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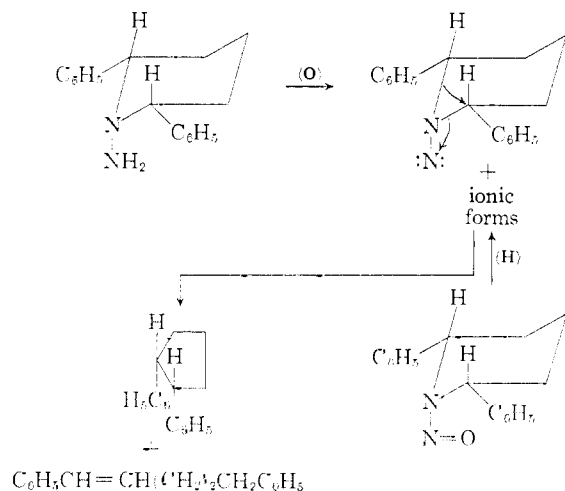
Stereochemistry of the Decomposition of N-Nitroso- and N-Amino- α,α' -dimethyldibenzylamine¹

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The synthesis of optically active N-amino- α,α' -dimethyldibenzylamine, the corresponding N-nitroso compound and the stereochemistry of their decomposition are described. Both the oxidation of the hydrazine and reduction of the nitrosamine gave 2,3-diphenylbutane which consisted of a mixture of the *meso* and partially optically active isomers. This indicates that elimination of nitrogen and formation of hydrocarbon does not proceed by a completely concerted process. Also reported is the catalytic hydrogenation of optically active N-methylbenzylidene- α -methylbenzylamine which proceeded with a high degree of asymmetric induction to generate a new optically active center.

Previous papers in this series have shown that the oxidation of appropriately substituted N-aminopiperidines proceeded with a high degree of stereospecificity to yield substituted cyclopentanes.³ Along with the cyclic products, linear unsaturated compounds also were formed. Similarly the reduction of *cis*-N-nitroso-2,6-diphenylpiperidine with sodium hydrosulfite also resulted in nitrogen elimination to give cyclic product with stereoretention of configuration.⁴ Moreover the ratio of cyclic product to olefin was very similar to that obtained from the oxidation of the corresponding N-amino compound. These results suggest that both reactions proceed *via* a common intermediate which subsequently collapses with a simultaneous loss of nitrogen and coupling of the 2,6-positions or formation of olefin.

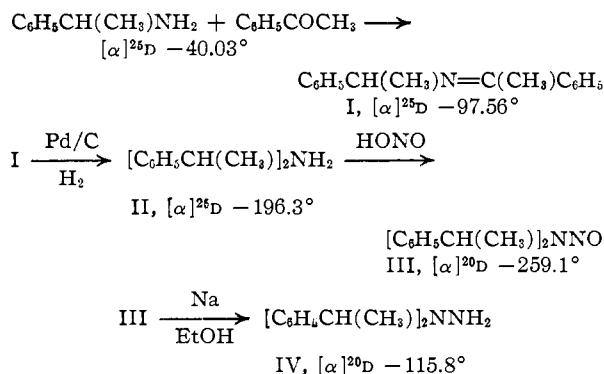


It may be argued that the observed stereoretention of configuration observed in the piperidine series is not the result of a truly concerted process but is a manifestation of the geometric restrictions placed on the system by a cyclic structure. For

this reason, it was important to determine the stereochemical fate of a linear nitrosamine and hydrazine.

Results and Discussion

The decision as to exactly what linear optically active compound to employ was restricted to one containing benzyl, furfuryl or α -cyano substituents since these are the only substituents reported at present to give the abnormal elimination reaction in fair to high yields. Because of the ready availability of optically active α -methylbenzylamine, the decision to synthesize optically active N-nitroso- and N-amino- α,α' -dimethyldibenzylamine followed logically. The desired compounds were successfully prepared by the reaction sequence



The Schiff base I was shown to be at least 96% optically pure since its acid hydrolysis regenerated α -methylbenzylamine with a specific rotation of -37.3° , which corresponded to a 96.6% content of the levorotatory isomer.

