

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 XI⁴ 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 $C_{24}N_8F_3(C_4H_9)_3N$: 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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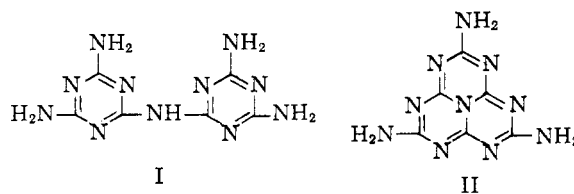
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Fusion of certain substituted amino-s-triazines with chloro-s-triazines resulted, depending on the substituents, in the formation of hepta-, octa-, or nona-substituted melams. Utilizing this method, melam derivatives composed of three s-triazine nuclei 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 Liebig¹ 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 prepa-



rations, involving high temperatures, are usually accompanied by the formation of I and 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 preparation 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.

(1) J. Liebig, *Ann.*, **10**, 4 (1834).

(2) L. Gmelin, *Ann.*, **15**, 252 (1835).

(3) L. Pauling and J. Sturdivant, *Proc. Natl. Acad. Sci.*, **23**, 615 (1937).

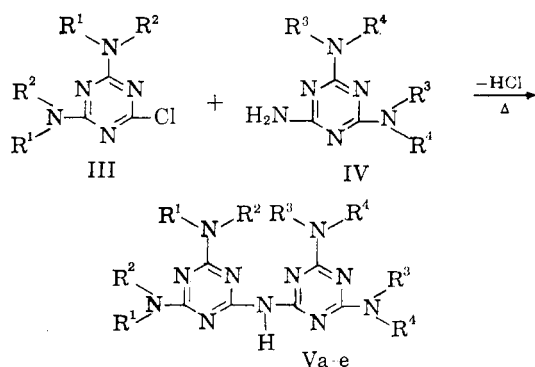
(4) C. E. Redeman and H. J. Lucas, *J. Am. Chem. Soc.*, **61**, 3420 (1939); **62**, 842 (1940).

TABLE I
 SECONDARY AROMATIC AMINES

Compound			B.P. (mm.)	n_D^{20}	t	Yield, %	Formula	Calcd., %			Found, %		
R ¹	R ²	R ³						C	H	N	C	H	N
H	CH ₃	C ₆ H ₅	158-164 (6.0) ^a	1.6269	29	49.2	C ₁₃ H ₁₃ N	85.20	7.15	7.65	84.49	7.72	8.04
CH ₃	CH ₃	<i>p</i> -CH ₃ C ₆ H ₄	125-132 (0.4)	1.6035	25	39.0	C ₁₅ H ₁₇ N	85.26	8.11	6.63	85.48	8.07	7.05
CH ₃	CH ₃	CH ₂ C ₆ H ₅	140-150 (0.65)	1.5922	26	78.0	C ₁₅ H ₁₇ N	85.26	8.11	6.63	85.67	7.89	6.76

^a M.p., 84-85°.

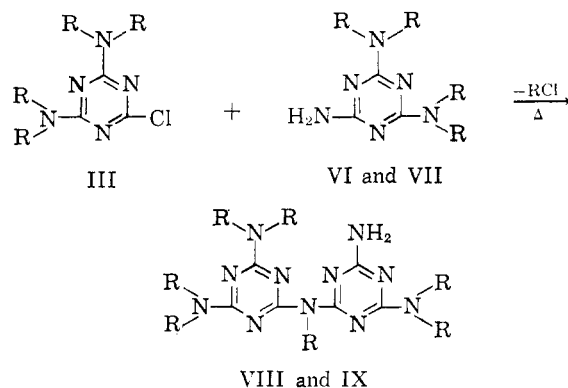
It has been found that fusion of 2,4-bis(*sec*-amino)-6-chloro-*s*-triazines (III) with certain 2-amino-4,6-bis(*sec*-amino)-*s*-triazines (IV) results with evolution of hydrogen chloride in the formation of the correspondingly substituted melams (Va-e).



