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

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[13] J. T. Adams, C. K. Bradsher, D. J. Breslow, S. T. Amore and C. R. Hauser, This Journal, **68**, 1317 (1946).

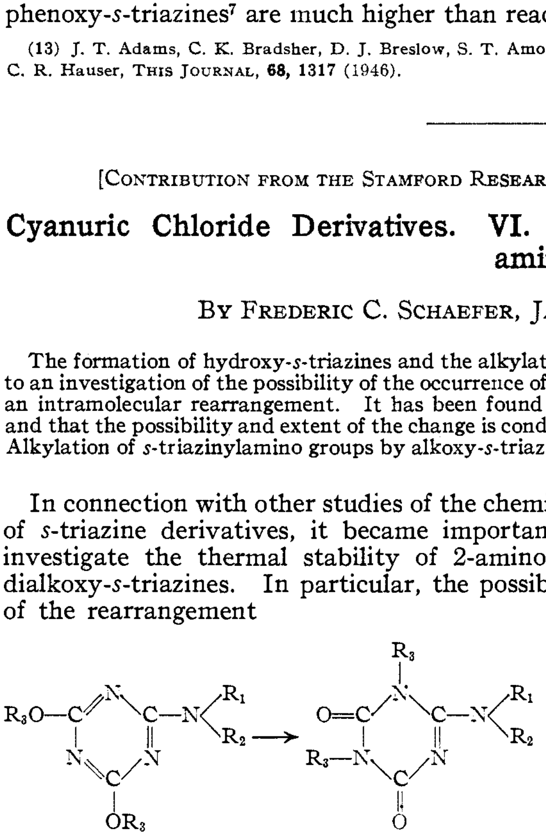
[Contribution from the Stamford Research Laboratories of the American Cyanamid Company]

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.

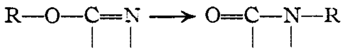
In connection with other studies of the chemistry of *s*-triazine derivatives, it became important to investigate the thermal stability of 2-amino-4,6-dialkoxy-*s*-triazines. In particular, the possibility of the rearrangement



(1)

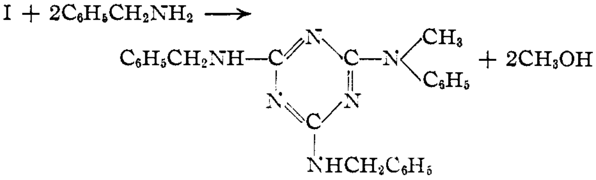
	R_1	R_2	R_3	
I	CH_3-	C_6H_5-	CH_3-	
II	H–	H–	C_4H_4-	
III	C_4H_4	H–	CH_3-	IV
V	C_6H_5	H–	CH_3-	VI

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



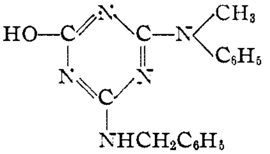
$$R{-}O{-}\underset{|}{C}{=}\underset{|}{N} \longrightarrow O{=}\underset{|}{C}{-}\underset{|}{N}{-}R \qquad (2)$$

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]



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).

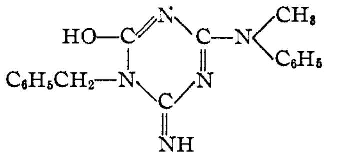
[2] A. W. Chapman, *J. Chem. Soc.*, 1992 (1925); 1743 (1927).

[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.



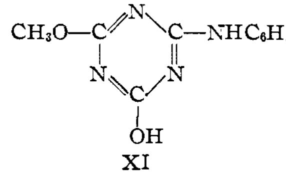
IX

It is not possible to establish which product had the structure VIII.

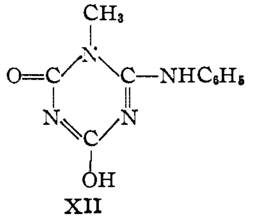
2-Amino-4,6-dibutoxy-*s*-triazine (II) appeared to undergo rearrangement at 170–200°, but no pure product could be isolated and identified. Hydroxy-*s*-triazines were also formed in considerable quantity if *p*-toluenesulfonic acid was used as a catalyst. On the other hand, 2-butylamino-4,6-dimethoxy-*s*-triazine (III) rearranged smoothly at 170–180° when heated alone or in the presence of *p*-toluenesulfonic acid to give 71–74% yields of the "normal" rearrangement product, 2-butylamino-1,4,5,6-tetrahydro-1,5-dimethyl-4,6-dioxo-*s*-triazine (IV) or its indistinguishable tautomers, the structure of which was proven by hydrolysis to dimethyl isocyanurate. The acid catalyst accelerated the rearrangement somewhat, but evidently it was not required. In this case no other reaction products were found. This dialkoxy-*s*-triazine (III) was not changed by long heating at 105°.

