"*p*-Urazine" and "Dithio-*p*-urazine"[1]

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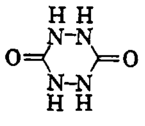
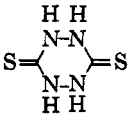
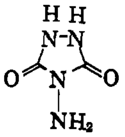
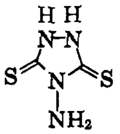
Two literature references purported to give *p*-urazine were re-examined and the product in each case shown to be biurea. A literature preparation claimed to be dithio-*p*-urazine was shown to be instead an isomer, N-aminodithiourazole. Certain other reaction discrepancies are also discussed.

The literature[2] records many times the synthesis of compounds presumed to have the structures of *p*-urazine (I)[3] and dithio-*p*-urazine (II). For example, Guha and De[4] have reported that the fusion of urea with carbohydrazide yields I. Re-examination of the product of this reaction by us has clearly established it to be not I nor its isomer III, but biurea.[5]


I


II


III

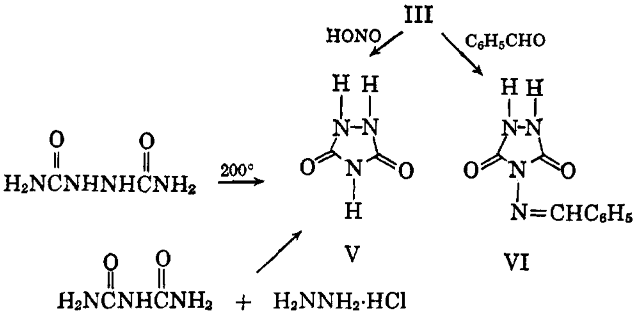

IV

Chattaway[6] has reported the synthesis of I from the action of ammonium hydroxide on chlorinated urea, but the product appears to be biurea again.[7] Consequently, the *p*-urazine reported by Datta and Gupta,[8] who varied the reaction of Chattaway only by using either allylamine or benzylamine instead of ammonium hydroxide, probably also is biurea.

Elemental analysis of the purified "*p*-urazine" obtained from the Guha and De preparation showed it to possess two additional hydrogen atoms and hence suggested it was biurea. This was established by comparison of its infrared spectra with an authentic sample of biurea as well as its conversion to urazole[9] (V) (Chart A). The latter compound, for comparison, was also prepared by heating biuret and hydrazine hydrochloride together.[10]

Confirmation of the structure assigned III (synthesized by two different routes[11]) was obtained *via* demonstration of the presence of a free primary amine group by preparing the known benzylidene derivative (VI), and deamination of III to give V. The infrared spectra of urazole (V) prepared by the three different routes shown in Chart A were identical with each other.

CHART A



A brief discussion of the infrared spectrum of III is pertinent. A double band between 1600 and 1650 cm.$^{-1}$ resembles that present in the spectrum of succinimide and is assigned to carbonyl absorption. A 1620-cm.$^{-1}$ band is due to NH deformation, while the broad absorption from 2700 to 3500 cm.$^{-1}$ is similar to absorption found in dimeric lactams.

It has been found that the $Na_3[Fe(CN)_5NH_3]$ reagent[12] is of diagnostic value for certain types of compounds discussed in this paper. An intense blue color is obtained with triazoles embodying either a –NHNH– or a $=$NNH— group within the ring.

Turning to the structure of dithio-*p*-urazine (II) it now has been also ascertained that the reaction of 3-thiocarbohydrazide with potassium ethyl xanthate in a sealed tube[4] does not give II,[13,14] but its isomer IV. Guha and De[4] were not able to obtain a benzylidene derivative of their "dithio-*p*-urazine," but we have found that *via* the ammonium salt of these authors' compound a readily recrystallizable benzylidene derivative (VII, Chart B) with m.p. 175–177° can be prepared. The benzylidene derivative reported by Arndt and Bielich[15] had low m.p. 136°. When Guha and De's compound was treated with nitrous acid, an intractable yellow powder was obtained, reacting sluggishly with NaN_3/I_2 reagent (test for thiol group) and having m.p. 105° (indefinite). Although attempts

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[1] Presented before the Division of Organic Chemistry at the 139th National Meeting of the American Chemical Society, St. Louis, Mo., March, 1961.

