soluble material). Treatment of a pentane solution of the N-chloro compound with dry hydrogen chloride gave a quantitative recovery of benzyl phenyl ketimine hydrochloride, m.p. 209–211° (lit.[9] m.p. 210–211°). Acidification of a methanol solution of the product (1 g./10 ml.) with 1:1 concentrated hydrochloric acid–water liberated chlorine. These observations are in accord with those of Campbell[9]; however, the compound appeared to be much more stable than reported by Campbell.

The Reaction of Hydrazine with 3,6-Diamino-*s*-tetrazine[1]

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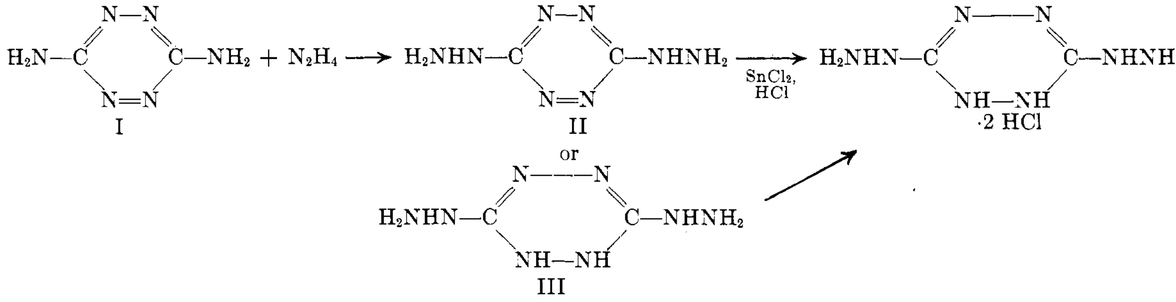
The reaction of hydrazine with 3,6-diamino-*s*-tetrazine was investigated. By suitable choice of reaction conditions, either 3,6-dihydrazino-*s*-tetrazine or the reduced form, 3,6-dihydrazino-1,2-dihydro-*s*-tetrazine, was isolated. The two products are interconvertible. Several derivatives of each are described.

The reaction of guanidine with hydrazine to yield triaminoguanidine has been reported in the literature.[2] As part of an investigation into the reaction of hydrazine with heterocyclic materials, the reaction of 3,6-diamino-*s*-tetrazine (I) with anhydrous hydrazine was investigated. Depending upon the reaction conditions chosen, it was found that this reaction produced either 3,6-dihydrazino-*s*-tetrazine (II) or 3,6-dihydrazino-1,2-dihydro-*s*-tetrazine (III).



If reaction is carried out at ambient temperatures, with no effort to exclude air, II is obtained. At slightly higher temperatures (40–50°), with rigorous exclusion of air, III results. When II is reduced with stannous chloride in hydrochloric acid, the product is identical with the hydrochloride salt prepared directly from III.

Hydrazine then is capable not only of formally displacing the amino groups from I, but also of acting as a reducing agent for the *s*-tetrazine ring. The reduction actually may have been accomplished by diimide or a substituted species of it,[3] although no effort was made to detect its existence, nor was any attempt made to investigate the reaction of diimide with I or II.

Attempts to verify the structure of II (or of III) by synthesis *via* alternate routes[4,5] were not successful, although some of the methods were not evaluated thoroughly. The structure of II was, however, established unequivocally by elemental analysis of the compound itself and of several derivatives (see Table I), and by conversion back to I. This was accomplished by treating it with nitrous acid to form the diazide, reducing the diazide with stannous chloride to 3,6-diamino-1,2-dihydro-*s*-tetrazime hydrochloride, and oxidizing the latter in aqueous base to yield a red, crystalline solid whose infrared spectrum and melting characteristics[6] proved it to be identical with the starting material. Thus the *s*-tetrazine ring remained intact during the hydrazinolysis of I and the reconversion of II to I.

