

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

THE REDUCTION OF AZOBENZENE, AZOXYBENZENE AND NITROSOBENZENE BY THE SYSTEM MAGNESIUM + MAGNESIUM IODIDE

By W. E. BACHMANN

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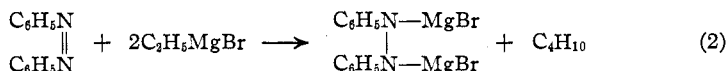
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Previous papers¹ have described the addition of the MgI group to the C=O group of various classes of compounds and to the trivalent C atom of triarylmethyls, the addition taking place when these compounds are treated with a mixture of magnesium and magnesium iodide in an ether-benzene solution. According to the hypothesis which was set forth, the active reducing agent is magnesium subiodide, generated by the interaction of the metal and metal halide

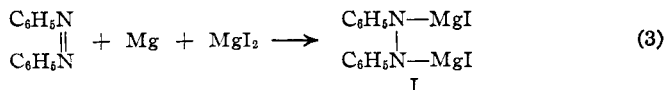


and present as such only in minute quantities at any one moment.

The behavior of the mixture, Mg + MgI₂, with azobenzene was of particular interest in view of the mechanism of the reduction of azobenzene by the Grignard reagent. Franzel and Deibel² found that ethylmagnesium bromide reduces azobenzene to a hydrazobenzene derivative and they formulated the reaction as follows



Addition of water gives hydrazobenzene.³ It is observed that the reduction of the azobenzene is occasioned by the addition of the MgX group of the Grignard reagent to each of the nitrogen atoms of the N=N group. It was, therefore, to be expected that the binary system, in virtue of its ability to furnish MgX, would readily accomplish a similar reduction. Such was found to be the case. A mixture of magnesium and magnesium iodide reduces azobenzene rapidly and completely according to the following reaction



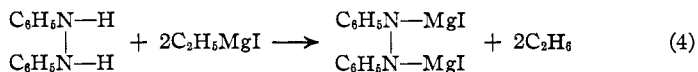
For each gram molecule of azobenzene, a gram atom of magnesium is dissolved and a gram molecule of iodomagnesium-hydrazobenzene (I) is formed. In the process of reduction the solution displays a series of intense colors, brown, reddish-brown and brown-black; at the end of the

¹ See Gomberg and Bachmann, *THIS JOURNAL*, **52**, 4967 (1930), for principal references.

² Franzel and Deibel, *Ber.*, **38**, 2716 (1905).

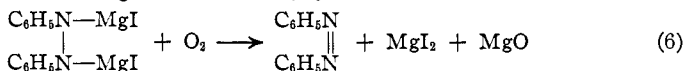
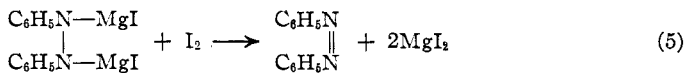
³ See also Gilman and Pickens, *THIS JOURNAL*, **47**, 2406 (1925); and Rheinboldt and Kirberg, *J. prakt. Chem.*, **118**, 1 (1928).

reaction the mixture is colorless. The play of colors is probably due to the formation of a complex between the iodomagnesium-hydrazobenzene and unreduced azobenzene, the complex being analogous to the quinhydrone-like compound which Schlenk and Appenrodt⁴ obtained by the action of sodium or potassium on azobenzene. They found that only one atom of potassium reacted for each molecule of azobenzene and they considered their dark violet-brown product to have the composition, $C_6H_5(K)N-N(K)C_6H_5 \cdot C_6H_5N=NC_6H_5$. Unlike sodium and potassium, the binary system is able to reduce the complex completely to the hydrazobenzene derivative. The identity of the product (I) as iodomagnesium-hydrazobenzene was established by its reactions and by its synthesis from hydrazobenzene through the action of a Grignard reagent.

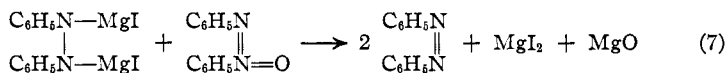


The iodomagnesium-hydrazobenzene (I) is very reactive. It is instantly decomposed by water into hydrazobenzene. The yield of hydrazobenzene obtained by hydrolysis of the reaction mixture varies between 85 and 90% of that calculated according to Equation 3. The remainder of the product consists of aniline produced by reduction beyond the hydrazobenzene stage; in agreement with this result is the fact that the amount of magnesium dissolved in the reaction is 10 to 15% greater than that required by Equation 3.

