

the intermediate is required, and our preferred procedure consisted of the direct fusion of cyanuric chloride and three moles of aniline at about 300°. Hydrogen chloride was evolved and N²,N⁴,N⁶-triphenylmelamine was formed in good yield. The use of benzene as a dilute in the initial reaction mixture served to moderate the exothermic reaction and to facilitate mixing of the reactants before the reaction mixture was heated.

Experimental^{6,7}

General Procedure.—One mole of the appropriate chloro-triazine was slurried in water (600–1000 ml.), and the amine was added. The molar quantity of the latter was such that there was one equivalent of amine for each chloro group to be replaced on the triazine. The mixture was slowly heated to reflux, and the refluxing temperature was maintained for one to two hours. During this time an aqueous solution of one equivalent of sodium hydroxide, carbonate or bicarbonate was added at such a rate that the reaction mixture remained neutral or slightly alkaline. The alkalinity could be conveniently controlled by the use of phenolphthalein in the reaction mixture. After cooling, the product was filtered from the reaction mixture, washed free of chloride ion with water and oven-dried. Purification was effected by crystallization from appropriate solvents.

Alternatively, twice the theoretical quantity of the amine was initially added to the reaction mixture, and no base was subsequently added. This variation was not preferred.

Monoarylmelamines.—The preparation of these compounds differed from the above procedure only in that the caustic was not added until the reaction was complete. Conversion of the hydrochloride of the product to the free base was effected with aqueous sodium hydroxide at 50–60° or at room temperature.

N²,N⁴,N⁶-Triphenylmelamine.⁸—A gentle reaction occurred when 301 g. (3.2 moles) of aniline was added to 184.4 g. (1.0 mole) of cyanuric chloride in 400 ml. of benzene over a period of two hours. The benzene was distilled as the bath temperature was then raised to 290–310° over a period of 1.5 hours. Hydrogen chloride was smoothly

(6) All melting points are uncorrected values for purified compounds.

(7) Comments on analytical procedures are given in footnote 8, reference 5.

(8) Also prepared according to Klason's method (ref. 2b). The direct method avoids the preparation of an intermediate and the use of excess aniline in the final step.

evolved in this temperature range, and the reaction was complete in 1.5 hours. After cooling, the solid cake was digested with methyl cellosolve. The yield was 92%, m.p. 229–231°. Recrystallization from methyl cellosolve gave m.p. 232–234°.

Pentaethylmelamine.—One mole of 2-chloro-4,6-bis-(diethylamino)-s-triazine and 2.4 moles of 70% aqueous ethylamine were heated for five hours at 110° under pressure in dioxane solution. One mole of aqueous sodium hydroxide was added, and the mixture was evaporated on a steam-bath. The yield of product, after extraction of the residue with benzene and removal of the solvent, was 95%. Purification of the liquid product was effected by distillation; b.p. 120–121° (0.4 mm.).

Anal. Calcd. for C₁₃H₂₆N₆: C, 58.61; H, 9.84; N, 31.55; neut. equiv., 266.4. Found: C, 58.62; H, 9.82; N, 30.84; neut. equiv., 267.6.

Hexaethylmelamine.—A solution of one mole of 2-chloro-4,6-bis-(diethylamino)-s-triazine in toluene was heated to reflux, and 2.2 moles of anhydrous diethylamine was added slowly to prevent flooding in the condenser. The addition required six hours. The product was isolated as described above; yield 93%. Purification was first effected by distillation, b.p. 151–154° (2–3 mm.), and then by crystallization from methanol, m.p. 46–47°.

Anal. Calcd. for C₁₅H₃₀N₆: C, 61.18; H, 10.27; N, 28.55. Found: C, 61.26; H, 10.25; N, 28.62.

Hexamethylmelamine.—A 26% aqueous solution of 3.3 moles of dimethylamine was added to one mole of cyanuric chloride in 800 ml. of acetone, maintaining the temperature at about 50° by intermittent cooling. One mole of aqueous sodium hydroxide was added, and the mixture was heated under reflux for one hour. The water and acetone were removed by distillation, finally adding xylene to completely remove the water by azeotropic distillation. Two moles of powdered sodium hydroxide were added, and the mixture was heated for three hours at 100°. Fractional crystallization of the product from methanol gave a 37% yield of hexamethylmelamine, m.p. 172–174°, and a 26% yield of 2-chloro-4,6-bis-(dimethylamino)-s-triazine, m.p. 62–63°.

Anal. Calcd. for C₉H₁₈N₆: N, 39.97. Found: N, 39.72.

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[CONTRIBUTION FROM THE STAMFORD RESEARCH LABORATORIES OF THE AMERICAN CYANAMID COMPANY]

Cyanuric Chloride Derivatives. III. Alkoxy-s-triazines

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A series of new trialkyl cyanurates, 2,4-dialkoxy-6-amino-s-triazines, and 2-alkoxy-4,6-diamino-s-triazines have been prepared for investigation of their use in a number of applications. Modifications in procedure have been developed, and a general method for the preparation of alkoxy-s-triazines from the corresponding chloro-s-triazines has been reported.

