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Triazines XV. The Conversion of Chloro-*s*-triazines into their Parent Compounds, *s*-Triazine and 2-Methyl-*s*-triazine[1,2]

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The procedure for the conversion of chloro-*s*-triazines into their parent compounds *via* the hydrogenolysis of the thiomethyl derivatives with Raney nickel has been improved. *s*-Triazine has been obtained by this method from cyanuric chloride. 2-Methyl-*s*-triazine, the first known representative of the monoalkyl-*s*-triazines, has been prepared.

Some time ago a method was described for the replacement of halogen atoms in *s*-triazines by hydrogen.[3] The procedure consisted of exchanging the halogen with a methylmercapto group and subsequent hydrogenolysis with a large excess of Raney nickel. This method has since been found useful in several cases, especially, where the direct catalytic hydrogenolysis of the chlorotriazines is not possible because of the poisoning effect of the triazine on the catalyst.[3,4,5]

Previous attempts to synthesize *s*-triazine (III) from cyanuric chloride (I) *via* the 2,4,6-trismethylmercapto-*s*-triazine (methyltrithiocyanurate) (II) failed,[6] possibly because at that time we were not aware of the high volatility and sensitivity to hydrolysis of *s*-triazine. In the meantime it was discovered that the well known, so called "dimeric hydrocyanic acid" was in reality the long sought *s*-triazine.[7,8]

With *s*-triazine (III) now at hand a careful study of its properties could be made. Such an investigation revealed that the best way to isolate small quantities of III from dilute solutions is by precipitation as the sesqui-hydrochloride, 2 $C_3H_3N_3 \cdot 3HCl$ (IIIa). The liberation of *s*-triazine from IIIa with quinoline, as described by Hinkel,[9] is not a procedure well suited for working with milligram quantities. We found that the sesqui-hydrochloride IIIa is neatly reconverted into the free *s*-triazine by ethereal diazomethane. *s*-Triazine does not react with diazomethane under these conditions. While this procedure is not suited for large scale preparation of III, it has the advantage that only very volatile by-products (N_2 and CH_3Cl) are formed. This facilitates isolation of small amounts of *s*-triazine.

Methyltrithiocyanurate (II) does not react with Raney nickel in boiling ether, apparently because the temperature is too low. Dioxane, which has been tried before,[6] is not suitable since its boiling point is so close to that of *s*-triazine that separation is impossible. We therefore tried inert and high-boiling solvents, removing the *s*-triazine formed in the reaction mixture by entrainment in a current of nitrogen. This method avoided the further reduction of the *s*-triazine.

So now by the procedure as described in detail in the experimental part, we were finally able to isolate *s*-triazine in very small quantities from the reaction of methyltrithiocyanurate with Raney nickel. This route is without practical importance as compared to other methods for the preparation of *s*-triazine. Its significance lies in the fact that this is the first synthesis of *s*-triazine from another *s*-triazine derivative of established structure.

As could be expected from previous experiences the conversion of the 4,6-dichloro-2-methyl-*s*-triazine (IV) by the same sequence into the 2-methyl-*s*-triazine (VI) runs much better, since the last step in this case involves only the removal of two methylmercapto groups. The volatility of VI, however, makes necessary special deviations from the original procedure which result in an optimum yield of 30%. The 2-methyl-*s*-triazine thus obtained as the first known representative of the monoalkyl-*s*-triazines is a very volatile crystalline compound, melting at 50–50.5°. Contrary to the parent compound it has a pronounced odor resembling crude acetamide. It is a weak base, forming in non-aqueous media a hygroscopic hydrochloride similar to *s*-triazine itself. The sensitivity of VI to hydrolysis by acids and bases is of the same order as that of the parent substance III; however, VI does not exhibit the characteristic ring cleavage of *s*-triazine (III) by primary amines forming N,N′-disubstituted formamidines.[10]

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[2] Preceeding communication: Schroeder and Grundmann, *J. Am. Chem. Soc.*, (in press).

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

[4] Grundmann and Kreutzberger, *J. Am. Chem. Soc.*, **77**, 44 (1955).

[5] Brandenberger and Schwyzer, *Helv. Chim. Acta*, **38**, 1396 (1955).

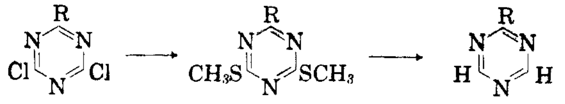
[6] Ulrich, *Diploma Thesis, Humboldt-University*, Berlin, Germany, 1952.

