furanoside (VI).—Reaction of 10 g. of V with 12 g. of the sodium salt of benzyl mercaptan in 300 ml. of ethanol under reflux for 3 hr. caused rapid precipitation of sodium toluenesulfonate and 7.8 g. of the sirupy thiobenzyl derivative VI, 91% yield, was isolated in the usual way.

Methyl 2,3-O-Isopropylidene-5-deoxy-5-mercapto-D-ribofuranoside (VII).—Reduction of 7.8 g. of VI with sodium in liquid ammonia gave 4.7 g. or 85.5% yield of (VII) as a sirup which by iodine titration had 80% of the sulfur in the form of free thiol groups. The sirup was dissolved in a solution consisting of 10 ml. each of methanol, acetic acid, and water. The solution was titrated with iodine solution and a small amount of water was added. Sirup separated but soon crystallized and 1.6 g. or a 35% yield of crystalline (VIII) was removed by filtration. The product was washed with water and recrystallized from ethanol, m.p. 67°, $[\alpha]^{25}D$ −124° (*c*, 1.04 in methanol).

Anal. Calcd. for $C_{18}H_{30}O_8S_2$: C, 49.31; H, 6.84; S, 14.61. Found: C, 50.05; H, 6.67; S, 14.49.

Reduction of 0.5 g. of VIII in 5 ml. of ether with lithium aluminum hydride (50 mg. in 2 ml. ether) and 1 hr. at 25° caused complete reduction. Excess reducing agent was destroyed with water and hydrochloric acid and the ether layer separated. Concentration of the ether solution gave 0.5 g. of VII as a sirup. Iodine titration showed 93% of the expected free thiol groups.

Methyl β-D-Ribothiapyranoside (IX).—A solution of 1 g. of methyl 2,3-O-isopropylidene-5-deoxy-5-mercapto-D-ribofuranoside was refluxed in 50 ml. of 1% methanolic hydrogen chloride for 5 hr., during which the thiol activity was reduced to 10% of the original value. Hydrogen chloride was absorbed on a 20-g. column of Dowex-1(OH). The effluent was concentrated to a sirup, 20 ml. of ether was added, and the mixture was kept at 0° for 3 days. The sirup crystallized and filtration gave 0.1 g. or a 12.2% yield of methyl β-D-ribothiapyranoside. This was recrystallized from ethyl acetate, m.p. 97°, $[\alpha]^{25}D$ + 18.6° (*c*, 0.59 in water).

Anal. Calcd. for $C_6H_{12}O_4S$: C, 40.00; H, 6.66; S, 17.77; OCH_3, 17.22. Found: C, 40.05; H, 6.46; S, 17.70; OCH_3, 17.11.

When hydrolyzed with 0.5 *N* hydrochloric acid solution at 75° the specific rotation of methyl β-D-ribothiapyranoside increased from + 18.6 to + 51.0° where it became constant after 0.5 hr.

When oxidized with sodium metaperiodate under the usual conditions at 25°, methyl β-D-ribothiapyranoside liberated 1 mole of formic acid per mole after 1 hr., with the formic acid increasing to 1.2 mole/mole after 8 hr.

Methyl β-D-2-Deoxyribothiapyranoside.—A solution of 10 g. of 2-deoxy-D-ribose was treated with 192 ml. of 0.1% methanolic hydrogen chloride for 12 min. at 25°. Acid was removed with Dowex-1(OH) and the neutral effluent concentrated to give 9.3 g. of the sirup, methyl 2-deoxy-D-ribofuranoside (X). A solution of this sirup in 100 ml. of pyridine was treated at 0–5° with a solution of 12.0 g. of tosyl chloride in 25 ml. of pyridine for 20 hr. The mixture was worked up in the usual way to give 9.3 g. or a 49% yield, of a sirup (XI). Reaction of XI with 12 g. of the sodium salt of benzyl mercaptan in 300 ml. of ethanol gave 7.7 g. of methyl 5-deoxy-5-thiobenzyl-2-deoxy-D-ribofuranoside (XII). Reduction of XII with sodium in liquid ammonia gave 3.1 g. or a 62.8% yield of the thiol (XIII), containing 95% of the sulfur as free thiol groups. Equilibration of XIII in 50 ml. of 1% methanolic hydrogen chloride under reflux caused the loss of 95% of the thiol activity in 20 min. Acid was removed with Dowex-1(OH) and the effluent concentrated to yield 2.2 g. of sirupy methyl β-D-2-deoxyribothiapyranoside (XIV), $[\alpha]^{25}D$ −26.9° (*c*, 5.29 in methanol).

Anal. Calcd. for $C_6H_{12}O_3S$: C, 43.90; H, 7.33; S, 19.51; OCH_3, 18.9. Found: C, 44.20; H, 6.98; S, 19.10; OCH_3, 18.4.

When hydrolyzed at 75° with 0.25 *N* hydrochloric acid in 50% aqueous methanol, the specific rotation increased to −4.16° after 1.5 hr.

Azo Compounds.[1] Preparation and Decomposition of 3,6-Dimethyl-3-phenyl-2,3,4,5-tetrahydropyridazine

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The addition of phenyllithium to 3,6-dimethyldihydropyridazine led to the formation of the monoaddition product, 3,6-dimethyl-3-phenyl-2,3,4,5-tetrahydropyridazine. Attempts to prepare the analogous cyclic azo compound from the cyclic hydrazine, obtained from the hydrazone by reduction over platinum oxide, led only to the formation of the parent cyclic hydrazone. The cyclic hydrazone could be decomposed at 250° to form nitrogen, propylene, α-methylstyrene, *cis*- and *trans*-1-phenyl-1,2-dimethylcyclobutane, and a small amount of acetophenone. The products are consistent with a mechanism involving the cyclic azo compound and a 1,4-biradical as intermediates.