Trialkyl cyanurates,¹ I, and alkyl ethers of ammelide² and ammeline derivatives,³ II and III, have long been known. However, the only reported

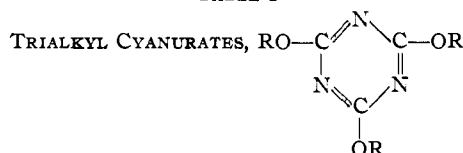
(1) (a) F. S. Cloez, *Compt. rend.*, **44**, 482 (1857); (b) E. Mulder, *Ber.*, **15**, 69 (1882); **16**, 390, 2763 (1883); *Rec. trav. chim.*, **1**, 63, 191 (1882); **2**, 133 (1883); **3**, 287 (1884); (c) J. Ponomareff, *Ber.*, **15**, 513 (1882); **18**, 3261 (1885); (d) P. Klason, *J. prakt. Chem.*, (2) **33**, 116 (1886); (e) A. Hantzsch and L. Mai, *Ber.*, **28**, 2466 (1895); (f) E. Büllmann and J. Bjerrum, *Ber.*, **50**, 503 (1917); W. Hentrick, U. S. Patent 2,306,440 (1942).

(2) A. W. Hofmann and O. Olshausen, *Ber.*, **3**, 269 (1870).

(3) (a) A. W. Hofmann, *Ber.*, **19**, 2061 (1886); (b) J. Controulis and C. K. Banks, *THIS JOURNAL*, **67**, 1946 (1945); (c) W. Pearlman and C. K. Banks, *ibid.*, **71**, 1128 (1949); (d) W. Pearlman, J. D. Mitulski and C. K. Banks, *ibid.*, **71**, 3248 (1949).

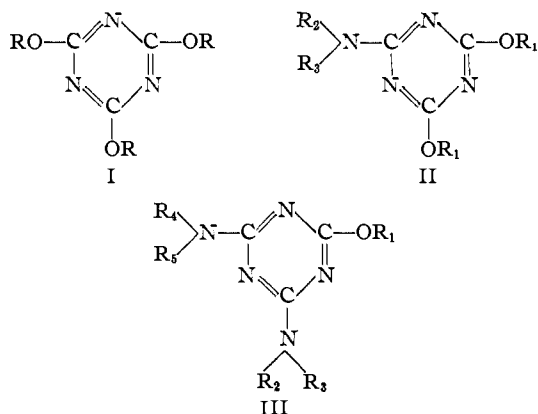
work on the development of a general and practical preparative method is that of Controulis and Banks,^{3b} who prepared an extensive series of 2-alkoxy-4,6-diamino-s-triazines. Their method, which gave acceptable yields in most cases, was similar to that used by Hofmann^{2a} to prepare cyanurates, *i.e.*, reaction of the chloro-s-triazine with the appropriate sodium alkoxide, generally in excess alcohol. They also mentioned the use of potassium carbonate or dry hydrogen chloride as condensing agents for reaction of the chloro-s-triazine with the alcohol, but these methods were considered inferior.

TABLE I



R	Yield, ^a %	Crystallized from	M.p., °C.	Formula	Analyses, %					
					Carbon		Hydrogen		Nitrogen	
					Calcd.	Found	Calcd.	Found	Calcd.	Found
Methyl ^b	98 ^c	Water	134–136	C ₆ H ₉ N ₃ O ₃	42.10	42.49	5.26	5.29	24.56	24.34
Allyl	85 ^d	Aq. methanol	31 ^e	C ₁₂ H ₁₅ N ₃ O ₃	16.87	17.11
Isobutyl	62	^f	37 ^f	C ₁₅ H ₂₇ N ₃ O ₃	14.13	13.87
Pentyl (mixed isomers)	68	^g	Oil ^g	C ₁₈ H ₃₃ N ₃ O ₃	12.38	12.26
<i>n</i> -Hexyl	63	^h	Oil	C ₂₁ H ₃₉ N ₃ O ₃	11.02	11.13
Cyanomethyl	81	Methanol	158–159	C ₆ H ₈ N ₆ O ₃	43.90	43.94	2.45	2.82
2-Chloroethyl-	...	Dioxane	154	C ₉ H ₁₂ Cl ₂ N ₃ O ₃	34.12	34.03	3.82	3.80	33.65	33.26

^a Yield of product as isolated from the reaction mixture. Most of the products were essentially pure, and little improvement in purity was effected by crystallization. ^b Ref. 1. ^c The yields were 70% when sodium hydroxide or pyridine was used. ^d Allyl alcohol containing 10% water was used. ^e The yield was determined after washing with 5% sodium hydroxide. A 10% yield of diallyl cyanurate was recovered by acidification of the washings; m.p. 137–138° after crystallization from water. *Anal.* Calcd. for C₉H₁₁N₃O₃: N, 20.08. Found: N, 20.23. ^f This compound could be distilled in small lots; b.p. 137–140 (2.5 mm.). Later attempts on a larger scale caused violent polymerization. ^g Purified by distillation; b.p. 146–155° (1.0 mm.). ^h Purified by steam distillation.



