

this later investigation and should be consulted for further comments.

### Summary

Five compounds were identified as high-boiling hydrolytic derivatives of lignin, in a yield of 15.5%. Together with the six low-boiling compounds in 27.5% yield, reported in an earlier pub-

lication, the total yield of the reaction came to 43.3%. The compounds identified were generally similar to known derivatives of lignin preparations. The experimental data were not considered adequate to support the proposal of a constitutional model.

SEATTLE, WASHINGTON RECEIVED NOVEMBER 18, 1946

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT OF THE LAKESIDE LABORATORIES, INC.]

## The Base Effect in Catalytic Hydrogenation. A Simple Synthesis of 6-Methoxy- $\alpha$ -tetralone

BY GILBERT STORK<sup>1</sup>

In an attempted preparation of  $\beta$ -tetralone by the catalytic hydrogenation of  $\beta$ -naphthol<sup>1a</sup> with Raney nickel a tetralol fraction was obtained which solidified and was found to consist mostly of the *phenolic ar*-tetrahydro- $\beta$ -naphthol. This result could not be reconciled with that of previous investigators who had studied the catalytic hydrogenation of  $\beta$ -naphthol to its tetrahydro derivative, using nickel or Raney nickel catalysts, and who had reported the product of the reaction to be the non-phenolic *ac*-tetrahydro- $\beta$ -naphthol.<sup>2</sup> Only one of these workers<sup>2c</sup> had reported the simultaneous formation of approximately equal amounts of both isomers.

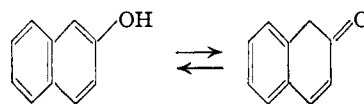
This lack of agreement prompted us to reinvestigate the catalytic hydrogenation of  $\beta$ -naphthol with Raney nickel. It was found that, contrary to the results previously reported with this catalyst,<sup>2d,e,f</sup> the absorption of two moles of hydrogen per mole of  $\beta$ -naphthol brings about the preferential saturation of the non-phenolic ring with the formation of the *phenolic ar*-tetrahydro- $\beta$ -naphthol. Some of the isomeric *ac*-tetrahydro- $\beta$ -naphthol is also formed, a typical yield being 66% of 5,6,7,8-tetrahydro- $\beta$ -naphthol and 33% of the non-phenolic isomer.<sup>3</sup> The two compounds can easily be separated by extraction of the *ar*-tetrahydro- $\beta$ -naphthol with very dilute (2%) sodium hydroxide solution. More concentrated solutions fail to dissolve the sodium salt. Once separated, the two isomers can be readily differentiated by comparing their behavior toward diazotized aromatic amines.

The finding that  $\beta$ -naphthol is reduced pre-

ferentially in the unsubstituted ring throws some doubt on Palfray's conclusion<sup>2f</sup> that a hydroxyl group facilitates the reduction of an aromatic ring. It is suggested that in a polycyclic aromatic compound that ring will become reduced, the reduction of which will result in the smallest loss of resonance energy by the system. If this be so, then one would expect that in a system like naphthalene almost any substituent introduced in one ring will stabilize that ring toward hydrogenation, and the normal product of the Raney nickel hydrogenation of  $\beta$ -naphthol would then be expected to be *ar*-tetrahydro- $\beta$ -naphthol, as was indeed found.

It should be pointed out, however, that this conclusion will be valid only in the absence of other factors which under the proper conditions may well play a determining part in directing the hydrogenation. For instance, it would not be expected that the presence of acid in the reduction medium would materially affect the course of the reduction of  $\beta$ -naphthol since this would cause little change in the molecule undergoing reduction. In the presence of some diethylamine hydrochloride or acetic acid in the alcohol solution the hydrogenation was somewhat slower than in a neutral medium, but the products from these reductions were qualitatively similar to those obtained without acid, and the main constituent was again the phenolic 5,6,7,8-tetrahydro- $\beta$ -naphthol.

