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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA, IOWA CITY, IOWA]

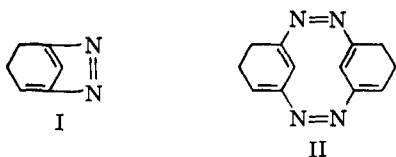
## Reactions of 1,3-Cyclohexanediones with Hydrazine : A Novel Pyridazinopyridazine Synthesis as a Result of Oxidation Promoted by Steric Strain

BY J. K. STILLE AND R. ERTZ<sup>1</sup>

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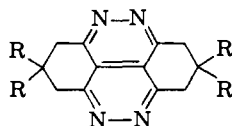
The reactions of 1,3-cyclohexanedione and 5,5-dimethyl-1,3-cyclohexanedione with excess hydrazine hydrate produce 1,4,5,8-bis-trimethylenepyridazino[4,5-*d*]pyridazine and 1,4,5,8-bis- $\beta,\beta$ -dimethyltrimethylenepyridazino[4,5-*d*]pyridazine, respectively. The mechanism of this reaction was demonstrated to involve formation of the cyclic azine and subsequent air oxidation to the aromatic pyridazine structure. This reaction represents a novel method of pyridazine formation.

The reaction of 1,3-cyclohexanedione with excess hydrazine hydrate has been reported<sup>2</sup> to afford a product  $C_6H_6N_2$ , whose structure was reported to be either 1,3-azo-1,3-cyclohexadiene (I) or its dimer II. It is evident that I is an unlikely candidate for the  $C_6H_6N_2$



compound and the formation of II would involve azine formation, tautomerization, and finally oxidation of the hydrazo tautomer to the azo compound. Further, it is unusual that such a facile isomerization and oxidation in the formation of II would take place to the exclusion of cyclic azine formation, since the formation and isolation of cyclic azines from diketones are the usual modes of reaction.<sup>3</sup> Under certain conditions acetylacetone reacts with hydrazine hydrate to form an associated dimer of a dimethyldihydropyridazine,<sup>4</sup> but this is a special case of the reaction with diketones.

The reaction of 1,3-cyclohexanedione with hydrazine hydrate does indeed form a light yellow, crystalline compound, whose elemental analysis and molecular weight verified the  $C_{12}H_{12}N_4$  compound described earlier. The infrared spectrum of this compound failed to reveal the characteristic  $C=N$  or  $N=N$  stretching and only a weak maximum at  $1625\text{ cm}^{-1}$ , which could be ascribed to the  $C=C$  moiety, was observed. The ultraviolet spectrum confirmed the absence of  $N=N$  absorption and showed a complicated absorption spectrum in the 250–310  $m\mu$  range. This spectral data and the n.m.r. spectrum established 1,4,5,8-bis-trimethylenepyridazino[4,5-*d*]pyridazine (III,  $R = H$ ) as the product of the reaction of 1,3-cyclohexanedione with hydrazine hydrate. The



III,  $R = H, CH_3$

quintet centered at  $7.67\ \tau$  (relative to tetramethylsilane) was assigned to the four internal methylene protons;

(1) Abstracted in part from the Ph.D. Thesis of R. Ertz, February, 1964.

(2) N. A. Domnin and N. S. Glebovskaya, *Zh. Obshch. Khim.*, **27**, 656 (1957).

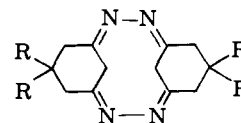
(3) C. G. Overberger, *Record Chem. Progr.*, **21**, 21 (1960).

(4) C. G. Overberger, N. R. Byrd, and R. B. Mesrobian, *J. Am. Chem. Soc.*, **78**, 1961 (1956).

the areas of the components of the quintet were the expected 1:3:5:3:1. The triplet centered at  $6.6\ \tau$  was assigned to the eight equivalent methylene protons; the areas of the components of the triplet approximated a 1:2:1 ratio. The relative number of triplet to quintet protons was 2:1.