In our early work on *s*-triazine derivatives we employed Hofmann's method for preparing trimethyl cyanurate. 2,4-Dimethoxy-6-anilino-*s*-triazine and 2-amino-4,6-dimethoxy-*s*-triazine were prepared similarly, and we obtained substantially the same results as have been reported by Contoulis and Banks in the preparation of a few 2-alkoxy-4,6-diamino-*s*-triazines. However, we found that sodium hydroxide could be used to replace the less practical sodium alkoxide in the preparation of a large number of compounds of structures I, II and III without decrease in yield. In those cases where sodium hydroxide was not useful because of its unnecessarily great basicity, sodium carbonate or tertiary amines were satisfactory as acid acceptors.

In our procedure the base was dissolved or suspended in an excess of the appropriate alcohol, and at a suitable temperature the chloro-*s*-triazine was added. Sodium carbonate was preferred for the preparation of the lower trialkyl cyanurates in order to moderate the vigorous reaction of cyanuric chloride, but sodium hydroxide was more effective for the preparation of the higher esters. Sodium hydroxide was also more effective in the preparation of alkoxyamino-*s*-triazines, II and III.

Table I lists the trialkyl cyanurates prepared. In general, lower yields were obtained with the

higher alcohols. However, this was also the case when Hofmann's method was used.

In addition to being difficult to obtain in dry form from our usual preparative process in aqueous acetone,⁴ 2-amino-4,6-dichloro-*s*-triazine and its mono-*N*-substituted derivatives were eye and nose irritants. Investigation disclosed that 5–10% of water in the alcohol generally was not appreciably detrimental in the preparation of the 2,4-dialkoxy-6-amino-*s*-triazines, so that anhydrous intermediates were not required in these cases. We found that it was not only easier and more comfortable to use the intermediates as obtained in a filter cake containing up to 50% of water, but that frequently better over-all yields of alkoxy-*s*-triazines could be obtained when decomposition on drying was thus avoided. Fortunately, the only cases in which the dry chloro-*s*-triazines were required for good yields were those in which the less reactive intermediates could be easily obtained in dry form.

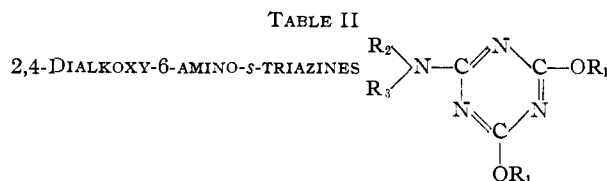
The 2,4-dialkoxy-6-amino-*s*-triazines and 2-alkoxy-4,6-diamino-*s*-triazines which we have prepared from the corresponding chloro-*s*-triazines are listed in Tables II and III, respectively. A particularly interesting member of the first class was 2,4-diallyloxy-6-amino-*s*-triazine, and its preparation was studied exhaustively.

The two factors, reaction temperature and base used, were most important in governing the extent to which the chlorine atoms in chloro-*s*-triazines could be replaced. A limited study of the stepwise replacement of chlorine atoms by alkoxy groups was made. 2,4-Dichloro-6-methoxy-*s*-triazine and 2-chloro-4,6-dimethoxy-*s*-triazine⁵ could be prepared in good yield by reaction of cyanuric chloride with methanol in the presence of sodium bicarbonate at suitable temperatures. Also, 2-allyloxy-4-amino-6-chloro-*s*-triazine could be prepared from 2-amino-4,6-dichloro-*s*-triazine in allyl alcohol in the presence of sodium carbonate.

The deactivation of the remaining chlorine atoms,

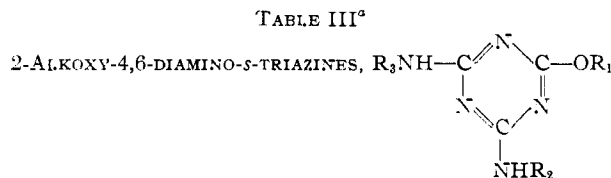
(4) J. T. Thurston, *et al.*, *THIS JOURNAL*, **73**, 2981 (1951).

(5) O. Diels and M. Liebermann, *Ber.*, **36**, 3191 (1903).



