

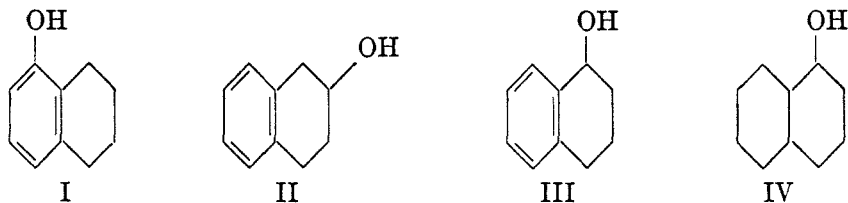
REDUCTIONS WITH NICKEL-ALUMINUM ALLOY AND AQUEOUS ALKALI. PART VI. NAPHTHALENE AND ITS SUBSTITUTION PRODUCTS¹

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Received November 22, 1948

In a previous publication (1) from these laboratories, the displacement of sulfonic acid groups by the action of a nickel-aluminum alloy in aqueous alkali was reported. In the case of naphthalene sulfonic acids, simultaneous reduction to tetrahydronaphthalenes accompanied hydrogenolysis of the sulfonic acid groups. This paper describes the results of our studies on the application of the Raney alloy reduction procedure to a variety of mono- and di-substituted naphthalene compounds.

The hydrogenation of naphthalene and naphthalene derivatives to the corresponding tetrahydro and decahydro compounds has been the subject of many investigations. The classical studies of Bamberger (2) on the reduction of naphthalene derivatives by means of sodium and alcohols established the marked difference in reactivity of the substituted and unsubstituted rings of the naphthols. While α -naphthol reduces almost exclusively in the unsubstituted ring to give the phenolic, *ar*- α -tetralol (I), β -naphthol reduces to the alcohol, *ac*- β -tetralol (II).



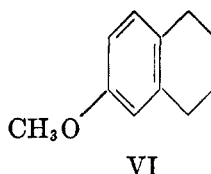
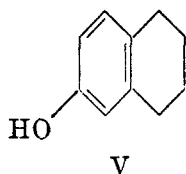
The course of the catalytic hydrogenation of the naphthols depends primarily upon the nature of the catalyst. With α -naphthol, there may be obtained in addition to I, the alcohols (III) and (IV), as well as tetralin, the latter resulting from the hydrogenolysis of (III) (3a). For example, with Raney nickel catalyst, α -naphthol gives (I) and (III) in a ratio of 5:3, whereas over copper chromite the ratio is 1:2 respectively. On the other hand, β -naphthol, over either catalyst, has been reported to hydrogenate almost exclusively in the oxygenated ring to the alcohol (II).

However, Stork (3d) has shown recently that β -naphthol² with "neutral" Raney nickel catalyst at 85–100° and at an initial pressure of about 3,500 lbs. is hydrogenated to the *ar*- β -tetralol (V) in 66% yield. Under identical condi-

¹ Presented in abstract before the Division of Organic Chemistry at the New York Meeting of the American Chemical Society on September 15, 1947.

² In studying the preparation of β -tetralone by the catalytic hydrogenation of β -naphthol with Raney nickel catalyst, Stock and Foreman (3c) isolated a tetralol fraction which consisted predominately of the phenolic *ar*- β -tetralol.

tions except for the presence of a small quantity of base, β -naphthol reduces preferentially in the substituted ring to the alcohol (II). β -Naphthyl methyl ether gave 60% of 6-methoxytetralin (VI) with "neutral" Raney nickel catalyst.

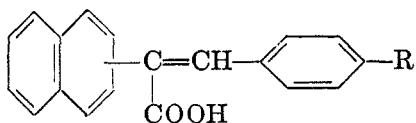


In general, catalytic hydrogenation of naphthalene or substituted naphthalenes to the decahydro derivatives is relatively simple; whereas the selective hydrogenation of one of the benzenoid nuclei is often difficult, particularly for substituted naphthalenes when hydrogenation of either the substituted or unsubstituted ring is desired. Although chemical reduction (sodium and alcohols) gives, almost without exception, the tetrahydro derivatives, preferential reduction of either ring is also not always feasible. Hydrogenolysis occasionally accompanies catalytic and chemical reduction, this side reaction being more frequently encountered in the catalytic procedures.

