

pH 2, and the filtered solution was concentrated. A total of 8.8 g. of crystalline material was obtained in three successive crops as the concentration was carried to a very small volume of residue. This material was resolved by fractional crystallization from water into (a) 2.7 g., m.p. 290–292°, obtained in leaflets as a hydrate unstable at 100°, and (b) a very water-soluble compound, m.p. > 360°. The substance melting at 290–292° was soluble in 7 parts of boiling water, was more soluble in dilute sodium hydroxide, and gave a red-violet, crystalline copper salt with ammoniacal cupric sulfate. These properties all agreed with identification of the compound as monomethyl isocyanurate (m.p. 296–297° cor.).¹⁰ (The phenolphthalein end-point was not sharp.)

Anal. Calcd. for C₄H₅N₃O₃: neut. equiv., 143. Found: neut. equiv., 144–151.

The compound melting above 360° gave a strongly acid water solution which contained sulfate ions. When the solution was made alkaline with sodium hydroxide and distilled, aniline was carried over into the distillate where it was identified by conversion to *N*-phenylbenzenesulfonamide, m.p. 109–110°.

Rearrangement of X to VI at 160°.—Only a trace of decomposition was brought about by heating 4 g. of X at 160 ± 3° for 18 hours.

Compound X (5.0 g.) was heated at 160° for 18 hours in 5.0 ml. of methyl carbitol. At the end of this time the insoluble material amounted to 3.9 g., m.p. 310–330°. Recrystallization from methyl cellosolve gave the pure compound, melting at approximately 325°. This substance was soluble in dilute sodium hydroxide, which indicated that it was a hydroxy-*s*-triazine. Analysis confirmed the identification of this compound as 1,6-dihydro-1-methyl-2-anilino-4-hydroxy-6-oxo-*s*-triazine (XII).

Anal. Calcd. for C₁₀H₁₀N₄O₂: C, 55.04; H, 4.62; N, 25.68. Found: C, 54.86; H, 4.52; N, 25.25.

A 4.0-g. sample of X was heated for 18 hours in 5.0 ml. of refluxing Varsol No. 1 (158°). By extraction of the solid material with ethanol and fractional crystallization of the extract from ethanol and from dioxane, 0.25 g. of compound VI, m.p. 225–227°, was isolated. There was also obtained approximately 2.5 g. of XII, melting at approximately 325°.

(10) E. Fischer and F. Frank, *Ber.*, **30**, 2615 (1897).

Rearrangement of 2-Anilino-4,6-dimethoxy-*s*-triazine at 105–110°.—An 80-g. lot of V, m.p. 128.5–130.5°, was recrystallized from 300 ml. of ethanol with the expectation of an elevation of the m.p. to 132–133°. The recovered crystals were dried in an open dish at 105° for 40 hours. At the end of this time the solid weighed 66 g., m.p. 100–120°, and a slight yellow color had developed. The material was extracted with hot ethanol, which left a residue of 34 g. of well-formed, white crystals which were identical with X. The yield of this product was 51% based on the recovered solid. Fractional crystallization of the ethanol extract yielded 12.5 g., m.p. approximately 205° (19%). This was impure VI.

In a better controlled experiment, 26.0 g. of V (m.p. 132–133°) was stored in a sealed container for six days at 110°. The solid fused partially after two days and subsequently resolidified. The resulting mass was worked up as described above, yielding 16.4 g. (63%) of compound X.

Rearrangement of 2-Anilino-4,6-dimethoxy-*s*-triazine under Other Conditions.—(1) When V was heated in the presence of 4% of *p*-toluenesulfonic acid for 1.5 hours at 150–210°, two isolable products were obtained. One of these was VI (60%), m.p. 217.5–219.5°. The other, XI (20%), m.p. 300–304°, was a relatively insoluble material which could be recrystallized from cellosolve. It was soluble in dilute alkali and therefore was a hydroxy-*s*-triazine.

Compound XI proved difficult to analyze, but the results supported its identification as 2-anilino-4-hydroxy-6-methoxy-*s*-triazine or an isomer.

Anal. Calcd. for C₁₀H₁₀N₄O₂: C, 55.04; H, 4.62; N, 25.68. Found: C, 54.61; H, 4.61; N, 26.16.