It was expected that catalytic hydrogenation of I would result in an equimolar mixture of one optical enantiomer and the *meso* isomer of α,α' -dimethyldibenzylamine (II). Since these would be diastereomers it was hoped that they would be separable by simple physical methods. Distillation of II, however, gave a constant boiling fraction in 96% yield, $[\alpha]^{25D} - 172.7^\circ$. Fractional crystallization of the hydrochloride salt gave 18.05 g. of salt with a rotation $[\alpha]^{20D} - 71.0^\circ$ to -71.8° and only 3 g. with a specific rotation of -16.5° . Decomposition of the salt, $[\alpha]^{25D} - 71.8^\circ$, regenerated II with a specific rotation of -196.3° . Furthermore it was shown that II with a rotation of -196.3° was essentially optically pure since its hydrolysis regenerated α -methylbenzylamine with a specific rotation of -38.1° , which corre-

(1) This is the 35th in a series of papers on the preparation and reactions of azo and diazo compounds. For the previous paper in this series, see G. C. Overberger and P. Chien, *J. Am. Chem. Soc.*, **82**, 5874 (1960). For a preliminary report of this work see C. G. Overberger, N. P. Marullo and R. G. Hiskey, *ibid.*, **81**, 1517 (1959).

(2) From a portion of the Dissertation submitted by N. P. Marullo in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Polytechnic Institute of Brooklyn.

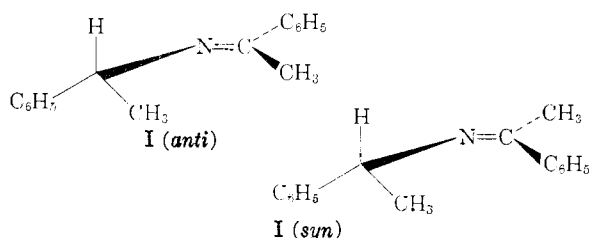
(3) (a) C. G. Overberger, J. G. Lombardino and R. G. Hiskey, *J. Am. Chem. Soc.*, **79**, 6430 (1957); (b) C. G. Overberger, G. Kesslin and P. Huang, *ibid.*, **81**, 3779 (1959).

(4) C. G. Overberger, L. G. Lombardino and R. G. Hiskey, *ibid.*, **80**, 3009 (1958).

sponds to a 97.5% content of the levorotatory isomer. Since the rotation of the initially distilled II had a rotation of -172.7° it appears that catalytic hydrogenation of I proceeded in a stereospecific manner to generate a new optically active center. Assuming that the difference in rotation between the crude and purified II was due to the presence of the *meso* isomer, the initially distilled secondary amine contained 88% of the levorotatory isomer.

There have been a number of cases reported where asymmetric induction has been observed in a catalytic hydrogenation reaction.⁵

It is interesting to explore the possible reasons for the observed high degree of stereospecificity in the catalytic reduction of I. Although geometric isomerism is possible for Schiff bases, there is no good evidence for the isolation of such isomers or of even their transitory existence.⁶ If, however, it is assumed that compound I can exist in solution as an equilibrium mixture of both isomers then the following would be the most stable conformers



Catalytic reduction of the more stable *anti* isomer (I) proceeding through the least hindered side would give the *meso*-amine, whereas reduction of the *syn* isomer would give the optically active amine. A rationale for the observed experimental result is that there is a very facile equilibrium between the *syn* and *anti* forms and that the *syn* isomer, being a higher energy state, is more easily reduced.

A chemical reduction of I using lithium aluminum hydride also gave an unequal mixture of isomers but to a lesser extent. The rotation of the amine obtained was 58% of that for optically pure II.

