Derivatives of Ditraizinylamine and Tritriazinylamine

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2-Arylamino-4,6-dichloro-*s*-triazine reacts with cyanuric chloride in the presence of alkali to yield *N*,*N*-bis(4,6-dichloro-*s*-triazin-2-yl)-arylamine. In like manner, 2-substituted *o*-chloro-, *p*-chloro-, *o*-nitro- and *p*-carbomethoxyphenylamino-4,6-dimethoxy-*s*-triazines react with cyanuric chloride to yield the corresponding 4,6-dichloro-*s*-triazin-2-yl-4′,6′-dimethoxy-*s*-triazin-2′-ylaryl-amine, while anilino-, *p*-toluidino, *o*- and *p*-methoxyphenylamino and *o*-carbomethoxyphenyl-amino derivatives did not.

The reaction of cyanuric chloride with 2,4-dichloro-6-ethylamino-*s*-triazine in the presence of alkali yields the condensation product of the ditriazinylamine type and the reaction of cyanuric chloride with ammonia yields *N*,*N*-bis(4,6-dichloro-*s*-triazin-2-yl)- or tris(4,6-dichloro-*s*-triazin-2-yl)amine.

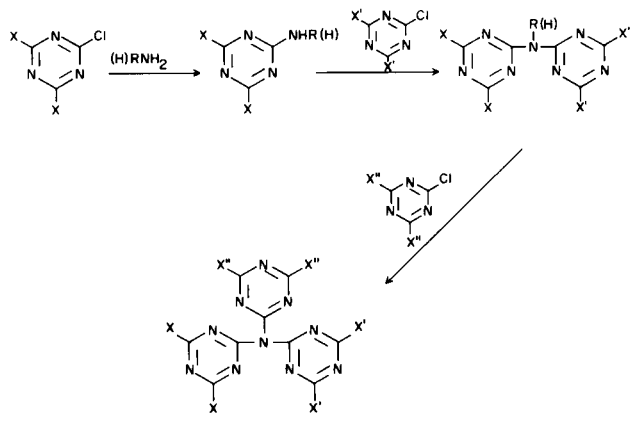
A. Introduction.

In the reaction of cyanuric chloride with ammonia or with amines, one, two or three chlorine atoms may be replaced by amino groups depending upon the reaction temperature and the molar ratio of reaction components (1-7).

A number of derivatives of aminodichloro-*s*-triazine, diaminochloro-*s*-triazine and melamine have been prepared by the condensation of cyanuric chloride with equimolar or excess amine (8-14). However, the reaction of cyanuric chloride or other chloro-*s*-triazines with ammonia or with amines using one mole of amine and two or three moles of chloro-*s*-triazine depending upon the number of active hydrogen atoms on the amines has not been studied.

Thus, it was of interest to investigate the reaction of amino-*s*-triazines with chloro-*s*-triazines to obtain derivatives of ditriazinylamine and tritriazinylamine.

The present work reports the condensation of amino-*s*-triazines with one or two moles of chloro-*s*-triazine to give novel derivatives of ditriazinylamine and tritriazinylamine in good yield.



B. Reaction of Cyanuric Chloride with Anilino-*s*-triazines.

The reaction of cyanuric chloride in the presence of sodium hydroxide with 2-anilino-4,6-dichloro-*s*-triazine (8a), the primary condensation product of cyanuric chloride with aniline, gave a secondary condensation product in good yield. This compound contains two dichloro-*s*-triazinyl groups attached to the same amino nitrogen atom and proved to be *N*,*N*-bis(4,6-dichloro-*s*-triazin-2-yl)aniline (XIII) as described in Experimental Section B (a).

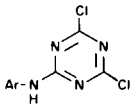
On the other hand, the desired derivative of ditriazinylamine was not obtained from the reaction of 2-anilino-4,6-dimethoxy-*s*-triazine (XXV) with cyanuric chloride under similar reaction conditions.

It is assumed that the difference in reactivity of these two anilino-*s*-triazines towards cyanuric chloride may be attributed to the difference in acidity of the NH group. In the case of the more acidic dichloro-2-anilino derivative the reaction took place smoothly, while with the less acidic dimethoxy-2-anilino-*s*-triazine derivative no reaction took place.

