nal fraction, b.p. 63–65°, probably consisted of an azeotrope. The yield of pure ester represents the minimum value for large mechanical losses were sustained in handling the small sample.

Acknowledgment. We are indebted to the Research Corporation for financial aid in the pursuance of this work.

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Triazines. XVI. A New Synthesis for 1,2,4-Triazoles

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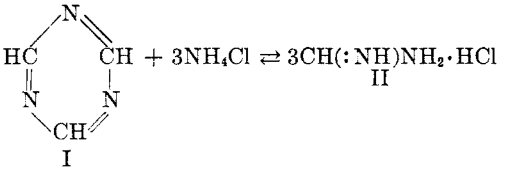
In our previous work on *s*-triazines it has been found that *s*-triazine (I) reacts with ammonia to form dark intractable resins.[3] However, with ammonium chloride in boiling ethanol a nearly quantitative reaction was observed which leads, with complete ring cleavage, to formamidine hydrochloride (II):[4]

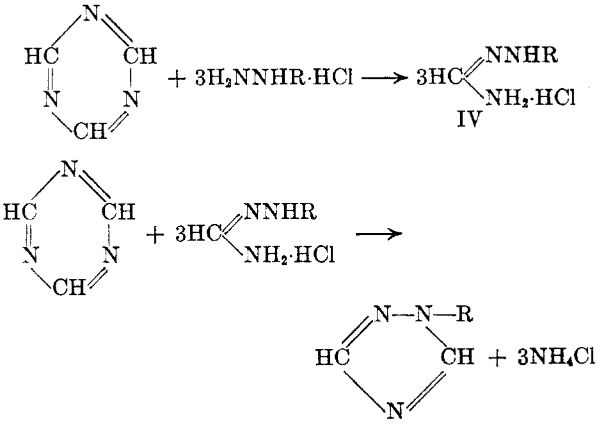


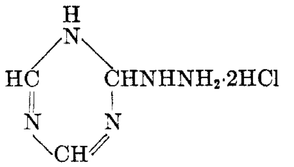
This reaction is essentially the reverse of the previously described formation of *s*-triazine by thermal decomposition of formamidine hydrochloride.[5] In contrast to its formation from *s*-triazine, the reconversion of the formamidine hydrochloride into I is far from being quantitative even in the presence of scavengers for hydrogen chloride.

The above described findings prompted us to attempt the reaction of I with hydrazine monohydrochloride (III) anticipating the formation of the yet unknown formamidrazone hydrochloride (IV, R = H). In boiling absolute ethanol I and III reacted promptly, but instead of IV, 1,2,4-triazole (V) and ammonium chloride were obtained in almost theoretical yields, according to the equation:

$$2C_3H_3N_3 + 3N_2H_4\cdot HCl \longrightarrow 3NH_4Cl + 3C_2H_3N_3$$

This reaction can be explained by a two-step process. First, one molecule of I undergoes the expected ring cleavage to IV. The formamidrazone then will react immediately with another molecule of *s*-triazine, in the same manner as recently described for *ortho*-diamines,[3] to yield 1,2,4-triazole and ammonia. This cyclization reaction seems to be favored since even with an excess of hydrazine monohydrochloride 1,2,4-triazole is the only isolable product.





VIII

V R = H
VI R = CH_3
VII R = C_6H_5

It seems that this reaction can be generalized in that use of mono-substituted hydrazine monohydrochlorides leads to 1-substituted 1,2,4-triazoles. Thus from methyl hydrazine monohydrochloride, 1-methyl-1,2,4-triazole (VI) is recovered and from phenylhydrazine monohydrochloride, 1-phenyl-1,2,4-triazole (VII) has been obtained. Good yields result in both cases.

Hydrazine dihydrochloride reacts in quite a different manner with I, since the only product isolated was an adduct, $C_3H_3N_3\cdot N_2H_4\cdot 2HCl$ which may tentatively be formulated as the dihydrochloride of 1,2-dihydro-2-hydrazino-1,3,5-triazine (VIII).

EXPERIMENTAL[6]

Formamidine hydrochloride from s-triazine. A mixture of 2.8 g. of *s*-triazine and 3.55 g. of ammonium chloride in 25 ml. of absolute alcohol was gently refluxed. After six hours, all of the NH_4Cl had gone into solution and the formamidine salt could be isolated by addition of an excess of ether. In

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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 Olin Mathieson Chemical Corporation, New York, N. Y.

[2] Preceding communication: Grundmann and Kober, *J. Org. Chem.*, 21, 641 (1956).

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

[4] This reaction has been found independently in the laboratories of the American Cyanamid Co. (private communication by I. Hechenbleikner at the 127th A.C.S. meeting in Cincinnati, March–April 1955).

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

[6] All melting points are determined with the Fisher-Johns apparatus. Microanalyses are by Galbraith Laboratories, Knoxville, Tenn., and Spang Microanalytical Laboratory, Ann Arbor, Michigan.

this way, 90% of the reaction product was isolated. An additional 8% was recovered by vacuum evaporation of the mother liquor. Formamidine hydrochloride was identified by analysis and by the mixture melting point of its picrate with an authentic sample of formamidine picrate.

Anal. Calc'd for CH_5ClN_2: N, 34.80; Cl, 44.10. Found: N, 34.43, 34.24; Cl, 43.63, 43.48.