Further support of the pyridazine structure (III,  $R = H$ ) was gained by an investigation of the product of the reaction of 5,5-dimethyl-1,3-cyclohexanedione with excess hydrazine hydrate. The infrared spectrum of this product showed no absorption associated with the  $C=N$  or  $N=N$  moiety. The ultraviolet spectrum failed to reveal the characteristic  $N=N$  absorption, but showed again a complicated absorption spectrum between 250 and 310  $m\mu$ . This spectral data and the n.m.r. spectrum established 1,4,5,8-bis- $\beta,\beta$ -dimethyltrimethylenepyridazino[4,5-*d*]pyridazine (III,  $R = CH_3$ ) as the product of the reaction of 5,5-dimethyl-1,3-cyclohexanedione with hydrazine hydrate. The singlet at  $8.83\ \tau$  (relative to tetramethylsilane) was assigned to the twelve methyl hydrogens and the singlet at  $6.72\ \tau$  corresponded to the eight methylene hydrogens. The relative number of methyl protons to methylene protons was 3:2.

The formation of III ( $R = H, CH_3$ ) presumably proceeds through the intermediate IV which contains two azine linkages, yet compounds containing two



IV,  $R = H, CH_3$

azine linkages formed in the condensation of acyclic diketones with hydrazine are stable enough to be isolated from the reaction mixture.<sup>3</sup> This would indicate that the intermediate IV must have a special reactivity associated with it and is not stable under the conditions of the reaction. Models of IV show that the hydrogens on the two internal methylene groups are no greater than 1.2 Å. apart, the van der Waals radius for hydrogen. Thus, because of the close proximity of the two internal methylene groups, IV, in the presence of an oxidizing agent, dehydrogenates with bond formation to produce the pyridazine III, and thereby relieves the strain imposed. It is significant that cyclodecapentaene, which is forced into the same type of steric crowding, has never been isolated, although its transitory existence has been indicated.<sup>5</sup> Several examples of this type of oxidation involving bond formation to afford the same ring system have been described in the

(5) M. Avram, C. D. Nentzescu, and E. Marica, *Ber.*, **90**, 1857 (1957).

literature,<sup>6,7</sup> but the conditions for these oxidations are not as mild as the ones we describe.

An attempt was made to isolate the intermediate IV ( $R = CH_3$ ) and detect the oxidizing agent by carrying out the condensation of 5,5-dimethyl-1,3-cyclohexanedione with hydrazine hydrate in an inert atmosphere. This reaction was used in preference to the reaction of 1,3-cyclohexanedione with hydrazine hydrate since it was expected that the intermediate IV ( $R = H$ ) would give a more complex n.m.r. spectrum.

Proof of the existence of IV ( $R = CH_3$ ) as the intermediate was exemplified by the fact that no III ( $R = CH_3$ ) formed when the condensation of 5,5-dimethyl-1,3-cyclohexanedione and hydrazine hydrate was carried out in an inert atmosphere. When the solution containing IV ( $R = CH_3$ ) was removed from the nitrogen atmosphere and exposed to air, however, crystals of III ( $R = CH_3$ ) immediately began to deposit. This demonstrated that air oxidation was necessary for the formation of III ( $R = CH_3$ ).

The n.m.r. spectrum of the product isolated in a nitrogen atmosphere was consistent with the spectrum expected for the intermediate IV ( $R = CH_3$ ). The appearance of the singlet at 5.71  $\tau$ , which was shifted downfield as expected, was assigned to the four internal methylene hydrogens. This peak could not be assigned to unchanged 5,5-dimethyl-1,3-cyclohexanedione, as the n.m.r. spectrum of the pure diketone showed no signals in the range of 5–6  $\tau$ . In addition to the singlet present at 5.71  $\tau$ , additional singlets at 7.75 ( $-CH_2-$ ) and 8.82  $\tau$  ( $-CH_3$ ) were detected. The hydrogen ratios of these three peaks were not exactly as expected for structure IV ( $R = CH_3$ ), probably a result of the presence of unchanged 5,5-dimethyl-1,3-cyclohexanedione, which, because of solubility problems, could not be separated completely from the intermediate.