Since an amino group attached to the *s*-triazine ring behaves in the same manner as an amide, the nucleophilic reactivity of the amino group of amino-*s*-triazine would be expected to be low.

It is generally considered that amino-*s*-triazine itself does not react with chloro-*s*-triazine, but that it reacts as an anion in the presence of alkali. In the case of amino-*s*-triazines of low acidity no anions are formed in alkali, and consequently their nucleophilic reactivity is low.

TABLE I



2-Arylamino-4,6-dichloro-*s*-triazines

Aryl		Yield %	M.p. (a) °C.	Recrystn. Solvent	Elemental Analysis Calcd. C	H	Found. C	H	Molecular Formula	Reference
C_6H_5-	(I)	90	136-137 (138)	Benzene-Ligroin					$C_9H_6Cl_2N_4$	(8a)
o-CH_3-C_6H_4-	(II)	92	162-164 (161-162)	Benzene					$C_{10}H_8Cl_2N_4$	(15)
p-CH_3-C_6H_4-	(III)	90	129.5-131 (132.5-133)	Benzene					$C_{10}H_8Cl_2N_4$	(15)
2,6-$(CH_3)_2$-C_6H_3-	(IV)	95	191.5-193.5	Benzene	49.09	3.75	49.21	3.78	$C_{11}H_{10}Cl_2N_4$	
o-CH_3O-C_6H_4-	(V)	83	173-174 (174.5-175.5)	Benzene					$C_{10}H_8Cl_2N_4O$	(15)
p-CH_3O-C_6H_4-	(VI)	93	170-173 (172.5-173)	Benzene					$C_{10}H_8Cl_2N_4O$	(15)
o-ClC_6H_4-	(VII)	85	159-160.5 (158-159)	Benzene					$C_9H_5Cl_3N_4$	(15)
p-ClC_6H_4-	(VIII)	80	186-188 (187-188)	Benzene					$C_9H_5Cl_3N_4$	(15)
o-$CH_3OOCC_6H_4$	(IX)	84	192-194	Benzene	44.17	2.70	44.24	2.79	$C_{11}H_8Cl_2N_4O_2$	
p-$CH_3OOCC_6H_4$-	(X)	60	295	Chloro-benzene	44.17	2.70	44.45	2.97	$C_{11}H_8Cl_2N_4O_2$	
o-NO_2-C_6H_4-	(XI)	70	196.5-197	Benzene	37.79	1.76	38.01	1.98	$C_9H_5Cl_2N_5O_2$	
1-$C_{10}H_7$-	(XII)	85	155 (149)	Benzene-Ligroin	53.63	2.77	54.09	2.90	$C_{13}H_8Cl_2N_4$	(2)

(a) Values in parentheses are described in the references.

Thus, it is reasonable to assume that the acidity of the NH group of amino-*s*-triazine is an important factor in this reaction. Based upon this assumption the influence of substituents on the reactivity of amino-*s*-triazine has been investigated.

C. Reaction of Cyanuric Chloride with Substituted Aromatic Primary Amines.

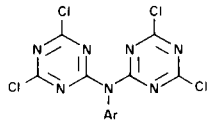
The two types of primary condensation products of substituted aromatic primary amines with chloro-*s*-triazines selected for this reaction were 2-arylamino-4,6-dichloro-*s*-triazine and 2-arylamino-4,6-dimethoxy-*s*-triazine.

In Table I are listed the starting materials of the 2-arylamino-4,6-dichloro-*s*-triazine type.

(a) Reaction of Cyanuric Chloride with 2-Arylamino-4,6-dichloro-*s*-triazines.

