Anal. Calcd. for $C_{21}H_{12}N_3O_3Cl_3$: N, 9.12; Cl, 23.10. Found: N, 9.17; Cl, 23.39.

Reaction of Chloro-*s*-triazines with Sodium Aryloxides in Aqueous Systems

2-Amino-4,6-diphenoxy-*s*-triazine (V).—2-Amino-4,6-dichloro-*s*-triazine was prepared as reported earlier[6d] and used at once without drying. A 3.0-mole batch of such material was added to a cold (10°) solution of 564 g. (6.0 moles) of phenol and 240 g. (6.0 moles) of sodium hydroxide in 3000 ml. of water. The mixture was stirred for two hours, during which time the temperature was allowed to rise to 25°. The reaction was only weakly exothermic. The temperature was then raised to 90–95° for four hours. The crude product was filtered, washed with water and with ethanol, and dried at 110°. The dry product weighed 718 g. (87% based on cyanuric chloride), m.p. 173–177°. Recrystallization from 5 ml. of butanol per gram raised the melting point to 181–182°.

Anal. Calcd. for $C_{15}H_{12}N_4O_2$: C, 64.29; N, 20.00. Found: C, 64.46; N, 20.17.

In other experiments in which the 2-amino-4,6-dichloro-*s*-triazine (1.0 mole) reacted with phenol (2.0 moles) in water in the presence of sodium carbonate (1.0 mole) at 35–65° or with sodium phenoxide (2.0 moles) in water at 0–10°, **2-amino-4-chloro-6-phenoxy-*s*-triazine** (VI) was obtained in crude yields of 85 and 56%, respectively. This compound melted at 224–227° after recrystallization from dioxane. It could be converted readily to V by reaction with aqueous sodium phenoxide at 75°. In these preparations of VI, excess phenol was used in expectation of the formation of V. Such an excess is unnecessary for the preparation of the intermediate.

2,4-Diamino-6-phenoxy-*s*-triazine (VII).—One mole of crude, wet 2,4-diamino-6-chloro-*s*-triazine[6d] was added to a solution of 99 g. (1.05 moles) of phenol and 42 g. (1.05 moles) of sodium hydroxide in 1000 ml. of water. The mixture was stirred briefly at room temperature and then was heated at reflux for four hours. The slurry was filtered hot, and the product was washed with water and with methanol and was dried at 105°. The crude product weighed 165 g. (82%, based on cyanuric chloride), m.p. 248–250°. The compound could be recrystallized from butanol or methyl cellosolve to give m.p. 255–258°, but large volumes of solvent were required.

Anal. Calcd. for $C_9H_9N_5O$: C, 53.19; H, 4.43; N, 34.48. Found: C, 53.35; H, 4.63; N, 34.16.

Triphenyl Cyanurate (I).—A mixture of 18.4 g. (0.1 mole) of cyanuric chloride and 150 ml. of acetone was stirred vigorously while a solution of 29.1 g. (0.31 mole) of phenol and 12.4 g. (0.31 mole) of sodium hydroxide in 150 ml. of water was run in gradually (15 minutes). The reaction temperature was held at 25° throughout by gentle cooling, and the mixture was stirred at 25° for an additional three hours. The crystalline solid was filtered, washed with water and with methanol and dried at 110°. The dry triphenyl cyanurate weighed 34.0 g. (95%), m.p. 232–235°.

Cyanuric chloride in its usual dense crystalline form would not react completely in the absence of the inert organic solvent, even at 75°.

2-Chloro-4,6-diphenoxy-*s*-triazine (VIII).[12]—To a mixture of 92.2 g. (0.5 mole) of cyanuric chloride and 375 ml. of acetone at 15–20° was added 1.0 mole of sodium phenoxide in 375 ml. of water. After 1.5 hours at 15–20° and one hour at 25°, the product was separated and dried in a vacuum desiccator. The yield was 145 g. (97%), m.p. 110–115°. Recrystallization from heptane gave m.p. 121–123°.

Anal. Calcd. for $C_{15}H_{10}N_3O_2Cl$: C, 60.11; H, 3.36; N, 14.02; Cl, 11.83. Found: C, 60.50; H, 3.61; N, 13.97; Cl, 11.47.

2-Chloro-4,6-bis-(pentachlorophenoxy)-*s*-triazine (IX) was prepared by the procedure described for compound VIII; m.p. approx. 300° (from tetrachloroethane); yield 93%.

This compound did not react with additional pentachlorophenol and sodium hydroxide in aqueous acetone at 25°. Probably this inactivity was due to the very low solubility of the triazine.