(2) A mixture of 46.4 g. of V, 1.0 g. of *p*-toluenesulfonic acid and 150 ml. of butanol was heated at reflux for three hours. The butanol was distilled, and the residue was extracted with methanol, leaving undissolved 11.5 g. (28%), m.p. 301–303°, which was identical with XI. From the methanol solution was recovered about 17 g. (37%) of X.

(3) Twenty-five grams of V was heated with 4% of sodium methoxide at 190–200° for 18 hours. Considerable solid material separated from the melt. The mixture was poured into 1000 ml. of water, and the crystalline material was filtered (15.0 g., m.p. 90–180°). Fractional crystallization of the crude product from alcohol yielded 0.5 g. of VI (2%) and 5 g. of X (20%).

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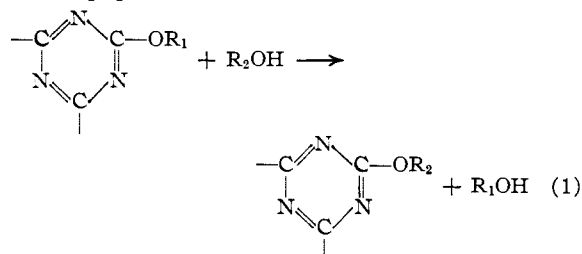
[CONTRIBUTION FROM THE STAMFORD RESEARCH LABORATORIES OF THE AMERICAN CYANAMID COMPANY]

Cyanuric Chloride Derivatives. VII. Transesterification Reactions of Alkoxy-*s*-triazines. Polyammide Ethers

BY JAMES R. DUDLEY, JACK T. THURSTON, FREDERIC C. SCHAEFER, CLARENCE J. HULL, DAGFRID HOLM-HANSEN AND PIERREPONT ADAMS

Transesterification has been investigated as a preparative method for monomeric and polymeric alkoxy- and alkoxyamino-*s*-triazines. Both classes undergo transesterification reactions with primary or secondary alcohols in the presence of catalytic amounts of sodium alkoxides. This affords a method of preparation for those derivatives which cannot be prepared directly from the corresponding chloro-*s*-triazines. Linear polyammide esters have been prepared by transesterification of 2-amino-4,6-dialkoxy-*s*-triazines with glycols. The effects of structural modifications and conditions of reaction are discussed.

It is often convenient to consider alkoxy-*s*-triazines as esters.¹ In extension of this analogy, the following general reaction which is the subject of this paper is classed as a transesterification



(1) J. T. Thurston, *et al.*, *THIS JOURNAL*, **73**, 2992 (1951).

We have studied this reaction to some extent as a method for the preparation of monomeric materials, but our chief interest has been the preparation of resinous compositions which might have usefulness in various industrial fields. It seems appropriate at this time to report the conditions required for the reaction, the catalysts used, structural influences, and the types of products obtainable.

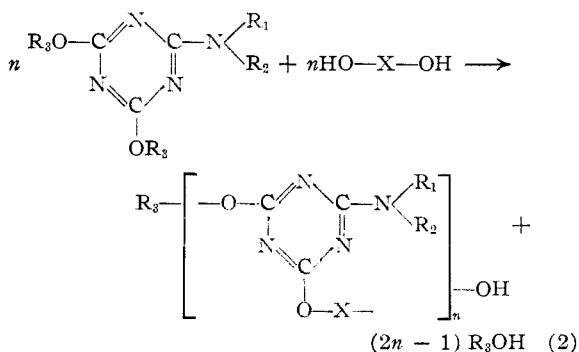
Hofmann prepared triethyl cyanurate from trimethyl cyanurate by heating the latter with an equivalent amount of sodium ethoxide in absolute ethanol.² We have demonstrated that only catalytic amounts of an alkoxide are required for such reactions, and that the method is also useful with

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

2-amino-4,6-dialkoxy-*s*-triazines. Transesterification of 2-alkoxy-4,6-diamino-*s*-triazines with alcohols has not been thoroughly investigated, although it has been shown that this class of compounds also reacts. Acid catalysts, *e.g.*, *p*-toluenesulfonic acid, which are useful for the transesterification of carboxylic esters, were not effective with 2-amino-4,6-dialkoxy-*s*-triazines. Possibly this was due to salt formation with these weakly basic compounds. However, the acid catalysts did seem to promote alkylation reactions leading to the formation of hydroxy-*s*-triazines. This subject has been covered in an earlier paper.³ The acid catalysts were not tried with cyanurates.

