J. 30 A. 3

STUDIES IN ANTIMALARIALS

Part VIII. Aryl-Cyanoguanidines from Aryl-Azo Cyanoguanidines

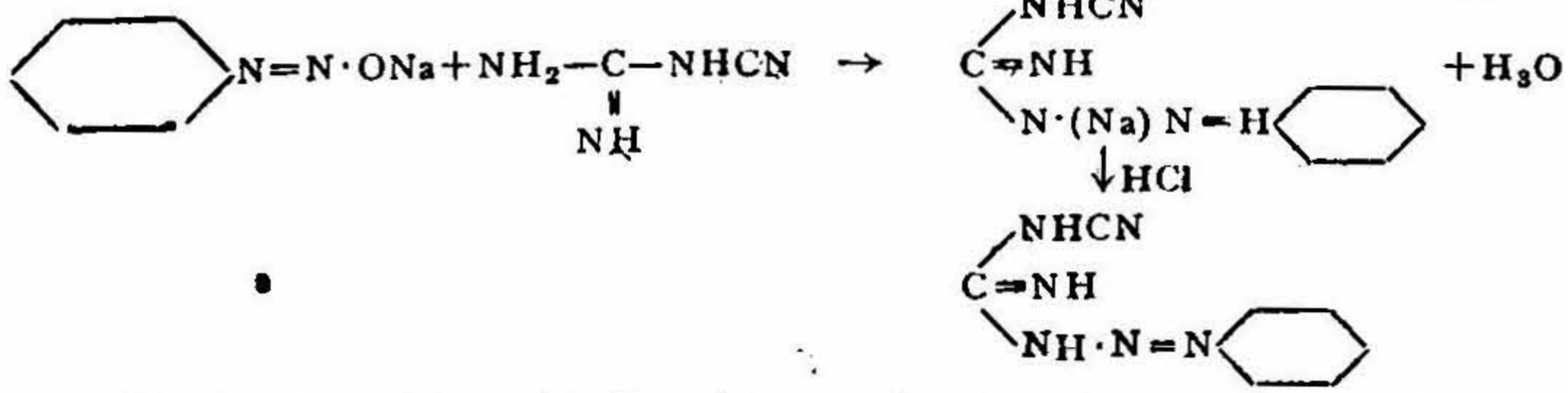
By H. L. Bami

With the discovery of Paludrine (N^1-*p*-Chlorophenyl-N^5-iso-propyl biguanide) (Curd and Rose, *J.C.S.*, 1946, 729; *cf.* Bami, Iyer and Guha, *J. Indian Inst. Sci.*, 1946, **29 A**, 1; *Sci. and Cult.*, 1947, **12**, 448) considerable interest has been developed in the field of substituted biguanides as potential antimalarials. Cyanoguanidines are important intermediates for the synthesis of biguanides. Phenyl-cyanoguanidine was first prepared by Wheeler and Jamieson (*J. Amer. Chem. Soc.*, 1903, **25**, 719) by *s*-methylation of the product obtained by interaction of phenylisothiocyanate and sodium cyanamide, and subsequent treatment by alcoholic ammonia. Recently this method has been extended to prepare phenanthrylcyanoguanidines and alkylcyanoguanidines, which have been used for the synthesis of new potential antimalarials (May, *J. Org. Chem.*, 1947, **12**, 437, 443; Everette and Mosettig, *ibid.*, 864). This method for the synthesis of substituted cyanoguanidines is tedious and gives poor yields in comparison to the other method discussed below. However, it is useful in cases where either the amine cannot be diazotised or fails to form the triazene and/or the cyanoguanidine.

Walther and Grieshammer (*J. fur. Prakt. Chem.*, 1915, **92**, 209) first described the formation of arylazocyanoguanidines by coupling the diazotised arylamines with dicyandiamide in alkaline solution and obtained the arylcyanoguanidines by decomposing their labile hydrochlorides (formed in ether) with warm water. This method has been further simplified by Curd and Rose (*loc. cit.*) and Bami, *et. al.* (*loc. cit.*) and the present work deals with (*a*) finding out the best procedure for the denitrogenation of arylazocyanoguanidines (referred to as triazenes) to the corresponding arylcyanoguanidines, (*b*) application of this method for the synthesis of new arylcyanoguanidines and (*c*) discussion of mechanism of these reactions.