The fact that the maximum yields of III ( $R = H, CH_3$ ) were only about 25% was not too unusual. The major side reaction in both cases was the formation of polymeric material and this is a common occurrence in the reactions of acyclic diketones with hydrazine.<sup>8</sup> It was shown (Table I) that a 4:1 molar excess of hydrazine hydrate to the diketone gave the best yield of III ( $R = H$ ) and this was not affected by using an inverse addition procedure. Equimolar amounts or a 2:1 molar excess of hydrazine hydrate to the diketone gave mostly polymeric material. A greater than 4:1 molar excess of hydrazine hydrate did not increase the yield appreciably. Neither was the yield increased when air was bubbled through the solution containing a 4:1 excess of hydrazine hydrate during the addition of the diketone.

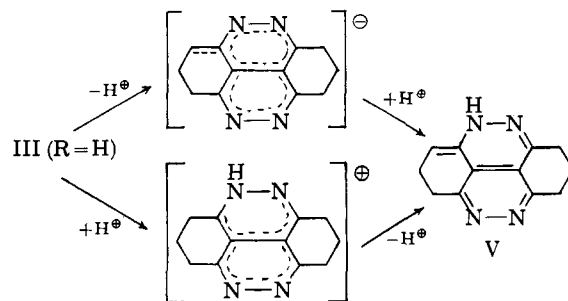
It was interesting to note that the bishydrazones of 5,5-dimethyl-1,3-cyclohexanedione and 1,3-cyclohexanedione were never isolated. Apparently bimolecular condensation involving azine formation was favored under the conditions of the reaction. It was thought that an intermediate of the type IV could be isolated from the reaction of 2,2,5,5-tetramethyl-1,3-cyclohexanedione with hydrazine hydrate since the 2-position was completely blocked and double bond formation could not occur. No reaction occurred between 2,2,5,5-tetramethyl-1,3-cyclohexanedione and hydrazine hydrate under the same reaction conditions which resulted in the formation of III. However, when a solution containing 2,2,5,5-tetramethyl-1,3-cyclohexanedione

and hydrazine hydrate was heated under reflux, the corresponding bishydrazone resulted.

Since the condensation of 2,5,5-trimethyl-1,3-cyclohexanedione with hydrazine hydrate yielded a polymeric solid, it appears that two  $\alpha$ -hydrogens are necessary if any product similar to III is to result. Evidently the stereochemistry of 1,3-cyclohexanedione and 5,5-dimethyl-1,3-cyclohexanedione favors bimolecular condensation with hydrazine hydrate to form the intermediate IV which readily dehydrogenates with double bond formation.

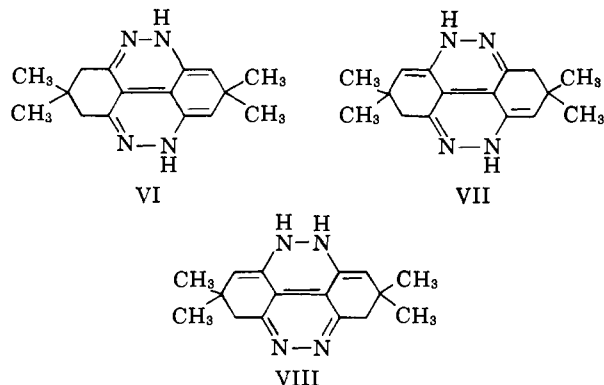
Both pyridazinopyridazines III ( $R = H, CH_3$ ), are quite stable and difficult to analyze, but the preparation of their respective picrates proved to give suitable derivatives. The pyridazine ring functions as a monoacid base<sup>9</sup> and gives a 1:1 adduct with picric acid. Since both compounds contain two fused pyridazine rings, it was possible that dipicrates would result. It was found that III ( $R = H$ ) functioned as a monoacid base and gave a 1:1 adduct with picric acid. Compound III ( $R = CH_3$ ), however, functioned as a diacid base and a dipicrate was formed.

It was found that III ( $R = H$ ) readily tautomerized to an unstable compound which exhibited basic properties. This was found to occur in either acid or base. The addition of acid to III ( $R = H$ ) followed by basic precipitation was found to be the best method for the preparation of this unstable tautomer. Since both the tautomer and III ( $R = H$ ) yielded identical monoadducts with picric acid, V, which has only one nitrogen proton, is suggested as the structure of the tautomer. The unstable tautomer V, having lost some of its



aromaticity, easily reverts to the more stable compound III ( $R = H$ ) immediately on solution in any of the common organic solvents or over a period of several hours on standing in the solid state.

