

Ethyl β -[5-Carboxy-3-(2-carboxyethyl)-4-methyl-2-pyrrolyl]- β -(4-carboxy-3,5-dimethyl-2-pyrrolyl)-propionate (XVII).—An intimate mixture of 306 mg. of α -carboxy-acrylic acid (VI) and 223 mg. of the pyrrolepropionic acid (XVIII) was heated for 8.5 hours at 119–124°. The viscous melt was then taken up in glacial acetic acid by heating on the water-bath. After addition of water to incipient turbidity, ethanol was gradually added until subsequent cooling caused separation of some solid. The oil which separated simultaneously was brought to crystallization by alternate brief heating and cooling of the mixture. After cooling slowly to room temperature, then refrigerating, the crystalline product A⁴⁵ was filtered off and washed with 1:1 ethanol-water. In order to separate acidic from non-acidic substances product A was dissolved in a little warm ethanol-water and potassium bicarbonate was added to the cessation of effervescence. The mixture was then added to about 15 ml. of water to precipitate product B, which was filtered off after standing for a few hours. Acidification of the filtrate to a pH of 5 with acetic acid caused separation of product C.

Concentration of the mother liquor from which product A had crystallized, and subsequent separation of the residue into acidic and non-acidic components by the above procedure, but employing centrifugation rather than filtration, yielded a small amount of viscous acidic product. This was

(45) Although in the experiment described here most of the β , β -dipyrrolylpropionic ester acid XVII was present in product A, such was not the case in other similar runs. Product A frequently consists largely of non-acidic by-product, the XVII remaining in the mother liquor.

combined with product C and recrystallized from minimum hot ethanol-water to give 148 mg. or 29% of XVII monohydrate. The analytically pure monohydrate was obtained by repeated recrystallization from hot ethanol-water. The substance did not melt sharply presumably because of gradual loss of its water of hydration. A 3 to 7° melting range was usually observed somewhere between the limits of 87 and 101°, depending upon the rate of heating and the state of subdivision of the sample. The melt began to resolidify when a temperature a little above the melting point was maintained for several minutes.

Anal. Calcd. for $C_{25}H_{34}O_8N_2 \cdot H_2O$: C, 59.04; H, 7.14; C_2H_5O , 26.58. Found: C, 59.30; H, 7.08; C_2H_5O , 26.61, 26.70.

The monohydrate was quantitatively dehydrated to the anhydrous β , β -dipyrrolylpropionic ester XVII by heating *in vacuo* at 75–80° for 30 minutes, then at 105–115° for 90 minutes.

Anal. Calcd. for $C_{25}H_{34}O_8N_2$: H_2O (of hydration), 3.54. Found: loss in weight on heating as above, 3.69, 3.72, 3.69.

The thus obtained anhydrous XVII melted at 150–152°.

Anal. Calcd. for $C_{25}H_{34}O_8N_2$: C, 61.21; H, 6.99; C_2H_5O , 27.56; mol. wt., 491. Found: C, 61.34; H, 6.88; C_2H_5O , 27.42; mol. wt., 496 ± 7 (ebullioscopic in chloroform).⁴⁶

(46) The authors wish to thank Mr. James Ogilvie for this determination of the molecular weight.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE OHIO STATE UNIVERSITY RESEARCH FOUNDATION]

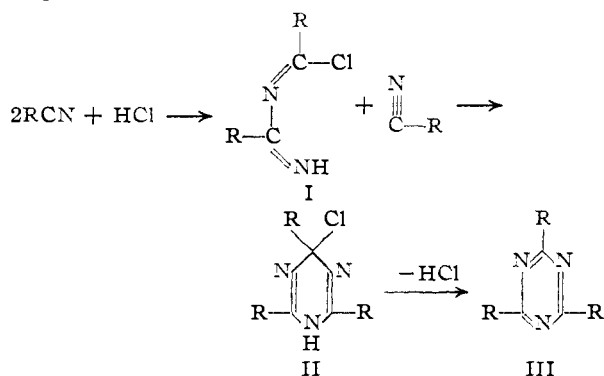
Triazines. IX. 1,3,5-Triazine and its Formation from Hydrocyanic Acid^{1,2}

