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.

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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]

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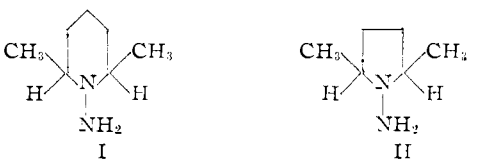
Convenient syntheses of some 1,1-disubstituted hydrazines are described. I, II and III were prepared by nitrosation of the corresponding secondary amines followed by reduction with lithium aluminum hydride in high yields. II was also prepared by two other methods: by the reaction of hydrazine and 2,5-dibromohexane 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.

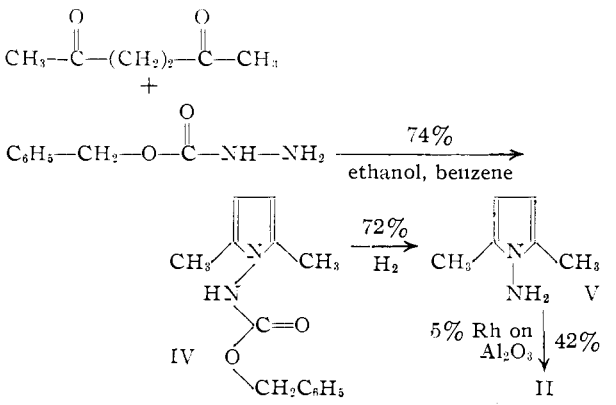
(6) (a) F. W. Schueler and C. Hanna, THIS JOURNAL, **73**, 4996 (1951); (b) C. Hanna and F. W. Schueler, *ibid.*, **74**, 3693 (1952).

(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).

trans-2,5-Dimethylpyrrolidine has been reported by Evans[10] by hydrogenation of the corresponding Δ^3-pyrroline. Evans did not report physical constants for the *trans* isomer but a picrate was reported melting at 128–130°; although no analysis was reported. A third synthesis of II is



The preparation of IV is similar to a recently reported synthesis of 1-benzoylamino-2,5-dimethylpyrrole.[11] The preparation of V by the above procedure is a new method for the synthesis of 1-amino-2,5-dimethylpyrrole. The physical properties and infrared spectra of II prepared by this method as well as the picrate and tetrazene were identical with II and the respective derivatives prepared by the other methods. Since two of the methods of synthesis of II involve reduction of a pyrrole ring catalytically, the *cis* configuration of the methyl groups are suggested.

All of the N-amino compounds (I, II and III) give tetrazenes. I was oxidized with yellow mercuric oxide to give the tetrazene in 76% yield. III was oxidized with quinone according to the general directions of Wieland and Fressel.[7b] II was converted to the tetrazene with potassium permanganate in acetone. This compound was previously reported by Tafel and Neugebauer[8] by oxidation of an impure N-amino compound with mercuric oxide.

Deamination of I over 5% rhodium on alumina catalyst proceeded with facility and gave the piperidine in 59% yield.

An inspection of the infrared spectra revealed the ease of distinguishing between NH and NH_2 groups.[1] The infrared spectrum of 1-amino-2,6-dimethylpiperidine revealed a medium strong peak in the 6.25 μ region, indicative of an NH_2 bending frequency. Furthermore, two peaks were also noted in the 3 μ area. 2,6-Dimethylpiperidine revealed only one peak in the 3 μ area and no absorption in the 6.25 μ region.

Comparison of the spectra of 1,1-dibenzylhydrazine and dibenzylamine with their respective analogs in the piperidine series, indicated similar peaks in the 3 μ area. In the 6.25 μ area, however, there is a phenyl absorption, and in carbon tetrachloride solution it appears that the phenyl and NH_2 absorptions overlap to give a stronger absorption maximum.

The infrared spectra of II and its precursors allowed similar comparisons.