Characteristics of II and III.—Compound II is a red solid, melting at 160–162° with decomposition. It reduces Fehling's solution in the cold. II crystallizes readily from dimethyl sulfoxide (DMSO) and is preferably recovered by the addition of alcohol. It is moderately soluble in hot sulfolane, dimethyl sulfoxide, and glacial acetic acid. Exothermic decomposition, however, appears to take place in the latter two solvents above 75°. Compound II is very slightly soluble in hot water and hot methanol. It is insoluble in the other aliphatic alcohols, dioxane, tetrahydrofuran, ethylene glycol dimethyl ether, acetonitrile, benzene, dimethylformamide, pyridine, chlorobenzene, and nitrobenzene. It decomposes rapidly in aqueous alkali and slowly in water. It is soluble in dilute hydrochloric

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[1] Contribution no. 312:62-105, Chemical Products Division, Aerojet-General Corp.

[2] (a) L. H. Diamond, Dissertation, University of Illinois, 1954, p. 98; (b) L. F. Audrieth and B. A. Ogg, "The Chemistry of Hydrazine," John Wiley and Sons, Inc., New York, N. Y., 1951, p. 215.

[3] E. E. van Tamelen, R. S. Dewey, M. F. Lease, and W. H. Pirkle, *J. Am. Chem. Soc.*, **83**, 4302 (1961).

[4] Among the routes investigated for compound II were the Hunsdiecker reaction with the silver salt of 3,6-dicarboxy-*s*-tetrazine; the bromination of *s*-tetrazine; and the fluorination of 3,6-dicarboxy-*s*-tetrazine. It was intended to replace the halogen of the 3,6-dihalo-*s*-tetrazine (had they been obtained) with hydrazine by direct metathesis. In addition, attempts were made to effect the oxidative ring-closure of S-methylthiocarbohydrazide hydriodide and the amination of I with hydroxylamine-O-sulfonic acid.

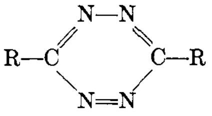
[5] Alternate routes investigated for the synthesis of III included the preparation of "*p*-dithiourazine" (prior to the disclosure of its structure as that of the isomeric N-aminodithiourazole) [A. W. Lutz, Abstracts, Division of Organic Chemistry, 139th National Meeting of the American Chemical Society, St. Louis, Mo., March, 1961, p. 3-O, and N. Petri, *Zeitschrift Naturforsch.*, **16B**, 767 (1961)], which was to be followed by alkylation and hydrazinolysis; the nitrosation of I with amyl nitrite, to be followed by reduction; and the hydrazinolysis of 3,6-diamino-1,2-dihydro-*s*-tetrazine. The latter compound, found to be stable in the form of its hydrochloride salt, was immediately oxidized to I in the presence of hydrazine.

[6] I does not melt up to 300°, but sublimes at about 200–240°.

TABLE I

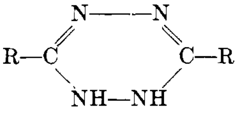
ELEMENTAL ANALYSIS

3,6-DISUBSTITUTED s-TETRAZINES



R	Formula	Carbon, %		Hydrogen, %		Nitrogen, %		Chlorine, %	
		Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
NH_2	$C_2H_4N_6$	21.46	21.52[a] 21.37	3.59	3.43 3.38	74.95	73.32 73.42		
$NHNH_2$	$C_2H_6N_8$	16.90	16.76[a] 16.81	4.26	4.27 4.19	78.84	78.92 79.17		
$NHNH_2 \cdot HCl$	$C_2H_8N_8Cl_2$ + 10.2% H_2O							29.6	29.97[b] 29.98
C_6H_5CHNNH	$C_{16}H_{14}N_8$	60.37	60.71[a] 60.63	4.43	4.52 4.66	35.20	35.15 34.99		
CH_3CHNNH	$C_6H_{10}N_8$	37.1	37.1[b]	5.18	5.09	57.7	55.0		
$CH_3CONHNH$	$C_6H_{10}N_8O_2$	31.9	32.1[b]	4.46	4.59	49.5	49.2		
$(CH_3CO)_2NN(COCH_3)$	$C_{14}H_{18}N_8O_6$	42.7	42.9[b]	4.60	4.71	28.4	27.7		