2,4-Diallyloxy-6-pentachlorophenoxy-*s*-triazine (X).—A mixture of 289 g. (1.57 moles) of cyanuric chloride, 750 ml. of acetone and 300 ml. of water was stirred at 0–5° while a hot (80–90°) solution of 420 g. (1.57 moles) of pentachlorophenol and 62.8 g. (1.57 moles) of sodium hydroxide in 1250 ml. of water was run in during 1.5 hours. The slurry was agitated for 30 minutes longer after completing this addition and was then filtered. The crude product was pumped as dry as possible, but it weighed 1029 g. and apparently contained approximately 379 g. of water. This material was added over a one-hour period to a solution of 129.5 g. (3.14 moles) of sodium hydroxide in 1500 ml. of allyl alcohol held at 10°. After an additional 30 minutes in the cold, the mixture was heated to 50–60° for 20 minutes. The slurry was diluted with an additional 500 ml. of allyl alcohol and was filtered hot. The product crystallized promptly from the filtrate, and the mother liquor was used to re-extract the filter cake. The combined crops of crystallized 2,4-diallyloxy-6-pentachlorophenoxy-*s*-triazine weighed 514 g. (72%), m.p. 91–95°. The compound was recrystallized with 91% recovery from ethanol, m.p. 94–95°.

Anal. Calcd. for $C_{15}H_{10}N_3O_3Cl_5$: C, 39.34; H, 2.19; Cl, 38.79. Found: C, 39.44; H, 2.36; Cl, 38.94.

Stamford, Connecticut Received July 14, 1950

[Contribution from the Stamford Research Laboratories of the American Cyanamid Company]

Cyanuric Chloride Derivatives. V. Reaction of Alkoxy-s-triazines and Aryloxy-s-triazines with Amines

By Jack T. Thurston, Frederic C. Schaefer, James R. Dudley and Dagfrid Holm-Hansen

The reaction of *s*-triazinyl ethers with amines has been investigated as an alternate method for the preparation of substituted melamines. N-Substituted amino-*s*-triazines may be prepared by the condensation of aryloxy-*s*-triazines with amines, and this is the best method for the preparation of some derivatives. On the other hand, the same reaction with alkoxy-*s*-triazines is not as well defined. A side reaction which becomes predominant with weakly basic amines leads to the formation of hydroxy-*s*-triazines, and the amine is alkylated.

It was observed by Ponomareff[1] that the ethoxy groups in triethyl cyanurate could be displaced by strong aqueous ammonia at 170–180° to give a mixture of melamine and ammeline. Trialkyl cyanurates and alkyl ethers or esters of ammeline and ammelide derivatives are readily available from cyanuric chloride[2] and would serve as intermediates for the preparation of substituted melamines if amines could be substituted for ammonia in this reaction. Most substituted melamines can be prepared directly from cyanuric chloride in good yield,[3] but in some cases isolation of the product is tedious and inefficient. It was hoped

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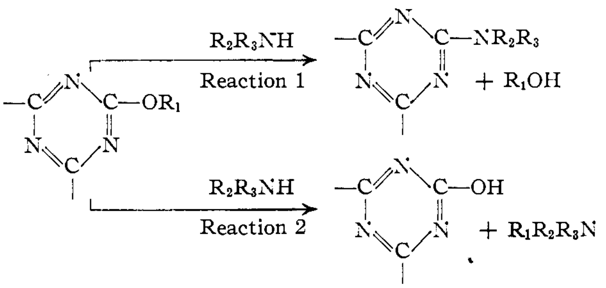
(1) J. Ponomareff, *Ber.*, **18**, 3261 (1885).

(2) J. R. Dudley, *et al.*, This Journal, **73**, 2986 (1951).

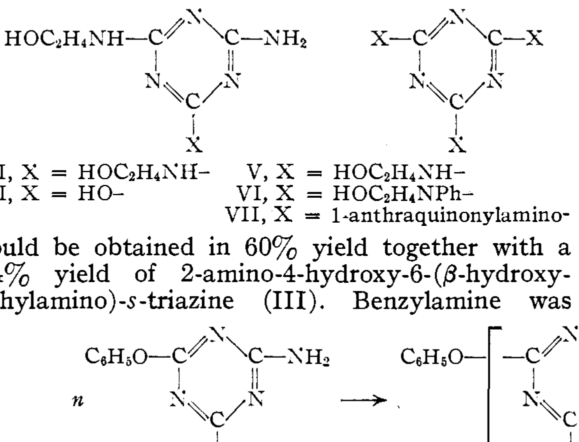
(3) A. W. Hofmann, *Ber.*, **18**, 2755 (1885); P. Klason, *J. prakt. Chem.*, [2] **33**, 290 (1886); H. H. Fries, *Ber.*, **19**, 2055 (1886); H. E. Fierz-David and M. Matter, *J. Soc. Dyers and Colourists*, **53**, 424 (1937); H. S. Mosher and F. C. Whitmore, This Journal, **67**, 662 (1945).

that certain melamines could be obtained more readily from the alkoxy-*s*-triazines.