Experimental[12]

Preparation of *cis*-2,6-Dimethylpiperidine.—A solution of freshly distilled 2,6-lutidine (53.5 g., 0.5 mole) in 100 ml. of glacial acetic acid was hydrogenated over 1 g. of 5% rhodium on alumina catalyst at 60° in a Parr reduction apparatus at 3 atmospheres. After the theoretical amount of hydrogen was adsorbed, the reaction mixture was filtered to remove catalyst, with the aid of infusorial earth. To the filtrate was added 40 ml. of water, followed by sufficient potassium hydroxide to neutralize the glacial acetic acid and the acetic acid salt of the 2,6-dimethylpiperidine. The resultant mixture was extracted four times with ether with further solid potassium hydroxide added to the solution after each extraction. The combined ethereal solution, after drying over anhydrous potassium carbonate, was fractionally distilled to yield 50 g. (88.5%) of product, b.p. 127–128° (b.p. 127.5–128.25° prepared by reduction of 2,6-lutidine with sodium and alcohol followed by separation of hydrochloride isomers[13]).

The picrate was prepared by adding an ether solution of the amine to an ether solution of picric acid, and melted at 166–166.5° dec. (m.p. of *cis* isomer, 162–164°[13]).

1-Nitroso-2,6-dimethylpiperidine.—The method used was adapted from that described by Hatt[5] who nitrosated dimethylamine. 2,6-Dimethylpiperidine (178 g., 1.58 moles) was dissolved in 158.4 g. (1.6 moles) of concd. hydrochloric acid in 500 ml. of water. The temperature of the mixture was kept at 75° and stirred while 113.6 g. (1.6 moles) of 97% sodium nitrite dissolved in 300 ml. of water was added dropwise over a two-hour period. After addition the heating and stirring were continued for an additional two hours. A yellow oily top layer was separated from the reaction mixture, while the bottom layer was extracted two times with ether. The combined ethereal washings and top layer were dried over anhydrous potassium carbonate, the ether was removed and the remaining yellow oil fractionally distilled to yield 162 g. (72.2%) of product, b.p. 83–85° (2.5 mm.), probably the *cis* isomer. The freshly distilled oil on standing tends to crystallize, m.p. 33–35°.

Anal.[14] Calcd. for $C_7H_{14}N_2O$: C, 59.15; H, 9.86; N, 19.72. Found: C, 59.22; H, 10.08; N, 19.72.

Starting material that has not reacted can be recovered by making the aqueous lower layer basic and extracting four times with ether.

N-Nitrosodibenzylamine.—The method employed was similar to the one used in the preparation of 1-nitroso-2,6-dimethylpiperidine. The product was a yellow crystalline precipitate which, after recrystallization from ligroin, melted at 60–61° (80%), (m.p. 61°, prepared by nitrosation of dibenzylamine, no yield given[15]).

1-Amino-2,6-dimethylpiperidine.—The procedure was similar to that reported by Schueler and Hanna[6] although the specific reaction conditions included herewith are important for successful results and safety. One pound of dry ether was added to 26.6 g. (0.70 mole) of freshly ground lithium aluminum hydride and the apparatus was arranged so that outside moisture was excluded. This slurry was allowed to stir at reflux for one hour, then 71 g. (0.5 mole) of 1-nitroso-2,6-dimethylpiperidine dissolved in 25 ml. of ether was added dropwise over a 2-hour period to the ice-cooled reaction mixture. The reaction mixture was allowed to stir at 0° for one hour after the addition, at which time it was allowed to come slowly to room temperature. During the warming period (approximately 1/2 hour) frothing and a general exothermic reaction occurs. Recooling with an ice-bath was necessary, and after one hour the reaction was completed. Excess lithium aluminum hydride was destroyed by adding small amounts of water dropwise to the cooled reaction mixture. The water addition was continued until the reaction mixture was completely white.

(10) G. G. Evans, THIS JOURNAL, **73**, 5230 (1951).

(11) H. L. Yale, K. Losee, J. Martins, M. Holsing, F. M. Perry and J. Bernstein, *ibid.*, **75**, 1933 (1953). We are grateful for a small sample of this benzoate donated by Dr. Yale of the Squibb Institute for Medical Research

(12) All melting points are corrected.

(13) A. Marcuse and R. Wolfenstein, *Ber.*, **32**, 2525 (1899).

(14) Analyses by Dr. K. Ritter, Basel, Switzerland, and Dr. F. Schwarzkopf, New York, N. Y.

(15) T. Curtius and H. Franzen, *Ber.*, **34**, 552 (1901).