In a continuation of the study of the preparation and behavior on oxidation of 1,2-disubstituted cyclic hydrazines,[3a] an attempt was made to prepare six-membered ring hydrazones, hydrazines, and azo compounds unsymmetrically substituted in the 3- and 6-positions. Earlier workers[3b] had reported the preparation and decomposition of 3-phenyl-3,4,5,6-tetrahydropyridazine to yield phenylcyclobutane as the only product. During the course of this study, Kuzmin[4] reported the preparation of a number of 3-aryl- and 3-aryl-6-alkyl-1,4,5,6-tetrahydropyridazines which were decomposed to give aryl- and alkylarylcyclobutanes and olefinic cleavage products.

(1) This is the 40th in a series of papers concerned with the preparation and decomposition of azo compounds. For the previous paper in this series, see C. G. Overberger and L. P. Herin, *J. Org. Chem.*, **27**, 2423 (1962).

(2) A portion of a thesis submitted by G. Kesslin in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the Polytechnic Institute of Brooklyn.

(3)(a) C. G. Overberger, G. Kesslin, and N. R. Byrd, **27**, 1568 (1962); (b) R. Ya. Levina, M. G. Kuzmin, and Yu. S. Shabarov, *Vestn. Mosk. Univ. Ser. Mat., Mekhan., Astron., Fiz. i Khim.*, **12**, No. 1, 170 (1957).

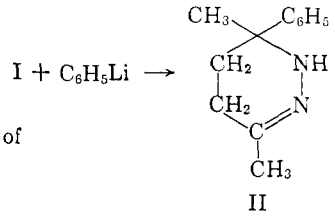
(4) R. Ya. Levina, Yu. S. Shabarov, M. G. Kuzmin, N. I. Vasilev, and E. G. Treschova, *Dokl. Akad. Nauk SSSR* **121**, 303 (1958).

The purpose of this work was to prepare unsymmetrical hydrazines and azo compounds starting with the high-boiling tautomer of 3,6-dimethyldihydropyridazine[5] and to compare the behavior on oxidative decomposition of such compounds with other 1,2-disubstituted hydrazines and azo compounds,[1,4-8] with the view toward elucidating the factors influencing the types of products formed and the mechanism of their formation.

The position of the double bonds in the high-boiling tautomer of 3,6-dimethyldihydropyridazine has not been firmly established. However both the high-boiling and low-boiling tautomers yield the same addition product with hydrogen cyanide[5] and therefore a common intermediate, formed by a suitable rearrangement of double bonds under the conditions of reaction, must be involved.

The attempt to add phenylmagnesium bromide to the high-boiling tautomer (I), based on the method of Overberger and DiGiulio[9] for linear azines, resulted in recovery of starting product and the formation of some biphenyl. The addition of thiophenol in benzene solution according to the method of Stacy[10] for Schiff bases, and of benzyl mercaptan in aqueous alkaline solution resulted in the isolation only of starting products and some disulfides of the respective thiols.

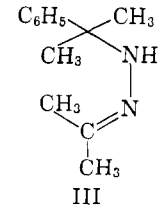
The addition of phenyllithium in ether, according to a modification of the method of Overberger and DiGiulio[9] for linear azines, resulted in the isolation of a monoaddition product (II). The



High-boiling tautomer of 3,6-dihydropyridazine

II

position of the double bond in II is not definitely assigned. However, analysis of its infrared spectrum revealed a single strong absorption band for NH stretching at 3.05 μ. There is a weak absorption band at 6.25 μ, but the presence of an aromatic ring in the molecule makes an assignment of this frequency of C=N difficult. This difficulty is pointed out by Overberger and DiGiulio who found the infrared spectrum of the open-chain analog of II, exhibited a C=N absorption as only a weak shoulder on the phenyl band at 6.22 μ The ultraviolet spectrum of II is characterized by a shoulder in the 230-mμ region, ϵ 6600. This was also found to be characteristic of nonconjugated hydrazones studied by Stevens, *et al.*,[11] and of



III

the open - chain analog (III), λ_{max} ~231 mμ, ϵ ~6000.

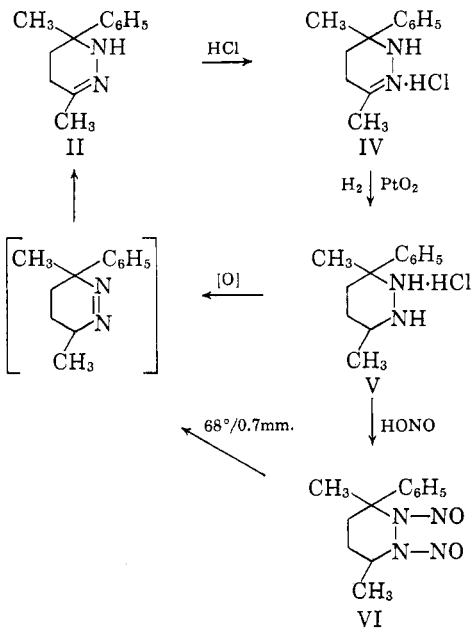
Freshly prepared, crystalline cyclic hydrazone (II) slowly changes to a viscous oil on standing in a closed bottle, possibly because of autoxidation.[12] Cyclic hydrazone hydrochloride (IV), prepared by passing anhydrous hydrogen chloride into a solution of free base in ethylene dichloride, is stable in melting point and crystalline form and represents the best form in which to store the cyclic hydrazone for long periods of time. The hydrochloride (IV) can be quantitatively hydrogenated to the hydrazine hydrochloride (V) over pre-reduced platinum oxide at room temperature and atmospheric pressure. Attempts to isolate the free cyclic hydrazine by neutralization with sodium ethylate resulted instead in the isolation of the cyclic hydrazone (II). This transformation apparently resulted from autoxidation of the liberated free hydrazine to the analogous azo compound followed by rearrangement to the hydrazone. Similar difficulty in the isolation of free linear and cyclic hydrazines, noted by other workers,[8,9,13-16] is presumably due to facile air oxidation and rearrangement to the more stable hydrazone.[17]

