m.p. 307–308°, after crystallization from aqueous ethanol. The dilute aqueous solution gave a blue fluorescence and the ultraviolet and infrared spectrum of this substance were identical with those from preparation *a* above.

Diquino[1,2-a,1',2'-c]imidazolium bromide (IIIb). This substance was prepared from ω,ω-dibromoquinaldine and quinoline using the method of Brown and Wild;[5] m.p. 306°. It was converted to the picrate; m.p. 267–270°.

Diquino[1,2-a,1',2'-c]imidazolium picrate (IIIc). This compound separated from an alcoholic solution of IIIa, prepared by method *a* or *b*, or from IIIb when alcoholic solutions of these preparations were treated with picric acid. It was recrystallized from ethanol; m.p. 267–270°[10]; mixed melting points using the three preparations were not depressed.

N(2-quinolylmethyl)carbostyril (IV). Two grams of IIIa was added to a solution of 15% potassium hydroxide in 50% water-ethanol. The solution was boiled for 20 min. After cooling, the dark oil which separated was extracted with chloroform. After removal of the chloroform, the residue was leached with 500 cc. of boiling pentane. Concentration of the pentane solution gave 200 mg. (21%) of colorless needles; m.p. 125–126° (after melting and resolidifying at 105–107°).

Anal. Calcd. for $C_{19}H_{14}N_2O$: N, 9.79. Found: N, 9.76.

The remainder of the above residue was dissolved in ethanol and converted to the picrate. Yield 1.5 g. (70%); m.p. 195–197°.[11] The overall conversion of IIIa to IV was 91%.

10-Methyldiquino[1,2-a,1',2'-c]imidazolium iodide (VI). Iodine, 12.7 g. was added to 8.0 g. of 2.6-dimethylquinoline and 30 cc. of quinoline. After heating for 12 hr. the mixture was extracted successively with ether, acetone, and water. The residue was crystallized from ethanol-water. Yield 8.0 g. (78% based on iodine); m.p. 319°.

Anal. Calcd. for $C_{20}H_{15}N_2I$: C, 58.54; H, 3.69. Found: C, 58.32; H, 3.88.

This compound gave no picryl chloride test.[2,8] Dilute solutions in polar solvents showed blue fluorescence. The infrared spectra and the ultraviolet spectra (Table 1) were similar to those of compound IIIa. Light absorption at a concentration of $1.34 \times 10^{-5}M$ in methanol: Max. at 390, 375, 350, 335, 310, 300, 295, 286, 260, 255, and 225 mμ (log ε 4.30, 4.36, 4.17, 3.87, 4.02, 4.43, 4.45, 4.31, 4.59, 4.50, 4.57); min. at 385, 360, 325, 275, and 240 mμ (log ε 4.13, 4.11, 3.65, 4.20, 4.42).

Acknowledgment. We wish to thank the American Cyanamid Company for a research fellowship.

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(10) Brown and Wild, ref. 5, reported the m.p. as 261–262°.

(11) Brown and White, ref. 7, reported m.p. 125° for the base and 189° for the picrate.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

Reactions of Terpenes with Acid and Thiourea III.[1] Preparation and Nitrosation of Some 1(*S*),8(*N*)-*p*-Menthyleneisothioureas

L. CARROLL KING AND ERIC W. STERN[2]

When limonene reacts with *p*-toluenesulfonic acid and methylthiourea or with phenylthiourea, the products are 3-methylamino-1,5,5-trimethyl-2-thia-4-azabicyclo[4.2.2]dec-3-ene and 3-anilino-1,5,5-trimethyl-2-thia-4-azabicyclo[4.2.2]dec-3-ene respectively. On methylation of 1(*S*),8(*N*)-*p*-menthyleneisothiourea, 3-imino-1,4,5,5-tetramethyl-2-thia-4-azabicyclo[4.2.2]-decane was produced. Each of the above compounds was nitrosated. The structure of these compounds and their nitroso derivatives is discussed herein.

In paper II of this series the preparation, properties, and structure of 1(*S*),8(*N*)-*p*-menthyleneisothiourea (I) were discussed.[1] This derived name was adopted because of its simplicity and suggestion of the terpene origin of I. However, in discussing the derivatives described herein the need for a more systematic nomenclature became evident. After consultation with L. T. Capell,[3] we chose the bicyclic system so that I becomes 3-amino-1,5,5-trimethyl-2-thia-4-azabicyclo[4.2.2.]dec-3-ene (II).

