[CONTRIBUTION FROM THE STAMFORD LABORATORIES, CENTRAL RESEARCH DIVISION, AMERICAN CYANAMID CO.]

Synthesis of the *sym*-Triazine System. I. Trimerization and Cotrimerization of Amidines

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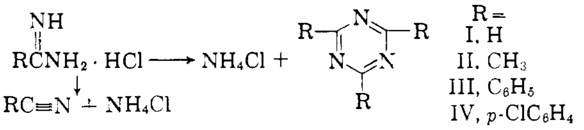
The conversion of amidines to *sym*-triazines has been investigated as a method of possible preparative value. This condensation trimerization is found to be useful only with formamidine and such electronegatively substituted amidines as 2,2,2-trichloracetamidine. However, these reactive compounds can be cotrimerized with other amidines to give substantial yields of mixed unsymmetrically substituted *sym*-triazines.

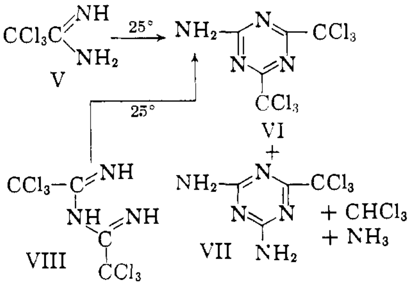
The discovery by Grundmann and Kreutzberger[1] that the compound formerly known as "hydrocyanic acid dimer" is in fact *sym*-triazine (I) stimulated great interest in our laboratories where the synthesis of this compound as an adjunct to our work with *sym*-triazine derivatives had been an unsolved challenge for many years. We began at once to investigate the chemistry of this interesting compound and to reappraise the methods for its preparation. Encouraged by our early results we soon extended the scope of our research to a general investigation of methods for the synthesis of the *sym*-triazine ring system. This paper is the first of a series which we plan to submit for publication describing new methods for the synthesis of hitherto rare or unknown types of *sym*-triazine compounds. Here are reported the results of our work on the preparation of *sym*-triazine compounds by trimerization and cotrimerization of amidines.

We have several times prepared *sym*-triazine for our purposes by the somewhat unsatisfactory reaction of "hydrogen cyanide sesquihydrochloride," $(2HCN,3HCl)_x$, with quinoline as described by Hinkel and Dunn.[2,3] The known alternative procedures[4] were also tried but were much less useful. However, in a continuing search for better methods, it was found that decomposition of formamidine hydrochloride on heating at 250° at 20 mm. pressure produced *sym*-triazine which sublimed from the reaction mixture and could be collected in a trap cooled with Dry Ice. Yields of approximately 72% were thus obtained. This mode of decomposition was subsequently mentioned by Grundmann and Kreutzberger[5] and later described by Grundmann, Schroeder and Ruske.[6] The yield reported, however, was only 9%, undoubtedly because in their experiment at ordinary pressure the unstable product was not removed quickly from the heated zone.

This efficient conversion of formamidine hydrochloride to I encouraged us to investigate the behavior of other amidine salts under similar conditions. Acetamidine hydrochloride was found to give 2,4,6-trimethyl-*sym*-triazine (II) in 13% yield[7] together with an 82% yield of acetonitrile, but propionamidine hydrochloride gave propionitrile exclusively. Benzamidine hydrochloride and *p*-chlorobenzamidine hydrochloride gave trace amounts of the 2,4,6-triaryl-*sym*-triazines, III and IV, respectively, when decomposed at 250° in sealed tubes, but substantially complete conversion to the nitrile was the predominant result.



An alternative procedure for the preparation of *sym*-triazine which was reported by Grundmann, *et al.*,[6] was the reaction of formamidine hydrochloride with quinoline at 150°. The yield was only 3%, however. We have not investigated this procedure extensively but have found that *sym*-triazine can be sublimed in 71% yield from an equimolar mixture of formamidine hydrochloride and tri-*n*-butylamine heated at reduced pressure. This again was a sufficiently promising lead to encourage our examination of the behavior of other free amidines. Pinner[8] had observed the formation of III together with benzonitrile when free benzamidine was heated at 115°. A more impressive reference, however, is the work of Dachlauer[9] who showed that 2,2,2-trichloroacetamidine (V) is unstable at room temperature and trimerizes spontaneously to give a mixture of 2-amino-4,6-bis-(trichloromethyl)-*sym*-triazine (VI) and 2,4-diamino-6-trichloromethyl-*sym*-triazine (VII). It



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(1) C. Grundmann and A. Kreutzberger, THIS JOURNAL, **76**, 632 (1954).