R ₁	R ₂	R ₃	Yield, ^a %	Crystallized from	M.p., °C.	Formula	Analyses, %					
							Carbon		Hydrogen		Nitrogen	
						Calcd.	Found	Calcd.	Found	Calcd.	Found	
Methyl ^{b,c}	H	H	94	Water	219	C ₈ H ₈ N ₄ O ₂	
Ethyl	H	H	78	Benzene	97-98	C ₇ H ₁₂ N ₄ O ₂ ^d	45.64	45.73	6.56	6.57	30.42	30.35
<i>n</i> -Propyl	H	H	71	Benzene	92-93	C ₉ H ₁₆ N ₄ O ₂	50.95	51.96	7.60	7.53	26.42	26.05
Isopropyl ^e	H	H	48	Benzene	96	C ₉ H ₁₆ N ₄ O ₂	50.95	51.07	7.60	7.52	26.42	26.41
<i>n</i> -Butyl	H	H	69	Butanol	101	C ₁₁ H ₂₀ N ₄ O ₂	54.98	55.21	8.39	8.35	23.32	23.27
Allyl ^f	H	H	91	Aq. ethanol	60-61 ^g	C ₉ H ₁₆ N ₄ O ₂	51.91	51.78	5.81	5.57	26.91	27.27
Methallyl	H	H	80	Pet. ether	88-89	C ₁₁ H ₁₆ N ₄ O ₂	55.92	55.84	6.82	6.82	23.73	23.47
Methyl ^h	H	Butyl	92	Aq. methanol	65-65.5	C ₉ H ₁₆ N ₄ O ₂ ⁱ	50.93	51.03	7.60	7.60	26.40	26.15
Methyl ^h	H	Cyclohexyl	80	Aq. methanol	127-129	C ₁₁ H ₁₈ N ₄ O ₂	55.46	55.11	7.56	7.61	23.53	23.54
Methyl ⁱ	H	Phenyl	96	Aq. methanol	133-134	C ₁₁ H ₁₂ N ₄ O ₂	56.89	56.42	5.21	5.04	24.13	23.91
Methyl	Methyl	Cyclohexyl	85	Heptane	61-62	C ₁₂ H ₂₀ N ₄ O ₂	57.14	57.21	7.94	7.96	22.22	22.16
Methyl ^j	Methyl	Phenyl	94	Aq. methanol	51-52	C ₁₂ H ₁₄ N ₄ O ₂ ^k	58.52	58.78	5.73	6.02	22.75	22.69
Methyl ^l	Ethyl	Ethyl	86	Benzene	33-34	C ₉ H ₁₆ N ₄ O ₂	26.40	26.18
Methyl	2-Hydroxy-ethyl	Phenyl	56	Ethanol	143-145	C ₁₈ H ₁₆ N ₄ O ₃	56.51	55.96	5.84	5.86	20.28	20.01
Ethyl ^m	H	Ethylene-(bis)	66	Heptane	163-166	C ₁₆ H ₂₄ N ₄ O ₄	48.72	48.60	6.64	6.52	28.41	28.53
Ethyl ⁿ	H	Phenyl	92	Methanol	106-107	C ₁₈ H ₁₆ N ₄ O ₂	21.53	21.36
Ethyl ⁿ	H	<i>p</i> -Sulfophenyl	75	Water	255-260	C ₁₂ H ₁₆ N ₄ O ₆ ·H ₂ O ^o	15.64	15.66
Allyl ^p	H	<i>n</i> -Dodecyl	82	Methanol	49-51	C ₂₁ H ₃₄ N ₄ O ₂	66.98	66.80	9.64	9.99
Allyl	H	2,5-Dichlorophenyl	84	Ethanol	89.5-90	C ₁₅ H ₁₄ Cl ₂ N ₄ O ₂	50.99	50.86	3.97	4.04	20.11	20.05
Allyl	2-Hydroxyethyl		14	Water	109-112	C ₁₈ H ₂₀ N ₄ O ₃	52.69	52.66	6.80	6.86	18.90	18.77

^a Unless otherwise specified, the aminochloro-*s*-triazine was freshly prepared from cyanuric chloride and used directly in moist condition for the preparation of the alkoxy-*s*-triazine. The yields in these cases are based on cyanuric chloride. Where indicated, the aminochloro-*s*-triazine was prepared as previously reported (ref. 4), and the yields are based on the intermediate. Figures represent yield of product as isolated from the reaction mixture. ^b Refs. 1 and 2. ^c Prepared from 2-amino-4,6-dichloro-*s*-triazine. ^d *Anal.* Calcd.: ethoxyl, 48.93. Found: ethoxyl, 48.71. ^e Could be purified in small lots by distillation, b.p. 151° (1.0 mm.). The bath temperature must be kept below 175° to avoid excessive polymerization. Larger quantities were successfully "flash" distilled at 0.2-0.4 mm. pressure from a flask heated to 275-300°. ^f Prepared from 2-*n*-butylamino-4,6-*s*-triazine. ^g *Anal.* Calcd.: methoxyl, 29.24. Found: methoxyl, 29.38. ^h Prepared from 2-cyclohexylamino-4,6-dichloro-*s*-triazine. ⁱ Prepared from 2-anilino-4,6-dichloro-*s*-triazine. ^j Prepared from 2-*N*-methylamino-4,6-dichloro-*s*-triazine. ^k *Anal.* Calcd.: methoxyl, 25.20. Found: methoxyl, 25.35. ^l Prepared from 2-diethylamino-4,6-dichloro-*s*-triazine. ^m This compound has the structure: (C₂H₅O)₂(C₃N₃)NHCH₂CH₂NH(C₃N₃)-(OC₂H₅)₂. ⁿ Prepared from 2-sodiumsulfoanilino-4,6-dichloro-*s*-triazine. ^o *Anal.* Calcd.: neut. equiv., 358.4. Found: neut. equiv., 354.5. ^p Prepared from 2-*n*-dodecylamino-4,6-dichloro-*s*-triazine.