Action of diazonium salts on alkylamines has been studied by various workers (Baeyer and Jagar, *Ber*, 1875, **8**, 148; Wallach, *Ann.* **235**, 233; Goldschmidt and Hohm, *Ber.* 1888, **21**, 1016; Goldschmidt and Badl., *Ber.*, 1889, **22**, 928; Korber, *Ber.*, 1890, **23**, 1028, 1032; Heussler, *Ann.*, 1890, **260**, 249; Hunter, *J.C.S.*, 1937, 320; Elks and Hey, *J.C.S.*,1943, 441;

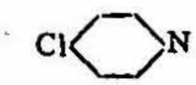
Dimroth, *Ber.*, 1905, **38**, 2328, 670; 1906, **39**, 3905; 1907, **40**, 2376; 1903, **36**, 909) but in spite of the acidic character of dicyandiamide, it was possible to obtain diazoamino compounds under certain conditions. On the addition of aryldiazoniumchloride to a strongly alkaline solution of dicyandiamide, the former is converted into an alkali diazotate and reacts with the latter as follows:—



On acidification of the alkali solution after 2–3 hours, the product is precipitated out with mineral acid due to its acidic character. After filtering out the triazene, the filtrate can be made alkaline again to get a little more of the product but generally this did not affect the yield materially except in the case of anilines having strongly electronegative substituents, *i.e.*, nitroanilines and dichloroanilines. The constitution of arylcyanoguanidines has been established by Walther and Grieshmmer (*loc. cit.*). These triazenes as obtained from various substituted anilines (*vide* Table 'B') are light yellow to orange in colour and are very unstable. They are insoluble in most of the common organic solvents excepting alcohol, acetic acid and pyridine and decompose at low temperatures with slight decomposition. Their decomposition points cannot be used for their characterisation. In these reactions the cyanoguanidine was always taken in slight excess in order to avoid the formation of diazoamino compounds. Longer keeping of the reaction mixture and higher temperature resulted in the formation of tarry products. These arylazo-cyanoguanidines form monoalkali salts and give silver salts as well.

For the present work, the triazenes have not been usually isolated in completely dry state but have been denitrogenated to the corresponding arylcyanoguanidines in acid mixtures of hydrolytic solvents by methods previously reported (Bami, Iyer and Guha, *loc. cit.*; *J. Indian Inst. Sci.*, 1946, **29 A**, 15). Curd and Rose (*loc. cit.*) used a mixture of β-ethoxyethanol and hydrochloric acid for the denitrogenation of the triazenes but now it has been possible to replace this solvent by other cheaper common organic solvents without affecting the yields of arylcyanoguanidines. Consequently a large number of organic solvents and acid mixtures were studied for the denitrogenation of *p*-chlorophenyl-azocyanoguanidines and the results have been tabulated in Table 'A'.

TABLE "A" *Denitrogenation of p-chlorophenylazocyanoguanidine into p-chlorophenylcyanoguanidine*