Iodine and oxygen react readily with the iodomagnesium-hydrazobenzene; the principal product of the reactions is azobenzene.



If an equivalent amount of azoxybenzene is added to the reduction product, the latter is oxidized and the azoxybenzene is reduced to one and the same product, azobenzene

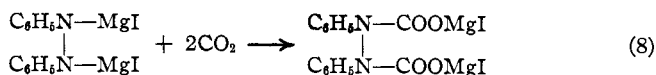


This reaction is analogous to the reaction between iodomagnesium-hydrobenzoinate and benzil, which yields benzoin as the sole product.⁵

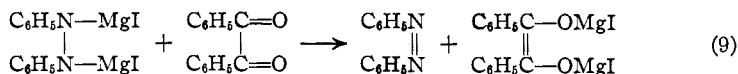
The iodomagnesium-hydrazobenzene reacts with benzoyl chloride, both MgI groups being replaced by benzoyl groups with the formation of dibenzoyl-hydrazobenzene. It reacts with carbon dioxide in the manner of a Grignard reagent giving the iodomagnesium salt of hydrazobenzene-N,N-dicarboxylic acid.

⁴ Schlenk and Appenrodt, *Ber.*, **47**, 4851 (1914).

⁵ Shankland and Gomberg, *THIS JOURNAL*, **52**, 4973 (1930).



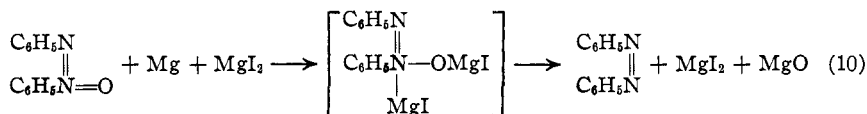
Benzil is able to abstract both MgI groups from the nitrogen atoms and attach them to its two C=O groups



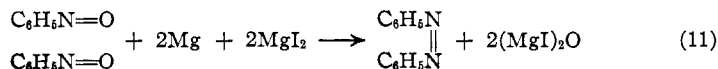
On hydrolysis azobenzene and benzoin⁶ are obtained in equivalent amounts. Benzaldehyde, however, behaves differently; it gives benzanilide as the chief product.

Para-substituted dimethyl-, dimethoxy- and diphenylazobenzene were reduced by the binary system; in all cases reduction occurred to a considerable extent (up to 49%) beyond the hydrazobenzene stage and an equivalent amount of the corresponding substituted aniline was found in the hydrolyzed products. The actual mechanism of this reduction to the aniline stage is unknown.

Azoxybenzene and substituted azoxybenzenes were found to react rapidly with a mixture of magnesium and magnesium iodide. If only one gram atom of metallic magnesium is employed for a gram molecule of azoxybenzene, azobenzene is obtained on hydrolysis of the reaction product. If twice that amount of reducing agent is present, reduction proceeds to iodomagnesium-hydrazobenzene. One may consider that the azoxybenzene is reduced to azobenzene (Equation 10) and that this is then reduced further according to Equation 3.



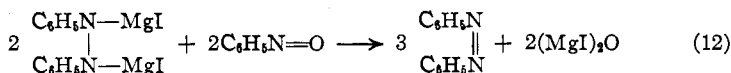
The reaction between nitrosobenzene and a mixture of magnesium and magnesium iodide is similar to the reduction of azobenzene and azoxybenzene. The principal reaction (to the extent of 70%) consists in the reduction of nitrosobenzene to azobenzene (Equation 11) followed by the reduction of the latter compound to iodomagnesium-hydrazobenzene.



When an amount of reducing agent corresponding to that given in Equation 11 is employed, azobenzene is the chief reduction product. By using an excess of reducing agent, iodomagnesium-hydrazobenzene is obtained.

Nitrosobenzene can also be reduced by iodomagnesium-hydrazobenzene; both reactants are converted to azobenzene in the reaction.

⁶ Compare the reduction of benzil by Mg + MgI₂, Gomberg and Bachmann, THIS JOURNAL, 49, 2584 (1927).