[2] P. F. Wiley, "The 1,2,4,5-Tetrazines" in "The Chemistry of Heterocyclic Compounds," Interscience Publishers, Inc., New York, N. Y., 1956, pp. 191–196.

[3] Confusion on this topic has been compounded by the use of "*p*-urazine" to mean both I and III (*e.g.*, ref. 11b and those references included therein). While neither "urazine" nor "urazole" are systematic names, the "ine" and "ole" endings imply six-membered and five-membered rings, respectively, and are so used in this paper.

[4] P. C. Guha and S. C. De, *J. Chem. Soc.*, **125**, 1215 (1924).

[5] After this work was completed, F. Eloy and C. Moussebois, *Bull. soc. chim. Belges*, **68**, 432 (1959), published a similar observation. These authors also have confirmed that the product of five previously reported reactions is III. *Chemical Abstracts* [**54**, 7625*h* (1960)] is misleading in that the abstract implies that the sole product of *all* reactions previously claimed to give I or III gave III, rather than just *some* reactions. We thank a referee for calling this to our attention.

[6] F. D. Chattaway, *J. Chem. Soc.*, **95**, 235 (1909).

[7] Since the completion of this work, C. S. Grove, G. F. Grillot, and R. C. Chang, *J. Org. Chem.*, **26**, 4131 (1961), have obtained from Chattaway's preparation a substance which appeared to them to be biurea. These authors also claim the preparation of authentic *p*-urazine (I) after the method of T. Curtius and K. Heidenreich, *Ber.*, **27**, 2684 (1894); *J. prakt. Chem.* [2]**52**, 454 (1895). However, since Curtius and Heidenreich reported their compound gave a benzylidene derivative which melted at 253°, the compound most certainly must be III and not I.

[8] R. L. Datta and S. D. Gupta, *J. Am. Chem. Soc.*, **35**, 1183 (1913).

[9] J. Thiele and O. Stange, *Ann.*, **283**, 1 (1894).

[10] G. Pellizzari and G. Cuneo, *Gazz. chim. ital.*, **24**, I, 499 (1894).

[11] (a) A. Purgotti, *ibid.*, **27**, II, 60 (1897); (b) L. F. Audrieth and E. B. Mohr, *Inorg. Syn.*, **4**, 29 (1953).

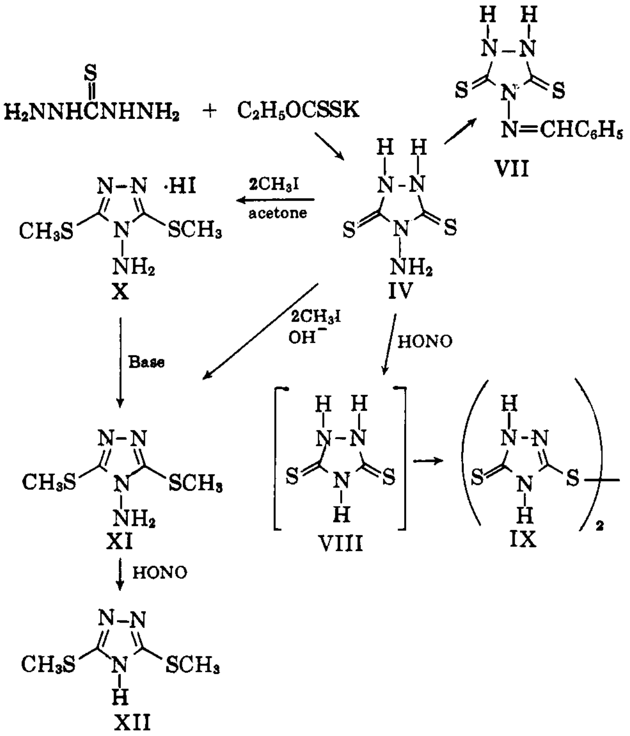
[12] F. Feigl, "Spot Tests. II. Organic Applications," Elsevier Publishing Co., New York, N. Y., 1954, pp. 212–213.