[7] Grundmann and Kreutzberger, *J. Am. Chem. Soc.*, **76**, 632 (1954).

[8] Grundmann and Kreutzberger, *J. Am. Chem. Soc.*, **76**, 5654 (1954).

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

[10] Grundmann and Kreutzberger, *J. Am. Chem. Soc.*, **77**, 6559 (1955).



I R=Cl II R=CH_3—S III R=H
IV R=CH_3 V R=CH_3 VI R=CH_3

EXPERIMENTAL[11]

Preparation of the Raney nickel catalyst. The yields obtained in the hydrogenolysis reactions described below were largely dependent on the quality of the Raney nickel employed. It was found especially important that the catalyst be free of the last traces of alkali and completely anhydrous. The catalyst was prepared from the commercial alloy according to Mozingo.[12] After the washing water has reached *p*H 7, the nickel must be washed at least 20 times more with distilled water. When the catalyst was used in a low-boiling solvent, the water was removed by the method of Mozingo. When a high-boiling solvent was used, water was removed from the Raney nickel by washing 20 to 30 times with absolute alcohol and then five times with the applied solvent. The catalyst, dispersed in the necessary amount of the solvent, then was heated to 160–180° for 24 hours. During the period a slow current of dry pure nitrogen was passed through in order to remove the last traces of all low-boiling solvents which, if not removed, would interfere with the isolation of the volatile triazines.

2,4,6-Tristhiomethyl-s-triazine (II). II was prepared from cyanuric chloride and sodium hydrogen sulfide in methanol *via* the trithiocyanuric acid in analogy with the procedure described by Klason.[13] Crude trithiocyanuric acid (38 g.) was dissolved in a solution of 30 g. of sodium hydroxide in 500 ml. of methanol, the insoluble material (3 g.) was filtered off, and 200 g. of methyl iodide was added with stirring. A crystalline precipitate formed immediately and was filtered off after three hours at room temperature. The pale yellow crystals were washed with ethanol and dried in a desiccator; m.p. 180–183°, yield: 85%. After one recrystallization from glacial acetic acid, II melts at 189° and is sufficiently pure for the hydrogenolysis. The reaction of cyanuric chloride with sodium methyl mercaptide in methanol which is recommended in the literature[13,14] for the preparation of II results, according to our experiences, in a much lower yield of a product contaminated with methoxytriazines and which is difficult to purify by recrystallization.[6]

4,6-Bisthiomethyl-2-methyl-s-triazine (V). To a solution of 11.5 g. of sodium in 500 ml. of absolute alcohol, 100 g. of methyl mercaptan was added while cooling with ice. To this an ice-cold solution of 41 g. of 4,6-dichloro-2-methyl-*s*-triazine[15] in 500 ml. of absolute alcohol and 400 ml. of dry acetone was added dropwise while stirring at 0°. The reaction mixture was stirred for four hours at 0° and then for 24 hours more at room temperature. The sodium chloride then was removed by vacuum-filtration and the solvents were removed by vacuum-distillation. The remaining residue was recrystallized from alcohol yielding white, long needles, m.p. 72–73°. Yield: 39.2 g. (84%).

Anal. Calc'd for $C_6H_9N_3S_2$: C, 38.48; H, 4.84; N, 22.44. Found: C, 38.46; H, 4.82; N, 22.50.

s-Triazine from s-triazine sesqui-hydrochloride and diazomethane. To a suspension of 3.8 g. of triazine sesqui-hydrochloride, $2\ C_3H_3N_3 \cdot 3\ HCl$, in 50 ml. of anhydrous ether a solution of 6 g. of diazomethane in 250 ml. of ether was slowly added while stirring at 0°. After storage of the solution for five days, insoluble by-products were filtered off and the excess diazomethane and ether were removed by fractional distillation using a Widmer column of 30-cm. length. At the end of the distillation, the *s*-triazine begins to crystallize from the ether. At this point the distillation is interrupted and the contents of the flask are kept for one day at −25°. The crystals then are rapidly filtered and dried between filter paper (0.49 g.). A second crop was isolated on further concentration of the mother liquor resulting in a total yield of 0.53 g. of *s*-triazine (47%). After one sublimation, the product had a melting point of 85–86°; with an authentic sample of *s*-triazine there was no depression of the melting point.

The 2,4,6-trichlorohexahydro-*s*-triazine sesqui-hydrochloride ("sesquihydrochloride of hydrocyanic acid") reacts vigorously with diazomethane; however, in this case only intractable resins, but no *s*-triazine, were isolated.