When II was treated in strong acid solution with aqueous sodium nitrite, no reaction occurred. Only the salt of II corresponding to the strong acid used was isolated. However when II was dissolved in glacial acetic acid and treated with aqueous sodium nitrite, a golden yellow solid, 3-nitrosoimino-1,5,5-trimethyl-2-thia-4-azabicyclo[4.2.2]decane (III), precipitated after a few minutes.

Compound III gave a positive Liebermann's nitrosoamine test. When warmed with concentrated hydrochloric acid, it evolved nitrous acid and gave II as the hydrochloride. When III was treated with dilute aqueous sodium hydroxide it was converted to sodium 1,5,5-trimethyl-2-thia-4-azabicyclo[4.2.2]dec-3-ene-3-diazoate (IV), a white compound. Compound IV regenerated III on acidification with glacial acetic acid. Combustion of the white compound IV gave the expected amount of ash.

Compound III was formulated as a primary rather than as a secondary nitrosoamine because of the intense color and because the reversible change III ⇆ IV would be difficult to explain in terms of the secondary nitrosoamine structure. Thus if the yellow compound had the structure V, the nitroso group would not be in conjugation with the CN group and the color would be expected to be like that of most secondary nitrosoamines. Furthermore, if the yellow compound had the structure V the addition of a base would predict disruption of a bond V → VI → VII, an irreversible procedure,

(1) Paper No. II of this series, L. C. King, L. A. Subluskey, and E. W. Stern, *J. Org. Chem.*, 21, 1232 (1956).

(2) From the Ph.D. thesis of Eric W. Stern (1954).

(3) Private communication.

whereas the action of base is reversed by addition of acid.

Absorption peaks in the infrared spectra of III and IV are in line with the proposed structures. The band at 6.17 μ in the spectrum of II, assigned to CN stretching[4] is shifted to 6.34 μ and 6.36 μ, respectively, in the spectra of III and IV. Such a shift would be expected for a system in which CN was conjugated to N=O. If the yellow compound had the structure V rather than III, the CN group would not be in conjugation with N=O and no shift of the 6.17 μ band of II would be expected.

The NH stretching bands, found at 2.90 and 3.00 μ in the spectrum of II are shifted to 3.25 μ and 3.34 μ in the spectrum of III. This is consistent with hydrogen bonding to the nitroso group as shown.

The bands at 7.54 μ and 9.27 μ in the spectrum of III have been assigned to the N=O group.[5] These bands disappear in IV giving way to a large absorption in the region 7.32 μ to 8.88 μ. A band similar to this is found in the spectra of the *cis*- and *trans*-potassium benzenediazoates.[6]

When 3-amino-1,5,5-trimethyl-2-thia-4-azabicyclo[4.2.2)dec-3-ene (II) is treated with methyl iodide, the product is 3-imino-1,4,5-5-tetramethyl-2-thia-4-azabicyclo[4.2.2]decane (VIII). The assignment of structure is based on analogy to the reaction of 2-aminothiazoline with methyl iodide wherein methylation occurs on the ring nitrogen[7] and on the fact that this compound on nitrosation gives an orange nitrosoamine IX. Furthermore, the alternate methylation product, 3-methylamino-1,5,5-trimethyl-2-thia-4-azabicyclo[4.2.2]dec-3-ene (X), was prepared by a different procedure and shown to give a colorless nitrosoamine. These relationships will be discussed further below.

When compound VIII in glacial acetic acid was treated with aqueous sodium nitrite an orange compound, 3-nitrosoimino-1,4,5,5-tetramethyl-2-thia-4-azabicyclo[4.2.2]decane (IX), was obtained. The orange color is associated with conjugation of the N=O and CN grouping as shown in IX. In addition the band at 6.18 μ in the infrared spectrum of VIII is shifted to 6.44 μ in IX as would be expected if CN were conjugated with N=O.

The other methylated isomer of II was prepared by treating limonene with methylthiourea and *p*-toluenesulfonic acid followed by conversion to the base by treatment with sodium hydroxide. This substance was assigned structure X since on nitrosation it gave a nearly colorless nitrosoamine. Of the two possible structures for the nitrosoamine, 3-methylimino-4-nitroso-1,5,5-trimethyl-2-thia-4-azabicyclo(4.2.2]decane (XI) and *N*-nitroso-3-methylamino-1,5,5-trimethyl-2-thia-4-azabicyclo-[4.2.2]dec-3-ene (XII), we prefer XI. Both of these compounds should be colorless.