[13] J. Sandström, *Acta Chem. Scand.*, **15**, 1295 (1961), has shown that heating 3-thiocarbohydrazide and carbon disulfide in a sealed tube [P. G. Guha and S. C. De, *J. Indian Chem. Soc.*, **1**, 141 (1925)] does not give II either.

[14] J. Sandström, *Acta Chem. Scand.*, **15**, 1575 (1961), herein reports the first authentic preparation of dithio-*p*-urazine (II).

[15] F. Arndt and F. Bielich, *Ber.*, **56**, 809 (1923).

Chart B



to purify this product for proper characterization were fruitless, it is assumed that this substance is the disulfide IX resulting from oxidation of the deamination product, dithiourazole (VIII). That this is a reasonable assumption is shown by a similar transformation of XVI to XIX. Arndt and Milde[16] and Fromm[17] both reported difficulties working with compound IX.

Evidence for a free amino group was obtained by converting IV to 4-amino-3,5-bis(methylthio)-4H-1,2,4-triazole (XI), which subsequently smoothly deaminated to the known 3,5-bis(methylthio)-4H-1,2,4-triazole (XII).[16,18] Finally, the Guha and De compound proved to be identical by melting point and infrared spectrum with a sample of IV prepared by the method of Hoggarth.[19]

In the course of this work a novel synthesis of an aminodithiourazole was discovered. When equimolar quantities of 3-thiocarbohydrazide and dimethyl dithioimidocarbonate hydrochloride reacted in water, a homogeneous white solid precipitated. It gave a positive test with NaN_3/I_2 reagent, dissolved in dilute sodium hydroxide, and was precipitated upon acidification. Four products are possible depending upon the cyclization route taken (Chart C). Elemental analysis excluded XIII and XIV, while XV was eliminated by the ready formation of a benzylidene derivative XVII (Chart D). Deamination of the reaction product afforded two known compounds, 3-methylthio-Δ^2-1,2,4-triazoline-5-thione (XVIII) and its oxidation product, the disulfide (XIX). These compounds agree in melting point with those prepared by Arndt and Milde[16] in different fashion. Therefore, the correct configuration of this previously unknown compound must be XVI.

Chart C

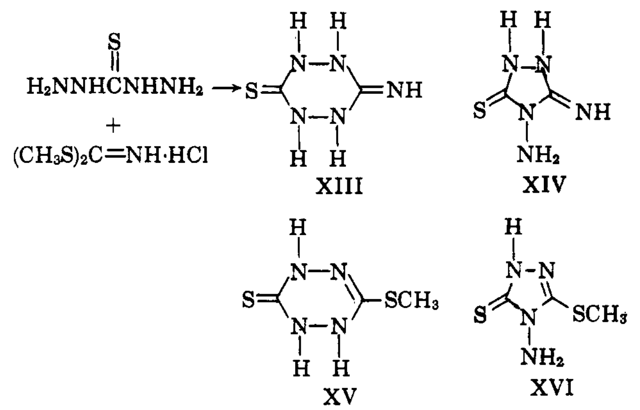
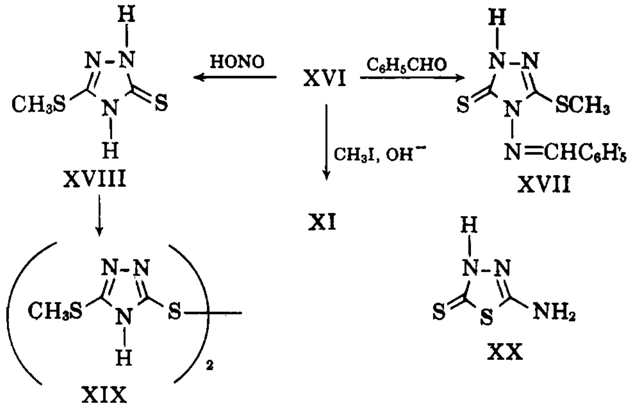
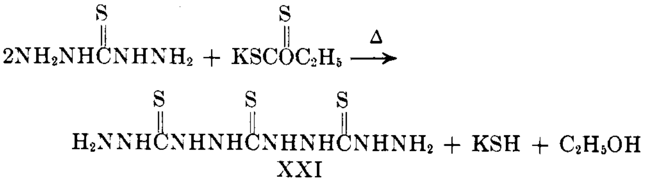