	R ¹	R ²	R ³	R ⁴
Va.	<i>n</i> -C ₄ H ₉	<i>n</i> -C ₄ H ₉	<i>n</i> -C ₄ H ₉	<i>n</i> -C ₄ H ₉
Vb.	<i>n</i> -C ₇ H ₁₅	<i>n</i> -C ₇ H ₁₅	<i>n</i> -C ₇ H ₁₅	<i>n</i> -C ₇ H ₁₅
Vc.	<i>n</i> -C ₇ H ₁₅	<i>n</i> -C ₇ H ₁₅	<i>n</i> -C ₄ H ₉	<i>n</i> -C ₄ H ₉
Vd.	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅
Ve.	<i>n</i> -C ₄ H ₉	C ₆ H ₅	<i>n</i> -C ₄ H ₉	C ₆ H ₅

While the fusion of III with IV, which gave the octa-substituted melams Va-e in high yields, proceeded as expected, unpredictable results were obtained when monochloro-*s*-triazines (III) were subjected to fusion with 2-amino-4,6-bis(diethylamino)-*s*-triazine (VI) or 2-amino-4,6-bis(di-*n*-propylamino)-*s*-triazine (VII). Instead of yielding melams of the general structure V, the reaction took an unexpected course to form, with elimination of ethyl chloride or *n*-propyl chloride, the hepta-substituted melams VIII and IX, respectively, which still have the primary amino group attached to that part of the moiety which stems from compounds VI and VII, respectively.

Similar dealkylations of aliphatic and mixed aliphatic-aromatic tertiary amines by means of cyanuric chloride have been reported recently.⁵ In the latter investigation a distinct difference between the reactivity of aliphatic and aromatic groups was observed in as far as aliphatic groups but not aromatic groups attached to the nitrogen



III. VI. VIII. R = C₂H₅
 III. VII. IX. R = *n*-C₃H₇

atom of tertiary amines were cleaved. The reaction of compounds IV, VI, and VII with monochloro-*s*-triazines (III), however, is marked not only by the difference in the tenacity of alkyl and phenyl groups attached to tertiary nitrogen atoms but also by the tendency of the lower alkyl groups to cleave more easily than the higher alkyl groups. While these findings can be explained with the rule established by von Braun,⁶ the interaction of the chlorine atom of compound III with a tertiary amino group instead of the primary amino group of VI or VII is still surprising. Therefore, it must be assumed that in the present systems the dealkylation of alkyl groups lower than *n*-butyl occurs already at temperatures not high enough to effect reaction of the primary amino group with the chlorine atom of compound III.

Nona-substituted melams (Xa-k) were obtained by the fusion of compounds of structure III with 2-anilino-4,6-bis(*sec*-amino)-*s*-triazines (XI). The formation of alkyl chlorides has not been observed when alkylamino-substituted melamines of structure XI were employed.

Our investigations were also extended to melams consisting of three substituted *s*-triazine rings connected by nitrogen bridges. The preparation of these compounds was again achieved by fusion of correspondingly substituted anilino- and chloro-*s*-triazines. Reaction of 2,4-bis(anilino)-6-diphenylamino-*s*-triazine (XII) with two mole equivalents of 2,4-bis(*sec*-amino)-6-chloro-*s*-triazines (XIII) as

(5) E. Kober and R. F. W. Rätz, *J. Org. Chem.*, **27** 2509 (1962).

(6) J. von Braun and K. Moldaenke, *Ber.*, **56**, 2165 (1923).