Hydrogenolysis of 2,4,6-trismethylmercapto-s-triazine (II). A suspension of 50 g. of Raney nickel in 150 ml. of anhydrous decalin was heated with 10 g. of methyltrithiocyanurate (II) to 150–160°, while a slow stream of dry nitrogen was passed through the reaction flask. The flask was connected to a Vigreux column which, in turn, was connected to a Dry Ice trap. After six hours a small amount of decalin containing the formed *s*-triazine had condensed in the receiver. After dilution with 50 ml. of anhydrous ether, the *s*-triazine was converted into the hydrochloride (IIIa) by passing hydrogen chloride through the solution until no more precipitate formed. The white, crystalline, very hygroscopic product was rapidly filtered off, washed with anhydrous ether, and dried over sodium calcium hydrate. Yield: 0.6 g. (10%).

Anal. Calc'd for $C_6H_9Cl_3N_6$: Cl, 39.17. Found: Cl, 37.12.

Free *s*-triazine, prepared from this hydrochloride by the procedure described above gave a melting point and mixture melting point of 85–86°.

To another sample of the decalin-triazine distillate an ethereal picric acid solution was added. After allowing this solution to stand for three hours at room temperature, long yellow needles of formamidine picrate were obtained, m.p. 237–238°. Formation of this picrate from *s*-triazine under these conditions has already been reported.[8] The formamidine picrate was identified by a mixture melting point with an authentic sample.

Hydrogenolysis of 4,6-bis-thiomethyl-2-methyl-s-triazine (V). Since attempts to carry out the reaction of V with Raney nickel in decalin resulted in a product which was difficult to separate from the adhering decalin, the use of a less volatile solvent was considered. A silicone oil (Dow Corning Fluid 200) proved unsatisfactory, only traces of 2-methyl-*s*-triazine being formed, apparently because of inactivation of the catalyst by the solvent. The best results so far were obtained with a purified high-boiling petroleum distillate (Phillips 66, Soltrol 170, distillation range about 215–245°).

The mixture of 6.5 g. of V and 100 g. of Raney nickel in 300 ml. of Soltrol 170 was kept between 140 and 160° for 40 hours with stirring, while a slow stream of dry nitrogen was passed through. The formed 2-methyl-*s*-triazine (VI) distilled through a Vigreux column and condensed in glittering leaflets in the upper parts of the Dry Ice trap, while in the bottom of the trap a solution of VI in Soltrol 170 was found. Thus 0.33 g. of 2-methyl-*s*-triazine was obtained directly and 1.16 g. of VI-hydrochloride was recovered by conversion of the VI in the Soltrol solution to the hydrochloride, as described above; over-all yield: 32%.

The 2-methyl-*s*-triazine is purified by sublimation at room temperature (using a Dry Ice- and acetone-cooled condenser) and by recrystallization at −25° from petroleum ether (b.p. 35–38°) yielding very volatile needles, m.p. 50–50.5°.

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(11) All melting points are corrected. The microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn., and Spang Microanalytical Laboratory, Plymouth, Mich.

(12) Mozingo, *Org. Syntheses*, **21**, 15 (1941).

(13) Klason, *J. prakt. Chem.*, [2] **33**, 116 (1886).

(14) Hofmann, *Ber.*, **18**, 2206 (1885).

(15) Hentrich and Hardtmann, U.S. Patent 1,911,689 (1933); *Chem. Abstr.*, **27**, 3952 (1933).

Anal. Calc'd for $C_4H_5N_3$: C, 50.51; H, 5.30; N, 44.19. Found: C, 50.63, 50.41; H, 5.32, 5.50; N, 44.20, 44.08.

Purification of the 2-methyl-*s*-triazine hydrochloride proved to be extremely difficult because of its hygroscopicity which even seems to surpass that of the *s*-triazine hydrochloride (IIIa). Therefore the analytical data obtained do not permit conclusive establishment of an empirical formula.

Anal. Found: N, 25.74; Cl, 29.48.

Treatment of the crude hydrochloride with quinoline in an analogous manner to the described procedure for *s*-triazine,[8] however, leads to the isolation of 2-methyl-*s*-triazine which is identical to the specimen obtained directly from the hydrogenolysis.

When 0.13 g. of VI were dissolved in 0.45 g. of aniline and the mixture was heated for three hours at 90°, not even traces of ammonia could be detected. The work up did not indicate the formation of any N,N'-diphenylformamidine or N,N'-diphenylacetamidine. The sensitivity of the method was proved by admixing about 5% of *s*-triazine with VI. This *s*-triazine was easily detectable in the form of the N,N'-diphenylformamidine.

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