Chart D





$$2NH_2NH\overset{S}{\overset{\|}{C}}NHNH_2 + KS\overset{S}{\overset{\|}{C}}OC_2H_5 \xrightarrow{\Delta}$$

$$H_2NNH\overset{S}{\overset{\|}{C}}NHNH\overset{S}{\overset{\|}{C}}NHNH\overset{S}{\overset{\|}{C}}NHNH_2 + KSH + C_2H_5OH$$

XXI

An attempt was made to prepare "monothio-*p*-urazine,"[4] but biurea was the product obtained.[20] Numerous efforts were made to repeat the preparation of IV by the acid cyclization of 1-thiocarbamylthiocarbohydrazide[21] using a sample of the latter compound synthesized after the method of Scott and Audrieth,[22] but the product proved to be 2-amino-Δ^2-1,3,4-thiadiazoline-5-thione (XX).[23]

During one of the preparations of the Guha and De "dithio-*p*-urazine," a shorter heating period was employed leading to the formation of a compound having the empirical formula, $C_3H_{10}N_8S_2$. Although no proof of structure is presented, 1,1′-(thiocarbonyl)bis(3-thiocarbohydrazide) (XXI) is offered as a possible structure. This compound has not been reported in the literature. It was thought that XXI might be an intermediate in the preparation of IV, particularly since it melts, resolidifies, and remelts at 203–205° dec. However, an attempt to effect this conversion on a 1-g. scale gave no IV.

Compounds IV, VIII, IX, XVI, XVIII, and XX showed medium to strong absorption in the infrared

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[16] F. Arndt and E. Milde, *Ber.*, **54B**, 2089 (1921).

[17] E. Fromm, *Ann.*, **426**, 313 (1922).

[18] L. Loewe and M. Türgen, *Rev. faculte sci. univ. Istanbul*, **14A**, 227 (1949).

[19] E. Hoggarth, *J. Chem. Soc.*, 4817 (1952).

[20] We thank Mr. D. W. Long of this laboratory for this experiment.

[21] See Guha and De reference in ref. 13.

[22] E. S. Scott and L. F. Audrieth, *J. Org. Chem.*, **19**, 742 (1954).

[23] H. Beyer and C. F. Kröger, *Ann.*, **637**, 126 (1960), have independently obtained similar results.

between 1500–1550 cm.$^{-1}$ attributed to the $\overset{\underset{\|}{\text{S}}}{\text{C}}\text{—NH}$ vibration.[24] There was also medium to strong absorption between 1190–1330 and 940–1060 cm.$^{-1}$ associated with the $\text{—}\overset{\underset{\|}{\text{S}}}{\text{C}}\text{NH}$ symmetric and asymmetric stretching vibrations.

Experimental

Melting points were determined in a Thomas-Hoover capillary melting point apparatus or on a Fisher-Johns block and are uncorrected. Microanalyses were performed by the microanalytical laboratory of the American Cyanamid Co. or by Galbraith Laboratories, Inc.

"*p*-Urazine." After Guha and De's Procedure.—This compound was purchased from the Aldrich Chemical Co. which had prepared it after the method of Guha and De.[4] Recrystallization from hot 0.1 *M* HCl and then water gave m.p. 250–252° dec. (block). It had an infrared spectrum identical with an authentic sample of biurea.

Anal. Calcd. for $C_2H_4N_4O_2$: C, 20.69; H, 3.47; N, 48.27. Found: C, 20.33; H, 5.03; N, 48.01. Biurea $C_2H_6N_4O_2$ required C, 20.34; H, 5.12; N, 47.43.