Since III ( $R = CH_3$ ) formed a dipicrate when treated directly with picric acid, it was thought that at least two dipicrates should be isolated since III ( $R = CH_3$ ) should be capable of tautomerizing to VI and VII or even VIII. Two different dipicrates were indeed iso-



lated; one from treating III ( $R = CH_3$ ) directly with picric acid and the other from treating the tautomerized

(6) W. Baker, J. F. W. McOmie, and J. M. Norman, *J. Chem. Soc.*, 1114 (1951).

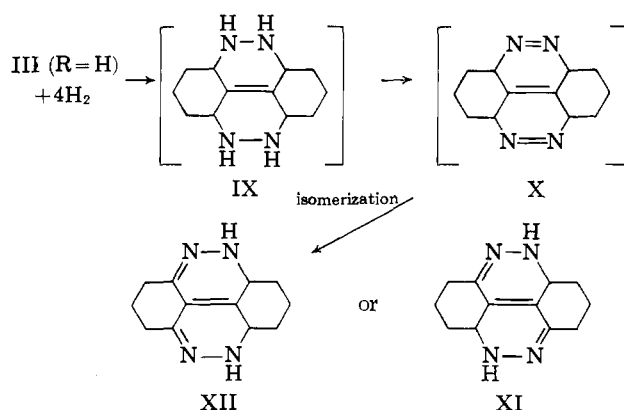
(7) V. Boekelheide and J. B. Phillips, *J. Am. Chem. Soc.*, **85**, 1545 (1963).

(8) C. G. Overberger and J. J. Monagle, *ibid.*, **78**, 4470 (1956).

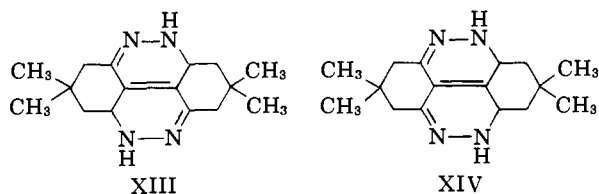
(9) S. Gabriel and J. Colman, *Ber.*, **32**, 395 (1899).

III (R = CH<sub>3</sub>) with picric acid. The compounds VI and VII are the most probable tautomers, but the third tautomer, VIII, cannot be seriously considered since it contains a hydrazine linkage and would be readily oxidized in the atmosphere.

The quantitative hydrogenation of III (R = H) showed the absorption of approximately 4 moles of hydrogen, but a preparative hydrogenation produced a product whose analysis indicated the absorption of 2 moles of hydrogen. The intermediate bishydrazine IX resulting from the addition of 4 moles of hydrogen was not isolated, but apparently oxidation involving the loss of 2 moles of hydrogen resulted in the formation of the bis-azo compound X, which isomerized readily to the conjugated dihydrazone XI or XII. The structure of the dihydrazone XI or XII is supported by its analysis, its infrared spectrum which revealed characteristic —N—H and C=N stretching maxima, its ultraviolet spectrum, and the fact that isomerizations of azo compounds to the more stable hydrazones are well documented in the literature.<sup>3,10,11</sup>



Similarly, either XIII or XIV results from the hydrogenation of III (R = CH<sub>3</sub>). The infrared and ultraviolet spectra supported either structure but



could not distinguish between the isomers. The complicated n.m.r. spectrum gives more support, however, to XIV as the appropriate structure because of the appearance of two distinct peaks in the methyl region—one at 9.08  $\tau$  (relative to tetramethylsilane) present as a doublet and the other at 8.79  $\tau$  present as a singlet. The relative areas of these two peaks were equal. A structure such as XIII would be expected to show only one methyl peak since each pair of methyl groups reside in identical environments. The ratio of methyl hydrogens to the remaining hydrogens attached to carbon was approximately 6:5, consistent with either XIII or XIV.