(2) C. Grundmann and A. Kreutzberger, *ibid.*, **76**, 5646 (1954).

(3) L. E. Hinkel and R. T. Dunn, *J. Chem. Soc.*, 1834 (1930).

(4) (a) J. U. Nef, *Ann.*, **287**, 337 (1895); (b) R. Willstätter and T. Wirth, *Ber.*, **42**, 1915 (1909).

(5) Reference 2. This paper was received in our laboratory for refereeing only a few days after our experiment. A. Gautier, *Ann. chim. phys.*, [4] **17**, 103 (1869), had stated that formamidine hydrochloride decomposed at 100° into hydrogen cyanide and ammonium chloride.

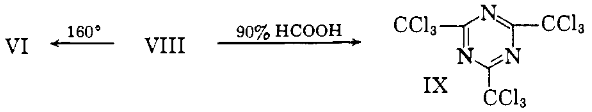
(6) C. Grundmann, H. Schroeder and Ruske, *Chem. Ber.*, **87**, 1865 (1954).

(7) Grundmann, *et al.* (ref. 6), produced a trace amount of 2,4,6-trimethyl-*sym*-triazine by dry distillation of acetamidine hydrochloride but were unable to isolate the product.

(8) A. Pinner, "Die Imidoäther und ihre Derivate," Robert Oppenheim (Gustav Schmidt), Berlin, Germany, 1892, p. 155.

(9) K. Dachlauer, "Reactions of Trichloroacetonitrile," PB 58825, Office of the Publication Board, Department of Commerce, Washington, D. C. This brief reference does not identify the decomposition products as VI and VII but there is no doubt that these structures were known by the author.

was also shown that N-(trichloroacetimidyl)-trichloroacetamidine (VIII), which is readily prepared from trichloroacetonitrile and aqueous ammonia and which may be considered a condensation dimer of V, decomposes in the same fashion when stored at room temperature. When III was treated with hot 90% formic acid cyclization to 2,4,6-tris-(trichloromethyl)-*sym*-triazine (IX) occurred, whereas heating alone gave nearly pure VI. Reactivity of this type has more recently been demonstrated with the perfluoroamidines by Reilly and Brown.[10]

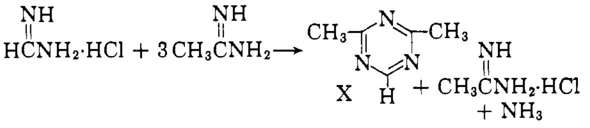


IX

We have further investigated the behavior of trichloroacetamidine and its dimer VIII and have confirmed the great ease with which these compounds form *sym*-triazines. However, a limited study of other amidines related to carboxylic acids of various strengths has convinced us that significant trimerization can be accomplished only with formamidine and those amidines in which the functional group is attached to a very strongly electronegative radical. Two techniques were employed in examining the thermal instability of amidines. Heating in sealed tubes for 2–3 hours as the temperature was raised from 150 to 250° was appropriate with the aromatic amidines which could be used as the crystalline free bases. Distillation of the dry amidine or of an alcoholic solution at gradually decreasing pressure was also used. Benzamidine and *p*-chlorobenzamidine gave trace yields of III and IV, respectively, but acetamidine and 2-isopropoxyacetamidine gave no detectable *sym*-triazine product. In all cases conversion to the nitrile was essentially complete. Experiments with lactamidine and 2-chloropropionamidine were abortive, unfortunately, only tarry products being obtained.

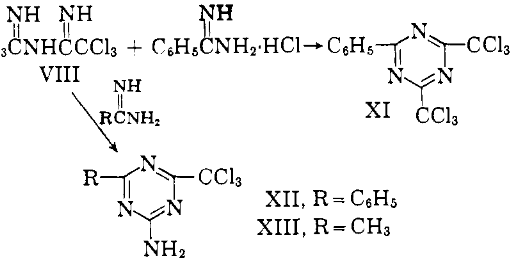
Hydrogen chloride appears to be a catalyst for the trimerization of amidines although in the limited work done the effect observed was not large. Thus, a 9:1 mixture of acetamidine and its hydrochloride gave an 11% yield of II, based on the total amidine. This result is to be compared with the formation of acetonitrile alone when free acetamidine is heated. Some other examples of the use of an amidine–amidine hydrochloride mixture will be found later.

