[Contribution from the Ohio State University Research Foundation]

Triazines. XVII. *s*-Triazine from *s*-Triazine-2,4,6-tricarbonic Acid

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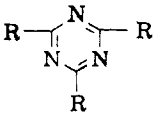
A method for the preparation of pure *s*-triazine-2,4,6-tricarbonic acid (II) through the acid chloride is described. II can be converted by thermal decarboxylation into *s*-triazine with an optimum yield of 34% under special conditions which prevent decomposition of the sensitive *s*-triazine. Some further reactions of the acid chloride of II are reported.

s-Triazine (IV) has previously been obtained from derivatives of hydrocyanic acid such as ethylformimidate hydrochloride,[3] thioformamide,[4] formamidine hydrochloride,[5] and from products whose structures have not yet been proved[6,7] unambiguously. Recently we have reported the conversion of cyanuric chloride (2,4,6-trichloro-*s*-triazine) into *s*-triazine.[8] This was the first time that IV was obtained from a *s*-triazine derivative of established structure. The yield, however, was extremely small. In this paper we describe the preparation of IV from another *s*-triazine derivative, namely, *s*-triazine-2,4,6-tricarbonic acid (II).

Trimerization of ethyl cyanoformate by means of hydrochloride acid yields triethyl *s*-triazine-2,4,6-tricarboxylate (I) almost quantitatively. By saponification with potassium hydroxide, I is converted into the tris-potassium salt. However, by acidification of an aqueous solution of this salt the free acid II is never obtained pure, because it has the marked tendency to adsorb strongly the formed inorganic potassium salts. Moreover, the tricarbonic acid is easily hydrolyzed by dilute acids to oxalic acid derivatives. The thermal decarboxylation of such impure samples of the tricarbonic acid II was tried in vain a long time ago by Weddige.[9] When 2-phenyl-*s*-triazine was recently prepared by decarboxylation of 2-phenyl-*s*-triazine-4,6-dicarbonic acid, a pronounced adverse effect was caused by the presence of neutral inorganic salts.[10] The possibility was therefore considered that a successful decarboxylation of II to *s*-triazine might still be achievable if a pure acid, especially free of inorganic material, would be used. Much effort then was spent to free the *s*-triazine-tricarbonic acid from the adhering potassium salts without appreciable success until it was found that the tripotassium salt of II is smoothly converted into the *s*-triazine-2,4,6-tricarbonic acid chloride (III) by phosphorus oxychloride. This acid chloride has been briefly described in a patent,[11] but the recommended procedure, reaction of II with a large excess of phosphorus pentachloride, gives a low yield of a very impure product which is not suitable for the purpose of this work.

The pure acid chloride III reacts normally with alcohols to produce the corresponding esters of *s*-triazine-2,4,6-tricarbonic acid, a reaction which proves its constitution. With water, however, even under moderated conditions, the main reaction products are cyanuric acid (V) and oxamic acid. This reaction, therefore, involves a fission of the originally formed tricarbonic acid II in a manner similar to the reported hydrolytic cleavage of II upon warming with water.[9] This hydrolysis of II can be avoided by treating the acid chloride with anhydrous formic acid, the only by-products in this case being hydrogen chloride and carbon monoxide. The acid thus prepared was ash-free and, after extensive drying, was used for the decarboxylation experiments which are described in detail in the experimental part.

s-Triazine can thus be obtained from the tricarbonic acid II in yields of 16 to 34%. In respect to yield this reaction is not attractive as a preparative method for *s*-triazine, but it does constitute another chemical proof for the structure of IV which, so far, has been mainly established from physical measurements and degradation reactions.



	R =
I	COOEt
II	COOH
III	COCl
IV	H
V	OH
VI	CHO
VII	COC_6H_5
VIII	CN_2—COOEt

The unusual decomposition of the acid chloride (III) with water is analogous to that of oxalyl chlo-

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[2] Preceding communication: Grundmann and Raetz, *J. Org. Chem.*, **21**, 1037 (1956).

[3] Nef, *Ann.*, **287**, 355 (1895).

[4] Willstätter and Wirth, *Ber.*, **42**, 1915 (1909).

[5] Grundmann, Schröder, and Ruske, *Chem. Ber.*, **87**, 1865 (1954).

[6] Hinkel and Dunn, *J. Chem. Soc.*, 1834 (1930).

