In an experiment in which the cyanurate was treated with an equimolar amount of triethylene glycol, samples were removed from the reaction mixture at suitable time intervals and were tested for solubility in butanol as a criterion of cross-linking. It was found that insoluble polymer was produced before the reaction was 13% completed.

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

## Cyanuric Chloride Derivatives. VIII. Vinylamino-s-triazines

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In the attempted preparation of vinylamino-s-triazines for use as monomers in the preparation of resinous materials, it has been found that the compounds which can be made are subject to constitutional limitations. An unusual intramolecular rearrangement has been discovered, which leads to the formation of vinylamino-s-triazines, and three such compounds have been prepared. The vinyl group in this new class of compounds appears to be stable with respect to peroxide-induced polymerization.

N-Vinyl derivatives of N-substituted aliphatic amides and of imides have been reported by Hanford and Stevenson<sup>1</sup> to give useful products when polymerized alone or copolymerized with vinyl or vinylidene compounds. This class of compounds, which can be prepared by pyrolysis of the corresponding N- $\beta$ -acetoxyethylamides, contains

the active structural unit,  $H_2C=CH-N-C-$ . Amino-s-triazines are known to have amide properties, and it was possible that N-vinylamino-s-triazines might also be useful monomers. They

would contain the group,  $H_2C=-CH-N-U$ , which may be considered an ammono analog of that in the N-vinylamides.<sup>2</sup>

It was found that N-vinylamino-s-triazines could not be prepared by pyrolysis of N- $\beta$ -acetoxyethylamino-s-triazines unless an alkoxy-s-triazine group was also present in the molecule. When this requirement was not met, the  $\beta$ -acetoxyethyl group was very stable. In those cases where a vinyl derivative was obtained, the reaction was not that expected

 $N C_{6}H_{5}$   $C - N - CH_{2}CH_{2}OCOCH_{5} \rightarrow$   $N C_{6}H_{5}$   $C - N - CH = CH_{2} + CH_{3}OOH (1)$ 

Instead, an alkyl acetate was evolved, and an hydroxy-N-vinylamino-s-triazine was produced, e.g.



(1) W. E. Hanford, et al., U. S. Patents 2,231,905 (1941) and 2,276,840 (1942).

(2) J. T. Thurston, et al., This Journal, 73, 2992 (1951).



The first experiments were directed toward the preparation of 2-N-vinylanilino-4,6-dimethoxy-striazine. It was considered that inclusion of only one active group in the molecule would make simpler both the preparation of this compound and the study of its reactivity. Also, the product would be expected to have physical properties comparable to those of 2-N-methylanilino-4,6dimethoxy-s-triazine,3 i.e., low melting point and high solubility in organic solvents, and so it would be similar to the useful N-vinylamides. The phenyl group was expected to confer additional, desirable amide character to the amino nitrogen 2-(N-β-Acetoxyethylanilino)-4,6-dimethatom. oxy-s-triazine (I) was prepared by acetylation of 2 - (N -  $\beta$  - hydroxyethylanilino) - 4,6 - dimethoxys-triazine and was pyrolyzed at 200-240° without isolation. No acetic acid could be detected in the evolved vapors. The residue yielded a compound which melted at 254-255°. Analytical data for this substance definitely showed loss of the acetoxy group from I, and the infrared absorption spectrum gave strong evidence for the presence of the vinyl group.

These data alone did not permit completely unequivocal identification of the product as 2-Nvinylanilino-4-hydroxy-6-methoxy-s-triazine (II) rather than 2-N-vinylanilino-4,6-dimethoxy-s-triazine, but the melting point and poor solubility of the compound strongly supported this conclusion. The yield of II was 60%. Preparation of the corresponding ethoxy-s-triazine derivative (IV) was carried out similarly to confirm the structure of II and if possible to obtain a lower melting and more soluble product. Compound IV was obtained in 48% yield. Analysis gave satisfactory confirmation of the assigned structure, but little was gained in solubility. In this preparation it was possible to isolate and identify ethyl acetate as the by-product.

(3) J. R. Dudley, et al., ibid., 73, 2986 (1951).