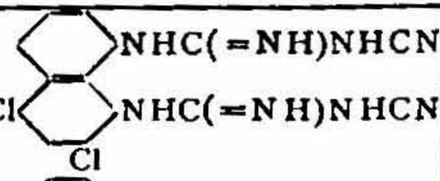
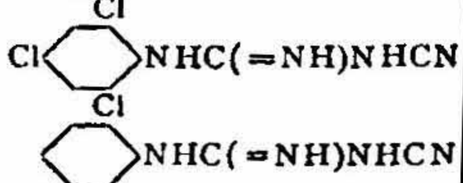
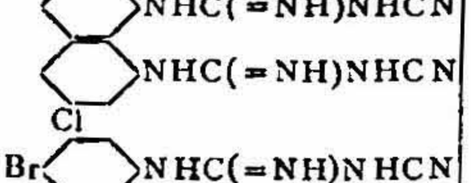
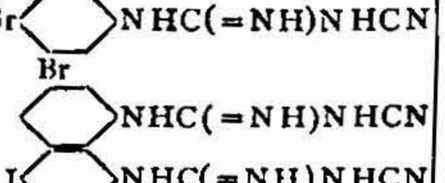
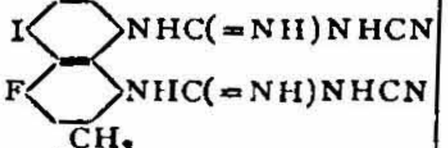
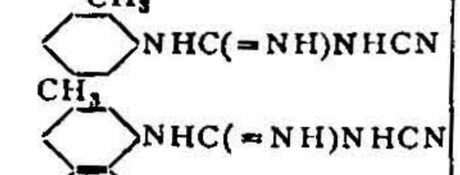
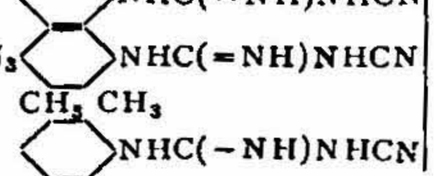
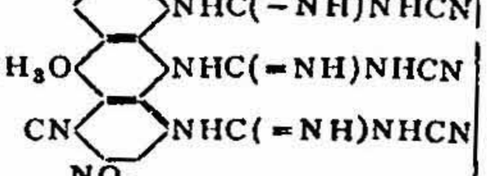
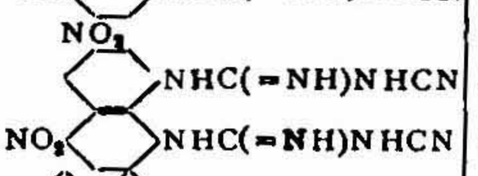
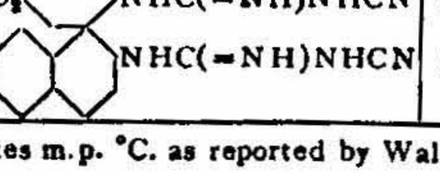
No.	p-Chlorophenylazocyanoguanidine in gm.		Solvent or med.	Quantity in c.c.	Acid	Quantity in c.c.	Tem. °C.	Time hrs.	Yield m.p. 203	Remarks
1		10	Nil	Nil	Nil	Nil	150–60	3	Nil	Heating in oil-bath
2	do	10	xylene	50	Nil	Nil	120–30	3	2g.	*vide* exptl. (I)
3	do	10	do	do	HCl	5	do	2	Nil	do
4	do	5	Liquid paraffin	25	Nil	Nil	Free flame	1	Nil	
5	do	5	Nil	Nil	HCl	30	60	1	0·5	
6	do	11	Acetone	60	Acetic acid	15	50–60	0·5	2	*vide* exptl. (II)
7	do	11	do	50	HBr	10	35	1	6·5	do
8	do	11	do	50	HCl	10	30–40	0·5	6·4	do
9	do	11	do	50	H_2SO_4	10	do	do	6·2	do
10	do	11	mathylethylketone	50	HCl	10	30	1·5	4·5	*vide* exptl. (I)
11	do	11	diethylketone	do	do	do	do	2	4	do
12	do	11	dioxane	25	do	7	do	0·5	6·4	*vide* exptl. (II)
13	do	11	ethylenechlorhydrine	50	do	10	do	0·75	5·5	do
14	do	11	methyl alcohol	do	do	do	40–50	1·5	2·7	do
15	do	11	ethy alcohol	do	do	do	do	do	4·3	do
16	do	11	normal propy alcohol	do	do	do	do	2	3·8	do
17	do	11	formic acid	do	do	do	do	do	2·7	do
18	do	11	acetic acid	do	do	do	30–40	do	5	do
19	do	11	do	100	HS_2O_4	15	do	0·5	6·4	do
20	do	11	do	do	HNO_3	do	do	do	3	do
21	do	11	Benzene	do	HCl(gas)	Sat. soln.	60–70	1	5·7	*vide* exptl. (III)
22	do	11	ether	do	do	do	do	do	5·8	*vide* exptl. (IV)

From Table 'A' it is evident that a mixture of acetone with hydrochloric acid, hydrobromic acid and sulphuric acid, dioxane with hydrochloric acid and acetic acid with sulphuric acid gives the maximum yield of *p*-chlorophenylcyanoguanidine, which has been selected as a representative of this series due to its being an intermediate for the synthesis of paludrine. In the case of these solvent acid mixtures, the time required was also less and the temperature fairly low; both these factors are of considerable importance for a good yield of the product which otherwise got saponified to *p*-chlorophenylguanylurea.

Attempts to denitrogenate the triazene by strong ammonia, by application of heat, by heating with acid alone and by heating in a non-hydrolytic solvent like xylene have not met with much success. These failures can be adequately explained when the possible mechanism of this reaction is discussed. Original procedure as adopted by Walther and Grieshmmer (*loc. cit.*) has also been modified and the yield of the required product has been fairly good although less than that in the case of solvent acid mixtures. This method cannot compete with the previous procedure, which is both easy and cheap in operation (Table 'A', No. 21, 22).