In the attempt to prepare the cyclic azo compound, oxidation of V after neutralization in solution, with yellow mercuric oxide in ethanol or in tetrahydrofuran resulted only in the formation of cyclic hydrazone (II). Similar results were obtained with potassium permanganate in acetone. Oxidation with bromine water yielded only a viscous oil which resisted characterization. An attempt was made to follow Thiele and Heuser's[18] technique in preparing azobisisobutyronitrile by dinitrosation of the hydrazobisisobutyronitrile and denitrosation with gentle heating Treatment of V with nitrous acid at low temperatures gave a yellow crystalline solid which decomposed at its melting point with the apparent evolution of nitric oxide. Formulation of the yellow solid as the N,N'-dinitroso compound (VI) is consistent with its analysis and its infrared spectrum which con-

(5) C. S. Overberger, N. R. Byrd, and R. B. Mesrobian, *J. Am. Chem. Soc.*, **78**, 1961 (1956).
(6) K. L. Rinehart, Jr., and T. V. VanAuken, *ibid.*, **82**, 5251 (1960).
(7) K. v. Auwers and F. Konig, *Ann.*, **496**, 252 (1932).
(8) C. H. Wang, S. Hsiao, E. Saklad, and S. G. Cohen, *J. Am. Chem. Soc.*, **79**, 6562 (1958).
(9) C. G. Overberger and A. V. DiGiulio. *ibid.*, **80**, 6562 (1958).
(10) G. W. Stacy, *ibid.*, **74**, 3885 (1952).
(11) C. L. Stevens, B. T. Gillis, J. C. French, and T. H. Haskell, *ibid.*, **78**, 3229 (1956).
(12) R. Criegee and G. Lohaus, *Chem. Ber.*, **84**, 219 (1951)
(13) C. G. Overberger, I. Tashlick, M. Bernstein, and R. G. Hiskey, *J. Am. Chem. Soc.*, **80**, 6556 (1958).
(14) C. G. Overberger and J. G. Lombardino, *ibid.*, **80**, 2317 (1958).
(15) R. L. Hinman, *ibid.*, **79**, 414 (1957).
(16) C. G. Overberger and M. Lapkin, *ibid.*, **77**, 4651 (1955).
(17) G. E. K. Branch and M. Galvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, p. 288.
(18) J. Thiele and K. Heuser, *Ann.*, **290**, 1 (1896).

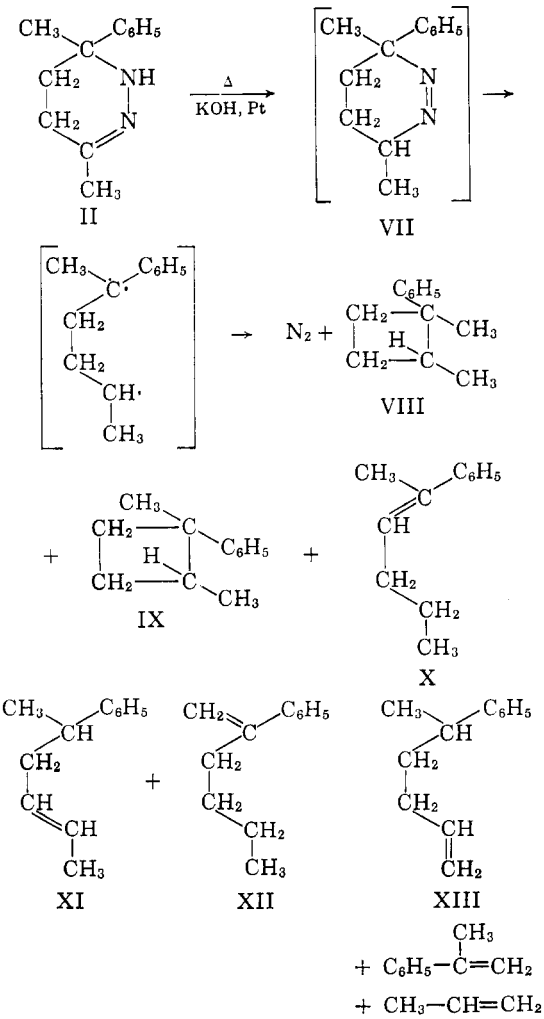
tained an N—N=O absorption band at 7.0 μ.[19,20] Heating the dinitroso compound in a vacuum sublimation apparatus gave no azo compound but resulted in the isolation of an 85% yield of cyclic hydrazone (II).

The difficulties encountered in isolating the free cyclic hydrazine by neutralization of its hydrochloride, and in isolating the cyclic azo compound by decomposition of the dinitroso compound or oxidation of cyclic hydrazine hydrochloride are consistent with the postulation of a facile rearrangement of initially formed cyclic azo compound to cyclic hydrazone.



Since paths to the isolation of the desired azo compound led only to hydrazone, it was decided to study the thermal decomposition of the hydrazone, which could be a source for the azo compound as an unstable intermediate formed at elevated temperatures. Conditions used for the reaction were similar to those of the Kishner reduction of the hydrazone derivatives of ketones.[21] When II was heated to 250–260° in the presence of potassium hydroxide and platinized pumice stone, decomposition occurred with the evolution of gas and formation of a colorless liquid distillate. Approximately one mole of gas was collected when the evolved gases were first passed through a Dry Ice trap before measurement and a colorless liquid was found in the cold trap. The temperature of the liquid collected in the cold trap was raised slowly and the gas evolved bubbled through a solution of 2,4-dinitrobenzenesulfenyl chloride (DNBS) in glacial acetic acid. Two DNBS adducts of propylene were formed and isolated according to the method of Kharasch and Buess.[22] These adducts were demonstrated to be the result of addition to the double bond of propylene in the Markownikoff and non-Markownikoff manner.[22]

The liquid distillate from the hydrazone decomposition was subjected to vapor phase chromatography and six peaks were observed. A consideration of the products to be expected from the decomposition (with nitrogen evolution) of the cyclic hydrazone *via* the intermediate formation of its isomeric azo compound suggested the following products:



The first peak in the vapor phase chromatogram represented the major component (VPC I) of the liquid distillate from the decomposition. As calculated, this peak amounted to 74.7% of the total decomposition products. Since the infrared spectrum of the original decomposition distillate was very similar to that of a commercial sample of α-methylstyrene, it was tentatively assumed that VPC I was α-methylstyrene. The same retention time as that for VPC I was obtained for authentic

(19) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1958.

