 N hydrochloric acid to a pH value of 5.5. The product precipitated was the same as the monohydrate of III obtained in the preceding section.

β-(4, 6-Diamino-*sym*-triazin-2-yl)propionamide (IV).—A solution of 2 g. of I and 0.1 g. of sodium hydroxide in 40 ml. of a 9% hydrogen peroxide aqueous solution was heated at 60—65°C for 40 min. The precipitate which was thus formed was collected by filtration and recrystallized from water, giving a monohydrate of IV; m. p. 250—251°C (decomp.).

Found: C, 36.33; H, 6.14; N, 42.26. Calcd. for $C_6H_{10}N_6O\cdot H_2O$: C, 36.00; H, 6.04; N, 41.98%.

The monohydrate was dehydrated by the same procedure as that used for III to give IV; m. p. 251—252°C (decomp.).

Found: N, 46.52. Calcd. for $C_6H_{10}N_6O$: N, 46.13%.

The Reaction of AS Resins with Dicyandiamide. —(Exp. No. 2). To a solution of 2 g. of AS1 in 20 ml. of dimethylformamide, 20 ml. of methyl cellosolve and 3 g. of dicyandiamide were added. The mixture was then heated at 130°C until a clear solution was obtained. To this solution there was added 0.2 g. of potassium hydroxide. The mixture was then kept at 130°C for 5 hr., after which it was poured into methanol. The polymer thus precipitated was filtered, washed with methanol, and purified by reprecipitation with a dimethylformamide-methanol system. The reduced specific viscosity of AS1 and of the modified polymer obtained here were, respectively, 0.84 and 0.78, at 30°C at the concentration of 0.2 g. of polymer in 100 ml. of dimethylformamide.

The other reactions of AS resins with dicyandiamide were carried out similarly; the results are summarized in Table III.

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