

lute ethanol at 60°, with 16.25 g. (0.075 mole) of yellow mercuric oxide evolved 99% of the theoretical quantity of nitrogen within 20 minutes. The mercuric oxide must be added slowly and the mixture stirred vigorously in order to avoid too violent a reaction.

The green reaction mixture was filtered through Celite and the filtrate, after drying with magnesium sulfate, was concentrated to 20 ml. by distillation of the solvent through a glass helices packed column. The residue was allowed to stand in the refrigerator for 1 week to give 2.46 g. (31.2%) of *meso*-2,3-diphenylbutane, m.p. 123–124°. Evaporation of the filtrate and distillation of the residue through a glass spiral column gave 3.45 g. (45%) of colorless oil, b.p. 68° (0.05 mm.), n_D^{20} 1.5546, $[\alpha]_D^{20}$ -36.4° (*c* 5, ethanol).

The ethanol distillates from the above "work-up" were combined and examined for styrene content using the same procedure as that described for the sodium hydrosulfite reduction of optically active *N*-nitroso- α,α' -dimethyldibenzylamine. On this basis the maximum total styrene content of the ethanolic distillates was less than 40 mg. (approximately 0.5% of theoretical).

Preparation of Racemic *p,p'*-Dinitro-2,3-diphenylbutane.—A modified procedure of Wright²⁵ was used. To 72 g. (0.34 mole) of racemic 2,3-diphenylbutane dissolved in 200 ml. of glacial acetic acid in an ice-bath was added dropwise with stirring an ice-cold solution of 200 ml. of glacial acetic acid and 125 ml. of fuming nitric acid. The rate of addition was controlled so that the temperature of the reaction medium did not go above 10°. After addition was complete the mixture was stirred at ice temperature for 10 hours and then at room temperature for 2 hours. The solution was cautiously poured onto a large excess of cracked ice and then concentrated sodium hydroxide added to give a pH of 6. The precipitate was taken up with ether, dried, and the ether solution evaporated. The residue was recrystallized from absolute ethanol giving 55 g. (54%), m.p. 131–132° (m.p. 133° (40% yield of crude)²⁵).

Preparation of Racemic *p,p'*-Diamino-2,3-diphenylbutane.—A solution of 30 g. (0.1 mole) of racemic *p,p'*-dinitro-2,3-diphenylbutane in 200 ml. of tetrahydrofuran containing 0.5 g. of 10% palladium-on-carbon was shaken in a Parr

apparatus. After the theoretical quantity of hydrogen was absorbed the mixture was filtered and dried over magnesium sulfate. After filtration, the solvent was evaporated leaving a viscous residue which was distilled to give 22 g. (92%), b.p. 177° (0.04 mm.), of a colorless glass. Crystallization from an ether-pentane solution and recrystallization from pentane gave analytically pure solid, 20.2 g. (83%), m.p. 84–85.5° (m.p. 75–78°, 88% yield, prepared by reduction with platinum⁷).

Anal. Calcd. for C₁₆H₂₀N₂: C, 79.95; H, 8.39; N, 11.66. Found: C, 80.08; H, 8.27; N, 11.33.

Resolution of Racemic *p,p'*-Diamino-2,3-diphenylbutane.—A solution of 48 g. (0.2 mole) of racemic *p,p'*-diamino-2,3-diphenylbutane in 500 ml. of absolute methanol was added to a hot solution of 56.4 g. (0.4 mole) of *D*-tartaric acid in 3 liters of absolute methanol. The solution was filtered, rapidly brought to a boil and stoppered. Slow cooling deposited 61 g. of salt having a specific rotation of +29.2° (*c* 2, deionized water). A second crop of 21 g. was obtained by concentration of the filtrate to 2.5 liters. Seventeen recrystallizations of the first crop from methanol gave 0.4 g. of pure salt, $[\alpha]_D^{20}$ +62.0°.