These results indicated that pyrolysis of the  $\beta$ acetoxyethylamino group to give the vinyl derivative was not a difficult reaction. Attention was then turned to pyrolysis of 2,4,6-tris-(N- $\beta$ -acetoxyethylanilino)-s-triazine (V), in which case no complex reactions seemed possible. This compound



was obtained in high yield from the hydroxyethylamino-s-triazine (VI). Surprisingly, it was found that V was very stable, and although decomposition could be brought about by long heating at  $350^\circ$ , no acetic acid was evolved. Apparently, the relatively easy pyrolysis obtained with I and III was the result of the possibility of simultaneous cleavage of an alkoxy-s-triazine group. Therefore, pyrolysis of V in the presence of trimethyl cyanurate and of 2-amino-4,6-diethoxy-s-triazine was attempted, but no reaction occurred.

Compound VI was prepared satisfactorily by condensation of triphenyl cyanurate with phenylethanolamine.<sup>3</sup> Prior to this, however, its preparation was attempted by reaction of cyanuric chloride with the amine in acetone. The results at the time were quite puzzling, but proved very instructive when it was discovered later that the acetone used had been contaminated by a large amount of methanol. The crude sirupy product obtained was assumed to be the melamine (VI) and was acetylated directly. It was evident that this did not give a useful amount of the desired product (V), but a high yield of 2-N-vinylanilino-4- $(N - \beta - hydroxyethylanilino) - 6 - hydroxy - s$ triazine (VII) was obtained. It was seen that VII could have arisen from a reaction similar to (2), which was particularly easy in this case

ylated at  $115^{\circ}$  in the usual way. Compound VII was obtained directly in 53% yield. Presumably, the monoacetate (IX) was quite unstable, and its rapid decomposition to VII, which was insoluble, prevented further acetylation to more than a small extent.

It might have been expected that acetylation of 2 - (N -  $\beta$  - hydroxyethylanilino) - 4,6 - dialkoxys-triazines at  $115-120^{\circ}$  would endanger the alkoxy groups because of their known susceptibility to anhydrous acids. It was also possible that pyrolysis of the acetates to give acetic acid might be accompanied by cleavage of the alkoxy groups by the acetic acid. However, the actual results are difficult to explain. Some dealkylation occurred during the preparation of I and III, but over half of VIII was dealkylated during acetylation, and a vinylamino group was always developed simultaneously. Cleavage of alkyl groups by acetic acid in the solvent would not have given nearly pure II as was the case, but rather a mixture of mono- and dihydroxy-s-triazines bearing both vinylamino and acetoxyethylamino groups. Likewise, VII would not have been obtained without a substantial amount of 2,4-bis-(N-\beta-acetoxyethylanilino)-6-hydroxy-s-triazine. Certainly, cleavage of alkyl groups was brought about by, or in conjunction with the loss of, acetic acid from the acetoxyethyl group. Conversely, it was apparent that acetic acid was not lost from an acetoxyethylamino-s-triazine group (except possibly at very high temperatures) unless an alkoxy-s-triazine group in the same molecule could be cleaved simultaneously. No acetic acid was detected in the volatile products of the pyrolysis of I or III, and no dihydroxy-s-triazines were produced. These facts and the failure of V to react with trimethyl cyanurate or 2-amino-4,6-diethoxy-s-triazine can lead only to the conclusion that II, IV and VII were formed by an intramolecular reaction or "rearrangement" which proceeds without side reactions at moderate temperatures. Unfortunately no reasonable mechanism can be proposed.



In order to demonstrate the plausibility of this route to the vinylamino-s-triazine (VII), the intermediate, 2,4-bis-(N- $\beta$ -hydroxyethylanilino)-6-methoxy-s-triazine (VIII), was prepared and acet-

The very low solubility of II, IV and VII in all solvents and their high melting points greatly limited the potential usefulness of materials of this type. It was also found that the vinyl group in

IV had no tendency to polymerize under conditions used with N-vinylamides. No extensive studies were made in this unpromising direction.