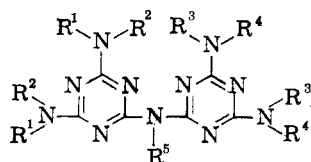
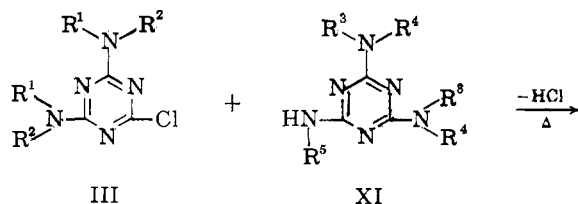
TABLE II
SUBSTITUTED 2,4-DIAMINO-6-CHLORO-S-TRIAZINES

Compound		M.P.	B.p. (mm.)	Yield, %	Formula	Calcd., %				Found, %				Prepared by Method
R ¹	R ²					C	H	N	Cl	C	H	N	Cl	
<i>n</i> -C ₇ H ₁₅	<i>n</i> -C ₇ H ₁₅	258 (4)	75	69.20	C ₂₁ H ₃₀ N ₃ Cl	69.20	11.17	13.03	6.60	71.48	11.61	13.32	6.90	A
<i>n</i> -C ₇ H ₁₅	C ₆ H ₅	233 (3)	38	67.38	C ₂₂ H ₂₃ N ₃ Cl	67.38	6.89	17.09	8.65	67.77	6.69	16.99	8.38	A
C ₆ H ₅	C ₆ H ₅	221-222	34	72.07	C ₂₇ H ₂₀ N ₃ Cl	72.07	4.48	15.57	7.88	72.33	4.65	15.44		B
CH ₃ C ₆ H ₄	CH ₃ C ₆ H ₄	163-164	91.8		C ₃₁ H ₂₃ N ₃ Cl				7.00				7.14	A
CH ₂ C ₆ H ₄	C ₆ H ₄ (CH ₃) ₂ (<i>o,p</i>)	37-40	98.7		C ₃₃ H ₂₃ N ₃ Cl				6.64				6.80	A

TABLE III
SUBSTITUTED MELAMINES

Compound		R ³	R ⁴	M.P.	B.P. (mm.)	Yield, %	Formula	Calcd., %				Found, %				Prepared by method
R ¹	R ²							C	H	N		C	H	N		
C ₂ H ₅	C ₂ H ₅	H	H	71-72 ^a		97	C ₁₁ H ₁₂ N ₆	55.43	9.31	35.26		55.57	9.03	35.39		A
<i>n</i> -C ₃ H ₇	<i>n</i> -C ₃ H ₇	H	H	67-68 ^b		95	C ₁₃ H ₁₆ N ₆	61.24	10.21	28.55		61.32	10.18	28.61		A
<i>n</i> -C ₄ H ₉	<i>n</i> -C ₄ H ₉	H	H	62 ^b		100	C ₁₅ H ₁₈ N ₆	65.20	10.85	23.98		64.94	10.97	24.17		A
<i>n</i> -C ₇ H ₁₅	<i>n</i> -C ₇ H ₁₅	H	H	38.5-40 ^b	239-244 (760)	80	C ₃₁ H ₄₂ N ₆	71.80	11.93	16.20		71.50	12.20	16.43		A
C ₆ H ₅	C ₆ H ₅	H	H	312-315 ^c		45	C ₂₅ H ₂₈ N ₆	75.33	5.15	19.52		75.25	4.97	19.46		C
<i>n</i> -C ₄ H ₉	<i>n</i> -C ₄ H ₉	H	H	143-144 ^d		34	C ₂₃ H ₃₀ N ₆	70.73	7.74	21.52		70.27	7.78	21.49		C
C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	H	59-61	214 (3)	76	C ₃₃ H ₃₆ N ₆	70.50	9.87	19.63		70.51	9.70	19.62		C
C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	H	273-274 ^e		78.2	C ₃₃ H ₃₆ N ₆	78.24	5.17	16.59		78.39	5.37	16.64		C
C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	218-219 ^f		44.2	C ₃₇ H ₄₂ N ₆	75.32	5.15	19.52		75.03	5.16	19.54		C
C ₆ H ₅	CH ₃	C ₆ H ₅	H	126-128 ^d		94.7	C ₂₃ H ₂₂ N ₆	72.23	5.79	21.98		72.59	6.22	21.93		C
CH ₃ C ₆ H ₄	CH ₃ C ₆ H ₄	C ₆ H ₅	H	131-132 ^g		85.7	C ₃₇ H ₄₄ N ₆	78.97	6.09	14.94		78.14	6.29	15.02		B
C ₆ H ₄ (CH ₃) ₂ (<i>o,p</i>)	C ₆ H ₄ (CH ₃) ₂ (<i>o,p</i>)	C ₆ H ₅	H	95-100 ^h		63.5	C ₃₉ H ₃₈ N ₆	79.29	6.48	14.23		78.57	6.82	14.60		C
CH ₂ C ₆ H ₄	C ₆ H ₄ (CH ₃) ₂ (<i>o,p</i>)	C ₆ H ₅	H	75-78 ^h		91	C ₃₅ H ₃₈ N ₆	79.29	6.48	14.23		79.65	6.67	13.95		C

