prepared from Fehling solution and glucose), and methanol (200 ml.) which had been saturated with ammonia at 0°, were heated in a stainless steel high pressure reactor at 200° for 18 hours. The contents were cooled to room temperature, transferred to a beaker, and the solvent was evaporated. The residue was thoroughly agitated with sodium hydroxide (0.5 *N*, 100 ml.) and allowed to stand overnight. The solid was separated from the basic solution by filtration and dissolved in boiling ethanol (95%, 100 ml.). This solution was decolorized with carbon and filtered. A small quantity of light green precipitate appeared, after the solution had stood overnight, and was removed. The nature of this precipitate has not been determined. The filtrate was evaporated to half volume and water was added to the hot solution to permanent cloudiness. The precipitate which formed was collected and recrystallized from benzene to give small white needles, of 2-(*p*-ethoxyphenyl)-4-amino-6-methyl-3(2H)-pyridazone, 1.5 g. (32%), m.p. 156–157°.

Anal. Calcd. for $C_{13}H_{15}N_3O_2$: C, 63.65; H, 6.16. Found: C, 63.52; H, 6.27.

AUBURN, ALABAMA

[CONTRIBUTION FROM THE OHIO STATE UNIVERSITY RESEARCH FOUNDATION]

Triazines. XI. Some Reactions of 1,3,5-Triazine[1,2]

BY CHRISTOPH GRUNDMANN AND ALFRED KREUTZBERGER

RECEIVED JULY 19, 1954

Chlorination of *s*-triazine yields cyanuric chloride and minor amounts of dichlorotriazine. Bromination gives at first a perbromide; at higher temperatures probably dibromotriazine hydrobromide is the main product, as its reaction with aniline yields dianilido-*s*-triazine. Sodium amide decomposes *s*-triazine to sodium cyanide and disodium cyanamide. *s*-Triazine is a powerful poison for noble metal hydrogenation catalysts; therefore catalytic hydrogenation was not possible. The constitution of the known double compounds of hydrocyanic acid and aluminum chloride and their behavior in the Friedel–Crafts reaction are discussed in view of their suggested triazine structure.

In previous papers[2,3] we have established that iminoformylcarbylamine ("dimeric hydrocyanic acid") is really 1,3,5-triazine (III) and furthermore suggested formulation of the dichloromethylformamidine hydrochloride ("sesquihydrochloride of hydrocyanic acid") as sesquihydrochloride of 2,4,6-trichloro-hexahydro-1,3,5-triazine (I) and the chloromethyleneformamidine as sesquihydrochloride of 1,3,5-triazine (II), mainly on the basis of their generic relationship with *s*-triazine itself, shown in the scheme below.

We present now further chemical evidence for the identity of the trimer of hydrocyanic acid with *s*-triazine by its conversion into *s*-triazine derivatives of known or established structure. With this purpose in mind we first studied the halogenation of *s*-triazine.

Chlorination of *s*-Triazine.—*s*-Triazine is not easily substituted by chlorine. At room temperature and in solution in carbon tetrachloride or chloroform a sluggish reaction takes place forming an insoluble precipitate. Application of ultraviolet light apparently increases the reaction to some extent. But the primary product is so extremely hygroscopic and also sensitive against elevated temperatures that all attempts to isolate a uniform compound failed so far. It is not improbable that the primary products of the chlorination are similar in structure to those obtained in the bromination of *s*-triazine which are described below, and that they decompose thermally in a similar manner. Chlorination in the vapor phase just above the boiling point of *s*-triazine or in CCl_4 at 100–110° in a sealed tube led only to the isolation of triazine sesquihydrochloride (II), which was identified by its known conversion with aniline into N,N'-diphenylformamidine.[4] The formation of II indicates that there must be a substitution reaction too, but also in this case we were unable to identify the other reaction products because of their instability.

At temperatures between 140 and 200° the chlorination of *s*-triazine in CCl_4 in a sealed tube yields about 25% of 2,4,6-trichloro-1,3,5-triazine, or cyanuric chloride (IV), which was further identified by its conversion with aniline into 2,4,6-trianilido-1,3,5-triazine (V). As a by-product (about 4%) 2,4-dichloro-1,3,5-triazine (VI) is formed, which could not be isolated as such but was identified after reaction of the mixture of the chlorination products with aniline as 2,4-dianilido-1,3,5-triazine (VII)[3a,6] No evidence for the presence of a monochlorotriazine could be found.