Guha and De's "*p*-urazine" has a solubility of 1 g./*ca.* 75 ml. hot 0.1 *M* HCl and is insoluble in DMF. Compound III has a solubility of 1 g./*ca.* 22 ml. hot 0.1 *M* HCl and is soluble in DMF; it could be quantitatively titrated in a 3:7 DMF–pyridine mixture with 0.1 *N* tetrabutylammonium hydroxide to give a value of 99.7% purity. The solution turned green at the end point suggestive of a polyphenol. Lack of solubility prevented titration of "*p*-urazine."

N-Aminourazole (III). (**a**).—The procedure used was that of Audrieth and Mohr[11b] with the one modification of reducing the reaction time from 4 to 2.5 hr. Heating of carbohydrazide (30.2 g.) in hydrochloric acid gave 6.34 g. of product after one recrystallization, with m.p. 269–274° dec. (capillary tube), 272–275° dec. (block) (lit. m.p. 275° dec.).

Anal. Calcd. for $C_2H_4N_4O_2$: C, 20.69; H, 3.47; N, 48.27. Found: C, 21.05; H, 3.50; N, 48.10.

(**b**).—The method followed was that of Purgotti.[11a] The reaction of biurea (23.5 g.) with hydrazine sulfate (26.0 g.) gave as a first crop of crude product 6.40 g., m.p. 254–258° dec. (capillary tube), and a second crop, 0.50 g., m.p. 241–245° dec. (lit. m.p. 266–267°).

The benzylidene derivative (VI) was prepared in hot 80% ethanol and recrystallized from 95% ethanol to give needles, m.p. 258–259° (lit.[11b] m.p. 253°). Guha and De's "*p*-urazine," when treated under similar conditions, failed to react.

Anal. Calcd. for $C_9H_7N_4O_2$: C, 53.20; H, 3.47; N, 27.57. Found: C, 53.21; H, 3.56; N, 27.53.

Urazole (V) from N-Aminourazole.—N-Aminourazole (1.2 g., 0.01 mole) was dissolved in 1 *N* HCl (20 ml.) and this solution diluted with water (50 ml.). The solution was rapidly cooled with stirring and to the fine suspension which resulted was added dropwise a solution of sodium nitrite (0.69 g. in 20 ml. water) at a temperature of 10–15°. The solid dissolved and the solution took on a faint yellow color. After evaporation to dryness the solid residue was recrystallized from water to give 0.38 g. of product, m.p. 229–238° dec. (capillary tube) (lit.[9,10] m.p. 244°). The infrared spectrum of this preparation and the spectra of the samples prepared according to these references were superimposable on each other.

N-Aminodithiourazole (IV). (**a**).—The procedure followed was that of Guha and De[4]; crude yield was 49.6%. Recrystallization from water gave a lemon-colored solid, m.p. 202–204°. The product, when dissolved in ammonium carbonate solution, treated with decolorizing charcoal, boiled until no ammonia evolution occurred, cooled, and then acidified, gave a white powder, m.p. 205–207° dec. (capillary tube).

Anal. Calcd. for $C_2H_4N_4S_2$: C, 16.21; H, 2.72; N, 37.80; S, 43.26. Found: C, 16.38; H, 2.96; N, 37.92; S, 43.18.

The benzylidene derivative (VII) was prepared by dissolving IV (0.74 g., 5 mmoles) in 10 ml. of ammonium hydroxide and boiling to discharge excess ammonia. A solution of benzaldehyde (1.06 g., 10 mmoles) in ethanol (5 ml.) was added and the mixture refluxed for 2 hr., whereupon the yellow solution was poured into water. The unchanged aldehyde was removed by ether extraction and the aqueous phase acidified to give a white gum. The gum was taken up in ether, water washed, and dried; ether was removed. The resulting gum (404 mg., 33.9%) hardened upon standing, and, after two recrystallizations from benzene followed by sublimation at 110° (0.3 mm.), gave an off-white solid, m.p. 175–177°.

Anal. Calcd. for $C_9H_8N_4S_2$: C, 45.74; H, 3.41; N, 23.71; S, 27.13. Found: C, 45.84; H, 3.38; N, 23.63; S, 26.97.