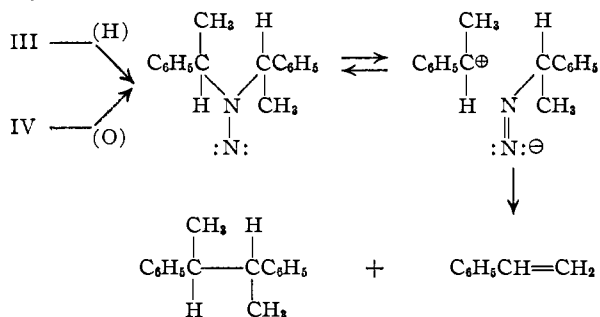
The nitrosation of II proceeded in good yield and without racemization to give the optically active nitrosamine III. In general, conversion of nitrosamines to hydrazines is best accomplished by reduction with lithium aluminum hydride. Reaction of optically inactive III with this reagent, however, gave a product which was not the expected hydrazine since it was unaffected by oxidizing agents. The nitrosamine III was successfully reduced to the optically active hydrazine IV by sodium in refluxing ethanol. Racemization was found not to occur since deamination of IV, $[\alpha]^{20D} -115.8^\circ$, gave the hydrochloride salt of II with a specific rotation of -69.6° which is 96% of the value obtained for the hydrochloride of optically pure II. The value of 96% is probably more

(5) (a) M. G. Vavon and B. Jakubowicz, *Bull. soc. chim.*, **53**, 1111 (1933); (b) D. Lipkin and T. D. Stewart, *J. Am. Chem. Soc.*, **61**, 3295 (1939); (c) C. L. Arcus and D. G. Smyth, *J. Chem. Soc.*, 34 (1955); (d) A. Pedrazzoli, *Chimica (Swits.)*, **10**, 260 (1956); (e) V. Prelog and H. Scherrer, *Helv. Chim. Acta*, **42**, 2227 (1959).

(6) (a) V. DeGaouck and R. J. Lefevre, *J. Chem. Soc.*, 1392 (1939); (b) J. Hires and J. Balog, *Acta Phys. et Chem. N.S.*, **2**, 87 (1956).

the results of contaminants other than isomers of II since the experimental work-up must be such as to yield a crude product. Extensive purification of the product would be objectionable since it could be argued that isomer fractionation occurred during purification.

By analogy with the mechanism proposed for the nitrogen elimination reactions in the piperidine series, the linear compounds III and IV should give one optical isomer of 2,3-diphenylbutane and styrene.



Reduction of the optically pure nitrosamine III with sodium hydrosulfite in base evolved 90% of the nitrogen and there was obtained 21.2% of crystalline *meso*-2,3-diphenylbutane and 42% of a mixture of liquid isomers of 2,3-diphenylbutane having a specific rotation of -45.5° . No polystyrene was isolated and only trace amounts of styrene were found. Oxidation of the hydrazine IV gave similar results. Oxidation of IV with mercuric oxide evolved 99% of the theoretical nitrogen and there was obtained 31.2% of *meso* coupled product, 45% of a mixture of liquid isomers of 2,3-diphenylbutane with a rotation $[\alpha]^{20D} -36.4^\circ$, and trace amounts of styrene.

The formation of *meso* hydrocarbon, coupled with the fact that the rotation of what is considered to be optically pure 2,3-diphenylbutane⁷ has a value of 95 to 99°, suggests that the formation of coupled product, at least in the linear series, does not proceed by a completely concerted process, and that fragmentation takes place. However, since the hydrocarbon obtained did possess some optical activity, it is improbable that the fragments have an independent existence in excess of time for racemization.⁸ This conclusion has

(7) H. H. Richmond, E. J. Underhill, A. G. Brook and G. F. Wright, *J. Am. Chem. Soc.*, **69**, 937 (1947); also see Experimental section of this paper.

(8) Absolute configuration: The configuration of (-)- α -phenylethanol has been related to (-)- α -phenylethyl chloride (J. Kenyon, H. Phillips and F. M. Taylor, *J. Chem. Soc.*, 173 (1933)) which in turn was related to (-)- α -methylbenzylamine (W. A. Cowdry, E. D. Hughes, C. K. Ingold, L. Masterson and A. Scott, *ibid.*, 1252 (1937)). These configurations subsequently were related to D- or R-glyceraldehyde (F. A. Abd Elhafez and D. J. Cram, *J. Am. Chem. Soc.*, **74**, 5849 (1952)). The prefix R is used according to the R, S system of R. S. Cahn, C. K. Ingold and V. Prelog, *Experientia*, **12**, 81 (1956). The preparation of I from D- or R-(-)- α -methylbenzylamine did not involve the participation of the asymmetric carbon and therefore it can be assumed that I also has a D- or R-configuration. This was substantiated by hydrolysis of I to D- or R-(-)- α -methylbenzylamine. The formation of II by catalytic hydrogenation of I was shown to proceed with a high degree of asymmetric induction to generate a new optically active center of the same configuration. Therefore II has a D,D- or R,R-configuration and this conclusion is supported by the hydrogenolysis of II to give D- or R-(-)- α -methylbenzylamine. The preparation of III and IV did not involve participation of the asym-