All of these primary condensation products were found

TABLE II



N,N-Bis(4,6-dichloro-*s*-triazin-2-yl)arylamines

Aryl		Yield %	m.p. °C	Recrystn. Solvent	Elemental Analysis Calcd C	H	Found C	H	Molecular Formula
C_6H_5-	(XIII)	82	182-183	Benzene-Ligroin	37.05	1.30	37.50	1.49	$C_{12}H_5Cl_4N_7$
o-$CH_3C_6H_4$-	(XIV)	68	170-172	Benzene	38.74	1.75	38.76	1.96	$C_{13}H_7Cl_4N_7$
p-$CH_3C_6H_4$-	(XV)	83	216-217	Benzene	38.74	1.75	38.64	1.95	$C_{13}H_7Cl_4N_7$
2,6$(CH_3)_2C_6H_3$-	(XVI)	72	246-248	Benzene	40.56	2.18	40.70	2.40	$C_{14}H_9Cl_4N_7$
o-$CH_3OC_6H_4$-	(XVII)	72	192-194	Benzene	37.26	1.68	37.72	1.87	$C_{13}H_7Cl_4N_7O$
p-$CH_3OC_6H_4$-	(XVIII)	80	217	Benzene	37.26	1.68	37.73	1.83	$C_{13}H_7Cl_4N_7O$
o-ClC_6H_4-	(XIX)	83	174-175	Benzene	34.03	0.95	34.39	1.16	$C_{12}H_4Cl_5N_7$
p-ClC_6H_4-	(XX)	71	245-245.5	Benzene	34.03	0.95	34.51	0.92	$C_{12}H_4Cl_5N_7$
o-$CH_3OOCC_6H_4$-	(XXI)	82	140-141	Benzene	37.61	1.58	37.97	1.67	$C_{14}H_7Cl_4N_7O_2$
p-$CH_3OOCC_6H_4$-	(XXII)	81	241-242	Benzene	37.61	1.58	37.95	1.70	$C_{14}H_7Cl_4N_7O_2$
o-$NO_2C_6H_4$-	(XXIII)	61	215.5-218	Benzene	33.21	0.93	33.48	1.01	$C_{12}H_4Cl_4N_8O_2$
1-$C_{10}H_7$-	(XXIV)	94	172-174	Benzene-Ligroin	43.77	1.61	44.19	1.74	$C_{16}H_7Cl_4N_7$

to condense with cyanuric chloride in acetone in the presence of sodium hydroxide to give secondary condensation products containing two dichloro-*s*-triazinyl groups attached to the same amino nitrogen atom.

The *N,N*-bis(4,6-dichloro-*s*-triazin-2-yl)arylamines obtained are listed in Table II.

These results indicate that the influence of electron-attracting and electron-donating substituents on the phenyl group of the 2-arylamino-4,6-dichloro-*s*-triazines is not significant as long as an *s*-triazinyl group possesses high electron attracting character due to two chlorine atoms. Furthermore, the 2,6-xylidino derivative, despite the two methyl groups occupying both *ortho* positions, formed smoothly, indicating that steric effects of substituents might also be relatively insignificant.

(b) Reaction of Cyanuric Chloride with 2-Arylamino-4,6-dimethoxy-*s*-triazine.

In Table III are listed the starting materials for the 2-arylamino-4,6-dimethoxy-*s*-triazines.

The reactions of cyanuric chloride with these dimethoxy derivatives were carried out under conditions similar to those described in section C (a). However, the desired derivatives of *N,N*-ditriazinylamine were not obtained in the case of anilino-, *p*-toluidino-, *o*- and *p*-methoxyphenylamino- and *o*-carbomethoxyphenylamino-4,6-dimethoxy-*s*-triazines.

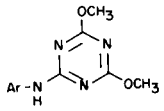
On the other hand, as shown in Table IV, the reaction of *o*-chloro-, *p*-chloro-, *o*-nitro- and *p*-carbomethoxyphenylamino-4,6-dimethoxy-*s*-triazines with cyanuric chloride gave the desired derivatives of *N,N*-ditriazinylamines in good yields.

Thus, it is clear that, in the reaction of the dimethoxy derivatives with cyanuric chloride, substituents on the phenyl group do affect the reaction process considerably.

The negative results of *p*-toluidino-, *o*- and *p*-methoxyphenylamino derivatives indicate that electron releasing groups prevent the reaction by lowering the acidity of the NH group, while the positive results of the chloro- and nitrophenylamino derivatives show that electron attracting groups increase the reactivity of starting compounds by enhancement of the acidity of the NH group.