(**b**).—Hoggarth's procedure[19] was adhered to as closely as possible using the same scale preparation. After the first acidification stage, 9.95 g. (m.p. 209–214° dec.) of a side product, 3,4-diamino-Δ^2-1,2,4-triazoline-5-thione, precipitated, and by allowing the filtrate to stand overnight at room temperature an additional 4.50 g. (m.p. 205–209° dec.) were obtained. Hoggarth obtained a total of 6.6 g. of the diaminotriazolinethione at this point. The filtrate from the above compound after further acidification gave IV (5.0 g., m.p. 197–200° dec.), contaminated with a trace of the diaminotriazolinethione as determined by its infrared spectrum. Purification gave a white solid (3.75 g.) with m.p. 199–205° dec. (block), 204–206° dec. (capillary). The infrared spectrum was identical in all respects with that of the sample prepared in part a.

Disulfide of Dithiourazole (IX).—IV (741 mg., 5.0 mmoles) was stirred into 12 ml. of 1 *N* HCl diluted with 50 ml. water at 75°. The suspension was rapidly cooled to 5° with stirring and a solution of sodium nitrite (355 mg., 5.0 mmoles in 20 ml. of water) added in small portions. The resulting solid was taken up in 95% ethanol and allowed to separate slowly at room temperature. A yellow powder was deposited, m.p. 105° (indefinite). The infrared spectrum was different from that of an authentic sample of dithiourazole (m.p. 219–220°).

4-Amino-3,5-bis(methylthio)-4H-1,2,4-triazole Hydriodide (X).—To a solution of IV (1.48 g., 0.01 mole) in 25 ml. of refluxing anhydrous acetone was added all at once excess methyl iodide (5.68 g., 0.04 mole). Warming was continued for 15 min., the solvent stripped, and the dark residue triturated with anhydrous ether to give a yellow solid, 1.25 g. (41.0%).

Two recrystallizations from absolute ethanol containing enough water to effect solution (addition of ether to the cooled solution aided crystallization) gave the analytical sample as white needles, m.p. 175–176.5°. The product darkened upon short standing (no infrared spectral changes), but the coloration was readily removed by an ether wash.

Anal. Calcd. for $C_4H_9IN_4S_2$: C, 15.79; H, 2.98; I, 41.72; N, 18.42; S, 21.08. Found: C, 16.16; H, 2.81; I, 41.50; N, 18.60; S, 20.69.

4-Amino-3,5-bis(methylthio)-4H-1,2,4-triazole (XI).—To a filtered solution of IV (10.0 g., 68 mmoles) in 136 ml. of 2 *N* sodium hydroxide (0.27 mole) was added 125 ml. of 95% ethanol, followed by methyl iodide (38.6 g., 0.27 mole). The mixture was permitted to stand at room temperature for several hours and evaporated to dryness. The residue was not very soluble in ether or in hot benzene, but could be dissolved in chloroform. After concentration of the chloroform extracts, filtration of the sodium iodide, and ice cooling, tan needles separated which partially turned purple upon air exposure. One recrystallization from ethyl acetate gave a yellow solid which again partially turned purple. Sublimation at 90° (0.5 mm.) removed the color bodies as volatiles leaving the unsublimed material as white needles, 8.46 g. (71.2%), m.p. 146–148°, identical by melting point and infrared spectrum with the free base prepared from the hydriodide (X).

Anal. Calcd. for $C_4H_8N_4S_2$: C, 27.26; H, 4.58; N, 31.79; S, 36.38. Found: C, 27.28; H, 4.98; N, 31.62; S, 36.12.