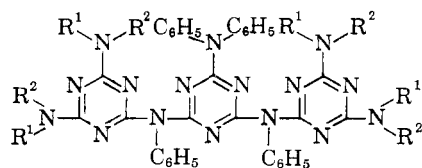
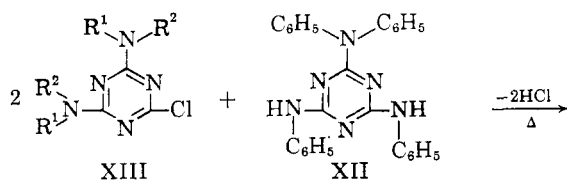
^a From 65% aqueous methanol. ^b From petroleum ether (b.p. 60-70°). ^c From diethylene glycol diethyl ether. ^d From ethanol. ^e From decalin. ^f From xylene. ^g Dissolved in toluene and precipitated with ethanol. ^h Attempts to recrystallize this material from various organic solvents were not successful.



Xa-k

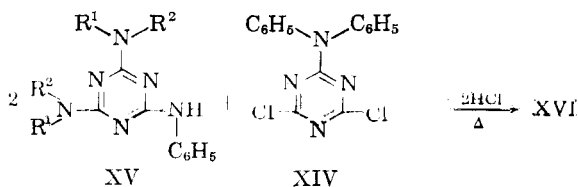
	R ¹	R ²	R ³	R ⁴	R ⁵
Xa.	<i>n</i> -C ₄ H ₉	<i>n</i> -C ₄ H ₉	<i>n</i> -C ₄ H ₉		
b.	C ₆ H ₅	C ₆ H ₅	CH ₃		
c.	CH ₃	C ₆ H ₅	CH ₃		
d.	CH ₃	C ₆ H ₅	C ₆ H ₅		
e.	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅		
f.	CH ₂ C ₆ H ₅	CH ₂ C ₆ H ₅	C ₆ H ₅		
g.	CH ₂ C ₆ H ₅	CH ₂ C ₆ H ₅	C ₆ H ₄ (CH ₃ - <i>p</i>)		
h.	CH ₂ C ₆ H ₅	C ₆ H ₃ (CH ₃) ₂ (<i>o,p</i>)	C ₆ H ₄ (CH ₃ - <i>p</i>)		
i.	CH ₂ C ₆ H ₅	CH ₂ C ₆ H ₅	CH ₃		
j.	CH ₃	C ₆ H ₅	C ₆ H ₄ (CH ₃ - <i>p</i>)		
k.	CH ₃	C ₆ H ₅	CH ₂ C ₆ H ₅		
				R ⁴	R ⁵
		<i>n</i> -C ₄ H ₉		C ₆ H ₅	
		C ₆ H ₅		C ₆ H ₃ (C ₂ H ₅) ₂ (<i>o,o</i>)	
		C ₆ H ₅		C ₆ H ₅	
		C ₆ H ₅		C ₆ H ₅	
		C ₆ H ₅		C ₆ H ₅	
		C ₆ H ₅		C ₆ H ₅	
		C ₆ H ₃ (CH ₃) ₂ (<i>o,p</i>)		C ₆ H ₅	
		C ₆ H ₃ (CH ₃) ₂ (<i>o,p</i>)		C ₆ H ₅	
		C ₆ H ₃ (CH ₃) ₂ (<i>o,p</i>)		C ₆ H ₅	
		C ₆ H ₃ (CH ₃) ₂ (<i>o,p</i>)		C ₆ H ₅	

well as reaction of 2,4-dichloro-6-diphenylamino-*s*-triazine (XIV) with two mole equivalents of 2-