### Experimental<sup>12</sup>

**1,4,5,8-Bistrimethylenepyridazino[4,5-d]pyridazine (III, R = H).**—To a solution of 9.3 g. (9 ml., 0.186 mole) of hydrazine hydrate in 50 ml. of absolute ethanol cooled in an ice bath at 0–5°, was added a solution of 5 g. (0.0447 mole) of 1,3-cyclohexanedione<sup>13</sup> in 125 ml. of absolute ethanol with stirring over a period of 1 hr. After addition was complete, the solution was

stirred an additional 5 hr. and then stored overnight at 0–5°. The ethanol solution was concentrated to about 20 ml. under reduced pressure leaving a dark red solution which slowly deposited crystals when left exposed to the atmosphere. The crystals were filtered from the dark red oil and recrystallized twice from absolute ethanol to yield 1.26 g. (26.6%) of light yellow needles which decomposed at approximately 260°.

*Anal.* Calcd. for C<sub>12</sub>H<sub>12</sub>N<sub>4</sub>: C, 67.92; H, 5.66; N, 26.41; mol. wt., 212. Found: C, 67.81; H, 5.69; N, 26.33; mol. wt., 213.

The infrared spectrum (mull) showed no absorption in the —N—H or N=N regions. The ultraviolet spectrum showed  $\lambda_{\max}$  at 308 m $\mu$ ,  $\epsilon$  5300; 297, 5750; 285, 4900; 272, 5750; and 263, 6400 in absolute ethanol. The n.m.r. spectrum determined at 60 Mc. in deuteriochloroform showed a quintet centered at 7.67  $\tau$  (relative to tetramethylsilane) and a triplet centered at 6.6  $\tau$ . No —N—H or vinyl protons were detected. The relative areas of triplet to quintet were 2:1.

A picrate of III (R = H) was prepared in the usual manner<sup>14</sup> from an ethanol solution of picric acid. After recrystallization from absolute ethanol, the picrate decomposed at approximately 190°.

*Anal.* Calcd. for C<sub>18</sub>H<sub>18</sub>N<sub>7</sub>O<sub>7</sub>: C, 48.98; H, 3.40; N, 22.22. Found: C, 48.81; H, 3.47; N, 22.19.

**Condensation of 1,3-Cyclohexanedione with Hydrazine Hydrate.**—Various experiments at 0–5° were carried out in order to determine the optimum yield of 1,4,5,8-bistrimethylenepyridazino[4,5-d]pyridazine. In all cases the reaction time and isolation techniques were the same as described previously, but the molar ratios of 1,3-cyclohexanedione to hydrazine hydrate and the order of addition were varied.

TABLE I  
CONDENSATION OF 1,3-CYCLOHEXANEDIONE WITH HYDRAZINE HYDRATE

Mole ratio of diketone to hydrazine hydrate	Order of addition	Yield of III, R = H, %
1:4	Ket. to hydr.	21–26.6
1:4	Hydr. to ket.	21.4
1:1	Ket. to hydr.	Black powder <sup>b</sup>
1:2	Ket. to hydr.	Black tar
1:4	Ket. to hydr. <sup>a</sup>	26.6
1:10	Ket. to hydr.	28

<sup>a</sup> Air was bubbled through the solution of hydrazine which contained a cupric oxide catalyst. <sup>b</sup> A yield of approximately 4% was isolated by using column chromatography.

**Determination of the Molecular Weight of 1,4,5,8-Bistrimethylenepyridazino[4,5-d]pyridazine at Various Concentrations.**—Using a vapor osmometer with chloroform as the solvent, it was demonstrated that the molecular weight did not vary with concentration. At concentrations ranging from 0.01 molal to 0.06 molal, molecular weights between the limits of 201 and 213 were obtained.

**Hydrogenation of 1,4,5,8-Bistrimethylenepyridazino[4,5-d]pyridazine.**—A solution of 1.08 g. (0.0046 mole) of 1,4,5,8-bistrimethylenepyridazino[4,5-d]pyridazine in 75 ml. of absolute methanol containing 0.105 g. of platinum oxide was hydrogenated at room temperature at an initial hydrogen pressure of 40 p.s.i. for 8 hr. The catalyst was then removed and the filtrate was concentrated under reduced pressure. A yellow solid remained which was decolorized and recrystallized twice from dilute ethanol. Light tan needles of XI or XII, m.p. 179–180° dec., were obtained.