3,5-Bis(methylthio)-4H-1,2,4-triazole (XII).—To a filtered solution of XI (4.41 g., 0.25 mmole) in 100 ml. of 0.5 *N* hydrochloric acid was added with stirring at 0–5° a solution of sodium nitrite (1.73 g., 0.25 mmole) in 10 ml. of water. The first few drops turned the colorless solution orange-brown, then, as the addition proceeded, gray, and finally blue. After the addition was completed (30 min.), the mixture was allowed to warm to room temperature (1 hr.), and a light blue solid (1.34 g., m.p. 90–91° dec., turned white upon standing) filtered off. The filtrate

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[24] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 350, assigns the 1470–1500-cm.$^{-1}$ region to this grouping.

upon evaporation left mostly as a residue the triazole hydrochloride, m.p. 148° (acetone). The hydrochloride salt was converted to the triazole by solution in a minimum amount of water and treatment with 6 *N* sodium hydroxide to give product with m.p. 93–94° (lit.[16,18] m.p. 91°, 93–94°). Total yield of product was 2.75 g. (68.3%). An analytical sample prepared by slow evaporation of an aqueous solution has m.p. 92.5–93°.

Anal. Calcd. for $C_4H_7N_3S_2$: C, 29.80; H, 4.38; N, 26.07; S, 39.77. Found: C, 29.97; H, 4.58; N, 26.22; S, 39.57.

Dimethyl Dithioimidocarbonate Hydrochloride.[25]—Addition of hydrogen chloride to about equal amounts of methyl mercaptan and methyl isothiocyanate in chloroform at 0° afforded the crystalline product (87%), m.p. 158–159° dec.

4-Amino-3-(methylthio)-Δ^2-1,2,4-triazoline-5-thione (XVI).—To a solution of 3-thiocarbohydrazide (5.31 g., 0.05 mole) in 75 ml. of water was added in small portions, over a 10-min. period, dimethyl dithioimidocarbonate hydrochloride with stirring. This reagent slowly dissolved with a steady evolution of methyl mercaptan. After 25 min., a solid began to precipitate. The thick paste which was present after 2 hr. was filtered to give 4.31 g., m.p. 174–208° (capillary). The filtrate was evaporated to dryness; the residue and product combined and recrystallized from a minimum amount of water to give 4.91 g., m.p. 186–190° (60.5%). Recrystallization again from water gave white fluffy needles, m.p. 197–197.5°.

Anal. Calcd. for $C_3H_6N_4S_2$: C, 22.21; H, 3.73; N, 34.54; S, 39.53. Found: C, 22.20; H, 4.34; N, 34.33; S, 39.43.

The benzylidene derivative (XVII) prepared at room temperature in ethanol containing a trace amount of hydrochloric acid had m.p. 205–207°.

Anal. Calcd. for $C_{10}H_{10}N_4S_2$: C, 47.99; H, 4.03; N, 22.39; S, 25.62. Found: C, 48.35; H, 4.23; N, 22.27; S, 25.58.

3-Methylthio-Δ^2-1,2,4-triazoline-5-thione (XVIII) and 3,3′-Dithiobis[5-(methylthio)-4H-1,2,4-triazole] (XIX).—XVI (4.05 g., 0.25 mmole) was dissolved in 250 ml. of water containing 60 ml. of 1 *N* hydrochloric acid and warmed to 75° to effect solution. To the solution, which was cooled rapidly to 5–10° with stirring (slush formed), a solution of sodium nitrite (1.72 g., 0.25 mmole) in 50 ml. of water was added dropwise with stirring. After the addition was complete, the reaction mixture was stirred at 5–10° for 15 min. and then allowed to warm to room temperature. A solid was removed and the filtrate was evaporated to dryness. The residual solid was extracted with boiling 95% ethanol several times to obtain additional product. The original precipitate was then dissolved in these combined extracts, the solution filtered, and three crops of crystals collected. Fractional crystallization of these crops from absolute ethanol and then acetone permitted the separation of three compounds. These were the triazolinethione, 0.85 g. (23.2%, least soluble absolute ethanol and acetone), the disulfide, 1.13 g. (30.9%), and unchanged starting material (most soluble). A final recrystallization of the triazolinethione from water gave white plates, m.p. 248–250° (lit.[16] m.p. 254°).

Anal. Calcd. for $C_3H_5N_3S_2$: C, 24.48; H, 3.42; N, 28.55; S, 43.56. Found: C, 24.47; H, 3.23; N, 28.45; S, 43.45.