After having established the condition for the preparation of arylazocyanoguanidines and their subsequent denitrogenation to the arylcyanoguanidines, it was thought of interest to extend this method for the synthesis of substituted cyanoguanidines derived from diazotisable amines. Consequently various new arylcyanoguanidines have been prepared (Table 'B') by general methods already established (Bami, Iyer and Guha, *loc. cit.*). Some of the anilines used in the present work namely 2:4-dichloroaniline, *p*-iodoaniline, *p*-fluoroaniline and *p*-cyanoaniline were specially prepared for the purpose because the corresponding cyanoguanidines will serve as important intermediates for the synthesis of biguanide derivatives. Except in a few cases the yield of cyanoguanidines was good. The products were high melting white crystalline powders (except nitro-derivatives which were light yellow) with fair solubility in alcohol, dioxane, acetic acid, acetone and alkalies. They were insoluble in benzene, ether, toluene and petrol, etc. Cyanoguanidines were purified by precipitation from their alkali solution with acid and subsequent crystallisation from alcohol or dilute acetone.

2:4:6-Tribromoaniline was diazotised in nitrosylsulphuric acid acetic acid mixture and the 2:4:6-tribromophenyldiazonium sulphate was obtained in solid form according to the method of Hodgson and Mahadevan (*J.C.S.*, 1947, 173). An aqueous solution of this diazonium salt failed to react with dicyandiamide in the absence of alkali which only goes to prove

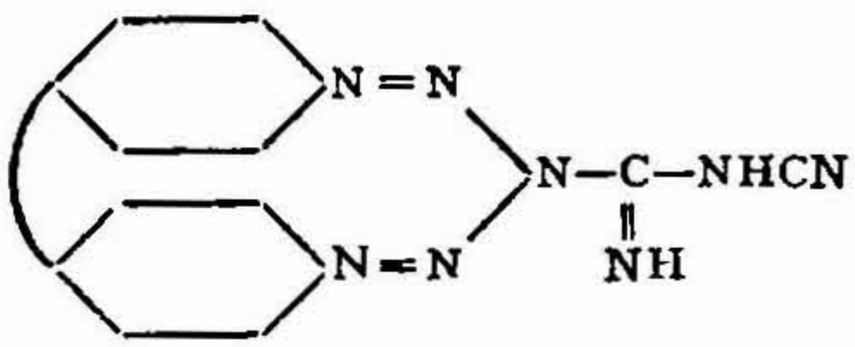
No.	Substituted aniline	Amount of diazotised	Cyanoguanidine	Solvent	Amount c.c.	Acid	Amount c.c.	Amount gms.	%	Aryl Cyanoguanidine	°C	Formula	Calc.	Found
1	Aniline	46 g.	44 .	acetone	300	HCl	56	35	48		190	(190–91*,190–91†)		
2	*p*-Chloraniline	32	22	acetic acid	250	do	50	25	51		203	(203*, 197–98†)		
3	2 : 4-dichloroaniline	18	10	acetone	100	do	25	5	21·5		217	$C_8H_6N_4Cl_2$	24·45	24·77
4	*o*-Chloraniline	10·5	7	do	do	do	20	4·5	28		170	$C_8H_7N_4Cl$	28·78	29·16
5	*m*-Chloraniline	21	15	do	150	do	25	9	28		232–233	$C_8H_7N_4Cl$	28·78	29·46
6	*p*-Bromoaniline	40	22	ethanol	200	do	50	20	36		198	(196–97†)		
7	*m*-Bromoaniline	12	7	acetone	100	do	25	6	36		233	$C_8H_7N_4Br$	24·68	25·06
8	*p*-Iodoaniline	44	20	ethanol	200	H_2SO_4	30	25	43		217	$C_8H_7N_4I$	19·58	19·65
9	*p*-Fluoraniline	7	6	acetone	100	HCl	20	3	27		211	$C_8H_7N_4F$	31·63	32·35
10	*o*-Toluidine	9	10	do	do	do	do	3	21		205	$C_9H_{10}N_4$	32·19	32·48
11	*m*-Toluidine	22	20	do	200	do	50	20	55		202	$C_9H_{10}N_4$	32·19	32·28
12	*p* Toluidine	27	25	do	250	do	45	24	54		211	(211–12*; 207–8†)		
13	2 : 3-Dimethylaniline	25	20	do	200	do	50	20	51		185	$C_{10}H_{12}N_4$	29·89	30·10
14	*p* Methoxyaniline	13	10	do	150	do	30	9	43		187	(188*)		
15	*p*-Cyanoaniline	3·9	3	do	50	do	10	1	16		244	$C_9H_7N_5$	37·83	38·05
16	*m*-Nitroaniline	13	10	do	120	do	30	6	31		229	$C_8H_7N_5O_2$	34·14	33·60
17	*p*-Nitroaniline	28	20	do	250	do	50	14	33		243	(242–43*)		
18	β-Napthylamine	28	20	do	200	do	50	3·6	8·7		237	$C_{12}H_{10}N_4$	26·66	26·98