In the preparation of monomeric compounds an excess of the transesterifying alcohol was helpful, but the reaction proceeded satisfactorily when equivalent amounts of reactants were used, either with or without an inert solvent. Generally, a low boiling alcohol was displaced by one less volatile, and high conversions were attained by distilling the product alcohol from the reaction mixture as it was formed. Descriptions of the preparations of tris-2-hydroxyethyl cyanurate (I), 2-amino-4,6-dibutoxy-*s*-triazine (II) and 2-anilino-4,6-dibutoxy-*s*-triazine (III) are given in the Experimental section. Inasmuch as compounds of these classes can usually be prepared directly and in good yield from cyanuric chloride,⁴ the transesterification method is recommended only when the alcohol contains more than one reactive group, *e.g.*, ethylene glycol, or when it is undesirable to use excess alcohol, *e.g.*, octadecyl alcohol.

A large number of thermoplastic polyammellide ethers (or esters) were prepared by transesterification of 2-amino-4,6-dialkoxy-*s*-triazines with glycols



It was not possible to achieve sufficiently high degrees of condensation to produce tough or fiber-forming resins. Generally, the degree of reaction was in the range of 85–90%, corresponding to an average degree of polymerization (n) of 3–5, when unsubstituted 2-amino-4,6-dialkoxy-*s*-triazines were used. Somewhat better conversions were possible with *N*-alkyl substituted and *N,N*-disubstituted 2-amino-4,6-dialkoxy-*s*-triazines, but these gave softer resins in general. Table I lists suitable resin preparations to illustrate the variations in the reaction and in the products which arise from structural differences in the reactants. The influences attributable to the triazine would, of

course, also operate in the preparation of monomeric compounds.

It was found that there was a lower limit of concentration below which the sodium alkoxide catalyst was not effective, which varied with the triazine used. The amount of catalyst required to give a satisfactory reaction rate increased with increasing acidity of the amino group in the triazine. The order of increasing catalyst requirement, and the minimum and optimum catalyst concentrations (mole per cent. of sodium alkoxide based on the triazine) were: 2-diethylamino-4,6-dimethoxy-*s*-triazine, 2-*N*-methylanilino-4,6-dimethoxy-*s*-triazine, 2-butylamino-4,6-dimethoxy-*s*-triazine (1.5, 4 mole %) < 2-amino-4,6-dimethoxy-*s*-triazine, 2-amino-4,6-dibutoxy-*s*-triazine (4, 5–8 mole %) < 2-anilino-4,6-dimethoxy-*s*-triazine (4, 8–10 mole %).

The range of reaction temperatures was generally limited to approximately 80–155°. The upper limit was set so as to avoid serious side reactions. If the reactions were run at a high temperature (170–180°) from the outset, the rate and the maximum degree of reaction were much lower than when the reactions were allowed to proceed approximately halfway at 80–120° before the temperature was raised. This effect was probably caused by rearrangement of the triazine to an unreactive form.³ The *N,N*-disubstituted 2-amino-4,6-dialkoxy-*s*-triazines, which are at least relatively stable toward rearrangement, could be used at higher initial temperatures, but these compounds gave very rapid reactions in any case. Temperatures above 155° for the last stage of the reaction were not employed except for short periods in order to avoid cross-linking of polymer chains through the amino groups and/or cleavage of amino groups by the glycol.

In all cases the reaction proceeded in two distinct stages, the first alkoxy group being displaced much more rapidly and at a lower temperature than the second. The observed effect was qualitatively much greater than could be expected from the decrease in concentration of the unreacted groups. The stepwise replacement of the two groups in 2-amino-4,6-dialkoxy-*s*-triazines by different alcohols or glycols which this effect suggested has not been investigated.