The combined filtrates from the above recrystallizations were evaporated and the residue added to the original second crop. Eight recrystallizations from methanol (in each case the solution was seeded with the previously isolated pure salt) gave 5.1 g. of salt, $[\alpha]_D^{20}$ +61.8°. The pure salts were dissolved in deionized water and excess aqueous ammonia was added. The mixture was allowed to stand in the refrigerator for 5 days and the precipitated solid diamine was filtered. Drying the solid in vacuum gave 2.4 g. (10%) of a tacky clear glass, $[\alpha]_D^{20}$ +103°, $[\alpha]_D^{20}$ +106°, m.p. 43.5–46° obtained from enriched (+)-diamine using camphorsulfonic acid as the resolving agent⁷).

Deamination of (+)-*p,p'*-Diamino-2,3-diphenylbutane.—The procedure employed was similar to that described in reference 7. Our product had a rotation of $[\alpha]_D^{20}$ +95.7° (*c* 4, ethanol) ($[\alpha]_D^{20}$ +98.9° (ethanol)⁷).

Acknowledgment.—We wish to acknowledge gratefully the support of this work by the National Science Foundation, Grant NSF-G5247.

(25) George F. Wright, *J. Am. Chem. Soc.*, **61**, 2106 (1939).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN, BROOKLYN 1, N. Y.]

Decomposition of Unsymmetrical Nitrosamines¹

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Unsymmetrically substituted 1,1-dibenzyl nitrosamines were prepared and decomposed to determine whether fragmentation occurred. The compounds prepared were *N*-nitroso-3-aminodibenzylamine and *N*-nitroso-3-amino- α,α' -dimethyldibenzylamine. Reduction of these compounds with sodium hydrosulfite gave high yields of the unsymmetrical bibenzyls and no detectable amount of cross-over product. These results, coupled with previous results, demonstrated that the fragments are effectively trapped within a solvent cage and are not free.

The previous paper in this series³ demonstrated that the mercuric oxide oxidation of optically active *N*-amino- α,α' -dimethyldibenzylamine (I) did not proceed with complete stereoretention of configuration of the benzyl carbons to give a single enantiomer of 2,3-diphenylbutane. There was instead isolated considerable amounts of the *meso* hydrocarbon and a mixture of isomers, the optical rotation of which was approximately 36% of the

rotation of optically pure 2,3-diphenylbutane. Approximately the same results were obtained upon reduction of optically active *N*-nitroso- α,α' -dimethyldibenzylamine (II). These results suggested that the decomposition of I and II does not proceed by a completely concerted process, and that fragmentation occurs to some extent.

It was to test this point that Hinman and Hamm⁴ oxidized several *p*-substituted 1,1-dibenzylhydrazines. If the product was formed by coupling of two fragments, then it would be expected that cross-over would occur. These authors, however, found no evidence for cross-over; the only products isolated were the 4-substituted bibenzyl.

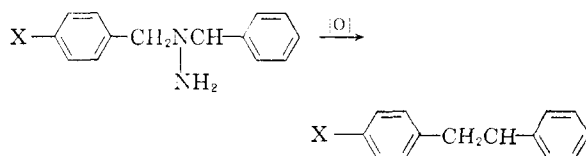
The hydrocarbon obtained from the decomposi-

(1) This is the 36th in a series of papers on the properties and reactions of azo and diazo compounds. For the previous paper see C. G. Overberger and N. P. Marullo, *J. Am. Chem. Soc.*, **83**, 1374 (1961).

(2) This paper comprises a portion of a thesis presented by N. P. Marullo in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the Polytechnic Institute of Brooklyn.

(3) C. G. Overberger, N. P. Marullo and R. G. Hiskey, *J. Am. Chem. Soc.*, **83**, 1374 (1961).