The reaction mixture was filtered, and the precipitated lithium aluminate treated with potassium hydroxide solution and then extracted with ether two times. The ether extracts were added to the filtrate and the volume reduced to 250 ml. by removing solvent. The solution was dried over anhydrous potassium carbonate and the residue fractionally distilled, to yield 53.7 g. (84%) of an evil smelling water-white liquid which boiled at 165–167°, $n^{25.5}$D 1.4688, probably the *cis* compound (b.p. 170–175°, no yield reported, prepared by electrolytic reduction[3]).

Anal. Calcd. for $C_7H_{16}N_2$: C, 65.63; H, 12.50; N, 21.99. Found: C, 65.74; H, 12.43; N, 22.13.

In general, care must be taken not to add large amounts of the nitroso compound too rapidly as a relatively long induction period was noted and the reaction can become violent and uncontrollable even with ice-bath cooling.

The picrate of 1-amino-2,6-dimethylpiperidine was prepared in ethereal solution. Recrystallization twice from ethanol gave a m.p. 168–169°.

Anal. Calcd. for $C_{13}H_{19}N_5O_7$: C, 43.70; H, 5.32; N, 19.61. Found: C, 43.57; H, 5.43; N, 19.45.

Preparation of 1,1-Dibenzylhydrazine.—This asymmetric hydrazine was prepared from N-nitrosodibenzylamine by a similar procedure to that used to prepare 1-amino-2,6-dimethylpiperidine. The product obtained was a white crystalline precipitate which was washed with petroleum ether (b.p. 30–45°), and melted at 60–61° (78%). The picrate was prepared by adding a dry ether solution of picric acid to an ether solution of the 1,1-dibenzylhydrazine; the product was recrystallized from ethanol and melted at 136–137° dec.

Anal. Calcd. for $C_{20}H_{19}N_5O_7$: C, 54.42; H, 4.31; N, 15.87. Found: C, 54.45; H, 4.31; N, 15.80

Tetrazene of 1,1-Dibenzylhydrazine.—The tetrazene was prepared according to the procedure of Wieland and Fressel,[7b] m.p. 99–100° after recrystallization from ether (m.p. 98–99°[7b]).

Tetrazene of 1-Amino-2,6-dimethylpiperidine.—To a suspension of 12.96 g. of yellow mercuric oxide and 20 ml. of dry ether, was added rapidly a solution of 3.84 g. (0.03 mole) of 1-amino-2,6-dimethylpiperidine in 20 ml. of dry ether. The reaction mixture discolored almost immediately to a murky grey-green color, with evolution of heat. The reaction was allowed to stir for three hours, and then filtered through infusorial earth. The precipitate was thoroughly washed with ether and the combined ether filtrates evaporated at room temperature to an approximate 10 ml. volume. To the ethereal solution was added enough low boiling petroleum ether (b.p. 30–45°) to cause cloudiness and the flask was cooled to −80° which resulted in 2.88 g. (76%) of product, m.p. 43–47°. Recrystallization from ethanol and water yielded white crystals melting at 45.5–46.5°, which after drying under vacuum melted at 44–45°.

Anal. Calcd. for $C_{14}H_{28}N_4$: C, 66.67; H, 11.11; N, 22.22. Found: C, 66.66; H, 11.21; N, 22.26.

Deamination of 1-Amino-2,6-dimethylpiperidine.—A solution of 10 g. (0.078 mole) of 1-amino-2,6-dimethylpiperidine, 60 ml. of methanol, 9.36 g. (1.56 moles) of glacial acetic acid and 2 g. of 5% rhodium on alumina catalyst was hydrogenated in a Parr apparatus. At 3 atm. of hydrogen and 55° one mole of hydrogen was absorbed within ½ hour. The catalyst was removed and 7.7 g. (0.078 mole) of concentrated hydrochloric acid and 25 ml. of water was added to the filtrate. The solution was heated on a water-bath to remove the methanol and then well cooled and carefully made basic with solid potassium hydroxide. After extraction with ether 4 times, the combined ethereal extracts were dried over anhydrous magnesium sulfate and after removal of the ether, the fraction boiling at 125–127° was collected, 5.2 g. (59%), $n^{26.5}$D 1.4352 (n^{25}D 1.4366[16]).

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

Infrared spectra of the picrate and the amine were identical with spectra obtained from the known 2,6-dimethylpiperidine and its picrate.