R ₁	R ₂	R ₃	Yield, ^b %	Crystallized from	M.p., °C.	Formula	Analyses, %					
							Carbon		Hydrogen		Nitrogen	
						Calcd.	Found	Calcd.	Found	Calcd.	Found	
Methyl ^c	H	H	93	Water	238	C ₄ H ₇ N ₅ O	34.04	33.76	5.00	4.77	49.65	49.72
<i>n</i> -Propyl ^c	H	H	78	Propanol	182-184	C ₆ H ₁₁ N ₅ O	42.60	42.39	6.55	6.51	41.42	41.56
Isopropyl ^c	H	H	58	Water	170-171	C ₆ H ₁₁ N ₅ O	42.60	42.67	6.55	6.54	41.42	41.73
<i>n</i> -Butyl ^c	H	H	73	Water	178	C ₇ H ₁₃ N ₅ O	45.90	45.85	7.16	7.10	38.25	38.19
Allyl ^c	H	H	88	Water	181-182	C ₈ H ₉ N ₅ O	43.11	42.98	5.38	5.52	41.92	42.01
Methyl ^d	Phenyl	Phenyl	100	Ethanol	165-166	C ₁₆ H ₁₅ N ₅ O ^e	65.51	65.69	5.15	5.29	23.88	23.93
<i>n</i> -Propyl ^d	Phenyl	Phenyl	93	Aq. ethanol	148-149	C ₁₈ H ₁₉ N ₅ O ^f	67.27	67.01	5.96	5.61	21.79	22.09
Allyl ^g	Butyl	H	78	Aq. dioxane	104.5-106	C ₁₀ H ₁₇ N ₅ O	31.36	30.87

^a Unless otherwise specified, the compounds were prepared from 2-amino-4,6-dichloro-*s*-triazine (ref. 4). ^b Yield of product as isolated from the reaction mixture. ^c Ref. 3b. ^d Prepared from 2-chloro-4,6-bis(anilino)-*s*-triazine. ^e *Anal.* Calcd.: methoxyl, 10.58. Found: methoxyl, 10.60. ^f *Anal.* Calcd.: propoxyl, 18.41. Found: propoxyl, 18.33. ^g Prepared from 2-chloro-4-amino-6-*n*-butylamino-*s*-triazine.

which is the result of stepwise reaction of cyanuric chloride with amines, is paralleled by a similar effect in the stepwise reaction with alcohols. However, in the latter case deactivation is much less, and 2,4-dialkoxy-6-chloro-*s*-triazines, for example, are considerably more reactive than 2,4-diamino-6-chloro-*s*-triazines. This difference makes possible an alternative route to certain

s-triazine derivatives which cannot be prepared satisfactorily by earlier methods. To cite one case, 2-chloro-4,6-bis-(*N*-β-hydroxyethylamino)-*s*-triazine cannot be prepared satisfactorily by reaction of phenylethanolamine with cyanuric chloride by the processes described in this paper because of the low reactivity of the initially formed dichloro-*s*-triazine and the very low basicity of the

amine. Furthermore, if it were available it would probably be very difficult to convert to this compound the corresponding methoxy derivative. However, 2,4-dichloro-6-methoxy-*s*-triazine reacted readily with phenylethanolamine to give 2-methoxy-4,6-bis-(*N*- β -hydroxyethylanilino)-*s*-triazine in about 95% yield.

Experimental^{6,7}

Trialkyl Cyanurates (I).—Three moles of sodium hydroxide was dissolved or suspended in 1000 ml. of the alcohol, and one mole of solid cyanuric chloride was added gradually while the reaction temperature was held at 25–30°. The addition generally required about one hour, and the mixture was subsequently stirred for another two hours at room temperature. The precipitated sodium chloride was then filtered from the solution, and the filtrate was evaporated to recover the soluble cyanurate. If the product did not crystallize during the evaporation, it was recovered as an oil by complete evaporation, sometimes followed by distillation of the product at low pressure, or if the alcohol used was water-soluble, the cyanurate could be thrown out by drowning the concentrate in water. The crystalline cyanurates could be recrystallized without difficulty from common solvents.