In the presence of added base, however, the situation is quite different. In the first place, the phenolic moiety will be more strongly adsorbed on the basic catalyst than the rest of the molecule, and secondly it will have the possibility of tautomerizing to the non-aromatic  $\alpha,\beta$ -unsaturated ketone system



As a matter of fact, when the catalytic hydrogenation of  $\beta$ -naphthol was conducted in the

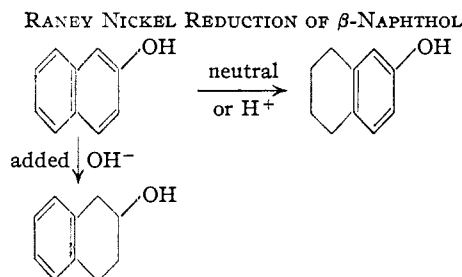
(1) Present address: Converse Memorial Laboratory, Harvard University, Cambridge, Massachusetts.

(1a) Stork and Foreman, *THIS JOURNAL*, **68**, 2172 (1946).

(2) (a) Schroeter, Svanoe, Einbeck, Geller and Riebenschahm, *Ann.*, **426**, 83 (1921); (b) Brochet and Cornubert, *Bull. soc. chim.*, **31**, 1280 (1922); (c) Kimura, *J. Chem. Soc. Japan*, **51**, 208 (1930); *C. A.*, **26**, 720 (1932); (d) Musser and Adkins, *THIS JOURNAL*, **60**, 664 (1938); (e) Palfray, *Compt. rend.*, **206**, 1976 (1938); (f) Palfray, *Bull. soc. chim.*, [5] **7**, 407 (1940).

(3) Professor Homer Adkins has told us that H. P. Schultz, working in his laboratory, had observed the formation of the phenolic 5,6,7,8-tetrahydro- $\beta$ -naphthol in a Raney nickel hydrogenation of  $\beta$ -naphthol.

presence of a small quantity of 40% sodium hydroxide solution only a small quantity of the phenolic *ar*-tetrahydro- $\beta$ -naphthol was formed and the major product was the alcohol, *ac*-tetrahydro- $\beta$ -naphthol. The speed of reduction or the temperature at which it proceeded (85°) were the same as without added base. This would not be expected and may be cited in favor of reduction by way of the unsaturated ketone tautomer.<sup>4</sup> The results which have been discussed above may be summarized in a chart.



Because we were interested in 6-methoxytetralin, it was of interest to see if the reduction of  $\beta$ -naphthyl methyl ether could be made to proceed in the unsubstituted ring. From the preceding discussion it would be expected that such a reduction of the unsubstituted ring should be the dominant reaction in a neutral or acidic medium. It was found that, in the presence of a small quantity of acetic acid in the alcoholic medium, hydrogenation took place very rapidly at 130°, being completed in about fifteen minutes. The product of the reaction was a colorless oil with a pleasant odor recalling that of  $\beta$ -naphthyl methyl ether. That this consisted mostly of the expected 6-methoxytetralin was shown by chromic oxide oxidation to the known 6-methoxy- $\alpha$ -tetralone, further identified by means of its known semicarbazone. In this manner, 6-methoxy- $\alpha$ -tetralone was obtained in 60% yield from the readily available  $\beta$ -naphthyl methyl ether. This method of synthesis is preferable to the alternate reduction of  $\beta$ -naphthol to *ar*-tetrahydro- $\beta$ -naphthol, as described above, followed by methylation to 6-methoxytetralin: while the preparation of the methyl ether of the tetrahydronaphthol necessitates the use of dimethyl sulfate, it is merely necessary to reflux a solution of  $\beta$ -naphthol in methanol containing some sulfuric acid to obtain  $\beta$ -naphthyl methyl ether in good yield.

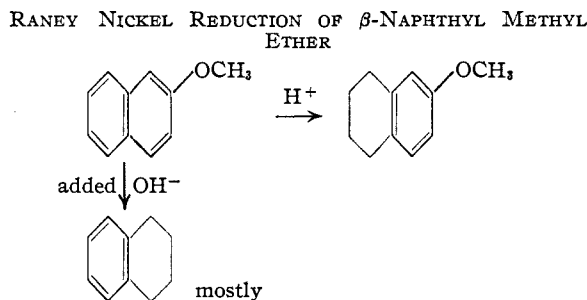
It seems that this synthesis of 6-methoxy- $\alpha$ -tetralone offers considerable advantage over the other methods which have been devised for its preparation,<sup>5</sup> and this interesting intermediate becomes readily available.