BY CHRISTOPH GRUNDMANN AND ALFRED KREUTZBERGER

RECEIVED MAY 22, 1954

The identity of the long known "dimer of hydrocyanic acid" with *s*-triazine, $C_3H_3N_3$, has been established. New chemical and spectroscopical data for *s*-triazine are presented. The formation of $C_3H_3N_3$ from HCN *via* the "sesquihydrochloride of hydrocyanic acid" and the "chloromethylene-formamidine" is discussed, and new structures for these intermediates are proposed. Other known modes of formation of dimeric HCN are discussed in view of the new structure.

The mechanism of the acid-catalyzed polymerization of nitriles to *s*-triazines has recently been explained as a kind of Diels-Alder reaction in which two molecules of the nitrile and one molecule of hydrochloric acid form at first an intermediate I which then adds another molecule of the nitrile, the resulting product II splitting off hydrochloric acid to give the *s*-triazine (III)³



(1) This article is based on work performed under project 116-B of The Ohio State University Research Foundation sponsored by the Mathieson Chemical Corporation, Baltimore, Md.

(2) Preceding communication: Ch. Grundmann and H. Schroeder, *Chem. Ber.*, **87**, 747 (1954).

(3) Ch. Grundmann, G. Weisse and S. Seide, *Ann.*, **577**, 77 (1952).

But as already reported our attempts to trimerize hydrocyanic acid to *s*-triazine failed, hydrocyanic acid and hydrochloric acid forming rapidly the long known so-called "sesqui-hydrochloride of hydrocyanic acid," $2HCN \cdot 3HCl$, to which formulas IVa⁴ and more recently IVb⁵ have been assigned. This compound under a variety of conditions readily loses two thirds of its hydrogen chloride content yielding a product formulated as chloromethylene-formamidine (V). As this has the structure expected for the intermediate of hydrocyanic acid in the trimerization (I, R = H), we tried to react this compound with another nitrile or hydrocyanic acid itself. As no condensation to the expected triazine took place, we assumed that the second intermediate (II, R = H) might be more stable in this special case, and we decided to carry out the reaction with addition of a tertiary base as a scavenger of hydrochloric acid in the last step (II \rightarrow III). We found then that this experiment had already been made by Hinkel, *et al.*, heating either the sesquihydrochloride of hydrocyanic acid or chloromethylene-formamidine with quinoline.⁶ Since free hydrocyanic acid is reported always to occur during these reac-

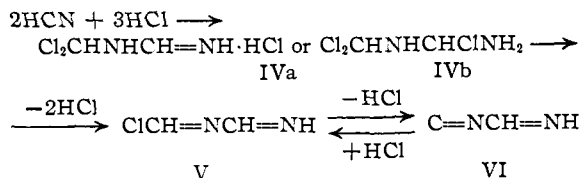
(4) L. Gattermann and K. Schnitzspahn, *Ber.*, **31**, 1770 (1898).

(5) (a) L. E. Hinkel and T. I. Watkins, *J. Chem. Soc.*, 647 (1944);

(b) L. E. Hinkel and R. Hullin, *ibid.*, 1033 (1949).

(6) L. E. Hinkel and R. T. Dunn, *ibid.*, 1834 (1930).

tions by some degradation of IV or V,⁷ the necessary conditions for a triazine synthesis are provided. The reaction of the sesquihydrochloride of hydrocyanic acid or the chloromethylene-formamidine with quinoline yields in fact a polymer of hydrocyanic acid which since its discovery by Nef⁸ by a different route has been regarded as a dimer, C₂H₂N₂. Nef postulated the formula HN=CH-CN, iminoglyoxylic acid nitrile, but as its hydrolysis yields only formic acid and ammonia, Michael and Hibbert⁹ first suggested the structure VI of iminoformylcarbylamine. Later this was confirmed by Hinkel,¹⁰ who in his detailed studies on hydrocyanic acid gives the following sequence for the reactions leading from hydrocyanic acid to the dimer.