3,6-DISUBSTITUTED 1,2-DIHYDRO-s-TETRAZINES



R	Formula	Carbon, %		Hydrogen, %		Nitrogen, %		Chlorine, %	
		Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
$NHNH_2$	$C_2H_8N_8$	16.6	17.2[b]	5.59	5.71	77.8	77.4		
$NHNH_2 \cdot HCl$	$C_2H_{10}N_8Cl_2$							32.67	33.52[b] 33.58
C_6H_5CHNNH	$C_{16}H_{16}N_8$	60.0	59.9[b]	5.04	5.20	35.0	35.0		
$(CH_3)_2CNNH \cdot HCl$	$C_8H_{18}N_8Cl_2$	32.4	32.0[b]	6.06	6.30	37.7	37.4		

[a] Truesdail Laboratories, Inc., Los Angeles, Calif. [b] Analytical Laboratory, Aerojet-General Corporation.

acid; from more concentrated solution the dihydrochloride precipitates in light orange crystals with about 10% water of hydration.

Although the dry II has shown itself to be stable for many months on storage at ambient temperatures, spontaneous decomposition, accompanied by flame, has occurred several times after partial air drying of the crude II. Recrystallized II has never decomposed spontaneously. One can, therefore, bypass this critical drying stage either by immediately recrystallizing II, or by converting it to the hydrochloride salt while it is still thoroughly wet.

Pure III is a colorless substance, but is so readily oxidized that it has been obtained in this form for only a few minutes. It is normally obtained as light tan or light pink crystals, in which form it may be kept for substantial periods of time in a nitrogen filled drybox. In the presence of air, III gradually changes to II within several hours; in water, this oxidation requires only a few minutes. This conversion also may be brought about rapidly by heating III in air to about 140°, just below the melting point of II.

III is readily soluble in glacial acetic acid, indicating increased basicity on loss of aromaticity. Addition of ether yielded a white precipitate which was rapidly oxidized. Elemental analysis was inconclusive, but indicated a mixture of III mono- and diacetate. A brief kinetic study was undertaken to determine whether III was capable of decomposition to II in an inert atmosphere. At 100°, a small amount of hydrogen was found, but the major product was nitrogen. Attempts to follow the rate of decomposition were not too successful, in that the decomposition was very slow and the rates were not reproducible. The decomposition residues were not analyzed. It was concluded that, if III did undergo thermal dehydrogenation to II, there were other modes of decomposition which were kinetically far more favored under the experimental conditions employed.

Derivatives of II and III.—Among the well characterized derivatives of II which were prepared are the hydrochloride, benzylidene, ethylidene, diacetyl[7] and hexaacetyl derivatives, as well as 3,6-diazido-s-tetrazine, the oxidation product of II with nitrous acid. This latter compound was not confirmed by elemental analysis, for the sensitivity of the dry material was such that mere contact with a polyethylene spatula caused its detonation. For the same reason, no molar extinction coefficient was obtained. Its infrared spectrum in carbon tetrachloride solution, however, shows the characteristic —N=N=N— stretching absorption[8] at 2130 cm.$^{-1}$, whereas there is no absorption whatever in the normal NH region of 3200–3500 cm.$^{-1}$. Its infrared spectrum, extreme sensitivity to impact, method of preparation, and convertibility to I comprise the reasons for the assigned structure. All of the listed derivatives of II are highly colored compounds (*cf.* Table II). Their visible spectra deviate in some cases from the absorption range of 500–600 mμ (or even narrower, within this range) previously considered characteristic of tetrazines.[9–11] Elemental analysis of the derivatives are included in Table I.

The derivatives of III which have been characterized include the hydrochloride salt, the diisopropylidene

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(7) We assume the diacetyl derivative of II to be the bis(β-acetylhydrazino)tetrazine. I is a very weak base (see ref. 10); acetylation of the β-nitrogen should, therefore, be favored.

(8) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 230.

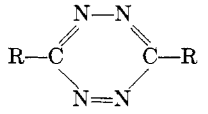
(9) E. Müller and L. Herrdegen, *J. prakt. Chem.*, **102**, 113 (1921).

(10) C. H. Lin, E. Lieber, and J. P. Horwitz, *J. Am. Chem. Soc.*, **76**, 427 (1954).