(4) Such an unsaturated tautomer has been postulated by Adkins to explain the reduction of  $\beta$ -naphthol over copper chromite; Adkins, *Ind. Eng. Chem.*, **32**, 1189 (1940).

(5) (a) Schroeter, *Ber.*, **63**, 1308 (1930); (b) Thompson, *J. Chem. Soc.*, 2310 (1932); (c) Robinson and Schlittler, *ibid.*, 1288 (1935); (d) Peak and Robinson, *ibid.*, 1581 (1937); (e) Burnop, Elliott and Linstead, *ibid.*, 727 (1940); (f) Bachmann and Thomas, *THIS JOURNAL*, **64**, 94 (1942); (g) Chuang and Huang *Ber.*, **69**, 1505 (1946).

With no added acid, previous workers have reported that the product of the catalytic hydrogenation of  $\beta$ -naphthyl methyl ether with Raney nickel is not 6-methoxytetralin, but the isomeric 1,2,3,4-tetrahydro- $\beta$ -naphthyl methyl ether.<sup>6</sup> If Arbit's proof of structure be accepted, the result can be explained as being due to the presence of a small quantity of base on the Raney nickel that was used. The effect of base would be to increase adsorption of the methoxylated ring on the catalyst through coordination with the positive center on the oxygen. It is of interest that the reductions carried out by Arbit,<sup>6</sup> Musser<sup>2d</sup> and Van Duzee<sup>6</sup> all required considerably higher temperature and longer time than the one described in this paper in which the non-substituted ring was reduced. From what has been said before this would be expected because of the stabilization of the substituted ring. In our experience the addition of base to the reduction medium, either as sodium methoxide or alcoholic potassium hydroxide, resulted in a very difficult reduction, the product of which was mostly the result of hydrogenolysis of the ether linkage, followed by reduction, *i. e.*, tetralin.

The results which we have obtained with  $\beta$ -naphthol methyl ether may be summarized as shown.



The observations which we have made on the influence of base on the course of the catalytic hydrogenation of  $\beta$ -naphthol and its methyl ether may be of general applicability. The increased adsorption of a positive center on Raney nickel in the presence of base has been termed the base effect. This is pictured to occur through a cancellation of the positive center through coordination with the base. The effect of base in facilitating the hydrogenation of simple phenols has been reported by Ungnade and his collaborators.<sup>7</sup> Another illustration is the increased rate of hydrogenation of carbonyl compounds in the presence of base.<sup>8</sup>

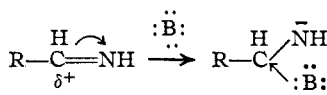
The effect of ammonia in increasing the yield of primary amine from the reduction of a nitrile over Raney nickel can also be explained in this way if the effectiveness of ammonia in suppressing

(6) Van Duzee and Adkins, *THIS JOURNAL*, **57**, 147 (1935); Arbit, *ibid.*, **68**, 1662 (1946).

(7) Ungnade and McLaren, *ibid.*, **66**, 118 (1944); Ungnade and Nightingale, *ibid.*, 1218 (1944).

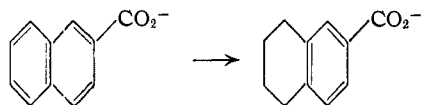
(8) Delépine and Horeau, *Compt. rend.*, **201**, 1301 (1935).

the formation of secondary amine<sup>9</sup> is pictured as being due to the cancellation of the positive center of the intermediate imine, resulting in strong adsorption on the catalyst and preventing addition of initially formed primary amine to the imine double bond.