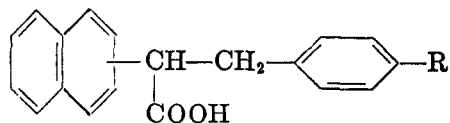
The use of an alkali solution together with Raney's alloy for effecting the reduction of organic compounds has been without effect on the hydrogenation of benzene or substituted benzene compounds. However, naphthalene and its derivatives reduce readily to the corresponding tetrahydro compounds by the alloy method; the hydrogenation of several compounds proceeds smoothly even at room temperature.

Naphthalene reduced in good yield to tetralin and many of the monosubstituted naphthalenes reduced exclusively in the non-substituted ring. For example, α -naphthol, α -nitronaphthalene, β -naphthoic acid, α -naphthaleneacetic acid and β -(2-naphthoyl)propionic acid yielded the corresponding *ar*-tetrahydro derivatives. With β -naphthol and α -naphthoic acid, reduction occurs in both the substituted and unsubstituted rings. In the former case, approximately 55-60% of *ar*- β -tetralol was formed. This result is somewhat unexpected in view of Stork's findings (3d). β -Naphthaleneacetic acid reduced in the substituted ring and an 85% yield of recrystallized *ac*- β -tetralylacetic acid was obtained. In the latter case there was no evidence that any reduction in the unsubstituted ring occurred.

Several α -(1- and 2-naphthyl)cinnamic and β -(1- and 2-naphthyl)- β -phenylpropionic acids of the following formulas (VII-XIV) reduced in either the sub-



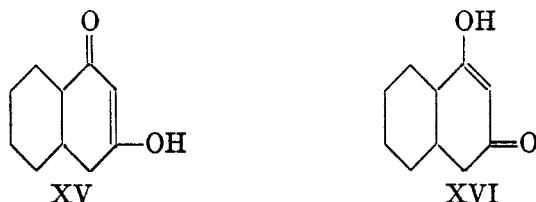
- VII α -C₁₀H₇-; R, H
 IX β -C₁₀H₇-; R, H
 XI α -C₁₀H₇-; R, OH
 XIII β -C₁₀H₇-; R, OH



- VIII α -C₁₀H₇-; R, H
 X β -C₁₀H₇-; R, H
 XII α -C₁₀H₇-; R, OH
 XIV β -C₁₀H₇-; R, OH

stituted or unsubstituted ring. Compounds VII and VIII gave approximately equal amounts of the *ar*- and *ac*-compounds, whereas IX and X gave a predominant amount of the *ar*-compound and only about 15% of the *ac*-compound. For XI–XIV inclusive, only one reduction product was isolated and identified, the *alpha* compounds, XI and XII, reducing in the substituted ring, whereas the *beta* compounds, XIII and XIV, reduced in the unsubstituted ring. The reduction products of compounds VII–XIV were identified by analysis and mixed melting point with authentic samples of α -(tetralyl)- β -phenylpropionic acid (4).

Several disubstituted naphthalenes wherein the substituents are on either one ring or on both rings have also been studied. The former are reduced in the unsubstituted ring, 3-hydroxy- β -naphthoic acid and 1-hydroxy- β -naphthoic acid yielding the corresponding *ar*- β -tetrahydro derivatives in good yield. However, 1,3-dihydroxynaphthalene gave an unusual reduction product, which analyzed for a dihydroxyhexahydronaphthalene of probable formula XV or XVI. In a patent (5), the catalytic reduction of 1,3-dihydroxynaphthalene is stated to yield a hexahydro derivative. However, neither the procedure for the catalytic reduction nor physical data for the compound is given.