The rearrangement of 2-anilino-4,6-dimethoxy-*s*-triazine (V) gave a mixture of products, the composition of which varied greatly with the particular conditions of reaction. The "normal" rearrangement product, 1,4,5,6-tetrahydro-1,5-dimethyl-2-anilino-4,6-dioxo-*s*-triazine (VI) was obtained in 50% yield, contaminated by only a small amount of a second isomeric product, 1,6-dihydro-1-methyl-2-anilino-4-methoxy-6-oxo-*s*-triazine (X), when III was heated for ten hours at 160°. When *p*-toluenesulfonic acid was present, a 60% yield of VI was obtained, but a hydroxy-*s*-triazine (XI) was also formed in 20% yield, and the mixture was difficult to separate. Compounds X (37%) and XI (28%) were both obtained when V was heated in refluxing butanol in the presence of *p*-toluenesulfonic acid. Compound X was most easily obtained, and in good yield (63%), when V was heated at 110° for 48 hours. Although a small amount of VI was also obtained under these conditions, this could easily be removed. These results might be summarized by the conclusion that at moderate temperatures formation of X was favored, while at higher temperatures formation of VI was predominant. Compound X was identified as an intermediate in the formation of VI and could be converted into the latter at 160°.

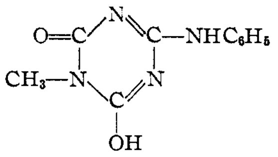
Compound XI was obtained in isolable amounts only when *p*-toluenesulfonic acid was present during the rearrangement process, but it may have been present in the crude rearrangement product in all cases. It was alkali-soluble, indicative of a hydroxy-*s*-triazine, and its analysis corresponded to the isomeric structures.



XI



XII



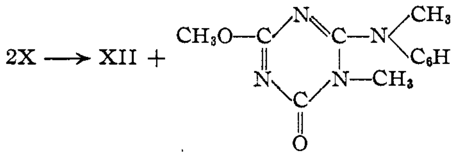
XIII

A fourth possible isomer was 2-N-methylanilino-4,6-dihydroxy-*s*-triazine, but this compound was obtained in another reaction[5] and was not identical with XI. It is suggested that XI was formed by an intermolecular alkylation reaction[7]

$$2\text{V} \longrightarrow \text{XI} + \text{I}$$

Compound I or its isomers, which would also be formed, have physical properties which would effectively prevent their discovery among the reaction products.

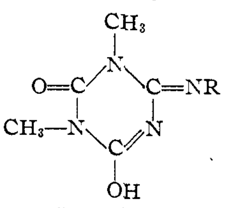
A hydroxy-*s*-triazine (XII) isomeric with XI, was obtained when X was heated at 160° in methyl carbitol or in a saturated hydrocarbon solvent. In the latter case it seems safe to assume that the liquid medium did not react, and this appears to be another example of alkylation of an amino-*s*-triazine by an alkoxy-*s*-triazine.



However, when methyl carbitol was the reaction medium the amount of XII recovered was equivalent to 83% of the X used. Methylation of the methyl carbitol must have taken place; and if this is the case, it is the first known example of alkylation of an alcohol by an alkoxy-*s*-triazine.

The structure assigned to XII therefore appears logical, but the structure assigned to XI is not established, since XIII is also a possibility.

The structures of IV and VI were established by hydrolysis of these compounds with 80% sulfuric acid, which produced dimethyl isocyanurate in both cases. These compounds were unexpectedly soluble in dilute alkali, and as their structures are usually written, the presence of the hydroxyl group is obscured. However the tautomeric structures XIV and XV probably make the principle contributions to the resonance state of the ions in alkaline solution.



XIV, R = C_4H_9- (tautomer of IV)
XV, R = C_6H_5- (tautomer of VI)

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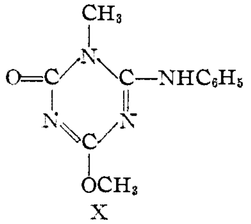
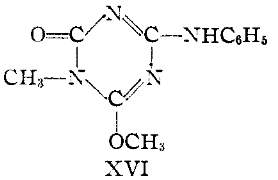
[7] An acid is not necessary for the alkylation reaction, although a catalytic influence is apparent from the present work. See ref. 4.