* Indicates m.p. ° C. as reported by Curd and Rose (*loc. cit.*). † Indicates m.p. °C. as reported by Walther and Grieshmmer (*loc. cit.*).

that this reaction cannot proceed in the absence of an alkali diazotate. However a strongly alkaline solution of the above diazonium salt also failed to react with cyanoguanidine and on acidification only a yellow precipitate separated out which was a mixture of 3:5-dibromodiazophenol and its trimolecular hydroxy condensation product (Ortan, *J.C.S.*, 1905, **87**, 99; 1907,, **91**, 1554; 1903, **83**, 796). The failure of this reaction may be attributed to the strong electro-negative nature of the substituted benzene ring and the instability of its diazonium salt. Similar experiments were done with 2:3:4-trichlor aniline and 2:4:5-trichloroaniline but in no case the desired triazene could be obtained.

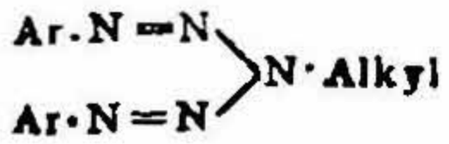
Out of the diazotisable heterocyclic amines, 2-aminothiazole was selected for the present study. The heterocyclic amine was diazotised according to the method of Morgan and Morrow (*J.C.S.*, 1915, **107**, 1291) but on basification of the diazotised solution, extremely unstable thiazole-2-diazohydroxide was formed (Hantzsch. *Ann.*, 1888, **249**, 1; Traumann, *ibid*, p. 35; Schatzmann, *ibid.*, 1891, **261**, 9; *cf.* Nef., *Ann.*, 1891, **265**, 110). Failure to obtain a stable diazotate from 2-aminothiazole may be the cause of non-formation of 2-thiazolylazocyanoguanidine. From the above failures it is evident that this method has general applicability only in the case of those amines which give stable diazotates apart from the question of denitrogenation which is discussed later.

In order to obtain benzidine-*p*-*p*'-bis (azocyanoguanidine), tetrazotised benzidine was reacted with an alkaline solution of dicyandiamide when a water-insoluble sodium salt of a product was obtained which on acidification with hydrochloric or acetic acid gave the corresponding acid salts which on analysis found to conform to structure (I).



(I)

This means that both the diazonium groups have combined with the same molecule of cyanoguanidine. Such a structure can be possible when we consider that in the field of arylalkyltriazenes firstly only bisdiazoamino compounds of the type (II) were formed (" The Aromatic Diazo Compounds," by Saunders, p. 130; Goldschmidt and Badl., *Ber.*, 1889, **22**, 933; Busch., *J. fur. Prakt. Chem.*, 1934, **140**, 127).