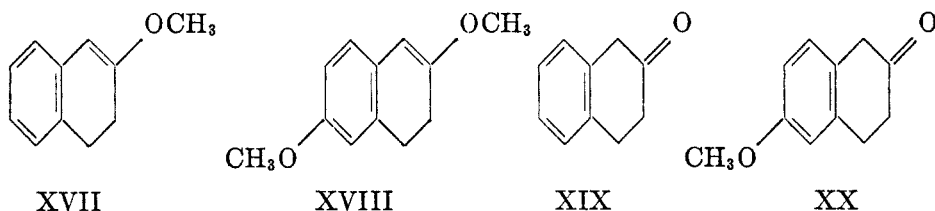


The disubstituted naphthalenes having one substituent on each ring gave in the case of 2,7-dihydroxy- and 1,8-dicarboxy-naphthalenes the expected 2,7-dihydroxy- and 1,8-dicarboxy-tetralins respectively. However, 1,5-dinitronaphthalene yielded *ar*-tetrahydro- α -naphthylamine, a nitro or an amino group being hydrogenolyzed in the course of the reaction.

A most unexpected result was obtained with 1,5-dihydroxy- and 1,6-dihydroxy-naphthalenes. Instead of the expected 1,5- and 1,6-dihydroxytetralins, there was obtained 5-hydroxy- and 6-hydroxy- α -tetralones respectively. It is difficult to reconcile these results with the known susceptibility of carbonyl groups to the Raney alloy (6) and Raney catalyst (7) reduction methods. It is apparent, especially in the case of 1,6-dihydroxynaphthalene, that the tetralone is the direct product of the reduction, further reduction of the carbonyl group being rendered difficult by the fact that it is essentially an acid carbonyl (8). The 6-hydroxy- α -tetralone can be recovered quantitatively after treatment with Raney's alloy and aqueous alkali. Although only a poor yield of 5-hydroxy- α -tetralone was obtained as the 5-methoxy compound, the 6-hydroxy- α -tetralone was secured in 70% yields on ten-gram reductions of 1,6-dihydroxynaphthalene. This procedure appears considerably simpler than those published for securing 6-methoxy- α -tetralone (3d, 9).

In the course of the reduction of the naphthalene nucleus, other groups susceptible to reduction by the alloy method such as the nitro groups, keto groups and double bonds are simultaneously reduced.

Hydrogenolysis was also encountered in the case of β -naphthyl methyl ether, the principal product of the reaction being tetralin. Approximately 30–35% of the β -naphthyl methyl ether was recovered unchanged. With sodium and alcohol, β -naphthyl methyl ether and 2,6-dimethoxynaphthalene reduce to the dihydro derivatives XVII and XVIII respectively (10). On hydrolysis, XVII



and XVIII yield the ketones XIX and XX. With Raney alloy and aqueous alkali, 1,6-dimethoxynaphthalene yielded several products, tetralin being the only one definitely identified.

EXPERIMENTAL

The reductions were carried out as previously described (1). It was necessary to modify the procedure for several compounds and the reduction for these compounds is described in detail. Except in those cases where the amounts of starting material are given, 10 g. of substance in 300 cc. of 10% sodium hydroxide solution was reduced with 20 g. of Raney's alloy. The yields are calculated to the purified reduction product. Alkali-insoluble compounds were reduced in a 2,000-cc. flask equipped with an adapter and efficient reflux condenser. All melting points have been corrected.

1. *Naphthalene* was reduced using 50 cc. of ethyl alcohol as solvent. A 74% yield of *tetralin* was obtained, b.p. 203–205°. With *phthalic anhydride*, the *o-tetrahydronaphthoylbenzoic acid* was obtained, m.p. 155–156° in agreement with the literature (11).

2. α -*Naphthol* gave an 85% yield of *ar-tetrahydro- α -naphthol*. Recrystallized from petroleum ether, m.p. 70–71°, literature 68.5–70° (12). Addition product with 1,3,5-trinitrobenzene was obtained as golden yellow needles, m.p. 103–110°, literature 106–107° (13).