The 2,4-dianilido-1,3,5-triazine (VII) was synthesized for comparison by the following route: 2,4-Dianilido-6-chloro-1,3,5-triazine[5] (VIII) was converted with sodium hydrosulfide into 2,4-dianilido-6-mercapto-1,3,5-triazine (IX), which was then methylated with methyl iodide to 2,4-dianilido-6-methyl-mercapto-1,3,5-triazine (X). The latter was converted into VII by treatment with Raney nickel in dioxane, a method recently developed for the replacement of halogen by hydrogen in the triazine series.[7]

Bromination of *s*-Triazine.—Bromine with *s*-triazine at 0° in carbon tetrachloride readily forms an orange-colored well-crystallized addition compound, $C_3H_3N_3.3Br$, or possibly an analog to the triazine sesquihydrochloride, $2C_3H_3N_3.3Br_2$. The compound has the properties of a perbromide of *s*-triazine. Dissolved in water or in aqueous ethanol, the compound dissociates completely. The total bromine content can then be titrated as free

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[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: J. Goubeau, E. L. Jahn, A. Kreutzberger and Ch. Grundmann, *J. Phys. Chem.*, **58**, 1078 (1954).

[3] (a) Ch. Grundmann and A. Kreutzberger, THIS JOURNAL, **76**, 632 (1954); (b) Ch. Grundmann and A. Kreutzberger, *ibid.*, **76**, 5646 (1954).

[4] F. B. Dains, *Ber.*, **35**, 2496 (1902); L. E. Hinkel and R. I. Dunn, *J. Chem. Soc.*, 1834 (1930).

[5] J. T. Thurston, *et al.*, THIS JOURNAL, **73**, 2981 (1951).

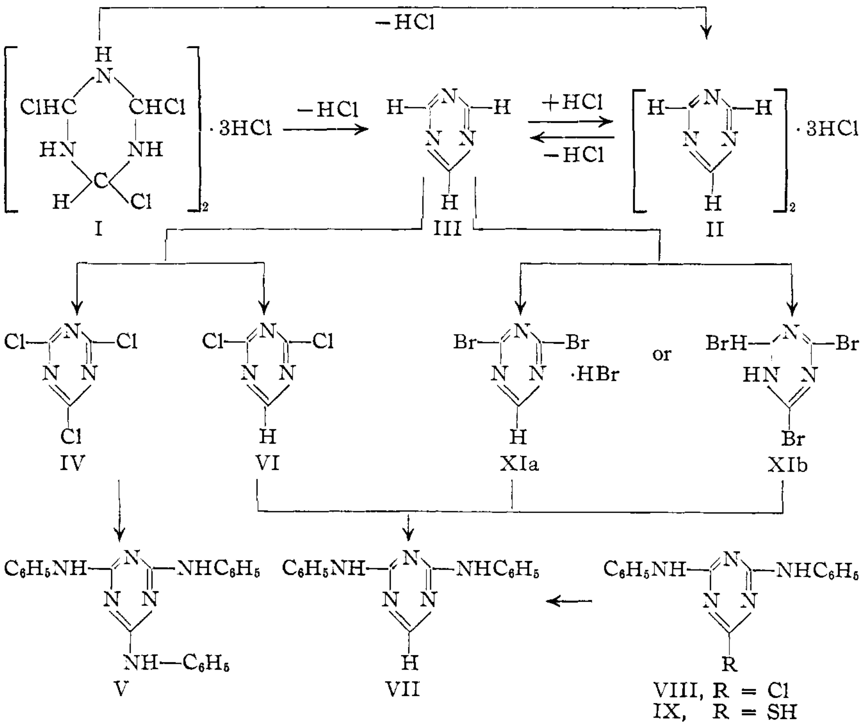
[6] I. Hechenbleikner, *ibid.*, **76**, 3032 (1954).

[7] Ch. Grundmann, H. Ulrich and A. Kreutzberger, *Ber.*, **86**, 181 (1953).

bromine, thus indicating that no substitution has taken place.

Analogous compounds are formed under the same conditions from 2,4,6-trimethyl-1,3,5-triazine and 2-phenyl-4,6-dimethyl-1,3,5-triazine, having the empirical compositions $C_6H_9N_3.2$ Br and $C_{11}H_{11}N_3.2$ Br, respectively. Also in these cases the whole bromine content can be determined by titration as free bromine. Perbromides of similar constitution and properties are well known in the pyridine series.