XVIa-d

	R ¹	R ²
XVIa.	C ₆ H ₅	C ₆ H ₅
b.	CH ₃	C ₆ H ₅
c.	CH ₂ C ₆ H ₅	CH ₂ C ₆ H ₅
d.	CH ₂ C ₆ H ₅	C ₆ H ₃ (CH ₃) ₂ (<i>o,p</i>)

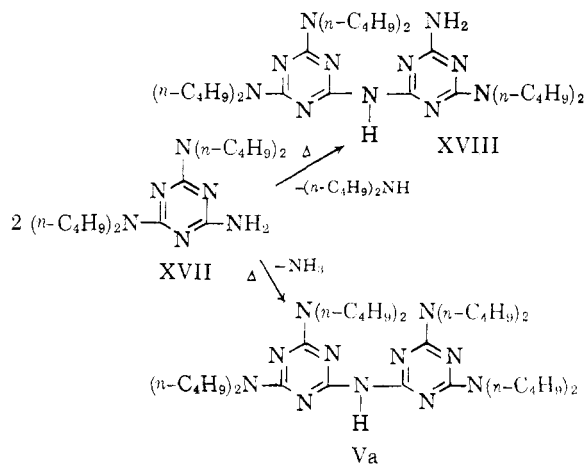


anilino-4,6-bis(*sec*-amino)-*s*-triazines (XV) led to the desired compounds (XVIa-d).

An attempt to synthesize substituted melams in analogy to the formation of the parent compound by heating a substituted melamine was not very successful. The principal product obtained by heating 2-amino-4,6-bis(di-*n*-butylamino)-*s*-triazine (XVII) to 350° was hexabutylmelam (XVIII). Apparently, the interaction of two moles of XVII proceeds mainly with elimination of one mole of dibutylamine and not, as expected, with evolution of ammonia. The desired product, octabutylmelam (Va), was obtained in very low yield only.

The attempt to prepare octaheptylmelam by melting 2-amino-4,6-bis(di-*n*-heptylamino)-*s*-triazine (XIX) and 2,4-bis(di-*n*-heptylamino)-6-phenoxy-*s*-triazine (XX) at 300° did not proceed with the elimination of phenol and, consequently, did not result in the formation of the desired melam. As to be expected from similar experiments reported by Thurston *et al.*⁷ Both reactants, XIX and XX, were recovered unchanged.

The exclusively aliphatic substituted melams are liquids at room temperature; in general, the melting points increase with the number of alkyl groups replaced by aryl groups. All of these compounds possess high volatilization temperatures and most are characterized by their remarkable thermal stability.



Experimental⁸

Procedure for the Preparation of Secondary Aromatic Amines.—Metallic potassium (1 g.-atom) was added in portions to excess amine, kept under nitrogen between 100 and 150° until complete solution had been achieved. After raising the temperature to 185°, a chloro- or bromoaryl compound (1 mole) was added dropwise. After 4 hr. of additional refluxing, the excess amine was removed by

(7) J. T. Thurston, F. C. Schaefer, J. R. Dudley, and D. Holm-Hansen, *J. Am. Chem. Soc.*, **73**, 2 (1951).

(8) Melting points were determined using a Fisher-Johns apparatus; microanalyses are by Central Analytical Department, Olin Mathieson Chemical Corporation, New Haven, Conn., and by Galbraith Micro-analytical Laboratories, Knoxville, Tenn.