***cis*-2,5-Dimethylpyrrolidine.**—2,5-Dimethylpyrrole was prepared by the method of "Organic Syntheses."[17] Reduction of 2,5-dimethylpyrrole was carried out with 42 g. (0.44 mole) of 2,5-dimethylpyrrole and 3 g. of 5% rhodium on alumina catalyst in 150 ml. of glacial acetic acid in a Parr apparatus at 40 lb. hydrogen pressure. Absorption of the first mole of hydrogen was rapid (1 hr.), but the second mole was taken up at a much slower rate. After removing the catalyst, a concentrated solution of sodium hydroxide was added slowly with cooling until the mixture was strongly basic. The organic layer was separated and the aqueous layer extracted four times with ether. The combined product layer and ethereal extracts were dried over potassium carbonate. Distillation gave 30.5 g. (70%), b.p. 106–106.7°, n^{25}D 1.4276, d^{20}_4 0.8205, of a water-white product. The infrared spectrum indicated an N-H stretching frequency at 3.06 μ. Some references to this product which do not involve hydrogenation of the pyrrole ring have been omitted for brevity (b.p. 106–108°, from reduction of the phenylhydrazene of acetonylacetone with sodium amalgam and acetic acid, no yield[18]) (from distillation of the hydrochloride of 2,5-diaminohexane, hydrochloride reported, no yield[8]) (b.p. 106–109°, d^{15}_{15} 0.813, from distillation of 2-amino-4-chlorohexane, no yield, probably both isomers present[19]) (b.p. 106°, n^{15}D 1.4357, hydrogenation of 2,5-dimethylpyrrole with a platinum oxide catalyst[20]) (b.p. 106°, derivatives reported from hydrogenation of Δ^1-pyrroline over platinum oxide and from hydrogenation of 2,5-dimethylpyrrole over platinum oxide[10]).

The picrate was prepared by adding the amine to a saturated ether solution of picric acid. Recrystallization from benzene gave a m.p. 119.5–121° (m.p. 117–118°[21]) (m.p. 120–121°[10]).

***cis*-1-Nitroso-2,5-dimethylpyrrolidine.**—The general procedure of "Organic Syntheses" was followed.[5] From 40 g. (0.40 mole) of 2,5-dimethylpyrrolidine was obtained 30 g. (58%), b.p. 72° (1.4 mm.), n^{25}D 1.4696 (prepared from 2,5-dimethylpyrrolidine, sulfuric acid and sodium nitrite, b.p. 135° (60 mm.), no yield stated[8]).

Anal. Calcd. for $C_6H_{12}N_2O$: N, 21.86. Found: N, 22.05.

***cis*-1-Amino-2,5-dimethylpyrrolidine.**—The above nitroso compound was reduced with lithium aluminum hydride according to the general procedure described previously. From 53 g (0.41 mole) of *cis*-1-nitroso-2,5-dimethylpyrrolidine, there was obtained 34 g. (72%), b.p. 56–57° (35 mm.), n^{25}D 1.4520, d^{20}_4 0.8774, of product (see later section for analysis (prepared from 1-nitroso-2,5-dimethylpyrrolidine, zinc and acetic acid but not isolated).[8] The picrate was made by the procedure described previously, m.p. 154–156° dec. (see later section).

The infrared spectrum indicated an NH_2 doublet at 3.00 and 3.12 μ and a medium strong absorption at 6.26 μ.

Reaction of 2,5-Dibromohexane with Hydrazine Hydrate.—A mixture of 294 g. (1.2 moles) of 2,5-dibromohexane and 165 g. (3.3 moles) of hydrazine hydrate in 3 liters of ethanol was refluxed for 23 hours. The reaction mixture was cooled in an ice-bath and concentrated sulfuric acid added slowly until the mixture was acidic. After filtration of the hydrazine hydrobromide crystals, the ethanol was removed by distillation. The remaining viscous oil was extracted twice with ether to remove any neutral components. Concentrated sodium hydroxide solution was then added until the mixture was strongly basic. The dark brown organic layer was separated from the aqueous layer and the aqueous layer extracted 3 times with ether. The crude product and ethereal extracts were dried over potassium carbonate. Distillation through a one foot helices packed column gave four fractions: fraction A, *cis*-1-amino-2,5-dimethylpyrrolidine, 51.3 g. (37%), b.p. 60–61° (40 mm.), n^{25}D 1.4520, d^{20}_4 0.8774. An infrared spectrum of this product was identical with the spectrum of 1-amino-2,5-dimethylpyrrolidine obtained from the reduction of the nitroso precursor.