It was found that alkoxy-*s*-triazines do not react cleanly with amines to form N-substituted amino-*s*-triazines (Reaction 1). A side reaction takes place in which the amine is alkylated and a hydroxy-*s*-triazine is formed (Reaction 2).



When 2,4-dimethoxy-6-N-methylanilino-*s*-triazine was heated with N-methylaniline (two equivalents) at 175–185°, 2,4-dihydroxy-6-N-methylanilino-*s*-triazine (I) was recovered in 37% yield, and no methanol was evolved. This experiment was repeated and N,N-dimethylaniline equivalent to 32% of the initial N-methylaniline was isolated. In neither case was the expected melamine found. Monoethanolamine, a stronger base than methylaniline, and 2-amino-4,6-dimethoxy-*s*-triazine reacted at 155° by both the alkylation reaction and the replacement reaction, and small yields of N^2,N^4-bis-(β-hydroxyethyl)-melamine (II) could be recovered. At a lower temperature this melamine could be obtained in 60% yield together with a 24% yield of 2-amino-4-hydroxy-6-(β-hydroxyethylamino)-*s*-triazine (III). Benzylamine was similar to monoethanolamine in its reaction with 2-amino-4,6-dimethoxy-*s*-triazine, and in its reaction with 2-methoxy-4,6-bis-anilino-*s*-triazine a 70% yield of 2-hydroxy-4,6-bis-anilino-*s*-triazine (IV) was formed.



II, X = HOC_2H_4NH– V, X = HOC_2H_4NH–

III, X = HO– VI, X = HOC_2H_4NPh–

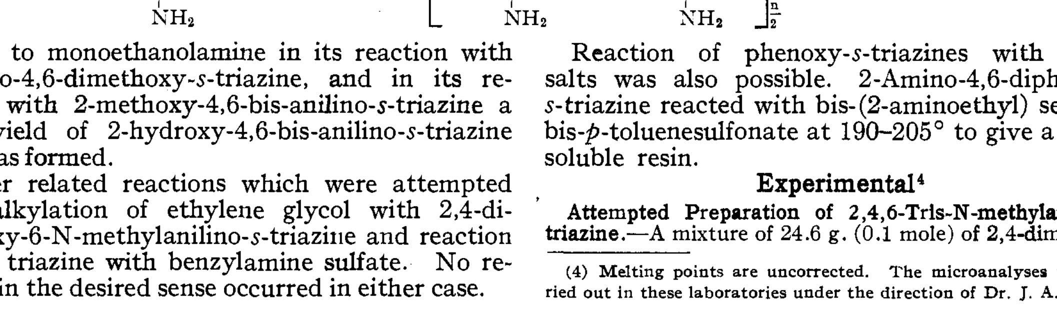
VII, X = 1-anthraquinonylamino-

Other related reactions which were attempted were alkylation of ethylene glycol with 2,4-dimethoxy-6-N-methylanilino-*s*-triazine and reaction of this triazine with benzylamine sulfate. No reaction in the desired sense occurred in either case.

Theoretical considerations indicated that aryloxy-*s*-triazines would be less likely than alkoxy-*s*-triazines to give the undesired side reaction producing hydroxy-*s*-triazines, and in subsequent work emphasis was placed on utilization of the phenoxy-*s*-triazines. These compounds were found to react smoothly with all classes of amines which were tried, and in several cases the reaction afforded the best method available for the preparation of the particular product. No hydroxy-*s*-triazine formation was observed in any case.

The conditions required for the reaction varied considerably depending upon the basicity of the amine used, weaker bases requiring higher temperatures and/or longer heating periods. 2-Amino-4,6-bis-phenoxy-*s*-triazine and triphenyl cyanurate each reacted nearly quantitatively with monoethanolamine (33–50% excess) at 180–210° in three to five hours, and the corresponding substituted melamines (II and V) were isolated in 93.5 and 75% yields, respectively. (Preparation of these compounds directly from cyanuric chloride is difficult because of problems in isolation.) The weaker base, N-phenylethanolamine, required a reaction temperature of about 250°, and reaction with triphenyl cyanurate was incomplete after 16 hours. In this case the substituted melamine (VI) was isolated in 43% yield. Triphenyl cyanurate did not react appreciably with the very weak base 1-aminoanthraquinone at temperatures below 250°, but at 350° nearly complete reaction occurred in one hour, as judged by the weight of phenol evolved. The desired melamine (VII) could not be recovered in pure form.