been independently confirmed by an initial study of the decomposition of unsymmetrical nitrosamines and will be described in a separate paper.

Experimental⁹

Preparation of Optically Active N-Methylbenzylidene- α -methylbenzylamine (I).—A solution of 24.2 g. (0.2 mole) of α -methylbenzylamine, $[\alpha]^{25}_D -40.03^\circ$ ($[\alpha]^{25}_D -40.30^\circ$,¹⁰ $[\alpha]^{25}_D -39.2^\circ$ to -39.7^{11}), and 24 g. (0.2 mole) of redistilled acetophenone in 175 ml. of benzene containing a catalytic amount of *p*-toluenesulfonic acid was refluxed under nitrogen while water was continuously removed by means of a Dean-Stark trap. After 3 days, 3.2 ml. (90%) of water was collected. The reaction mixture was cooled in an ice-bath and rapidly washed once with 25 ml. of dilute ice-cold sodium bicarbonate, twice with ice-cold saturated aqueous sodium chloride and then dried over anhydrous magnesium sulfate. Benzene was removed at reduced pressure and the oily residue was vacuum distilled through a 6-inch Vigreux column, in a nitrogen atmosphere, to yield 35 g. (86%) of colorless oil, b.p. 106° (0.2 mm.), n^{25}_D 1.5790, d^{25}_4 1.0002, λ_{max}^{MeOH} 238 m μ , ϵ_{max} 12,200, $[\alpha]^{25}_D -97.56^\circ$. An infrared spectrum showed strong absorption at 1630 cm.⁻¹ characteristic of an azomethine.

Anal. Calcd. for C₁₆H₁₇N: C, 86.05; H, 7.68; N, 6.27. Found: C, 86.12; H, 7.71; N, 6.52.

The inactive Schiff base, prepared in a similar manner using racemic α -methylbenzylamine, was a colorless oil, b.p. $107-109^\circ$ (0.4 mm.), n^{25}_D 1.5785. The infrared spectrum was identical with that of the optically active compound.

Hydrolysis of Optically Active N-Methylbenzylidene- α -methylbenzylamine (I).—A mixture of 6.7 g. (0.03 mole) of optically active N-methylbenzylidene- α -methylbenzylamine in 15 ml. of benzene and 25 ml. of 3 *N* hydrochloric acid was stirred on a steam-bath for 2 hours. The benzene layer was removed and the aqueous phase washed twice with benzene, made alkaline with solid sodium hydroxide and extracted four times with ether. After drying, the ether was evaporated and the residue distilled to give 2.4 g. (67%) of α -methylbenzylamine, b.p. 70° (10 mm.), n^{25}_D 1.5248, $[\alpha]^{25}_D -37.3^\circ$.

Preparation of Optically Active α,α' -Dimethyldibenzylamine (II). Procedure (a).—A solution of 21 g. (0.094 mole) of optically active I in 100 ml. of tetrahydrofuran containing 0.5 g. of 10% palladium-on-charcoal was shaken in a Parr hydrogenator. Reduction proceeded rapidly; the theoretical quantity of hydrogen was absorbed in 20 minutes. After filtration of the catalyst, solvent was evaporated at reduced pressure and the residue vacuum distilled to yield 20.5 g. (96%) of colorless oil, b.p. $103-105^\circ$ (0.3 mm.), n^{25}_D 1.5508, d^{25}_4 0.9870, $[\alpha]^{25}_D -172.7^\circ$. Infrared analysis showed weak NH absorption at 3340 cm.⁻¹. Redistillation through an 8-inch glass spiral column gave analytically pure material with the same physical constants.