Anal. Calcd. for $C_6H_{14}N_2$: C, 63.11; H, 12.36; N, 24.54. Found: C, 63.32; H, 12.49; N, 24.49.

The picrate was prepared by adding the compound to a saturated ether solution of picric acid. Recrystallization from benzene gave a picrate, m.p. 154–156° dec. A mixed melting point with the picrate obtained *via* the reduction procedure was not depressed.

(16) I. M. Heilbron, "Dictionary of Organic Compounds," Oxford University Press, Revised Ed., 1953, Vol. II, p. 333.

(17) D. M. Young and C. F. H. Allen, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 219.

(18) J. Tafel, *Ber.*, **22**, 1854 (1889).

(19) G. Merling, *Ann.*, **264**, 310 (1891).

(20) M. de Jong and J. P. Wibaut, *Rec. trav. chim.*, **49**, 237 (1930).

Anal. Calcd. for $C_{12}H_{17}N_5O_7$: C, 41.98; H, 4.99; N, 20.40. Found: C, 42.14; H, 5.06; N, 20.32.

A derivative with *p*-nitrobenzaldehyde was made according to the general procedure of Shriner and Fuson[21] and recrystallized from a water–ethanol mixture, m.p. 67.5–68°.

Anal. Calcd. for $C_{13}H_{17}N_3O_2$: C, 63.16; H, 6.93; N, 16.99. Found: C, 63.31; H, 6.74; N, 17.11.

Fraction B gave 28.5 g. (21%), b.p. 56° (20 mm.), $n^{25}D$ 1.4580, d^{20}_4 0.9004, the *trans* isomer of 1-amino-2,5-dimethylpyrrolidine. The infrared spectrum indicated an NH_2 doublet at 3.01 and 3.1 μ and a single absorption at 6.22 μ.

Anal. Calcd. for $C_6H_{14}N_2$: C, 63.11; H, 12.36; N, 24.54. Found: C, 63.38; H, 12.31; N, 24.66.

The picrate was prepared using the procedure described for fraction A, m.p. 162–164° dec.

Anal. Calcd. for $C_{12}H_{17}N_5O_7$: C, 41.98; H, 4.99; N, 20.40. Found: C, 42.00; H, 5.14; N, 20.32.

Fraction C gave 1.65 g. (1.2%), b.p. 65–66° (7 mm.), $n^{18}D$ 1.4711. This fraction was identified as a 3,6-dimethyltetrahydropyridazine by comparison of its picrate with the picrate of a known compound[9] and by comparison of their infrared spectra which were similar but not identical due to some impurity in the 3,6-dimethyltetrahydropyridazine prepared here.

The picrate was prepared as described previously, m.p. 109–110°. A mixed melting point with the known compound was not depressed and infrared spectra were identical.

Anal. Calcd. for $C_{12}H_{16}N_5O_7$: C, 42.23; H, 4.43; N, 20.52. Found: C, 42.47; H, 4.47; N, 20.82.

Fraction D, 4 g., could not be characterized.

Tetrazene of *cis*-1-Amino-2,5-dimethylpyrrolidine.—A general procedure of Wieland[22] was followed although they did not report this compound. The N-amino compound, 2 g. (0.0175 mole) was added to a small amount of acetone and a saturated acetone solution of potassium permanganate was added dropwise at 0° until the color of permanganate remained. After filtration and evaporation of the acetone, there was obtained 1 g. (51%) of white plate-like crystals. Recrystallization from an ethanol–water mixture gave a m.p. 43.5–45° (m.p. 43°, prepared from 1-amino-2,5-dimethylpyrrolidine and mercuric oxide[8]).

Anal. Calcd. for $C_{12}H_{24}N_4$: C, 64.24; H, 10.78; N, 24.97. Found: C, 64.18; H, 10.61; N, 24.84.

Tetrazene of *trans*-1-Amino-2,5-dimethylpyrrolidine.—The oxidation was carried out according to the directions employed for the *cis* compound. From 2 g. (0.0175 mole) of the N-amino compound there was obtained 0.9 g. (46%), m.p. 67.8–68.8°.