3. To 25 g. of β -*naphthol* dissolved in 600 cc. of 10% sodium hydroxide, there was added 40 g. of Raney's alloy. The reduction product was extracted with chloroform from the acidified solution, the chloroform extract washed, dried and evaporated; yield 17.5 g., m.p. 56–58°. Recrystallized from petroleum ether, it had m.p. 60–61°; literature 59–60° (3b). The *ac- β -tetralol* was lost by steam distillation during the reduction.

4. *Reduction of 1,3-dihydroxynaphthalene*. Five grams of 1,3-dihydroxynaphthalene was reduced in 250 cc. of 10% sodium hydroxide solution with 20 g. of Raney's alloy. The reduction was carried out in an atmosphere of nitrogen. The reduction product was worked up and after two recrystallizations from *n*-hexane it melted at 108–110°.

Anal. Calc'd for $C_{10}H_{14}O_2$: C, 72.25; H, 8.48.

Found: C, 72.19; H, 8.35.

5. *1,5-Dihydroxynaphthalene*. To one liter of 5% sodium hydroxide in a two-liter, three-necked flask carrying a condenser and gas delivery tube, there was added 10 g. of 1,5-dihydroxynaphthalene. After replacing the air with nitrogen, the reaction mixture was heated to 40–50° and 25 g. of Raney's alloy added in small portions over a period of 1½–2 hours. The reaction temperature rose to 65–70° and after one hour at this temperature the reaction mixture was filtered into a mixture of ice and hydrochloric acid. The acidified solution was extracted with ether and after removing the solvent in a nitrogen atmosphere, 7.4 g. of a brown crystalline mass was obtained. The crude reduction product was methylated with dimethyl sulfate and the product separated into 1,5-dimethoxynaphthalene

(m.p. 182–184°) and 5-methoxy- α -tetralone [yield 2.1 g., m.p. 87–88°; literature m.p. 89–89.5° (14)] by recrystallization from petroleum-ether. The semicarbazone of 5-methoxy- α -tetralone melted at 249–250° in agreement with the literature (14).

6. Technical 1,6-dihydroxynaphthalene was recrystallized from benzene, m.p. 137–138°. Ten grams was reduced as described for the 1,5-dihydroxy compound. The reaction mixture was filtered directly into a mixture of ice and concentrated hydrochloric acid, stirred to completely dissolve the aluminum salts, and then extracted with ether. The ether residue yielded 7 g. of a tan product, m.p. 137–141°. Recrystallized from water, 6.1 g. of 6-hydroxy- α -tetralone was obtained, m.p. 150–152°, literature m.p. 150° (15).

Anal. Calc'd for $C_{10}H_{10}O_2$: C, 74.04; H, 6.22.

Found: C, 73.64; H, 6.22; 5.87.

The semicarbazone was prepared in the usual manner and recrystallized from alcohol, m.p. 216.5–217.5°.

Anal. Calc'd for $C_{11}H_{13}N_3O_2$: C, 60.25; H, 5.98; N, 19.17.

Found: C, 59.98; H, 6.23; N, 19.24.

The 6-acetoxy- α -tetralone was prepared as described (16) and after recrystallization from aqueous methyl alcohol melted at 60–61°, literature 61–62°.

7. 2,7-Dihydroxynaphthalene gave an 86% yield of the tetrahydro derivative, m.p. 123–132°. Recrystallized from water, m.p. 146–147°.

Anal. Calc'd for $C_{10}H_{12}O_2$: C, 73.12; H, 7.32.

Found: 73.19; H, 7.25.

8. α -Naphthoic acid gave a mixture of the *ar*- and *ac*-tetrahydro- α -naphthoic acid. From 20 g. of α -naphthoic acid, 16 g. of the mixed acids was obtained which melted at 70–86°. This product was converted to the ethyl esters, yield 16 g.; b.p. 102–103°/1 mm.

Anal. Calc'd for $C_{13}H_{16}O_2$: C, 76.42; H, 7.91.

Found: C, 76.55; H, 8.14.

The mixed esters were saponified but attempts to separate the two isomeric acids by crystallization or by formation of the amides were fruitless.