Substitution occurs when *s*-triazine is heated with bromine to 115–120°, obtaining in good yield a product which according to analysis contains three atoms of bromine per C_3N_3 unit but is not identical with the known 2,4,6-tribromo-1,3,5-triazine (cyanuric bromide). Reaction of this compound with aniline yields exclusively the 2,4-dianilido-1,3,5-triazine (VII), thus indicating that the starting material is either a 2,4-dibromo-1,3,5-triazine hydrobromide (XIa) or a tribromodihydrotriazine, for instance XIb. We feel that the insolubility of our bromo compound in all non-polar organic solvents supports the formula XIa. The same compound XI is formed by heating the above-described addition product of *s*-triazine and bromine to 150–160° in a sealed tube.



Attempts to brominate *s*-triazine by means of N-bromosuccinimide were unsuccessful.

Reaction of *s*-Triazine with Sodium Amide.—As pyridines and also pyrimidines[8] are aminated with sodium amide, we expected an analogous reaction of *s*-triazine which should lead to mono- or di- or triamino-*s*-triazine, all well-known compounds, and thus support the assumed structure of the starting material. But the reaction product of sodium amide with *s*-triazine in xylene at about 160° was extremely soluble in water to a strongly alkaline solution, thus ruling out the formation of any of the expected aminotriazines. We could prove qualitatively the presence of cyanide ion in this solution. Furthermore during the reaction much ammonia was evolved. The primary product when reacting with *n*-butyl bromide yielded di-*n*-butyl cyanamide $(C_4H_9)_2N{\cdot}CN$, which led to the conclusion that the starting material contained also disodium cyanamide. Based on these facts we suggest the following course of the reaction between sodium amide and *s*-triazine

$$C_3H_3N_3 + 3NaNH_2 = 3NaCN + 3NH_3$$
$$3NaCN + 3NaNH_2 = 3Na_2N{-}CN + 3H_2$$

Attempted Catalytic Hydrogenation of *s*-Triazine.—With palladium or platinum catalysts *s*-triazine could not be hydrogenated under atmospheric pressure in liquid phase, because of a pronounced inhibitory effect of *s*-triazine itself on the catalyst. The catalytic hydrogenation of cyclohexene, for instance, with a very active platinum catalyst is almost completely stopped by adding a small amount of *s*-triazine. Thus *s*-triazine appears to be a very effective poison for noble metal hydrogenation catalysts. This explains the previously reported failure to obtain *s*-triazine by the catalytic hydrogenolysis of cyanuric chloride.[7,9]

Friedel–Crafts Reactions of *s*-Triazine and its Hydrogen Chloride Derivatives.—In a series of papers Hinkel, *et al.*,[10] have carefully studied the interrelationships between hydrocyanic acid, the trichlorohexahydrotriazine sesquichloride, the triazine sesquichloride and triazine itself, and their various double compounds with aluminum chloride. In the light of our present knowledge the picture given by them should be modified as shown (Δ stands for $C_3H_3N_3$). As already recognized by Hinkel, aluminum chloride in all the above double compounds apparently weakens the C–N bonds in the triazine part of the molecule, thus giving rise to an easy depolymerization of these triazine derivatives. This is most evidently demonstrated by the fact that the compound XI—formed either from *s*-triazine and $AlCl_3$

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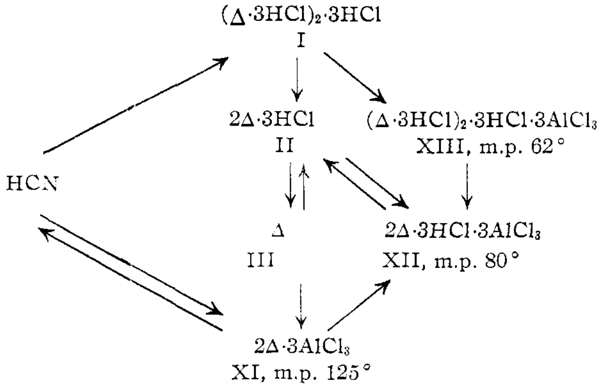
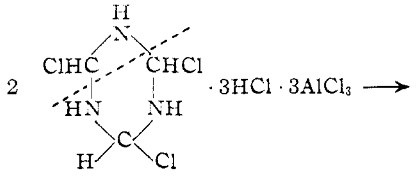
[8] E. Ochiai and M. Karii, *J. Pharm. Soc. Japan*, **59**, 18 (1939); *C. A.*, **33**, 3791⁶ (1939).