3-Anilino-1,5,5-trimethyl-2-thia-4-azabicyclo-[4.2.2]dec-3-ene (XIII) was prepared from phenylthiourea, limonene, and *p*-toluenesulfonic acid. On nitrosation it gave 3-phenylimino-4-nitroso-1,5,5-trimethyl-2-thia-4-azabicyclo[4.2.2]decane (XIV). Assignment of structures for XIII and XIV is by method of preparation and analogy to X and XI above.

In Table I data for the colors and the melting points of the nitroso compounds described herein are summarized. Table 2 lists pertinent infrared data and assignments of bands. Other data including preparation of derivatives of VIII, X, and XIII and analysis of all compounds are listed in the Experimental part.

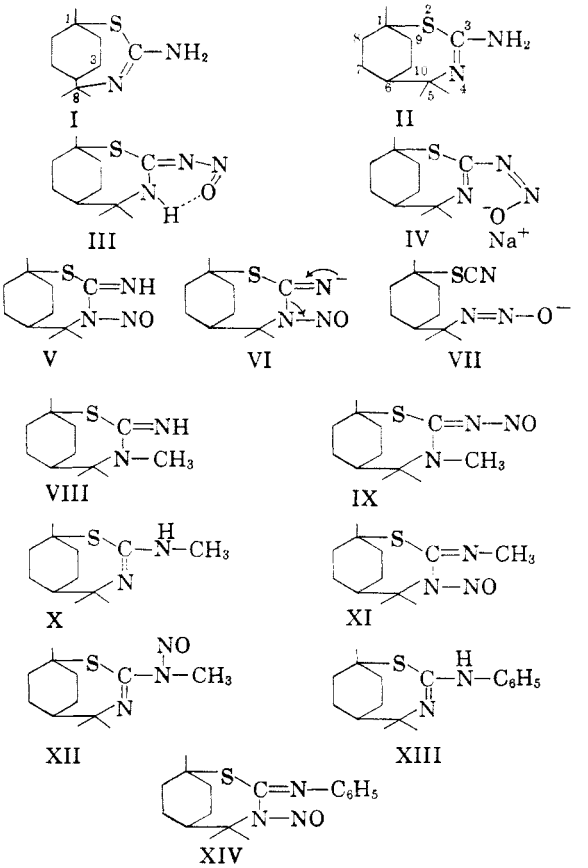

TABLE I

Compound	Color	Melting Point	Liebermann's Test
III	Golden yellow	Explosively 149–150° (dec.)	+
IV	White	290–291° (dec.)	
IX	Orange	117–118° (dec.)	+
XI	Yellowish white	39–40°	+
XIV	Yellowish white	115–116°	+

(4) N. B. Colthup, *J. Opt. Soc. Am.*, **40**, 397 (1950).

(5) R. N. Haszeldine and J. Jandor, *J. Chem. Soc.*, 695 (1954).

(6) R. J. W. Lefevre, M. F. O'Dwyer, and R. L. Werner, *Australian J. Chem.*, **6**, 341 (1953).

(7) S. Gabriel, *Ber.*, **22**, 1141 (1889).

TABLE II[a]

MAJOR PEAKS IN THE 2–12 MICRON REGION OF THE INFRARED SPECTRUM

Compound	Solvent	Wave Length (Microns) and Assignment
II	$CHCl_3$	2.90, 3.00 (N—H nonbonded), 3.30 (N—H bonded), 6.17 (C=N), 6.36 (NH_2)
III	$CHCl_3$	3.25, 3.34 (N—H), 6.34 (C=N), 7.54, 9.27 (N=O)
IV	KBr pellet	6.36 (C=N), 7.32–8.88 broad poorly resolved absorptions (diazotate ?)
VIII	$CHCl_3$	2.94, 3.01, 3.09 (N—H nonbonded), 3.26 (N—H bonded), 6.18 (C=N)
IX	$CHCl_3$	6.44 (C=N), 7.43, 9.32 (N=O)
X	$CHCl_3$	2.97 (N—H nonbonded), 3.22 (N—H bonded), 6.22 (C=N)
XI	$CHCl_3$	6.25 (C=N), 7.48, 9.73 (N=O)
XIII	$CHCl_3$	3.01 (N—H nonbonded), 3.33 (N—H bonded), 6.18 (C=N)
XIV	$CHCl_3$	6.23 (C=N), 7.52, 9.36 (N=O)

[a] Spectra were taken on a Baird Recording infrared spectrophotometer using a rock salt prism and matched 0.1-mm. cells.