(11) V. A. Grakauskas, A. J. Tomasewski, and J. P. Horwitz, *ibid.*, **80**, 3155 (1958).

TABLE II

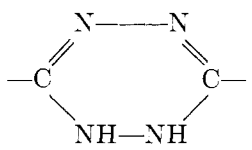
VISIBLE ABSORPTION MAXIMA OF *s*-TETRAZINES



R	Solvent	λ_{max}, mμ	ϵ_{max}	log ϵ_{max}
NH_2	Water	428^a	1,340	3.13
	Dioxane	428^a	1,980	3.30
		528^a	590	2.77
	Dimethyl sulfoxide	446		
		$\sim$520 (shoulder)		
	Methanol	433		
$NHNH_2$	Water	454	1,110	3.05
		$\sim$490 (shoulder)	1,080	3.03
	1,4-Dioxane	455	1,590	3.20
		$\sim$500 (shoulder)	1,187	3.07
	Dimethyl sulfoxide	465	1,340	3.13
		$\sim$500 (shoulder)	1,125	3.05
$CH_3CONHNH$	Water	424	1,810	3.26
		$\sim$475 (shoulder)		
	Dioxane	410	2,094	3.32
		516	718	2.86
$(CH_3CO)_2NN(COCH_3)$	Dioxane	356	1,682	3.23
		524	552	2.74
C_6H_5CHNNH	Dimethyl sulfoxide	350	27,600	4.44
		493	1,297	3.11
CH_3CHNNH	Dimethyl sulfoxide	482	1,220	3.09
		$\sim$500 (shoulder)	1,170	3.07
N_3	Carbon tetrachloride	371		
		517		
		527		
		536		
		549		

[a] Data taken from Ref. 10.

(also as the salt), and the dibenzylidene. These compounds are all colorless. The III-dibenzylidene is also oxidized to the II-dibenzylidene on prolonged standing, but is much more stable than III itself at ambient temperatures. Upon attempted recrystallization from dimethyl sulfoxide, however, only the II-dibenzylidene was recovered. Unlike the latter, the III-dibenzylidene reduces Fehling's solution in the cold, indicative of the following ring structure.



Experimental[12]

3,6-Dihydrazino-*s*-tetrazine (II).—Fifteen grams (0.134 mole) of crude I was suspended in a mixture of 82 ml. of hydrazine ($\sim$2.5 moles, minimum 95% free base) and 10 ml. of methanol in a 500-ml. round-bottom flask. After stirring at 20 ± 5° for 4 hr., no starting material remained. The volume of the dark brown solution was 100 ml. The hydrazine and methanol were removed under vacuum and the residue was treated with 25 ml. of cold water. After standing overnight, the solid was filtered and washed, first with ice-water and then with alcohol. The crude, dry 3,6-dihydrazino-*s*-tetrazine weighed 7.1 g. (38%), m.p. 146–147° dec. Occasionally, spontaneous decomposition has occurred while the crude product, only partially dry, was exposed to air.

An alternate, simpler method of isolation consists of quenching the reaction mixture by the addition of 3–5 vol. of cold water, followed by filtration and washing, as described. The yields are slightly lower (30–35%).

Three grams of crude II was dissolved in 80 ml. of dimethyl sulfoxide (J. T. Baker, reagent grade) at 60–80°.[13] The hot, deep red solution was filtered through cotton and diluted, first with 50 ml. of hot ethanol, which was added in a thin stream with stirring, and then with 30 ml. of cold 2-propanol. The addition of the alcohol caused immediate precipitation of II as glistening red crystals. The mixture was chilled to 10–15° while stirring, and the product filtered and washed with a few milliliters of a 50–50 mixture of dimethyl sulfoxide and 2-propanol. After a second recrystallization, which was carried out similarly, the dark red crystalline product weighed 2.0 g. (67% recovery). It melted at 160–162° dec.