[9] A. Burger and E. D. Hornbaker, This Journal, **75**, 4579 (1954).

[10] (a) L. E. Hinkel and R. T. Dunn, *J. Chem. Soc.*, 3343 (1931); (b) L. E. Hinkel, E. E. Ayling and W. H. Morgan, *ibid.*, 2793 (1932); (c) L. E. Hinkel, E. E. Ayling and J. H. Beynon, *ibid.*, 674 (1935); (d) L. E. Hinkel and T. I. Watkins, *ibid.*, 407 (1940); (e) L. E. Hinkel and R. P. Hullin, *ibid.*, 1033 (1949); (f) L. E. Hinkel and G. H. R. Summers, *ibid.*, 2813 (1952).



or from HCN and $AlCl_3$—completely dissociates on simple dissolution in ether, or on moderate heating, into hydrocyanic acid, which can be isolated as such. In analogy one may expect similar dissociations of the double compounds XII and XIII, which would give (besides HCN) formimido chloride, HN=CHCl and formamido dichloride, $H_2N{-}CHCl_2$, respectively, as unstable intermediates. Under the conditions of the Friedel–Crafts reaction these intermediates will probably react at a very high rate with the aromatic compound present, yielding thus the numerous aromatic aldehyde derivatives observed by Gattermann, Hinkel and others. On the other hand, the depolymerization of XIII, if occurring stepwise, may generate a C_2-unit XIV as an unstable intermediate (besides formimido chloride)



XIII

$$2HN{=}CH{-}NH{-}CHCl_2 + 2NH{=}CHCl + 3HCl + 3AlCl_3$$

XIV

This intermediate XIV would then be responsible for the formation of derivatives of benzhydrylamine first obtained by Gattermann and Schnitzspahn.[11] In the case of mesitylene, Hinkel and Summers[10f] recently isolated besides the dimesitylmethylamine, derived from XIV, the mesitylaldehyde too, which according to the above sequence is generated from C_1-unit (formimido chloride) formed in the breakdown of the triazine ring.

The above-mentioned formation of benzhydrylformamidine hydrochloride (XV) from the "sesquihydrochloride of hydrocyanic acid"[11] seemed at first to be inconsistent with our formula I for the latter compound, as the authors claim to have obtained XV in yields as high as 85% of the theory based on their equation A. Our formula I would result in equation B, which allows only two moles of XV to be formed from the two C_3-units available in I. Therefore the yield based on Gattermann's equation A should not exceed 66.7%. A careful repetition of his work confirmed our anticipation. The maximum yield of XV was 53.5% based on equation A, corresponding to 80.5% calculated on equation B.

$$\text{(A)}\quad 2C_6H_6 + 2HCN{\cdot}3HCl \xrightarrow{AlCl_3} \underset{\text{XV}}{(C_6H_5)_2{-}CH{-}NH{-}CH{=}NH{\cdot}HCl} + 2HCl$$

$$\text{(B)}\quad 4C_6H_6 + \underset{\text{I}}{(C_3H_6N_3Cl_3)_2{\cdot}3HCl} \longrightarrow 2(C_6H_5)_2{-}CH{-}NH{-}CH{=}NH{\cdot}HCl + 5HCl + \underset{\text{XXV}}{2HN{=}CHCl}$$

A reinvestigation of the reactions of *s*-triazine and its hydrogen chloride derivatives with phenols and amines is at present in progress.

Acknowledgment.—We are very much indebted to the Mathieson Chemical Corporation for their generous support of this work. We wish to acknowledge furthermore the valuable assistance of Miss Mary W. Renoll in obtaining halogen determinations of some of the above described compounds.

Experimental[12]

Chlorination of *s*-Triazine at 100°.—A solution of 8 g. of chlorine in 32 g. of dry carbon tetrachloride was added to 3 g. of *s*-triazine, and the mixture was heated in a sealed tube at 100–110° for 7 hours. After cooling, the tube was opened and the formed brownish solid (2.3 g.) was separated by suction filtration. When this solid was sublimed up to 140° at normal pressure, 1.4 g. (27.7%) of a very hygroscopic white sublimate was obtained. In the sublimation flask a carbonized residue remained. The chlorine analysis of the white sublimate was in agreement with that calculated for *s*-triazine sesquihydrochloride (II).