(20) J. C. Earl, R. J. W. LeFevre, A. G. Pulford, and A. Walsh, *J. Chem. Soc.*, 2207 (1951).

(21) R. Adams, "Organic Reactions," Vol. IV, John Wiley & Sons, Inc., New York, N. Y., 1948, p. 378.

(22) N. Kharasch and C. M. Buess, *J. Am. Chem. Soc.*, **71**, 2724 (1949).

α-methylstyrene. In addition, careful fractionation of a typical liquid decomposition distillate gave a fraction having the boiling point and density reported for α-methylstyrene. Oxidation with chromic acid yielded acetophenone, identified as the semicarbazone by melting point and mixture melting point with an authentic sample. The amount of α-methylstyrene indicated by vapor phase chromatographic analysis corresponded to a 78% yield based on cyclic hydrazone decomposed.

VPC II, represented by the second peak, was a minor component of the liquid distillate from the decomposition. It amounted to only 2.7% of the liquid decomposition products. Its retention time was identical with that found for a minor impurity in commercial α-methylstyrene. Since it has been reported that α-methylstyrene generally distils with the formation of a small amount of acetophenone due to air oxidation,[23] it seemed reasonable to ascribe the peak for VPC II to acetophenone. Liquid phase chromatography of the original decomposition distillate resulted in the elimination of the peak for VPC II as was shown when the petroleum ether-eluted products were examined by vapor phase chromatography. Subsequent elution of the liquid phase chromatogram with a mixture of benzene and ether yielded a small amount of oil which could be converted to the semicarbazone of acetophenone with semicarbazide hydrochloride chloride.

VPC III and VPC IV occurred in approximately equal concentrations. Each represented approximately 10% of the liquid decomposition products. Careful fractionation of the decomposition distillate resulted only in slight enrichment of their combined total without altering their relative proportion. By collecting VPC III and VPC IV, in a cold trap, from repeated chromatograms of decomposition distillate, slightly enriched in these components by preliminary fractionation, it was possible to collect approximately 0.10 g. of each of liquid VPC III and liquid VPC IV in chromatographically pure condition. Analyses of both were identical and conformed to the empirical formula $C_{12}H_{16}$, which is consistent with their formulation as the dimethylphenylcyclobutanes (VIII) and (IX), or as the isomeric linear unsaturated hydrocarbons (X), (XI), (XII), and (XIII). Their ultraviolet spectra were almost identical and contained two maxima at 261 and 255 mμ with molar extinction coefficients of the order of 200, similar to other phenyl substituted alicyclic compounds.[24] On the basis of ultraviolet spectra, linear unsaturated hydrocarbons (X) and (XII), containing double bonds conjugated with a phenyl ring and requiring λ_{max} ~243 mμ and ϵ ~10,900 similar to α-methylstyrene,[25] are unlikely as possible formulations. Linear unsaturated hydrocarbons (XI) and (XIII) are considered unlikely structural representations on the basis of the absence of C=C stretching frequencies in the 6-μ region and the C—H out-of-plane bending frequencies for linear olefins in the 10.2-μ region[19] of their infrared spectra. VPC III and VPC IV are therefore believed to be *cis*- and *trans*-1,2-dimethyl-1-phenylcyclobutane (VIII) and (IX).

The concentration of VPC V and VPC VI was too small to permit isolation, and their identity was not further pursued.

Stereochemistry and Mechanism of the Decomposition.—The first application of Kishner conditions to the decomposition of six-membered ring cyclic hydrazones was reported by Kuzmin[4] who pointed out the structural similarity between such compounds and 2-pyrazolines, five-membered ring hydrazones, which are known to undergo decomposition with the formation of cyclopropanes.[21] In explanation of the formation of both coupled and cleavage products he proposed an initial rearrangement of 3-methyl-6-phenyl-2,3,4,5-tetrahydropyridazine to a cyclic azo compound followed by a decomposition yielding a 1,4-biradical which could couple to give cyclobutanes or cleave to give styrene and propylene. Rearrangement of a hydrazone to a short-lived isomeric azo compound, under these conditions, has been proposed by other workers.[21,25-28] Since similar coupling and cleavage products have resulted from the present work, it is therefore reasonable to postulate that the first step in the decomposition of 3,6-dimethyl-3-phenyl-2,3,4,5-tetrahydropyridazine (II) involves rearrangement to the cyclic azo compound previously shown to be too unstable for isolation because of the *cis* azo linkage and the tertiary carbon adjacent to the azo group. The decomposition of the cyclic azo compound with the evolution of nitrogen and the formation of a 1,4-biradical is consistent with the work of Cohen, *et al.*,[3] Kuzmin,[4] and Overberger, *et al.*[1] It is supported by the formation of α-methylstyrene and propylene as cleavage products.

The isolation of equal parts of *cis*- and *trans*-cyclobutane derivatives in this study and the similar results of Kuzmin[4] is evidence that the 1,4-biradical is probably free enough to lose stereoidentity before coupled products are formed. The 2-pyrazoline studied by Jones likewise forms coupled products with extensive loss of stereochemical purity upon thermal decomposition.[27] Rinehart and Van Auken[6] also report the formation of nonstereospecific products in the thermal decomposition of 1-pyrazolines. These authors find the

(23) R. H. Boundy and R. F. Boyer, "Styrene—Its Polymers, Copolymers and Derivatives," Reinhold Publishing Corp., New York 36, N. Y., 1952.

(24) W. W. Robertson, J. F. Music, and F. A. Matsen, *J. Am. Chem. Soc.*, **72**, 5260 (1950).