[7] The product obtained by the methods referred under (3), (4), and (6) is erroneously described as dimeric hydrocyanic acid (iminoformyl carbylamine), *cf.* Grundmann and Kreutzberger, *J. Am. Chem. Soc.*, **76**, 832, 5646 (1954).

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

[9] Weddige, *J. prakt. Chem.*, [2] **10**, 212 (1874).

[10] Grundmann, Kreutzberger, and Ulrich, *Chem. Ber.*, **86**, 181 (1953).

[11] Ott, Swiss Patent 111,562 (1924).

ride, but unlike that compound, III was found to be quite stable thermally, boiling without decomposition at 221° at atmospheric pressure. Attempts to convert the acid chloride into the *s*-triazine-2,4,6-trialdehyde (VI) have been unsuccessful. The Rosenmund reduction could not be initiated, probably because of the catalyst-poisoning effect of *s*-triazines.[12] With lithium aluminum hydride only resins were obtained, both from III directly and from the tris-N-methylanilide of II according to Weygand's procedure.[13] The reaction of tristhiomethylester of II with Raney nickel did not yield either the aldehyde VI or the expected corresponding triole. On the other hand the acid chloride underwent a normal Friedel-Crafts reaction leading to 2,4,6-tribenzoyl-*s*-triazine (VII). From the reaction of III with diazomethane the expected tris-diazoketone could not be isolated, possibly because of its instability, but with the less reactive ethyldiazoacetate the corresponding 2,4,6-tris-(carbethoxy-diazoacetyl)-*s*-triazine (VIII) was obtained.

EXPERIMENTAL[14]

Ethyl cyanoformate and *triethyl-s-triazine-2,4,6-tricarboxylate* (I) are best prepared according to the procedure given by Ott.[15]

The tris-potassium salt of *s*-triazine-2,4,6-tricarbonic acid is obtained in better yield by the following modification of Weddige's original procedure:

The finely powdered triethyl ester (I) (39 g.) was added in small portions to a stirred, ice-cooled aqueous 2 *N* potassium hydroxide solution (175 ml.). Stirring was continued for about three hours until only traces of the ester remained undissolved and the alkalinity had dropped to *p*H 7–8. The solid ester remaining was removed by filtration and the filtrate was mixed with 1000 ml. of absolute ethanol. The crystallized potassium salt was vacuum-filtered, washed thoroughly with absolute ethanol, and dried *in vacuo* over calcium chloride. Yield: 43 g. (99%).

The free acid II, as precipitated from an aqueous solution of this salt, showed the same behavior as reported by Weddige.[9] No better results were obtained when the acid was liberated by formic or acetic acid. Although potassium formate and potassium acetate are extremely soluble in water, we found it impossible to free the tricarbonic acid (II) from these salts by extensive washing with water. Furthermore, the analysis of such samples revealed that hydrolytic cleavage had already taken place to a considerable extent.

s-Triazine-2,4,6-tricarbonic acid chloride (III). The finely powdered potassium salt of the *s*-triazine tricarbonic acid (37 g.) was introduced in small portions, with stirring, into 160 g. of phosphorus oxychloride at room temperature, over a period of 10 minutes, the temperature rising to 70°. When the spontaneous reaction had ceased, the mixture was refluxed for two hours. After cooling, the dark brown product was extracted three times with 100-ml. portions of anhydrous ether, leaving only inorganic material behind. The combined ethereal extracts were heated under a slight vacuum by a steam-bath, the ether and the excess phosphorus oxychloride distilling off. The acid chloride then distilled, at 114–115° and 0.2 mm., as a slightly yellow liquid with the characteristic pungent smell of the lower acid chlorides. Yield: 21.8 g. (73%), d_4^{20} 1.647. Upon standing it crystallizes completely, m.p. 54.5–56°.

Anal. Calc'd for $C_6Cl_3N_3O_3$: C, 26.85; Cl, 39.63; N, 15.66. Found: C, 26.82, 27.00; Cl, 40.07, 39.60; N, 15.89, 15.89.

The acid chloride III reacted with ethanol in a 91% yield to regenerate the triethyl ester (I), identified by melting point (169–170°) and mixture melting point with an authentic sample. With methanol the trimethyl ester (II) was obtained in a similar manner; white needles from methanol, m.p. 159.5–162° (Weddige[9] gives 154°). In this case, however, the yield was only 44%. The trimethyl ester is apparently much less stable than the triethyl ester; unlike I, it soon dissolves in boiling water undergoing extensive decomposition.