It has been found possible to take advantage of the propensity of formamidine to trimerize by using this compound in co-reaction with another amidine. Yields of mixtures of alkyl or aryl-*sym*-triazines of the order of 60% were realized from the reactions which occurred when acetamidine, propionamidine or benzamidine hydrochlorides were fused with formamidine hydrochloride in equimolar amounts. Mono- and disubstituted *sym*-triazines were the predominant products but considerable *sym*-triazine was also formed and the aliphatic amidines gave some trisubstituted *sym*-triazine as well.[11] (It was interesting that the cotrimerization reaction of propionamidine and formamidine hydrochlorides gave 2,4,6-triethyl-*sym*-triazine in small yield although none could be obtained from propionamidine hydrochloride alone.) A variation which permitted the use of lower temperatures and which therefore may have some advantage was the reaction of formamidine hydrochloride with acetamidine base. The procedure involved liberation of free acetamidine from its hydrochloride in methanol solution, addition of formamidine hydrochloride at room temperature and subsequent distillation of the reaction products. When a ratio of formamidine hydrochloride to acetamidine of 1:3 was used, the yield of 2,4-dimethyl-*sym*-triazine (X) was approximately 21%, but a substantial amount of 2,4,6-trimethyl-*sym*-triazine was also obtained. Acetamidine hydrochloride was recovered as a by-product in 77% yield. Under these conditions the ideal reaction would be represented



Although the unsatisfactory selectivity of such reactions limits their utility, the rare mono- and disubstituted *sym*-triazines are thus made more readily available than by previously published procedures. We have chosen to limit our work on this reaction in view of the inherent advantages of alternative methods which will be reported in succeeding articles.

We have also had some success in cotrimerizing 2,2,2-trichloroacetamidine (in the form of its dimer, VIII) with other amidines. Thus, fusion of a mixture of VIII with benzamidine hydrochloride gave 2-phenyl-4,6-bis-(trichloromethyl)-*sym*-triazine (XI). Reaction of VIII with free benzamidine, however, gave 2-amino-4-phenyl-6-trichloromethyl-*sym*-triazine (XII). Free acetamidine reacted similarly giving 2-amino-4-methyl-6-trichloromethyl-*sym*-triazine (XIII). Open-chain structures were apparently also present in the reaction products, and the yields were not high. These reactions were not studied further in view of the satisfactory procedures already available for the preparation of both 2-R-4,6-bis-



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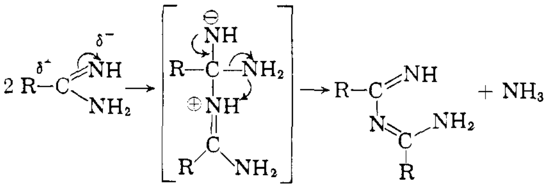
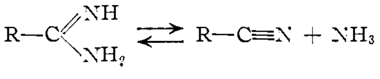
[10] W. L. Reilly, Doctoral Dissertation, University of Florida, 1955; W. L. Reilly and H. C. Brown, *J. Org. Chem.*, **22**, 698 (1957).

[11] Fractional distillation of the complex product mixtures containing methyl- or ethyl-*sym*-triazines gave unsatisfactory results in that analytically pure compounds were not obtained. The yield data were therefore calculated from the results of mass spectroscopic analyses.

(trichloromethyl)-*sym*-triazines[12] and 2-amino-4-R-6-trichloromethyl-*sym*-triazines.[13]

The exploratory experiments reported here cannot be considered to establish a mechanism for the formation of *sym*-triazine compounds from amidines. However, the pattern of results strongly suggests the nature of the process, and a qualitative understanding of the factors involved seems fairly clear. In our view the steps proceeding from the amidine structure must be successive condensation reactions leading to a linear trimer, which then cyclizes to the resonance-stabilized *sym*-triazine system. The first stage of this polycondensation process may be represented as shown below for the case of the free amidine. The subsequent stages are not essentially different and all will involve the following influences although with some variation in degree: (1) R groups of greater electronegativity will enhance the electrophilic character of the carbon atom of the functional group and tend to favor formation of the intermediate adduct. (2) Increase in the electronegativity of R will cause a decrease in the basic strength and nucleophilic character of the amidine group and thus tend to inhibit formation of the intermediate but probably this effect will be smaller than that in (1). (3) An increase in the size of the group R will tend to inhibit the reaction and this influence will become greater at succeeding stages. These three effects would be expected to cause a complex dependence of the over-all reaction rate upon the nature of R. To give a practical process this rate would have to be appreciably greater than that of the alternative reaction in which the nitrile is regenerated





$$\text{R—C}\begin{smallmatrix}\text{NH}\\ \text{NH}_2\end{smallmatrix} \rightleftarrows \text{R—C}{\equiv}\text{N} + \text{NH}_3$$