Viewed in this light, the repression of secondary amine formation by ammonia would be expected to occur also with other bases. In this connection, a recently reported observation of Fluchaire and Chambret<sup>10</sup> takes added significance. They found that benzyl cyanide gave almost exclusively the primary amine when hydrogenated with Raney nickel in the presence of a little sodium hydroxide. This is in contrast to the large quantity of secondary amine which they obtained with a thoroughly washed catalyst. This result makes it appear that it would be well to study the base effect in the reduction of other nitriles.

The preferential hydrogenation of a phenolic ring in a polycyclic aromatic compound in the presence of base would not be expected to be shown by compounds in which the phenolic hydroxyl has been replaced by a carboxyl group. In that case, the negative charge on the anion cannot affect adsorption of the ring since it is not conjugated with it. In fact, when  $\beta$ -naphthoic acid was reduced with Raney nickel, in the presence of either a small amount or an excess of sodium hydroxide, the only product formed was the product of reduction in the unsubstituted ring; 5,6,7,8-tetrahydro- $\beta$ -naphthoic acid.



In view of this result it is difficult to accept without question Robinson and Rydon's proof of structure of their  $\alpha$ -norestrone,<sup>11</sup> based as it is on the assertion that a carboxyl greatly facilitates reduction of the aromatic ring to which it is attached.

With the base effect in mind it becomes possible to understand many apparently irreconcilable results recorded in the literature. For example, the catalytic hydrogenation of  $\alpha$ -naphthol with a nickel catalyst<sup>2b</sup> or with Raney nickel<sup>2f</sup> is stated to give almost exclusively the product of reduction in the substituted ring, *ac*-tetrahydro- $\alpha$ -naphthol, while other investigators report that hydrogenation takes place in the non-phenolic ring with the formation of *ar*-tetrahydro- $\alpha$ -naph-

thol.<sup>2d,12</sup> Another example, perhaps amenable to the same explanation, is the catalytic hydrogenation of 1-alkyl-2-naphthols which some workers report to take place with saturation of the phenolic ring,<sup>2d</sup> while others have obtained reduction in the non-phenolic ring, using apparently identical conditions.<sup>13</sup>

## Experimental

**Reduction of  $\beta$ -Naphthol with Raney Nickel in Neutral or Acidic Medium.**—A solution of 72 g. of  $\beta$ -naphthol in commercial absolute alcohol was prepared so that the total volume was 250 ml. A few cc. of Raney nickel catalyst<sup>14</sup> was added and the hydrogenation was conducted in a high pressure rocking hydrogenation bomb in the customary manner. The initial pressure was 3400 psi. The hydrogenation was completed after two to three hours at 85°. On working up as indicated below there was obtained 50 g. of *ar*-tetrahydro- $\beta$ -naphthol, m. p. 57–58°, as well as a small amount of the non-phenolic isomer. In the same manner, but in the presence of 5 g. of diethylamine hydrochloride, reduction proceeded at a similar rate at a temperature of 125° giving 45 g. of *ar*-tetrahydro- $\beta$ -naphthol, m. p. 56–57°. Similarly, but in the presence of 1 ml. of glacial acetic acid, the reduction proceeded rapidly at 115° (three hours). After filtering off the catalyst, the alcohol was removed and the reduction products were distilled in vacuum, giving 69.5 g., b. p. 169–172° at 30 mm. of a mixture of reduction products. After the addition of about 250 ml. of ether, the phenolic material was extracted with 2 liters of 2% sodium hydroxide solution, in about five portions. From the ether layer 18 g. of *ac*-tetrahydro- $\beta$ -naphthol, b. p. 153–155° at 20 mm., was recovered. The aqueous alkaline layer was made acid to Congo red, and the liberated oil was extracted with ether. The oil remaining after removal of the ether was recrystallized from petroleum ether (b. p. 65–80°) with the help of decolorizing charcoal. On cooling *ar*-tetrahydro- $\beta$ -naphthol crystallized, m. p. 59–60°; the quantity obtained was 42 g. Addition of a cold diazotized solution of *p*-nitroaniline to the phenol in dilute sodium hydroxide gave an immediate brick-red precipitate of the coupling product. Under the same conditions, the non-phenolic isomer gave no precipitate.