Anal. Calc'd for $C_9H_9N_3O_6$: N, 16.47. Found: N, 16.38, 16.39.

s-Triazine-2,4,6-tricarbonic acid (II). Hydrolysis of an ethereal solution of the acid chloride with ice-water yielded a crude acid which we tried to purify by recrystallization from glacial acetic acid. A considerable part of the material, however, was found to be insoluble in this solvent and was identified as cyanuric acid (V) both by analysis and by its characteristic reaction with Cu(II)-salts.

Anal. Calc'd for $C_3H_3N_3O_3$: C, 27.92; H, 2.34; N, 32.56. Found: C, 27.71; H, 2.59; N, 32.20.

The fraction of the original material which crystallized from hot acetic acid proved to be *oxamic acid*.

Anal. Calc'd for $C_2H_3NO_3$: C, 26.97; H, 3.40; N, 15.73. Found: C, 26.81; H, 4.13; N, 15.50.

s-Triazine-2,4,6-tricarbonic acid chloride (14.4 g.) was added dropwise with stirring to 50 g. of anhydrous formic acid at 0°. Stirring then was continued for 14 hours at room temperature during which time carbon monoxide and hydrogen chloride were evolved and a white precipitate of II formed. After two more days at room temperature, the tricarbonic acid was vacuum-filtered, washed thoroughly with ether, and dried *in vacuo* over potassium hydroxide. Yield: 9.4 g. (82%). As this product still had a slight smell of formic acid, it was extracted in a Soxhlet apparatus with ether for 48 hours. The acid then was white and odorless. The analysis showed the correct ratio of C and N, but the H values indicated a water content which could not be eliminated by drying the acid below its decomposition temperature. When heated in a capillary tube, the tricarbonic acid slowly started to decompose above 160° and carbonized gradually up to 350° without melting.

Anal. Calc'd for $C_6H_3N_3O_6$: C, 33.81; H, 1.42; N, 19.72. Found: C, 31.95, 31.92; H, 2.37, 2.15; N, 18.99, 18.84.

s-Triazine (IV) *from* II. Essential for the recovery of *s*-triazine was the knowledge of its properties gained from previous work.[16,8] The isolation procedure must especially take into account the high volatility of IV and its sensitivity to hydrolysis. Addition of copper improved the yields, but is not essential for the decarboxylation, while quinoline had no beneficial effect.

The pure acid III (2.0 g.) and copper powder (0.2 g.) were mixed intimately and heated over a free flame in a sublimation apparatus the condenser of which was cooled by Dry Ice and acetone. After a small forerun, consisting mainly of water and ammonium carbonate, the main portion of the sublimate condensed as a white crystalline mass which was extracted immediately with anhydrous ether. If this step was delayed for only 20 minutes, the yield dropped to less than 2%. The ether-insoluble part of the sublimate proved to be *ammonium carbonate*. The ether was removed from the extract by slow distillation through an

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(12) Grundmann and Kreutzberger, *J. Am. Chem. Soc.*, **77**, 44 (1955).

(13) Weygand and Eberhardt, *Angew. Chem.*, **64**, 458 (1952).

(14) All melting points are determined with the Fisher-Johns apparatus, microanalyses are from Galbraith Laboratories, Knoxville, Tenn.

(15) Ott. *Ber.*, **52**, 661 (1919).

(16) Grundmann and Kreutzberger, *J. Am. Chem. Soc.*, **76**, 5646 (1954).

efficient column until crystalline IV began to appear in the distillation flask. The flask then was removed from the column, cooled to −20° for several hours, and the *s*-triazine was separated by vacuum-filtering on a pre-cooled Buchner funnel (0.26 g.; 34.1%). In other experiments, quinoline which had been dried over potassium hydroxide and freshly distilled over aluminum amalgam, was used. The reaction mixture of II (3.8 g.), copper powder (0.9 g.), and quinoline (47 g.) was refluxed for six hours, while a moderate stream of dry nitrogen passed through the liquid to carry off the formed volatile products through an air-cooled reflux condenser and into a trap chilled with Dry Ice and acetone. By re-sublimation of the dark product thus collected a white material was obtained, which was purified in the same way as the sublimate described above (yield: 0.34 g.; 23.6%). In all cases the *s*-triazine was identified by a mixture melting point with an authentic sample. In view of the volatility and the sensitivity of IV it is obvious that the reported yields are minimum values.[17]