To at least a first approximation, the position of this equilibrium is controlled by the electronegativity of R. The addition of ammonia to nitriles has been studied and it is recognized that, for example, the amount of acetamidine in equilibrium with acetonitrile would be very small unless the amidine is stabilized as an acid salt[14] or as a metal derivative.[15] In contrast to this, trichloroacetonitrile and perfluoronitriles absorb ammonia essentially quantitatively.

In view of the considerations above one would predict that those amidines in which R is strongly electronegative would have a much greater ability to produce *sym*-triazines than those in which R is a relatively neutral group. In the latter case regeneration of the nitrile would be expected. These deductions are in agreement with the observed facts except for the remarkable reactivity of formamidine which is to be attributed to the negligible steric effect when R is hydrogen. The results, show, as the qualitative considerations do not, that nitrile regeneration nearly completely overrides *sym*-triazine formation except when R is very strongly electronegative.

Although this discussion has been limited to the case of the free amidines, the use of amidine salts merely complicates the mechanistic detail without changing the general picture. The carbon atom of the functional group in an amidinium ion is more electrophilic than in the free amidine but the ion is also less nucleophilic. As is shown by one experiment, a small amount of the amidine salt acts as a catalyst for the trimerization reaction which presumably proceeds most readily by attack of a nucleophilic amidine molecule upon the activated amidinium ion.

As Grundmann, *et al.*,[1,6] pointed out, there is a noteworthy structural similarity in the conversion of formamidine, ethyl formimidate[4a] and thioformamide[4b] to *sym*-triazine. However, rather than invoking an "activated" form of hydrogen cyanide, $\text{H}\overset{\oplus}{\text{C}}{=}\overset{\ominus}{\text{N}}$, as a common intermediate which trimerizes in these processes, we prefer to picture all three as polycondensation reactions in the manner indicated above.

Experimental Section[16]

Preparation of *sym*-Triazine (I). A. Thermal Decomposition of Formamidine Hydrochloride.—Five grams of formamidine hydrochloride[17] (0.062 mole) was heated gradually to 250° at 20 mm. pressure. Visible decomposition began at a bath temperature of 120°. Volatile decomposition products were passed into a receiver chilled with Dry Ice. Crystalline I which collected weighed 1.2 g., m.p. 80–81°,[18] yield 72%.

B. Reaction of Formamidine Hydrochloride with Tri-*n*-butylamine.—A mixture of 52 g. (0.28 mole) of tri-*n*-butylamine and 22.7 g. (0.28 mole) of formamidine hydrochloride was stirred vigorously and heated at a pressure of 80–90 mm. in a distilling apparatus. A large-diameter air condenser was used, connected to a receiver which was cooled in a Dry Ice–acetone-bath. Sublimation of *sym*-triazine into the condenser was first apparent when the temperature of the reaction mass reached 65–70°. Ammonia was evolved continuously as the temperature was raised to 110° during one hour. In this period a substantial deposit of *sym*-triazine crystals collected in the condenser. The reaction mixture was heated two hours longer at 125°. During this time additional *sym*-triazine sublimed and some crystalline material separated in the reaction mixture although this consisted chiefly of two liquid phases throughout the process. No significant amount of tri-*n*-butylamine distilled during the reaction. The *sym*-triazine collected

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(12) K. Dachlauer, German Patent 682,391, October, 1939; C. Grundmann, G. Weisse and S. Seide, *Ann.*, **577**, 77 (1952); C. Grundmann and G. Weisse, *Ber.*, **84**, 684 (1951).

(13) A. Kreutzberger, This Journal, **79**, 2629 (1957).

(14) P. Oxley, M. W. Partridge and W. F. Short, *J. Chem. Soc.*, 303 (1948).

(15) E. F. Cornell, This Journal, **50**, 3311 (1928).

(16) Melting points were determined by the capillary method and are uncorrected. Microanalyses were carried out in these laboratories under the direction of Dr. J. A. Kuck. Infrared absorption spectra were obtained and interpreted by Dr. J. E. Lancaster. Mass spectroscopic analyses were carried out under the supervision of Mr. A. H. Struck.

(17) Reference 8, p. 93.