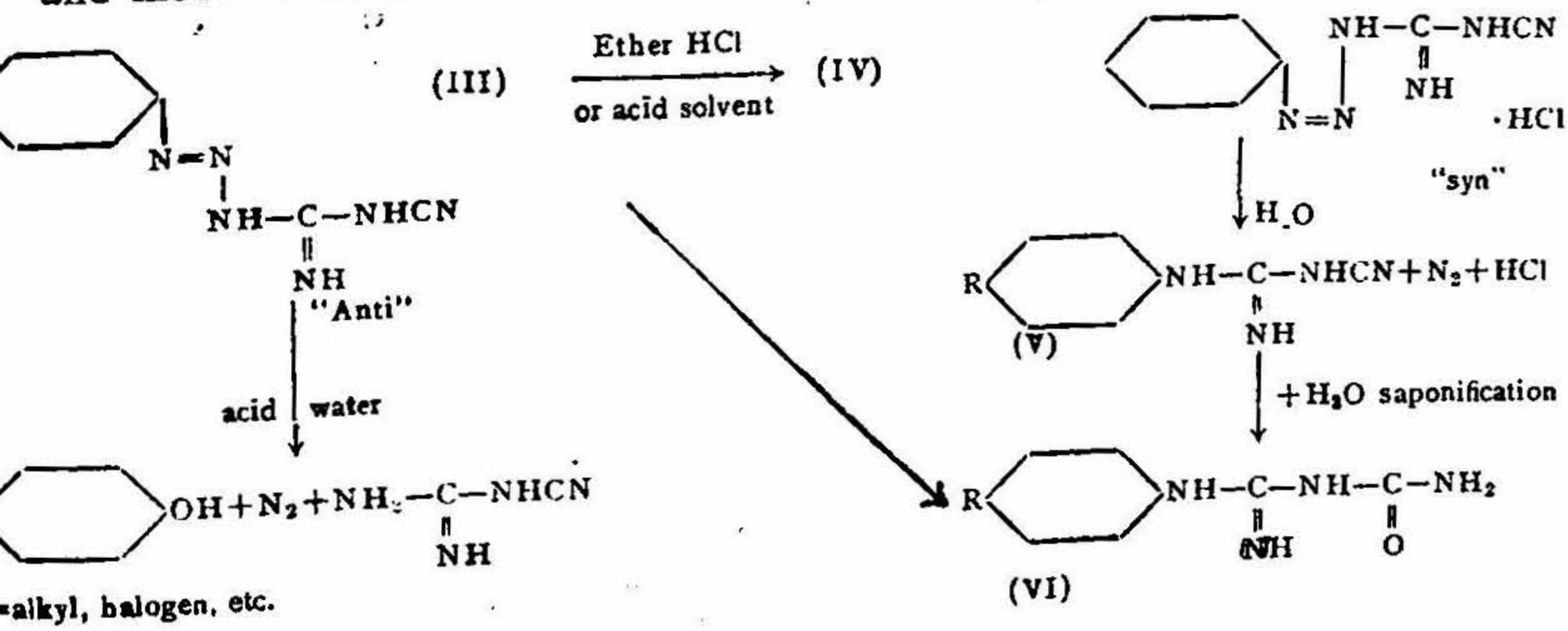


(II)

Another important fact is that if a diazo compound is free to combine with an amino or imino group, then the combination is with the primary amino group (Pinner, *Ber.*, 1889, **22**, 1609). The product (I) was a brown amorphous precipitate which became dark red on drying. The acid salts of the compound (I) were insoluble in water and usual organic solvents and were very sensitive to heat and mineral acids. In a mixture of acetone and hydrochloric acid this compound gave out nitrogen. When heated dry, there was a sudden evolution of nitrogen at 150° and some ammonia was also given out. The product changed into a colourless amorphous powder which did not melt upto 360°. This new product was insoluble in usual organic solvents and in both acid and alkalies. Further work on the constitution of these products is deferred for the time being.

After the first part of this work had been completed, a patent by Broadbent and Rose (U.S.P. 2409832, 1946. *cf. Amer. Chem. Abst.*, 1947, **41**, 1243) was published where a few of the arylcyanoguanidines reported by Curd and Rose (*loc. cit.*), have been prepared from the triazines by the denitrogenation process in suitable solvent acid mixtures.

It is generally accepted that in alkali solution, the diazonium salts form alkali isodiazotates which are stable and may correspond to Hantzsch's antiform ("Unit Processes in Organic Chemistry," by Groggins, p. 155). These isodiazotates in strong alkali solution, have very little capacity for coupling in the usual way because the normal form (Labile syn. form) is completely suppressed (Hantzsch, *Ber.*, 1900, **33**, 2517. *cf.* "The aromatic diazo compounds" by Saunders, p. 81, 183). Accordingly the aryl-azo-cyanoguanidines obtained by the reaction of diazonium salt on dicyandiamide in alkaline solution must have an antiform (III) due to its stability and mode of formation. The decomposition of these triazines in aqueous



=alkyl, balogen, etc.

or acidic solutions have only led to the formation of aromatic phenol, nitrogen and dicyandiamide, but when a suspension of the product in ether was treated with hydrochioric acid gas, a labile hydrochloride (IV) was formed which according to Walther and Greishmmer (*loc. cit.*) may have a "syn" configuration.

Assumption of a "syn" structure for (IV) is very necessary for the formation of (V) because only such a structure can decompose in this way. The above explanation receives support from the recent work on diazocyanides (Anderson, *et. al.*, *J.C.S.*, 1947, **445**, 457; Sheppard and Sutherland, *ibid.*, 453) and azobenzene (Hartley, *J.C.S.*, 1938, 633, 1939, 531; Robertson, *ibid.*, 232). Treatment of (IV) with hot water led to the formation of (V). In the case of denitrogenation in the solvent acid medium it was quite possible that before (V) was formed from (III,) an intermediate labile salt (IV) was formed which was immediately acted upon by water available in the mixture itself.

Walther and Grieshmmer (*loc. cit.*) have prepared arylguanylurea (VI) from (III) directly by evaporating a mixture of (III) in alcoholic hydrochloric acid. In this case also intermediate labile hydrochloride (IV) as well as the cyanoguanidine (V) was not isolated and hence (V) was directly saponified to (VI) under these conditions. In experiments reported in this paper it was also observed that if the denitrogenation of (III) into (V) was done during a longer period of reaction and at a higher temperature, the yield of (V) was greatly reduced with corresponding increase in the amount of (VI) formed. In fact, as soon as the conversion of (III) into (V) was over, the denitrogenation mixture was diluted and chilled to separate out the product and arrest its saponification into (VI). In one experiment when the denitrogenation mixture after the evolution of nitrogen was left overnight, no aryl cyanoguanidine could be obtained after diluting the solution next morning and the entire triazene passed into arylguanylurea (VI).