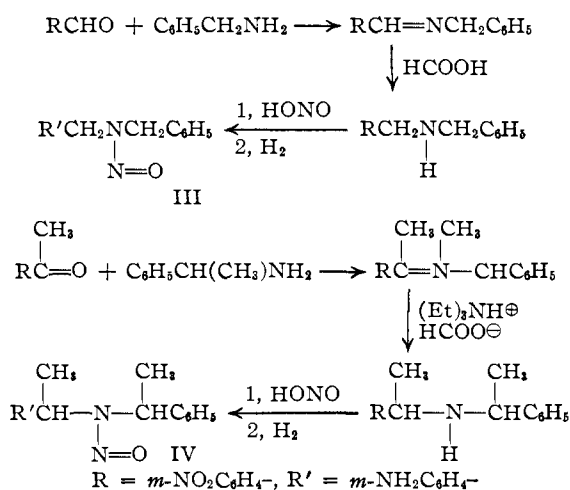
(4) R. Hinman and K. Hamm, *ibid.*, **81**, 3294 (1959).



tion of I and II had specific rotations of 36% and 45%, respectively, of that for the single enantiomer of 2,3-diphenylbutane. If racemization is the result of a reaction path which involves loss of nitrogen and formation of two residues which subsequently combine to form product, then the fragments must be short lived. Consequently, a cross-over experiment should be designed to permit the detection of small yields of a cross-over product. Since this was an important point, we decided to check the results of reference 4 carefully; we have substantiated these results completely. The compounds chosen were N-nitroso-3-aminodibenzylamine (III) and N-nitroso-3-amino- α,α' -dimethyl-dibenzylamine (IV).

The choice and position of the substituent was dictated by several factors, most important of which was that it be either acidic or basic. If cross-over occurred then one of the products would be the neutral unsubstituted hydrocarbon which could be isolated by a simple extraction method. The other consideration was that it be as small as possible thereby minimizing steric contributions, and that it be located in the *m*-position thereby minimizing possible resonance effects. For these reasons a *m*-amino substituent was chosen. The experiment with the *m*-amino substituent on the cross-over experiments is not unequivocal. If, for example, fragmentation occurred in an ionic fashion, the *m*-amino portion could direct cleavage to favor the formation of *m*-aminobenzylcarbonium ion. Mixed products, *i.e.*, cross-over products, would then be unfavorable.

These compounds were prepared according to the scheme



The synthesis of III and IV necessitated that the nitro group not be reduced until after nitrosation of the secondary amine. For this reason the Schiff bases could not be catalytically hydrogenated.

The nitro substituted amines were successfully prepared by a modification of the Leuckart procedure.^{5,6}

When 3-nitrobenzylidenebenzylamine was heated with anhydrous formic acid, carbon dioxide was evolved smoothly and a 67% yield of 3-nitrodibenzylamine was obtained. Attempts to reduce N-(α -methyl-3-nitrobenzylidene)- α -methylbenzylamine with formic acid, however, gave low yields (0-4%). Employing triethylammonium formate as the reducing agent under a variety of conditions gave erratic results. The yield, however, was improved and ranged from 4-20%.

Reduction of III with sodium hydrosulfite in base at 63° gave the theoretical nitrogen evolution. Extraction of the reaction mixture with aqueous acid in order to remove basic components gave only 0.2% of suspected neutral material. An infrared spectrum of this material showed a broad absorption between 3500 and 3300 cm^{-1} and derived from bibenzyl. From the acidic extracts 72% of 3-aminobibenzyl was isolated. This clearly shows that no "cross-over" has occurred.

Reaction of IV with sodium hydrosulfite also resulted in the theoretical evolution of nitrogen. Because of the easy hydrolysis of the hydrochloride salt of the basic components, an extraction procedure could not be used to isolate possible neutral compounds. Alumina chromatography, however, gave no 2,3-diphenylbutane under conditions where it was shown that this hydrocarbon was completely removed from the column. There was isolated a 79% yield of 3-amino- α,α' -dimethylbiphenyl. These results also show that no cross-over has taken place.

If the reaction path involves fragmentation and subsequent combination, then the results of the cross-over experiments dictate that these fragments be effectively trapped within a solvent cage. Recent work on the base-catalyzed decomposition of tosylhydrazones indicates that both carbenoid and cationoid decomposition of the diazo intermediate can occur.⁷ A carbonium ion intermediate however, could not be captured when the reaction was carried out in excess thiophenol.⁸ These results also help substantiate the idea of trapped short lived fragments.