Although the polyethylene glycols in general reacted readily, ethylene glycol reacted principally as a monohydric alcohol, probably due to steric effects. Decamethylene and hexamethylene glycols were somewhat sluggish, but 2-ethyl-1,3-hexanediol containing a secondary hydroxyl group was surprisingly reactive. This was unexpected because isopropyl alcohol and *s*-butanol reacted less readily than *n*-butanol with 2-amino-4,6-dimethoxy-*s*-triazine, and the complete failure of *t*-butanol to react with this triazine had further indicated a general decrease in the reactivity of alcohols in the order primary > secondary > tertiary.

Progressive substitution in the amino group of the 2-amino-4,6-dialkoxy-*s*-triazine led to decreased hardness and increased organic solubility in the polymers. The polymethylene glycols gave greater hardness than the polyethylene glycols, and

(3) F. C. Schaefer, *et al.*, *THIS JOURNAL*, **73**, 2996 (1951).

(4) J. R. Dudley, *et al.*, *ibid.*, **73**, 2988 (1951).

TABLE I
 PREPARATION OF POLYAMMELIDE ESTERS

2,4-Dialkoxy- 6-amino- <i>s</i> - triazine	Glycol	Mole % sodium ^a	Reaction conditions			Degree of reaction, ^b %	Description of resinous product
			Time, hr.	Temp., °C.	Pressure, mm.		
ABDT ^c	Decamethylene	5	4	120	2	65	Hard, brittle, softening point <i>ca.</i> 80°
			+2.5	170	2	88	
ADBT	Decamethylene	10	2	165	15	55	Hard, brittle ^d
			+6	180	2	82.5	
ADBT	Triethylene	4	1.75	117	100→2	60	Moderately soft, solid ^d
			+2.5	155	2	87	
ADBT	Triethylene	10	2	180	760→15	66	Tacky solid ^d
			+6.5	180	15	72.5	
ADBT	Triethylene	3	1	120	10	0	
ADMT ^e	Decamethylene	4	0.75	120	100	55	Hard, brittle ^d
			+2	155	2	75	
ADMT	Diethylene	8	2	65-90	28	..	Tacky, brittle ^f
			+4	135-150	11	83	
ADMT	Triethylene	8	2	60-100	30	..	Tacky ^f
			+3	140-155	1	89	
ADMT	"Polyethylene Glycol 200" ^g	8	2	79-97	54	..	Moderately soft solid ^h
			+2	148	1	89	
ADMT	"Polyethylene Glycol 400" ^g	8	2	70-95	45	..	Soft ^h
			+2	150	45	90	
ADMT	"Carbowax 1500" ⁱ	8	2	97	22	..	Wax ^h
			+2	150	2	97	
ADET ^k	Diethylene	8	1.5	75-125	Hard, brittle ^l
			+3	150-160	1	85	
ADET	Hexamethylene	4	2	100	18	..	Hard, brittle ^l
			+3	150	10	86	
ADET	Decamethylene	8	1	105-125	75	..	Hard, brittle ^l
			2	150	2	84	
DEADMT ^m	Ethylene	5	2	120	200→1	73	Wax
			+1	150	1	No change	
DEADMT	Diethylene	5	1.25	115	100→2	92	Tacky gum ^f
			+0.25	160	2	94-98	
DEADMT	Triethylene	4	0.83	117	100→2	88	Viscous sirup
DEAMDT	Triethylene	1.5	1.5	120	2	Slight	
DEADMT	Decamethylene	4	1.6	120	300	72	Viscous sirup ^f
			+6.5	150-185	2	96	
DEADMT	Decamethylene	10	2.5	120	25	87	Viscous sirup ^f
			+4	150-180	1	97	
DEADMT	2-Ethyl-1,3-hexanediol	4	0.5	120	400→2	90-98	Hard brittle, softening point <i>ca.</i> 65°
DEADMT	2-Ethyl-1,3-hexanediol	0	4	200	760	Partial decompu. only	
AnDMT ⁿ	Triethylene	8	2	120	20	66	Hard, brittle, softening point <i>ca.</i> 50°
			+1.5	150	15	70	
AnDMT	Decamethylene	10	3	120	200→2	66	Moderately hard, brittle, softening point, <i>ca.</i> 50° ^f
			+2	170	2	No change	
AnDMT ^o	2-Ethyl-1,3-hexanediol	4	1	120-140	15	42	
			+0.5	190	160	48	
AnDMT	2-Ethyl-1,3-hexanediol	8	1	100-110	20	67	Very hard, brittle, softening point, <i>ca.</i> 80° ^f
			+1.5	160-165	50	78	
BADMT ^o	Triethylene	4	0.5	115	160	63	Soft, tacky
			+0.5	115-150	160	83	
			+0.5	180	15	91	
DoADMT ^{p,4}	"Polyethylene glycol 300"	8	11	70-150	70-12	67	Soft ^h
MAnDMT ^q	Triethylene	4	1.5	120	400→2	89	Soft, tacky