*Anal.* Calcd. for C<sub>12</sub>H<sub>16</sub>N<sub>4</sub>: C, 66.67; H, 7.41; N, 25.92; mol. wt., 216. Found: C, 66.75; H, 7.13; N, 25.54; mol. wt., 225.

The infrared spectrum (mull) showed absorption maxima at 3350–3100 (—N—H str.) and 1670 cm.<sup>-1</sup> (C=N str.). The ultraviolet spectrum showed a broad  $\lambda_{\max}$  at approximately 267 m $\mu$ ,  $\epsilon$  approximately 2000, in absolute ethanol. A meaningful n.m.r. spectrum could not be obtained owing to its solubility properties.

**Quantitative Hydrogenation of 1,4,5,8-Bistrimethylenepyridazino[4,5-d]pyridazine.**—To a semimicro hydrogenator containing 0.0152 g. of pre-reduced platinum oxide in 40 ml. of absolute methanol was added 0.0884 g. (0.000417 mole) of 1,4,5,8-bistrimethylenepyridazino[4,5-d]pyridazine. In 6 hr. the material absorbed 89% of the theoretical number of moles of hydrogen for a structure containing four double bonds.

(14) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th Ed., John Wiley and Sons, Inc., New York, N. Y., 1957, p. 229.

(10) C. G. Overberger and J. P. Anselme, *J. Am. Chem. Soc.*, **84**, 869 (1962).

(11) S. G. Cohen and R. Zand, *ibid.*, **84**, 586 (1962).

(12) Melting points are corrected.

(13) R. B. Thompson, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 278.

All attempts made to isolate a tetrpicrate or a tetrahydrochloride from the intermediate bishydrazine failed.

**Tautomerization of 1,4,5,8-Bistrimethylenepyridazino[4,5-*d*]-pyridazine (Method A).**—A solution of 0.6 g. (0.0028 mole) of 1,4,5,8-bistrimethylenepyridazino[4,5-*d*]pyridazine in 50 ml. of water containing 1 ml. of concentrated hydrochloric acid was prepared. Concentrated sodium hydroxide was added to the above solution until it was basic to litmus. From the basic solution a precipitate separated which was removed by filtration and recrystallized from aqueous ethanol to give a quantitative yield of the unstable tautomer V, which decomposed at approximately 260°. Upon standing several hours exposed to the atmosphere, this tautomer (V) reverted to starting material.

The unstable tautomer showed strong absorption maxima in the infrared region (mull) at 3390 and 3290  $\text{cm}^{-1}$  ( $-\text{N}-\text{H}$  str.) in addition to maxima at 1690 ( $\text{C}=\text{C}$  str.) and 1665  $\text{cm}^{-1}$  ( $\text{C}=\text{N}$  str.).

A picrate of the unstable tautomer was prepared immediately from an ethanol solution of picric acid. After recrystallization from absolute ethanol, a picrate which decomposed at approximately 190° resulted. The melting point of a mixture of this picrate and the picrate prepared directly from 1,4,5,8-bistrimethylenepyridazino[4,5-*d*]pyridazine decomposed at approximately 187°. Their infrared spectra (mull) were superimposable.

**Tautomerization of 1,4,5,8-Bistrimethylenepyridazino[4,5-*d*]-pyridazine (Method B).**—A solution of 0.6 g. (0.0028 mole) of 1,4,5,8-bistrimethylenepyridazino[4,5-*d*]pyridazine in absolute methanol was prepared. To this was added 1 g. (0.025 mole) of sodium hydroxide dissolved in 10 ml. of water. The solution was stirred at room temperature for 6 hr. Upon concentration under reduced pressure, a precipitate formed which was removed and recrystallized twice from aqueous ethanol to yield 0.4 g. (67%) of the unstable tautomer V.