From the results reported in this work and those of the previous paper, it is clear that two major possibilities must be considered to explain the stereochemical results. The formation of tight ion pairs or radicals within a solvent cage which are not free fragments can explain the loss of asymmetry and the "cross-over" results. An alternative explanation is that the racemization observed might be due to racemization of the reactive intermediate to (B) as indicated.

There are many examples of polar reactions which proceed through tight ion pairs where the rate of racemization is greater than the rate of formation of a titratable ion from the ion pair.⁹

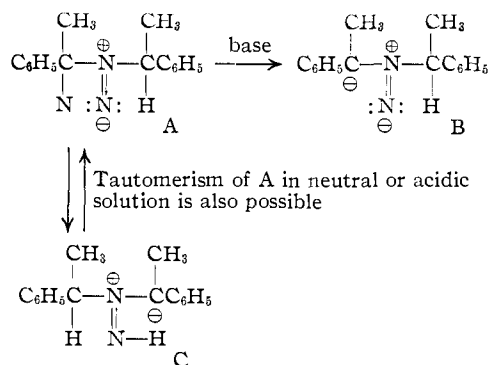
(5) E. Staple and E. C. Wagner, *J. Org. Chem.*, **14**, 559 (1949).

(6) E. R. Alexander and R. Wildman, *J. Am. Chem. Soc.*, **70**, 1187 (1948).

(7) L. Friedman and H. Shechter, *ibid.*, **81**, 5513 (1959).

(8) C. H. DePuy and D. H. Froemsdorf, *ibid.*, **82**, 635 (1960).

(9) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, pp. 304-306.



An equilibrium giving C is considered unlikely especially in the case of the hydrosulfite reduction of nitrosamines which is carried out in a highly alkaline medium.

The question as to whether the reactive intermediate undergoes initial racemization might be resolved by the oxidation of an optically active hydrazine under conditions where the intermediate would not go on to form product and the original hydrazine was regenerated. McBride and Kruse¹⁰ found that when the oxidation of simple aliphatic 1,1-disubstituted hydrazines was carried out in a solution of high acid concentration, two equivalents of oxidant was consumed but tetrazine was not formed. If the oxidized hydrazine was treated with a reducing agent the original hydrazine was regenerated, whereas when the solution was made alkaline, tetrazine was formed. This affords good evidence for the existence of a diazo-like intermediate which is stabilized when protonated.

The aim of stabilizing a benzyl-substituted hydrazine, however, was not realized. Addition of potassium bromate to 1,1-dibenzylhydrazine in a solution of high acid concentration caused evolution of nitrogen. Subsequent addition of base gave no additional significant amount of nitrogen. These results indicate that under the oxidizing conditions used, the intermediate is not stable and rapidly proceeds to form products.

Experimental¹¹

Preparation of 3-Nitrobenzylidenebenzylamine.—This compound was prepared from *m*-nitrobenzaldehyde and benzylamine in the same way as described previously for the preparation of *N*-benzylidene- α -methylbenzylamine.¹² Evaporation of the benzene and crystallization of the product by addition of pentane gave a 96% yield, m.p. 60–62°. Recrystallization from methanol gave 3-nitrobenzylidenebenzylamine, m.p. 62–64° (m.p. 62°, no yield given¹²). An infrared spectrum showed bands at 1655 (C=N), 1534 and 1354 cm^{-1} (NO₂) and none for aromatic carbonyl.

Preparation of 3-Nitrodibenzylamine.—A solution of 24 g. (0.1 mole) of 3-nitrobenzylidenebenzylamine in 100 ml. of *o*-xylene was heated to 120°. To this was added 9.2 g. (0.2 mole) of 98% formic acid which previously was dried over Drierite for 2 weeks. The reaction mixture was vigorously stirred at 120° until no more carbon dioxide was evolved. The reaction mixture was poured into cold water and made alkaline. The organic layer was separated, washed twice with water and then refluxed for 24 hours with 9 *N* hydrochloric acid. Concentration of the mixture pre-

cipitated the hydrochloride salt which then was refluxed with 100 ml. of absolute ethanol to give 18.7 g. (67%) of the amine hydrochloride, m.p. 220°.