The wide applicability of the reaction of phenoxy-*s*-triazines with amines was further shown by the behavior of 2-amino-4,6-bis-phenoxy-*s*-triazine and 2,4-diamino-6-phenoxy-*s*-triazine when heated alone above their melting points. Each of these compounds underwent intermolecular condensation at 260–280° with evolution of 75% or more of the theoretical yield of phenol based on the polymerization reactions



Reaction of phenoxy-*s*-triazines with amine salts was also possible. 2-Amino-4,6-diphenoxy-*s*-triazine reacted with bis-(2-aminoethyl) sebacate bis-*p*-toluenesulfonate at 190–205° to give a water-soluble resin.

Experimental[4]

Attempted Preparation of 2,4,6-Tris-N-methylanilino-*s*-triazine.—A mixture of 24.6 g. (0.1 mole) of 2,4-dimethoxy-

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[4] Melting points are uncorrected. The microanalyses were carried out in these laboratories under the direction of Dr. J. A. Kuck.

6-N-methylanilino-*s*-triazine, 21.4 g. (0.2 mole) of N-methylaniline and 0.1 g. (0.004 mole) of metallic sodium was heated at 120° at atmospheric pressure for 1.5 hours. No methanol was evolved. Considerable solidification took place on heating for an additional four hours at 175–185°, but no methanol was formed. Distillation at low pressure and extraction of the solid residue with boiling ethanol left 8 g. of an alkali soluble material which melted at 293–295° after recrystallization from water. Analysis indicated it to be **2,4-dihydroxy-6-N-methylanilino-*s*-triazine** (I); it was obtained in 37% yield, based on the original triazine.

Anal. Calcd. for $C_{10}H_{10}N_4O_2$: C, 55.04; H, 4.62; N, 25.68. Found: C, 54.90; H, 4.72; N, 25.70.

No crystalline material could be isolated from the ethanol extract.

Methylation of N-Methylaniline by 2,4-Dimethoxy-6-N-methylanilino-*s*-triazine.—A mixture of 24.6 g. (0.1 mole) of 2,4-dimethoxy-6-N-methylanilino-*s*-triazine and 21.4 g. (0.2 mole) of N-methylaniline (redistilled, n^{22}D 1.5698) was heated for five hours at 170–175°. Partial solidification took place. The cooled reaction mixture was filtered, and the solid was found to be identical with (I); it was obtained in 20% yield.

Distillation of the liquid portion at low pressure gave 18.5 g. of distillate, n^{25}D 1.5648. This refractive index corresponded to a mixture of 32% N,N-dimethylaniline and 68% N-methylaniline. Further distillation through a 2-ft. spiral column gave a 15.4-g. fraction, b.p. 112–113° at 59 mm. Refractive indices of separate portions of this fraction again indicated the whole to be a 32–68 mixture of dimethylaniline and monomethylaniline. Separation by the Hinsberg method gave N-methyl-N-phenylbenzenesulfonamide, m.p. 78–79°, equivalent to 65% of the 15.4-g. amine mixture. Distillation of the tertiary amine gave N,N-dimethylaniline, b.p. 113.5° (66 mm.), n^{25}D 1.5555. The identity of this compound was confirmed by a positive malachite green test[5] (not given by the N-methylaniline) and by the preparation of a derivative, *p*-nitrosodimethylaniline, m.p. 86–87°.

Reaction of 2-Amino-4,6-dimethoxy-*s*-triazine with Two Equivalents of Monoethanolamine.—2-Amino-4,6-dimethoxy-*s*-triazine (78.0 g., 0.5 mole), 61.0 g. (1.0 mole) of monoethanolamine, and 0.6 g. (0.025 mole) of metallic sodium were heated for 1.5 hours at 120° at 650 to 200 mm. pressure. A 58% yield of methanol was evolved, and the residue gradually solidified. The temperature was raised to 155° to obtain sufficient fluidity for stirring and was held at 155–165° at 200 mm. for an additional 30 minutes. This increased the yield of methanol to 71%, and some amine was also distilled from the reaction flask. A further 1.5-hour period at 165–175° with an additional 0.5 mole of monoethanolamine caused no change. All volatile material was then distilled at low pressure. Extraction of the solid residue with 180 ml. of butanol which contained 2.0 ml. of acetic acid and 10 ml. of water, followed by evaporation of the solvent from the extract, gave a sirupy residue from which a small amount of crystalline N^2,N^4-bis-(β-hydroxyethyl)-melamine (II), m.p. 159–161°, was obtained. This substance was identical with the product prepared from 2-amino-4,6-dichloro-*s*-triazine and monoethanolamine.[6]

The butanol-insoluble residue, m.p. 280°, was soluble in both dilute sodium hydroxide and dilute hydrochloric acid. This material was shown to be chiefly **2-amino-4-hydroxy-6-(β-hydroxyethylamino)-*s*-triazine** (III); yield 40%. It formed a **sodium salt** which could be recrystallized from water. The recrystallized salt was washed with boiling cellosolve, and samples of the purified compound were titrated by dissolving the substance in excess standard hydrochloric acid and back-titrating with sodium hydroxide. *Anal.* Calcd. for $C_5H_8N_5O_2Na$: neut. equiv., 193. Found: neut. equiv., 195.