Anal. Calcd. for $C_3H_9N_6Cl_3$ (II): Cl, 39.16. Found: Cl, 38.64.

Further evidence for II could be obtained by its reaction with aniline. When 0.5 g. of II was heated with 5 g. of aniline for a few minutes, cooled, and diluted with 15 ml. of acetone, followed by 40 ml. of water, small needles precipitated, which we identified as N,N'-diphenylformamidine, m.p. 141–142°.

Anal. Calcd. for $C_{13}H_{12}N_2$: C, 79.56; H, 6.16; N, 14.28. Found: C, 79.65, 79.73; H, 6.04, 6.25; N, 13.98, 13.89.

Chlorination of *s*-Triazine at 200°.—A mixture of 3 g. of *s*-triazine and 40 g. of a saturated carbon tetrachloride–chlorine solution was heated in a sealed tube at 200° for 7 hours. After cooling, a considerable excess of hydrogen chloride was noted on opening the tube. The contents of the tube were filtered off (filtrate A), leaving 4.8 g. of a reddish-brown solid. In order to identify this solid, it was suspended in 50 ml. of benzene and then 15 g. of aniline was added to it dropwise, whereby a reaction occurred with evolution of heat. A temperature of 145° was maintained for 4.5 hours, and then the reaction mixture was allowed to cool. By filtration, 7.1 g. of brownish solid was separated from the benzene filtrate (filtrate B). The solid was freed of any aniline hydrochloride by boiling with methanol and filtering to obtain 0.6 g. of 2,4-dianilido-1,3,5-triazine (VII), which, after recrystallization from aqueous acetic acid, melted at 316°. Mixed m.p. with an authentic sample of VII gave no depression.

On evaporation of the solvent from filtrate B *in vacuo* a reddish-brown resinous residue remained which could be dried on a porous plate and on recrystallization from benzene gave 0.4 g. of 2,4,6-trianilido-1,3,5-triazine (V), m.p. 236–237°. The material showed no melting point depression when mixed with an authentic sample.[13] An amount of 0.4 g. of 2,4,6-trianilido-1,3,5-triazine corresponds to 0.2 g. of cyanuric chloride (IV) originally formed.

The greater quantity of IV was obtained upon evaporation under reduced pressure of filtrate A; the crude substance was a white needle-like solid which had a strong lachrymatory property. Recrystallization from petroleum ether yielded 1.5 g. of cyanuric chloride which melted at 147–148° and

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[11] L. Gattermann and K. Schnitzspahn, *Ber.*, **31**, 1770 (1898).

[12] All melting points are corrected; microanalyses were by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

[13] P. Klason, *J. prakt. Chem.*, [2] **33**, 294 (1886).

showed no depression in melting point when mixed with authentic cyanuric chloride. A total yield of 1.7 g. of cyanuric chloride (24.9%) was obtained.

Anal. Calcd. for $C_3N_3Cl_3$: Cl, 57.69. Found: Cl, 57.41.

2,4-Dianilido-6-chloro-1,3,5-triazine (VIII).—The procedure used for the preparation of this compound was a modification of that described by Thurston, *et al.*[5] An amount of 124 g. of aniline was added dropwise to a stirred suspension of 62 g. of cyanuric chloride in 400 ml. of benzene at such a rate that the temperature of the reaction did not exceed 40°. The solid was filtered off, shaken for 0.5 hour with 500 ml. of water, filtered again and oven-dried. The yield was 93.5 g. (93.6%). Recrystallized from 70% ethanol, an amount of 74.8 g. of VIII in form of white needles was obtained, m.p. 201–202°.

Anal. Calcd. for $C_{15}H_{12}N_5Cl$: Cl, 11.91. Found: Cl, 11.99, 11.85.

2,4-Dianilido-6-mercapto-1,3,5-triazine (IX).—The required solution of sodium hydrosulfide was prepared by bubbling a CO_2 stream into a solution of 10 g. of $Na_2S \cdot 9H_2O$ in 300 ml. of tetrahydrofurfuryl alcohol until the necessary amount of sodium hydrocarbonate was precipitated. The precipitate was filtered off and the filtrate, containing the NaSH, boiled with 10 g. of 2,4-dianilido-6-chloro-1,3,5-triazine (VIII) at 150–155° for 3.5 hours. Allowed to stand overnight, the reaction mixture was acidified with hydrochloric acid, the white precipitate filtered and washed thoroughly with water. Since the material is insoluble in all common organic solvents, it could not be recrystallized. It was freed from any sodium salts by boiling with water and dried *in vacuo;* yield 8.5 g. (85.6%), m.p. 384–386°.