A final recrystallization of the disulfide from absolute ethanol gave white prisms, m.p. 210–211° (lit.[16] m.p. 203°).

Anal. Calcd. for $C_6H_8N_6S_4$: C, 24.64; H, 2.76; N, 28.74; S, 43.85. Found: C, 24.88; H, 3.09; N, 28.75; S, 43.98.

Attempted Preparation of IV from 1-Thiocarbamylthiocarbohydrazide.—The hydrazide[22] (11.3 g.) in 50 ml. of concentrated hydrochloric acid was heated for 40 min. at 90°. This solution after evaporation to dryness left a solid residue which was recrystallized twice from water to give tan needles, 1.1 g., m.p. 228–231° dec. Sublimation gave raised m.p. 230–232° dec., no melting point depression upon admixture with authentic 2-amino-Δ^2-1,3,4-thiadiazoline-5-thione.[26] The infrared spectra of the two samples were identical.

Anal. Calcd. for $C_2H_3N_3S_2$: C, 18.04; H, 2.27; N, 31.56; S, 48.16. Found: C, 18.39; H, 2.24; N, 30.92; S, 48.38.

1,1′-(Thiocarbonyl)bis(3-thiocarbohydrazide) (XXI).—3-Thiocarbohydrazide (50.0 g., 0.47 mole) and potassium ethyl xanthate (75.5 g., 0.47 mole) were heated in 500 ml. of 95% ethanol in a rocking autoclave at 100° for 2 hr. (instead of 5 hr.). The contents were washed out of the autoclave with water (300–500 ml.) and filtered from some gray solid. The latter was extracted with boiling water, and the extracts were combined with the original solution. The yellow solid (22.4 g.) which separated upon acidification of the reaction mixture was recrystallized from 500 ml. of hot water to give 18.0 g. (31.4%) of tan needles, m.p. 163–166°, with resolidification and remelting at 202–204° dec. Recrystallization from water three times gave a pure sample, m.p. 170–172° (203–205°).

Anal. Calcd. for $C_3H_{10}N_8S_3$: C, 14.17; H, 3.96; N, 44.07; S, 37.82. Found: C, 14.29; H, 4.18; N, 43.95; S, 37.77.

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[25] We thank Dr. R. W. Addor of this laboratory for this preparation.

[26] L. L. Bambas, "Five-Membered Heterocyclic Compounds with Nitrogen and Sulfur or Nitrogen, Sulfur, and Oxygen," Interscience Publishers, Inc., New York, N. Y., 1952, pp. 149-153.

Reaction of Eugenol with Synthesis Gas. Synthesis of 5,6,7,8-Tetrahydro-3-methoxy-2-naphthol

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The reaction of eugenol with synthesis gas, in the presence of dicobalt octacarbonyl, leads to a ring closure with the formation of 5,6,7,8-tetrahydro-3-methoxy-2-naphthol. The isolation of 5,6-dihydro-3-methoxy-2-naphthol in short time experiments suggests a mechanism of ring closure with the latter as precursor. For testing purpose, 4-(3-methoxy-4-hydroxyphenyl)-1-butanol and 1(2H)-3,4-dihydro-6-methoxy-7-hydroxynaphthalenone were synthesized and treated under the same conditions.

In previous work from this laboratory,[1] it was shown that the reaction of wood or lignin with pressurized synthesis gas, in the presence of dicobalt octacarbonyl, provides good yields of phenols through an homogeneous phase catalyzed hydrogenation and/or hydroformylation of these materials.

In order to acquire some insight in the reaction occurring with wood, we have now treated eugenol and isoeugenol, as lignin model compounds, under "hydroformylation conditions."[2] Experiments with eugenol were carried out at 120–180° under a pressure of

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[1] F. Gaslini (to Vita Mayer and Co.), U. S. Patent 2,947,739 (Aug. 2, 1960).

[2] The term "hydroformylation conditions" has the same meaning as in I. Wender, H. W. Sternberg, and M. Orchin, *J. Am. Chem. Soc.*, **75**, 3041 (1953).