The salt was further purified by decomposition to the free base and distillation; the fraction boiling at 150–160° (0.1 mm.) was collected. This was dissolved in 500 ml. of anhydrous ether and gaseous hydrogen chloride added to reprecipitate the amine hydrochloride, m.p. 227°.

Anal. Calcd. for C₁₄H₁₅N₃O₃Cl: C, 60.32; H, 5.43; N, 10.06. Found: C, 60.21; H, 5.88; N, 10.36.

The infrared spectrum of the free base showed bands at 3340 (NH), 1534 and 1355 (NO₂) and none at 1655 cm^{-1} (C=N).

Preparation of *N*-Nitroso-3-nitrodibenzylamine.—The general procedure of Hatt¹³ was used. From 48 g. (0.17 mole) of 3-nitrodibenzylamine hydrochloride dissolved in 50% aqueous ethanol there was obtained 45 g. (94%) of light yellow solid, m.p. 61–63°. Recrystallization from ethanol-water gave analytically pure solid, m.p. 62.5–64°. The infrared spectrum showed strong bands characteristic of nitroso and aromatic nitro groups, and none at 3340 cm^{-1} (NH).

Anal. Calcd. for C₁₄H₁₃N₃O₃: C, 61.98; H, 4.83; N, 15.49. Found: C, 62.05; H, 4.95; N, 15.19.

Preparation of *N*-Nitroso-3-aminodibenzylamine (III).—A solution of 34 g. (0.125 mole) of *N*-nitroso-3-nitrodibenzylamine in 250 ml. of absolute ethanol was shaken with 1.0 g. of 5% palladium-on-carbon in a Parr apparatus. The theoretical quantity of hydrogen was absorbed rapidly. The reaction mixture was filtered and concentrated to a volume of 75 ml., warmed, and water added until the solution became cloudy and then allowed to crystallize to yield 28 g. (92%) of solid, m.p. 44–46.8°. The infrared spectrum showed bands at 3450, 3350, 1624 and 1610 cm^{-1} (NH₂) as well as those corresponding to the nitroso group.

Anal. Calcd. for C₁₄H₁₅N₃O: C, 69.69; H, 6.27; N, 17.42. Found: C, 69.90; H, 6.39; N, 17.27.

Reaction of *N*-Nitroso-3-aminodibenzylamine with Sodium Hydrosulfite.—A solution of 35 g. (0.141 mole) of *N*-nitroso-3-aminodibenzylamine dissolved in 500 ml. of a 1:1 mixture of absolute ethanol and 20% aqueous sodium hydroxide was prepared. The solution was maintained at 63° in a water-bath and stirred under a stream of nitrogen for 30 minutes. Then 52.2 g. (0.3 mole) of sodium hydrosulfite was placed in the solids addition tube and the system sealed. Half the solid was added and nitrogen began to evolve almost immediately. After approximately 50% of the theoretical quantity was evolved the remaining sodium hydrosulfite was added. After 4 hours the theoretical nitrogen had been evolved. The reaction mixture was poured into an equal volume of salt water and extracted five times with 100-ml. portions of ether. The combined ether extracts were washed twice with saturated aqueous sodium chloride. The ether layer was cooled in an ice-bath and shaken with 150 ml. of 1 *N* hydrochloric acid. The ether layer was separated and extracted with five 50-ml. portions of 1 *N* hydrochloric acid and then dried over anhydrous magnesium sulfate. Evaporation of the ether gave 0.074 g. (0.2% based on weight of starting material) of a waxy solid which became dark brown on exposure to air. Infrared examination of this material gave a broad absorption in the 3500 to 3300 cm^{-1} region.

The ether extracts from above were made alkaline with concentrated sodium hydroxide and extracted with three 100-ml. portions of ether. After drying over magnesium sulfate and evaporation of the ether, the residue was distilled to yield a colorless liquid, b.p. 126° (0.03 mm.). Crystallization from pentane yielded 20 g. (72%) of 3-aminobenzyl, m.p. 50.5–51° (b.p. 180° (6 mm.), m.p. 51°¹⁴).

