dec., which was not depressed by genuine tropinone hydrochloride (m.p. 188°[20]). The crude picrate (m.p. 207° dec.), prepared in benzene, did not depress the m.p. of authentic tropinone picrate (m.p. 215°[20]). Finally, the infrared spectrum (chf.) of the oil was superposable on that of pure tropinone over the entire region with but minor exceptions.

Hofmann Degradation of Pseudotropine (IV).—A warm aqueous solution of pseudotropine methiodide (obtained with methyl iodide in ether) was treated with one equivalent of silver oxide and digested at 50° for 1 hr. The cooled mixture was filtered and the filtrate distilled at atmospheric pressure; after removal of the water the portion with b.p. 230–245° was collected. Redistilled twice in vacuum, the des-base V was a colorless, viscous liquid, b.p. 110–112° (2 mm.). On refrigeration the oil formed a hygroscopic solid (m.p. 41–44°, sealed tube).

The corresponding benzoate was prepared with benzoic anhydride in refluxing benzene (8 hr.) and converted to the hydrochloride salt as described by Willstätter.[16] This derivative had m.p. 169° (reported 166–167°) and was crystallized from an anhydrous mixture of alcohol–ether.

Bromination and Cyclization to 2-Bromopseudotropine Methobromide (VII).—To the des-base (V, 0.50 g.) obtained above, in 2 cc. of water was added 1.2 g. of 34% hydrobromic acid. This solution then was cooled in ice and shaken vigorously while a solution of bromine (0.54 g.) in chloroform (5.0 g.) was introduced slowly at a rate governed by the rate of discharge of the bromine color (10–20 min.). Sodium bisulfite was added to decolorize unchanged bromine, and the cold mixture was made alkaline with solid sodium carbonate and shaken well. The chloroform layer was separated, the aqueous layer was promptly extracted with more chloroform, and the combined organic layers were filtered through anhydrous sodium sulfate. Warming the filtrate effected cyclization of the des-base dibromide, and crystals of 2β-bromopseudotropine methobromide started to precipitate almost immediately. After concentration to a volume of 8 cc. the mixture was cooled and the solid collected; 0.33 g., m.p. 240° dec. (vacuum, dependent on rate of heating). Crystallization from ethanol improved the appearance but did not alter the m.p. (reported 237–238°[16]).

(20) R. Willstätter, *Ber.*, **29**, 393 (1896).

Conversion of the Bromohydrin III to the Methobromide Salt VII.—An anhydrous ethanolic solution of III (m.p. 120–124°) was treated with excess methyl bromide, and the stoppered flask allowed to stand 24 hr. The transparent rhombs that formed were collected, washed with a little ethanol, then with ether; m.p. 245° dec. Additional material was obtained by concentration of the mother liquor and precipitation with ether. The 2β-bromopseudotropine methobromide prepared this way and the one prepared by the cyclization procedure described above gave infrared spectra (in Nujol) that were superposable.

Hofmann Degradation of Tropine (Epimer of IV).—Tropine was degraded to the corresponding des-base (epimer of V) by the same procedure as was used for pseudotropine. After being redistilled twice, the olefin had b.p. 110–111° (2 mm.) and was a viscous oil with a faint yellow tinge.

The hydrochloride salt of the corresponding benzoate ester was obtained by heat treatment of the des-base with benzoyl chloride for a few minutes. The mixture stood overnight and then was diluted with ether. Crystallized from ethanol–ether (both anhydrous) the solid had m.p. (uncor.) 175–177° (reported 171–172°[16]).

Preparation of the Epimer of VI.—The des-base obtained from tropine was treated with bromine as described above for the pseudo series. During the bromine addition the chloroform layer became filled with a white solid. The cold mixture was filtered and the solid washed with cold chloroform then with dry ether; 0.46 g., m.p. 168° dec. Recrystallized from ethanol this hydrobromide salt had m.p. 178–178.5° dec. (reported 178°[16]).