EXPERIMENTAL[8]

3-Nitrosoimino-1,5,5-trimethyl-2-thia-4-azabicyclo[4.2.2]-decane (III). A solution of 10 g. II[9] in 50 cc. glacial acetic acid was cooled on an ice bath, 60 cc. of ice cold 10% aqueous sodium nitrite was added, and the mixture was allowed to stand at ice bath temperature. An excess of nitrous acid was demonstrated by the fact that a drop of solution turned starch–potassium iodide paper blue. After standing for 20 min., during which time the solution turned progressively darker yellow, a golden yellow solid began to precipitate. The mixture was allowed to stand overnight, warming up slowly to room temperature. It was then cooled and the yellow crystalline material collected on a suction filter. Yield 9.5 g. (83.6%); decomposed explosively 142–143°. Washing the crude material with water containing a little ethanol raised the decomposition temperature to 145–146°. Recrystallization from absolute ethanol further raised the point of decomposition to 149–150°.

Anal.[10] Calcd. for $C_{11}H_{19}N_3SO$: N, 17.41. Found: N, 17.38.

A small amount of compound III was treated with 2 cc. cold concentrate sulfuric acid, and a few small crystals of phenol were added. On gentle warming, the solution turned dark green. Careful dilution with water turned the solution red, while making it alkaline turned it green once more. This constituted a positive Liebermann's test for *N*-nitrosoamines.[11]

When the compound III was warmed with excess concentrated hydrochloric acid on the steam bath, nitrous acid was evolved rapidly. After 5 min., precipitation of a white crystalline material began. The mixture was evaporated to dryness and the residue recrystallized from dilute hydrochloric acid, after decolorization with Norit A. The compound did not depress the melting point of the hydrochloride of II,[1] and treatment with dilute base regenerated II.[1] This constituted further evidence that the compound was an *N*-nitrosoamine.[12]

Sodium 1,5,5-trimethyl-2-thia-4-azabicyclo[4.2.2]dec-3-ene-3-diazotate (IV). A portion of III was placed in 4*N* sodium hydroxide, the solution heated to boiling and then set aside to cool overnight. A yellowish oil precipitated which hardened gradually to a white solid. The solid was separated and dissolved in benzene. The solution was heated to boiling and Norit A added. At this point the solid precipitated and would not redissolve in benzene. A few drops of ethanol were therefore added, the mixture heated until the compound dissolved, the solution filtered, and the filtrate evaporated to dryness. The residue was dissolved in warm water and the white compound salted out with sodium sulfate after cooling. The crystals were washed on the filter with $CHCl_3$ and ether; dec. 290–291°. The compound was ashed to the sulfate.

Anal. Calcd. for $C_{11}H_{18}N_3SONa$: N, 15.96; % ash, 26.9. Found: N, 15.50; % ash, 26.6.

Treatment with cold glacial acetic acid resulted in immediate regeneration of III.

3-Imino-1,4,5,5-tetramethyl-2-thia-4-azabicyclo[4.2.2]decane (VIII). Several grams of II were dissolved in a minimum of dry ether, excess methyl iodide was added, and the mixture heated on the steam bath for several minutes. The flask was then stoppered tightly and allowed to stand overnight. The crystals which formed were separated, washed with several portions of dry ether, and crystallized from absolute ethanol-ether. This substance is the hydriodide salt of VIII, m.p. 216–217°.

Anal. Calcd. for $C_{12}H_{23}N_2SI$: C, 40.68; H, 6.50; N, 7.91. Found: C, 41.22; H, 6.50; N, 8.14.

The hydriodide was treated with 33% potassium hydroxide and the mixture warmed on the steam bath. A colorless oil with a strong fishy odor separated. The latter was extracted with ether, the extract dried over anhydrous sodium sulfate, and the solvent evaporated. The residual oil crystallized slowly on standing. Recrystallization from petroleum hexane (Skellysolve B) yielded white crystals of VIII; m.p. 94–95°.