Reaction of 2-Amino-4,6-dimethoxy-*s*-triazine with a Large Excess of Monoethanolamine.—A mixture of 78.0 g. (0.5 mole) of 2-amino-4,6-dimethoxy-*s*-triazine, 183 g. (3.0 moles) of monoethanolamine and 0.6 g. (0.025 mole) of metallic sodium was heated at 125–135° at 180 mm. for 5.5 hours. Considerable crystalline material formed, and 75% of the theoretical amount of methanol was evolved. All volatile material was distilled at low pressure. The crude reaction product was extracted once with 100 ml. of hot water containing 2.0 ml. of acetic acid and twice with 100-ml. portions of hot water. This left a residue of 17.0 g., m.p. 300° (incomplete), which was soluble in dilute alkali. This material was crude III. The aqueous extracts deposited crystals of II, m.p. 159–161°, when cooled. Fractional crystallization of the mother liquors yielded additional amounts of the II and III, bringing the yields of these compounds to 60 and 24%, respectively.

Reaction of 2-Amino-4,6-dimethoxy-*s*-triazine with Benzylamine.—When benzylamine and 2-amino-4,6-dimethoxy-*s*-triazine were heated together in the presence of a catalytic amount of sodium, only about 34% of the expected methanol was evolved during three hours at 120–150°. However, during this time a solid product was formed to a considerable extent. This was composed of hydroxytriazines. No attempt was made to isolate any definite products from this reaction.

Reaction of 2-Methoxy-4,6-bis-anilino-*s*-triazine with Benzylamine.—A mixture of 29.4 g. (0.1 mole) of the triazine and 10.7 g. (0.1 mole) of benzylamine was heated at 180° for 4.5 hours under a reflux air condenser. The reaction mixture solidified rapidly during the heating period. The crude product was broken up and extracted with hot methanol, leaving 27 g. of insoluble material, m.p. 275°. Further extraction with boiling ethanol left 19.5 g., which melted at near-red heat. This product was not detectably soluble in acid or alkali or in any of the usual solvents. The analytical data and physical properties of the unrecrystallized product were consistent with the identification of this compound as **2-hydroxy-4,6-bis-anilino-*s*-triazine** (IV); yield 70%.

Anal. Calcd. for $C_{15}H_{13}N_5O$: C, 64.50; H, 4.69; N, 25.08. Found: C, 63.99; H, 4.95; N, 25.30.

Attempted Reaction of 2,4-Dimethoxy-6-N-methylanilino-*s*-triazine with Benzylamine Neutral Sulfate.—Benzylamine (25.0 g., 0.233 mole), 24.6 g. (0.1 mole) of the triazine and 1.0 g. (0.01 mole) of sulfuric acid were heated together at 100–110° for five hours and at 120–130° for five hours. During the latter period approximately 2.0 ml. of liquid distilled. This was chiefly methanol, but evidently the amine sulfate was not an active reagent.

Attempted Methylation of Ethylene Glycol by 2,4-Dimethoxy-6-N-methylanilino-*s*-triazine.—A mixture of 49.2 g. (0.2 mole) of the triazine and 24.8 g. (0.4 mole) of ethylene glycol was heated at 165–170° for 10 hours under a reflux condenser. No apparent change occurred. The volatile material was distilled at low pressure, giving a two-phase distillate, one layer of which contained methylaniline. Redistillation of the glycol layer gave no indication of the presence of methyl cellosolve. The non-volatile residue from the reaction mixture appeared to be resinous.

N^2,N^4-Bis-(β-hydroxyethyl)-melamine (II).—A mixture of 276 g. (1.0 mole) of 2-amino-4,6-diphenoxy-*s*-triazine[7] and 183 g. (3.0 moles) of monoethanolamine was heated for three hours at reflux (180°). The volatile material was then distilled as completely as possible at reduced pressure. The dark-colored, sirupy residue, while still hot, was stirred and diluted with 400 ml. of butanol, and a solution of 4 g. of sodium hydrosulfite in 15 ml. of water was added at once. The color was largely discharged, and the product crystallized rapidly. After the mixture had cooled to room temperature, the crystals were filtered, washed with butanol and with acetone, and dried at 105°. The nearly white product weighed 200 g. (93.5%), m.p. 160–162°. It could be recrystallized from water, from which it separated slowly with about 60% recovery but with no elevation in melting point. However, the product as obtained was satisfactory for most contemplated applications.