(25) G. H. Beaver and E. A. Johnson, *J. Chem. Soc.*, 654 (1957).

(26) D. Todd, *J. Am. Chem. Soc.*, **71**, 1356 (1949).

(27) W. M. Jones, *ibid.*, **82**, 3136 (1960).

(28) L. Gattermann and H. Wieland, "Laboratory Methods of Organic Chemistry," Macmillan and Co., Ltd., London, 1952, p. 384.

coupled products can be formed stereospecifically, however, by conducting the decomposition with sunlight at normal temperatures. The apparent freedom of the 1,3-biradical to lose stereoidentity at elevated temperatures is not an entirely general phenomenon, since other workers[7,29] have reported that thermal decomposition of 1-pyrazolines can lead to stereospecific coupled products. Further work in this area is presently in progress.[29]

Experimental

3,6-Dimethyldihydropyridazine. The High-Boiling Tautomer.—The high-boiling tautomer of 3,6-dimethyldihydropyridazine was prepared in 81.3% yield, b.p. 120° (2 mm.), $n^{25}D$ 1.5318, by the method of Overberger, *et al.* (b.p. 108° (1 mm.), $n^{30}D$ 1.5330, 72% yield).[5]

3,6-Dimethyl-3-phenyl-2,3,4,5-tetrahydropyridazine. The Cyclic Hydrazone.—The addition of phenyllithium to the high-boiling tautomer was carried out by a modification of the method of Overberger and DiGiulio.[9] To 2.0 moles of phenyllithium prepared in 1500 ml. of anhydrous ether[31] was added, with agitation, 97.5 g. (0.887 mole) of the high-boiling tautomer dissolved in 500 ml. of anhydrous ether. The addition was made over 90 min. with the temperature rising, without cooling, from 23 to 31°. The mixture was agitated 1 hr. longer and allowed to stand overnight at room temperature. The reaction mixture was then quenched on 750 g. of crushed ice in 750 ml. of water. The ether layer was separated and the aqueous layer extracted with two portions of 400 ml. of ether. The combined ether layers were washed with two portions of 200 ml. each of water, dried over anhydrous magnesium sulfate, filtered, and evaporated free of ether. The residual oil, 133.5 g., was distilled through a 6-in. electrically heated column equipped with a total reflux partial take-off distilling head, under 0.2–0.3 mm. of mercury pressure. A first fraction, b.p. 50–60°, 10.1 g. was collected, mainly diphenyl [b.p. 51° (3 mm.)] by infrared spectrum, an intermediate fraction of 12.4 g., b.p. 60–90°, and the crude 3,6-dimethyl-3-phenyl-2,3,4,5-tetrahydropyridazine, 95.2 g. (57%), b.p. 90–105°. The product crystallized in the receiver on cooling. Recrystallization of the crude from 100 ml. of 1:1 petroleum ether (b.p. 40–60°) and toluene, with cooling to −12°, resulted in the isolation of 48.5 g. (29.1%) of yellow crystals, m.p. 79–86°. A second recrystallization from a mixture of 60 ml. of toluene and 200 ml. of petroleum ether (b.p. 40–60°) yielded 38.9 g. (23.3%) of pure product, m.p. 83.0–87.5°. An analytical sample prepared by recrystallization from ether and analyzed within 3 hr. after isolation had a m.p. 84.5–87.5°.

Anal. Calcd. for $C_{12}H_{16}N_2$: C, 76.55; H, 8.57; N, 14.88. Found: C, 76.30; H, 8.40; N, 14.60.[32]

Five recrystallizations of product, m.p. 83.0–87.5°, gave no improvement in melting point beyond 84.5–87.5°. Redistillation followed by recrystallization did not narrow the melting point range. Liquid phase chromatography on alumina resulted in the isolation of oily solid of poor melting point. Fractional sublimation at 50° (0.5 mm.) gave m.p. 82.2–86.8° for the purest fraction. A sample of hard, white crystals, m.p. 84.5–87.5°, changed to m.p. 76–85° after 1 week and to a yellow-orange viscous liquid after 3 months. Samples submitted at two different times for analysis by Weiler and Strauss in Oxford, England, resulted in nitrogen analyses no higher than 13.1–13.9%.

The infrared spectrum of the crystalline cyclic hydrazone showed bands at 3.05 (NH), 6.25, 13.05, and 14.25 μ (monosubstituted phenyl.) The ultraviolet spectrum in ethanol showed λ_{max} (shoulder) 225–230 mμ, ε 6600.

Cyclic Hydrazone Hydrochloride.—Into 14.78 g. (0.0787 mole) of 3,6-dimethyl-3-phenyl-2,3,4,5-tetrahydropyridazine, m.p. 77.0–87.5°, dissolved in 50 ml. of methanol was passed 3.76 g. (0.103 mole) of anhydrous hydrogen chloride. The solution was treated with carbon and evaporated free of solvent at 30° under reduced pressure. Crystallization of the viscous residue was induced by scratching with a glass rod or seeding with previously isolated hydrochloride. Recrystallization of the amorphous, white solid from 140 ml. of ethylene dichloride with cooling to −12°, resulted in the isolation of 14.52 g. (82.4%) of light tan crystals, m.p. 164.8–166.6°. An analytical sample was prepared by a second recrystallization, m.p. 165.8–167.8°.

Anal. Calcd. for $C_{12}H_{17}N_2Cl$: C, 64.13; H, 7.62; N, 12.47; Cl, 15.78; neut. equiv. 224.7. Found: C, 64.41; H, 7.53; N, 12.71; Cl, 15.55; neut. equiv., 226.0.

The infrared spectrum showed bands at 3.22 (NH), 4.0, and 5.0 μ (C=NH^+),[19] 13.15 and 14.35 μ (monosubstituted phenyl).

Regeneration of the free base was readily accomplished with sodium methylate in methanol, followed by recrystallization from toluene–petroleum ether (b.p. 40–60°), m.p. 83.5–87.5°. A mixture melting point with cyclic hydrazone, m.p. 84.0–87.5°, prepared directly by the phenyllithium addition reaction gave a m.p. 83.6–87.5°.