In the course of our work on sulphabiguanides (Bami, *et al.*, *loc. cit.*) it was desired to convert the N^4-amino group of sulphanilamide into a cyanoguanidine group (V; $R=SO_2NH_2$) by the above methods. Although a triazene could be obtained from sulphanilamide (III; $R = SO_2NH_2$) in the usual way, it was not possible to convert it into (V; $R = SO_2NH_2$) by following either of the two methods for the removal of azo nitrozen. In ethereal suspension this triazene failed to give a labile hydrochloride, which is very necessary for obtaining the corresponding cyanoguanidine. In acid-solvent medium also the product only decomposed into a tar with evolution of nitrogen. This means that with increasing acidity of (III) the possibility

of obtaining a labile hydrochloride (IV) decreases. The decomposition product of (III) in this case gave a phenolic tar and dicyandiamide which show that the product decomposed in the antiform and did not pass through a "syn" phase which is perhaps necessary for obtaining substituted cyanoguanidines.

Similar experiments were repeated with sulpha-diazine, sulphamerazine, sulphamethazine and metachloridine with simlar negative results. In order to see if the free amido hydrogen in the sulphonamido group of the triazene (III; $R = SO_2NH_2$) has anything to do with the failure of this reaction, two alkali-insoluble sulphanilamides, namely N^1-dimethylsulphanilamide and sulphaguanidine (K. Ganapthi, *Proc. Indian Acad. Sci.*, 1941, **13 A**, 386) were diazotised and denitrogenated in the usual manner but the previous results with sulphanilamide were confirmed.

p-Arsinilic acid and *p*-aminobenzoic acid as well as ethylester of the latter also failed to give the corresponding cyanoguanidines (V; R = COOH, COOEt, etc.). All these experiments show that strong electronegative nature of the substituent in the phenyl ring of the triazene (III) will not allow the formation of (V) which decidedly limits the scope and applicability of this reaction.

It will be interesting to point out here that neither the labile hydrochloride (IV) could be analysed due to its great instability nor could the free "syn" form be generated by using sodium acetate for neutralising the mineral acid (Walther and Grieshmmer, *loc. cit.*). In other words, a concrete proof for the existence of a syn form (IV) under the conditions is lacking but the mechanism of reaction and the general considerations from the field of diazocyanides and relative fields greatly support the explanation now offered.

Experimental

p-Chlorophenylcyanoguanidine from p-chlorophenylazocyanoguanidine:—

Using xylene, methyl ethylketone and diethylketone (I).—*p*-Chlorophenylazocyanoguanidine (11 gm.) was added to the mixture of ketone (50 c.c.) and hydrochloric acid (10 c.c.). The mixture was well stirred for ½ an hour and when the evolution of nitrogen was over, the ketone was extracted with dilute sodium hydroxide solution (10%, 50 c.c.) twice and the alkaline solution on acidification gave the desired product. It was purified by crystallisation from alcohol. Ketone after extraction was evaporated when a little more of the product was obtained. In the case of xylene a similar procedure was repeated but the results were less satisfactory.

Using hydrolytic solvents with acids (II).—*p*-Chlorophenylazocyanoguanidine was added to a mixture of the solvent and the acid in such a way that the temperature did not rise above 30°. This mixture was vigorously stirred and after ½ an hour when the evolution of nitrogen ceased the clear solution was diluted with water and chilled. The crystalline product was filtered off dissolved in alkali, treated with norite, filtered and precipitated with mineral acid, finally purified by crystallising from alcohol.

Using Benzene and Hydrochloric Acid Gas (III).—*p*-Chlorophenylazocyanoguanidines (11 gm.) was suspended in benzene (100 c.c.) and dry hydrochloric acid gas passed for 2 hours at 0° C. The labile hydrochloride was filtered off, washed with little ether and warmed with water (50° c.c.) at 60–70° C. for one hour. The product was filtered and purified as described under (II).

Using Ether and Hydrochloric Acid Gas (IV).—The details were similar to those described under (III) except that the ether was evaporated in an open dish to get the labile hydrochloride after passing the hydrochloric acid gas in the etherial suspension of the triazene.