Spectral examination, in methanol in the presence of sodium methoxide of the 2-arylamino-4,6-dimethoxy-*s*-triazines obtained, revealed that new absorption bands due to an anion appeared in the long wave length region in the

TABLE III

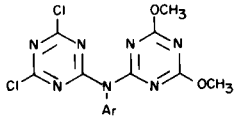


2-Arylamino-4,6-dimethoxy-*s*-triazines

Aryl		Method (a)	Yield %	m.p. (b) °C	Recrystn. Solvent	Elemental Analysis Calcd. C	H	Found C	H	Molecular Formula
C_6H_5-	(XXV)	A	Quant.	133-134 (133-134)	Ligroin					$C_{11}H_{12}N_4O_2$
o-$CH_3C_6H_4$-	(XXVI)	A	Quant.	128-129.5	Ligroin-	58.53	5.73	58.43	5.66	$C_{12}H_{14}N_4O_2$
p-$CH_3C_6H_4$-	(XXVII)	A	Quant.	133-134	Benzene	58.53	4.73	58.05	5.52	$C_{12}H_{14}N_4O_2$
2,6-$(CH_3)_2C_6H_3$-	(XXVIII)	A	Quant.	127-128	Benzene	59.99	6.20	60.43	6.47	$C_{13}H_{16}N_4O_2$
o-$CH_3OC_6H_4$-	(XXIX)	A	Quant.	134-135	Benzene-Ligroin	54.95	5.38	55.30	5.43	$C_{12}H_{14}N_4O_3$
p-$CH_3OC_6H_4$-	(XXX)	A	Quant.	136-137	Benzene-Ligroin	54.95	5.38	55.31	5.45	$C_{12}H_{14}N_4O_3$
o-ClC_6H_4	(XXXI)	A	Quant.	103.5-104	Petro.ether-Acetone	49.50	4.15	49.74	4.22	$C_{11}H_{11}ClN_4O_2$
p-ClC_6H_4-	(XXXII)	A	Quant.	163-164	Benzene-Ligroin	49.50	4.15	49.36	4.30	$C_{11}H_{11}ClN_4O_2$
o-$CH_3OOCC_6H_4$-	(XXXIII)	B	66	156-157	Benzene	53.79	4.86	53.69	4.78	$C_{13}H_{14}N_4O_4$
p-$CH_3OOCC_6H_4$-	(XXXIV)	B	54	195-197	Benzene	53.79	4.86	53.64	5.14	$C_{13}H_{14}N_4O_4$
o-$NO_2C_6H_4$-	(XXXV)	A	Quant.	174-176	Acetone	47.66	4.08	47.74	4.08	$C_{11}H_{11}N_5O_4$

(a) Refer to Experimental Section C. (b) Value in parenthesis is described in the reference (8b).

TABLE IV



4,6-Dichloro-*s*-triazin-2-yl-4′,6′-dimethoxy-*s*-triazin-2′-ylarylamines

Aryl		Yield %	M.p. °C	Recrystn. Solvent	Elemental Analysis Calcd. C	H	Found C	H	Molecular Formula
o-$CH_3C_6H_4$-	(XXXVI)	56	154-155.5	Petro.ether-Acetone	45.70	3.32	45.96	3.65	$C_{15}H_{13}Cl_2N_7O_2$
2,6-$(CH_3)_2$-C_6H_3-	(XXXVII)	10	159.5-160	Petro.ether-$CHCl_3$	47.07	3.70	47.47	3.87	$C_{16}H_{15}Cl_2N_7O_2$
o-Cl-C_6H_4-	(XXXVIII)	73	106.5-107.5	Petro.ether-$CHCl_3$	40.55	2.43	40.55	2.73	$C_{14}H_{10}Cl_3N_7O_2$
p-ClC_6H_4-	(XXXIX)	41	160-161	Petro.ether-Acetone	40.55	2.43	40.79	2.63	$C_{14}H_{10}Cl_3NO_2$
p-CH_3OOC-C_6H_4-	(XL)	70	171	Acetone	43.85	2.99	44.30	3.21	$C_{16}H_{13}Cl_2N_7O_4$
o-$NO_2C_6H_4$-	(XLI)	94	164.5-166.5	$CHCl_3$	39.55	2.37	39.21	2.25	$C_{14}H_{10}Cl_2N_8O_4$

case of *o*-chloro-, *o*-nitro- and *p*-carbomethoxy derivatives, but not with *p*-methyl- nor with the *o*- and *p*-methoxy derivatives. These results are shown in Figures 1, 2, 3 and 4.