Experimental

For rapid reaction magnesium was used in the form of powder or turnings; when magnesium powder was employed, the reaction was completed in several hours. In most cases magnesium rods were used because they can be withdrawn from the solution at any time and the weight of magnesium that has reacted can be accurately determined. Best results were obtained when the reaction was carried out at room temperature. Moisture, oxygen and carbon dioxide must be excluded from the reaction mixture; this was accomplished most conveniently by carrying out the reaction in stoppered glass cylinders or heavy test-tubes of such a capacity that the solutions practically filled the tube.

Reduction of Azobenzene.—To a filtered solution of magnesium iodide, prepared from 27 g. of iodine in a mixture of 40 cc. of ether and 80 cc. of benzene, was added 18.2 g. of azobenzene and a rod of magnesium. The tube was quickly stoppered and shaken mechanically at room temperature. Frequently the reaction started in a few minutes, as was evidenced by the appearance of a dark brown color. During the reduction the solution became dark brown, reddish-brown and brown-black (like dark-oak stain) in color. The color gradually disappeared and after two days the mixture was practically colorless and contained a large amount of finely-divided grayish-white solid. The magnesium rod was withdrawn from the mixture, washed with alcohol and weighed. The loss in weight was 2.70 g., which is 111% of that calculated (2.43 g.) according to Equation 3. Numerous determinations showed that from 10–15% reduction occurred beyond the hydrazobenzene stage.

The mixture was poured into ice and water that had been saturated with carbon dioxide, and all subsequent operations were carried out in an atmosphere of carbon dioxide in order to prevent oxidation. Dilute acetic acid was used to dissolve the magnesium hydroxide which was produced on hydrolysis. After the ether-benzene solution had been washed with water, the solvents were removed by distillation under reduced pressure at 30–35° (at high temperatures hydrazobenzene is decomposed into azobenzene and aniline). The solid residue was treated with warm petroleum ether in order to remove azobenzene and aniline; the insoluble colorless residue of hydrazobenzene weighed 14.7 g. The petroleum ether filtrate was evaporated to dryness under reduced pressure and the residue was treated with a cold solution of 30% acetic acid in order to extract aniline; this acid extract yielded 1.2 g. (6%) of aniline. The residue which was insoluble in acetic acid was heated with dilute hydrochloric acid in order to convert the hydrazobenzene in it to benzidine. The azobenzene which remained weighed 0.25 g. (1%) and the benzidine (isolated as sulfate) corresponded to 1.6 g. of hydrazobenzene. The total weight of hydrazobenzene was 16.3 g. (89%) and agrees with that expected from the amount of magnesium that had reacted.

Attempts were made to reduce the product more completely to aniline by employing an excess of magnesium and magnesium iodide and allowing a long period of time for the reaction. The results were no different from those given above.

It is possible to reduce a gram molecule of azobenzene completely without using a full mole of magnesium iodide; this indicates that magnesium iodide is split off from the iodomagnesium-hydrazobenzene and is thus made available for further reaction. The rate of reaction when smaller proportions of magnesium iodide are used is, however,

greatly decreased. Using 50% of magnesium iodide, complete reduction was effected in one week (112% Mg loss); when only 25% of magnesium iodide was employed, two weeks were required for reduction (111% Mg loss).

Reaction of the Reduction Product with Benzoyl Chloride.—The colorless mixture obtained by reducing 7.28 g. of azobenzene was treated with a solution of 11 g. of benzoyl chloride in 20 cc. of benzene. The benzoyl chloride was added in small portions and the mixture was kept cold throughout the reaction. A vigorous reaction ensued and a dark reddish-brown solution resulted. After five hours the mixture was hydrolyzed and it yielded 3.3 g. of dibenzoylhydrazobenzene; m. p. 158°. The product was found to be identical with dibenzoylhydrazobenzene prepared from hydrazobenzene and benzoyl chloride.