3,6-Dihydrazino-*s*-tetrazine Dihydrochloride.—Five grams (0.035 mole) of crude II was added slowly to 20 ml. of concentrated hydrochloric acid at 5–10°. The temperature rose to 20°. Much stirring was required to break up the lumps of II. After all the II had been converted, the mixture was chilled below 10°, filtered, and washed first with 15 ml. of cold concentrated hydrochloric acid, and then with two 15-ml. portions of 2-propanol. The air-dried orange product weighed 5.8 g. (64%). No more hydrochloride could be isolated from the filtrate.

The salt was purified by recrystallization first from 45% aqueous 2-propanol and then from 4 *N* hydrochloric acid. It was found by gas chromatography to contain 10.2% water. On heating in a capillary tube, it turned bright orange-red at 80–90° (dehydration), and decomposed at 180–182°.

3,6-Bis(benzylidenehydrazino)-*s*-tetrazine.—A 25-ml. round-bottom flask was charged with 1.0 g. (0.007 mole) of II, 20 ml. of methanol, 3 drops of glacial acetic acid, and 2.65 g. (0.025 mole, 75% excess) of benzaldehyde. Reaction took place in the cold, accompanied by slight evolution of heat and a change in color of the solid from dark red to dull purple. The mixture was refluxed on the steam bath for 10 min, and the product filtered off, washed successively with ethanol and ether, and air dried. The crude benzal weighed 2.3 g. (100%) and decomposed at 249–251°. It was recrystallized twice from dimethyl sulfoxide. The glistening purplish platelets decomposed at 256–257°.

3,6-Bis(salicylidenehydrazino)-*s*-tetrazine.—A 20-ml. round-bottom flask was charged with 1.0 g. (0.007 mole) of crude II, 15 ml. of methanol, 3 drops of glacial acetic acid, and 3.05 g. (0.025 mole, 75% excess) of salicylaldehyde. After 10-min. reflux, the product was isolated in the same manner as the benzal. The crude disalicylal weighed 2.3 g. (94%) and melted with decomposition at 283–287°. The solid was dull purplish in color. A sample twice recrystallized from dimethyl sulfoxide decomposed at 286–287°. It was not submitted for elemental analysis.

3,6-Diethylidenehydrazino-*s*-tetrazine.[14]—One-hundredth mole of II (1.42 g.) and 0.88 g. of acetaldehyde (0.02 mole) were added to 25 ml. of dry dimethylformamide at 10° in a vessel equipped with a Dry Ice condenser. After 2 hr. at 25°, and 2 additional hr. at 50°, the mixture was concentrated to about 5 ml. The product crystallized in the form of brown-red clumps. It melted over an extended range, 168 to 190° with decomposition. A suitable method for the recrystallization of this derivative was not found. Elemental analysis was carried out on the unpurified product.

3,6-Diazido-*s*-tetrazine.—Five milliliters 4 *N* hydrochloric acid was placed in a large test tube, and 0.14 g. (0.001 mole) of once-recrystallized II added in small increments. The first portions dissolved quickly with the formation of a yellow-orange color; the last ones formed a yellow precipitate. The mixture was chilled to 2–3° and stirred with a magnetic ball. Over 18 min., 2.5 ml. of 1.0 *N* (0.0025 mole) of sodium nitrite solution was added dropwise at 3–6°. An orange precipitate separated soon after the addition was begun, and the stirring became rather ineffective. Toward the end of the addition, manual stirring with a thermometer had to suffice. The mixture was then allowed to stand with occasional stirring for 30 min. at 3–5°. The orange solid was filtered and washed thoroughly with water. A small portion was dried on a porous plate, m.p. 128–130° dec.

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[12] Melting and decomposition temperatures are uncorrected. All such temperatures were determined on a Fisher-Johns block, unless noted otherwise.

[13] It appeared that decomposition took place above 75° at such a rate as to cause a temperature increase. Care was, therefore, taken not to exceed this temperature.

[14] This work was performed by Dr. O. L. McCurdy.

The main portion of the wet azide was recrystallized by repeatedly pouring hot ethanol through the funnel, until a substantial quantity appeared to have gone into solution. To the red ethanol solution (estimated 10 ml.) was added about 2 ml. of water. After cooling in ice, the azide was collected as orange-red platelets, m.p. 130–131° dec. A sample of the recrystallized azide on an unglazed porcelain plate detonated on contact with a polyethylene spatula. Elemental analysis was not obtained because of the extreme sensitivity of the compound.