**1,4,5,8-Bis- $\beta,\beta$ -dimethyltrimethylenepyridazino[4,5-*d*]pyridazine (III, R =  $\text{CH}_3$ ).**—The preparation of III (R =  $\text{CH}_3$ ) from 5 g. (0.0357 mole) of 5,5-dimethyl-1,3-cyclohexanedione<sup>15</sup> and 9.3 g. (9 ml., 0.186 mole) of hydrazine hydrate was carried out as described for III (R = H). Isolation of the product in the manner described previously yielded 1.2 g. (25%) of the crystalline product, which after recrystallization from ethanol decomposed at approximately 270°.

*Anal.* Calcd. for  $\text{C}_{18}\text{H}_{26}\text{N}_4$ : C, 71.64; H, 7.46; N, 20.90; mol. wt., 268. Found: C, 71.34; H, 7.64; N, 20.84; mol. wt., 267.

The infrared spectrum (mull) showed no absorption in the  $\text{N}=\text{N}$  or  $\text{C}=\text{C}$  region. The ultraviolet spectrum showed  $\lambda_{\text{max}}$  at 308  $\text{m}\mu$ ,  $\epsilon$  4400; 297, 5000; 283, 4700 273, 5800; and 264, 6400 in absolute ethanol. The n.m.r. spectrum determined at 60 Mc. in deuteriochloroform showed a singlet at 8.83  $\tau$  (relative to tetramethylsilane) and a singlet at 6.72  $\tau$ . The relative areas of the two singlets were 3:2.

A picrate of III (R =  $\text{CH}_3$ ) was prepared in the usual manner from an ethanol solution of picric acid. After recrystallization from absolute ethanol, yellow prisms, m.p. 171–172° dec., were obtained.

*Anal.* Calcd. for  $\text{C}_{28}\text{H}_{36}\text{H}_{10}\text{O}_{14}$ : C, 46.28; H, 3.58; N, 19.28. Found: C, 46.45; H, 3.90; N, 19.64.

**Hydrogenation of 1,4,5,8-Bis- $\beta,\beta$ -dimethyltrimethylenepyridazino[4,5-*d*]pyridazine.**—A solution of 0.88 g. (0.0033 mole) of 1,4,5,8-bis- $\beta,\beta$ -dimethyltrimethylenepyridazino[4,5-*d*]pyridazine in absolute ethanol containing 0.064 g. of platinum oxide was hydrogenated at room temperature at an initial hydrogen pressure of 35 p.s.i. for 7 hr. The catalyst was removed and the yellow solution was concentrated under reduced pressure. A yellow solid remained which was decolorized and recrystallized twice from aqueous ethanol. The purified product, consisting of a yellow amorphous powder, m.p. 219–220° dec., weighed 0.6 g. (67%).

*Anal.* Calcd. for  $\text{C}_{18}\text{H}_{24}\text{N}_4$ : C, 70.59; H, 8.82; N, 20.59; mol. wt., 272. Found: C, 70.40; H, 8.37; N, 20.65; mol. wt., 277.

The infrared spectrum (chloroform solution) showed absorption maxima at 3410 ( $-\text{N}-\text{H}$ ) and 1630  $\text{cm}^{-1}$  ( $\text{C}=\text{N}$  str.). The ultraviolet spectrum showed a broad  $\lambda_{\text{max}}$  at approximately 258

$\text{m}\mu$ ,  $\epsilon$  approximately 5100, in absolute ethanol. The n.m.r. spectrum obtained at 60 Mc. in deuteriochloroform showed a doublet centered at 9.08  $\tau$  (relative to tetramethylsilane), a singlet at 8.79  $\tau$ , absorption centered at 8.1  $\tau$ , a singlet at 7.54  $\tau$ , and a singlet at 7.02  $\tau$ . The ratio of methyl hydrogens to the remaining hydrogens attached to carbon was approximately 6:5.