Reaction of 2-Amino-4,6-bis-phenoxy-*s*-triazine with Bis-(2-aminoethyl)-sebacate Bis-*p*-toluenesulfonate.[8]—An equimolar mixture of the reactants was heated at 190–205° for 1.5 hours at 30 mm. pressure. Eighty-one per cent of the theoretical yield of phenol was evolved. The clear, glassy resinous product was water-soluble.

N^2,N^4,N^6-Tris-(β-hydroxyethyl)-melamine (V).—Triphenyl cyanurate (657 g., 1.83 moles) and 447 g. (7.32

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[5] S. P. Mulliken, "Identification of Pure Organic Compounds," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1916, p. 145.

[6] D. W. Kaiser, *et al.*, This Journal, **73**, 2984 (1951).

[7] F. C. Schaefer, *et al.*, *ibid.*, **73**, 2990 (1951).

[8] This compound was prepared by heating 1.0 mole of sebacic acid, 2.0 moles of monoethanolamine, and 2.0 moles of *p*-toluenesulfonic acid in refluxing toluene until the theoretical amount of water was collected in a moisture trap. The insoluble product was obtained in quantitative yield, m. p. 170–175°.

moles) of monoethanolamine were heated together at 200–210° for five hours. The volatile material was then distilled as completely as possible at low pressure, and the residue was crystallized from 1400 ml. of butanol. The product which separated slowly weighed 352 g. (75%), m.p. 94–95°. The dark-colored compound was recrystallized from butanol (2.0 ml. per gram) after treatment with activated carbon, with 84% recovery. The white crystals obtained melted at 98–100°. This compound was identical with that prepared by reaction of 2-chloro-4,6-bis-(β-hydroxyethylamino)-*s*-triazine with monoethanolamine.[6].

2,4,6-Tris-(N-β-hydroxyethylanilino)-*s*-triazine (VI).—A mixture of 126 g. (0.353 mole) of triphenyl cyanurate and 242 g. (1.765 moles) of N-phenylethanolamine was heated at 250° in a distilling apparatus for 16 hours. During the first two hours it was possible to distil about 50 g. of material boiling below 210° (b.p. of N-phenylethanolamine, 286°). Later very little material distilled. The dark-colored reaction mixture was cooled to about 100° and diluted with 1000 ml. of ethanol. Crystallization began promptly and was completed at 0°. The crystals were separated and washed with ethanol until the washings were colorless. The nearly white product weighed 67 g., m.p. 146–152°. Another 5 g. was recovered with difficulty from the filtrate, bringing the yield of the melamine to 43%. The crude product could be recrystallized from 5 ml. of propanol or 12 ml. of benzene per gram or from 5% sulfuric acid. The analyzed sample had m.p. 163–164°.

Anal. Calcd. for $C_{27}H_{30}N_6O_3$: C, 66.65; H, 6.21; N, 17.27. Found: C, 66.71; H, 6.26; N, 17.51.

Reaction of Triphenyl Cyanurate with 1-Aminoanthraquinone.—A mixture of 7.00 g. (0.0314 mole) of recrystallized 1-aminoanthraquinone and 3.57 g. (0.0100 mole) of triphenyl cyanurate was heated for one hour at 350° at atmospheric pressure. At first a little 1-aminoanthraquinone sublimed, but within 15 minutes phenol began to distil. At the end of one hour, 2.7 g. of distillate had collected (90–94%). The black residue was broken up and extracted with hot methyl cellosolve, which left 7.20 g. undissolved. A lighter colored dye could not be extracted from the black product, which produced only a very weak, orange-yellow when applied to cotton cloth from a hydrosulfite vat.

This reaction was very incomplete after six hours when it was attempted at 270–285° in an effort to reduce the amount of decomposition. No reaction occurred in refluxing decalin (195°) during 5.5 hours.

Polymerization of 2,4-Diamino-6-phenoxy-*s*-triazine and 2-Amino-4,6-bis-phenoxy-*s*-triazine.—2,4-Diamino-6-phenoxy-*s*-triazine (1.5 g.) gave a clear, colorless melt when heated carefully at the melting point (255–258°), but when heated further to about 265° the melt began to boil vigorously and partially resinified almost at once. After a few minutes, the mixture was cooled and extracted with dry ether. The ether solution was evaporated, leaving a residue of 0.6 g. (75%) which was identified as phenol by odor, coloration with ferric chloride, and conversion to picric acid, m.p. 120–122°. The white residue from the ether extraction was infusible and insoluble in hot hydrochloric acid or hot formalin.

A 10.0-g. sample of 2-amino-4,6-bis-phenoxy-*s*-triazine, m.p. 181–182°, was heated at 280–300° under an air condenser. Boiling began within a few minutes and soon became vigorous. No solid separated, but the melt became progressively more viscous without darkening. After one hour the mixture was cooled and the glassy resin extracted with dry ether. Evaporation of the ether solution left 2.5–3.0 g. of phenol (75–90%). The residue from the extraction was a white powder which softened at 220–250°.

