sired amine in 120 ml. of chloroform was added in small portions keeping the temperature below 10°. After standing at 5° for 1 hr., the solution was poured into water, the product extracted with chloroform, and the extracts washed with water, dried, and evaporated. The crude products were purified by recrystallization from the appropriate solvent (see Table I).

Reactions using compound VIIb were run at room temperature instead of 0–5°. The 3-hydrazino compounds (VIII. Y = $NHNH_2$, R = H or CH_3) were prepared in ethanol solution at room temperature using a fivefold excess of hydrazine hydrate.

3-Alkoxypyrido[2,3-*e*]-*as*-triazine 1-Oxides (VIII. Y = OR).—The appropriate sodium alkoxide (0.21 mole) in 250 ml. of the corresponding dry alcohol was chilled to 5°, and a solution of 0.1 mole of VIIa in 100 ml. of the same alcohol added with stirring over a 0.5-hr. period. The product was filtered, washed with water to remove sodium chloride, and purified as shown in Table I.

3-Mercaptopyrido[2,3-*e*]-*as*-triazine 1-Oxide (IXa).—Six grams (0.033 mole) of VIIa was dissolved in ethanol containing 6.0 g. of thiourea. The solution was refluxed for 1 hr., cooled, and the dark red product isolated by suction filtration. The crude product was purified by dissolution in aqueous alkali and reprecipitation with acetic acid, to obtain 4.1 g. (69.5%) of a dark red solid, m.p. 197–198° dec. See Table I for the elemental analyses.

3-Aminopyrido[2,3-*e*]-*as*-triazine (XI). A. By Catalytic Hydrogenation of IIIa.—3-Aminopyrido[2,3-*e*]-*as*-triazine 1-oxide (IIIa) (0.82 g., 5.0 mmoles) was dissolved in 100 ml. of glacial acetic acid containing 0.05 g. of 10% palladium on barium sulfate and hydrogenated at 2 atm. in a Parr shaker. Uptake of hydrogen was complete in 15 min. The catalyst was removed by filtration to give a clear yellow filtrate.[14] This solution was evaporated to dryness *in vacuo*, the residue taken up in 12 ml. of water and a solution of 2.5 g. of potassium ferricyanide in 10 ml. of water quickly added. The resulting solution was made basic with concentrated ammonium hydroxide, filtered to remove a black flocculent impurity, and chilled to 0° to precipitate the product as yellow needles, m.p. 246–250° dec., 0.4 g. (56%). Recrystallization from water with Norit gave bright yellow needles, m.p. 242–244° dec.

Anal. Calcd. for $C_6H_5N_5$: C, 48.97; H, 3.43; N, 47.60. Found: C, 49.11; H, 3.21; N, 47.57.

B. By Sodium Dithionite Reduction of IIIa.—Compound IIIa (4.9 g., 0.03 mole) was added to a solution of 10.6 g. (0.061 mole) of sodium dithionite (sodium hydrosulfite) in 75 ml. of water and stirred at room temperature for 1 hr. The bright yellow IIIa disappeared rapidly during this period and was replaced by a cream-colored precipitate of the 1,2-dihydro compound (X). This material (4.8 g.) was removed by suction filtration and converted to the aromatic compound (XI) by dissolving in 70 ml. water containing 22.5 g. of potassium ferricyanide and enough ammonium hydroxide to render the solution quite basic.[15] An immediate precipitation of XI occurred as a yellow solid. The mixture was chilled, filtered, with suction, and the product washed with cold water to give 2.5 g. (57%) of material, m.p. 235–240° dec. The infrared spectrum of this compound was identical to that of the compound prepared by method A.

Acknowledgment.—The authors are indebted to Mr. E. F. Shelberg and his staff for the microanalyses, Mr. W. Washburn and his staff for the infrared spectra, and to Mr. M. Freifelder for the catalytic hydrogenations.

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(14) This yellow solution quickly turns deep violet upon exposure to the air and should therefore be worked up without delay, preferably under a nitrogen atmosphere. Reduction using palladium on charcoal was also successful, however platinum on charcoal gave only deeply colored mixtures from which no product could be isolated.

(15) The dihydro compound (X) was quite unstable and quickly turned violet upon prolonged exposure to the air. It could not be purified for analysis because of this extreme instability.

The Reaction of Tertiary Amines with Halo-*s*-triazines and Halopyrimidines[1a]

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Trialkylamines, aryldialkylamines, and *N*-alkyl saturated nitrogen heterocycles, such as *N*-alkylpiperidines and *N*-alkyl morpholines, react with halo-*s*-triazines and halopyrimidines to form *s*-triazines and pyrimidines substituted by secondary amino groups.