Compound VI shows many peculiar reactions, but none of those characteristic for the isonitriles. With the considerations discussed above in mind, we reinvestigated the molecular weight of the alleged dimer of hydrocyanic acid and found that this compound is in fact a trimer, C₃H₃N₃. Since its hydrolysis under very mild conditions yields quantitatively formic acid and ammonia,⁷ any formula with C-C or N-N groups is definitely excluded, and the compound is now believed to be 1,3,5-triazine (X),¹¹ the hitherto unknown parent compound of the *s*-triazines which many chemists have long tried in vain to prepare.¹² We were able to support our formula by conversion of the trimer into *s*-triazine derivatives of established structure.¹¹

s-Triazine crystallizes from the vapor phase in highly refracting well-formed rhombohedral crystals,¹³ m.p. 86°, b.p. 114° (760 mm.). The compound is extremely volatile, subliming far below its melting point. In this property it resembles other organic compounds of highly symmetrical structure. A comparison of the melting and boiling points of *s*-triazine, pyrimidine and pyridine is given in Table I.

(7) L. E. Hinkel, E. E. Ayling and J. H. Beynon, *J. Chem. Soc.*, 674 (1935).

(8) J. U. Nef, *Ann.*, **287**, 337 (1895).

(9) A. Michael and H. Hibbert, *ibid.*, **364**, 70 (1909).

(10) See ref. 6, 7, L. E. Hinkel and T. I. Watkins, *J. Chem. Soc.*, 407 (1940).

(11) Ch. Grundmann and A. Kreutzberger, *THIS JOURNAL*, **76**, 632 (1954).

(12) (a) O. Diels, *Ber.*, **32**, 691 (1899) (reduction of cyanuric chloride with HI + PH₄I); (b) O. Diels and M. Liebermann, *ibid.*, **36**, 3191 (1903) (reduction of cyanuric chloride with zinc dust and water); (c) A. Burger and E. D. Hornbaker, *THIS JOURNAL*, **75**, 4579 (1953); (d) Ch. Grundmann and E. Beyer, *ibid.*, **76**, 1948 (1954) (reduction of cyanuric chloride with LiAlH₄); (e) Ch. Grundmann, H. Ulrich and A. Kreutzberger, *Chem. Ber.*, **86**, 181 (1953) (catalytic reduction of cyanuric chloride); (f) A. Weddige, *J. prakt. Chem.*, [2] **10**, 212 (1874) (decarboxylation of *s*-triazinetricarboxylic acid); (g) H. Wieland, *Ber.*, **42**, 803 (1909) (reduction of *s*-triazinetrioxide); (h) Ch. Grundmann and H. Ulrich, unpublished work (hydrogenolysis of trimethyl thiocyanurate with Raney Ni, thermal decomposition of 1,3,5-tribenzoyl-hexahydro-1,3,5-triazine). The now-known properties of *s*-triazine, especially its sensitiveness to hydrolytic cleavage, make all the above-mentioned failures to prepare this compound easily understandable.

(13) L. A. Siegel and E. F. Williams, *J. Chem. Phys.*, **22**, 1147 (1954).

TABLE I

	B.p., °C. (760 mm.)	M.p., °C.	ΔT, °C.
1,3,5-Triazine	114	86	
1,3-Diazine	123	22	64
Pyridine	116	-42	64

The boiling points are little changed by introducing one and two nitrogens successively in *m*-positions into the pyridine nucleus but the melting points rise in an exact linear function. With more material available it might be interesting to study whether this is a general rule.

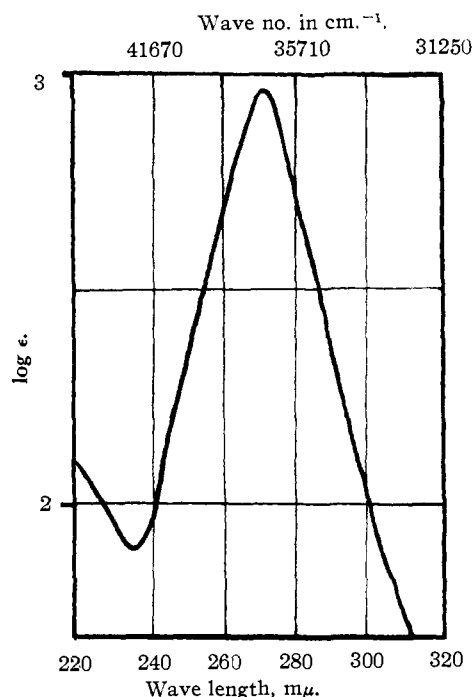


Fig. 1.—Ultraviolet absorption spectrum of 1,3,5-triazine in iso-octane solution.