Cyclization of the Dibromide Salt to the Epimer of VII.—The epimer of VI (0.40 g.) was added to a funnel containing 4 cc. of water, 5 cc. of chloroform and 0.6 g. of sodium carbonate, and the mixture shaken. The aqueous phase was extracted again with chloroform, and the combined organic layers were filtered through sodium sulfate and boiled down on a steam-cone for 15 min. The solid that precipitated was collected and dried; 0.18 g., m.p. 236° dec. Recrystallized from dry alcohol–ether, the 2β-bromotropine methobromide had m.p. 237° dec. (dependent on rate of heating); reported m.p. *ca.* 233°.[16] The preparation of this compound was performed also without isolation of the intermediate dibromide salt as was done in the pseudo series.

BRYN MAWR, PENNA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, INSTITUTE OF POLYMER RESEARCH, POLYTECHNIC INSTITUTE OF BROOKLYN]

Azo Compounds.[1] A Re-examination of the Structure of the Product from the Reaction of Heptane-2,6-dione with Hydrazine Sulfate and Sodium Cyanide in Dilute Solution

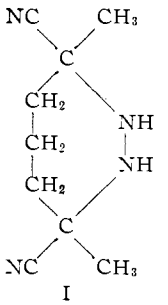
BY C. G. OVERBERGER AND BURTON S. MARKS[2]

RECEIVED JANUARY 18, 1955

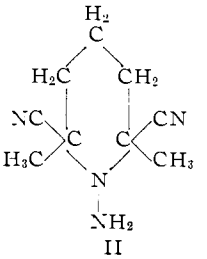
The reaction betweenheptane-2,6-dione, hydrazine sulfate and sodium cyanide has been re-examined. It has been shown that the product is II, 1-amino-2,6-dicyano-2,6-dimethylpiperidine instead of I, 3,7-dicyano-3,7-dimethylhomopiperidazine, previously reported.

In previous work[3] we had reported that the reaction between heptane-2,6-dione, hydrazine sulfate and sodium cyanide had resulted in the formation of I.

Structure I was proposed based on the following evidence. Oxidation of the product with bromine in ethanol gave a quantitative evolution of nitrogen and three well characterized products, indicative of biradical formation on decomposition of an unstable azo intermediate. The analogous behavior of linear hydrazines of similar structure to form azo compounds on oxidation and the known mechanism of the decomposition of linear azo compounds of this



I



II

(1) This is the 12th in a series of articles on the preparation and decomposition of azo compounds. For the 11th paper in this series see C. G. Overberger, W. F. Hale, M. B. Berenbaum and A. B. Finestone, THIS JOURNAL, **76**, 6185 (1954).

(2) A portion of a thesis submitted by Burton S. Marks 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, T. B. Gibbs, Jr., S. Shibnik, P. Huang and J. J. Monagle, THIS JOURNAL, **74**, 3290 (1952); (b) C. G. Overberger, P. Huang and T. B. Gibbs, Jr., *ibid.*, **75**, 2082 (1953).

type gave support to structure I.[4] Furthermore, failure to isolate a product on reaction with benzaldehyde and a faulty interpretation of the infrared spectra also suggested I. The basicity of the compound was interpreted in favor of structure I.

A comparison of the spectra of a reference compound, 1-amino-2,6-dimethylpiperidine[5] with the product II showed striking similarities.

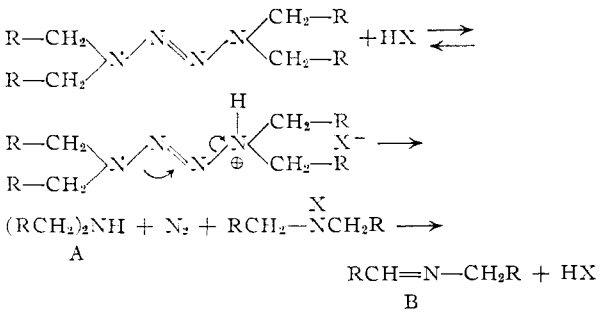
In particular, a peak at 6.18–6.25 μ was identical for both compounds. From other work[5] and the carefully studied spectra of methylhydrazine,[6a] 1,2-dimethylhydrazine[6a] and hydrazine,[6b] it was clear that this peak could be attributed to an NH_2 bending frequency not present in structure I. Twin peaks in the 3 μ area were also indicative of an NH_2 group, although they did not rule out two separate NH peaks or hydrogen bonding with an NH group. Chemical evidence was then obtained to support structure II.