9. β -Naphthoic acid yielded 85% of *ar*-tetrahydro- β -naphthoic acid which melted at 152.5–153.5° after two recrystallizations from dilute methyl alcohol. Previously reported m.p. 143° (17), 153° (18). This compound has been secured by the Friedel-Crafts reaction between tetralin and acetyl chloride with the subsequent oxidation of the 2-acetyl derivative (17). It has also been obtained by catalytic reduction with Raney nickel (3d).

Anal. Calc'd for $C_{11}H_{12}O_2$: C, 74.96; H, 6.82.

Found: C, 74.65; H, 7.16.

10. To 50 g. of α -naphthalenaecetic acid dissolved in 1,000 cc. of 10% sodium hydroxide, was added gradually 75 g. of Raney's alloy. The reduction product was isolated in the usual manner and after recrystallization from benzene-petroleum ether 36 g. of *ar*- α -tetrahydro-naphthaleneacetic acid³ melting at 131–132° was obtained; mixed m.p. with α -naphthaleneacetic acid 115–118°.

Anal. Calc'd for $C_{12}H_{14}O_2$: C, 75.75; H, 7.42.

Found: C, 75.79; H, 7.64.

The reduction product readily underwent a Perkin condensation with *p*-hydroxybenzaldehyde (4). Oxidation with alkaline permanganate gave hemimellitic acid, m.p. 188–190° after recrystallization from dilute aqueous hydrochloric acid; literature m.p. 190° (dec.) (19). The anhydride melted at 194–196°, literature 196° (19).

³ *Ac*- α -tetralylacetic acid has been obtained by the Reformatsky reaction from α -tetralone and ethyl bromoacetate, followed by dehydration, saponification and reduction. It is reported as a viscous oil [Schroeter, *Ber.*, **58**, 713 (1925)] and a solid, m.p. 35–36° [v. Braun, Gruber, and Kirschbaum, *Ber.*, **55**, 3664 (1922)]. In an attempt to obtain β -(α -naphthyl)-ethyl alcohol, de Pommereau [*Compt. rend.*, **175**, 105 (1922)] reduced ethyl α -naphthylacetate with sodium and alcohol. Instead of the expected substituted ethyl alcohol, a tetralylacetic acid was obtained melting at 131°. Although no proof of structure for this acid was given, its melting point is in agreement with that of our *ar*- α -tetralylacetic acid.

11. Twenty grams of β -naphthaleneacetic acid was reduced in 500 cc. of 10% sodium hydroxide with 40 g. of Raney's alloy. The crude tetrahydro acid was recrystallized from petroleum ether, yield 17 g.; m.p. 53.5–55°. Recrystallized for analysis, m.p. 54–55°.

Anal. Calc'd for $C_{12}H_{14}O_2$: C, 75.75; H, 7.42.

Found: C, 75.94; H, 7.56.

The reduction occurred in the substituted ring to give the *ac*- β -tetralylacetic acid since the *ar*- β -tetralylacetic acid prepared by an unequivocal synthesis melted at 97–98° (4).

12. Naphthalic anhydride was reduced to tetralin-1,8-dicarboxylic acid, yield 86%; m.p. 185–186° after recrystallization from aqueous alcohol, literature 185° (20).

Anal. Calc'd for $C_{12}H_{12}O_4$: C, 65.42; H, 5.50.

Found: C, 65.40; H, 6.02.

13. 1-Hydroxy- β -naphthoic acid was prepared as follows (21): 14.4 g. of α -naphthol was added gradually to 2.5 g. of powdered sodium in 150 cc. of dry toluene. The mixture was heated to boiling and a stream of carbon dioxide bubbled in for 1½ hours. After cooling, the unreacted sodium was destroyed with 50 cc. of ethyl alcohol and the solvents removed by steam distillation. The steam-distillation residue was cooled and carbon dioxide was bubbled into the solution. The unreacted α -naphthol was filtered off and the filtrate acidified with sulfuric acid. The 1-hydroxy- β -naphthoic acid was filtered and purified through the sodium salt, yield, 8.6 g.; m.p. 186–188°; literature 185–186°; 186–188° (22).