3,6-Dimethyl-3-phenylpiperidazine Hydrochloride. The Cyclic Hydrazine Hydrochloride.—When hydrogenation was attempted in ethanol over 10% palladium-on-carbon catalyst, no hydrogen uptake was observed. The hydrochloride of the cyclic hydrazone, 10 g. (0.0446 mole), m.p. 65–67°, was hydrogenated in 85 ml. of ethanol in the presence of 0.50 g. of pre-reduced platinum oxide catalyst at room temperature and atmospheric pressure. The theoretical uptake of hydrogen was observed in approximately 6 hr. The reaction mixture was filtered free of catalyst and the solvent evaporated at 50° under reduced pressure. The viscous oil which first resulted could be solidified by scratching with a glass rod. The off-white, amorphous solid was solved in 30 ml. of isopropyl alcohol by warming to 40–50°, cooled to room temperature, diluted with 300 ml. of ether, treated with carbon and then refrigerated at −12° for 5 days. The precipitated white hydrochloride was filtered and dried, 8.5 g. (84.2%), m.p. 184.0–196.0°. An analytical sample prepared by a second recrystallizaton gave a m.p. 186.0–188.0°.

Anal. Calcd. for $C_{12}H_{19}N_2Cl$: C, 63.56; H, 8.45; N, 12.36; Cl, 15.64; neut. equiv., 226.8. Found: C, 63.95; H, 8.73; N, 12.00; Cl, 15.50; neut. equiv., 231.0.

The infrared spectrum showed a band at approximately 3.15 μ (NH), a series of three bands at 3.75, 3.92, and 4.10 μ (secondary amine hydrochloride), and bands at 6.33 μ (NH_2^+ deformation) and 13.05 and 14.25 μ (monosubstituted phenyl).

Attempted Isolation of Cyclic Hydrazine.—To 1.0 g. (0.00442 mole) of cyclic hydrazine hydrochloride, m.p. 186–188°, dissolved in 20 ml. of methanol was added sufficient 10% sodium in methanol to make the mixture neutral to phenolphthalein. After evaporation of the solvent, the residue was dissolved in ether and separated from any insoluble salt by filtration. Evaporation of the ether yielded a thin, colorless liquid residue. Attempts to recrystallize the residue resulted only in the precipitation of an oil. Upon evaporation of solvent and allowing the residue to stand overnight, an oily crystalline solid, 0.675 g., formed. Recrystallization from 5 ml. of 25% toluene in petroleum ether (b.p. 40–60°) with cooling to −9°, yielded 0.218 g. (26.3%) of crystals, m.p. 84.5–87.5°. A mixture melting point with cyclic hydrazone, m.p. 84.0–87.0°, gave a m.p. 84.0–87.2°. The infrared spectrum was identical with that of the cyclic hydrazone.

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

(30) All melting points are corrected. Analyses by Drs. G. Weiler and F. B. Strauss, Oxford, England.

(31) R. Adams, *Org. Reactions*, **VI**, 353 (1948).

(32) Analysis by Dr. S. Blackman, Burroughs-Wellcome, Tuckahoe, New York.

N,N'-Dinitroso Compound of 3,6-Dimethyl-3-phenylpiperidazine.—The procedure used for nitrosation was a modification of the method of Thiele and Heuser.[18] The cyclic hydrazine hydrochloride, 0.50 g. (0.00221 mole) was added to a solution of 1.50 g. (0.0218 mole) of sodium nitrite in 5 ml. of concentrated hydrochloric acid, 10 ml. of isopropyl alcohol, and 100 ml. of water, and agitation, at 10–15°. The oil which first precipitated turned to a yellow crystalline solid. The mixture was stirred overnight at room temperature and then filtered and air-dried. The crude dinitroso compound weighed 0.389 g. (71.1%), m.p. 66.4° (gas). Recrystallization from a mixture of isopropyl alcohol and petroleum ether (b.p. 40–60°), without warming above room temperature, yielded a product, m.p. 67.8° (gas). Attempted recrystallization with warming to 40–50° was attended by decomposition, the appearance of a brown vapor and the characteristic odor of nitrogen dioxide.

Anal. Calcd. for $C_{12}H_{16}O_2N_4$: C, 58.05; H, 6.50; N, 22.57. Found: C, 58.57; H, 6.67; N, 22.00

The infrared spectrum showed bands at 7.0 μ (N—N=O),[19,20] 13.05 and 14.20 μ (monosubstituted phenyl).

Attempted Preparation of Cyclic Azo Compound. 1. Decomposition of the Dinitroso Compound.—In the attempt to prepare the cyclic azo compound, the dinitroso compound was subjected to thermal decomposition by a modification of the method of Thiele and Heuser.[18]

The dinitroso compound, 0.21 g. (0.000347 mole), was subjected to thermal decomposition in a vacuum sublimation apparatus at 68° (0.7 mm.). The white crystalline sublimate weighed 0.135 g. (84.7%), m.p. 84.5–87.5°. A mixture melting point with cyclic hydrazone, m.p. 84.0–87.0°, gave a m.p. 84.2–87.2°. The infrared spectrum was identical with that of the cyclic hydrazone.