TABLE IV
SUBSTITUTED MELAMS

	R ¹	R ²	R ³	R ⁴	R ⁵	R ⁶	R ⁷
Va	<i>n</i> -C ₄ H ₉	<i>n</i> -C ₄ H ₉	<i>n</i> -C ₄ H ₉	<i>n</i> -C ₄ H ₉	<i>n</i> -C ₄ H ₉	<i>n</i> -C ₄ H ₉	H
Vb	<i>n</i> -C ₇ H ₁₅	<i>n</i> -C ₇ H ₁₅	<i>n</i> -C ₇ H ₁₅	<i>n</i> -C ₇ H ₁₅	<i>n</i> -C ₇ H ₁₅	<i>n</i> -C ₇ H ₁₅	H
Vc	<i>n</i> -C ₈ H ₁₇	<i>n</i> -C ₈ H ₁₇	<i>n</i> -C ₈ H ₁₇	<i>n</i> -C ₈ H ₁₇	<i>n</i> -C ₈ H ₁₇	<i>n</i> -C ₈ H ₁₇	H
Vd	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	H
Ve	<i>n</i> -C ₄ H ₉	C ₆ H ₅	<i>n</i> -C ₄ H ₉	C ₆ H ₅	<i>n</i> -C ₄ H ₉	C ₆ H ₅	H
VIII	C ₆ H ₅	C ₆ H ₅	H	H	C ₆ H ₅	C ₆ H ₅	C ₂ H ₅
IX	<i>n</i> -C ₃ H ₇	<i>n</i> -C ₃ H ₇	H	H	<i>n</i> -C ₃ H ₇	<i>n</i> -C ₃ H ₇	<i>n</i> -C ₃ H ₇
Xa	<i>n</i> -C ₄ H ₉	<i>n</i> -C ₄ H ₉	<i>n</i> -C ₄ H ₉	<i>n</i> -C ₄ H ₉	<i>n</i> -C ₄ H ₉	<i>n</i> -C ₄ H ₉	C ₆ H ₅
Xb	C ₂ H ₅	C ₂ H ₅	CH ₃	C ₆ H ₅	CH ₃	C ₆ H ₅	C ₆ H ₅ (C ₂ H ₅) ₂ (<i>o,o</i>)
Xc	CH ₃	C ₆ H ₅	CH ₃	C ₆ H ₅	CH ₃	C ₆ H ₅	C ₆ H ₅
Xd	CH ₃	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅
Xe	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅
Xf	CH ₂ C ₆ H ₅	CH ₂ C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅
Xg	CH ₂ C ₆ H ₅	CH ₂ C ₆ H ₅	C ₆ H ₄ CH ₃ (<i>p</i>)	C ₆ H ₃ (CH ₃) ₂ (<i>o,p</i>)	C ₆ H ₄ CH ₃ (<i>p</i>)	C ₆ H ₃ (CH ₃) ₂ (<i>o,p</i>)	C ₆ H ₅
Xh	CH ₂ C ₆ H ₅	C ₆ H ₃ (CH ₃) ₂ (<i>o,p</i>)	C ₆ H ₄ CH ₃ (<i>p</i>)	C ₆ H ₃ (CH ₃) ₂ (<i>o,p</i>)	C ₆ H ₄ CH ₃ (<i>p</i>)	C ₆ H ₃ (CH ₃) ₂ (<i>o,p</i>)	C ₆ H ₅
Xi	CH ₂ C ₆ H ₅	CH ₂ C ₆ H ₅	CH ₃	C ₆ H ₅	CH ₃	C ₆ H ₅	C ₆ H ₅
Xj	CH ₃	C ₆ H ₅	C ₆ H ₄ CH ₃ (<i>p</i>)	C ₆ H ₃ (CH ₃) ₂ (<i>o,p</i>)	C ₆ H ₄ CH ₃ (<i>p</i>)	C ₆ H ₃ (CH ₃) ₂ (<i>o,p</i>)	C ₆ H ₅
Xk	CH ₃	C ₆ H ₅	CH ₂ C ₆ H ₅	C ₆ H ₃ (CH ₃) ₂ (<i>o,p</i>)	CH ₂ C ₆ H ₅	C ₆ H ₃ (CH ₃) ₂ (<i>o,p</i>)	C ₆ H ₅
XVIII ^d	<i>n</i> -C ₄ H ₉	<i>n</i> -C ₄ H ₉	H	H	<i>n</i> -C ₄ H ₉	<i>n</i> -C ₄ H ₉	H

^a From toluene. ^b Distilled at 0.025 mm. 350° oil bath temperature. ^c Dissolved in decalin and precipitated with ethanol. ^d From xylene. ^e Dissolved in toluene and precipitated with petroleum ether (b.p. 90–97°). ^f Washed with petro-

distillation. The potassium halide formed was then dissolved by addition of water and the secondary amine extracted with ether. Removal of the ether and fractional distillation through a Vigreux column yielded the desired product.