The use of tertiary amines as acid scavengers is well known. In a great number of experiments, using tertiary amines as hydrochloride acceptors for the preparation of substituted *s*-triazines from the corresponding chloro-*s*-triazines, we observed the formation of by-products for which no well defined structures could be established. Analytical data and properties of these by-products did show that these compounds were not quaternary ammonium salts which—according to an Austrian patent[2]—are formed when tertiary amines are added to solutions of chloro-*s*-triazines in a nonpolar solvent.

A first hint on the nature of these products was obtained when we synthesized 2-chloro-4-*n*-butoxy-6-trichloromethyl-*s*-triazine by treating 2,4-dichloro-6-trichloromethyl-*s*-triazine (I)[3] with *n*-butyl alcohol in the presence of triethylamine. From this experiment, a by-product was isolated and identified as 2-*n*-butoxy-4-diethylamino-6-trichloromethyl-*s*-triazine (II). Apparently, in a side reaction a quaternary triethylammonium salt (III) had been formed as an intermediate

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(1)(a) This article is based on work performed under Project 116-B of The Ohio State University Research Foundation sponsored by the Olin Mathieson Chemical Corp., New York, N. Y.; (b) Olin Mathieson Chemical Corp., New Haven, Conn.

(2) Austrian Patent 174,377.

(3) E. Kober and Ch. Grundmann, *J. Am. Chem. Soc.*, **81**, 3769 (1959).

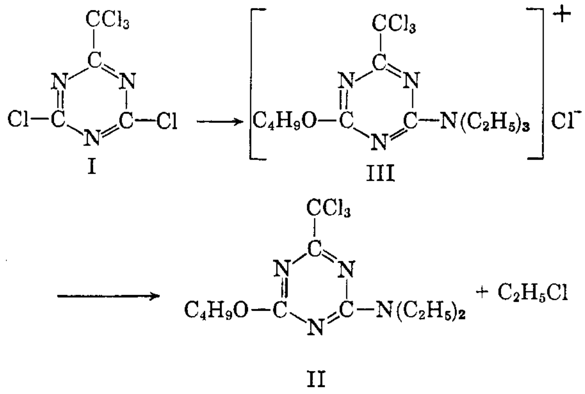
TABLE I

REACTIONS OF CYANURIC CHLORIDE (IV) WITH TERTIARY AMINES

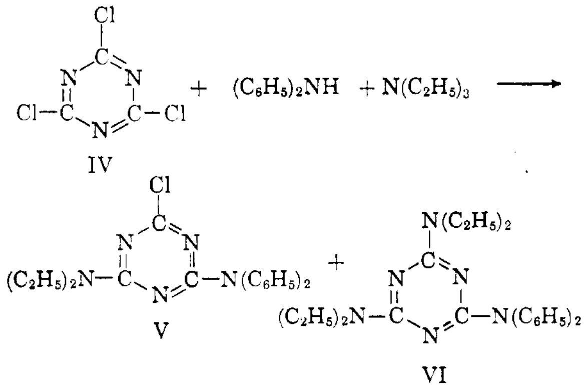
Compound	Tertiary Amine Employed	Mole Ratio IV–*tert.* Amine	Solvent	Reaction Temp., °C.	Reaction Time, Hr.	Yield, %
2-Chloro-4,6-bis(diethylamino)-*s*-triazine	Triethylamine	1:2	None	95	2	93.5
2-Chloro-4,6-bis(diethylamino)-*s*-triazine	Triethylamine	1:3	Toluene	110	1.5	99
2-Chloro-4,6-bis(di-*n*-propylamino)-*s*-triazine	Tri-*n*-propylamine	1:2	None	95	2	91
2,4-Dichloro-6-di-*n*-butylamino-*s*-triazine	Tri-*n*-butylamine	1:1	None	110	1	72
2-Chloro-4,6-bis(di-*n*-butylamino)-*s*-triazine	Tri-*n*-butylamine	1:2	Toluene	110	1.5	95
2,4,6-Tris(di-*n*-butylamino)-*s*-triazine	Tri-*n*-butylamine	1:3	None	200	1.5	78
2,4,6-Tris(*N*-methyl-*n*-dodecylamino)-*s*-triazine	*N*,*N*-Dimethyl-*n*-dodecylamine	1:3	None	220	3	95
2,4,6-Trismorpholino-*s*-triazine	*N*-Methylmorpholine	1:2	Toluene	110	2	66
2-Chloro-4,6-bis(*N*-methylphenylamino)-*s*-triazine	*N*,*N*-Dimethylaniline	1:3	Toluene	110	1.5	91
2,4,6-Tris(*N*-methylphenylamino)-*s*-triazine	*N*,*N*-Dimethylaniline	1:3	Decaline	185	1.5	30

[a] Glassy solid at room temperature.

which was decomposed upon distillation of the reaction mixture to form compound II and ethyl chloride.