The identical results were obtained from iodomagnesium-hydrazobenzene prepared from hydrazobenzene and ethylmagnesium iodide (Equation 4). A solution of ethylmagnesium iodide was prepared from 4.5 cc. of ethyl iodide in a mixture of 30 cc. of ether and 60 cc. of benzene and to the filtered solution solid hydrazobenzene was added in small portions until no further evolution of ethane took place (3.82 g. of hydrazobenzene). This mixture behaved in all respects like the reduction mixture from azobenzene. Addition of 5 cc. of benzoyl chloride gave 1.8 g. of dibenzoylhydrazobenzene.⁷

Reaction with Iodine.—Five grams of iodine was added in portions to the colorless reduction mixture from 3.64 g. of azobenzene. Cooling was necessary because a considerable amount of heat was developed in the reaction. At first the solution became dark-blue in color, then black-brown and finally reddish-brown. After two hours, hydrolysis gave 3.3 g. (90%) of azobenzene, 0.2 g. of hydrazobenzene and 0.1 g. of a black material. The iodomagnesium-hydrazobenzene prepared from hydrazobenzene and a Grignard reagent reacted with iodine in the same manner; the same color changes were observed and azobenzene was obtained in practically the same yield.

Reaction with Oxygen.—When a colorless solution of iodomagnesium-hydrazobenzene is exposed to the air for but an instant, the solution immediately becomes opaque blue-black and then brown-black in color. These colors, like the colors produced during the process of reduction, are due, as explained before, to the formation of quinhydrone-like complexes between the iodomagnesium-hydrazobenzene and azobenzene (the latter compound being furnished here by oxidation).

Dry air was passed into a solution of iodomagnesium-hydrazobenzene for two hours; the following color changes were observed: deep blue, greenish-brown, reddish-brown, dark brown. Hydrolysis gave a 90% yield of azobenzene and no hydrazobenzene. A similar result was obtained when air was passed into iodomagnesium-hydrazobenzene which had been prepared from hydrazobenzene.

Reaction with Carbon Dioxide.—Dry carbon dioxide was passed into the colorless reduction mixture prepared from 7.28 g. of azobenzene; the mixture was kept at 20° throughout the reaction. The grayish-white precipitate which was originally present disappeared completely after one hour and two liquid layers were obtained. After one and one-half hours of carbonation, a mixture of ice and water was added; a large amount of the salt of hydrazobenzene-N,N-dicarboxylic acid (Equation 8) precipitated in the aqueous solution. The benzene-ether solution which was removed was found to contain only 0.72 g. (10%) of product. The aqueous solution was filtered from the solid; the clear filtrate rapidly became cloudy because the salt of the acid loses carbon dioxide and gives hydrazobenzene. When the aqueous solution was acidified, the free acid was precipitated as a solid; it decomposed in a short time into carbon dioxide and hydrazobenzene. Schlenk and Appenrodt observed the same kind of reaction in the case of the sodium addition products of azobenzene.

⁷ Compare Gilman and Pickens, *THIS JOURNAL*, 47, 2406 (1925).

Practically identical results were obtained from iodomagnesium-hydrazobenzene which had been prepared from hydrazobenzene (3.15 g.) and ethylmagnesium iodide. Hydrolysis of the carbonated mixture gave an aqueous solution of the salt of the dicarboxylic acid; acidification of the filtered aqueous solution gave 1.76 g. of hydrazobenzene.

Reaction with Azoxybenzene.—Nine and one-tenth grams of azobenzene was reduced and the colorless reduction mixture was treated with 9.9 g. of azoxybenzene in portions; cooling was necessary. The mixture became dark blue, then opaque brown and finally brown-red in color. After twenty hours at room temperature, the solution was hydrolyzed; there was obtained 17 g. of azobenzene and no hydrazobenzene.

Reaction with Benzil.—A solution of 10.5 g. of benzil in 30 cc. of benzene was added in the course of five minutes to the iodomagnesium-hydrazobenzene from 9.1 g. of azobenzene. The dark reddish-brown solution which resulted was hydrolyzed after six hours. The solid residue of azobenzene and benzoin which remained after removal of the organic solvents was extracted in a Soxhlet extractor with petroleum ether (40–60°) until the siphoning liquid was colorless. From the extract, 5.6 g. of azobenzene was obtained. The colorless benzoin in the extraction thimble weighed 6.8 g.; by recrystallization from acetic acid it was obtained in the form of colorless needles melting at 132–133°.