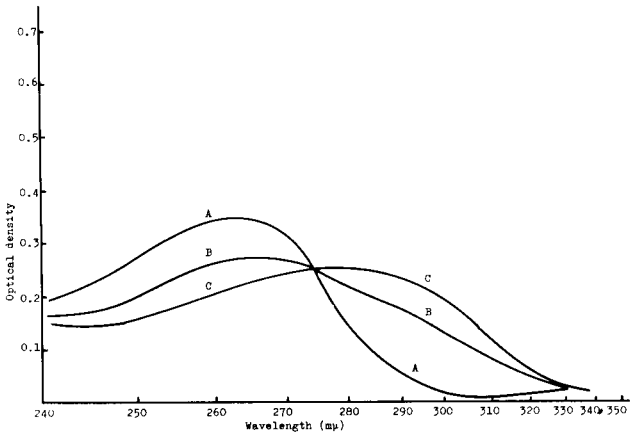


Figure 1. Absorption spectra of 2-(*o*-chloroanilino)-4,6-dimethoxy-*s*-triazine, (XXXI). 2.0 x 10^{-5} *M* in ethanol at room temperature. A, sodium ethoxide 0.00*M*; B, Sodium ethoxide 0.12*M*; C, Sodium ethoxide 0.61*M*.

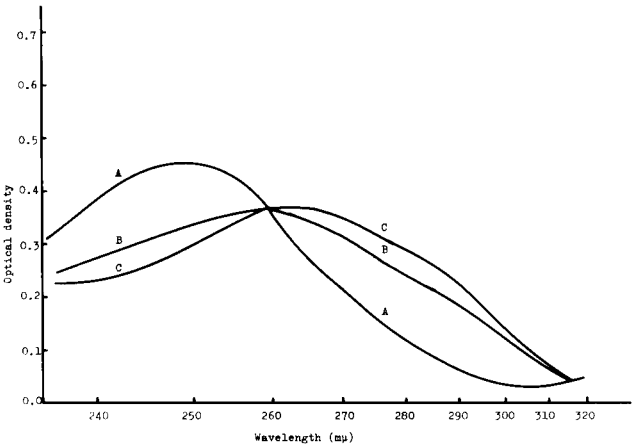


Figure 2. Absorption spectra of 2-(*o*-nitroanilino)-4,6-dimethoxy-*s*-triazine, (XXXV), 2.0 x 10^{-5} *M* in methanol at room temperature. A, Sodium methoxide 0.00*M*; B, Sodium methoxide 0.24*M*; C, Sodium methoxide 0.48*M*.

With respect to the carbomethoxy derivatives as described in Table IV, the *p*-isomer gave ditriazinylamine, while the *o*-isomer did not.

These data indicate that the position of a carbomethoxy phenylamino-*s*-triazine, and it is assumed that the intramolecular hydrogen bond between the imino hydrogen and carbonyl group may be the reason for the low reactivity of the *o*-isomer.

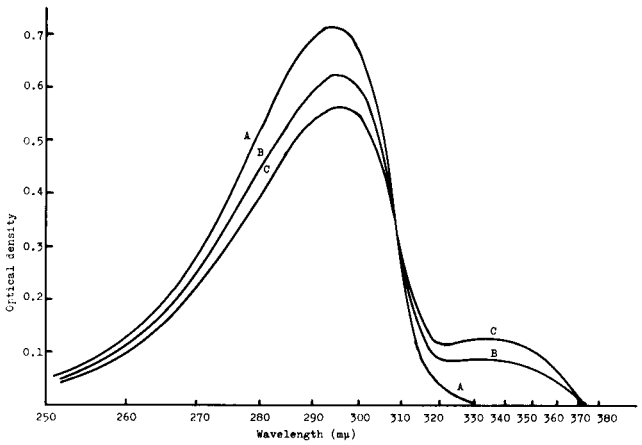


Figure 3. Absorption spectra of 2-(*p*-carbomethoxyanilino)-4,6-dimethoxy-*s*-triazine, (XXXIV), 2.0 x 10^{-5} M in methanol at room temperature. A, Sodium methoxide 0.00*M*; B, Sodium methoxide 0.62*M*; C, Sodium methoxide 0.83*M*.