(18) Various values have been reported for the m.p. of *sym*-triazine. J. U. Nef,[4a] gave the very high value of 87°. This was contested by Willstätter and Wirth[4b] who obtained 81–82°. Hinkel and Dunn[3] found 85° and Grundmann and Kreutzberger[2b] have more recently reported 86°. We find a melting point of 81.5 to 82.0° cor. (capillary) for *sym*-triazine which has been repeatedly sublimed and contains less than 0.1 mole per cent. of impurities according to mass spectroscopic analysis.

in the condenser tube weighed 5.4 g. (71%), m.p. 80–81°. The liquid in the receiver weighed only 0.2 g. after evaporation of condensed ammonia. The solid which had separated in the reaction flask was ammonium chloride (0.12 mole). The upper, more fluid of the two liquid phases remaining was essentially pure tri-*n*-butylamine (approx. 0.18 mole). The viscous lower phase was tri-*n*-butylamine hydrochloride.

Thermal Decomposition of Amidine Hydrochlorides. A. Acetamidine Hydrochloride.—Acetamidine hydrochloride[19] (53.0 g., 0.565 mole) was heated slowly to 300° at a pressure of 10–20 mm. The volatile products were collected in a receiver cooled in a Dry Ice–acetone-bath. Crystals which collected in the cooler parts of the distillation apparatus were extracted with petroleum ether and the solution was combined with the liquid distillate. Fractional distillation of the products gave 11 g. of acetonitrile and 1.7 g. of **2,4,6-trimethyl-*sym*-triazine** (II), m.p. 59–60°.[20] The residue in the reaction flask weighed 22 g. and was found to be essentially pure starting material. The yield of II was 13% and that of acetonitrile 82% based on unrecovered acetamidine hydrochloride.

B. Propionamidine Hydrochloride.—Fifteen grams of propionamidine hydrochloride[21] was heated to 260° at 15–25 mm. A 64% yield of propionitrile distilled; 33% of the starting material was recovered by extraction of the residue and some crystalline sublimate with ethanol.

C. Benzamidine Hydrochloride.—Decomposition of 12.6 g. (0.080 mole) of anhydrous benzamidine hydrochloride[22] during 6 hours in a sealed tube at 250° produced a 3% yield of **2,4,6-triphenyl-*sym*-triazine** (III), m.p. 226–230° (lit.[23] 232°) and an approximately 97% yield of benzonitrile.

D. *p*-Chlorobenzamidine Hydrochloride.—When 3.6 g. (0.019 mole) of *p*-chlorobenzamidine hydrochloride[24] was heated for 3 hours in a sealed tube at 250°, *p*-chlorobenzonitrile, m.p. 89–91°, was obtained in 95% yield and 0.025 g. (1%) of 2,4,6-tris-*p*-chlorophenyl-*sym*-triazine (IV),[23] m.p. 344° dec., was also found.

Preparation[25] and Decomposition of 2,2,2-Trichloroacetamidine (V).—A mixture of trichloroacetonitrile[26] (17.0 g., 0.12 mole) and 50 cc. of benzene was cooled to 10° and 4.0 g. (0.23 mole) of ammonia was added under a Dry Ice–acetone condenser. The mixture was allowed to stand overnight at room temperature. The benzene and excess ammonia were then evaporated at reduced pressure leaving a pale yellow oil which already weighed only 85% of the theoretical amount. On standing the oil gradually solidified. After two weeks the product was extracted with petroleum ether which left undissolved 8.45 g. (64%) of crude **2-amino-4,6-bistrichloromethyl-*sym*-triazine** (VI).[27] After recrystallization from wet ethanol the product melted at 164–166°.

In another experiment, the crude trichloroacetamidine prepared as described above from 15 g. (0.10 mole) of trichloroacetonitrile was heated gradually to 200° after removal of the benzene. Some chloroform distilled leaving a residue of 11.4 g. of crude VI which melted at approximately 135°; yield approximately quantitative.

Preparation and Decomposition of N-(Trichloroacetimidyl) - trichloroacetamidine (VIII).[9]—Trichloroacetonitrile (29.0 g., 0.20 mole) was added dropwise at 7–10° to 13.0 cc. of 29.8% aqueous ammonia (0.10 mole) diluted with 25 cc. of water. The mixture was stirred for 1.5 hours at 10° to complete crystallization of the product. The colorless needles obtained were dried over sulfuric acid; yield 30 g. (99%), m.p. approx. 30–35° (lit.[9] 36°).