In another experiment in which we tried to synthesize 2-chloro-4,6-bis(diphenylamino)-*s*-triazine from cyanuric chloride (IV) and two moles of diphenylamine in the presence of triethylamine,



we did not obtain the desired product but instead 2-chloro-4-diethylamino-6-diphenylamino-*s*-triazine (V), 2,4-bis(diethylamino)-6-diphenylamino-*s*-triazine (VI), and ethyl chloride. The isolation of compounds V and VI and especially of ethyl chloride clearly indicated that triethylamine reacted not only as a hydrogen chloride scavenger but also with chlorine atoms of IV to form *s*-triazines substituted by diethylamino groups.

These findings prompted us to investigate the reaction of cyanuric chloride (IV) with a variety of tertiary amines. We observed that certain tertiary amines form, upon addition to a solution of cyanuric chloride in an inert, nonpolar solvent, crystalline intermediates, apparently quaternary ammonium salts, and that these intermediates are thermolabile and decompose on warming into alkyl halides and *s*-triazines substituted by secondary amino groups. Whether or not this reaction occurs, depends largely on the tertiary amine employed. In general, it can be stated that tertiary aromatic amines are completely inert to this type of reaction, while trialkylamines, aryldialkylamines, and *N*-alkyl saturated nitrogen heterocycles, such as *N*-alkylpiperidines and *N*-alkylmorpholines, react quite readily. The reaction proceeds also with alkyldiarylamines but requires rather rigid conditions. Thus, cyanuric chloride reacted with two mole equivalents of *N*-methyldiphenylamine in the absence of a solvent at 250° to result in the evolution of one mole equivalent of methyl chloride which was identified by infrared analysis. The solid reaction product consisted of a mixture of chlorodiphenylamino-*s*-triazines and tris(diphenylamino)-*s*-triazine which could not be separated.

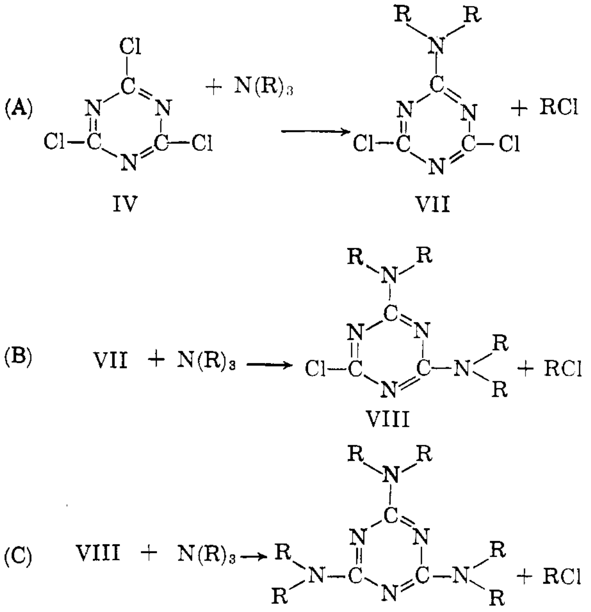
With most of the tertiary amines subjected to this reaction the substitution of the cyanuric chloride (IV) by secondary amino groups proceeds stepwise, involving one, two, or three chlorine atoms of IV, as shown by the following scheme.

Whether the reaction proceeds according to equation A or whether it continues to form compounds of type VIII or IX depends on the mole ratio of cyanuric chloride and tertiary amine, on the reaction conditions, and largely on the reactivity of the tertiary amine employed. Lower temperatures and the use of an inert solvent favor reaction A, while elevated temperatures or working without a

TABLE I (*continued*)