Reaction of 2 : 4 : 6-*tribromobenzenediazonium salt with dicyandiamide*:—

2 : 4 : 6-Tribromoaniline (10 gm.) was diazotised according the method of Hodgson and Mahadevan (*loc. cit.*), and ether (250 c.c.) was added to the diazotising sulphuric acid-acetic acid mixture at 0° C., when a crystalline white precipitate of 2 : 4 : 6-tribromobenzenediazonium sulphate separated. It was collected by filtration and dissolved in water (200 c.c.). This solution was rapidly poured into a chilled solution of sodium hydroxide (26 g. in 250 c.c. water), when a little light yellow product separated out. The solution was filtered and the filtrate was made strongly alkaline. Dicyandiamide (5 g.) was also dissolved in the alkaline solution and kept for 2–3 hrs. at 0° C. When the solution was acidified with mineral acid, a thick yellow precipitate gradually separated out which was not the required triazene but a mixture of diazoxides, yield 6 gm., m.p. 82° C. (decomp.) (m.p. 85° C. decomp. according to Ortan; *J.C.S.*, 1903, **83**, 796).

An aqueous solution of the above diazonium sulphate and dicyandiamide did not react, while alkalization with sodium bicarbonate gave similar results.

Reaction of diazotised 2-*aminothiazole with dicyandiamide*:—

2-Aminothiazole (2 g.) was diazotised according to the procedure adopted by Morgan and Morrow (*loc. cit.*) and a solution of dicyandiamide (2 g., 200 c.c. water) was added to it. The mixture was alkalised with either

sodium carbonate or sodium hydroxide solution, but in either case dark brown, mucky precipitate started separating gradually which further decomposed when acidified with hydrochloric acid. The products in all probabilities were labile diazohydroxides derived from 2-aminothiazole and not the required triazene.

Reaction of tetrazonium salt of benzidine with dicyandiamide:—

Benzidine (9 gm.) was added to a solution of hydrochloric acid (25 c.c. in 25 c.c. water) and boiled for a few minutes. The amine hydrochloride was tetrazotied with a sodium nitrite solution (8 gm. in 25 c.c. water) at 0° C. in the usual way. The tetrazotised solution was filtered and added to a solution of dicyandiamide (10 g. in 500 c.c. water) and the mixture strongly made alkaline with sodium hydroxide solution (50 gm. in 100 c.c. water). A clear red colour developed but in about twenty minutes thick blood red precipitate of the sodium salt of a product separated out. After one hour the precipitate was filtered off and washed with little water and alcohol. Yield 15 gm.

The sodium salt was dissolved in hot water, treated with norite and filtered. The filtrate was acidified with hydrochloric acid, the product filtered, washed well with water, and then with alcohol and ether. Finally it was dried in the air oven. A dark brown powder; insoluble in the usual organic solvents was obtained. On heating the salt, suddenly decomposed at about 150° C. and was converted into a light coloured powder which did not melt up to 360° C. and was insoluble in the usual organic solvents. (Found: N, 34·61%, $C_{14}H_{11}N_8Cl$ requires N, 34·25%.)

The acetate salt was prepared similarly and had similar properties. (Found: N, 31·56%; 32·25%. $C_{16}H_{14}N_8O_2$ requires N, 32·18%).

p-Sulphonamidophenylazocyanoguanidine and its decomposition:—

Sulphanilamide (17·2 gm.) was diazotised in hydrochloric acid solution (25 c.c. in water, 50 c.c.) with sodium nitrite solution (7 gm. in 50 c.c. water) at 0° C. The clear solution was added on to the solution of dicyandiamide (10 gm. in 1000 c.c. of water) and the mixture made strongly alkaline. After 3 hours, the solution was acidified and the triazene was filtered, washed with water and dried in a desiccator. Yield 20 gm., m.p. 85° C. decomp.

The triazene was treated with gaseous hydrochloric acid in ether according to the method described, but no labile hydrochloride was obtained and the etherial mixture on evaporation decomposed into a tar.

The above triazene (20 gm.) was added to a mixture of acetone (200 c.c.) and hydrochloric acid (50 c.c.) and stirred for half an hour. The clear solution after dilution with ice-cold water (1500 c.c.) separated a semisolid red paste which could not be crystallised but solidified on keeping in contact with porous plate. m.p. 60° decomposition. This semisolid product was tested with ferric chloride solution and gave a positive test for phenols. Libermann's reaction also confirmed the presence of phenolic residues in the mass. The filtrate after the removal of the above product was neutralised, evaporated and extracted with alcohol. The alcohol extract was evaporated and the residue dissolved in water and gave a silver salt with silver nitrate proving the presence of dicyandiamide.

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