The ultraviolet absorption spectrum of X is shown in Fig. 1, having a broad maximum at 272 mμ and probably a second one below 220 mμ, where we were unable to measure it,¹⁴ corresponding to 2,4,6-trimethyl-1,3,5-triazine (λ_{max} 264 mμ, ε_{max} 700, in hexane).¹⁵ The Raman spectrum of *s*-triazine has been determined by Goubeau and Jahn, who found it in excellent agreement with the structure X; furthermore, it has a striking resemblance to the Raman spectrum of benzene, thus indicating that *s*-triazine must be considered as an aromatic system.¹⁶ The infrared spectra of *s*-tria-

(14) Following our previous communication,¹¹ Dr. R. C. Hirt, American Cyanamid Co. Research Laboratories, Stamford, Conn., kindly informed us that they recently measured the ultraviolet absorption spectrum of *s*-triazine in the vapor phase, thus obtaining a much more detailed spectrum. They found these data in agreement with their predicted spectrum of *s*-triazine on the basis of theoretical considerations (R. C. Hirt and D. J. Salley, *J. Chem. Phys.*, **21**, 1181 (1953)). R. C. Hirt, F. Halverson and R. G. Schmitt, *J. Chem. Phys.*, **22**, 1148 (1954).

(15) We owe these data to the courtesy of Dr. L. Paoloni, Istituto Superiore di Sanita, Rome, publication in the *Gazz. chim. ital.*, in press.

(16) Full details will be published in the *J. Phys. Chem.* We are very much indebted to Prof. Goubeau, Technische Hochschule Stuttgart, Germany, for his kind permission to bring the results of his work here *in extenso*.