The product was not seriously changed after storage for one month at 0°, but at 25° decomposition was well advanced in two to three days. Both **2-amino-4,6-bis-(trichloromethyl)-*sym*-triazine** (VI) **and 2,4,6-tris-(trichloromethyl)-*sym*-triazine** (IX) were formed. When a 3.6-g. sample of VIII (0.0117 mole) was heated at 20 mm. pressure at 160–250° for 20 minutes much of the material evaporated and recovery was low. However, the residue, which weighed 0.98 g. and melted at approximately 80°, was nearly pure IX (35% yield). Recrystallization from ethanol gave needles, m.p. 93–5° (lit.[28] 96°). Decomposition of VIII by gradual heating to 250° at atmospheric pressure produced a 94% yield of VI.

Catalysis of the Trimerization of Acetamidine by Hydrogen Chloride.—To a partial solution of 14.6 g. (0.27 mole) of sodium methoxide in 50 cc. of methanol was added 28.4 g. (0.300 mole) of acetamidine hydrochloride. After being mixed for several minutes the resultant slurry was filtered to remove the precipitated sodium chloride. After evaporation of the solvent below 30° at 40 mm., the pressure was reduced to 20 mm. and the temperature gradually increased. Distillation of the volatile material present occurred at a bath temperature of 160–200° and was completed in about 20 minutes. The distillate weighed 2.5 g. and boiled at 50–60° at 20 mm. Infrared examination showed that the distillate contained a substantial amount of 2,4,6-trimethyl-*sym*-triazine (II). Analysis of the material by mass spectroscopy gave the following approximate composition (mole %): II, 27; acetamide, 19; acetamidine, 6; methanol, 46. From these data the yield of II was calculated to be 11% based on acetamidine hydrochloride used.

Cotrimerization of Formamidine Hydrochloride with Acetamidine Hydrochloride.—A mixture of 40.3 g. (0.50 mole) of formamidine hydrochloride and 47.3 g. (0.50 mole) of acetamidine hydrochloride was stirred and heated gradually to 250° at 50–100 mm. pressure. The distillate which collected in an ice-cooled receiver weighed 20.5 g. (60% of the theoretical maximum). Redistillation failed to accomplish a sharp separation of the constituents of the product mixture. The fractions collected were analyzed by mass spectroscopy and the following approximate composition of the 20.5 g. was calculated (mole %): acetonitrile < 13; *sym*-triazine, 20; **2-methyl-*sym*-triazine**,[29] 31; **2,4-dimethyl-*sym*-triazine** (X), 35; 2,4,6-trimethyl-*sym*-triazine, 1. Dilution of the highest boiling fraction, 4 g., b.p. above 60° at 50 mm., with petroleum ether caused crystallization of 2 g. of X, m.p. 46–48° (lit.[30] 46°).

Cotrimerization of Formamidine Hydrochloride with Acetamidine.—Sodium methoxide (16.2 g., 0.30 mole) was dissolved in 50 cc. of methanol and 28.4 g. (0.30 mole) of acetamidine hydrochloride was added. The mixture was stirred occasionally during 30 minutes and then was filtered to remove precipitated sodium chloride. To the acetamidine solution was added 8.05 g. (0.10 mole) of formamidine hydrochloride, and the mixture was allowed to stand at 25° for 18 hours. Distillation of the solution yielded a 5.6 g. fraction which boiled at 130–140°. Infrared spectroscopy showed this to be a mixture of methyl-*sym*-triazines with considerable methanol present. Mass spectroscopic analysis gave the following composition (mole %): *sym*-triazine, 0.4; 2-methyl-*sym*-triazine, 2.8; 2,4-dimethyl-*sym*-triazine, 25.2; 2,4,6-trimethyl-*sym*-triazine, 15.2; methanol, 56.3. On this basis the yield of *sym*-triazine compounds was 27%, based on the total weight of starting amidines. Alternatively, the yield of II was 13% based on acetamidine hydrochloride used, and the yield of X was 21% based on the equation given in the text; 77% of the acetamidine hydrochloride used was recovered in the distillation residue.

Cotrimerization of Formamidine Hydrochloride with Propionamidine Hydrochloride.—A mixture of 37.4 g. (0.465 mole) of formamidine hydrochloride and 50.4 g. (0.465 mole) of propionamidine hydrochloride was heated at 20–40 mm. pressure. Distillation took place at a bath temperature of 185–245°. The distillate which was collected in an ice-cooled receiver was redistilled to separate the *sym*-triazines obtained from some sublimed ammonium chloride and amidine hydrochloride. The 23.2 g. of crude *sym*-triazines recovered amounted to 66% of the theoretical maximum. This material was analyzed by mass spectroscopy

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[19] Reference 8, p. 107.