Reaction of 1-amino-2,6-dicyano-2,6-dimethylpiperidine (II) with benzaldehyde and acetic anhydride gave the hydrazone (III). Examination of the infrared spectrum revealed the loss of the peaks at 3 μ and a new peak at 6.12 μ which was consistent with a C=N bending frequency.[7,8]

The tetrazene (IV) was prepared by oxidation with potassium permanganate in 20% yield after negative results were obtained with yellow mercuric oxide and benzoquinone as oxidizing agents. Examination of molecular models reveals the steric difficulties for formation of the tetrazene because of the interference of the methyl and nitrile groups between the two halves of the molecule. The infrared spectra of the tetrazene was consistent with its structure.

Acid decomposition of the tetrazene followed the general path outlined by Wieland and Fressel[9] to give 44% of 2,6-dicyano-2,6-dimethylpiperidine (V) as a major product. This reaction course was also confirmed by the acid decomposition of the tetrazene of 1-amino-2,6-dimethylpiperidine to give a 30% yield of 2,6-dimethylpiperidine.

The general acid decomposition of tetrazenes was studied by Wieland[9] and may be pictured in the following way.

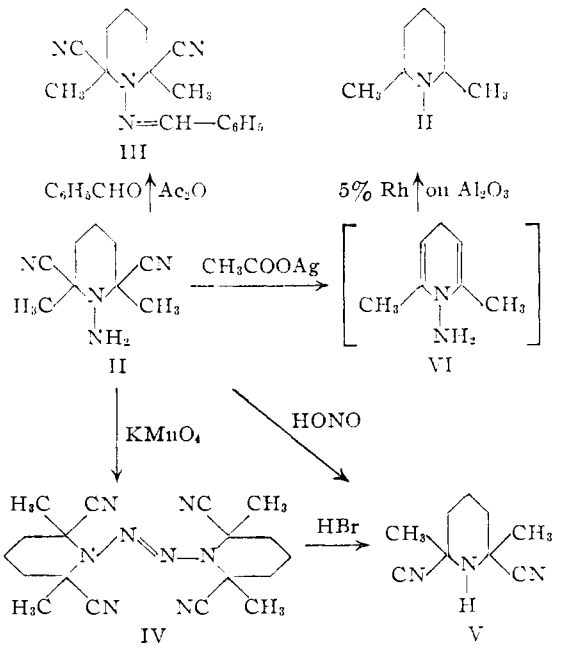


The fragment corresponding to B or its hydrolysis products was always more difficult to isolate than fragment A. We were unable to isolate fragments corresponding to B in the decomposition of the tetrazene of either II or 1-amino-2,6-dimethylpiperidine and always observed formation of resinous materials in the latter case. The decomposition of the tetrazenes in petroleum ether or dry ether does not proceed as indicated; acetone is necessary for the reaction to proceed as shown.

The synthesis of V was also accomplished in 64% yield by the reaction of II with nitrous acid. This reaction has been reported for N-aminopyrroles[10a] and 1,1-disubstituted hydrazines[10b] and we are presently investigating its generality. The infrared spectrum of 2,6-dicyano-2,6-dimethylpiperidine is consistent with the proposed structure and is similar to the spectra of 2,6-dimethylpiperidine in the 3 and 6 μ regions.

We were then able to convert II to 2,6-dimethylpiperidine. II was treated with silver acetate below 60° in a dioxane–water solution for periods of about 20 minutes. The reaction conditions are extremely critical. The intermediate reaction product could not be isolated directly but was immediately reduced catalytically over a 5% rhodium on alumina catalyst at 55° to give 2,6-dimethylpiperidine. The product resulted from elimination of 2 moles of hydrogen cyanide followed by saturation of the two double bonds and hydrogenolysis of the N–N bond. Under identical conditions, 1-amino-2,6-dimethylpiperidine undergoes hydrogenolysis in 59% yield.[5]

It seems clear that the structure of the product is best represented as II.