Anal. Calc'd for *formamidine picrate* $C_7H_7N_5O_6$: C, 30.75; H, 2.56; N, 25.61. Found: C, 30.76, 30.90; H, 2.56, 2.66; N, 25.53, 25.57.

1,2,4-Triazole (V). To a solution of 16.2 g. (0.2 mole) of 1,3,5-triazine in 600 ml. of absolute alcohol (previously distilled from metallic sodium), there was added 20.55 g. (0.3 mole) of well-powdered hydrazine monohydrochloride. The mixture then was refluxed for eight hours. After cooling, 9 g. of ammonium chloride was filtered off. An additional amount (7 g.) was precipitated upon addition of ether to the filtrate, thus resulting in an almost quantitative yield (Calc'd 16.35 g.). The red-colored alcohol-ether filtrate was evaporated *in vacuo* to dryness. The remainder, 21 g., was recrystallized from chloroform yielding pure 1,2,4-triazole (95%). A mixture melting point with an authentic sample was without depression.

Anal. Calc'd for $C_2H_3N_3$: N, 60.87. Found: N, 60.80, 60.70.

1-Methyl-1,2,4-triazole. To a solution of 3.24 g. of *s*-triazine in 30 ml. of absolute ethanol 4.95 g. of methyl hydrazine hydrochloride was added. The reaction started immediately with evolution of heat and was completed by refluxing for eight hours. The precipitated ammonium chloride (2.2 g.) then was filtered off and the alcohol was removed through an efficient column. The oily residue was extracted with ether and an additional 0.9 g. of ammonium chloride which remained undissolved was removed by filtration. From the ethereal filtrate the ether was distilled leaving behind 4.0 g. of a yellowish oil which was almost pure 1-methyl-1,2,4-triazole. By distillation under atmospheric pressure the base was obtained colorless; b.p. 175–176°; m.p. 20°; yield: 81%.

Anal. Calc'd for $C_3H_5N_3$: N, 50.57. Found: N, 50.12, 50.10.

1-Phenyl-1,2,4-triazole (VI). A mixture of 16.2 g. of *s*-triazine and 43.4 g. of phenylhydrazine hydrochloride in 200 ml. of absolute alcohol was refluxed for 12 hours. After cooling, 12.5 g. of ammonium chloride was filtered off and the filtrate was distilled to remove the alcohol. There remained 36 g. of a light colored oil which crystallized upon storage in an icebox and consisted of almost pure 1-phenyl-1,2,4-triazole. By distillation under atmospheric pressure the base was obtained pure; b.p. 268–270°; m.p. 47°; yield: 83%.

Anal. Calc'd for $C_8H_7N_3$: N, 28.95. Found: N, 28.63, 28.68.

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Some Derivatives of Dihydroxyacetone

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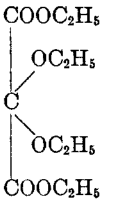
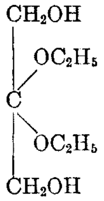
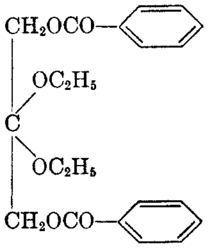
In connection with a study on carbohydrates it was necessary to prepare the diethyl acetal of dihydroxyacetone. Various methods of ketalation of dihydroxyacetone were investigated without success. However it was found that reduction of diethoxy diethyl malonate (I) with lithium aluminum hydride, afforded the desired acetal (II) in very good yield.



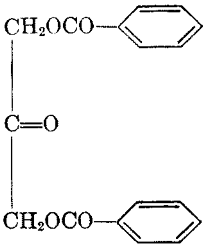
I



II



III



IV

This acetal is a crystalline substance which can be stored for long periods without decomposition. It does not reduce Fehling's solution. Mineral acids immediately cause hydrolysis and the resulting solution reduces Fehling's solution, even at room temperature.

The diethyl acetal can be benzoylated very easily to the corresponding dibenzoate (III) and the hydrolysis of the acetal grouping in III gave dibenzoxyacetone (IV) in almost quantitative yield.

EXPERIMENTAL[1]

We would like to thank Mrs. A. González from Syntex, S. A., for the microanalyses and Mr. F. Casas for technical assistance.

Diethoxy diethyl malonate was prepared from dibromo diethyl malonate according to Bischoff.[2]

Diethyl acetal of dihydroxyacetone (II). Diethoxy diethyl malonate (I) (50 g.) was dissolved in 400 ml. of anhydrous ether. The solution was added at room temperature during 2 hours with mechanical stirring to a slurry of 10 g. of lithium aluminum hydride in 300 ml. of ether, the mixture was refluxed 15 minutes, and the excess of hydride was destroyed with ethyl acetate; 20 ml. of a saturated solution of sodium sulfate was added with stirring and then enough anhydrous sodium sulfate until a clear solution was formed. The inorganic solids were filtered and thoroughly washed with ethyl acetate. The combined liquors were evaporated and the oily residue was crystallized by addition of hexane giving 27 g. of diethyl acetal (II) (81% yield) m.p. 79–80°. The analytical sample was obtained by repeated crystallization from ether-hexane. The product appears as long needles, m.p. 87–89°.

Anal. Calc'd for $C_7H_{16}O_4$: C, 51.20; H, 9.81. Found: C, 51.40; H, 9.83.

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(1) The melting points are uncorrected.

(2) Bischoff, *Ber.*, **30**, 487 (1897).