Anal. Calcd. for $C_{12}H_{22}N_2S$: C, 63.66; H, 9.80; N, 12.38. Found: C, 63.76; H, 9.51; N, 12.68.

Picrate: Recrystallized from ethanol; m.p. 166–168°.

Anal. Calcd. for $C_{18}H_{25}N_5SO_7$: C, 47.46; H, 5.53; N, 15.38. Found: C, 47.65; H, 5.77; N, 15.65.

Phenylthiourea: Recrystallized from ethanol; m.p. 182–183°.

Anal. Calcd. for $C_{19}H_{27}N_3S_2$: C, 63.11; H, 7.53; N, 11.62. Found: C, 63.59; H, 7.41; N, 11.76.

3-Nitrosoimino-1,4,5,5-tetramethyl-2-thia-4-azabicyclo-[4.2.2]decane (IX). Compound VIII was treated in cold glacial acetic acid solution with an excess of cold 10% aqueous sodium nitrite. After 1 hr., an oil began to separate which solidified on standing overnight. The orange crystals were separated and recrystallized from benzene-hexane yielding shiny orange plates; dec. 117–118°.

Anal. Calcd. for $C_{12}H_{21}N_3SO$: C, 56.44; H, 8.29; N, 16.45. Found: C, 56.91; H, 8.04; N, 16.22.

3-Methylamino-1,5,5-trimethyl-2-thia-4-azabicyclo[4.2.2]-dec-3-ene (X). A mixture consisting of 100 g. (0.735 mole) +-limonene, 99 g. (1.1 mole) methylthiourea, and 171 g. (0.9 mole) *p*-toluenesulfonic acid monohydrate was heated and stirred on the steam bath for three days. The product was washed with ether and water and then warmed with excess 4*N* sodium hydroxide. The brown solid produced was filtered off, washed with cold water, recrystallized from petroleum hexane, decolorized with Norit A, and recrystal-

(8) All melting points were taken on a Fisher-Johns block. Analyses are by H. Beck, J. Sorenson, and C. White.

(9) Prepared as directed in Ref. 1.

(10) Some difficulty was experienced in obtaining a carbon analysis in this series. In several attempts, the compounds exploded on combustion, and, even when explosion was avoided, decomposition was accompanied by rapid evolution of nitrogen oxides which apparently found their way into the CO_2 absorption tube causing a high carbon analysis.

(11) W. J. Hickinbottom, *Reactions of Organic Compounds*, 2nd ed., Longmans, Green and Co., London, 1948, p. 358.

(12) W. J. Hickinbottom, *Reactions of Organic Compounds*, 2nd ed., Longmans, Green and Co., London, 1948, p. 327.

lized from hexane again. Yield 57.4 g. (34.6%); m.p. 147–148°.

Anal. Calcd. for $C_{12}H_{22}N_2S$: C, 63.66; H, 9.80; N, 12.38. Found: C, 63.76; H, 9.62; N, 12.60.

Picrate: Recrystallized from ethanol; m.p. 207–208°.

Anal. Calcd. for $C_{18}H_{25}N_5SO_7$: N, 15.38. Found: N, 15.71.

Benzamide: Recrystallized from ethanol-water; m.p. 86–87°.

Anal. Calcd. for $C_{19}H_{26}N_2SO$: N, 8.48. Found: N, 8.71.

3-Methylimino-4-nitroso-1,5,5-trimethyl-2-thia-4-azabicyclo-[4.2.2]decane (XI). A solution of 3 g. of X in 25 cc. glacial acetic acid was treated with excess cold 10% aqueous sodium nitrite. An oil formed after several minutes which solidified on standing in the cold overnight. The light yellow solid was collected on a suction filter and washed with cold water. Crystallization was accomplished by dissolving the compound in ethanol, warming the solution slightly, adding water to cloudiness, warming until solution occurs again, and allowing the solution to cool slowly in a stoppered test tube placed in water bath. Clear, cubic, faintly yellow crystals, m.p. 39–40°, were produced.

Anal. Calcd. for $C_{12}H_{21}N_3SO$: N, 16.45. Found: N, 16.81.

The compound gave a positive Liebermann's test and evolved nitrous acid when treated with concentrated hydrochloric acid.