The sodium hydroxide could be added as a concentrated solution in water in some cases, but was best used as a dry powder. In this form it dissolved rapidly at room temperature in the lower alcohols and was easily kept in fine suspension in the higher alcohols by ordinary mechanical stirring. Heat was not used to increase the rate of solution of sodium hydroxide in the alcohols because this caused discoloration which persisted in the product.

Sodium carbonate could be used in place of sodium hydroxide in the reaction mixture. A longer reaction time was required, and the reaction mixture was usually agitated at 30–40° for a total of five hours, after which it was heated briefly at 60–80°.

Tris-(cyanomethyl) Cyanurate.—Cyanuric chloride (92.2 g., 0.50 mole) was suspended in 94 g. (1.65 moles) of glycolonitrile at 5° by mechanical stirring. To the suspension 60 g. of pyridine was gradually added over a two-hour period while the low temperature was maintained. During the more rapid addition of another 60 g. of pyridine the temperature was allowed to rise to 8°, and finally an additional 80 g. of pyridine was added rapidly. The mixture was held at about 10° for another hour and at 25° overnight. Water (200 ml.) was added and the excess pyridine was neutralized with dilute hydrochloric acid. The product which crystallized when the water solution was cooled to 5° was filtered and dried at 110°. The dry, yellow solid weighed 100 g. (81%), m.p. 154–158°. Recrystallization from methyl cellosolve after treatment with activated carbon gave a product with m.p. 158–159°.

2,4-Dialkoxy-6-amino-*s*-triazines (II).—Two moles of powdered sodium hydroxide were dissolved or suspended in 600–1000 ml. of the alcohol, and to this mixture one mole of the appropriate 2-amino-4,6-dichloro-*s*-triazine was added gradually at 30–40°. The latter was generally added in solid form, although in some cases an acetone solution or a moist filter cake of a freshly prepared intermediate was used successfully. This temperature was maintained for 30 minutes, and the mixture was then heated to 60–75° for 0.5 to 3 hours. The product was recovered in various ways depending upon its solubility. 2-Amino-4,6-dimethoxy-*s*-triazine was recovered by pouring the reaction mixture into an equal volume of water and filtering the insoluble product. In some cases, the reaction mixture was filtered cold, and the filter cake was extracted with water to remove the sodium chloride from the product. In many cases, the sodium chloride was filtered from the hot reaction mixture, and the product was recovered by evaporation of the filtrate. The longer reaction time given was necessary when the less reactive *N,N*-disubstituted 2-amino-4,6-dichloro-*s*-triazines or the higher alcohols were used. Sodium carbonate or calcium hydroxide could be substituted for sodium hydroxide, but longer reaction times were then required, and the products were much less pure. Trisodium phosphate could be

used successfully, but this made product isolation difficult because of the solubility of disodium phosphate in alcohols.

2,4-Diallyloxy-6-amino-*s*-triazine.—The general method just given for compounds of this type gave a 91% yield of this compound when the reaction was run at 20–25°. When aqueous ammonia was added at 0–5° to a slurry of cyanuric chloride in allyl alcohol in the presence of sodium carbonate to give the intermediate 2-amino-4,6-dichloro-*s*-triazine, and the reaction mixture was subsequently heated to reflux after the addition of the necessary amount of inorganic base, the desired product was generally not obtained in good yield. Hydroxy-*s*-triazines and 2-allyloxy-4-amino-6-chloro-*s*-triazine were always found. When the inorganic base was sodium carbonate, yields of 70–75% of the latter compound were obtained, m.p. 175–176°. It was found that this compound was stable in allyl alcohol in the presence of sodium carbonate at 150°.

Anal. Calcd. for C₈H₇N₄OCl: N, 30.02. Found: N, 29.80, 29.54.

Addition of cyanuric chloride (1.0 mole) at 5–10° to a mixture of allyl alcohol, ammonia (1.0 mole) and sodium hydroxide (3.0 moles) followed by a heating period of two hours at 60° gave yields of 69–71% of triallyl cyanurate. If the amount of ammonia was increased to two moles and the sodium hydroxide decreased to two moles, there was formed mainly 2-allyloxy-4,6-diamino-*s*-triazine (71%). Attempts to prepare 2,4-diallyloxy-6-chloro-*s*-triazine by reaction of cyanuric chloride with allyl alcohol in the presence of sodium bicarbonate failed. Hydroxy-*s*-triazines were the principal products.