It has not been possible to demonstrate that free radicals are formed from the oxidation of II although the products of the decompositions are in-

(4) (a) C. G. Overberger, M. T. O'Shaughnessy and H. Shalit, THIS JOURNAL, **71**, 2661 (1949); (b) C. G. Overberger and M. B. Berenbaum, *ibid.*, **73**, 4883 (1951).

(5) C. G. Overberger, L. Palmer, B. S. Marks and N. R. Byrd, *ibid.*, **77**, 4100 (1955).

(6) (a) D. W. Axford, G. J. Janz and K. E. Russell, *J. Chem. Phys.*, **19**, 705 (1951); (b) D. W. Scott, C. D. Oliver, M. E. Gross, W. N. Hubbard and H. M. Hoffman, THIS JOURNAL, **71**, 2293 (1949).

(7) B. Witkop and J. B. Patrick, *ibid.*, **75**, 4474 (1953).

(8) P. L. Pickard and G. W. Polly, *ibid.*, **76**, 5169 (1954).

(9) H. Wieland and H. Fressel, *Ann.*, **392**, 133 (1912).

(10) (a) C. Bulow and F. Kleinman, *Ber.*, **40**, 4749 (1907); (b) N. V. Sidgwick, "The Organic Chemistry of Nitrogen," the Clarendon Press, Oxford, England, 2nd revised edition, 1942, p. 380.

dicative of a biradical. A study of this and similar oxidations will be reported separately.

Experimental[11]

Preparation of 1-Benzimine-2,6-dicyano-2,6-dimethylpiperidine (III).—In 10 ml. of methanol was dissolved 0.25 g. (0.0014 mole) of 1-amino-2,6-dicyano-2,6-dimethylpiperidine and 0.2 g. (0.0019 mole) of benzaldehyde. The reaction mixture was heated on a steam-bath for three minutes, one drop of acetic anhydride was added and the heating at reflux continued for 15 minutes. Water was added, the orange-yellow oil which separated was removed from the water–methanol solution and the oil dissolved in ether. Petroleum ether (b.p. 30–45°) was added and the solution cooled at Dry Ice temperatures to yield a yellow-white precipitate which was dried under vacuum. The 0.1 g. of dried precipitate melted at 129–138° and after two recrystallizations from ether–petroleum ether (b.p. 30–45°) there was obtained 0.08 g. (21.4%) of shiny white needles, m.p. 147–148° (dec.). The infrared spectrum showed no N–H peak in the 3 μ area, but did show the C=N frequency at 6.12 μ.

Anal.[12] Calcd. for $C_{16}H_{18}N_4$: C, 72.18; H, 6.77; N, 21.05; mol. wt.,[13] 266. Found: C, 72.28; H, 7.01; N, 21.01; mol. wt., 290 (the isopiestic method of Signer-Barger).[14]

Preparation of the Tetrazene of 1-Amino-2,6-dicyano-2,6-dimethylpiperidine (IV).—A large excess of finely ground potassium permanganate and 30 ml. of acetone was placed in a flask fitted with an efficient stirrer. To this slurry was added, over a three-minute period, 3 g. (0.0169 mole) of 1-amino-2,6-dicyano-2,6-dimethylpiperidine dissolved in 30 ml. of acetone. The reaction mixture turns brown and an exothermic reaction ensues. The reaction mixture was allowed to stir for six hours, and then filtered through infusorial earth. To the purple filtrate was added 25 ml. of water, followed by enough sodium bisulfite to reduce the permanganate. The brown precipitated manganese dioxide was removed by filtration with the aid of infusorial earth, and the filtrate was evaporated at room temperature to yield a yellow oil and a water layer. The oil and water layers were extracted with ether four times and the combined ethereal extracts were dried over anhydrous magnesium sulfate. The ether solution was evaporated to approximately 10 ml., petroleum ether, b.p. 30–45°, was added and the product was crystallized with some difficulty at Dry Ice temperatures. The 1 g. of yellow precipitate melted at 53–60° and after two recrystallizations from ether there was obtained 0.6 g. (20.1%) of shiny yellow crystals, m.p. 65–65.3°. The infrared spectrum of the tetrazene showed no N–H peaks in the 3 μ area nor any NH_2 bending frequencies in the 6.25 μ area and was consistent with what would be expected for this structure.