Compound X was identified as the intermediate rearrangement product by isolation of monomethyl isocyanurate and aniline (as N-phenylbenzenesulfonamide) from the products of its hydrolysis with 65% sulfuric acid. The intermediate might have structure X or XVI


X


XVI

However, if XVI were the correct structure, the compound would be soluble in alkali as are IV and VI. Since this was not the case, the structure must be X.

Experimental[8]

Attempted Rearrangement of 2-N-Methylanilino-4,6-dimethoxy-*s*-triazine.—This triazine[4] was essentially unaffected after five hours at 230–250°, or after 18 hours at 185–195° in the presence of sodium methoxide.

Reaction of 2-N-Methylanilino-4,6-dimethoxy-*s*-triazine with Benzylamine.—A mixture of 24.6 g. (0.1 mole) of I, 21.4 g. (0.2 mole) of benzylamine and 0.1 g. of metallic sodium was heated for six hours at 140–200°. Approximately 40% of the theoretical amount of methanol was evolved, and the reaction mixture partly crystallized. The excess benzylamine was distilled, and the residue was washed with dilute hydrochloric acid and with water. The crude product weighed 28.0 g. and melted at 300–320°. Extraction with hot ethanol left a 9.0-g. residue, m.p. 345–350°. This substance was soluble in boiling 1 *N* hydrochloric acid, and crystals were obtained on cooling the solution. The recovered hydrochloride was unstable at 105°, and drying at this temperature gave a hydrogen chloride-free product, m.p. 355–360° (A). This was not soluble in aqueous alkali. The ethanol extract was fractionally crystallized, and approximately 2.5 g. of a compound melting at 201–204° was isolated (B). This substance was not alkali-soluble but dissolved in by dilute hydrochloric acid. Analysis showed these two products to be isomeric.

Anal. Calcd. for $C_{17}H_{17}N_5O$: C, 66.43; H, 5.57; N, 22.79. Found for A: C, 65.68; H, 5.66; N, 23.26. Found for B: C, 66.26; H, 5.65; N, 22.25.

An attempt was made to hydrolyze A with 67% sulfuric acid to a derivative which would indicate its structure. A solid product separated from the reaction mixture, but this proved to be the sulfate of the base, m.p. 216–219° (from glacial acetic acid).

Anal. Calcd. for $C_{17}H_{19}N_5O_5S$: C, 50.36; H, 4.72; N, 17.28. Found: C, 50.43; H, 4.95; N, 16.81.

More vigorous hydrolytic conditions caused excessive decomposition, and no hydrolysis product could be isolated.

Attempted Rearrangement of 2-Amino-4,6-dibutoxy-*s*-triazine.—A mixture of 25.0 g. of the triazine[4] (m.p. 100.5–101.5°) and 1.0 g. of *p*-toluenesulfonic acid was heated slowly from 100 to 150°. An exothermic reaction was apparent, and this became vigorous at 150°. The temperature rose rapidly to 230°, and the mixture solidified. After ten minutes at 170–200°, the mixture was extracted with boiling ethanol, which left an insoluble residue of 8.0 g., m.p. *ca.* 300°, which was alkali-soluble. The ethanol solution yielded 4.0 g., m.p. 135–150°, which could not be resolved successfully.

In another experiment, 2-amino-4,6-dibutoxy-*s*-triazine was heated with 6% of sodium butoxide at 190–200° for 18 hours. No apparent change took place, and no new compound could be isolated from the melt. However, it would seem that some reaction had occurred, since the starting material could not be recovered.

Rearrangement of 2-Butylamino-4,6-dimethoxy-*s*-triazine.—Fifty grams of II[4] (m.p. 65.0–65.5°) was heated at 160–170° for 18 hours. The melt crystallized at once on cooling to room temperature. The solid was recrystallized from ethanol to give 35.5 g. (71%) of a compound melting at 168–170°; further recrystallization from 5 ml. of ethanol per gram, m.p. 172–173°. The product was soluble in dilute sodium hydroxide solution as well as in dilute acids (acetic, hydrochloric). Analysis showed this compound to be isomeric with II.

Anal. Calcd. for $C_9H_{16}N_4O_2$: C, 50.93; H, 7.61; N, 26.40. Found: C, 51.15; H, 7.45; N, 26.58.