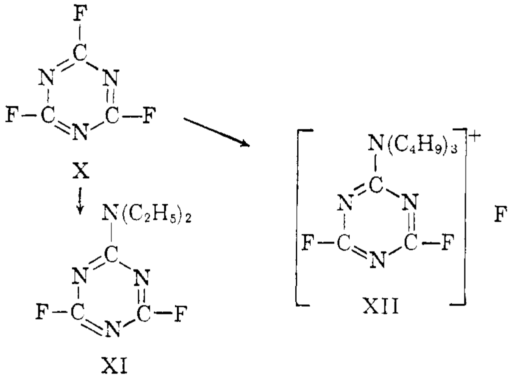
B.P. (mm.)	Refractive Index	Calcd.				Found			
		C	H	N	Cl	C	H	N	Cl
168 (10)	n^{25}_D 1.5222	51.83	7.83	27.22	13.78	52.15	7.83	28.09	11.92
135 (2)	n^{23}_D 1.5273								
142–144 (1)	$n^{28.5}_D$ 1.5128	57.40	8.99	22.31	...	57.33	9.11	22.24	...
124 (2)	n^{23}_D 1.5201	47.66	6.55	20.21	25.58	48.21	6.32	20.40	24.87
178 (1)	n^{27}_D 1.5046	61.68	9.81	18.93	9.58	62.07	9.56	18.84	9.75
189 (2)	n^{27}_D 1.4948	...	...	17.99	...	...	...	17.82	...
		75.02	12.50	12.50	...	74.96	12.27	12.22	...
M.p. 270–273		53.61	7.15	...	...	53.65	7.17	...	...
214–217 (2)		62.67	4.95	21.50	10.88	62.57	4.83	21.63	10.82
258–260 (2)[a]		72.20	6.10	21.20	...	72.06	6.16	20.92	...

solvent tend to cause the progression of the reaction to compounds of type VIII or IX. That the degree to which this reaction proceeds is also very much influenced by the reactivity of the tertiary amine employed, is indicated by the fact that with *N*-methylmorpholine the reaction resulted in the quantitative formation of the trisubstituted product of type IX even under conditions which favored with other tertiary amines the formation of di-substituted products of type VIII.



Our results on the reaction of cyanuric chloride (IV) with tertiary amines are summarized in Table I.

We observed that the reaction of tertiary amines also takes place with cyanuric fluoride (X).[3] The formed intermediate quaternary ammonium fluorides, however, do not undergo thermal decomposition to alkylhalides and *s*-triazines substituted by secondary amino groups as readily as the corresponding quaternary ammonium chlorides formed from IV. While 2,4-difluoro-6-diethylamino-*s*-triazine (XI) could be obtained, although in a very low yield, from X and triethylamine, the quaternary ammonium salt XII from X and tris-*n*-butylamine was distillable *in vacuo* without noticeable decomposition, thus indicating that compound XII is relatively thermostable. The isolation of a similar quaternary ammonium salt, namely the 2-*o*-chloroanilino-4-fluoro-*s*-triazinyl-(6)-triethylammonium fluoride has already been reported in connection with other investigations.[4]



Since the literature[2] describes also the formation of quaternary ammonium salts from chloropyrimidines and tertiary amines, we extended our investigation to the reaction of halopyrimidines with tertiary amines.[5]

Contrary to our finding in the series of reactions with cyanuric chloride we found that the degree to which the corresponding reaction of 2,4,6-trichloropyrimidine (XIII) and tertiary amine proceeds does not depend on the mole ratio of the two reactants and is very little or not influenced at all

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(4) E. Kober, H. Schroeder, R. Rätz, H. Ulrich, and Ch. Grundmann, *J. Org. Chem.*, **27**, 2577 (1962).

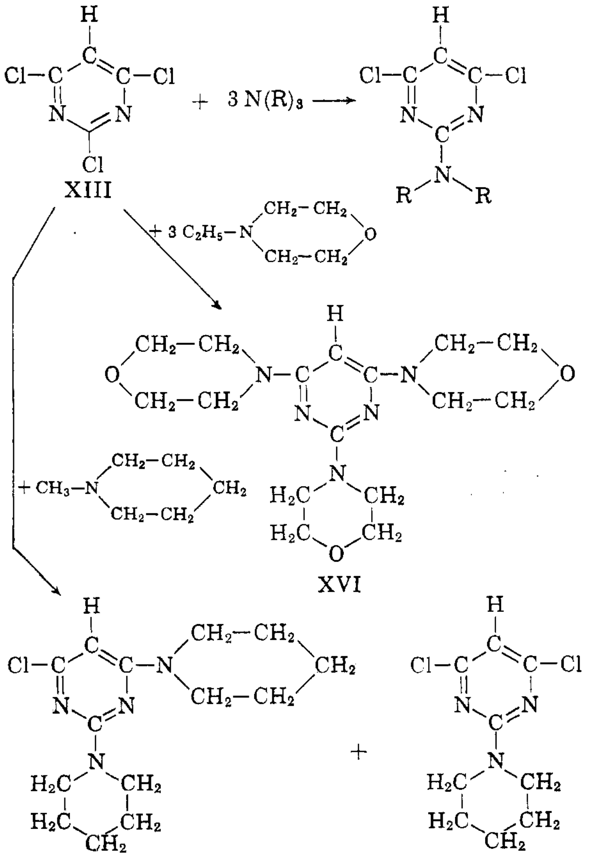
(5) The formation of 2,4,6-tris(*N*-methylphenylamino)pyrimidine by refluxing 2,4,6-trichloropyrimidine and *N*,*N*-dimethylaniline without a solvent has been reported by Sin' Iti Kawai and Takashige Miyoshi, *Sci. Papers, Inst. Phys. Chem. Res.* (Tokyo), **16**, 20 (1931).