Anal. Calcd. for $C_{18}H_{24}N_8$: C, 61.36; H, 6.82; N, 31.82; mol. wt., 352. Found: C, 61.41; H, 6.72; N, 31.60; mol. wt., 354, 358 (cryoscopic in 1,2-dibromoethane).

2,6-Dicyano-2,6-dimethylpiperidine (V). Method A.—In 50 ml. of ether was dissolved 1 g. (0.00284 mole) of the tetrazene of 1-amino-2,6-dicyano-2,6-dimethylpiperidine, and into this solution was bubbled hydrogen bromide gas for ten minutes. Then 25 ml. of acetone was added with continued hydrogen bromide addition. Upon the acetone addition, a marked increase in gas evolution from the reaction mixture was noted and a white precipitate appeared. The white hydrogen bromide salt of the product was removed by filtration and washed with acetone, m.p. 145–149°. After treatment with potassium hydroxide solution, the basic solution was extracted two times with methylene chloride, the combined methylene chloride extracts were washed two times with water, and dried over anhydrous magnesium sulfate. The solvent was distilled to yield 0.55 g. of a slightly discolored white precipitate, m.p. 116–127°. Sublimation at very low pressure gave 0.41 g. of sublimate, m.p. 123–126.5° (44.2%). An analytical sample of white needles could be obtained by dissolving the material in ethanol and allowing the solution to remain at Dry Ice temperatures overnight, m.p. 125.5–127°. The infrared spectrum showed one peak at 3.01 μ indicative of an N–H frequency, and gave no maximum for the NH_2 bending frequency in the 6.25 μ area.

Anal. Calcd. for $C_9H_{13}N_3$: C, 66.26; H, 7.98; N, 25.77. Found: C, 66.47; H, 7.99; N, 25.61.

Method B.—In 35 ml. of glacial acetic acid was dissolved 5 g. (0.028 mole) of 1-amino-2,6-dicyano-2,6-dimethylpiperidine, and this mixture was cooled to 15°. To this stirred cooled solution was added dropwise, over a one-hour period, 2.05 g. (0.029 mole) of 97% sodium nitrite dissolved in 15 ml. of water. The reaction was allowed to stir for an extra hour, and then cooled in an ice-bath. Solid potassium hydroxide pellets were added slowly, with the temperature kept below 25°, until the solution was basic. The solution was extracted four times with methylene chloride and the combined extracts dried over anhydrous magnesium sulfate. Removal of the methylene chloride yielded 4.18 g. of yellow tinted white precipitate, which was washed with ether to remove the yellow color. The 2.12 g. of product remaining melted at 125.5–127°. A further 0.8 g. of product was obtained from the ether washings, total 2.92 g. (64%). A mixed m.p. with the compound synthesized by method A gave no depression, m.p. 125.5–127°. Infrared spectra of the compounds prepared by methods A and B were identical.