## Experimental<sup>4</sup>

2-N-Vinylanilino-4-hydroxy-6-methoxy-s-triazine (II).—A nixture of 27.6 g. (0.1 mole) of 2-(N- $\beta$ -hydroxyethylanilino)-4,6-dimethoxy-s-triazine<sup>3</sup> and 30.6 g. (0.3 mole) of acetic anhydride was heated for three hours at reflux. Water was then added, and the mixture was neutralized with sodium carbonate. Extraction with ether brought about crystallization of 2.0 g., m.p. 234–237°. The ether solution of crude 2-(N- $\beta$ -acetoxyethylanilino)-4,6-dimethoxys-triazine (I) was dried over anhydrous sodium sulfate, after which it was concentrated at low temperature. The residue was heated in a distilling apparatus at 200–240° for one hour while evolved vapors were condensed in a Dry Ice trap. Crystals formed in the residue, beginning when the temperature reached 220°, and the residue was completely solid after cooling to room temperature. Extraction with hot acetone left 13 g. of a crystalline material which melted at 252–255°. This compound was not soluble in aqueous alkali nor in a 1:1 mixture of methanol and 50% aqueous potassium hydroxide, and it did not reduce bromine in carbon tetrachloride. The solid obtained directly from the acetylation reaction was a less pure form of this compound.

Anal. Calcd. for  $C_{12}H_{12}N_4O_2$ : C, 59.01; H, 4.95; N, 22.94. Found: C, 59.38; H, 5.44; N, 22.94.

Infrared absorption near 3090 cm.<sup>-1</sup>, 1620 cm.<sup>-1</sup> and 905–1000 cm.<sup>-1</sup> indicated that the vinyl group was present in the molecule as a terminal radical.

The liquid distillate from the pyrolysis (7.2 g.) contained no acetic acid. It was redistilled through a small spiral column and found to contain 30-40% of diethyl ether. Distillation of the remainder was unsatisfactory, but nearly all boiled below  $55^{\circ}$ . Methyl acetate (b.p.  $57^{\circ}$ ) might have been present, but this was not proven.

2.N-Vinylanilino.4-hydroxy-6-ethoxy-s-triazine (IV).—2- $(N-\beta-hydroxyethylanilino)-4,6-diethoxy-s-triazine was prepared by reaction of cyanuric chloride with phenylethanolamine and ethanol in ethanol solution.<sup>3</sup> The crude product was an oil. To this material (0.5 mole) was added 153 g. (1.5 moles) of acetic anhydride, and the mixture was stirred on a steam-bath for 3.5 hours. Water was then added, the mixture was neutralized with sodium hydroxide, and the crude 2-(N-<math>\beta$ -acetoxyethylanilino)-4,6-diethoxy-s-triazine (III) was extracted with ether. About 4 g. of water-insoluble, ether-insoluble solid, m.p. 270-300°, separated at this point.

The ether extract was dried and evaporated to a sirup weighing 133 g. (theory 173 g. of III). This material was heated at  $245-250^{\circ}$  for 2.5 hours in a distilling apparatus at 100 mm. The residue from this pyrolysis formed a glass at room temperature, which crystallized when extracted with hot acetone. The recovered solid weighed 60 g. (48%), m.p. 215-220°. Recrystallization from methyl cellosolve or dioxane raised the m.p. to  $225-228^{\circ}$ .

Anal. Caled. for  $C_{13}H_{14}N_4O_2$ : C, 60.45; H, 5.46; N, 21.69. Found: C, 60.33; H, 5.52; N, 21.70.

This compound exhibited the characteristic infrared absorption of the terminal vinyl group near 3090 cm.<sup>-1</sup>, 1620 cm.<sup>-1</sup> and 905-1000 cm.<sup>-1</sup>. The vapors evolved during the pyrolysis were trapped and redistilled. Ethyl acetate  $(n^{22}D \ 1.3704)$  was obtained in 20-30% yield based on the original cyanuric chloride.

Compound IV (5 g.) was recovered unchanged after being heated with 1% of benzoyl peroxide in 75 ml. of methyl

(4) Melting points are uncorrected. Microanalyses were carried out in these laboratories under the direction of Dr. J. A. Kuck. Infrared absorption measurements were made by J. L. Johnson. cellosolve at  $100-110^{\circ}$  for 8.5 hours. Gelation of a fumaric polyester resin at  $100^{\circ}$  in the presence of benzoyl peroxide was considerably retarded by the addition of IV, indicating poor copolymerizability for this material.