^a Based on triazine or glycol used. ^b Degree of reaction was calculated on a basis of 100% for complete displacement of the simple alcohol. However, the true maxima were lower, because the sodium retained approximately equivalent amounts of the simple alcohol and the glycol as alkoxides. ^c 2-Amino-4,6-dibutoxy-*s*-triazine. ^d Soluble in hot methyl cellosolve, insoluble in butanol. ^e 2-Amino-4,6-dimethoxy-*s*-triazine. ^f Soluble in hot butanol. ^g Principally tetraethylene glycol, average molecular weight 220. ^h Soluble in water. ⁱ Principally nonaethylene glycol, average molecular weight 423. ^j A mixture of high molecular weight polyethylene glycols, average molecular weight, 1440. ^k 2-Amino-4,6-diethoxy-*s*-triazine. ^l Soluble in formalin. ^m 2-Diethylamino-4,6-dimethoxy-*s*-triazine. ⁿ 2-Anilino-4,6-dimethoxy-*s*-triazine. ^o 2-Butylamino-4,6-dimethoxy-*s*-triazine. ^p 2-Dodecylamino-4,6-dimethoxy-*s*-triazine. ^q 2-N-Methylanilino-4,6-dimethoxy-*s*-triazine.

this compound to give trivinyl cyanurate. An insoluble resin was produced under relatively mild conditions, and ethylene glycol was identified as a by-product, demonstrating that the polymerization was at least principally due to transesterification rather than vinyl group polymerization. The polymerization was catalyzed by alkalis and was observed at temperatures as low as 100°.

Experimental⁵

Tris-2-hydroxyethyl Cyanurate (I).—A mixture of 102.6 g. (0.60 mole) of trimethyl cyanurate,⁴ 450 g. (7.3 moles) of ethylene glycol, and 0.02 mole of sodium methoxide (dissolved in 11.5 ml. of methanol) was heated at 100–110° for two hours in a distilling apparatus at 65–85 mm. During this time, 62 g. of methanol (92%) distilled. The catalyst was neutralized with 10% hydrochloric acid, and the excess glycol was distilled at 60° at 1–2 mm. The viscous residue was taken up in a small quantity of dioxane, and the product was crystallized from this solution by cooling. After further recrystallization from dioxane, the compound weighed 109 g. (69%), m.p. 130–132°.

Anal. Calcd. for C₉H₁₅N₃O₆: C, 41.38; H, 5.79; N, 16.09. Found: C, 41.40; H, 5.86; N, 16.12.

Attempts were made to pyrolyze I alone and in the presence of sodium carbonate at 150° to give trivinyl cyanurate. At this temperature a vigorous reaction took place with immediate polymerization to an infusible and insoluble resin. At 140° polymerization was slower and a liquid by-product was obtained. This was identified as ethylene glycol by its reaction with triphenylchloromethane to give ethylene bis-triphenylmethyl ether, m.p. 186–187°. Polymerization of the cyanurate was also observed at 100°, an insoluble product being obtained when the compound was dried at this temperature.

2-Amino-4,6-dibutoxy-s-triazine (II).⁴—A mixture of 234 g. (1.5 moles) of 2-amino-4,6-dimethoxy-s-triazine,⁴ 800 ml. (8.5 moles) of butanol and 1.4 g. (0.06 mole) of sodium was heated at a high reflux ratio under a fractionating column. During four hours, 103 ml. (86%) of methanol, b.p. 64–68°, was distilled, and at the end of this time the reaction had virtually stopped. Five ml. of acetic acid was added to the solution, and the excess butanol was distilled until the partly crystalline residue weighed 460 g. (theory 360 g.). Addition of 1000 ml. of water completed the crystallization of the crude product, which was then filtered and recrystallized from 500 ml. of ethanol. The recrystallized compound weighed 243 g. (68%), m.p. 99.5–100.50. The remainder of the product was recovered by diluting the mother liquor with water, m.p. ca. 75°. This material could be recycled.