Anal. Calcd. for $C_{15}H_{13}N_5S$: C, 61.00; H, 4.43; N, 23.72. Found: C, 60.63, 60.81; H, 4.22, 4.48; N, 23.65, 23.69.

2,4-Dianilido-6-methylmercapto-1,3,5-triazine (X).—The methylation of IX either with iodomethane or dimethyl sulfate did not proceed easily, therefore we found it more convenient to prepare X directly from VIII as follows: twenty-seven grams of a 70% grade NaSH was dissolved in 100 g. of hot tetrahydrofurfuryl alcohol. To this solution 10 g. of 2,4-dianilido-6-chloro-1,3,5-triazine (VIII) was added and the mixture heated for 3.5 hours at 160–170°, cooled and filtered. Iodomethane (10 g.) was added in small portions to the clear filtrate with intense shaking, and the mixture became quite hot. After allowing the reaction mixture to stand for 1 hour, it was poured into 800 ml. of water, whereupon an oily substance separated, which, after some standing, solidified on grinding, yield, 8.5 g. (81.6%). Insoluble in water, ether and petroleum ether, the substance is soluble in all other common organic solvents. Two subsequent recrystallizations from 60% ethanol afforded the analytically pure compound, m.p. 170–171°.

Anal. Calcd. for $C_{16}H_{15}N_5S$: C, 62.11; H, 4.89; N, 22.64. Found: C, 61.83, 61.80; H, 5.04, 5.05; N, 22.78, 22.89.

2,4-Dianilido-1,3,5-triazine (VII).—Raney nickel from 125 g. of the alloy was added to a stirred solution of 6 g. of 2,4-dianilido-6-methylmercapto-1,3,5-triazine (X) in 200 ml. of dioxane. The mixture was stirred and heated at 60–70° for 5 hours, then the temperature was increased to 100° for a few minutes, the catalyst was filtered off and washed with hot dioxane. The combined washings and the filtrate deposited white crystals upon cooling. An additional amount of these crystals was obtained by evaporating the dioxane. The total yield was 1.9 g. or 38.2% based on X. The substance obtained upon recrystallization from aqueous acetic acid melted at 316°.

Anal. Calcd. for $C_{15}H_{13}N_5$: C, 68.42; H, 4.98; N, 26.60. Found: C, 68.05; H, 4.62; N, 26.42.

Bromination of *s*-Triazine at 0°.—To a solution of 3 g. of *s*-triazine in 40 ml. of dry carbon tetrachloride in a 250-ml. flask fitted with a stirrer, was added dropwise under exclusion of atmospheric moisture a solution of 19.0 g. of bromine in 40 ml. of dry carbon tetrachloride with cooling and stirring. When about one-third of the bromine solution had been added, an orange crystalline solid began to precipitate. The reaction mixture was allowed to stand overnight, then rapidly filtered with suction (filtrate A) and washed with small quantities of ice-cold dry carbon tetrachloride. The crude orange crystals (8.7 g.) melted at 68° and proved to be unstable at 20–30°, splitting off bromine and forming a resin. However, the material could be stored for months under exclusion of atmospheric moisture at 0°. Although soluble in all common organic solvents, any attempt to recrystallize the substance failed. It could be purified by sublimation at 40° under normal pressure; care had to be taken that the condensation surface was well cooled with ice water. Thus bright orange crystals were obtained, m.p. 70° dec.

Filtrate A, after being allowed to stand for one more week under refrigeration, afforded an additional 1.3 g. of orange crystals, so that a total yield of 10.0 g. (84.4%) was obtained.

The active bromine content of the triazine perbromide could be determined as follows: In 50 ml. of 50% aqueous ethanol 1.5 g. of potassium iodide and a weighed amount of 1,3,5-triazine tribromide in a gelatine capsule were dissolved. Iodine was liberated immediately, and after standing for 0.5 hour the solution was titrated with 0.1 *N* sodium thiosulfate solution.

Anal. Calcd. for $C_3H_3N_3Br_3$: Br, 74.75. Found: Br, 75.05 (Carius); 74.33 (titration).