2. Oxidation of the Cyclic Hydrazine. a. With Mercuric Oxide in Ethanol.—This procedure is a modification of the technique of Overberger and Lombardino.[14] Cyclic hydrazone hydrochloride, 2.0 g. (0.0089 mole), m.p. 166.0–167.0°, was hydrogenated in 50 ml. of ethanol in the presence of 0.2 g. of pre-reduced platinum oxide until the theoretical volume of hydrogen was absorbed. The reaction mixture was filtered free of catalyst and neutralized to phenolphthalein indicator with a solution of 10% sodium in methanol. To the freshly prepared cyclic hydrazine, *in situ*, was added 15.5 g. (0.0717 mole) of yellow mercuric oxide and the mixture agitated for 20 hours at room temperature. The solution turned green in color, the solids were filtered with the aid of Celite and the filtrate evaporated free of solvent at 40° under reduced pressure. The viscous, oily residue, 1.90 g., which first formed, slowly crystallized. Recrystallization from 25% toluene in petroleum ether (b.p. 40–60°) yielded 0.91 g. (54.3%), m.p. 81.0–87.0°. A mixture melting point with authentic cyclic hydrazone, m.p. 84.0–87.0°, gave a m.p. 82.0–86.8°. The infrared spectrum was identical with that of the cyclic hydrazone.

b. **With Potassium Permanganate in Acetone.**—This procedure is based on a modification of the method of Overberger, Byrd, and Mesrobian.[5] To 0.50 g. (0.00221 mole) of cyclic hydrazine hydrochloride dissolved in 25 ml. of acetone, and cooled to 2°, was added, with agitation, sufficient 10% sodium in methanol to neutralize the mixture to phenolphthalein indicator. To this was immediately added 0.402 g. (0.00254 mole) of potassium permanganate and agitation continued for 30 min. at 2°. Manganese dioxide was precipitated, but no nitrogen was evolved. The mixture was filtered, and the filtrate evaporated in the cold under reduced pressure. The residue was dissolved in 20 ml. of ether and filtered. Evaporation of the solvent yielded, 0.326 g. (78%) of yellow, viscous oil which, on cooling, crystallized to a solid, m.p. 81.0–87.0°. A mixture melting point with cyclic hydrazone, m.p. 84.0–87.0, gave a m.p. 82.0–86.6°. The infrared spectrum was identical with that of the cyclic hydrazone.

Decomposition of 3,6-Dimethyl-3-phenyl-2,3,4,5-tetrahydropyridazine.—The procedure for decomposition of the cyclic hydrazone is based on the method of Kishner[21] for the decomposition of linear hydrazones.

A mixture of 9.80 g. (0.0522 mole) of cyclic hydrazone, 0.80 g. (0.0143 mole) of potassium hydroxide pellets, and five platinized pumice stones (1/4 in. stones impregnated with 5% potassium platinic chloride solution and dried at 100°) was introduced into a Claisen flask. The flask was stoppered and inserted into a silicone fluid bath pre-heated to 250° and maintained at 250–260° throughout the decomposition. Within approximately 8 min., regular gas evolution was observed. Over 70% of the total gas was collected in 60 min. After approximately 254 min., gas evolution had ceased and a total of 2015 ml. of gas had been collected at S.T.P. This corresponded to 172.5% of the calculated theoretical volume of nitrogen, and therefore indicated the presence of still another gaseous product. During the course of the decomposition a colorless liquid distilled into a test-tube receiver. The liquid distillate amounted to 5.73 g. A further 0.70 g. was obtained by the application of slight vacuum to the apparatus, giving a total of 6.43 g. of liquid.

The liquid distillate was subjected to vapor phase chromatography at 152° through a 2 m., 1/4 in. o.d. column packed with a polypropylene glycol stationary liquid phase deposited on diatomaceous earth (Perkin-Elmer Column R). The instrument used was a Perkin-Elmer Vapor Fractometer, Model 154D. The carrier gas was helium; column pressure, 20 p.s.i.; flowmeter setting, 40 mm.; detector voltage, 7.8. A 10 μl. sample was taken for analysis.

The vapor phase chromatogram showed six peaks representing components VPC I–VI. The following proportions of components were observed, representing the indicated weight of component in the total liquid distillate.

	%	G.
VPC I	74.7	4.80
VPC II	2.7	0.176
VPC III	9.3	.60
VPC IV	10.1	.65
VPC V	2.2	.142
VPC VI	1.0	.062
Total	100.0	6.43

The infrared spectrum of the liquid distillate showed great similarity to that of authentic α-methylstyrene except for an extra absorption band at 5.92 μ indicative of C=O.

In another decomposition performed under identical conditions and with the same proportion of reagents, the evolved gases were passed through two Dry Ice traps, connected in series, prior to measurement in an inverted graduated cylinder. In this experiment, approximately 1250 ml. of gas at S.T.P. were collected, corresponding to 107% of the theoretical nitrogen. The difference in volume (1090 ml. at S.T.P.) represented the quantity of condensable gas collected as a colorless liquid in the Dry Ice traps. This trapped liquid was saved for identification as described in a later section titled "The Gaseous Product."

The Liquid Products. a. VPC I.—This product was the major component (74.7%), and probably the lowest boiling of the liquid decomposition distillate, as indicated by vapor phase chromatography. Careful fractionation of 6.26 g. of decomposition distillate, through a 6-in. electrically heated column with a total reflux, partial take-off stillhead, yielded 2.53 g. of first fraction, b.p. 53.6–55.0° (14 mm.), which was 98.5% pure VPC I as indicated by vapor phase chromatography. Four succeeding fractions were taken at 60.4–69.0°, 1.50 g.; 70.0–78.6°, 1.0 g.; 81.0–92.5°, 0.75 g.; and 92.5–96.0°, 0.25 g. The residue amounted to 0.20 g. The latter fractions were all mixtures of the six original components with increasing quantities of VPC II–IV, and decreasing quantities of VPC I.

Fraction I, b.p. 53.6–55.0° (14 mm.), d_{25}^{25} 0.9080, $n^{20}D$ 1.5370, had the identical chromatographic retention time (9 min.) and infrared spectrum to that of authentic α-

methylstyrene [54.5–5.0° (14 mm.),[33] d_{25}^{25} 0.9062,[23] $n^{17.4}D$ 1.5384[33]].