Anal. Calcd. for C₁₆H₁₉N: C, 85.28; H, 8.49; N, 6.22. Found: C, 85.44; H, 8.36; N, 6.44.

A 19.1-g. sample of the above amine was converted to the hydrochloride salt and fractionally crystallized by slow addition of the amine to a stirred hot solution of 300 ml. of water containing 10 ml. of concentrated hydrochloric acid. Slow cooling gave 15.1 g. (68%) of solid, $[\alpha]^{20}_D -71.8^\circ$ (*c* 4, ethanol). Concentration of the filtrate to 150 ml. deposited a second crop of 2.45 g. (11%), $[\alpha]^{20}_D -71.4^\circ$. Concentration of the filtrate to 75 ml. gave a third fraction of 0.5 g. (2.3%), $[\alpha]^{20}_D -71.0^\circ$. Evapora-

metric centers and therefore they also have a D,D- or R,R-configuration. If the optically active hydrocarbon obtained from the decomposition of III and IV was a consequence of stereoretention of configuration, then levorotatory 2,3-diphenylbutane has a D,D- or R,R-configuration. This is substantiated by the results of Greene (F. Greene, *J. Am. Chem. Soc.*, **77**, 4869 (1955)) who isolated levorotatory 2,3-diphenylbutane from the decomposition of D- or R-methylphenylacetyl chloride with sodium peroxide.

(9) All melting points are uncorrected. Elemental analysis by Schwarzkopf Microanalytical Laboratories, Long Island City, New York. The authors are grateful to Mr. H. Talts for carrying out many of the infrared determinations.

(10) W. Theilacker and H. Winkler, *Chem. Ber.*, **87**, 690 (1954).

(11) A. W. Ingersoll, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 506.

tion of the resulting filtrate to dryness gave 3 g. (14%) of solid, $[\alpha]^{20}_D -16.5^\circ$. Decomposition of the hydrochloride salt (crop I) with aqueous base regenerated secondary amine having a rotation $[\alpha]^{20}_D -196.3^\circ$. The hydrochloride salt did not melt at temperatures up to 300° .

Anal. Calcd. for C₁₆H₂₀NCl: C, 73.28; H, 7.63; N, 5.34. Found: C, 73.25; H, 7.87; N, 5.31.

The picrate prepared in ether crystallized after 3 days at refrigerator temperature, m.p. $180-182^\circ$. An analytical sample was prepared by recrystallization twice from absolute ethanol; m.p. $181-182^\circ$.

Anal. Calcd. for C₂₂H₂₂N₄O: C, 58.05; H, 4.86; N, 12.33. Found: C, 58.07; H, 4.95; N, 12.56.

Procedure (b).—A solution of 2.23 g. (0.01 mole) of I in 25 ml. of purified tetrahydrofuran was added to a suspension of 0.38 g. (0.01 mole) of lithium aluminum hydride in 75 ml. of tetrahydrofuran. The resulting mixture was refluxed under nitrogen for 20 hours and then decomposed first by dropwise addition of ethanol and then water. The mixture was filtered, the aluminates washed several times with ether and the filtrate evaporated. The residue was warmed on a steam-bath with 20 ml. of 1 *N* hydrochloric acid for 1 hour, and then washed twice with benzene. The aqueous layer was made alkaline with 20% sodium hydroxide, extracted several times with ether and the combined ether extracts dried over magnesium sulfate. After evaporation of solvent the residue was stirred at 75° and 10 mm. for 1 hour in order to remove any primary amine and then treated with 12 ml. of 1 *N* hydrochloric acid. The resulting mixture was evaporated to give 1.05 g. (40%) of secondary amine hydrochloride, $[\alpha]^{20}_D -42.0^\circ$.