2,4,6-Trimethyl-1,3,5-triazine Dibromide.—This substance was obtained from 2,4,6-trimethyl-1,3,5-triazine and bromine quite analogous to the above-described triazine perbromide; yellow needles, decomposing above 30°, yield 70.3%.

Anal. Calcd. for $C_6H_9N_3Br_2$: Br, 56.50. Found: Br, 56.48 (Carius); 56.21 (titration).

2-Phenyl-4,6-dimethyl-1,3,5-triazine Dibromide.—This compound was prepared from 2-phenyl-4,6-dimethyl-1,3,5-triazine and bromine as described above. This bromide is apparently much more stable than the two aforementioned triazine perbromides; orange prisms, m.p. 138–139° dec., yield 93.3%.

Anal. Calcd. for $C_{11}H_{11}N_3Br_2$: Br, 46.32. Found: Br, 46.81 (Carius), 45.86 (titration).

Bromination of *s*-Triazine at 120°.—In a typical experiment, a mixture of 4 g. of *s*-triazine and 24 g. of bromine was heated in a sealed tube for 5 hours at 120–125°. Hydrogen bromide was formed during the heating period, as evidenced by escape of this gas with some force when the tube was opened. The brownish-red mass was purified by alternating treatment with dry carbon tetrachloride and ether. Thus 14.8 g. (94.0%) of a yellow powder was obtained, which on heating decomposed at 290–300°.

Anal. Calcd. for $C_3HN_3Br_2 \cdot HBr$: Br, 74.97. Found: Br, 73.18.

2,4-Dibromo-1,3,5-triazine hydrobromide (XI) also was obtained, when the above described 1,3,5-triazine tribromide (8 g.) was heated in a sealed tube at 150–160° for 4 hours.

2,4-Dianilido-1,3,5-triazine from XI.—Twenty-five grams of aniline was added dropwise to a stirred suspension of 9.5 g. of XI in 100 ml. of dry ether. The temperature was maintained at 60–70° for the first hour, then slowly raised to 150°, thereby distilling off all of the ether. After 3 hours at 140–150°, the reaction mixture was allowed to cool and then filtered. To dissolve all aniline hydrobromide, the filter cake was boiled out with methanol; filtration then resulted in 0.8 g. (10.2%) of 2,4-dianilido-1,3,5-triazine (VII), which after recrystallization from aqueous acetic acid melted at 316°. No depression occurred when this was melted with an authentic sample of VII.

Reaction of *s*-Triazine with Sodium Amide.—A mixture of 6 g. of *s*-triazine and 8.7 g. of sodium amide in 20 ml. of dry xylene was heated in an autoclave for 2 hours at 135–140° and for 6 additional hours at 160°. After cooling, the formed ammonia was released, and the brownish granular reaction product filtered off (10.9 g.). This product dissolved readily in twice its weight of water to form a strongly alkaline solution, giving the reactions of the cyanide ion. The crude reaction product (10.9 g.) as formed in xylene suspension was treated with 30 g. of *n*-butyl bromide in the autoclave for 7 hours at 150°. After cooling, the contents of the autoclave were filtered, the remaining solid was several times extracted with boiling xylene and *n*-butyl bromide, and the combined extracts and filtrate were freed from the solvents by distilling up to 200°. The remainder was then distilled *in vacuo*, yielding 6.2 g. of di-*n*-butylcyanamide, identified by analysis and by comparison with an authentic sample[14]; b.p. 81–82° (2 mm.), n^{25}_D 1.4369, d^{25}_4 0.8705.

Anal. Calcd. for $C_9H_{18}N_2$: C, 70.08; H, 11.76; N, 18.16. Found: C, 70.06, 70.01; H, 11.60, 11.89; N, 18.02, 18.17.

Attempted Catalytic Reduction of *s*-Triazine. (A) With Palladium-on-charcoal Catalyst.—After being found active on maleic anhydride, the 16.6% palladium-on-charcoal catalyst (0.1 g.) was added to a solution of 2 g. of *s*-triazine in 20 ml. of cyclohexane and the mixture shaken with hydrogen for 2 hours at room temperature and thereafter for 2 additional hours at 70–75°. However, no absorption of hydrogen occurred.

(B) With Platinum Catalyst.—The attempted hydrogenation of 2 g. of *s*-triazine, using 0.08 g. of platinum from platinum dioxide in 25 ml. of cyclohexane also was unsuccessful both at room temperature and at an elevated temperature of 70–75°.