[20] T. Cairns, A. Larcher and B. McKusick, THIS JOURNAL, **74**, 5633 (1952).

[21] Reference 8, p. 115.

[22] Reference 8, p. 152.

[23] A. H. Cook and D. G. Jones, *J. Chem. Soc.*, 278 (1941).

[24] C. Grundmann and G. Ottmann, Canadian Patent 510,525 (1955).

[25] This is essentially the procedure of K. Dachlauer, German Patent 671,784 (1939). An improvement over this method is reported by H. Schroeder and C. Grundmann, THIS JOURNAL, **78**, 2447 (1956).

[26] L. Bisschopinck, *Ber.*, **6**, 731 (1873).

[27] A. Weddige, *J. prakt. Chem.*, [2] **33**, 81 (1886), gives m.p. 165–166°.

[28] E. T. McBee, O. R. Pierce and R. O. Bolt, *Ind. Eng. Chem.*, **39**, 391 (1947).

[29] C. Grundmann and E. Kober, *J. Org. Chem.*, **21**, 641 (1956).

[30] H. Schroeder and C. Grundmann, THIS JOURNAL, **78**, 2447 (1956).

and was found to have the following composition (mole %): *sym*-triazine, 7; **2-ethyl-*sym*-triazine**, 42; **2,4-diethyl-*sym*-triazine**, 42; 2,4,6-triethyl-*sym*-triazine,[19] 9. Attempted fractional distillation failed to give analytically pure samples of these products.

Cotrimerization of Formamidine Hydrochloride with Benzamidine Hydrochloride.—A mixture of 8.05 g. of formamidine hydrochloride (0.10 mole) and 15.65 g. (0.10 mole) of benzamidine hydrochloride was heated to 250° at 10–20 mm. pressure in a distilling apparatus. Some solid sublimed into the condenser and 1.0 g. of liquid was collected in the receiver which was immersed in a Dry Ice–acetone-bath. The residue in the distilling flask (14.0 g.) was extracted with water and the remaining 8.0 g. of solid was recrystallized from methanol whereby 4.5 g. of 2,4-diphenyl-*sym*-triazine was obtained, m.p. 87–88° (lit.[31] 88.5°). The sublimate from the condenser was united with the mother liquor. Steam distillation of the mixture gave an oil which crystallized as the distillate cooled. This was **2-phenyl-*sym*-triazine**, m.p. 60–62° (63–65° from methanol; lit.[30] 63.5°). An additional 2 g. of crude 2,4-diphenyl-*sym*-triazine crystallized from the steam distillation residue. The yield of this product was 56% based on benzamidine hydrochloride used, and the yield of 2-phenyl-*sym*-triazine was 20% based on formamidine hydrochloride used. The liquid distillate obtained was chiefly benzonitrile (10% yield).

Anal. (2-phenyl-*sym*-triazine) Calcd. for $C_9H_7N_3$: C, 68.77; H, 4.49; N, 26.74. Found: C, 68.36; H, 4.79; N, 26.71.

Anal. (2,4-diphenyl-*sym*-triazine) Calcd. for $C_{15}H_{11}N_3$: C, 77.23; H, 4.75; N, 18.02. Found: C, 76.99; H, 4.88; N, 17.90.

Cotrimerization of N-(Trichloroacetimidyl)-trichloroacetamidine (VIII) with Benzamidine Hydrochloride.—A mixture of 1.5 g. (0.010 mole) of benzamidine hydrochloride and 3.0 g. (0.010 mole) of VIII was fused in a test-tube. At about 120° a homogeneous melt was obtained and ammonia evolution was evident. Heating was continued for 15 minutes at about the same temperature. The reaction mixture was then cooled and the solid obtained was recrystallized from wet ethanol. The product (1.9 g.) melted at 76–79°. Further recrystallization from aqueous acetone and other solvents failed to raise this melting point. The product, nevertheless, was virtually identical, according to infrared comparison, with authentic 2-phenyl-4,6-bis-(trichloromethyl)-*sym*-triazine (XI), m.p. 96–8°, prepared by the cotrimerization of benzonitrile and trichloroacetonitrile.[32] Analysis of the low-melting product gave the following fairly satisfactory results.