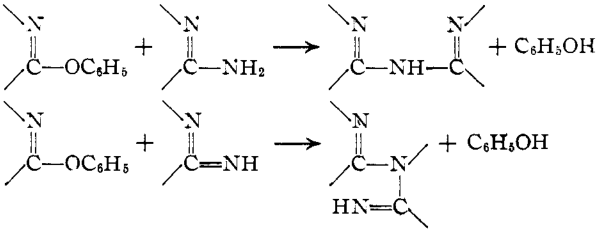
Discussion

Cyanuric chloride clearly is to be classed as an acyl halide, amino-*s*-triazines react as amides and *s*-triazinyl ethers are very similar to esters. The reaction of an amine with an *s*-triazinyl ether to produce a substituted amino-*s*-triazine (Reaction 1) is analogous to the formation of an amide from a carboxylic ester, and undoubtedly proceeds by the same mechanism. The ease of reaction would be expected to parallel the basic strength of the amine, and this has been observed in the limited series of amines studied.

Because the *s*-triazine nucleus is not devoid of aromatic character, there is some resistance to carbonyl reactions, and side reactions may occur when this possibility is present. In alkoxy-*s*-triazines the electrophilic effect of the *s*-triazine system acts in the same direction as the inductive effect of the alkyl group. The electronic configuration offers a seat of acceptor activity to a nucleophilic reagent, and Reaction 2 becomes more pronounced. When it was attempted to force the sluggish reaction of monoethanolamine with 2-amino-4,6-dimethoxy-*s*-triazine, Reaction 2 became a serious side reaction, although at a lower temperature the desired substituted melamine was obtained in fair yield. Methylaniline, a weaker base than monoethanolamine, presumably could not form an intermediate which would favor Reaction 1 at temperatures below that required for the alkylation reaction, which occurred exclusively.

On the other hand, in aryloxy-*s*-triazines the electron affinities oppose, and no fractional positive charge is developed on the attached carbon atom of the aryl group. An "arylation" reaction was not possible in the case of the aryloxy-*s*-triazines, and strenuous reaction conditions could be used when necessary to force Reaction 1, as in the reaction of triphenyl cyanurate with N-phenylethanolamine at 250° or with 1-aminoanthraquinone at 350°.

The polycondensation reactions which took place when aminophenoxy-*s*-triazines were heated at about 280° were interesting because of the very low basic strength of the amino groups in these cases. Reaction could have occurred by either route indicated



Phenol is well known as a catalytic solvent for condensation reactions of cyanuric chloride[9] and 9-chloroacridines[10] with amines. The 9-chloroacridines react easily at 90–100° with excess phenol to form 9-phenoxyacridines,[10a,11] and these compounds react at the same temperature with aliphatic amines or their hydrochlorides to give N-substituted 9-aminoacridines.[10a,10b,11,12]

Consequently it has been reasonable to consider the 9-phenoxyacridines to be intermediates in the one-step reactions in phenol solution.[10a] Similarly, 4-phenoxy-1,5-naphthyridine appears to be an intermediate in the preparation of N-substituted 4-amino-1,5-naphthyridines from the 4-chloro com-

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[9] W. Franz, U. S. Patent 1,994,602 (1935).

[10] (a) D. T. Magidson and A. M. Grigorowsky, *Ber.*, **69**, 396 (1936); (b) D. J. Duprē and E. A. Robinson, *J. Chem. Soc.*, 549 (1945); (c) D. M. Hall and E. E. Turner, *ibid.*, 694 (1945).

[11] I. G. Farbenindustrie A.-G., German Patent 553,027 (1932).

[12] R. R. Goodall and W. O. Kermack, *J. Chem. Soc.*, 1546 (1936).

pound.[13] However, such an explanation for the observed catalytic effect of the solvent phenol upon chloro-*s*-triazine reactions cannot be correct. The temperatures required for reaction of these compounds with phenol (170–210°) to give phenoxy-*s*-triazines[7] are much higher than reaction temperatures used to prepare N-substituted amino-*s*-triazines in phenol solution (100–120°). Furthermore, feebly basic amines such as 1-aminoanthraquinone, which react readily with cyanuric chloride in phenol at this low temperature, require very strenuous conditions for reaction with triphenyl cyanurate.

STAMFORD, CONNECTICUT RECEIVED JULY 14, 1950

(13) J. T. Adams, C. K. Bradsher, D. J. Breslow, S. T. Amore and C. R. Hauser, THIS JOURNAL, **68**, 1317 (1946).