Reduction of 5 g. of this acid gave 4.1 g. of the 1-hydroxy-*ar*-tetrahydro- β -naphthoic acid which melted after recrystallization from dilute alcohol at 156–158°. A deep reddish-brown dye was obtained with nitrodiazobenzene.

Anal. Calc'd for $C_{11}H_{12}O_3$: C, 68.71; H, 6.30.

Found: C, 69.09; H, 6.19.

14. 3-Hydroxy- β -naphthoic acid gave 3-hydroxy-*ar*-tetrahydro- β -naphthoic acid in 85% yield. Recrystallized from dilute methyl alcohol, m.p. 179–180°, literature 182° (23).

Anal. Calc'd for $C_{11}H_{12}O_3$: C, 68.71; H, 6.30.

Found: C, 69.05; H, 6.67.

The acetate was prepared in the usual manner and recrystallized from benzene-petroleum ether, m.p. 140–142°.

Anal. Calc'd for $C_{13}H_{14}O_4$: C, 66.70; H, 6.03.

Found: C, 66.64; H, 6.35.

15. Reduction of β -(2-naphthoyl)propionic acid. Ten grams of the acid was dissolved in 1,000 cc. of 10% sodium hydroxide and the reduction carried out in the usual manner with 50 g. of Raney's alloy. The reaction mixture was filtered from the nickel, acidified, and extracted with ether. The ether residue was distilled, yield 6 g.; b.p. 184–190°/3 mm. Recrystallized from petroleum ether, the γ -(5,6,7,8-tetrahydro- β -naphthyl)butyric acid melted at 49–50° in agreement with the literature (24).

16. α -Nitronaphthalene gave *ar*-tetrahydro- α -naphthylamine which was isolated by steam distillation, yield 65%; b.p. 261–263°. This substance on diazotization coupled readily with β -naphthol. The acetyl derivative, after recrystallization from water, melted at 156–157°; literature 158° (25). The *ar*-tetrahydro- α -naphthylamine hydrochloride was prepared in the usual manner and melted at 259–261°.

Anal. Calc'd for $C_{10}H_{11}ClN$: Cl, 19.32. Found: Cl, 19.49.

17. Reduction of 1,5-dinitronaphthalene. To 500 cc. of 10% sodium hydroxide solution, 10 g. of 1,5-dinitronaphthalene and 50 cc. of ethyl alcohol were added. After heating the reaction mixture to approximately 40°, 40 g. of Raney's alloy was added in small portions in a course of 2 hours. The reaction mixture was heated for an additional two hours on the steam-bath and then steam distilled. The steam-distillate was extracted with ether, the ether dried and evaporated. The residue was taken up in anhydrous benzene and gaseous hydrochloric acid passed in until precipitation of the amine hydrochloride was complete. After recrystallizing from absolute alcohol and ether, 4.4 g. of the pure hydrochloride was obtained, m.p. 257.5–258°. Mixed melting point with 5,6,7,8-tetrahydro- α -naphthylamine hydrochloride, 258–259°.

18. Reduction of β -naphthyl methyl ether. To 500 cc. of 10% sodium hydroxide in a 2-l.

flask equipped with adapter and condenser, there was added 20 g. β -naphthyl methyl ether, 50 cc. of ethyl alcohol and 50 cc. of toluene. After heating the mixture to about 50°, 30 g. of Raney's alloy was gradually added over a period of 1½–2 hours. The reaction mixture was filtered, diluted with 500 cc. of water, extracted with chloroform, dried and fractionally distilled. Fraction I, yield 2.5 g.; b.p. 85–100°/11 mm.; fraction II, yield 10 g.; b.p. 135°/10 mm., m.p. 69–71°. Fraction I was redistilled, b.p. 86–88°/20 mm.; yield 1.7 g. This was identified as *tetralin*, m.p. and mixed m.p. of *o*-tetrahydronaphthoylbenzoic acid, 156–158°. Fraction II was identified as starting material, m.p. and mixed m.p. 72.5–73°; *picrate*, m.p. and mixed m.p. 116–117°.