TABLE II

REACTIONS OF HALOPYRIMIDINES WITH TERTIARY AMINES

	Starting Materials[a]					
Compound	Halopyrimidine	Tertiary Amine	Solvent	Reaction Temp., °C.	Reaction Time, Hr.	Yield, %
2-Diethylamino-4,6-dichloropyrimidine	XIII	Triethylamine	None	25	200	85
2-Diethylamino-4,6-dichloropyrimidine	XIII	Triethylamine	Toluene	110	8	75
2-Di-*n*-butylamino-4,6-dichloropyrimidine	XIII	Tri-*n*-butylamine	Toluene	110	7	88
2-Di-*n*-butylamino-4,6-dichloropyrimidine	XIII	Tri-*n*-butylamine	Decaline	185	6	98
2-*N*-Methylphenylamino-4,6-dichloropyrimidine	XIII	*N*,*N*-Dimethylaniline	Toluene	110	8	82
2-*N*-Methylphenylamino-4,6-dichloropyrimidine	XIII	*N*,*N*-Dimethylaniline	Decaline	185	5	96
2-Piperidino-4,6-dichloropyrimidine	XIII	*N*-Ethylpiperidine	Toluene	110	8	84
2,4-Bis(piperidino)-6-chloropyrimidine	XIII	*N*-Ethylpiperidine	Toluene	110	8	5
2,4,6-Trimorpholinopyrimidine	XIII	*N*-Methylmorpholine	Toluene	110	5	94
2-Diethylamino-4,5,6-trichloropyrimidine	XVII	Triethylamine	Toluene	110	1	96
2-Di-*n*-butylamino-4,5,6-trichloropyrimidine	XVII	Tri-*n*-butylamine	Toluene	110	2	92
2-Di-*n*-butylamino-4,5,6-trichloropyrimidine	XVII	Tri-*n*-butylamine	Decaline	185	5	82
2-*N*-Methylphenylamino-4,5,6-trichloropyrimidine	XVII	*N*,*N*-Dimethylaniline	Toluene	110	8	96
2-Piperidino-4,5,6-trichloropyrimidine	XVII	*N*-Ethylpiperidine	Toluene	110	5	99
2-Morpholino-4,5,6-trichloropyrimidine	XVII	*N*-Methylmorpholine	Toluene	110	7	100
2-Diethylamino-4,6-difluoro-5-chloropyrimidine	XVIII	Triethylamine	Toluene	110	6	5
2-*N*-Methylphenylamino-4,6-difluoro-5-chloropyrimidine	XVIII	*N*,*N*-Dimethylaniline	Toluene	110	8	53

[a] A mole ratio 1: >3 was used in all experiments. [b] Melting point after recrystallization from methanol or ethanol. [c] This compound is converted by melting into a modification which has a melting point of 92.5–94°.



by the temperature at which the reaction is carried out. The influence of the character of the tertiary amine, however, is very significant. As in the case of cyanuric chloride, tertiary aromatic amines do not react at all. With tertiary aliphatic amines, such as triethylamine and di-*n*-butylamine, as well as with mixed aromatic aliphatic amines, such as *N*,*N*-dimethylaniline, only one chlorine atom of XIII is replaced by a secondary amino group, although these tertiary amines were applied in considerable excess and the reactions were carried out in refluxing toluene or decaline. It is tentatively postulated that the substitution occurred in the 2-position, since the electron-withdrawing effect of two adjacent nitrogen atoms should make the 2-chlorine atom more reactive than those in 4- or 6- position. When *N*-ethylpiperidine reacted with compound XIII, a small amount of 2,4-bis(piperidino)-6-chloropyrimidine (XIV) was formed besides 2-piperidino-4,6-dichloropyrimidine (XV) and—as with cyanuric chloride (IV)—*N*-methylmorpholine was found to be especially reactive indicated by the nearly quantitative formation of 2,4,6-trimorpholinopyrimidine (XVI).