This procedure was found to be more advantageous than the reaction in an autoclave. Results and characteristics of compounds thus prepared are compiled in Table I.

Methods for the Preparation of Substituted 2,4-Diamino-6-chloro-*s*-triazines.—These compounds were prepared either by adding secondary amines (2 moles) to a slurry of cyanuric chloride (1 mole) in acetone–water in the presence of sodium hydroxide (2 moles) (method A)⁹ or by treating cyanuric chloride (1 mole) with a secondary amine (2 moles) in decalin between 150–195° (method B). The relevant results and characteristics of the triazines thus obtained are compiled in Table II. 2,4-Bis(diethylamino)-6-chloro-*s*-triazine, 2,4-bis(di-*n*-propylamino)-6-chloro-*s*-triazine, and 2,4-bis(di-*n*-butylamino)-6-chloro-*s*-triazine were prepared from cyanuric chloride and the appropriate aliphatic tertiary amines according to a method described recently.⁵

Procedures for the Preparation of Substituted Melamines.—Substituted melamines were prepared either by treating 2-amino-4,6-dichloro-*s*-triazines (1 mole) with secondary amines (4 moles) in toluene between 60° and 100° (method A), by treating 2-anilino-4,6-dichloro-*s*-triazine (1 mole) with dibenzylamine (4 moles) in refluxing xylene (method B), or by heating the appropriate substituted or unsubstituted 2-amino-4,6-dichloro-*s*-triazines (1 mole) or 2,4-diamino-6-chloro-*s*-triazines (1 mole) with the appropriate amine (2–3 moles) without a solvent at temperatures between 150–300° under a blanket of nitrogen (method C).

Compounds prepared by these methods are compiled in Table III.

Procedure for the Preparation of Substituted Melams.—Appropriate substituted amino- and chloro-*s*-triazines were mixed in a mole ratio of 1:1 and heated gradually to and kept between 300 and 350° in a two neck flask, fitted with a gas inlet tube and a 25-cm. air-cooled vertical condenser containing a 10-cm. layer of glass wool in its upper part. A slow stream of dry nitrogen passed through the apparatus into a solution of 0.1 *N* sodium hydroxide in order to determine the amount of hydrogen chloride formed during the reaction. Heating was terminated after titration of the sodium hydroxide solution showed that hydrogen chloride formation had ceased. The reaction mixture was then allowed to cool to room temperature and the product was purified by either distillation or recrystallization. Substituted melams obtained by this procedure are compiled in Table IV.

The same method was also employed for the preparation of melams containing three *s*-triazine rings. In this case, appropriate substituted *s*-triazines were employed in a mole ratio of 1:2. Two moles of hydrogen chloride were formed during the formation of these compounds which are compiled in Table V.

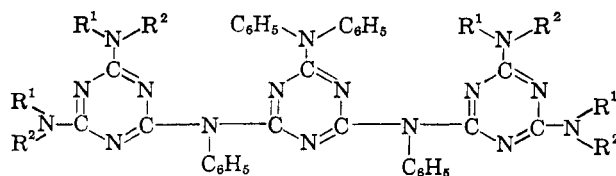
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TABLE IV (continued)