The same product was obtained in 74% yield when II was heated for seven hours at 170° in the presence of 4% of *p*-toluenesulfonic acid. The rearrangement product was hydrolyzed with 80% sulfuric acid at 160–165° for 16 hours.[9] (Milder condition had proven ineffective.) When the cooled and diluted hydrolyzate was made alkaline, unhydrolyzed starting material was precipitated. The filtered solution was acidified with acetic acid and evaporated to a small volume. The residue was made alkaline and filtered to remove crystallized sodium sulfate, and this process was repeated until a dry residue of small volume was obtained. Hot ethanol containing acetic acid extracted from the residue a mixture of sodium acetate and the hydrolysis product. The latter was recovered by recrystallization of the extract from water or by further extraction with benzene, m.p. 218–220°. Recrystallization of the hydrolysis product from water gave m.p. 219–222°. Analysis indicated this compound to be dimethyl isocyanurate[1] (m.p. 222°).

Anal. Calcd. for $C_5H_7N_3O_3$: C, 38.22; H, 4.49; N, 26.74. Found: C, 38.33; H, 4.56; N, 26.45.

Compound II was essentially unchanged after two days at 105°. The melting point was depressed to 50–55°, but no evidence of rearrangement was found.

Rearrangement of 2-Anilino-4,6-dimethoxy-*s*-triazine at 160°.—Fifty grams of V[4] (m.p. 132–133°) was heated for ten hours at 160°. Gradual solidification occurred. The crude product was washed with boiling ethanol to remove unchanged starting material, leaving a residue weighing 26 g., m.p. 220–230° (incomplete). Successive fractional recrystallization of this material from methyl cellosolve, dioxane and ethanol yielded approximately 25 g. (50%), m.p. 224–226°, (compound VI) and 1 g. (2%) of material which melted at 290–300° after an apparent transition at 230–240° (compound X). Compound VI was soluble in dilute aqueous sodium hydroxide as well as in dilute mineral acids. It crystallized slowly in long needles when an alkaline solution was acidified with acetic acid. Compound X was soluble in dilute hydrochloric acid but not in alkali. The analytical data showed that both VI and X were isomeric with V.

Anal. Calcd. for $C_{11}H_{12}N_4O_2$: C, 56.89; H, 5.21; N, 24.13. Found for VI: C, 56.97; H, 5.08; N, 24.10. Found for X: C, 56.55; H, 4.91; N, 24.38.

A small portion of VI was heated for 18 hours at 160–170°. At the end of this time, the solid was brown in color but still melted completely at 220–225°. This compound was equally stable when heated at 160° in suspension in Varsol No. 1 (a saturated hydrocarbon mixture).

Determination of the Structure of VI.—Twelve grams of VI was hydrolyzed with 80% sulfuric acid at 160–165°. The sulfuric acid was removed from the hydrolysate by addition of barium carbonate, and the filtered solution was evaporated to a small volume. An infusible barium salt (6.0 g.) crystallized. This substance was redissolved in hot water, and the solution was acidified with sulfuric acid. The mixture was filtered and cooled, whereupon crystallization yielded 2.5 g. of colorless plates, m.p. 220–222°. This compound was identified as dimethyl isocyanurate. Therefore, compound VI was the "normal" rearrangement product, **1,4,5,6-tetrahydro-1,5-dimethyl-4,6-dioxo-2-anilino-*s*-triazine.**

Determination of the Structure of X.—Hydrolysis of 11.4 g. of X with 65% sulfuric acid was carried out at 165° for 18 hours. The solution was diluted and was neutralized with barium hydroxide. Sulfuric acid was then added to give

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

[9] A. W. Hofmann, *Ber.*, **18**, 2787 (1885). Strong mineral acids hydrolyze amino or imino groups attached to an *s*-triazine nucleus, but hydrocarbon residues attached to ring nitrogen atoms are unaffected.

*p*H 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 $C_4H_5N_3O_3$: 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 $C_{10}H_{10}N_4O_2$: 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°.

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 $C_{10}H_{10}N_4O_2$: 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%).

STAMFORD, CONNECTICUT RECEIVED JULY 14, 1950

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

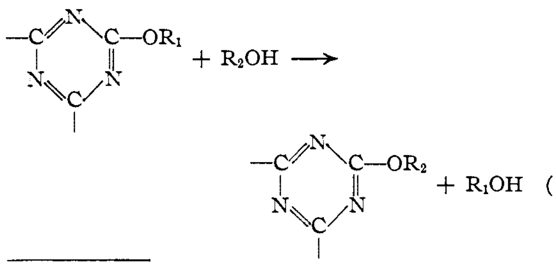
[CONTRIBUTION FROM THE STAMFORD RESEARCH LABORATORIES OF THE AMERICAN CYANAMID COMPANY]

Cyanuric Chloride Derivatives. VII. Transesterification Reactions of Alkoxy-s-triazines. Polyammelide 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 polyammelide 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)

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

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

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