The reaction of 2,4,5,6-tetrachloropyrimidine (XVII) led under various conditions without any exception to the substitution of only one chlorine atom by a secondary amino group. Even with such reactive tertiary amines as methylmorpholine or *N*-ethylpiperidine monosubstitution only could be achieved, although these amines were applied in a large excess. This indicates that the chlorine atom in 5- position reduces the reactivity of the chlorine atoms in 4- and 6-position as compared to

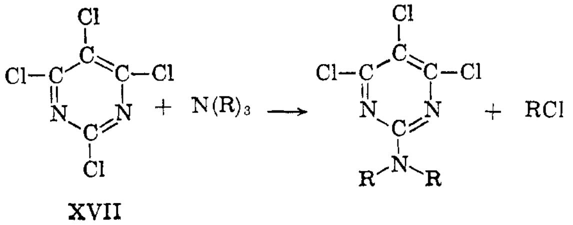
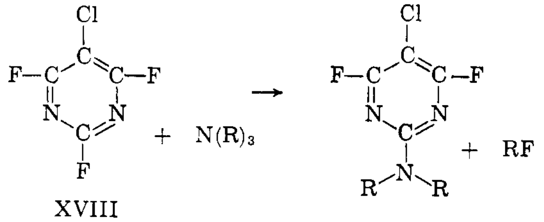


TABLE II (*continued*)

B.P. (mm.)	Refractive Index	Calcd.					Found				
		C	H	N	Cl	F	C	H	N	Cl	F
86–87.5 (1)	n^{26}D 1.5499	43.65	5.04	19.09	32.22		43.65	5.01	19.05	32.21	
85–87 (0.7)	n^{24}D 1.5506	43.65	5.04	19.09	32.22		43.65	5.60	19.22	32.24	
111–115 (0.3)	n^{30}D 1.5231	52.22	6.94	15.22	25.69		52.14	7.11	15.21	25.78	
91–99 (0.15)	n^{24}D 1.5252										
76–78^{b,c}		51.99	3.57	16.53	27.91		52.18	3.62	16.40	27.87	
76–78^{b,c}					27.91					27.70	
81–82^{b}		46.57	4.78	18.10	30.55		46.38	4.73	17.97	30.62	
106–109^{b}		59.88	7.54	19.96	12.62		61.76	7.58	19.86	10.91	
278–281^{b}		57.30	7.51	20.88			57.45	7.58	20.92		
78.5–79^{b}		37.75	3.96	16.51	41.79		37.99	3.91	16.40	41.67	
136–139 (0.65)	$n^{21.5}$D 1.5438	46.39	5.84	13.53	34.24		46.55	5.92	13.70	34.08	
127–138 (0.35)	n^{17}D 1.5436										
96–97^{b}		45.78	2.79	14.56	36.86		46.15	2.55	14.26	36.82	
73.5–74.5^{b}		40.55	3.78	15.75	39.90		40.51	4.44	15.72	39.50	
140–142^{b}		35.78	3.00	15.65	39.61		35.85	2.97	15.29	39.62	
55–57 (0.6)		43.35	4.55	18.96	16.00	17.15	43.39	4.64	18.45	15.99	17.21
96–105 (0.2)	n^{27}D 1.5706	51.68	3.16	16.43	13.87	14.86	52.26	3.88	16.32	13.52	14.11

the corresponding chlorine atoms of 2,4,6-trichloropyrimidine (XIII).

Finally, the reaction of tertiary amines with 2,4,6-trifluoro-6-chloropyrimidine (XVIII)[6] was investigated.



XVIII

As in the case of XVII, products of which only one fluorine atom was replaced by a secondary amino group were obtained.

Our results on the reaction of halopyrimidines with tertiary amines are summarized in Table II.