**Reduction with Raney Nickel in the Presence of Base.**—The hydrogenation in the presence of base was conducted as before, but 2 ml. of a 40% sodium hydroxide solution was added to the alcohol solution before reduction. The reaction was complete in about two hours at 85°. On working up as above, 8 g. of the phenolic *ar*-tetrahydro- $\beta$ -naphthol, m. p. 57–59°, was obtained while the main product was *ac*-tetrahydro- $\beta$ -naphthol (50 g.), b. p. 152° at 15 mm.

**$\beta$ -Naphthyl Methyl Ether.**—A mixture of 500 g. of  $\beta$ -naphthol, 600 ml. of methanol and 100 ml. of concentrated sulfuric acid was refluxed five hours. The solution was cooled, the precipitate filtered, washed with water, dilute sodium hydroxide, and again with water. The methyl ether was obtained in 85% yield on recrystallization from methanol and had m. p. 71–72°.

**Reduction of  $\beta$ -Naphthyl Methyl Ether to 6-Methoxytetralin.**—A suspension of  $\beta$ -naphthyl methyl ether in absolute alcohol was prepared by adding the alcohol to 79 g. of the ether until the total volume was 250 ml. Several cc. of Raney nickel catalyst and 1 ml. of glacial acetic acid were added and the hydrogenation was conducted as usual. The initial pressure was 3400 psi. At 130° the reduction took place very rapidly and was complete in about fifteen minutes. Distillation of the reduction product gave 74 g. of a colorless oil, b. p. 134–137°

(9) Winans and Adkins, *THIS JOURNAL*, **54**, 306 (1932); Schwoegler and Adkins, *ibid.*, **61**, 3499 (1939); Howk, U. S. Patent 2,166,150 and 2,166,151; Lazier and Howk, U. S. Patent 2,292,949.

(10) Fluchaire and Chambret, *Bull. soc. chim.*, **11**, 22 (1944).

(11) Robinson and Rydon, *J. Chem. Soc.*, 1394 (1939).

(12) Bachmann and Ness, *THIS JOURNAL*, **64**, 536 (1942).

(13) Martin and Robinson, *J. Chem. Soc.*, 491 (1943).

(14) "Organic Syntheses," Vol. 21, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 15. The catalyst used was neutral to pH Hydrion paper.

at 17 mm. This was shown to be mostly 6-methoxy-tetralin by the oxidation to 6-methoxy- $\alpha$ -tetralone which is described below.

**6-Methoxy- $\alpha$ -tetralone.**—The product of the reduction above was oxidized by the method of Burnop, Elliott and Linstead.<sup>15</sup> After completion of the oxidation the product was isolated by the method of Schwenk and Papa.<sup>15</sup> The crude 6-methoxy- $\alpha$ -tetralone thus obtained was recrystallized from dilute methanol. In this way, 6-methoxy- $\alpha$ -tetralone was obtained in 60–65% yield and had m. p. 78–79° (reported m. p. 77.5°,<sup>16</sup> 80°,<sup>16a</sup> 82°<sup>16b</sup>). The semicarbazone prepared in methanol in the presence of pyridine had m. p. 236–237° (reported m. p. 235°).<sup>16b</sup>

**Hydrogenation of  $\beta$ -Naphthoic Acid in the Presence of Base.**—The hydrogenation was carried out in the usual manner, using a solution of 43 g. of  $\beta$ -naphthoic acid in warm dioxane (total volume of 250 ml.). In the presence of several cc. of Raney nickel and 3 ml. of a 40% sodium hydroxide solution. The initial pressure was 3400 psi. After about two hours at 150° the hydrogenation was completed. The only product isolated was 5,6,7,8-tetrahydro- $\beta$ -naphthoic acid, m. p. 153–154° from benzene-ligroin (reported m. p. 154–155°).<sup>16</sup> The isomeric 1,2,3,4-tetrahydro- $\beta$ -naphthoic acid has m. p. 96°.<sup>17</sup>

This reduction was repeated using enough alkali so the acid would be entirely in the form of its salt: 1.72 g. of  $\beta$ -naphthoic acid was placed in a small hydrogenation bomb with 20 ml. of water and 0.4 g. of sodium hydroxide. One gram of Raney nickel was added to the suspension and

hydrogenation was conducted under the same conditions of temperature and pressure as above. The reduction was complete in less than an hour. Acidification of the filtered solution gave 1.3 g. of the tetrahydro acid, m. p. 145–150°, raised by recrystallization from benzene-ligroin to 153–155°.