3,6-Diacetylhydrazino-*s*-tetrazine.—Approximately 0.7 g. of II was added to 10 ml. of acetic anhydride. The temperature rose to 37°, and a voluminous orange precipitate soon formed. Complete solution of the starting material was not attained. After 30 min., the mixture was filtered, and the precipitate was washed with a little acetic acid. The crude diacetyl II melted at 254–260° dec. The material was recrystallized first from water, and then from aqueous methanol. The purified product melted with decomposition at 265–268°.

3,6-Hexaacetylhydrazino-*s*-tetrazine.—One gram (0.007 mole) of II was refluxed for 15 min. with 15 ml. of acetic anhydride. The dark red solution was filtered through glass wool, chilled, and poured onto ice. Hydrolysis of the excess acetic anhydride was accelerated by occasional stirring. After 0.5 hr., the aqueous layer was decanted from the crude product, which was in the form of a semisolid. The latter was stirred with 2-propanol and the salmon powder which was obtained was filtered, washed with 2-propanol, and air dried. The yield was 0.24 g. (9%), m.p. 215–230° dec.

The crude product was again refluxed with 1.5 ml. of acetic anhydride for 10 min. in order to complete the acetylation. On cooling the intense magenta solution, salmon-colored crystals separated, which were filtered and washed, first with a little acetic anhydride and then with 2-propanol. Followingre crystallization from acetic anhydride (about 4 ml.), the purified hexaacetylated II melted at 226–232° dec.

Structure Proof. Reconversion of II to I. A.—The preparation of 3,6-diazido-*s*-tetrazine from II and nitrous acid was carried out as described. One millimole of II was used as the starting material in this particular preparation.

B.—The water-wet filter cake of diazidotetrazine was added to a cold solution of stannous chloride in concentrated hydrochloric acid. Immediate gas formation (nitrogen) was noted, and a colorless precipitate formed. After chilling the reaction vessel in ice for 10 min. with occasional stirring, the product was filtered and washed with a little cold concentrated hydrochloric acid.

The colorless salt was dissolved in a little water, the solution was chilled, and made basic by the dropwise addition of 1*N* sodium hydroxide solution. Almost immediately, bright red crystals separated from the mixture. The product was filtered, washed with water and alcohol, and air dried. It did not melt up to 300°, although some sublimation was noted near 220°. This behavior is characteristic of I.[10] Its infrared spectrum was identical in every respect with that of authentic I.

The nature of the reduction product was independently established as 3,6-diamino-1,2-dihydro-*s*-tetrazine hydrochloride by the reaction of I with stannous chloride in hydrochloric acid. The colorless reduction product was filtered, and washed with a little hydrochloric acid and then with ethanol. It decomposed at 220–225°, and reduced Fehling's solution in the cold. The addition of ammonium hydroxide to an aqueous solution of the salt caused precipitation of bright red crystals of I, further identified by its melting characteristics.

3,6-Dihydrazino-1,2-dihydro-*s*-tetrazine (III). A. Preparation by Reduction of II.—II (2.8 g., 0.02 mole) was added in portions to a solution of 19 g. of stannous chloride dihydrate (0.084 mole, A.R.) in 30 ml. of concentrated hydrochloric acid. A clear, colorless solution was obtained in about 15 min. A little ethanol (about 10 ml.) was added to the solution, causing immediate separation of a colorless oil and some crystals. After storage in an icebox overnight, the oil had solidified. The mixture was filtered, and the colorless solid washed with ethanol. The solid turned salmon at about 165° and decomposed near 170°. It was soluble in water, but insoluble in ethanol or concentrated hydrochloric acid. Three grams (70%) was obtained.

The hydrochloride was dissolved in water and filtered through filter-aid. The volume of clear, colorless filtrate was 14 ml. Addition of 12 ml. of concentrated hydrochloric acid caused the precipitation of the product hydrochloride which was chilled, filtered, and washed with cold 6 *N* hydrochloric acid. The wet filter-cake was dissolved in 6 ml. of water and the product precipitated by the addition of an equal volume of ethanol. The weight of purified III·2HCl was 1.2 g. (40% over-all recovery). The product decomposed at 170–172°.