Hydrogenolysis of Optically Active II.—A solution of 5.0 g. (0.022 mole) of optically active II, 25 ml. of absolute ethanol, 5 ml. of glacial acetic acid and 2 ml. of concentrated hydrochloric acid was hydrogenated at room temperature and atmospheric pressure with 1 g. of 10% palladium-on-carbon. After approximately 7 hours, the theoretical quantity of hydrogen was absorbed and the reaction was stopped. The reaction mixture, after filtration and concentration at reduced pressure, was made alkaline with aqueous sodium hydroxide, extracted four times with petroleum ether (b.p. $30-60^\circ$) and dried over sodium hydroxide. Evaporation of the solvent at reduced pressure and distillation of the residue gave 1.20 g. (44%) of α -methylbenzylamine, b.p. $68-70^\circ$ (9-10 mm.), n^{25}_D 1.5246, $[\alpha]^{25}_D -38.1^\circ$.

Inactive α,α' -Dimethyldibenzylamine. Procedure (a).—The inactive secondary amine was prepared by catalytic hydrogenation of the corresponding Schiff base to give a colorless oil, b.p. $128-129^\circ$ (1.9 mm.), n^{25}_D 1.5496.

Procedure (b).—N-Benzylidene- α -methylbenzylamine was prepared by refluxing a benzene solution of equimolar quantities of racemic α -methylbenzylamine and benzaldehyde for 8 hours. Water was removed by means of a Dean-Stark trap. Distillation gave an 88% yield of colorless oil, b.p. $148-153^\circ$ (2.5-3 mm.), n^{25}_D 1.5874, (b.p. 170° (14 mm.), no yield given.¹² The ultraviolet spectrum gave λ_{max}^{MeOH} 248 m μ , ϵ_{max} 26,700.

The general method of addition of Grignard reagents to Schiff bases¹³ was used. To a solution of 6.0 g. (0.05 mole) of methylmagnesium bromide (6.0 g., 0.05 mole) prepared in 25 ml. of ether was added, dropwise under reflux in a nitrogen atmosphere, 5.2 g. (0.025 mole) of N-benzylidene- α -methylbenzylamine dissolved in 15 ml. of ether. After refluxing for an additional 2 hours the mixture was allowed to stand at room temperature overnight and then poured onto a mixture of ice containing 8 ml. of concentrated hydrochloric acid. The aqueous layer was washed three times with ether, made alkaline with 20% sodium hydroxide and extracted three times with ether and then dried over potassium hydroxide to yield 1.9 g. (36%) of colorless oil, b.p. $128-130^\circ$ (2 mm.), n^{25}_D 1.5502. The infrared spectrum of this material was identical with that obtained by procedure (a), the boiling point and refractive index being identical with the optically active product.

Inactive α,α' -dimethyldibenzylamine has been reported several times in the literature.¹⁴⁻²⁰ In most cases it was a

(12) K. Von Auwers and H. Wunderling, *Ber.*, **65B**, 78 (1932).

(13) K. N. Campbell, C. H. Helbing, M. P. Florkowski and B. K. Campbell, *J. Am. Chem. Soc.*, **70**, 3868 (1948).

(14) M. Busch and L. Leefhelm, *J. prakt. Chem.*, **77**, 1 (1908).

(15) A. Mailhe and M. Murat, *Bull. soc. chim.*, **9**, 465 (1911).

low yield by-product and the physical properties described by the various authors were in conflict. The boiling point has been given as 145–148°, 17 267–269°, 14 295–298°, 15 169–171° (18 mm.), 14 and 61–62° (0.2 mm.). 15 The only other reported physical constants for the free base were d_{43} 1.018 and n_D 1.573 15; the melting point of the hydrochloride salt was given as 240° 14 and 201° 16.

Optically Active N-Nitroso- α,α' -dimethyldibenzylamine (III).—The nitrosation was carried out according to the method of Hatt 21 except that 100 ml. of water and 25 ml. of ethanol was used as solvent. From 17.6 g. (0.067 mole) of secondary amine hydrochloride, there was obtained 16.5 g. (95%) of crystalline solid, m.p. 53–54.5°. Recrystallization from ethanol–water and then from petroleum ether (b.p. 30–60°) gave 15.5 g. (91.2%) of light yellow solid, m.p. 56–57°, $[\alpha]^{20}_D$ –259.1° (*c* 5%, ethanol). The solid gave a positive Liebermann nitroso test and an infrared spectrum indicated the presence of a nitroso group by strong absorption bands at 1430, 1335 and 1170 cm^{-1} .