Anal. Calcd. for $C_{11}H_5N_3Cl_6$: N, 10.72; Cl, 54.40. Found: N, 11.21; Cl, 54.32.

Cotrimerization of VIII with Benzamidine.—A solution of benzamidine in ethanol was prepared by treating 7.8 g. (0.050 mole) of benzamidine hydrochloride with a solution of 2.7 g. (0.050 mole) of sodium methoxide in 25 cc. of ethanol. The precipitated sodium chloride was filtered after 15 minutes, and 15.3 g. (0.050 mole) of VIII was added to the filtrate. The reaction mixture was heated for 1.5 hours 50–60° and then was allowed to stand at room temperature. Slow crystallization gave 6.75 g., m.p. *ca.* 130°. This material melted at 135–136° after recrystallization from aqueous alcohol. It appears to be an open chain compound rather than a *sym*-triazine but remains unidentified. The filtrate from this product was concentrated to crystallize 3.4 g. of 2-amino-4-phenyl-6-trichloromethyl-*sym*-triazine (XII), m.p. 172–174° (from wet ethanol; lit.[12] 175–176° cor.), yield 23%. Infrared comparison showed this compound to be identical with an authentic sample prepared by reaction of XI with ammonia as described by Kreutzberger.[12]

Cotrimerization of VIII with Acetamidine.—A solution of 0.033 mole of acetamidine was prepared by reaction of equimolar amounts of acetamidine hydrochloride and sodium methoxide in 10 cc. of ethanol. To this was added 10 g. of VIII. The mixture was allowed to stand overnight at room temperature. It was then evaporated at reduced pressure to remove the solvent, and the residue was heated to 180° during one hour. The dark reaction product was extracted with hot ethanol. From the extract was isolated 1.8 g., m.p. 146–150°. This was found to be crude **2-amino-4-methyl-6-trichloromethyl-*sym*-triazine (XIII)**. Recrystallization from ethanol raised the m.p. to 156–158° (lit.[12] 158–159° cor.). Infrared examination of by-product fractions from the reaction mixtures indicated that no other *sym*-triazine compound was present in significant amount.

Anal. Calcd. for $C_5H_3N_4Cl_3$: C, 26.40; H, 2.22. Found: C, 26.68; H, 2.43.

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[31] G. Grundmann, H. Ulrich and A. Kreutzberger, *Chem. Ber.*, **86**, 181 (1953).

[32] K. Dachlauer, German Patent 682,391 (1939).

[CONTRIBUTION FROM THE STAMFORD LABORATORIES, CENTRAL RESEARCH DIVISION, AMERICAN CYANAMID CO.]

Synthesis of the *sym*-Triazine System. II.[1] Preparation of Monosubstituted *sym*-Triazines by Reaction of *sym*-Triazine with Amidines

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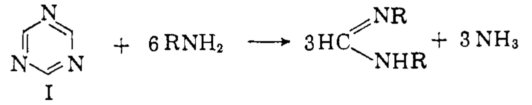
The reaction of amidino compounds with *sym*-triazine is reported as an efficient and broadly applicable method for the preparation of monosubstituted *sym*-triazines.

The dominant characteristic of the chemistry of *sym*-triazine (I) is the suceptibility of the ring system to cleavage and destruction by nucleophilic



I

reagents. Among such reagents amino compounds have received most attention. The literature[2] on "hydrocyanic acid dimer," as it was then called, discloses the reaction of I with aniline which produces N,N′-diphenylformamidine. Grundmann and Rätz[3] and, independently, Dr. Hechenbleikner in our laboratory have also shown the reaction of *sym*-triazine with ammonium chloride to be very clean and to lead to formamidine hydrochloride in essentially quantitative yield. Application of this degradation reaction for the preparation of such heterocyclic formamidines as benzimidazole and 3-aminotriazole has also been reported.[4] Undoubtedly such reactions proceed in a stepwise manner, and it occurred to us that if the reagent used was an

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[1] Paper I, F. C. Schaefer, I. Hechenbleikner, G. A. Peters and V. P. Wystrach, THIS JOURNAL, **81**, 1466 (1959).

[2] L. E. Hinkel and E. F. Ayling and J. H. Beynon, *J. Chem. Soc.*, 678 (1935).

[3] C. Grundmann and R. Rätz, *J. Org. Chem.*, **21**, 1037 (1956).

[4] C. Grundmann and A. Kreutzberger, THIS JOURNAL, **77**, 6559 (1955).