Compound II was also obtained in small yield when equivalent amounts of the reactants were heated with 0.05 equivalent of sodium methoxide in boiling benzene or toluene and the liberated methanol was distilled (as an azeotrope). *p*-Toluenesulfonic acid and sulfuric acid brought about no methanol evolution under similar conditions.

2-Anilino-4,6-dibutoxy-s-triazine (III) was prepared from 2,4-dimethoxy-6-anilino-s-triazine⁴ in the manner described for II. A theoretical yield of methanol was recovered. The yield of III was 39 g. (95%), m.p. 56.5–58.0°. Recrystallization from a concentrated benzene solution gave m.p. 58–60°.

When *p*-toluenesulfonic acid was tried as a catalyst for this reaction in boiling butanol transesterification did not proceed to an appreciable extent. No more than a trace of methanol was liberated, and alkylation and rearrangement products could be isolated from the reaction mixture.³

Transesterification of 2-Amino-4,6-dimethoxy-s-triazine with Isopropyl Alcohol.—A mixture of 78 g. (0.5 mole) of the triazine,⁴ 0.04 mole of sodium isopropoxide, and 250 ml. of isopropyl alcohol was heated for seven hours at the boiling point. During this time only a 20% yield of methanol was distilled.

Attempted Transesterification of 2-Amino-4,6-dimethoxy-s-triazine with *t*-Butanol.—A mixture of 0.5 mole of the triazine, 0.02 mole of sodium *t*-butoxide and 250 ml. of *t*-butanol was heated at the boiling point for six hours. No methanol was liberated.

(5) Melting points are uncorrected. Microanalyses were carried out in these laboratories under the direction of Dr. J. A. Kuck.

Transesterification of 2-Butylamino-4,6-dimethoxy-s-triazine with *s*-Butanol.—A 25% yield of methanol was obtained when 0.25 mole of the triazine,⁴ 0.02 mole of sodium *s*-butoxide and 150 ml. of *s*-butanol was heated at the boiling point for 5 hours.

Transesterification of 2,4-Diamino-6-methoxy-s-triazine with *n*-Butanol.—A mixture of 1.65 mole of the triazine,⁴ 0.04 mole of sodium butoxide and 200 ml. of butanol was refluxed for ten hours. During this time 43% of the expected methanol was obtained.

Preparation of Resins by Transesterification of 2-Amino-4,6-dialkoxy-s-triazines with Glycols.—The general procedure by which the resins described in Table I were prepared is as follows:

The glycol was introduced into a round-bottom flask of convenient size (250 ml. for a 0.1-mole run), and the required amount of metallic sodium was dissolved in the glycol, by heating if necessary. (In some cases, the sodium was added as sodium methoxide in methanol.) An equimolar quantity of the triazine was then added, and the flask was fitted with a stirrer and distilling head. A condenser, a receiver cooled in Dry Ice, and a pumping system were arranged in the usual manner. The pressure used depended upon the rate of methanol evolution, the boiling point of the glycol, and the foaming tendency of the reaction mixture. Usually pressures of 200–400 mm. were used at the start of the reaction, and the pressure was decreased gradually to 1–10 mm. The degree of reaction at any time was calculated from the weight of material lost from the reaction flask (or found in the receiver). The identity of the volatile material was checked by the refractive index of the distillate. In certain cases where glycol was carried out of the reaction flask by the volatile alcohol, the composition of the distillate was calculated from its refractive index, and the degree of reaction was calculated from this. The reactions were continued until it was apparent that alcohol evolution had virtually stopped.

Simultaneous Transesterification of Two 2-Amino-4,6-dialkoxy-s-triazines with Glycols.—The resin preparations summarized in Table II were carried out in the usual manner, at optimum temperatures between 100 and 150°, until it was evident that the reactions had stopped. The composition of the mixed alcoholic distillate was calculated from its refractive index.