Transformation of 1-Amino-2,6-dicyano-2,6-dimethylpiperidine (II) to 2,6-Dimethylpiperidine.—A solution of 100 ml. of commercial dioxane, 50 ml. of water, 5 g. (0.028 mole) of 1-amino-2,6-dicyano-2,6-dimethylpiperidine and 11.19 g. (0.056 mole, 20% excess) of silver acetate was mixed and then heated with efficient stirring on a steam-bath for 20 minutes with the temperature not permitted to rise over 60°. The color of the slurry almost immediately changed from a light gray to a gray black. After 20 minutes of heating, the stirring was continued for 1.5 hours at room temperature. The reaction mixture was filtered through infusorial earth to remove the silver cyanide and excess silver acetate, and the precipitate was washed with a small quantity of dioxane, followed by water. The filtrate and washings were reduced in a Parr apparatus at 55° and 3 atmospheres of hydrogen with 2 g. of 5% rhodium on alumina as catalyst. The reaction ceased to adsorb hydrogen after 90% of the theoretical three moles had been absorbed. The catalyst was removed and 2.78 g. (0.028 mole) of concentrated hydrochloric acid was added to the filtrate. The filtrate was removed under vacuum and nitrogen until approximately 25 ml. of solution remained. To this was added 10 ml. of water, and with cooling solid pellets of potassium hydroxide were added until the solution became strongly basic. The mixture was extracted five times with ether and the combined ethereal extracts dried over anhydrous potassium carbonate. The ether was carefully removed by fractionation and all material boiling between 54 and 128° was collected. This material was treated with ethereal picric acid to yield a picrate equivalent to 0.509 g. (16.1%) of 2,6-dimethylpiperidine, m.p. 166–166.5°. A mixed m.p. with the known picrate was not depressed and the infrared spectra of both picrates were identical.

Acid Decomposition of the Tetrazene of 1-Amino-2,6-dimethylpiperidine.—Into a stirred mixture of 27 ml. of a 50% ethanol and 5.04 g. (0.022 mole) of the tetrazene of 1-amino-2,6-dimethylpiperidine was added dropwise 16.25 g. of 40% hydrogen bromide. Evolution of nitrogen was measured overnight. The gas obtained amounted to 40% of total nitrogen in the compound. The reaction mixture was extracted three times with ether after diluting the solution with a salt solution to four times its volume. The water layer was then cooled and made basic with solid potassium hydroxide pellets. After four ether extractions, these combined ethereal extracts were dried over anhydrous magnesium sulfate and the solution was then fractionally distilled to remove the ether. The fraction boiling at 124–127° was collected, $n^{25}D$ 1.4372, 1.5 g. (30.2%).

(11) All melting points are corrected. The infrared spectra referred to in this article have been deposited as Document number 4500 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $1.25 for photoprints or $1.25 for 35 mm. microfilm in advance by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

(12) Analysis by D. F. Schwarzkopf, New York, N. Y., and Dr. K. Ritter, Basel, Switzerland.

(13) Molecular weights by Dr. F. Schwarzkopf, New York, N. Y., and Arnold London, New York, N. Y.

(14) E. P. Clark, *Ind. Eng. Chem., Anal. Ed.*, **13**, 820 (1941).

The picrate of this compound melted at 165–166° and a mixed melting point with the picrate of 2,6-dimethylpiperidine was not depressed.

Infrared Spectra.—A Perkin-Elmer model 21 double beam recording infrared spectrophotometer was employed with a sodium chloride prism to study the 2–15 μ range.

Acknowledgment.—We wish to gratefully acknowledge the support of this work by the Office of Ordnance Research, Contract No. DA30-069-ORD-1158.

BROOKLYN, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, INSTITUTE OF POLYMER RESEARCH, POLYTECHNIC INSTITUTE OF BROOKLYN]

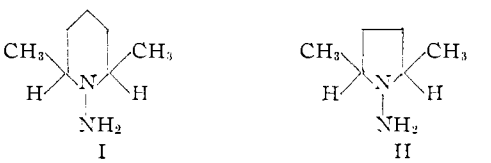
Azo Compounds.[1] Biradical Sources. The Synthesis of Some 1,1-Disubstituted Hydrazines

BY C. G. OVERBERGER, LOUIS C. PALMER,[2] BURTON S. MARKS[2] AND NORMAN R. BYRD[2]

RECEIVED JANUARY 25, 1955

Convenient syntheses of some 1,1-disubstituted hydrazines are described. I, II and III were prepared by nitrosation of the corresponding secondary amines followed by reduction with lithium aluminum hydride in high yields. II was also prepared by two other methods: by the reaction of hydrazine and 2,5-dibromohexane and by reaction of the N-carbobenzoxy derivative of hydrazine with acetonylacetone followed by reduction. This latter method represents a new use for the protective carbobenzoxy group. A number of novel reduction procedures with the use of the new 5% rhodium on alumina catalyst are reported.