Reaction with Benzaldehyde.—Addition of 10.6 g. of benzaldehyde in 10 cc. of benzene to the reduction product from 9.1 g. of azobenzene developed a large amount of heat (cooling necessary) and a dark reddish-brown solution resulted. After standing overnight at room temperature, the mixture was hydrolyzed; some aniline and 4.5 g. of benzanilide were obtained. After recrystallization from acetone, the benzanilide melted at 161–162°; the same melting point was observed when the compound was mixed with authentic benzanilide. Benzanilide has been found to be the product when azobenzene is heated at 200° with benzaldehyde.⁸

TABLE I
REDUCTION OF SUBSTITUTED AZOBENZENES BY Mg + MgI₂

Compound	G.	Mg reacted, %	Substituted hydrazobenzene	Substituted aniline
4,4'-Dimethylazobenzene	4.20	149	1.80	1.0
4,4'-Dimethoxyazobenzene	4.84	146	...	1.0
4,4'-Diphenylazobenzene	3.34	160	1.08	1.0

In all cases the hydrazobenzene was contaminated with some of the corresponding azobenzene. The reaction with dimethoxyazobenzene is a complex one; the product was a dark oil from which only traces of dimethylhydrazobenzene could be isolated.

In order to obtain some idea concerning the formation of *p*-toluidine (and of aniline from azobenzene), a solution of iodomagnesium-dimethylhydrazobenzene, prepared from dimethylhydrazobenzene (4.2 g.) and the Grignard reagent, was allowed to react with a mixture of magnesium and magnesium iodide. After six days of shaking at room temperature, 0.23 g. (48%) of magnesium had reacted and hydrolysis gave 2.0 g. of a mixture of dimethylhydrazobenzene and dimethylazobenzene and 1.0 g. of *p*-toluidine. Several formulations for the reaction suggest themselves but the correct one cannot be decided at this time.

Reduction of Azoxybenzene (One Equivalent of Magnesium).—A mixture of 3.96 g. (0.02 mole) of azoxybenzene, 0.486 g. (0.02 atom) of magnesium ribbon and 5.5 g. of magnesium iodide in ether and benzene was shaken until all of the magnesium had disappeared. The reddish-brown solution which contained a small amount of precipitate was hydrolyzed; 3.4 g. of azobenzene and no hydrazobenzene was obtained.

⁸ Bamberger, *Ber.*, 57, 2085 (1924); Bigiavi, *Gazz. chim. ital.*, 57, 160 (1927).

Reduction of Azoxybenzene (Two Equivalents of Magnesium).—To a filtered solution of magnesium iodide, prepared from 6 g. of iodine in 20 cc. of ether and 40 cc. of benzene, was added 4.95 g. of azoxybenzene and a magnesium rod. After three days of shaking the mixture was colorless and contained a precipitate; the mixture had the appearance of the reduction mixture obtained from azobenzene; loss in magnesium, 1.20 g.; calculated, 1.21 g. Hydrolysis gave 4.2 g. (92%) of hydrazobenzene.

The product obtained by the complete reduction of azoxybenzene was identical with the reaction product obtained by reduction of azobenzene. It reacted with azoxybenzene, with iodide and with oxygen, giving azobenzene as the principal product in each case.

TABLE II
REDUCTION OF SUBSTITUTED AZOXYBENZENES BY Mg + MgI₂

Compound	G.	Mg reacted, %	Substituted hydrazobenzene	Substituted aniline
4,4'-Dichloroazoxybenzene	5.34	96	4.0	..
4,4'-Dimethoxyazoxybenzene	4.30	110	0.5	..
4,4'Diphenylazoxybenzene	1.75	123	.83	0.35

Reduction of Nitrosobenzene to Hydrazobenzene.—To a filtered solution of magnesium iodide, prepared from 36 g. of iodine in a mixture of 40 cc. of ether and 80 cc. of benzene, was added 10.7 g. of nitrosobenzene and a rod of magnesium. The nitrosobenzene dissolved and a reddish-brown solution was obtained; however, after two minutes a complex of nitrosobenzene and magnesium iodide precipitated as an oil which quickly solidified. After ten minutes a large amount of the tan-colored crystals of the complex was present.