Fraction I, VPC I, 1.0 g. (0.01668 mole) was oxidized in 25 ml. of glacial acetic acid by the addition of 2 g. of chromium trioxide dissolved in 2 ml. of water. The mixture evolved heat, was cooled to room temperature and allowed to stand for 24 hr. It was then quenched in 250 ml. of water and extracted with two portions of 25 ml. each of ether. The ether layers were combined and dried over anhydrous magnesium sulfate. The ether was evaporated and the residue, which had the odor of acetic acid, was treated with a solution of 2 g. of semicarbazide hydrochloride and 1 g. of sodium acetate in 25 ml. of water. After 1 hr. of agitation at room temperature, the mixture was allowed to stand overnight to complete reaction. The crystalline precipitate was filtered and recrystallized from aqueous methanol yielding white crystals of acetophenone semicarbazone, 0.6 g. (22.7%), m.p. 199.4–201.0°. A mixture melting point with authentic acetophenone semicarbazone, m.p. 201.8–203.0°, and with semicarbazone prepared similarly from authentic α-methylstyrene gave no depression.

b. **VPC II.**—This product was a minor component (2.7%) of the liquid decomposition distillate as indicated by vapor phase chromatography. It was identified by isolation as a crude oil by liquid phase chromatography of decomposition distillate and derivatization.

Liquid distillate from a decomposition, 1.453 g., was chromatographed on activated alumina. Fractions 6 and 7, 0.05 g., were treated with semicarbazide hydrochloride in aqueous methanol. A slight amount of crystalline solid formed on standing overnight. Filtration and recrystallization from aqueous methanol yielded a white crystalline solid, 0.01 g., m.p. 198.0–200.0°. A mixture melting point with authentic acetophenone semicarbazone, m.p. 201.8–203.0°, gave a m.p. 199.4–201.6°.

c. **VPC III and VPC IV.**—These products each represented approximately 10% of the decomposition distillate as determined by vapor phase chromatography.

As described in the Experimental under VPC I, careful fractionation of 6.26 g. of decomposition distillate yielded five fractions and a residue with the following VPC III and VPC IV contents: fraction 1, negl., negl.; 2, 4.4%, 3.4%; 3, 10.5%, 8.7%; 4, 23.2%, 22.0%; 5, 25.0%, 27.0%; residue, 21.6%, 32.3%. Repeated vapor phase chromatograms of 50-μl. quantities of fractions 4 and 5 through a 2 m., 1/4-in. o.d. column, under conditions identical with those previously described, resulted in the isolation of 0.125 g. of crude VPC III and 0.118 g. of VPC IV, by condensation of the eluent in a Dry Ice trap. The isolated samples were re-processed through the Vapor Fractometer to obtain chromatographically pure material. Pure VPC III, 0.103 g., and VPC IV, 0.096 g. were colorless liquids with characteristic hydrocarbon odors.

Anal. Calcd. for $C_{12}H_{16}$ (VPC III): C, 89.94; H, 10.06. Found: C, 89.25; H, 10.00.

Anal. Calcd. for $C_{12}H_{16}$ (VPC IV): C, 89.94; H, 10.06. Found: C, 90.10; H, 10.20.

The infrared spectra for VPC III and VPC IV were very similar. Each showed bands at 13.1 and 14.25 μ (monosubstituted phenyl) and neither contained evidence of C=C absorption in the 6- or 10.2-μ region. The ultraviolet spectra in cyclohexane were almost identical with each other showing two maxima and one minimum: VPC III, λ_{max} 254 mμ, ε 189; 260 mμ, ε 215, λ_{min} 234 mμ, ε 110; VPC IV, λ_{max} 255 mμ, ε 208, 261 mμ, ε 239, λ_{min} 234 mμ, ε 59.

The Gaseous Product.—The gas evolved from the decomposition of 9.80 g. (0.0522 mole) of cyclic hydrazone with 0.80 g. (0.0143 mole) of potassium hydroxide pellets, and five platinized pumice stones at 250–260° was passed through two Dry Ice traps connected in series. A colorless liquid was collected in the traps which was equivalent to 0.0342 mole as calculated from the loss of volume of measured gas resulting from the removal of condensable gas by the Dry Ice traps.

The liquid collected in the cold traps was allowed to evaporate slowly by gradual warming of the traps, and the gas evolved was bubbled through a solution of 5 g. (0.0213 mole) of 2,4-dinitrobenzenesulfenyl chloride in 100 ml. of glacial acetic acid over a period of 30 min. The mixture was allowed to stand at room temperature for 36 hr. and then quenched in 500 ml. of water. A yellow, opaque solution resulted which, upon cooling at 4° for 6 hr., deposited a crystalline yellow solid. The solution was filtered and the crystals washed with water. The wet crystals were refluxed with 50 ml. of absolute ethanol and filtered hot. Approximately 0.8 g. of light, yellow solid of high-melting point was collected and was apparently 2,4-dinitrobenzenedisulfide, m.p. 240–280° dec.[34] The filtrate was cooled to 5° and the precipitated yellow crystals filtered and air-dried, 2.43 g., m.p. 54–65°.

The crystalline adduct mixture, 2.43 g., was refluxed with 50 ml. of ether and the insoluble yellow solid, 0.77 g., m.p. 71–95°, filtered off. Cooling the ether filtrate to room temperature overnight yielded 0.61 g. of yellow crystals, m.p. 72–78°. Two recrystallizations of the ether insoluble portion, 0.7 g., from absolute ethanol and one from ether, yielded 0.33 g. of high-melting propylene adduct, m.p. 108.0–109.5° (108.5–109.5°).[22] Recrystallization of the ether-soluble yellow crystals, 0.61 g., m.p. 72–78°, from absolute ethanol yielded the low-melting propylene adduct, 0.20 g., m.p. 73.0–75.0° (75–76°).[22]

The weight of propylene trapped in Dry Ice corresponded to 0.0342 mole and represents 65.5% of the theoretical propylene based on cyclic hydrazone decomposed.

(33) I. Heilbron, "Dictionary of Organic Compounds," Vol. III Oxford University Press, New York, N. Y., 1953, p. 507.

(34) N. Kharasch, H. L. Wehrmeister, and H. Tigerman, *J. Am. Chem. Soc.*, **69**, 1612 (1947).