Anal. Calcd. for $C_{12}H_{24}N_4$: C, 64.24; H, 10.78; N, 24.97. Found: C, 64.47; H, 10.70; N, 25.19.

Reduction of *trans*-1-Amino-2,5-dimethylpyrrolidine to *trans*-2,5-Dimethylpyrrolidine.—The N-amino compound (5.5 g., 0.048 mole) in 20 ml. of acetic acid and 0.3 g. of platinum oxide catalyst was reduced in a Parr apparatus at 48 lb. hydrogen pressure. The theoretical amount of hydrogen was absorbed in 1 hour. After removing the catalyst, concentrated sodium hydroxide solution was added until the solution was strongly basic. The organic layer was separated and the aqueous layer extracted 4 times with ether. The product was dried over potassium carbonate and on distillation there was obtained 3.2 g. of product (67%), b.p. 108–109°, $n^{23}D$ 1.4291.

The infrared spectrum indicated a NH stretching frequency at 3.05 μ and no NH_2 frequency in the 6.25 μ region.

Anal. Calcd. for $C_6H_{13}N$: C, 72.66; H, 13.21; N, 14.13. Found: C, 72.88; H, 13.05; N, 13.86.

The picrate was made by the method described previously, m.p. 130–131°.

Anal. Calcd. for $C_{12}H_{16}N_4O_7$: C, 43.90; H, 4.91. Found: C, 44.01; H, 5.03.

Nitrosation of *trans*-2,5-Dimethylpyrrolidine.—The same procedure was used as that employed for the *cis* isomer. From 8 g. (0.081 mole) of 2,5-dimethylpyrrolidine there was obtained 5.7 g. (54%) of product, b.p. 57° (1 mm.), $n^{25}D$ 1.4673.

Anal. Calcd. for $C_6H_{12}N_2O$: C, 56.21; H, 9.44. Found: C, 56.05; H, 9.40.

Reduction of *trans*-1-Nitroso-2,5-dimethylpyrrolidine.—The same procedure was used as that employed for the *cis* isomer. From 5 g. (0.039 mole) of the nitroso compound there was obtained 3.1 g. (70%) of product, b.p. 57° (22 mm.), $n^{25}D$ 1.4580.

The picrate was prepared, m.p. 162–164° dec. A mixed melting point with the picrate from fraction B was not depressed. Its infrared spectrum was identical with that of fraction B.

Preparation of Carbobenzoxy Derivative of Hydrazine.—Benzyl carbonate was first prepared. To 432 g. (4 moles) of benzyl alcohol dissolved in 800 g. (7.92 moles) of triethylamine cooled in an ice-bath was added 630 g. (3.7 moles) of carbobenzoxy chloride[23] dissolved in 1000 g. of toluene. The carbobenzoxy chloride was prepared immediately before use and was not isolated but allowed to remain in the toluene. After all the carbobenzoxy chloride was added, the solution was stirred for one hour at room temperature, the triethylamine hydrochloride removed by filtration and the filtrate washed with water until neutral to *p*H paper. The organic layer was dried over anhydrous magnesium sulfate and after removal of the solvent at reduced pressure, a cloudy orange oil, 555 g., was distilled to give 470 g. (52%) of benzyl caronate, b.p. 157° (1.1 mm.), $n^{28}D$ 1.5448 (204° (14 mm.), from benzyl alcohol and phosgene in toluene, no yield given[24]).

The hydrazine derivative was prepared according to the method described by Rabjohn[25a] who referred to a general method reported by Diels.[25b]

From 234 g. (4 moles) of 85% hydrazine hydrate dissolved in 750 ml. of refluxing ethanol and 470 g. (1.94 moles) of benzyl carbonate, there was obtained 280 g. (86.5%) of tan, pasty crystals, m.p. 60–65°. Recrystallization from a 1:1 benzene–ether mixture gave 182 g. (56%) of white crystals, m.p. 68–69° (69–70°[25a]).