Cyclohexene (1.0 g.) in 30 ml. of decalin was completely hydrogenated with 0.17 g. of the same catalyst in 45 minutes. After adding 0.1 g. of *s*-triazine to such a run, no adsorption of hydrogen took place in 5 hours. The presence of 0.01 g. of *s*-triazine stopped the hydrogenation after 25% of the required hydrogen had been taken up in 3 hours.

Friedel–Crafts Reaction of 2,4,6-Trichlorohexahydro-1,3,5-triazine Sesquihydrochloride (I) with Benzene.—A vigorous reaction occurred when 7 g. of aluminum chloride was added in small portions to a stirred suspension of 10 g. of I in 11 g. of benzene. The reaction, when ceasing, was completed by heating the mixture for 1 hour on the steam-bath; the evolution of hydrogen chloride, noticed at the beginning of the heating, slackened after 0.5 hour. The reaction mixture, after cooling, was poured into 150 g. of ice-water slightly acidified by hydrochloric acid. The addition of more concentrated hydrochloric acid precipitated XV as a white solid which after separation and drying amounted to 8.1 g.

COLUMBUS, OHIO

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Configuration and Reactivity of 9-Substituted Decalins

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trans-9-Decalincarboxylic acid has been prepared from 2-keto-10-carbethoxy-$\Delta^{1(9)}$-octahydronaphthalene and its stereo chemistry established by conversion to *trans*-9-methyldecalin by way of the *trans*-9-decalylcarbinol and the tosylate. Previous workers had assigned a *cis* structure to this series of compounds. The acid also has been converted to *trans*-9-decalylamine and the material is in stereochemical agreement with the arbitrarily assigned structures. *trans*-9-Hydroxydecalin was prepared from Δ^9-octalin epoxide by lithium aluminum hydride reduction. The steric course of the reaction of the 9-aminodecalins with nitrous acid to yield 9-hydroxydecalins and octalins has been reinvestigated and the results discussed.

To date, various 9-substituted decalins have been prepared either by direct substitution on decalin itself or by proceeding from Δ^9-octalin by addition reactions. For example, nitration of *trans*-decalin has been reported[2,3] to yield only 9-nitrodecalin whereas the preparation of 9-chlorodecalin[4] by an exchange reaction with *t*-butyl chloride and aluminum chloride is accompanied by the simultaneous formation of lesser amounts of other isomers. Similarly, direct oxidation of decalin with oxygen gives rise to a 9-hydroperoxide[5] while ozone yields the 9-decalols.[6] In all of these compounds, the stereochemistry of the ring juncture has been arbitrarily assigned.[7] The preparation of 9-bromo- and 9-iododecalin[8] by addition of hydrogen bromide and hydrogen iodide to Δ^9-octalin, however, should yield *trans*-isomers while the stereochemistry of the products (*i.e.*, 9-nitroso, 9-amino and 9-hydroxy[3]) resulting from transformation of the addition compound obtained from this octalin and nitrosyl chloride again have been arbitrarily assigned.[7] The steric configuration of the isomeric 9-methyldecalins, on the other hand, is well established[9,10] and these compounds would serve as excellent reference points in a study pertaining to the 9-substituted decalins.

Before investigating the steric aspects of the reaction of nitrous acid with 9-aminodecalins, it was desirable to first establish with certainty, the configuration of the 9-amino- and 9-hydroxydecalins. A convenient procedure to accomplish such a correlation of configuration of amines and alcohols has been utilized in the *cis*-2-decalin series[11] where a carboxylic acid was degraded *via* stereospecific reactions to each type of compound. In order to employ a similar reaction sequence in the 9-decalin series, the preparation of a 9-decalincarboxylic acid was undertaken.

Preparation of *trans*-9-Decalincarboxylic Acid.—Recently, Hussey, Liao and Baker[12] reported the synthesis of a 9-decalincarboxylic acid by a sequence of reactions starting with 2-keto-10-carbethoxy-$\Delta^{1(9)}$-octahydronaphthalene (I), a compound previously prepared by DuFeu, McQuillin and Robinson[13] from 2-carbethoxycyclohexanone and 1,1-diethylamino-3-butanone methiodide. Hydrogenation of I followed by Wolff–Kishner reduction yielded a crystalline acid, the stereochemistry of which was stated to have been established by con-

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