## 3-Amino-*as*-triazines

By John G. Erickson[1]

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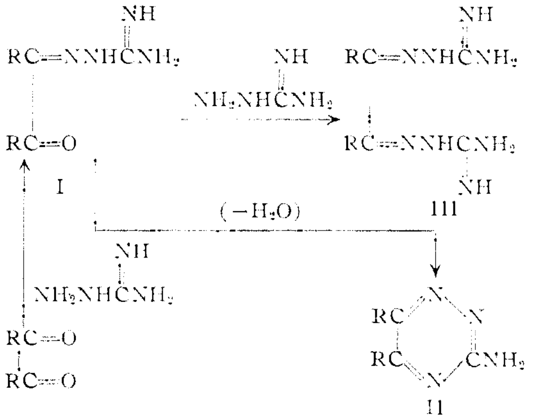
Thiele and Dralle[2] have studied the reactions of aliphatic 1,2-dicarbonyl compounds with certain aminoguanidine salts. Using glyoxal, biacetyl and dioxytartaric acid with aminoguanidine hydrochloride or nitrate in aqueous solution, they obtained no ring compounds. The monoguanylhydrazones (I), rather than cyclizing to *as*-triazines (II), reacted with a second mole of aminoguanidine and only osazone-like compounds (III) were isolated.



We have found that glyoxal and biacetyl react readily with aminoguanidine bicarbonate in aqueous medium at room temperature. 3-Amino-*as*-triazine (II, R = H) and 3-amino-5,6-dimethyl-*as*-triazine (II, R = $CH_3$) were obtained in this manner in good yields. These successful results are no doubt due to a difference between aminoguanidine bicarbonate and the hydrochloride and nitrate. The bicarbonate is relatively insoluble in water; its solutions therefore contain much lower concentrations of aminoguanidine salt than was the case with the hydrochloride or nitrate. As a result, monoguanylhydrazones are given a greater chance to cyclize before reacting further with aminoguanidine to form the osazones.

3-Amino-*as*-triazine appears to be the simplest *as*-triazine known.

**Acknowledgment.**—Analyses were performed by the Microanalytical Group of these laboratories.

### Experimental

**3-Amino-*as*-triazine.**—Thirty per cent. glyoxal solution in water (80 g., 0.41 mole of glyoxal) was added to a suspension of aminoguanidine bicarbonate (76.5 g., 0.56 mole) in 1200 ml. of water at 25°. The evolution of carbon dioxide began almost immediately. The mixture was stirred for two hours; at the end of this period the evolution of gas had virtually ceased. After standing overnight, the mixture was filtered and the filtrate was evaporated to dryness under reduced pressure. The residue was extracted with 1 liter of cold methanol. The methanol solution was filtered, evaporated to 100 ml., chilled and filtered again, yielding 24.0 g. (60.3%) of crude product as brown crystals. Recrystallization from acetonitrile gave fine, white needles, m.p. 171.5–172.5° (cor.), soluble in water.

*Anal.* Calcd. for $C_3H_4N_4$: C, 37.50; H, 4.19; N, 58.31. Found: C, 38.03, 38.03; H, 4.35, 4.30; N, 58.44, 58.05.

**3-Amino-5,6-dimethyl-*as*-triazine.**—A solution of biacetyl (64.4 g., 0.75 mole) in 250 ml. of water was added to a suspension of aminoguanidine bicarbonate (102 g., 0.75 mole) in 1250 ml. of water at 25°. The reaction was slow at first but carbon dioxide began gradually to be evolved. After standing for 22 hours at 25°, the mixture was warmed to 50° for an hour, then chilled and filtered, yielding 60.6 g. of nearly white solid, m.p. 208–210° (cor.). Concentration of the filtrate to 400 ml., followed by chilling and filtration, gave an additional 6.2 g. of product; total yield of crude product, 66.8 g. (82.6%). Recrystallization from toluene–ethanol (3:1 by volume) gave a very light yellow product, m.p. 211–212° (cor.). It is approximately 1% soluble in water at 25°.

*Anal.* Calcd. for $C_5H_8N_4$: C, 48.37; H, 6.50; N, 45.13. Found: C, 48.25, 48.52; H, 6.46, 6.73; N, 45.13, 45.13.

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[2] J. Thiele and E. Dralle, *Ann.*, **302**, 275 (1898).

## Preparation of N-Bis-(2-cyanoethyl)-acetamide[1]

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In the course of certain researches carried on in this Laboratory, a quantity of N-bis-(2-cyanoethyl)-acetamide was required. A search of the literature revealed two reports of this compound. In an attempt to characterize β,β′-iminodipropionitrile, Kost[2] reported the preparation of the acetyl derivative, N-bis-(2-cyanoethyl)-acetamide, and indicated a melting point of 146°. No details of the method of preparation are given, but it must be concluded from our findings that the reaction used was that between β,β′-iminodipropionitrile and acetyl chloride, inasmuch as the compound actually obtained was the hydrochloride[3] and not the acetyl derivative of β,β′-iminodipropionitrile.

In a patent[4] by McQueen, a preparation of N-bis-(2-cyanoethyl)-acetamide is described which involves the base-catalyzed reaction of acetamide and acrylonitrile.[5] The product was isolated as a liquid boiling at 210–225° and 2 mm., but no other physical constants are given. Several attempts to repeat the reaction in this Laboratory by adding acrylonitrile dropwise to a stirred solution of acetamide and catalytic amounts of Triton B in dioxane at about 30° were unsuccessful. The acetamide was recovered and a polymer of acrylonitrile was isolated.

We have obtained N-bis-(2-cyanoethyl)-acetamide as a solid (m.p. 50°) using very slightly more than two moles of amine to one mole of acid chloride. The excess amine permits complete reaction of the acid chloride by accepting the hydrogen chloride generated in the reaction.

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[2] A. N. Kost, *Vestnik, Moskov. Univ.*, No. 2, 141 (1947); *C. A.*, **42**, 3722 (1948).

[3] In a subsequent publication, the preparation of the hydrochloride of β,β′-iminodipropionitrile was reported, and its melting point was listed as 147–148°. No remark was made of the earlier erroneous report of the constants for the supposed acetyl derivative. See A. P. Terent'ev, *et al.*, *Zhur. Obschei Khim.*, **20**, 1073 (1950); *C. A.*, **44**, 9349 (1950); **45**, 1968 (1951).

[4] D. M. McQueen, U. S. Patent 2,424,664 (1947).

[5] In the review article on "Cyanoethylation," by H. A. Bruson, "Organic Reactions," Vol. V, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 79 *et seq.*, the reaction is represented as giving a 72% yield. However, no indication is given of the low conversion, 24%, reported by McQueen.