The acetanide was prepared using acetic anhydride, m.p. 128° (m.p. 128–129°¹⁴).

Preparation of *N*-(α -Methyl-3-nitrobenzylidene)- α -methylbenzylamine.—A solution of 33 g. (0.2 mole) of 3-nitroacetophenone and 24.2 g. (0.2 mole) of racemic α -methylbenzylamine in 300 ml. of toluene containing a catalytic amount of *p*-toluenesulfonic acid was refluxed for 20 hours. During this time the theoretical quantity of water (3.6 ml.) had distilled into a Dean-Stark trap. The

(10) W. R. McBride and H. W. Kruse, *J. Am. Chem. Soc.*, **79**, 572 (1957).

(11) All melting points are uncorrected. Elemental analysis by F. Schwarzkopf Microanalytical Laboratories, New York, N. Y. The authors are grateful to Mr. H. Talts for carrying out the infrared determinations.

(12) C. K. Ingold and H. A. Piggot, *J. Chem. Soc.*, 2385 (1922).

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

(14) F. Bergmann and D. Shapiro, *J. Org. Chem.*, **12**, 57 (1947).

solvent was evaporated at reduced pressure to give a dark brown oily residue. This was dissolved in 150 ml. of methanol, treated with Norite and filtered. Seed crystals, which were obtained from a previous experiment by freezing the oil in a Dry Ice-acetone-bath and allowing to come to room temperature over a 3-day period, were added to the clarified solution. Overnight cooling at -10° gave 27.3 g. (51%), of product, m.p. $42-45^{\circ}$. Concentration of the filtrate to 50 ml. gave an additional 21.4 g. (40%). An analytical sample was obtained by recrystallization once from benzene-pentane and then from methanol; m.p. $47-48.5^{\circ}$. The infrared spectrum showed bands at 1644 ($C=N$), 1530 and 1352 cm.^{-1} (NO_2) and none for aromatic carbonyl.

Anal. Calcd. for $C_{16}H_{16}N_2O_2$: C, 71.62; H, 6.01; N, 10.44. Found: C, 71.89; H, 6.08; N, 10.61.

Preparation of 3-Nitro- α,α' -dimethyldibenzylamine.—The procedure of Alexander and Wildman⁶ for the reduction of benzalaniline with triethylammonium formate was used. The first two times this procedure was used the formate salt of the product precipitated from the reaction mixture during benzene extraction of the crude reaction mixture which had been added to water. The yield in each case was 20%. Subsequent preparations of this compound using apparently identical conditions did not result in precipitation of the formate salt and work up of the reaction mixture in the usual manner⁶ gave yields of 0-8%.

Attempts to improve the yield by substituting pyridine for triethylamine or by conducting the reaction at various temperatures using different solvents such as xylene, dioxane and diethyl Cellosolve with anhydrous formic acid were not successful; the yields ranged from 4-8%.

The product, obtained by treating the formate or hydrochloride salt with base, was distilled to give a viscous oil, b.p. $138-140^{\circ}$ (0.01 mm.), n_D^{20} 1.5698. The infrared spectrum showed bands at 3410 (NH), 1530 and 1346 cm.^{-1} (NO_2), and none at 1644 cm.^{-1} ($C=N$).

Anal. Calcd. for $C_{16}H_{16}N_2O_2$: C, 71.09; H, 6.71; N, 10.36. Found: C, 71.24; H, 6.74; N, 10.03.

A picrate was prepared in ether and recrystallized from ethanol; m.p. $180.5-183^{\circ}$.

Anal. Calcd. for $C_{22}H_{21}N_5O_3$: C, 52.90; H, 4.24; N, 14.02. Found: C, 53.12; H, 4.27; N, 14.08.