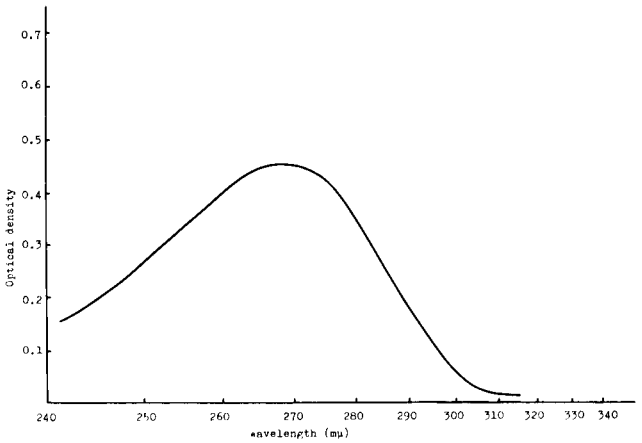
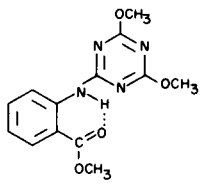


Figure 4. Absorption spectra of 2-(*p*-toluidino)-4,6-dimethoxy-*s*-triazine, (XXVII), 2.0 x 10^{-5} *M* in methanol at room temperature. Sodium methoxide, 0.00*M*; 0.10*M*; 0.20*M*; 0.52*M*.



From Table III, it can be seen that the *o*-methyl- and 2,6-dimethyl derivatives gave the desired compounds, but the *p*-methyl derivative did not. Thus, it is obvious that a methyl group in the *ortho* position facilitates the reaction significantly. However, neither of them showed an ab-

sorption band attributable to an anion in the presence of alkali and the reason for the reactivity difference between *o*-methyl and *p*-methyl derivatives still remains to be determined.

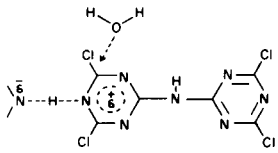
D. Reaction of Cyanuric Chloride with Ethylamine.

The reaction of cyanuric chloride with 2,4-dichloro-6-ethylamino-*s*-triazine (13) in the presence of sodium hydroxide gave the desired secondary condensation product (XLII) of the ditriazinylamine type in good yield.

However, the desired derivative of ditriazinylamine was not obtained when 2-ethylamino-4,6-dimethoxy-*s*-triazine (16) was used in place of 2,4-dichloro-6-ethylamino-*s*-triazine. The limitation of this reaction is consistent with that of the aniline derivatives described in section C (b).

E. Reaction of Cyanuric Chloride with Ammonia.

The reaction of cyanuric chloride with 2-amino-4,6-dichloro-*s*-triazine (8a) in a molar ratio of 1:1 in the presence of sodium hydroxide gave two kinds of products. One is soluble in alkali and the other is insoluble. The former is a fairly strong acid and was found to be the desired secondary condensation product of cyanuric chloride with ammonia and contains two dichlorotriazinyl groups and one hydrogen atom attached to the same nitrogen atom. The acidity of the NH group of this compound is expected to be strong due to the two dichlorotriazinyl groups. Since attempts to purify this compound by crystallization were unsuccessful due to rapid hydrolysis even in the presence of trace amounts of water, this compound was purified by sublimation. The ready hydrolysis of *N,N*-bis(4,6-dichloro-s-triazin-2-yl)amine (XLIII) may be explained by acid catalysis by the acidic imino proton as shown below.



The alkali insoluble product was found to be fairly stable to hydrolysis and to be a tertiary condensation product containing three dichlorotriazinyl groups attached to the same nitrogen atom since the mass spectral data were consistent with the calculated values for XLIV and the infrared spectrum did not show a band characteristic of the N-H group.

Tris(4,6-dichloro-*s*-triazin-2-yl)amine (XLIV) was also prepared by the reaction of *N,N*-bis(4,6-dichloro-*s*-triazin-2-yl)amine (XLIII) with cyanuric chloride in the presence of sodium hydroxide.

When 2-amino-4,6-dimethoxy-*s*-triazine (8b) was used in place of 2-amino-4,6-dichloro-*s*-triazine to obtain a secondary condensation product, no desired ditriazinylamine was obtained.

From these results, it can be generally concluded that in order to prepare derivatives of ditriazinylamine or tritriazinylamine from the reaction of amino-*s*-triazine with cyanuric chloride, the amino group of the amino-*s*-triazine must be sufficiently acidic to produce an anion with alkali.