**Tautomerization of 1,4,5,8-Bis- $\beta,\beta$ -dimethyltrimethylenepyridazino[4,5-*d*]pyridazine.**—The tautomerization of 1,4,5,8-bis- $\beta,\beta$ -dimethyltrimethylenepyridazino[4,5-*d*]pyridazine to its unstable tautomer (VI or VII) was carried out by either method A or B in a manner described for the tautomerization of III (R = H). A white solid resulted which reverted to III (R =  $\text{CH}_3$ ) upon standing in the atmosphere for several hours. The infrared spectrum (mull) showed absorption maxima at 3400 ( $-\text{N}-\text{H}$  str.) and 1630  $\text{cm}^{-1}$  ( $\text{C}=\text{N}$  str.).

A picrate of the unstable tautomer was prepared immediately in the usual manner. Long needles resulted which decomposed at approximately 230° after recrystallization twice from absolute ethanol.

*Anal.* Calcd. for  $\text{C}_{28}\text{H}_{36}\text{N}_{10}\text{O}_{14}$ : C, 46.28; H, 3.58; N, 19.28. Found: C, 46.52; H, 3.89; N, 19.65.

**Condensation of 5,5-Dimethyl-1,3-cyclohexanedione with Hydrazine Hydrate in an Inert Atmosphere.**—To a solution of 9.3 g. (9 ml., 0.186 mole) of hydrazine hydrate in 50 ml. of deoxygenated absolute ethanol was added 5 g. (0.0357 mole) of 5,5-dimethyl-1,3-cyclohexanedione in 125 ml. of deoxygenated ethanol in a nitrogen atmosphere at 0–5° over a period of 1 hr. After addition was complete, the light yellow solution was allowed to stand an additional hour at 0–5° in the inert atmosphere. The ethanol and excess hydrazine hydrate were removed completely under reduced pressure. A yellow-orange solid remained which was transferred immediately to a drybox. A solution of the solid in deoxygenated deuteriochloroform was prepared and its n.m.r. spectrum was immediately determined. The n.m.r. spectrum showed singlets at 5.71, 7.75, and 8.82  $\tau$ .

It was noted that III (R =  $\text{CH}_3$ ) did not form when 5,5-dimethyl-1,3-cyclohexanedione was added to hydrazine hydrate in the manner described above. If the solution were concentrated to approximately 15 ml. and allowed to stand in a nitrogen atmosphere for a period of 2 days, no crystals of III (R =  $\text{CH}_3$ ) separated; however, upon exposure to air, the solution immediately darkened and crystals of III (R =  $\text{CH}_3$ ) began to deposit within an hour.

**Bishydrazone of 2,2,5,5-Tetramethyl-1,3-cyclohexanedione.**—A solution of 5 g. (0.0298 mole) of 2,2,5,5-tetramethyl-1,3-cyclohexanedione<sup>16</sup> in 75 ml. of absolute ethanol containing 9.3 g. (9 ml., 0.186 mole) of hydrazine hydrate was heated at the reflux temperature for 6 hr. The ethanol was removed under reduced pressure and a yellow-orange solid remained. This was removed by filtration and recrystallized twice from benzene to yield 2.5 g. (43%) of white plates, m.p. 127–130°.

*Anal.* Calcd. for  $\text{C}_{10}\text{H}_{20}\text{N}_4$ : C, 61.22; H, 10.21; N, 28.57. Found: C, 61.36; H, 10.46; N, 28.67.

The infrared spectrum (mull) showed absorption maxima at 3390 ( $-\text{N}-\text{H}$  str.) and 3250 ( $-\text{N}-\text{H}$  str.) in addition to a strong maximum at 1635  $\text{cm}^{-1}$  ( $\text{C}=\text{N}$  str.).

No reaction occurred when 2,2,5,5-tetramethyl-1,3-cyclohexanedione was treated with hydrazine hydrate under the same reaction conditions and molar amounts which resulted in the formation of III.

**Reaction of 2,5,5-Trimethyl-1,3-cyclohexanedione with Hydrazine Hydrate.**—A solution of 2.5 g. (0.0162 mole) of 2,5,5-trimethyl-1,3-cyclohexanedione<sup>17</sup> in 50 ml. of absolute ethanol at 0–5° was stirred, over a period of 1 hr. The resulting solution was stirred an additional 5 hr. at 0–5° and then stored overnight in the refrigerator. The solution was concentrated under reduced pressure to give a yellow oil which gradually turned to a brittle polymeric solid.

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