1-Carbobenzoxyamide-2,5-dimethylpyrrole.—Acetonylacetone (125 g., 1.09 moles) was dissolved in 500 ml. of ethanol and the solution was heated to gentle reflux. To this, with stirring, was added 182 g. (1.09 moles) of the carbobenzoxy derivative of hydrazine dissolved in 1 liter of an ethanol–benzene mixture. Some precipitate began to form during the course of the addition but then redissolved to give a deep red-colored solution. When the addition was complete, the solution was allowed to remain at room temperature overnight, the solvent was removed at reduced pressure, and water was added to the residual oil until a solid mass precipitated, 200 g. (74.2%) of a fine red powder, m.p. 88–94°. Recrystallization from a 1:1 benzene–petroleum ether (b.p. 60–68°) mixture gave 190 g. (71%) of small pink crystals, m.p. 104–106°. An analytical sample was prepared by successive recrystallizations and sublimations to give small white crystals, m.p. 107.5–108°.

Anal. Calcd. for $C_{14}H_{16}N_2O_2$: C, 68.83; H, 6.60; N, 11.47. Found: C, 68.75; H, 6.86; N, 11.28.

1-Amino-2,5-dimethylpyrrole.—A modification of a hydrogenolysis procedure[26] for removal of the carbobenzoxy group was employed. In their usual procedure, Bergmann and Zervas[26] used an open system and bubbled hydrogen through a 1 *M* hydrochloric acid, 1:1 water–methanol solution of their compound in the presence of palladium–black catalyst.

To 48.8 g. (0.2 mole) of the carbobenzoxyamidopyrrole, in 200 ml. of ethanol and 20 ml. of glacial acetic acid was added 2 g. of 10% palladium on charcoal and the resultant solution hydrogenated at 3 atmospheres. After 50% of the hydrogen had been absorbed (30 minutes) the reaction stopped. The gases were evacuated and hydrogenation was continued for 1 hour, at which time the theoretical amount of hydrogen was absorbed. The catalyst was removed by filtration, the solvent removed under reduced pressure, the residue was made basic and the organic layer separated. The aqueous solution was extracted with two 50-ml. portions of methylene chloride and the extracts com-

(21) R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., 3rd Ed., New York, N. Y., 1948, p. 171.

(22) H. Wieland, *Ber.*, **41**, 3498 (1908).

(23) H. F. Carter, R. L. Frank and H. W. Johnston, *Org. Syntheses*, **23**, 13 (1943).

(24) C. A. Bischoff and A. von Hedenstrom, *Ber.*, **35**, 3431 (1902).

(25) (a) N. Rabjohn, THIS JOURNAL, **70**, 1181 (1948); (b) O. Diels, *Ber.*, **47**, 2183 (1914).

(26) M. Bergmann and L. Zervas, *ibid.*, **65**, 1192 (1932).

bined with the organic layer and dried over anhydrous potassium carbonate. Removal of the solvent under reduced pressure and nitrogen gave a mass of pasty, brown crystals which were recrystallized twice from "Skelly A" to give 16 g. (72.5%) of a yellow crystalline material, m.p. 46–49°. An analytical sample was prepared by successive recrystallization followed by chromatographing on alumina followed by recrystallization, m.p. 51.5–52.0° (52°, no yield reported from diacetosuccinic ethyl ester and hydrazine followed by saponification and decarboxylation[27]) (52°, from acetonylacetone and the formyl derivative of hydrazine followed by saponification, no yield reported[28]).

Anal. Calcd. for $C_6H_{10}N_2$: C, 65.41; H, 9.15; N, 25.43. Found: C, 65.34; H, 9.21; N, 25.12.

Benzoylation of 1-Amino-2,5-dimethylpyrrole.—A benzoyl derivative was prepared by treating 2.25 g. (0.02 mole) of 1-amino-2,5-dimethylpyrrole with benzoyl chloride in pyridine[29] to obtain 2.1 g. (49%) of crystals, m.p. 178–183°. Recrystallization from 85% ethanol gave crystals, m.p. 184–185.5°. A mixed melting point with a sample prepared according to the procedure described in reference 11 was not depressed, m.p. 180–182° (177–179°, no yield, from N-aminopyrrole[27]) (184–185°, 60–66%, from reaction of acetonylacetone with benzoyl derivative of hydrazine[11]).