Stepwise Transesterification of 2-*N*-Methylanilino-4,6-dimethoxy-s-triazine and 2-Amino-4,6-diethoxy-s-triazine with Triethylene Glycol.—A mixture of 0.15 mole of 2-*N*-methylanilino-4,6-dimethoxy-s-triazine⁴ and 0.20 mole of triethylene glycol containing 4 mole % of sodium based on the glycol was heated at 115–130° for one hour. During this time the theoretical amount of methanol was evolved. Then 0.05 mole of 2-amino-4,6-diethoxy-s-triazine⁴ was added, and heating was resumed. No reaction occurred during two hours at 120–150°.

The experiment above was repeated. However, the first stage was carried out at 95–115° and was run to 95% completion. Following the addition of the 2-amino-4,6-diethoxy-s-triazine, a heating period of 30 minutes at 120° brought about no reaction. A total of 50% of the theoretical ethanol was obtained by heating the reaction mixture at 155–175° for 35 hours.

In a third experiment, the first stage was carried to 89% completion and an additional 4 mole % of sodium was added with the second triazine. Further heating for one hour at 120°, one hour at 130° and 15 minutes at 150° gave 100 and 89%, respectively, of the theoretical yields of methanol and ethanol. Thus, the over-all reaction was 97% complete, and a degree of polymerization of about 15–20 was obtained. The product was clear, soft and tacky.

Transesterification of Triallyl Cyanurate with Glycols.—When triallyl cyanurate and di-, tri-, tetra- or hexaethylene glycol in equimolar quantities were heated with 4–10 mole % of sodium methoxide based on the triazine for one to three hours at 100–140°, 85–93% of the theoretical amount of allyl alcohol was evolved. In all cases the products were rubbery gels which were insoluble in water, heptane, butanol or xylene. When two moles of the cyanurate to one of the glycol was used, viscous oils were obtained. These were also insoluble. Ethylene glycol with one or two moles of triallyl cyanurate gave, respectively, 50 and 48% yields of allyl alcohol, again demonstrating the behavior of this glycol as a monohydric alcohol under any except forcing conditions.

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

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

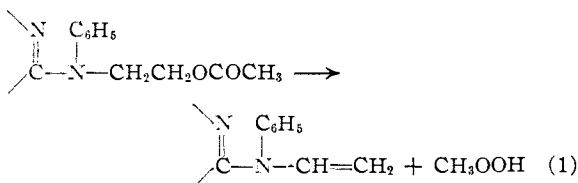
In the attempted preparation of vinylamino-*s*-triazines for use as monomers in the preparation of resinous materials, it has been found that the compounds which can be made are subject to constitutional limitations. An unusual intramolecular rearrangement has been discovered, which leads to the formation 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 Stevenson¹ 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- β -acetoxyethylamides, contains

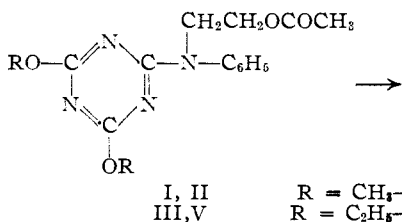
the active structural unit, $\text{H}_2\text{C}=\text{CH}-\text{N}-\overset{\text{O}}{\parallel}{\text{C}}$. Amino-*s*-triazines are known to have amide properties, and it was possible that N-vinylamino-*s*-triazines might also be useful monomers. They

would contain the group, $\text{H}_2\text{C}=\text{CH}-\text{N}-\overset{\text{N}}{\parallel}{\text{C}}$, which may be considered an ammono analog of that in the N-vinylamides.²

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

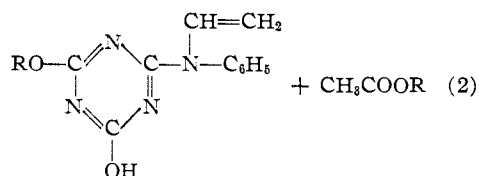


Instead, an alkyl acetate was evolved, and an hydroxy-N-vinylamino-*s*-triazine was produced, e.g.



(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-*s*-triazine. 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-4,6-dimethoxy-*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 atom. 2-(N- β -Acetoxyethyl-anilino)-4,6-dimethoxy-*s*-triazine (I) was prepared by acetylation of 2-(N- β -hydroxyethyl-anilino)-4,6-dimethoxy-*s*-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-N-vinylanilino-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).