2-Alkoxy-4,6-diamino-*s*-triazines (III).—The required 2-chloro-4,6-diamino-*s*-triazine was added to the appropriate alcoholic solution or suspension of sodium hydroxide at 50°, and the mixture was refluxed for 2–3 hours. The products when insoluble were separated by filtration and washed with water or, if soluble, were recovered by concentration of the alcoholic solution. The higher alcohols reacted slowly, and hydroxy-*s*-triazines were always formed to some extent. A large part of this poor reactivity in the case of some of the 2-chloro-4,6-diamino-*s*-triazines was due to poor solubility in the alcohol. The unsubstituted compound reacted very sluggishly with propanol or butanol, but 2-chloro-4,6-bis-anilino-*s*-triazine and 2-chloro-4,6-bis-cyclohexylamino-*s*-triazine gave good yields of the corresponding 2-alkoxy-4,6-diamino-*s*-triazines in 1.5–2.0 hours.

2-Chloro-4,6-dimethoxy-*s*-triazine.—To 45 g. of methanol and 5 g. of water were added 16.8 g. (0.2 mole) of sodium bicarbonate and 18.5 g. (0.1 mole) of cyanuric chloride. Carbon dioxide was liberated at a moderate rate as the temperature rose to 35°. The mixture was refluxed for 30 minutes after gas evolution had nearly ceased. It was then cooled, diluted with water, and filtered. The crystalline product was washed with water until chloride free and was dried in a vacuum desiccator. The crude product weighed 13 g. (74%), m.p. 74–76°. Recrystallization from heptane gave m.p. 75–76°.

Anal. Calcd. for C₈H₈N₄O₂Cl: C, 34.19; H, 3.42; N, 23.93; Cl, 20.23. Found: C, 34.34; H, 3.57; N, 23.41; Cl, 20.31.

2,4-Dichloro-6-methoxy-*s*-triazine.—To 200 ml. of methanol and 25 ml. of water were added 33.6 g. (0.4 mole) of sodium bicarbonate and 36.8 g. (0.2 mole) of cyanuric chloride. This mixture was stirred at 30° for 30 minutes until the evolution of carbon dioxide had nearly ceased, and water was then added. The crystalline solid which separated was filtered, washed with water, and dried in a vacuum desiccator. The yield of crude 2,4-dichloro-6-methoxy-*s*-triazine was 10.5 g. (58%), m.p. 87–89°. After recrystallization of the product from heptane the m.p. was 88–90°.

Anal. Calcd. for C₈H₈N₄OCl₂: C, 26.67; H, 1.67; N, 23.35; Cl, 39.44. Found: C, 26.96; H, 1.84; N, 23.25; Cl, 39.19.

2-Methoxy-4,6-bis-(*N*- β -hydroxyethylanilino)-*s*-triazine.—A mixture of 19.5 g. (0.108 mole) of 2,4-dichloro-6-methoxy-*s*-triazine and 150 ml. of water was stirred vigorously at 0–10° while 30.2 g. (0.22 mole) of phenylethanolamine was added dropwise during 30 minutes. There was a weakly exothermic reaction and a creamy solid was formed. Sodium carbonate (11.7 g., 0.11 mole) was added after the reaction mixture had been allowed to warm up to room tem-

(6) All melting points are uncorrected values for purified compounds.

(7) Comments on analytical procedures are given in footnote 8, ref. 4.

perature. The mixture was stirred briefly and then was heated slowly to 80°. Heating was continued for two hours at 80–85°. The solid was converted to a viscous oil which formed coarse crystals as the stirred mixture was cooled. The product was filtered, washed with water, and dried in a vacuum desiccator. The yield of material melting at 115–125° was 40 g. (95%). This compound was very soluble in all organic solvents, but none was found from which it could be crystallized without an intermediate oil being obtained. From methanol the oil rapidly crystallized in fine

needles, which appeared to go through a transition at 119–120° and to melt at 130°.

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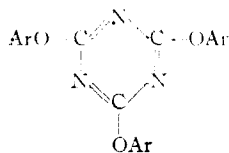
[CONTRIBUTION FROM THE STAMFORD RESEARCH LABORATORIES OF THE AMERICAN CYANAMID COMPANY]

Cyanuric Chloride Derivatives. IV. Aryloxy-*s*-triazines

BY FREDERIC C. SCHAEFER, JACK T. THURSTON AND JAMES R. DUDLEY

The reaction of chloro-*s*-triazines with phenols has been studied, and several new compounds of the following classes have been prepared: triaryl cyanurates, 2-amino-4,6-diaryloxy-*s*-triazines, 2-amino-4-aryloxy-6-chloro-*s*-triazines, 2-aryloxy-4,6-dichloro-*s*-triazines and 2,4-diaryloxy-6-chloro-*s*-triazines. The reaction of chloro-*s*-triazines with sodium aryloxides in aqueous systems to produce aryloxy-*s*-triazines has been developed as a general preparative method. Triaryl cyanurates have been prepared in high yield by heating cyanuric chloride directly with phenols at elevated temperatures.