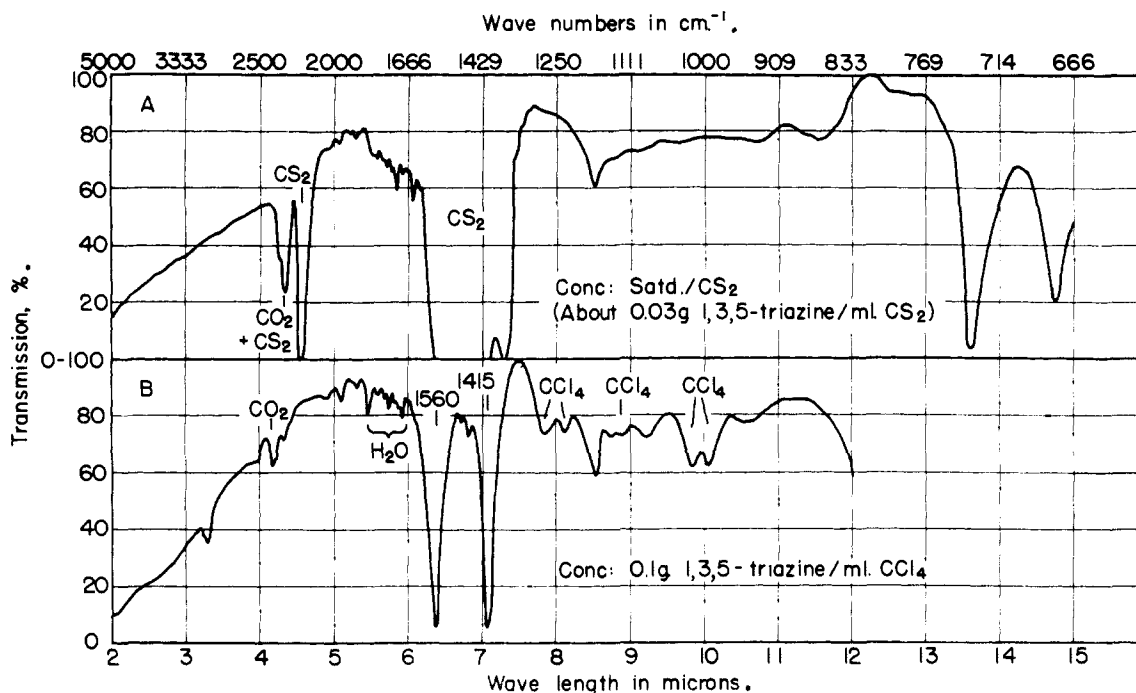


Fig. 2.—Infrared absorption spectra of 1,3,5-triazine as determined in carbon disulfide solution (curve A) and carbon tetrachloride solution (curve B) in a cell 0.005 in. thick.

zine in carbon tetrachloride and carbon disulfide are represented in Fig. 2. Characteristic are two strong bands at 1560 and 1415 cm^{-1} and two at 735 and 673 cm^{-1} . Very similar bands are also found in other simple triazine derivatives.¹⁶

s-Triazine is highly soluble in water and fairly soluble in most organic solvents. While its thermal stability seems to be remarkable,¹⁷ it is very sensitive to solvolysis not only in water but also in alcohols or other solvents containing hydroxyl groups which therefore are generally not suited for handling *s*-triazine. In a 10% solution in distilled water no more triazine can be detected after standing for 10 minutes at 25°; in presence of small amounts of mineral acids hydrolysis occurs almost instantly, ammonium formate being the only isolable product. As already recorded by Nef,⁸ in the presence of alkali formamide (as its dibenzoyl derivative) is obtained as an intermediate. Formamide is also isolated as picrate from alcoholic solutions of triazine and picric acid. This instability of *s*-triazine has not been fully recognized by previous workers and is the explanation for many reactions of the compound which seemed to support the earlier formula VI.¹⁸

s-Triazine gives addition products with several silver salts, *e.g.*, with silver nitrite and silver nitrate, the latter already having been obtained by Nef who gave to it the formula $\text{AgC}_2\text{HN}_2 \cdot \text{H}_2\text{O}$,⁸ while Hinkel after recognizing water as an unsuitable solvent and preparing it from alcohol suggested $2\text{AgNO}_3 \cdot 5\text{HCN}$.⁷ We have found that depending on the mode of preparation quite different analytical data can be obtained for this compound. Furthermore, the addition product once isolated

(17) L. E. Hinkel and T. I. Watkins, *J. Chem. Soc.*, 407 (1940).

(18) A detailed discussion of some of the known reactions of *s*-triazine and its precursors will be given in a following paper.

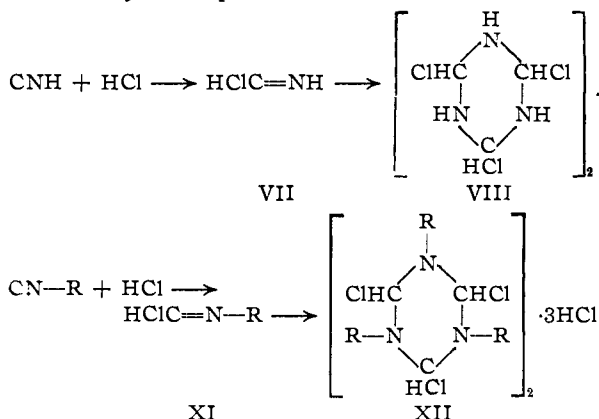
tends to lose triazine constantly by volatilization, so that this compound in spite of its beautiful, well-crystallized appearance is not suitable for identification purposes. Reasonable and constant analytical results are obtained only by working in media which do not react with *s*-triazine itself, *e.g.*, acetonitrile. The formula $\text{AgNO}_3 \cdot 2\text{C}_3\text{H}_3\text{N}_3$ now established is in accordance with the composition of the previously described silver nitrate addition compounds of 2-phenyl-1,3,5-triazine and 2-phenyl-4,6-dimethyl-1,3,5-triazine.^{12e} That silver nitrite in acetonitrile gives a product $\text{AgNO}_2 \cdot \text{C}_3\text{H}_3\text{N}_3$ indicates that there may be different types of addition compounds as in the pyridine series.¹⁹ For an addition compound with mercuric chloride, Hinkel⁷ has already established the correct formula $\text{HgCl}_2 \cdot 3\text{HCN}$ (or $\text{HgCl}_2 \cdot \text{C}_3\text{H}_3\text{N}_3$) probably because this one has been prepared in benzene as an inert solvent. It may be noted that, though neither this formula nor that of the silver salt is compatible with VI for the assumed dimer of hydrocyanic acid, no explanation is given by Hinkel for these deviations.