Therefore, when an electron releasing group such as the methoxyl group is introduced into the triazinyl group, the additional introduction of an electron attracting group in an other part of a molecule, for example in the phenyl group, is necessary to increase the acidity of the amino-*s*-triazine sufficiently to obtain the desired reaction product.

EXPERIMENTAL

Infrared spectra were measured in potassium bromide discs on a Jasco D-301 spectrophotometer.

Ultraviolet spectra were recorded on a Hitachi SPU-2-spectrophotometer. Mass spectra were determined with a Hitachi RMS-4 mass spectrometer. Elemental analyses were performed in the Microanalytical Center of the University of Gunma.

A. 2-Arylamino-4,6-dichloro-*s*-triazines (8).

A typical preparation is noted below in the case of 2-(*o*-carbomethoxyanilino)-4,6-dichloro-*s*-triazine (IX).

A solution of 8.9 g. (0.06 mole) of methyl anthranilate in 20 ml. of acetone was added dropwise with stirring during 20 minutes at 0° to 5° to a solution of 100 ml. of acetone in which 10.9 g. (0.06 mole) of cyanuric chloride was dissolved at the same temperature. After an additional 30 minutes' stirring the mixture was neutralized with sodium carbonate and poured into 500 ml. of ice-water. The precipitate was collected by filtration and dried over phosphorus pentoxide. Recrystallization from benzene yielded 14.7 g. (84%), m.p. 192-194°; infrared cm^{-1}, (NH) 3200; (C=O) 1690.

B. *N,N*-Bis(4,6-dichloro-*s*-triazin-2-yl)arylamines.

(a) *N,N*-Bis(4,6-dichloro-*s*-triazin-2-yl)aniline (XIII).

To keep the reaction mixture alkaline, a solution of 0.8 g. (0.02 mole) of sodium hydroxide in 8 ml. of water was added dropwise with stirring at 0° to 5° to a solution of 50 ml. of acetone in which 4.8 g. (0.02 mole) of 2-anilino-4,6-dichloro-*s*-triazine and 3.7 g. (0.02 mole) of cyanuric chloride were dissolved at the same temperature. After an additional 1.5 hours' stirring, the mixture was processed according to the procedure for IX. Recrystallization from ligroin-benzene yielded 6.4 g. (82%), m.p. 182-183°; infrared cm^{-1}, (triazine) 850.

Infrared spectrum of this compound did not show a band characteristic of the N-H group and its molecular weight was found to be 387 by a micro Rast method (calculated molecular weight 389.12 for XIII).

To 30 ml. of methyl alcohol containing 0.3 g. (0.0013 mole) of sodium was added 1.3 g. (0.0033 mole) of this compound at room temperature. The reaction mixture was allowed to stand at room temperature for 24 hours. The mixture was poured into 100 ml. of ice-water, neutralized with hydrochloric acid, filtered and dried. Recrystallization from ligroin yielded 0.7 g. of XXV. The

filtrate was concentrated to two thirds of its original volume and extracted with benzene. The benzene layer was evaporated *in vacuo* to about 2 ml. to produce the precipitate. Recrystallization from benzene yielded 0.2 g. of trimethyl cyanurate. This result suggests that two 4,6-dichloro-*s*-triazin-2-yl groups are attached to the same nitrogen atom of aniline. These results and the elemental analysis correspond to the structure for XIII.

(b) *N,N*-Bis(4,6-dichloro-*s*-triazin-2-yl)-p-carbomethoxyaniline (XXII).

A solution of 0.6 g. (0.015 mole) of sodium hydroxide in 6 ml. of water was added dropwise with stirring at 0° to 5° during about 2 hours to 400 ml. of acetone in which 1.5 g. (0.005 mole) of 2-(*p*-carbomethoxylanilino)-4,6-dichloro-*s*-triazine and 2.8 g. (0.015 mole) of cyanuric chloride were dissolved at the same temperature. After stirring an additional 6 hours, the mixture was processed according to the procedure for IX. Recrystallization from benzene yielded 1.8 g. (81%), m.p. 241-242°; infrared cm^{-1}, (C=O) 1725; (triazine) 852.