2,4,6-Ťris-(N- $\beta$ -acetoxyethylanilino)-s-triazine (V).—A mixture of 9.4 g. (0.0195 mole) of 2,4,6-tris-(N- $\beta$ -hydroxyethylanilino)-s-triazine (VI),<sup>2</sup> 11.9 g. (0.117 mole) of acetic anhydride and 1 drop of sulfuric acid was heated at 115–125° for four hours. Addition of water to the clear solution caused separation of 11.0 g. (93%) of the triacetate (V), m.p. 110–112°. Recrystallization from water gave m.p. 110.5–112.0°.

Anal. Calcd. for  $C_{33}H_{36}N_6O_6$ : C, 64.69: H, 5.92; N, 13.72. Found: C, 65.07; H, 5.85; N, 14.04.

Attempted Pyrolysis.—A 2.0-g. sample of this compound was heated in an open test-tube at 200° for one hour. Some fumes came from the tube, but these were not acidic. Decomposition to a charred mass occurred during two hours at 350°, but no evidence of acetic acid evolution was seen.

Attempted Reaction with Trimethyl Cyanurate.—A mixture of 6.07 g. (0.01 mole) of V and 1.71 g. (0.01 mole) of trimethyl cyanurate<sup>3</sup> was heated for one hour at 130–140° in a suitable apparatus for trapping any evolved methyl acetate. No reaction occurred.

Attempted Reaction with 2-Amino-4,6-diethoxy-s-triazine. --A mixture of 0.01 mole of V and 0.03 mole of 2-amino-4,6-diethoxy-s-triazine<sup>3</sup> was heated at 135-145° for 6.5 hours. No vapors were evolved. Similarly no change occurred during eight hours at 175-185° at 200 mm. Reaction of Cyanuric Chloride with Phenylethanolamine

Reaction of Cyanuric Chloride with Phenylethanolamine in Acetone–Methanol.—To a mixture of 0.5 mole of cyanuric chloride and 400 ml. of acetone containing 20-40% methanol was added 1.5 moles of phenylethanolamine at  $25-50^{\circ}$  during one hour. Sodium carbonate (0.75 mole) and 75 ml. of water were added, and the mixture was heated for 1.5 hours at 60°. Most of the solvent was then distilled and replaced by 400 ml. of dioxane and 100 ml. of water, and heating was continued for 15 hours at  $85-90^{\circ}$ . Approximately 80% of the carbonate was consumed, nearly all within the first three hours. The dioxane solution was separated from the lower aqueous solution and was evaporated to a sirup weighing 230 g.

Acetylation of 100 g. of this crude product in the usual way gave only 24 g. of ether-soluble material. The major product (58 g.) was a solid which was insoluble in water, ether, alcohol or 10% sodium hydroxide. Recrystallization from methyl cellosolve and from nitrobenzene gave a chlorine-free compound, m.p. 228.5–229.5°, which analysis showed to be 2-N-vinylanilino-4-(N- $\beta$ -hydroxyethylanilino)-6-hydroxy-s-triazine (VII).

Anal. Caled. for  $C_{19}H_{19}N_{5}O_{2}:$  C, 65.31; H, 5.48; N, 20.05. Found: C, 65.37; H, 5.50; N, 20.49.

When the reaction of cyanuric chloride with phenylethanolamine was carried out in dioxane solution only one chlorine atom was replaced. Inasmuch as dioxane and acetone have always been equivalent solvents for reactions of this type, the high degree of reaction in acetone-methanol must have been caused by the formation of an intermediate methoxy-s-triazine, probably 2,4-dichloro-6-methoxy-s-triazine, which is reactive toward phenylethanolamine.<sup>8</sup>

2-N-Vinylanilino-4-(N- $\beta$ -hydroxyethylanilino)-6-hydroxys-triazine (VII).—Compound VIII<sup>3</sup> (33.0 g., 0.867 mole) was heated at reflux for six hours with 35.8 g. (0.35 mole) of acetic anhydride and 0.15 ml. of sulfuric acid. At the end of this time there was considerable solid material present in the reaction mixture. Approximately 500 ml. of water and 100 ml. of ether were added, precipitating additional solid material. The solid product, amounting to 16 g. (approx. 53%), m.p. 195–215°, was a mixture of VII and its acetate. The crude material was saponified at room temperature with dilute sodium hydroxide and was then recrystallized from methyl cellosolve to give m.p. 227–229°.

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