3-Anilino-1,5,5-trimethyl-2-thia-4-azabicyclo[4.2.2]dec-3-ene (XIII). A mixture consisting of 50 g. (0.369 mole) +-limonene, 99 g. (0.65 mole) phenylthiourea, and 92.5 g. (0.485 mole) *p*-toluenesulfonic acid was heated and stirred on the steam bath for three days. The brown oily product was washed with ether and water and then warmed with excess 4*N* sodium hydroxide. The solid, which was produced, was separated and recrystallized from ethanol; yield 22 g. (20.6%), m.p. 165–166°.

Anal. Calcd. for $C_{17}H_{24}N_2S$: C, 70.78; H, 8.39; N, 9.71. Found: C, 70.70; H, 8.25; N, 9.93.

Picrate: Recrystallized from methyl ethyl ketone; m.p. 237–238°.

Anal. Calcd. for $C_{23}H_{27}N_5SO_7$: C, 53.37; H, 5.26; N, 13.53. Found: C, 54.38; H, 5.35; N, 14.00.

Benzamide: Recrystallized from hexane-cyclohexane; m.p. 140–141°.

Anal. Calcd. for $C_{24}H_{28}N_2SO$: C, 73.43; H, 7.19; N, 7.14. Found: C, 73.90; H, 6.98; N, 7.51.

3-Phenylimino-4-nitroso-1,5,5-trimethyl-2-thia-4-azabicyclo-[4.2.2.]decane (XIV). A solution of 5 g. in 25 cc. cold glacial acetic acid was treated with excess cold 10% aqueous sodium nitrite. A yellow oil precipitated which solidified on standing overnight. The solid was collected on a suction filter. Recrystallization from absolute ethanol yielded light yellow crystals; m.p. 115–116°.

Anal. Calcd. for $C_{17}H_{23}N_3SO$: N, 13.24. Found: N, 12.46.

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[CONTRIBUTION FROM THE OHIO STATE UNIVERSITY RESEARCH FOUNDATION]

Products from Reaction of Hydrazine and Thionooxamic Acid and Their Conversion into Heterocyclic Compounds[1]

RUDI RÄTZ AND HANSJUERGEN SCHROEDER

Received June 15, 1958

Contrary to literature statements free thionooxamic acid, $H_2N—CS—COOH$, could be isolated and was found to be absolutely stable in the solid state. This acid is highly reactive to hydrazine and yielded, depending on the amount of hydrazine, oxalamidrazone and oxalhydrazidine. Oxalamidrazone was used for the synthesis of new 1, 2, 4-triazinecarbonic esters.

Thionooxamic acid (I), $NH_2—C(=S)—COOH$, has been reported only in the form of its salts and derivatives, *e.g.* esters, amides, etc. All attempts to prepare the free acid from alkali salts, even under mild conditions, resulted in failure, since the aqueous solution of I, obtained by adding the required amount of dilute mineral acid to the aqueous solution of an alkali thiono-oxamate, undergoes rapid decomposition with separation of elemental sulfur. Therefore I was described as incapable of existence in the free state.[2]

We have found, however, that immediate extraction of the aqueous solution of I by certain organic solvents, such as diethyl ether or ethyl acetate, leads to stable yellow prismatic crystals of I, m.p. 113°. These crystals of I have been stored for over two years without signs of decomposition.

Due to the presence of a free carboxylic and a thioamide group in its molecule, I represents a highly reactive compound. In order to obtain components for the synthesis of *N*-heterocyclics, the reaction of I with hydrazine (II) was studied.

Depending on the conditions different reaction products may be obtained from I and II. In ethanolic solution I reacted with one mole of anhydrous II to give the hydrazinium thionooxamate (III) which reacted vigorously with cold water to hydrogen sulfide and oxamic acid hydrazone (IV) (oxalamidrazone). Upon heating at 200°, IV decomposed with loss of ammonia and carbon dioxide. The yet unknown formamidrazone (V) could not be isolated as an intermediate during this thermal reaction, since at least under these conditions immediate self-condensation with formation of 4-amino-1,2,4-triazole (VI) occurred. This reaction and earlier observations[3] indicate

(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 Corp., New York, N. Y.

(2) H. Weddige, *J. prakt. Chem.* (2), **9**, 137 (1874).

(3) Ch. Grundmann and R. Rätz, *J. Org. Chem.*, **21**, 1037 (1956).