19. *Reduction of α -(α -naphthyl)cinnamic acid (4)*. Ten grams of this acid was reduced in the usual manner and the acidified solution extracted with ether. The combined ether extracts after drying were evaporated and the resulting oily residue partially crystallized on standing overnight. The crystalline product was freed of oil by filtration and washing with petroleum ether. Yield 5 g.; m.p. 132–134°. Recrystallized from ligroin (b.p. 75–90°) for analysis, m.p. 136–137°.

Anal. Calc'd for $C_{19}H_{20}O_2$: C, 81.38; H, 7.20.

Found: C, 81.48; H, 7.13.

After removing the petroleum ether, the oily product was esterified with ethanol and sulfuric acid and the crude ester distilled and saponified; yield 2.6 g.; m.p. 109–110° after recrystallization from *n*-hexane. Mixed m.p. with α -(5,6,7,8-tetrahydro- α -naphthyl)- β -phenylpropionic acid (4) 109–111°. The product m.p. 136–137° is therefore the isomeric α -(1,2,3,4-tetrahydro- α -naphthyl)- β -phenylpropionic acid.

20. *α -(α -naphthyl)- β -phenylpropionic acid* was reduced as described for the corresponding cinnamic acid. From the oily residue obtained from the ether extracts 5 g. of α -(1,2,3,4-tetrahydro- α -naphthyl)- β -phenylpropionic acid was obtained; m.p. 136–137° after recrystallization from ligroin (b.p. 75–90°). Mixed melting point with the product from experiment 19, 136–137°.

Anal. Calc'd for $C_{19}H_{20}O_2$: C, 81.38; H, 7.20.

Found: C, 81.18; H, 7.03.

The oily residue obtained from the evaporation of the recrystallization solvent was seeded with pure α -(5,6,7,8-tetrahydro- α -naphthyl)- β -phenylpropionic acid. After standing for several days a small amount of crystalline material was obtained which melted at 107–109° after recrystallization from *n*-hexane. Mixed m.p. 108–109°.

21. *Reduction of α -(β -naphthyl)cinnamic acid*. To 20 g. of the cinnamic acid in 600 cc. of 10% sodium hydroxide there was added, in the course of 3 hours, 50 g. of Raney's alloy. The crude reduction product was oily and after standing overnight at 0° it partially solidified. The crystalline product was filtered off, yield 2 g. Recrystallized from ligroin (b.p. 65–68°), yield 1.5 g.; m.p. 132–134°. Recrystallized for analysis, m.p. 137–138°.

Anal. Calc'd for $C_{19}H_{20}O_2$: C, 81.38; H, 7.19.

Found: C, 81.46; H, 7.46.

The residual oily product was esterified in the usual manner and the ester distilled, yield 12 g.; b.p. 187–190°/1 mm.; n_D^{25} 1.5600.

Anal. Calc'd for $C_{21}H_{24}O_2$: C, 81.77; H, 7.85.

Found: C, 82.02; H, 7.83.

Two grams of the ester was saponified and the product recrystallized from petroleum ether. Yield 1.5 g., m.p. 87–88°. Recrystallized for analysis, m.p. 90–91°.

Anal. Calc'd for $C_{19}H_{20}O_2$: C, 81.38; H, 7.19.

Found: C, 81.20; H, 6.82.

The latter product was identified by melting point and mixed melting point of 89–90° as α -(5,6,7,8-tetrahydro- β -naphthyl)- β -phenylpropionic acid (4). The product m.p. 137–138° is undoubtedly the isomeric α -(1,2,3,4-tetrahydro- β -naphthyl)- β -phenylpropionic acid.