Basic properties of *s*-triazine undoubtedly will be very difficult to demonstrate in aqueous or similar systems, because of the sensitivity of the compound to hydrolysis. However in non-polar solvents stable adducts are formed with hydrohalogen acids, from which the hydrogen chloride addition product has been closely examined. Nef⁸ originally claimed that the sesquihydrochloride of hydrocyanic acid (IV) is formed again. Later Hinkel⁷ found that only the chloromethylene-formamide (V) is formed from the components in such inert solvents as ether. Even with a large excess of hydro-

(19) L. Kahlenberg and R. K. Brewer, *J. Phys. Chem.*, 12, 287 (1908).

gen chloride it is impossible to reconvert V into IV. This seemed peculiar in view of the ease with which the reactions from IV to V proceed. We have re-investigated this reaction and have confirmed his experimental findings. *s*-Triazine forms quantitatively a compound of the empirical formula $2\text{HCN}\cdot\text{HCl}$, and from this product *s*-triazine is easily recovered by removing the hydrogen chloride with a tertiary base, e.g., quinoline.⁶ We therefore consider this adduct as the sesquihydrochloride of 1,3,5-triazine, $3\text{HCl}\cdot 2\text{C}_3\text{H}_3\text{N}_3$ (IX). The insolubility of IX in all non-polar solvents and its tendency to sublime *in vacuo* without decomposition agree much better with structure IX than with V. The almost quantitative formation of IX from the "sesquihydrochloride" under very mild conditions, e.g., merely by standing in a vacuum, suggests that the latter contains the triazine ring system. To correspond with the empirical formula we would then have to formulate the "sesquihydrochloride of hydrocyanic acid" as the sesquihydrochloride of 2,4,6-trichlorohexahydro-1,3,5-triazine (VIII). This structure explains at once the easy formation of IX from VIII as a dehydrochlorinating aromatization for which many close analogies exist in the aromatic series, e.g., the formation of trichlorobenzenes from the hexachlorocyclohexanes. Furthermore, the relative difficulty with which the last third of the chlorine content of VIII is removed now becomes understandable, while it could hardly be explained on the basis of the previous formulas IVa, or IVb, and V for these compounds. Unfortunately a direct proof for the assumed structures VIII and IX cannot be given by direct molecular weight determinations, since so far no solvent has been found in which they are soluble without change, nor are they vaporizable without decomposition or dissociation.

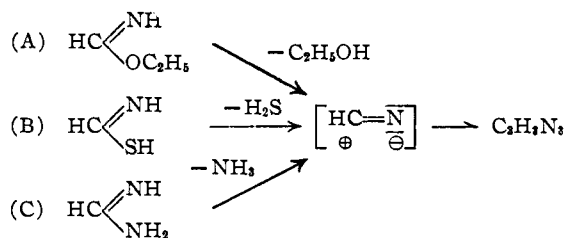
The formation of VIII from hydrocyanic acid may be explained through the intermediate formylimidochloride (VII), which we consider the first intermediate of the reaction between hydrocyanic and hydrochloric acid. VII trimerizes spontaneously to the trichlorohexahydro-*s*-triazine which stabilizes itself as the sesquihydrochloride (VIII). The whole course of the reaction between hydrocyanic and hydrochloric acid leading to *s*-triazine may be represented by the sequence



A striking analogy exists between the reaction product VIII of hydrocyanic and hydrochloric acids and those of the isonitriles of empirical composition

