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°.

Acknowledgment.—We are indebted to Mr. Eric I. Hoegberg, Dr. Donald W. Kaiser, and Mr. Lennart A. Lundberg for aid in the preparative work. Microanalyses were carried out in these laboratories under the direction of Dr. J. A. Kuck.

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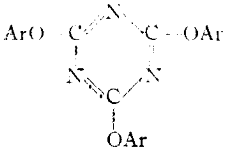
[CONTRIBUTION FROM THE STAMFORD RESEARCH LABORATORIES OF THE AMERICAN CYANAMID COMPANY]

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 chloride[1] or with cyanuric chloride.[2] Otto[3] 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 Mai[4] from spontaneous trimerization of diphenyl iminocarbonate with loss of phenol. In 1922 Swiss Patents[5] 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 Hamilton[7] 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 = C_6H_5–
II, Ar = 3,5-$(CH_3)_2C_6H_3$–
III, Ar = *p*-$(CH_3)_3CCH_2C(CH_3)_2C_6H_4$–
IV, Ar = *p*-ClC_6H_4–

The accelerating catalytic effect of phenolic solvents upon the reactions of chloro-*s*-triazines 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 reported[10] 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. Graham[11] 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-

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(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).

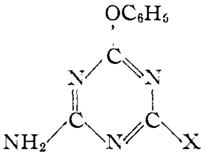
(8) F. Wieners, U. S. Patent 1,994,602 (1935).

(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).

azine also reacted with phenol in this temperature range, presumably forming the corresponding aminophenoxy-*s*-triazines. These, however, underwent further changes. Some cleavage of amino groups occurred and a small amount of triphenyl cyanurate was isolated from the reaction product in the former case. The major products of these reactions, however, were insoluble resins. At a lower temperature 2,4-diamino-6-chloro-*s*-triazine gave a low yield of 2,4-diamino-6-phenoxy-*s*-triazine. The nature of the polymerization reactions at high temperatures will be considered in a later paper.



V, X = C_6H_5O–
VI, X = Cl–
VII, X = NH_2–

The aminophenoxy-*s*-triazines (V and VII) which were not available from a fusion process were prepared by reaction of the chloro-*s*-triazines with sodium phenoxide in aqueous systems, a method which was developed more fully than is reported in the literature.[5,7] The general usefulness of such a process suggested by the Swiss patent specifications has been confirmed, and satisfactory general preparative procedures have been worked out with certain important compounds as examples. 2-Amino-4,6-dichloro-*s*-triazine reacted with aqueous sodium phenoxide at 10° or with phenol in aqueous sodium carbonate at 65° to form 2-amino-4-chloro-6-phenoxy-*s*-triazine (VI). This compound reacted further with aqueous sodium phenoxide at 75° to give 2-amino-4,6-diphenoxy-*s*-triazine (V). Compounds V and VI could each be isolated in yields of 85% or better, based on the original cyanuric chloride. Although the intermediate (VI) need not be isolated in the preparation of V, best results were obtained when the first stage of the reaction was run at low temperature. If the reaction mixture was heated at once the suspended reactants tended to coalesce and become unreactive. 2,4-Diamino-6-chloro-*s*-triazine was converted to VII in high yield by reaction with an equivalent amount of sodium phenoxide in water at 100°.

In view of the success of this method for the preparation of these amino-*s*-triazine derivatives, it was also investigated as an alternative method for the preparation of triaryl cyanurates. It was found that triphenyl cyanurate could be obtained in 95% yield by reaction of cyanuric chloride with sodium phenoxide in aqueous acetone at 25°. Furthermore, the product was a colorless, granular material of high purity. By limiting the amount of sodium aryloxide used to one or two moles per mole of cyanuric chloride and operating at slightly lower temperatures, the mono- or diaryloxy-*s*-triazines could be obtained in good yield. 2-Chloro-4,6-diphenoxy-*s*-triazine[12] and 2-chloro-4,6-bis-(pentachlorophenoxy)-*s*-triazine were prepared by reaction of cyanuric chloride with two equivalents of the sodium aryloxide at 15–20°. 2,4-Dichloro-6-pentachlorophenoxy-*s*-triazine was prepared by reaction of cyanuric chloride with one equivalent of sodium pentachlorophenoxide at 0–5°. In the last case the product was not isolated but was converted at once to 2,4-diallyloxy-6-pentachlorophenoxy-*s*-triazine by an adaptation of the method reported earlier for the preparation of alkoxy-*s*-triazines.[6d] An over-all yield of 72% was realized.

(Hydroxyphenoxy)-*s*-triazines could not be prepared by reaction of cyanuric chloride with resorcinol, insoluble and infusible polymeric products being obtained in poor yield. It was thought that tris-(*m*-hydroxyphenyl) cyanurate might be obtained by alkaline hydrolysis of tris-(*m*-acetoxyphenyl) cyanurate. However, this compound could not be prepared readily by the usual process from resorcinol monoacetate because the aryloxychloro-*s*-triazines were formed as gummy products. These intermediates may have been unreactive because of their physical condition.

An unsuccessful attempt was made to convert III to 2,4,6-tris-(2′-hydroxy-5′-*p*-diisobutylphenyl)-*s*-triazine under the conditions of the ortho Fries rearrangement.[13] Instead a water-stable aluminum chloride complex was obtained. This suggested that III might be the desired triaryl-*s*-triazine, obtained directly, which would be expected to have some basic character. However, hydrolysis of III with sodium hydroxide gave *p*-diisobutylphenol, confirming the cyanurate structure.

Experimental[14]

Preparation of Triaryl Cyanurates by the Fusion Process

Triphenyl Cyanurate (I).—Cyanuric chloride (184.4 g., 1.0 mole) was heated with a small excess of phenol (3.0–4.0 moles) at 185–210° for five hours under a reflux air condenser. Hydrogen chloride was evolved vigorously during the first few hours. The crude reaction product was extracted with boiling methanol, which left a white, crystalline residue of triphenyl cyanurate, m.p. 234–336°, in 95% yield. The product could be recrystallized from large volumes of benzene, methyl cellosolve or dioxane to give fine needles, m.p. 235–236°, but this was very impractical for any purpose in which the compound was to be used as an intermediate.

This reaction is not considered dangerous. The gas evolution can easily be slowed or stopped by controlling the source of heat. However, the reaction flask should not be more than half filled, and a large bore air condenser should be provided.

Tris-(3,5-xylyl) cyanurate (II) was prepared in a manner similar to compound I; m.p. 268.5–269.5°; yield 80%.

Anal. Calcd. for $C_{27}H_{27}N_3O_3$: N, 9.52. Found: N, 9.40.

Tris-(*p*-diisobutylphenyl) cyanurate (III) was prepared in a manner similar to compound I; m.p. 294–295°; yield 85%.

Anal. Calcd. for $C_{45}H_{63}N_3O_3$: C, 77.88; H, 9.15. Found: C, 77.69; H, 8.84.

The structure of III was proven by degradation with sodium hydroxide in boiling diethylene glycol, yielding the sodium salt of *p*-diisobutylphenol, m.p. 163–165°. From this the free phenol was obtained, m.p. 84–85°.

Compound III was recovered nearly quantitatively by decomposition with alkali of the complex compound formed when III and aluminum chloride (3.5 moles) were heated in nitrobenzene at 120°.

Tris-*p*-chlorophenyl cyanurate (IV) was prepared in a manner similar to compound I; m.p. 200–205°; yield 84%.

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[12] Ges. für Chemische Industrie Basel, Swiss Patent 106,382 (1924).

[13] A. H. Blatt, "The Fries Reaction" in "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942.

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

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).