Reduction of 1-Amino-2,5-dimethylpyrrole to 1-Amino-2,5-dimethylpyrrolidine.—Hydrogenation of 11 g. (0.1 mole) of 1-amino-2,5-dimethylpyrrole in 65 ml. of glacial acetic acid with 2 g. of 5% rhodium on alumina catalyst was carried out at 3 atmospheres. Hydrogen absorption amounted to 112%, based on two double bonds, at room temperature in 2 hours. The catalyst was removed, the solution made basic with potassium hydroxide, and then extracted with methylene chloride. The extract was dried over anhydrous potassium carbonate and the solvent removed under reduced pressure to give 10 g. of a brown liquid. Distillation resulted in 4.5 g. (39%) of 1-amino-2,5-dimethylpyrrolidine, b.p. 36–37° (13 mm.), $n^{24}D$ 1.4488.

A picrate was prepared from a solution of picric acid in ether, m.p. 154–156° dec. A mixed melting point with the picrate prepared by the hydrogenation of the N-nitroso compound melted at 154–156° dec.

The tetrazene was prepared by oxidation with potassium permanganate as described previously, m.p. 43–44°. A mixed melting point with the sample prepared by oxidation of the N-amino product from reduction of the nitroso intermediate melted at 41–43°.

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

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(27) C. Bulow, *Ber.*, **35**, 4311 (1902).
(28) E. E. Blaise, *Compt. rend.*, **172**, 221 (1921).
(29) Reference 21, p. 177.

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

Azo Compounds. Oxidation Studies of 1,1-Disubstituted Hydrazines[1]

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

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The oxidation of 1,1-dibenzylhydrazine with bromine in ethanol and with *t*-butyl hypochlorite followed by reaction with base has been studied. Two reaction paths are proposed, one to form bibenzyl by an unusual nitrogen elimination and two, the formation of a tetrazene and its decomposition products, benzylamine, dibenzylamine and benzaldehyde. From the bromine oxidation, ethyl benzoate was also isolated. From the oxidation with the hypochlorite in addition to normal products some tribenzylhydrazine was found. The oxidation of 1-amino-2,6-dicyano-2,6-dimethylpiperidine with permanganate was examined and the products compared with the previously reported bromine oxidation of the same compound. It is concluded that resonance stabilization of the intermediate after loss of nitrogen favors the abnormal reaction, that is, nitrogen elimination without tetrazene formation.

A large number of oxidations of 1,1-disubstituted hydrazines are recorded, many of which were reported by Wieland.[3] These oxidations were carried out with commonly employed oxidizing agents, including benzoquinone, potassium permanganate, bromine, sodium hypochlorite, ferric chloride, mercuric oxide, etc. A tetrazene was the usual primary product.

As a result of a review of this previous work, two anomalous results from these oxidations were noted. The first example was reported by Busch and Weiss[4] who treated 1,1-dibenzylhydrazine with mercuric oxide and obtained bibenzyl as the only product along with the theoretical evolution of nitrogen. Curtius and Franzen[5] performed the same oxidation with mercuric oxide, using as a solvent, instead of ethanol, chloroform. They obtained, in good yield, tetrabenzyltetrazene, and do not report any bibenzyl. Wieland[6] repeated this oxidation and obtained small amounts of tetrazene and largely bibenzyl.

Michaelis[7,8] treated 1-allyl-1-phenylhydrazine with mercuric oxide and obtained instead of the expected tetrazene the rearranged benzeneazopropene-2, indicative of a type of allylic rearrangement. If, however, ferric chloride was used instead of mercuric oxide, then the expected tetrazene was obtained.[7] Similarly, 1-allyl-1-*p*-tolylhydrazine reacted with mercuric oxide to give *p*-tolylazopropene-2[8] but yielded the tetrazene with ferric chloride.

Bromine oxidation of a compound reported to

(1) This is the 14th 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, L. C. Palmer, B. S. Marks and N. R. Byrd, THIS JOURNAL, **77**, 4100 (1955).
(2) This paper comprises a portion of a thesis presented by B. 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) H. Wieland, "Die Hydrazine," Verlag von Ferdinand Enke, Stuttgart, 1913, pp. 38, 39.
(4) M. Busch and B. Weiss, *Ber.*, **33**, 2701 (1900).
(5) T. Curtius and H. Franzen, *ibid.*, **34**, 552 (1901).
(6) H. Wieland and H. Fressel, *Ann.*, **392**, 133 (1912).
(7) A. Michaelis and C. Claessen, *Ber.*, **22**, 2233 (1889).
(8) A. Michaelis and K. Luxembourg, *ibid.*, **26**, 2174 (1893).