The first reported preparation of an aryloxy-*s*-triazine was by A. W. Hofmann, who obtained triphenyl cyanurate (I) by treating sodium phenoxide in phenol with cyanogen chloride¹ or with cyanuric chloride.² Otto³ employed the latter method to prepare a series of triaryl cyanurates from alkylphenols and from α - and β -naphthol. He also obtained 2,4-diamino-6-phenoxy-*s*-triazine (VII) by substituting 2,4-diamino-6-chloro-*s*-triazine for the cyanuric chloride and using an equivalent amount of sodium phenoxide. With excess sodium phenoxide triphenyl cyanurate was obtained. Triphenyl cyanurate was also obtained by Hantzsch and Mai⁴ from spontaneous trimerization of diphenyl iminocarbonate with loss of phenol. In 1922 Swiss Patents⁵ were issued which disclosed that cyanuric chloride or aminochloro-*s*-triazines would react in water suspension with sodium aryloxides in much the same way as was known for stepwise reaction with amines.⁶ Recently Witt and Hamilton⁷ have used this method to prepare nitrophenoxy derivatives from 2,4-diamino-6-chloro-*s*-triazine and 2-amino-4-chloro-6-ethylamino-*s*-triazine.



- I, Ar = C₆H₅-
 II, Ar = 3,5-(CH₃)₂C₆H₃-
 III, Ar = *p*-(CH₃)₃CCH₂C(CH₃)₂C₆H₄-
 IV, Ar = *p*-ClC₆H₄-

The accelerating catalytic effect of phenolic solvents upon the reactions of chloro-*s*-triazines

- (1) A. W. Hofmann, *Ber.*, **18**, 764 (1885).
 (2) A. W. Hofmann, *ibid.*, **19**, 2061 (1886).
 (3) R. Otto, *ibid.*, **20**, 2236 (1887).
 (4) A. Hantzsch and L. Mai, *ibid.*, **28**, 2472 (1895).
 (5) Ges. für Chemische Industrie Basel, Swiss Patents 106,098; 106,099, 106,111, 106,113, 106,118, 106,382, 106,392, 106,393 (1924).
 (6) (a) H. H. Fries, *Ber.*, **19**, 242 (1886); (b) H. E. Fierz-David and M. Matter, *J. Soc. Dyers Colourists*, **53**, 424 (1937); (c) H. S. Mosher and F. C. Whitmore, *This Journal*, **67**, 662 (1945); (d) J. T. Thurston, *et al.*, *ibid.*, **73**, 2981 (1951).
 (7) I. H. Witt and C. S. Hamilton, *ibid.*, **67**, 1078 (1945).

with feebly basic amines was disclosed by Wieners.⁸ Attempts in this Laboratory to obtain such catalysis in other reactions of chloro-*s*-triazines in phenol solution led to results which were explainable only if interaction of the chloro-*s*-triazine and phenol to give a phenoxy-*s*-triazine was assumed. Such a reaction was not to be expected in view of early published work by Klason.⁹ This author classified phenol with alcohols, which at their boiling points reacted with cyanuric chloride to give mainly alkyl chlorides and cyanuric acid. Cyanuric esters and hydrogen chloride were formed to only a very slight extent. It has also been reported¹⁰ that cyanuric chloride and α -naphthol react at 140° in the absence of solvent or added catalyst to give 2,4,6-tris-(4-hydroxy-1-naphthyl)-*s*-triazine, or at -5 to 15° in carbon disulfide to give 2-chloro-4,6-bis-(4-hydroxy-1-naphthyl)-*s*-triazine. Graham¹¹ has concluded from variations in the product of the reaction of 1-aminoanthraquinone with cyanuric chloride in phenol according to Wieners' process that cyanuric chloride and phenol may react under the conditions used. However, the manner of reaction was not suggested as different from the two possible modes reported earlier, and it appears unlikely that any reaction would be appreciable at the temperature mentioned, 100–120°.

In this Laboratory we have frequently found corroboration for Klason's statement, insofar as alcohols are concerned, but it was found that cyanuric chloride and monocyclic phenols reacted at 170–210° in the absence of solvents to give high yields of triaryl cyanurates. No hydrogen chloride acceptor was required, and no hydroxy-*s*-triazines have been found. In this way, triphenyl cyanurate (I), tris-(3,5-xylyl) cyanurate (II), tris-(*p*-diisobutylphenyl) cyanurate (III) and tris-*p*-chlorophenyl cyanurate (IV) have been prepared in 80–100% yields. 2-Amino-4,6-dichloro-*s*-triazine and 2,4-diamino-6-chloro-*s*-tri-

- (8) F. Wieners, U. S. Patent 1,994,602 (1935).
 (9) P. Klason, *J. prakt. Chem.*, [2] **34**, 152 (1886).
 (10) H. Fritzsche and P. Schaedeli, U. S. Patent 1,551,095 (1925).
 (11) D. P. Graham, U. S. Patent 2,373,826 (1945).