**Acknowledgment.**—The author wishes to express his appreciation to Dr. E. Leon Foreman for his interest in this work.

### Summary

The catalytic hydrogenation of  $\beta$ -naphthol over Raney nickel is described. It is shown that in neutral or acidic medium the product is mainly *ar*-tetrahydro- $\beta$ -naphthol, while *ac*-tetrahydro- $\beta$ -naphthol becomes the principal product in the presence of added base.

The catalytic hydrogenation of  $\beta$ -naphthyl methyl ether over Raney nickel in an acidic medium is shown to result in the reduction of the unsubstituted ring with the formation of 6-methoxytetralin.

A simple preparation of 6-methoxy- $\alpha$ -tetralone is outlined.

The theoretical implications of these findings are discussed.

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(15) Schwenk and Papa, *THIS JOURNAL*, **67**, 1432 (1945).

(16) Newman and Zahm, *THIS JOURNAL*, **65**, 1097 (1943).

(17) v. Sowiński, *Ber.*, **24**, 2354 (1891).

[CONTRIBUTION FROM THE PIONEERING RESEARCH SECTION, RAYON TECHNICAL DIVISION, E. I. DU PONT DE NEMOURS AND COMPANY, INC.]

## The Preparation of N-Substituted Diamines<sup>1</sup>

BY EMERSON L. WITTBECKER, RAY C. HOUTZ AND W. W. WATKINS

A number of disecundary and secondary-primary diamines were required for an investigation of N-substituted polyamides. The reduction of aldimines was chosen for the syntheses of these intermediates since this method has been one of the most successful for the preparation of secondary aliphatic amines.<sup>2</sup>

Dialdimines were readily prepared by adding two moles of an aldehyde to an aqueous solution of one mole of diamine. With compounds such as *i*-butyraldehyde or benzaldehyde, it was necessary only to keep the reaction temperature below the boiling point of the aldehyde. With butyraldehyde, propionaldehyde and acetaldehyde, the temperature was kept at 0–5°, since the dialdimines derived from lower or less complex aldehydes were less stable. N,N'-Di-*i*-butylidenehexamethylenediamine, for example, could be distilled in good yields, while N,N'-diethylidenehexamethylenediamine became resinous and only a 29% yield could be obtained on distillation. It was desirable, therefore, to purify the aldehydes and diamines used and then to hydrogenate the

dialdimines without drying or distilling. If the water separated as a layer, it was removed, otherwise it remained during the hydrogenation. This is in contrast to recent work<sup>2</sup> where it was reported that secondary aliphatic amines were obtained only when the aldimines were dried and distilled before hydrogenation.

Monoalldimines were prepared by adding one mole of an aldehyde to two moles of an aqueous diamine solution. While dialdime formation was not precluded, it was reduced to such an extent that good yields of N-monosubstituted diamines were obtained after hydrogenation of the reaction mixture.

Three methods of carrying out the reduction of aldimines have been tried. A sodium-ethanol reduction was used successfully in two cases, but the most convenient laboratory method was found to be a low-pressure catalytic hydrogenation with platinum oxide catalyst. In most cases, no solvent was used except a small amount of ethanol to assure homogeneity of the undried dialdime layer. A high pressure catalytic hydrogenation with Raney nickel catalyst was used in the preparation of N,N'-dibenzylhexamethylenediamine and N-benzylhexamethylenediamine and the

(1) This paper was presented before the Organic Division at the Atlantic City meeting of the American Chemical Society, April, 1946.

(2) Campbell, Sommers and Campbell, *THIS JOURNAL*, **66**, 82 (1944).