Anal. Calcd. for $\text{C}_{16}\text{H}_{18}\text{N}_2\text{O}$: C, 75.55; H, 7.13; N, 10.91. Found: C, 75.55; H, 7.3; N, 10.95.

Inactive N-nitroso- α,α' -dimethyldibenzylamine was prepared in a similar manner in 92.7% yield, m.p. 58.5–60°.

The stability of optically active N-nitroso- α,α' -dimethyldibenzylamine toward alkali was demonstrated by heating a solution of 0.50 g. of III in 25 ml. of ethanol and 25 ml. of 20% aqueous sodium hydroxide for 10 hours at 70°. After removal of ethanol at reduced pressure the reaction mixture was extracted four times with petroleum ether (b.p. 30–60°) and dried over potassium carbonate. Concentration of the petroleum ether extract to 5 ml. and subsequent cooling gave 0.44 g. (88%) of starting material, m.p. 55–57°, $[\alpha]^{20}_D$ –258.9°.

Denitrosation of Optically Active N-Nitroso- α,α' -dimethyldibenzylamine.—A solution of 2.0 g. (0.008 mole) of III, $[\alpha]^{20}_D$ –259.1°, in 50 ml. of tetrahydrofuran was refluxed while a stream of anhydrous hydrogen chloride was passed through the solution. The reaction was continued (about 1 hour) until the evolution of oxides of nitrogen stopped as evidenced by a negative starch–iodide test. The resulting solution was concentrated to 5 ml. and 50 ml. of warm hexane added to precipitate the secondary amine hydrochloride. The mixture was filtered while hot and washed several times with warm hexane to yield 2.0 g. (97%) of the hydrochloride, $[\alpha]^{20}_D$ –71.2°.

Reaction of Optically Active III with Sodium Hydrosulfite.—A slightly modified procedure from that of reference 4 was used. Optically active III (12.7 g., 0.05 mole), dissolved in 150 ml. ethanol and 75 ml. of 20% aqueous sodium hydroxide, was stirred at 70° under a stream of nitrogen for 0.5 hour. The system then was sealed and approximately 25% of the total of sodium hydrosulfite (35 g., 0.2 mole) contained in a solids addition tube was added. After 5 minutes, nitrogen began to evolve and was collected in a 1-liter graduate by displacement of water. Additional one-fourth portions of sodium hydrosulfite were added as the rate of nitrogen evolution began to decrease markedly. After approximately 10 hours, 90% of the theoretical nitrogen was collected. The cooled reaction mixture was added to an equal volume of salt solution and just enough water added to dissolve any remaining sodium hydrosulfite. A small amount of gray solid remained suspended and was removed by filtration. An infrared examination of this solid indicated that it was not polystyrene. This product was insoluble in water, benzene and methyl ethyl ketone. The filtered reaction mixture was extracted with five 100-ml. portions of ether and the combined ether extracts were then washed twice with saturated aqueous sodium chloride and dried over magnesium sulfate.

The solvent was removed by fractional distillation through an 8-inch glass helices packed column, after which the column was washed down with 15 ml. of ethanol—the washings being returned to the distilling flask. The result-

ing solution was allowed to stand in the refrigerator for 1 week. The precipitated *meso*-2,3-diphenylbutane, 2.23 g. (21.2%), m.p. 123–124°, was collected and the filtrate after evaporation of ethanol was distilled through an 8-inch glass spiral column to give 4.52 g. (43%) of colorless oil, b.p. 72–74° (0.07 mm.), n^{20}_D 1.5544, $[\alpha]^{20}_D$ –45.5° (*c* 5, ethanol).

The ethanol distillates from the above "work-up" were combined and examined for styrene content. An ultraviolet spectrum gave an absorption maximum at 248 $\text{m}\mu$. Assuming this absorption was due to styrene (λ_{max} 248 $\text{m}\mu$, ϵ_{max} 16,620), 22 the total styrene content of the ethanolic distillates was less than 40 mg. (0.5% theoretical). A microhydrogenation using Adams catalyst absorbed 0.5 millimole of hydrogen, corresponding to a total maximum styrene content of 0.6%.