In connection with current studies on the oxidation of disubstituted hydrazines, we have prepared and characterized some 1,1-disubstituted hydrazines by a number of convenient synthetic routes. This paper will describe the preparation and characterization of 1-amino-2,6-dimethylpiperidine (I), 1-amino-2,5-dimethylpyrrolidine (II) and 1,1-dibenzylhydrazine (III).



I

II

$(C_6H_5—CH_2)_2—N—NH_2$

III

I was previously reported by electrolytic reduction of the N-nitroso compound, but no yields were given.[3] I was prepared here by catalytic reduction of 2,6-lutidine over a 5% rhodium on alumina catalyst[4] to form the 2,6-dimethylpiperidine in 88% yield followed by nitrosation[5] (72%) and reduction with lithium aluminum hydride[6] (84%).

The initial reduction of the 2,6-lutidine was also accomplished with a platinum oxide catalyst but longer times were required. The reduction of the nitroso compound proceeds smoothly but the addition of the nitroso compound must be slow in order to avoid a violent reaction since an induction period is often observed. III was prepared in a similar manner in high yields. It has previously been prepared by the reaction of benzyl chloride and hydrazine hydrate in 50% yield.[7]

The *cis*-1-amino-2,5-dimethylpyrrolidine (II) was prepared in three ways. The above method was used satisfactorily, starting with 2,5-dimethylpyrrole. Tafel and Neugebauer[8] had previously reported the reduction of the N-nitroso precursor with zinc and acetic acid. II (*cis*) was also synthesized from the reaction of 2,5-dibromohexane and hydrazine hydrate in alcoholic solution in 37% yield. The physical properties of this product and the infrared spectra were identical with II prepared by the reduction method. A mixed melting point of the picrates was not depressed. This reaction also resulted in the formation of other products, part of which were characterized. 3,6-Dimethyltetrahydropyridazine was isolated and characterized by comparison with a known sample prepared by a method described elsewhere.[9] The evidence indicated that a third product was a stereoisomer of the 1-amino-2,5-dimethylpyrrolidine obtained in 21% yield. Analysis indicated the same empirical formula as the N-amino compound from reduction above but the physical properties and infrared spectrum were indicative of a structure change. Furthermore, a picrate and a tetrazene were not identical when compared with the picrate and tetrazene obtained from a product *via* the reduction method. Reduction of this stereoisomer over a platinum oxide catalyst resulted in hydrogenolysis to give a 2,5-dimethylpyrrolidine, not identical with the compound obtained on reduction of the 2,5-dimethylpyrrole. Nitrosation and reduction gave the same N-amino compound as was obtained directly from the distillation indicating no isomerization during hydrogenolysis, nitrosation and reduction. Infrared spectra of all of these compounds were consistent with the structures reported. It would appear that this isomer is the *trans*-1-amino-2,5-dimethylpyrrolidine.

(1) This is the 13th in a series of papers concerned with the preparation and decomposition of azo compounds. For the 12th paper in this series, see C. G. Overberger and B. S. Marks, THIS JOURNAL, **77**, 4097 (1955).

(2) This paper contains portions of theses submitted by L. C. Palmer, B. S. Marks and N. R. Byrd in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the Polytechnic Institute of Brooklyn.

(3) F. B. Ahren and Sollmann, *Chem. Zeit.*, **2**, 414 (1902–1903).

(4) Available from the Baker Chemical Company.

(5) H. H. Hatt, "Organic Syntheses," Col. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 211.

(6) (a) F. W. Schueler and C. Hanna, THIS JOURNAL, **73**, 4996 (1951); (b) C. Hanna and F. W. Schueler, *ibid.*, **74**, 3693 (1952).

(7) (a) H. Busch and B. Weiss, *Ber.*, **33**, 2701 (1900); (b) H. Wieland and H. Fressel, *Ann.*, **392**, 133 (1912).

(8) J. Tafel and A. Neugebauer, *Ber.*, **23**, 1544 (1890).

(9) C. G. Overberger and N. R. Byrd, THIS JOURNAL, **77**, in press (1955).