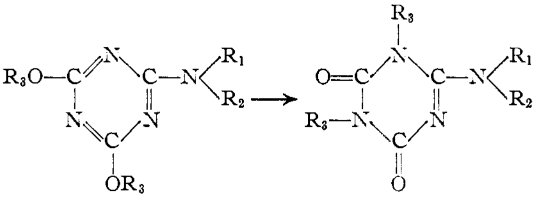
[CONTRIBUTION FROM THE STAMFORD RESEARCH LABORATORIES OF THE AMERICAN CYANAMID COMPANY]

Cyanuric Chloride Derivatives. VI. Rearrangement Reactions of 2,4-Dialkoxy-6-amino-s-triazines

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

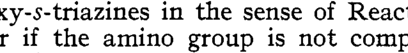
The formation of hydroxy-*s*-triazines and the alkylation of the amine in the reaction of alkoxy-*s*-triazines with amines led to an investigation of the possibility of the occurrence of a self-alkylation reaction in 2,4-dialkoxy-6-amino-*s*-triazines through an intramolecular rearrangement. It has been found that such a rearrangement does occur under the influence of heat, and that the possibility and extent of the change is conditioned by the nature of the substituents on the amino nitrogen atom. Alkylation of *s*-triazinylamino groups by alkoxy-*s*-triazines is also possible at temperatures of 120° or higher.

In connection with other studies of the chemistry of *s*-triazine derivatives, it became important to investigate the thermal stability of 2-amino-4,6-dialkoxy-*s*-triazines. In particular, the possibility of the rearrangement


(1)

	R_1	R_2	R_3	
I	CH_3–	C_6H_5–	CH_3–	
II	H–	H–	C_4H_4–	
III	C_4H_4	H–	CH_3–	IV
V	C_6H_5	H–	CH_3–	VI

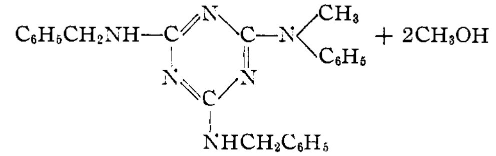
was to be studied. Such a rearrangement was to be expected at elevated temperatures in view of the known rearrangement of trialkyl and dialkyl cyanurates to isocyanurates,[1] the closely analogous rearrangement of aryl N-phenyliminobenzoates to N,N-diarylbenzamides,[2] and other rearrangements brought about by heat alone,[3] which in general may be represented



$$\mathrm{R{-}O{-}\underset{|}{C}{=}\underset{|}{N}} \longrightarrow \mathrm{O{=}\underset{|}{C}{-}\underset{|}{N}{-}R} \qquad (2)$$

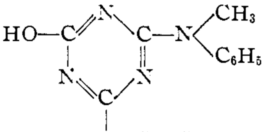
It was found that rearrangement of 2-amino-4,6-dialkoxy-*s*-triazines in the sense of Reaction 1 does occur if the amino group is not completely substituted, *i.e.*, if it bears at least one hydrogen atom. 2-N-Methylanilino-4,6-dimethoxy-*s*-triazine[4] (I) was essentially stable at temperatures of 185–250°. A rearrangement did occur in the reaction of I with benzylamine in an attempt to prepare 2-N-methylanilino-4,6-bis-benzylamino-*s*-triazine (VII) according to the reaction[5]

$I + 2C_6H_5CH_2NH_2 \longrightarrow$



VII

Some methanol was evolved, but the melamine, VII, was not obtained. Two isomeric products were recovered, one melting at 355–360° and the other at 201–204°. Neither compound was alkali-soluble, but both were soluble in dilute hydrochloric acid. Their empirical formula, $C_{17}H_{17}N_5O$, corresponded to the structure[6]



VIII

or to its rearrangement products. The formation of a compound having the structure shown might have been predicted since this parallels the formation of 2-amino-4-hydroxy-6-(β-hydroxyethylamino)-*s*-triazine under similar conditions from 2-amino-4,6-dimethoxy-*s*-triazine and monoethanolamine.[4] Because the melamine, VII, or the hydroxy-*s*-triazine, VIII, were the only products which could be expected on the basis of earlier work, it is suggested that one of the products obtained was this hydroxy-*s*-triazine. The isomeric product could then have a rearranged structure such as

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(1) A. W. Hofmann, *Ber.*, **19**, 2061 (1886).

(2) A. W. Chapman, *J. Chem. Soc.*, 1992 (1925); 1743 (1927).

(3) C. D. Hurd, "The Pyrolysis of Carbon Compounds," The Chemical Catalog Company, Inc. (Reinhold Publishing Corp.), New York, N. Y., 1929, p. 205.

(4) J. R. Dudley, *et al.*, THIS JOURNAL, **73**, 2986 (1951).

(5) J. T. Thurston, *et al.*, *ibid.*, **73**, 2992 (1951).

(6) Generally, the structures given in this paper will represent only one of the possible tautomers. It is not possible to distinguish between these rapidly convertible modifications of amino- and hydroxy-*s*-triazines.