$2\text{R}\text{---}\text{NC}\cdot 3\text{HCl}$.²⁰ In this case the reaction leading first to the unstable intermediate XI, analogous to VII, ends with the formation of compound XII, as aromatization is impossible here because of the group R attached to the nitrogen. The addition compounds of isonitriles and hydrochloric acid must then be considered as sesquihydrochlorides of 2,4,6-trichloro-1,3,5-trialkyl-(or -aryl)-hexahydro-1,3,5-triazines (XII). One may then speculate that hydrocyanic acid reacts in this case also in the postulated iso form $|\text{C} \rightleftharpoons \text{NH}$, which would explain why the formation of analogous *s*-triazine derivatives is not observed in the nitrile series. In the case of acetonitrile a compound $2\text{CH}_3\text{---}\text{CN}\cdot 3\text{HBr}$ has been described among others²⁰ but we have convinced ourselves that these products as well as the above discussed addition products of nitriles and hydrochloric acid of the formula $2\text{RCN}\cdot\text{HCl}$ (I) are decomposed by quinoline exclusively to the original monomeric nitrile. No trace of the corresponding 1,3,5-triazine is formed, while from the true trimethyl-*s*-triazine hydrochloride²¹ the base can easily be recovered by the same treatment.

The literature reports two further modes of formation for *s*-triazine, (A) the decomposition of iminoethylformate hydrochloride by sodium hydroxide, the method by which Nef first discovered this compound,⁸ and (B) the thermal decomposition of thioformamide.²² We can now add a third: (C) the decomposition of formamidine hydrochloride, either thermally or (better) by interaction of a tertiary base, e.g., quinoline.²³ All these reactions apparently follow the same scheme, if we suppose that thioformamide also reacts in the imido form.



In each case one can assume an activated or polar transition state of hydrocyanic acid as an intermediate which spontaneously trimerizes to *s*-triazine.

Formamide exists predominantly in the true amide form; it is therefore understandable that an analogous reaction is not observed here. Dehydration leads exclusively to the monomer, hydrocyanic acid.

Acknowledgment.—We are very much indebted to the Mathieson Chemical Corporation for their generous support of this work. We wish to acknowledge the valuable assistance of Mr. J. A.

(20) A. Gautier, *Ann. chim.*, [4] 17, 176 (1869).

(21) Ch. Grundmann and G. Weisse, *Chem. Ber.*, 84, 684 (1951).

(22) R. Willstätter and T. Wirth, *ibid.*, 42, 1915 (1909).

(23) Ch. Grundmann, H. Schröder and W. Ruske, *ibid.*, in press.

Curtis, Mathieson Chemical Corporation, Research Department, Niagara Falls, N. Y., by spectroscopic and molecular weight determinations.

Experimental²⁴

Preparation of *s*-Triazine (X).—The procedure given by Hinkel, *et al.*,^{6,7} was followed but we were not able to attain the yields reported. In repeated experiments we obtained only 44%, compared with 60% and more given by Hinkel. We are inclined to attribute these discrepancies to the quality of the quinoline (Eastman synthetic) used, as it is known that *s*-triazine and its precursors react easily with primary, secondary and some tertiary aromatic amines, which might have been present in small quantities. This view is further confirmed by the fact that a technical grade quinoline (Eastman) yielded less than 10% of *s*-triazine. The two-stage process gave essentially the same results, although the conversion of VIII into the sesquihydrochloride of *s*-triazine (IX) could be brought up to 87% by distilling VIII under 30 mm. from an oil-bath at 160–180°. Sodium cinnamate, recommended by Hinkel as a dehydrochlorinating agent, was found unsatisfactory as well as sodium benzoate and potassium phthalimide, the resulting *s*-triazine being in all cases contaminated with the corresponding organic acid. Anhydrous sodium acetate and sodium formate gave no triazine at all, probably because rapid hydrolytical changes were caused by the liberated organic acids.