In a 25-ml. erlenmeyer flask, 0.22 g. (0.001 mole) of III dihydrochloride was dissolved in 3.0 ml. of deionized water and chilled in ice during the purging and neutralization. Nitrogen was bubbled through this solution for 0.5 hr. prior to use, and during the subsequent neutralization. The 1.0 *N* aqueous sodium hydroxide solution which was used for this purpose was also purged with nitrogen for 0.5 hr. before use. After about one-half of the theoretical quantity had been added, a colorless solid precipitated (probably the monohydrochloride). The addition of base was continued until the mixture was basic to phenolphthalein. A trace of III dihydrochloride was then added, resulting in a colorless mixture which was neutral to litmus. After 10 min. the faintly pink solid was filtered off under a nitrogen blanket, washed with a little water, and dried in a vacuum desiccator. Both the wash water and the desiccator had been purged with nitrogen before use.

A 0.1-g. sample of III·2HCl, neutralized similarly but with no attempt to exclude air, resulted in the exclusive isolation of II, identified by its color, decomposition temperature, and infrared spectrum.

B. Preparation by Hydrazinolysis of I.—In a three-neck. 100-ml. flask equipped with a 50-ml. pressure-equalized dropping funnel, nitrogen inlet, and nitrogen outlet, was placed 10 ml. of 95% hydrazine, 2.0 g. (0.018 mole) of I and 1.0 ml. of methanol. This mixture was heated, with stirring, at 45–50° for 3 hr. Addition of 50 ml. of degassed water and cooling to −5° produced an essentially colorless precipitate which was filtered under nitrogen and washed with cold ethanol. The initially colorless material became light pink on contact with the degassed wash solution. Drying in a drybox gave 0.5 g. (20%) of powdered III.

A small sample of III obtained in this manner was suspended in 10 ml. of methanol. While chilling, hydrogen chloride gas was introduced until no more appeared to be absorbed. The nearly colorless crystals were filtered and washed with cold methanol. After one recrystallization from 4 ml. 6 *N* hydrochloric acid, the product decomposed at 170–172° and gave an infrared spectrum identical with that of the compound obtained by the reduction of II with stannous chloride.

3,6-Bis(benzylidenehydrazino)-1,2-dihydro-*s*-tetrazine.—A 25-ml. round-bottom flask was charged with 8 ml. of methanol, 1.15 g. (0.0108 mole) of benzaldehyde, 0.42 g. (0.0029 mole) of III, and 2 drops of glacial acetic acid. Reaction took place upon mixing, with slight evolution of heat. After 10 min. reflux the mixture was cooled to room temperature, and the light tan precipitate of benzal filtered, washed well with methanol, and dried under nitrogen. The yield of crude product, calculated as the dibenzal, was quantitative.

The crude benzal was recrystallized from glacial acetic acid. The solution was light yellow. Upon cooling, a voluminous, colorless, crystalline precipitate separated. The solid was filtered and washed first with glacial acetic acid, and then with methanol. On contact with the latter, the solid turned to an extremely fine, light grey powder. An additional recrystallization from glacial acetic acid-alcohol provided a sample for elemental analysis, m.p. 243–246° dec.

The remainder of the crude benzal was dissolved in 20 ml. of dimethyl sulfoxide at 100°. This solution was red. A little methanol was added, and the solution was left at room temperature overnight. Purplish crystals were obtained which decomposed at 252–254° and whose infrared spectrum was identical with that of the dibenzylidene derivative of II.

3,6-Bis(isopropylidenehydrazino)-1,2-dihydro-*s*-tetrazine.—The dihydrochloride of III was washed on the funnel with acetone. This treatment was sufficient to effect the formation of the hydrazone. The colorless salt was then reprecipitated three times by dissolving in methanol and adding an equal volume of acetone. The product decomposed at 176–178°.

Acknowledgment.—We are indebted to the Bureau of Naval Weapons for the financial support of this work.