2-Triazine-2,4,6-tricarboxy-N-methylanilide. A mixture of 16.05 g. of N-methylaniline, 12 g. of anhydrous pyridine, and 100 ml. of ether was added dropwise over a period of 20 minutes with stirring to a solution, held at 0°, of 13.5 g. of III in 110 ml. of ether. The reaction mixture was stirred for two hours more at room temperature, and the precipitate was filtered off, washed with ether, and dried over potassium hydroxide. The crude N-methylanilide of II was recrystallized from large amounts of methanol or aqueous acetone (21.3 g.; 88.8%), m.p. 277–278°.

Anal. Calc'd for $C_{27}H_{24}N_6O_3$: C, 67.48; H, 5.04; N, 17.49. Found: C, 67.09; H, 4.86; N, 17.27.

Trimethyl-2,4,6-trithiolcarboxy-s-triazine. A solution of 13.4 g. of III in 300 ml. of anhydrous ether was added dropwise with stirring to 100 ml. of methanethiol held at −20°. After gradually warming up to room temperature the yellowish micro-crystalline powder which formed was vacuum-filtered and washed with ether. Two subsequent recrystallizations from ligroin (b.p. 90–98°) and chloroform yielded the pure thiolmethyl ester of II as small needles (m.p. 177–178°).

Anal. Calc'd for $C_9H_9N_3O_3S_3$: C, 35.63; H, 2.99; N, 13.85; S, 31.70. Found: C, 35.07; H, 3.05; N, 13.93; S, 32.09.

2,4,6-Tribenzoyl-s-triazine (VII). The Friedel-Crafts reaction of V must be carried out at room temperature, otherwise dark and resinous products predominate. The acid chloride III (13.4 g.) was dissolved in 250 ml. of anhydrous benzene and 34 g. of anhydrous aluminum chloride was added, while the reaction flask was surrounded with ice-water. The mixture was stirred for 17 hours at 20–25°, then poured upon a mixture of 500 g. of crushed ice and 500 ml. of conc'd hydrochloric acid. The organic products were extracted with benzene. The benzene layer, after drying over calcium chloride, was evaporated on the steam-bath and the residue was extracted six times with 900-ml. portions of ligroin (b.p. 90–98°). Upon cooling, VII crystallized from these extracts (13.2 g., 75%). After two recrystallizations from ligroin VII was obtained in colorless leaflets (m.p. 157–161°).

Anal. Calc'd for $C_{24}H_{15}N_3O_3$: C, 73.27; H, 3.84; N, 10.68. Found: C, 73.36; H, 3.77; N, 10.47.

2,4,6-Tris-(carbethoxydiazoacetyl)-s-triazine (VIII). A solution of 6.7 g. of III in 100 ml. of ether was added dropwise to a mixture of 18.8 g. of ethyl diazoacetate and 70 ml. of ether, held at 0°. An immediate evolution of nitrogen was observed. The mixture was gradually warmed to room temperature which was maintained for three days. The reaction was finally completed by refluxing for four hours. After distilling off ether, excess diazoester and the formed ethyl chloroacetate were removed under a vacuum at 84–89°/7 mm. The residue, an orange-colored oil, was precipitated several times from ether-petroleum ether, aqueous acetone, and ether-petroleum ether again. Finally, the oil crystallized, while in the refrigerator, to a yellow micro-crystalline powder (3.6 g.; 28.8%), m.p. 36–39°, which slowly decomposes at room temperature with evolution of nitrogen.

Anal. Calc'd for $C_{18}H_{15}N_9O_9$: C, 43.12; H, 3.02. Found: C, 43.16, 43.31; H, 3.03, 3.15.

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(17) Also from Weddige's crude acid *s*-triazine may be obtained, but in much lower yield. Especially in this case the crude reaction product always contained considerable amounts of water, ammonia, and other by-products which tend to decompose the formed triazine rapidly. If the purification of such crude products was delayed, even for a very short time, only traces of *s*-triazine could be isolated. This may explain the negative results of Weddige and others to prepare *s*-triazine by this reaction.