Preparation of N-Nitroso-3-amino- α,α' -dimethyldibenzylamine (IV).—The nitrosation of 3-nitro- α,α' -dimethyldibenzylamine was carried out by the method of Hatt¹³ except that 75% aqueous ethanol was used as solvent. From 5.4 g. (0.02 mole) of the secondary amine there was obtained 4.9 g. (83%) of N-nitroso-3-nitro- α,α' -dimethyldibenzylamine as a light yellow glass. The infrared spectrum of this material was consistent with its structure. Except for an additional absorption at 1380 cm.^{-1} , characteristic for C-methyl, it was very similar to that obtained for N-nitroso-3-nitrodibenzylamine. Attempts to crystallize this compound from a variety of solvents before and after alumina chromatography were not successful.

Catalytic reduction using 10% palladium-on-carbon and tetrahydrofuran as a solvent rapidly resulted in the theoretical quantity of hydrogen being absorbed. The product, N-nitroso-3-amino- α,α' -dimethyldibenzylamine, was a glass

which failed to crystallize using a variety of solvents. The infrared spectrum showed bands at 3450, 3350, 1624 and 1610 cm.^{-1} (NH_2) as well as those corresponding to the nitroso group.

A benzenesulfonamide was prepared by reaction of IV with benzenesulfonyl chloride in pyridine. An analytical sample was obtained by recrystallization from methanol-water; m.p. $145.6-147^{\circ}$.

Anal. Calcd. for $C_{22}H_{23}N_3O_2S$: C, 64.52; H, 5.66; N, 10.26. Found: C, 64.39; H, 5.78; N, 10.43.

Reaction of N-Nitroso-3-amino- α,α' -dimethyldibenzylamine with Sodium Hydrosulfite.—The same procedure as described for the hydrosulfite reduction of N-nitroso- α,α' -dimethyldibenzylamine³ was used. Reaction of 2.32 g. (0.0083 mole) of the nitroso compound dissolved in 50 ml. of ethanol and 25 ml. of 20% aqueous sodium hydroxide with 4.33 g. (0.0249 mole) of sodium hydrosulfite at 70° gave 92% of the theoretical nitrogen evolution within 20 hours. The reaction products after evaporation of solvent were chromatographed through neutral alumina (Woelm, activity one). Elution with 250 ml. of a 2:1 pentane-ether solution gave no residue on evaporation of the eluent. Subsequent elution with 500 ml. of ether gave 1.48 g. (79%) of 3-amino- α,α' -dimethylbibenzyl as a soft solid. The infrared spectrum was almost identical, except for the additional C-methyl absorption, with that obtained for 3-aminobibenzyl and the product was analyzed without further purification.

Anal. Calcd. for $C_{16}H_{19}N$: C, 85.28; H, 8.50; N, 6.22. Found: C, 85.48; H, 8.55; N, 6.27.

In a control experiment, 100 mg. of *meso*-2,3-diphenylbutane, m.p. $124-125^{\circ}$, was placed on an alumina column and eluted with a 2:1 pentane-ether solution. The first 150 ml. of eluent contained 102 mg. of *meso*-2,3-diphenylbutane, m.p. $124-125^{\circ}$.

Oxidation of 1,1-Dibenzylhydrazine in Concentrated Acid.—To 12.5 g. (0.05 mole) of dibenzylhydrazine hydrochloride in 200 ml. of ethanol and 50 ml. of 12 N hydrochloric acid was added slowly 68 ml. of a 0.25 M solution of potassium bromate in water. The temperature of the solution was maintained at 0° . During the addition of oxidant, 220 ml. (20%) of nitrogen was evolved. When addition was complete, the ice-bath surrounding the reaction mixture was replaced by acetone-Dry Ice and excess concentrated sodium hydroxide was added to the reaction mixture at such a rate that the temperature did not rise above 5° . No significant amount of gas evolution occurred during addition of the base. The reaction mixture was poured into water and extracted several times with ether. Concentration of the solution deposited 4.9 g. of a white solid, m.p. $78-80^{\circ}$. Recrystallization from ethanol raised the melting point to $80-81.5^{\circ}$ and the solid subsequently was identified as the dibenzylhydrazone of benzaldehyde by a mixed melting point and infrared comparison with an authentic sample.

Since the reaction obviously did not proceed in the desired manner no further product work up was attempted.

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