C. 2-Arylamino-4,6-dimethoxy-*s*-triazine.

Typical preparations were noted in the case of 2,4-dimethoxy-6-(*o*-nitroanilino)- (XXXV) and 2,4-dimethoxy-6-(*o*-carbomethoxyanilino)-*s*-triazines (XXXIII).

Method (A) (12) 2,4-Dimethoxy-6-(*o*-nitroanilino)-*s*-triazine. (XXXV).

To a solution of 400 ml. of methanol containing 1.8 g. (0.08 mole) of sodium was added 5.8 g. (0.02 mole) of 2,4-dichloro-6-(*o*-nitroanilino)-*s*-triazine. The mixture was stirred for 6 hours at 35° to 40°, poured into 500 ml. of ice-water, neutralized with hydrochloric acid and filtered. Recrystallization from acetone yielded 5.4 g. (quantitative), m.p. 174-176°; infrared cm^{-1}, (NH) 3380; (triazine) 820.

Method (B) 2,4-Dimethoxy-6-(*o*-carbomethoxyanilino)-*s*-triazine (XXXIII).

A solution of 30 ml. of acetone containing 7.3 g. (0.048 mole) of methyl anthranilate and 8.6 g. (0.048 mole) of 2-chloro-4,6-dimethoxy-*s*-triazine was stirred for about 10 hours at 50°. A sodium carbonate solution was added at intervals to keep the mixture alkaline. Then the mixture was processed according to the procedure for IX. Recrystallization from pyridine yielded 9.2 g. (66%), m.p. 156-157°; infrared cm^{-1}, (NH) 3245; (C=O) 1684; (triazine) 820.

D. Ethyl-bis(4,6-dichloro-*s*-triazin-2-yl)amine (XLII).

A solution of 0.4 g. (0.001 mole) of sodium hydroxide in 4 ml. of water was added dropwise with stirring during 20 minutes at 0° to 5° to a solution of 50 ml. of acetone, in which 1.93 g. (0.01 mole) of 2-ethylamino-4,6-dichloro-*s*-triazine and 1.85 g. (0.01 mole) of cyanuric chloride were dissolved at the same temperature. After an additional 6 hours' stirring, the mixture was processed according to the procedure for IX. Recrystallization from ligroin yielded 2.2 g. (64.5%), m.p. 142.5-143.5°; infrared cm^{-1}, (triazine) 838.

Anal. Calcd. for $C_8H_5Cl_4N_7$: C, 28.18; H, 1.48. Found: C, 28.62; H, 1.41.

E. Bis- and Tris(4,6-dichloro-*s*-triazin-2-yl)amine (XLIII), (XLV).

A solution of 1.2 g. (0.03 mole) of sodium hydroxide in 12 ml. of water was added dropwise with stirring during 30 minutes at 0° to 5° to a solution of 100 ml. of acetone in which 4.95 g. (0.03 mole) of 2-amino-4,6-dichloro-*s*-triazine and 5.55 g. (0.03 mole) of cyanuric chloride were dissolved at the same temperature. After an additional 5 hours' stirring, the mixture was poured into 500 ml. of ice-water containing 3 g. of sodium carbonate. The precipitate which had separated was collected by filtration and dried over phosphorous pentoxide. Recrystallization from chlorobenzene yielded 0.4 g. (12%), m.p. >360°; infrared cm^{-1}, (triazine) 855; mass spectrometry, m/e 458. (strong, attirbutable to parent peak).

Anal. Calcd. for $C_9N_{10}Cl_6$: C, 23.45; H, 0.00; Cl, 46.2. Found: C, 23.95; H, 0.36; Cl, 46.6.

These results indicate this compound to be tris(4,6-dichloro-*s*-triazin-2-yl)amine (XLIV).

The filtrate was neutralized with hydrochloric acid and the precipitate was collected by filtration and dried over phosphorous pentoxide. Sublimation under reduced pressure (5.0 mm) yielded 2.2 g. (30%), m.p. 204°; infrared cm^{-1}, (NH) 3480; (triazine) 860; mass spectrometry, m/e 311 (strong, attributable to parent peak).

Anal. Calcd. for $C_6HCl_4N_7$: C, 23.03; H, 0.32; Cl, 45.3. Found: C, 23.65; H, 0.92; Cl, 44.9.

These results indicate this compound to be bis(4,6-dichloro-*s*-triazin-2-yl)amine (XLIII).

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