Experimental[7]

2-*n*-Butoxy-4-diethylamino-6-trichloromethyl-*s*-triazine (II) and 2-*n*-Butoxy-4-chloro-6-trichloromethyl-*s*-triazine.—A mixture of *n*-butyl alcohol (0.8 g.) and triethylamine (11.4 g.) in ether (150 ml.) was added at 0°, with stirring, to the solution of 2,4-dichloro-6-trichloromethyl-*s*-triazine (I) in ether. After stirring for 5 hr. at 0°, the precipitated triethylamine hydrochloride was filtered. The ether was removed from the filtrate and the oily remainder distilled *in vacuo* to give two fractions, one boiling at 110–111.8° (0.25 mm.) (11.65 g.), the other fraction boiling at 128–135° (0.15 mm.) (5.32 g.). The two fractions were separately fractionated; 2-butoxy-4-chloro-6-trichloro-methyl-*s*-triazine, b.p. 114–116° (0.4 mm.), n^{25}D 1.5222, was isolated from the first cut.

Anal. Calcd. for $C_8H_9N_3Cl_4O$: C, 31.50; H, 2.97; N, 13.78; Cl, 46.50. Found: C, 31.66; H, 3.00; N, 14.15; Cl, 46.40.

From the second cut 2-butoxy-4-diethylamino-6-trichloromethyl-*s*-triazine (II), b.p. 128–128.5° (0.1 mm.), $n^{26.5}$D 1.5185, was obtained.

Anal. Calcd. for $C_{12}H_{19}N_4Cl_3O$: C, 42.18; H, 5.60; N, 16.40; Cl, 31.13. Found: C, 42.01; H, 5.26; N, 17.53; Cl, 32.25.

2-Chloro-4-diethylamino-6-diphenylamino-*s*-triazine (V) and 2,4 - Bis(diethylamino) - 6 - diphenylamino - *s* - triazine (VI).—A solution of cyanuric chloride (IV, 9.23 g., 0.05 mole), diphenylamine (16.92 g., 0.1 mole), and triethylamine (10.1 g., 0.1 mole) in toluene (180 ml.) was refluxed for 5 hr. An amount of 3.2 g. of ethyl chloride had condensed in a Dry Ice-cooled trap. After filtration of the formed triethylamine hydrochloride (6.5 g.) the toluene was removed by vacuum distillation. The remaining semicrystalline residue was dissolved in ether and washed two times with small portions of water. After removal of the ether, 50 ml. of ligroin was added to the residue, leaving undissolved 4.8 g. of V, m.p. 166–168° (from ligroin); yield, 30%. From the petroleum ether-soluble part diphenylamine (9.4 g.) was recovered by vacuum distillation at 121° (4 mm.). The residue (11.4 g.) consisted of VI, m.p. 75–76° (from ligroin); yield, 45%.

Anal. Calcd. for $C_{19}H_{20}N_5Cl$: C, 64.49; H, 5.70; N, 19.79; Cl, 10.02. Found: C, 65.98; H, 5.63; N, 19.51; Cl, 9.69.

Anal. Calcd. for $C_{23}H_{30}N_6$: C, 70.73; H, 7.74; N, 21.52. Found: C, 70.13; H, 7.39; N, 21.08.

General Procedure for the Reaction of Cyanuric Chloride with Tertiary Amines. Preparation of 2-Chloro-4,6-bis-(diethylamino)-*s*-triazine. (a). Without a Solvent.—A mixture of cyanuric chloride (IV, 9.23 g., 0.05 mole) and triethylamine (10.5 g., 0.1 mole) was slowly heated to 70° at which temperature a gentle running reaction started. Within 30 min., an amount of 6.5 g. of ethyl chloride (identified by infrared spectrum) had condensed in a Dry Ice-cooled trap. The heating was continued at 100° for another 90 min. and the resulting oily reaction mixture distilled *in vacuo* to give 93.5% of 2-chloro-4,6-(diethylamino)-*s*-triazine.

(b). In Toluene.—A solution of cyanuric chloride (IV, 9.23 g., 0.05 mole) in toluene (100 ml.) was added to a solu-

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[6] H. Schroeder, E. Kober, H. Ulrich, R. Rätz, H. Agahigian, and Ch. Grundmann, *J. Org. Chem.*, **27**, 2580 (1962).

[7] All melting points are determined with the Fisher-Johns apparatus. Microanalyses are from Galbraith Microanalytical Laboratories, Knoxville, Tenn., and from Spang Microanalytical Laboratory, Ann Arbor, Mich.

tion of triethylamine (30.3 g., 0.15 mole) in toluene (80 ml.). After refluxing for 90 min., 6.3 g. of ethyl chloride (identified by infrared spectrum) had condensed in a Dry Ice-cooled trap. This corresponds well to the calculated amount of 6.45 g. or 0.1 mole of ethyl chloride. After filtering a very small amount of triethylamine hydrochloride, the solvent and the excess amine were removed by distillation *in vacuo.* The remaining slightly yellowish oil (13.1 g.) was purified by distillation, yielding 99% of 2-chloro-4,6-bis(diethylamino)-*s*-triazine.