Authentic *meso*- and *rac*-2,3-diphenylbutane prepared and separated by a known procedure (*meso*, m.p. 124°; DL-racemate, b.p. 153–156° (14 mm. 23)) had identical physical properties and infrared spectra with the *meso* and liquid hydrocarbon obtained from the oxidation reaction described (*meso*, m.p. 124–125°, b.p. 70° (0.05 mm.), n^{20}_D 1.5546).

Preparation of Optically Active N-Amino- α,α' -dimethyldibenzylamine (IV).—A solution of 38.1 g. (0.15 mole) of N-nitroso- α,α' -dimethyldibenzylamine, $[\alpha]^{20}_D$ –258.8°, in 300 ml. of absolute ethanol was refluxed for 15 minutes in a nitrogen atmosphere after which 77 g. (3.3 g. atoms) of sodium was added in approximately 5-g. portions. The reaction mixture was vigorously stirred and heated sufficiently to maintain reflux during addition of the sodium and barely enough ethanol was added to avoid crystallization of sodium ethoxide.

After all the sodium had been added, the reaction mixture was refluxed an additional 30 minutes, placed in an ice-bath and an equal volume of deoxygenated water slowly added. The hydrolyzed reaction mixture then was cooled to ice temperature while in a nitrogen atmosphere and then quickly extracted with five 150-ml. portions of very anhydrous ether. After drying the combined ether extracts with magnesium sulfate, the solvent was evaporated at reduced pressure giving a colorless oily residue. Distillation through an 8-inch glass spiral column gave 25 g. (70%) of a colorless highly viscous liquid, b.p. 93–94° (0.05 mm.), n^{20}_D 1.5677. Redistillation gave analytically pure material, b.p. 120° (0.1 mm.), n^{20}_D 1.5684, $[\alpha]^{20}_D$ –115.8° (*c* 5%, ethanol). An infrared spectrum showed weak absorption at 3375 cm^{-1} and the absence of nitroso peaks.

Anal. Calcd. for $\text{C}_{16}\text{H}_{18}\text{N}_2$: C, 79.95; H, 8.39; N, 11.66. Found: C, 80.14; H, 8.21; N, 11.44.

The hydrazine is very sensitive to oxidation; the odor of 2,3-diphenylbutane can be detected upon exposure to air for several minutes. The free base is stable indefinitely when stored at refrigerator temperature in a nitrogen atmosphere.

The picrate was prepared in ether and then recrystallized from ethanol; m.p. 138.5° dec.

Anal. Calcd. for $\text{C}_{22}\text{H}_{23}\text{N}_5\text{O}_7$: C, 56.26; H, 4.94; N, 14.92. Found: C, 56.40; H, 5.08; N, 14.74.

The inactive N-amino- α,α' -dimethyldibenzylamine was prepared in the same way as the optically active compound; b.p. 116–118° (0.15 mm.), n^{20}_D 1.5680.

Deamination of Optically Active N-Amino- α,α' -Dimethyldibenzylamine (IV).—The procedure of Overberger and Marks 24 was used. From 2.4 g. (0.01 mole) of the hydrazine there was obtained by crystallization 0.85 g. (37.8%) of the secondary amine hydrochloride having $[\alpha]^{20}_D$ –71.9°. Evaporation of the aqueous acidic filtrate to dryness gave an additional 0.104 g. (4.4%) of product having a rotation of $[\alpha]^{20}_D$ –50.5°. Combination of the values obtained for the two crops gives a calculated rotation of $[\alpha]^{20}_D$ –69.6°.

Oxidation of Optically Active N-Amino- α,α' -dimethyldibenzylamine.—The procedure of reference 3a for the mercuric oxide oxidation of dibenzylhydrazines was employed. Reaction of 9.0 g. (0.0375 mole) of optically active N-amino- α,α' -dimethyldibenzylamine, dissolved in 150 ml. of abso-

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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).

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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.

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