During this time reduction had begun and after half an hour the mixture was black in color. This color gradually disappeared and at the end of the reaction the mixture was light brown in color and contained a finely divided solid. The loss in weight of the magnesium rod was 3.76 g.; calculated, 3.65 g. (Equations 11 and 3). Half a dozen similar experiments gave exactly the same loss (103% of the calculated value) of magnesium. Hydrolysis of the mixture gave 6 g. (66%) of hydrazobenzene. Although the amount of magnesium that reacted corresponded closely to that required by Equations 11 and 3, nevertheless the yield of hydrazobenzene was never more than 70% of the calculated amount, which indicates that side reactions occur. The by-products appear to be of the nature of aniline-black. No reduction of nitrosobenzene occurred when it was shaken with magnesium without the addition of magnesium iodide.

When the reaction mixture was treated with iodine or with oxygen, azobenzene was obtained in 65–70% yields.

Reduction of Nitrosobenzene to Azobenzene.—A mixture of 5.35 g. of nitrosobenzene, 1.216 g. of magnesium ribbon and 15 g. of magnesium iodide in 20 cc. of ether and 40 cc. of benzene was shaken until all of the magnesium had disappeared. Hydrolysis of the black mixture gave 3.26 g. (71%) of azobenzene and no hydrazobenzene (Equation 11).

It was considered that azoxybenzene might be formed prior to azobenzene. However, when just enough reducing agent was employed to convert all of the nitrosobenzene to azoxybenzene (0.608 g. of magnesium for 5.35 g. of nitrosobenzene), the product consisted of a mixture of unchanged nitrosobenzene and azobenzene (33% yield).

Reaction of the Reduction Mixture with Nitrosobenzene.—To the fully reduced product from 5.35 g. of nitrosobenzene was added 2.68 g. of nitrosobenzene. A vigorous reaction took place with evolution of heat and a dark black mixture resulted. After twenty hours the mixture was hydrolyzed, and gave 4.8 g. (70% of that calculated in Equation 12) of azobenzene.

Summary

Azobenzene is reduced by the system $\text{Mg} + \text{MgI}_2$ to iodomagnesium-hydrazobenzene according to the reaction $\text{C}_6\text{H}_5\text{N}=\text{NC}_6\text{H}_5 + \text{Mg} + \text{MgI}_2 \longrightarrow \text{C}_6\text{H}_5(\text{MgI})\text{N}-\text{N}(\text{MgI})\text{C}_6\text{H}_5$.

Azoxybenzene is reduced by the binary system to azobenzene or to the hydrazobenzene derivative according to the amount of reducing agent employed.

Substituted azobenzenes and azoxybenzenes react in the manner of the unsubstituted compounds except that in certain instances reduction proceeds to a considerable extent beyond the hydrazobenzene stage.

Nitrosobenzene is reduced principally to iodomagnesium-hydrazobenzene according to the following formulation: $2\text{C}_6\text{H}_5\text{N}=\text{O} + 3\text{Mg} + 3\text{MgI}_2 \longrightarrow \text{C}_6\text{H}_5(\text{MgI})\text{N}-\text{N}(\text{MgI})\text{C}_6\text{H}_5 + 2(\text{MgI})_2\text{O}$. Azobenzene is formed as an intermediate product in this reaction.

The results obtained, in agreement with those of previous studies, lend support to the hypothesis that the active reducing agent is MgX , generated by interaction of magnesium and magnesium halide.

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CONDENSATIONS OF SECONDARY AMINES WITH NAPHTHOLS AND ALDEHYDES. II

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In earlier papers by the authors a description has been given, of the preparation¹ of a few condensation products of the type which might be associated with the intermediates formed in the Claisen or Knoevenagel reactions, and the resolution of one of these condensation products (1-(α -1-piperidylbenzyl)-2-naphthol),² into its optical antipodes. The present paper describes the preparation of several more condensation products involving other aromatic and aliphatic aldehydes. A preparation is also described in which α -naphthol is used in place of β -naphthol in these condensations.

The mechanism of the α -naphthol condensation was shown to be the same as that of the β -naphthol condensation by the preparation of the α -naphthol derivative through the interaction of benzylidene-dipiperidine and α -naphthol.

The structure of the naphthol derivative (2-(α -1-piperidylbenzyl)-1-

¹ Littman and Brode, *THIS JOURNAL*, **52**, 1655 (1930).

² Brode and Littman, *ibid.*, **52**, 5056 (1930).