22. *Reduction of α -(β -naphthyl)- β -phenylpropionic acid*. This acid was reduced as described for the corresponding α -naphthyl compound, experiment 20. After extracting the acidified solution with ether, the ether extracts were dried and evaporated to dryness. The residue on standing partially crystallized and the crystals were filtered off and washed

with cold petroleum ether. The crystalline product amounted to 2.4 g. and melted after recrystallization from ligroin (b.p. 65–68°) at 135–136°. Mixed melting point with product obtained under experiment 21 showed no depression.

The residual oily product was esterified, the ester distilled and then saponified as described under experiment 21. The yield of α -(5,6,7,8-tetrahydro- β -naphthyl)- β -phenylpropionic acid was 6 g.; m.p. 87–88°. Mixed m.p. 87–89°.

23. *Reduction of α -(α -naphthyl)- p -hydroxycinnamic acid.* Five grams of the cinnamic acid (4) was reduced with 20 g. Raney's alloy in 400 cc. of 10% sodium hydroxide; yield 5 g.; m.p. 183–189°. Recrystallization from benzene yielded long, fine, white needles, m.p. 198–199°.

Anal. Calc'd for $C_{19}H_{20}O_3$: C, 76.99; H, 6.87.

Found: C, 76.88; H, 7.08.

This product is the α -(1,2,3,4-tetrahydro- α -naphthyl)- β -(p -hydroxyphenyl)propionic acid since the isomeric α -(5,6,7,8-tetrahydro- α -naphthyl)- β -(p -hydroxyphenyl)propionic acid melts at 175–176° (4).

24. *The reduction of α -(α -naphthyl)- β -(p -hydroxyphenyl)propionic acid (4) gave an 85% yield of α -(1,2,3,4-tetrahydro- α -naphthyl)- β -(p -hydroxyphenyl)propionic acid, m.p. 197.5–198°; mixed m.p. with product of experiment 23, 198–199°. The residue from the recrystallization melted at about 165° and attempts to isolate a compound of definite melting point were unsuccessful.*

25. *Reduction of α -(β -naphthyl)- p -hydroxycinnamic acid.* To a solution of 20 g. of the acid (4) in 750 cc. of 10% sodium hydroxide there was added 45 g. of Raney's alloy in the course of 3–3½ hours. The reduction product was isolated in the usual manner, yield 20 g.; m.p. 186–188°. Recrystallized from aqueous alcohol or benzene-petroleum ether, m.p. 199–200°.

Anal. Calc'd for $C_{19}H_{20}O_3$: C, 76.98; H, 6.81.

Found: C, 76.81; H, 6.50.

The reduction product was α -(5,6,7,8-tetrahydro- β -naphthyl)- β -(p -hydroxyphenyl)propionic acid (4), mixed m.p. 200–201°.

26. *Reduction of α -(β -naphthyl)- β -(p -hydroxyphenyl)propionic acid.* To 5 g. of the propionic acid in 200 cc. of 10% sodium hydroxide, was added in the course of 1½ hours 15 g. of Raney's alloy. The crude reduction product was obtained in quantitative yield, m.p. 182–188°. Recrystallized from benzene-petroleum ether, yield 4.5 g.; m.p. 199–201°. Mixed m.p. with product of experiment 25, 199–200°.

ACKNOWLEDGMENTS

The authors wish to express their appreciation to Dr. Helen Ginsberg for her assistance during the early phases of this work (1942–1943); to Miss Virginia Peterson for technical assistance; to Mr. Edwin Conner of our microanalytical laboratories for most of the analyses reported herein; and to Mr. J. D. Nantz of National Aniline Division of Allied Chemical and Dye Corporation, and Dr. J. Werner of General Aniline for generous samples of 1,6-dihydroxynaphthalene.

SUMMARY

Naphthalene and its substitution products are reduced readily to the tetrahydro derivatives with Raney's alloy and aqueous alkali. In general, mono- and di-substituted naphthalenes give the corresponding tetralins in good yield. Unusual reduction products were obtained in the case of 1,5- and 1,6-dihydroxy naphthalenes, 5-hydroxy- and 6-hydroxy- α -tetralones being obtained respectively.

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