From the residue of the distillation 0.1 g. of crystalline 2-hydroxy-4,6-bis(diethylamino)-*s*-triazine was isolated. After recrystallization from ligroin, small needles, m.p. 166–168°, were obtained. This compound is soluble in warm 2 *N* sodium hydroxide.

Anal. Calcd. for $C_{11}H_{21}N_5O$: C, 55.20; H, 8.85; N, 29.27. Found: C, 56.68; H, 8.77; N, 27.53.

2,4-Difluoro-6-diethylamino-*s*-triazine (XI).—One mole of cyanuric fluoride (X) and 2 moles of triethylamine were refluxed in 2000 ml. of toluene for 24 hr. The ethyl fluoride which was evolved was condensed in a system of traps cooled with Dry Ice and acetone; the collected amount corresponded to 90% of the theory. After removing the toluene by distillation, XI was obtained as a solid residue which was recrystallized from ligroin to give colorless leaflets, m.p. 101°; yield, 4%. A mixed melting point with an authentic sample of XI[4] showed no depression.

Anal. Calcd. for $C_7H_{10}N_4F_2$: C, 44.67; H, 5.36; N, 29.74; F, 20.19. Found: C, 44.67; H, 5.30; N, 29.67; F, 20.22.

2,4-Difluoro-*s*-triazinyl-(6)-tris-*n*-butylammonium Fluoride (XII).—Cyanuric fluoride (X, 7.2 g.) in toluene (20 ml.) was added to a solution of tri-*n*-butylamine (20.2 g.) in toluene (40 ml.). Upon addition, a mild exothermic reaction occurred. The mixture was refluxed at 125° for 4 hr. After removal of the excess tri-*n*-butylamine and the toluene, a reddish brown, heavy oil remained. Fractional distillation of the residue afforded 16 g. of XII, b.p. 91° (2 mm.). The product crystallized upon standing at 0°; the crystals which formed showed a m. p. of 16–17°.

Anal. Calcd. for $C_3N_3F_3(C_4H_9)_3N$: C, 56.30; H, 8.44; N, 17.46; F, 17.80. Found: C, 56.48; H, 8.81; N, 17.21; F, 18.73.

General Procedure for the Reaction of Halopyrimidines with Tertiary Amines.—A halopyrimidine (XIII, XVII, or XVIII) was refluxed with a tertiary amine in the applied solvent. Low-boiling alkyl halides (identified by infrared spectrum) formed in the reaction were condensed in a Dry Ice-cooled trap. The reaction was complete when the formation of the alkyl halide had ceased. The excess tertiary amine, the solvent, and, in experiments with tri-*n*-butylamine, the *n*-butyl chloride formed (identified by infrared spectrum) were removed from the reaction mixture by distillation. Liquid residues were purified by vacuum distillation, while solid residues were recrystallized.

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The Synthesis of Substituted Melams

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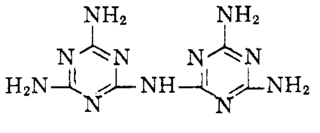
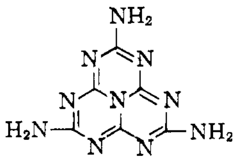
Fusion of certain substituted amino-*s*-triazines with chloro-*s*-triazines resulted, depending on the substituents, in the formation of hepta-, octa-, or nona-substituted melams. Utilizing this method, melam derivatives composed of three *s*-triazine nuclei have been prepared. Other approaches to synthesize substituted melams were less successful.

Melam (I) and melem (II) are carbon-nitrogen compounds which have been known for more than 100 years. These products were considered remarkable by their discoverers, two of whom were Liebig[1] and Gmelin,[2] because of their unusual thermal stability, a property which caused doubt as to whether to classify them as organic or inorganic compounds. Their structures were finally established by Pauling and his disciples.[3,4] These compounds are derivatives of melamine and are related to this parent compound in about the same manner as the polynuclear aromatics are related to benzene.

The relation of I and II to melamine is especially supported by the observation that melamine preparations, involving high temperatures, are usually accompanied by the formation of I and II.



I



II

While melamine has become an increasingly important chemical commodity, I and II have received little attention and, consequently, no derivatives of these two compounds are known. This and the unusual thermal stability of the two parent compounds prompted the preparaton of a series of substituted melams as well as of substituted melems. While the latter will be in part the subject of a separate paper, the present investigation represents a study on the novel class of substituted melams.

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