M.P.	B.P. (mm.)	n_D^{20}	Yield, %	Formula	Calcd., %			Found, %			
					C	H	N	C	H	N	
148-151 ^a	242-254 (0.007)		81	C ₃₈ H ₇₈ N ₁₁	66.80	10.62	22.55	66.48	10.52	23.25	
	310-329 (4)	1.5058	27	C ₅₂ H ₁₂₁ N ₁₁	73.10	11.88	15.11	72.83	11.48	15.17	
	290-300 (4)	1.5092	25	C ₅₀ H ₉₇ N ₁₁	70.45	11.47	18.08	69.07	11.92	18.65	
			71.5	C ₅₄ H ₄₁ N ₁₁	76.94	4.78	18.28	76.88	4.74	18.25	
	290-302 (0.004)		95	C ₄₆ H ₅₇ N ₁₁	72.41	7.40	20.20	71.90	7.43	20.36	
	226 (3)		80	C ₂₀ H ₃₇ N ₁₁	55.66	8.59	35.75	55.63	8.61	35.70	
	225 (2)		75	C ₂₇ H ₅₁ N ₁₁	61.30	9.65	29.05	60.84	0.55	29.60	
	295 (0.5)	1.5372	30	C ₄₄ H ₇₇ N ₁₁	69.53	10.12	20.35	69.42	91.13	20.74	
	49-55	280-290 (0.1)		63.5	C ₃₈ H ₄₉ N ₁₁			23.34			23.31
	95-98 ^b			44.8	C ₄₀ H ₃₇ N ₁₁	71.51	5.55	22.94	71.57	5.30	22.93
191-192 ^c			30.2	C ₅₀ H ₄₁ N ₁₁	75.45	5.19	19.36	74.76	5.45	19.50	
230 ^d			57.5	C ₅₀ H ₄₅ N ₁₁	78.32	4.93	16.75	78.24	4.95	16.75	
118-121 ^e			36	C ₄₄ H ₃₃ N ₁₁			15.76			15.62	
103-108 ^f			87	C ₇₀ H ₆₅ N ₁₁			14.53			15.24	
114-118 ^g			84.2	C ₇₂ H ₄₉ N ₁₁	79.45	6.39	14.16	79.34	6.49	14.62	
94-98 ^h			71	C ₅₄ H ₄₇ N ₁₁			18.13			19.12	
146-148 ^h			80.5	C ₅₆ H ₅₃ N ₁₁			17.51			18.15	
112-115 ^f			80	C ₄₆ H ₄₅ N ₁₁			17.51			18.29	
	260-280 (0.007)		18	C ₅₀ H ₄₆ N ₁₁	62.89	9.77	26.65	63.20	9.83	26.75	

leum ether (b.p. 90-97°). ^a From ethanol. ^b Washed with hot petroleum ether (b.p. 90-97°) and hot ethanol. ^c This product was obtained by heating 2-amino-4,6-bis(di-*n*-butylamino)-*s*-triazine.

TABLE V
MELAM DERIVATIVES CONTAINING THREE *s*-TRIAZINE RINGS

Compound	R ¹		M.P.	Yield, %	Formula	Calcd., %			Found, %		
	R ¹	R ²				C	H	N	C	H	N
XVIa	C ₆ H ₅	C ₆ H ₅	235-236 ^a	41.4	C ₈₁ H ₆₀ N ₁₆	77.36	4.81	17.82	77.25	4.74	18.00
XVIb	CH ₃	C ₆ H ₅	139-143 ^b	96	C ₆₁ H ₅₂ N ₁₆	72.60	5.19	22.21	72.63	5.13	21.22
XVIc	CH ₂ C ₆ H ₅	CH ₂ C ₆ H ₅	125-126 ^c	76.6	C ₈₉ H ₇₆ N ₁₆	78.04	5.39	16.37	77.02	5.36	12.25
XVIId	CH ₂ C ₆ H ₅	C ₆ H ₅ (CH ₂) ₂ (<i>o,p</i>)	134-137 ^d	91	C ₉₂ H ₈₄ N ₁₆			15.72			16.12

^a From xylene. ^b Washed with hot ethanol. ^c Dissolved in toluene and reprecipitated with petroleum ether (b.p. 90-97°). ^d Washed with hot petroleum ether (b.p. 90-97°).