Calcium oxide gave a very poor yield of an impure product, because of hydrolysis by the water formed during the reaction. Liquid ammonia reacts moderately with VIII but after evaporation of the excess ammonia a violent reaction occurs when almost all of the solvent has disappeared, and from the remaining dark brown tarry residue no triazine could be isolated. Better results were obtained when a suspension of VIII in *m*-cresyl methyl ether was treated with gaseous ammonia under cooling until no more production of heat was observed. Distilling the reaction mixture then in a current of warm dry air yielded about 20% of *s*-triazine, which is a considerable improvement over the similar previously reported experiments in ether.²² Diphenyl ether and high boiling white mineral oil gave less favorable yields. As these results seemed to indicate that *s*-triazine once formed is easily destroyed in the reaction mixture, another experiment was carried out in which the triazine formed was removed from the reaction as soon as possible by passing a fast current of warm dry air together with gaseous ammonia over the finely powdered, well-stirred dry salt VIII. The flow rate of the ammonia was so regulated that the reaction mixture did not heat up above 50°. This experiment resulted in a 20% yield of *s*-triazine.

Triazine can be purified without appreciable loss by repeated distillation over metallic sodium. Like trimethyltriazine, crystals of the pure substance poured on the surface of water exhibit the Leidenfrost phenomenon known as the

(24) Melting points are corrected; analyses are by Galbraith Micro-analytical Laboratories, Knoxville, Tenn., if not otherwise indicated.

“camphor dance,” characteristic of many solid substances with a high vapor pressure and surface tension.²⁵

Molecular Weight Determination of *s*-Triazine.—Besides the data already reported,¹¹ cryoscopic determinations in benzene were made after having checked the reliability of the method, in this case with 2,4,6-trimethyl-1,3,5-triazine.²⁶

Anal. Calcd. for C₃H₃N₃: mol. wt., 81. Found: mol. wt., 89; 91.

Reaction of *s*-Triazine with Picric Acid.—A solution of 0.3 g. of *s*-triazine in 10 ml. of ethanol was mixed at room temperature with 50 ml. of a saturated solution of picric acid in the same solvent and kept for 12 hours at 0°. The resulting small yellow needles were filtered off and washed with some absolute ethanol; m.p. 258°, mixed melting point with an authentic sample of formamidinpicric acid, 257–258°.

Addition Compounds of *s*-Triazine with Silver Salts.—The different modes of preparation and the analytical results obtained from the reaction product of *s*-triazine and silver nitrate are shown in Table II.

TABLE II

Calcd. for AgNO₃·2C₃H₃N₃: N, 29.54; Ag, 32.50.

Method of preparation	Found	
	N	Ag
In CH ₃ OH, excess AgNO ₃ ^a	16.50, 16.46	36.45, 36.59
In C ₂ H ₅ OH, excess AgNO ₃ ^a	16.82, 17.01	28.65, 28.44
In CH ₃ OH, 1AgNO ₃ :2C ₃ H ₃ N ₃ ^a	19.35, 19.38	46.44, 46.44
	^b 19.46, 19.42	44.00, 43.75
In C ₂ H ₅ OH, 1AgNO ₃ :2C ₃ H ₃ N ₃ ^a	19.69, 19.90	31.30, 31.17
	^b 27.88, 27.80	33.96, 34.09
In CH ₃ CN, 1AgNO ₃ :2C ₃ H ₃ N ₃ ^c	28.48, 28.47	31.72, 32.42
	^c 25.02	35.15

^a Data by the analytical laboratories, Mathieson Chemical Corporation, Research Department. ^b From a different batch. ^c From the same batch as the previous analysis but after some standing in open air. The pure compound AgNO₃·2C₃H₃N₃ melts at 203° (dec.). No analytical difficulties were encountered with the addition compound of *s*-triazine and silver nitrite, which deposited in small yellowish prisms from acetonitrile solutions of the components. The product after being filtered from the mother liquor was washed with some acetonitrile and analyzed immediately after drying on the suction funnel.

Anal. Calcd. for AgNO₂·C₃H₃N₃: N, 23.84; Ag, 45.92. Found: N, 24.12; Ag, 45.55.

COLUMBUS, OHIO

(25) See N. K. Adam, “Physics and Chemistry of Surfaces,” Oxford University Press, New York, N. Y., 1941.

(26) Data from Hoffman Microanalytical Laboratories, Wheatridge, Col.