

12. The Constitution of ψ -Santonin. Part II. The Preparation of Certain Dimethyl Naphthols.

By WESLEY COCKER.

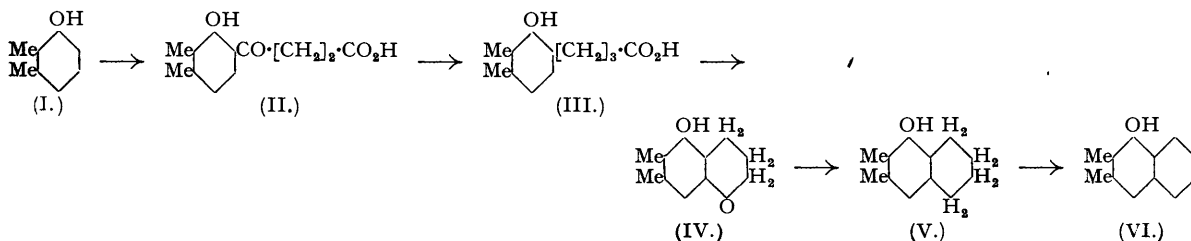
The preparations of 1 : 3-dimethyl-2-naphthol, 3 : 4-dimethyl-2-naphthol, and 2 : 3-dimethyl-1-naphthol are now described.

DEGRADATION of desmotropo- ψ -santonin by fusion with potassium hydroxide gave a dimethyl naphthol (Clemo and Cocker, this vol., p. 32) which, by analogy with the degradation product of *l*-santonin, was expected to be a dimethyl- β -naphthol with all substituents in the same ring. Only one of the three possible dimethyl- β -naphthols of this type had been described, namely 1 : 4-dimethyl-2-naphthol (Cannizzaro and Carnelutti, *Ber.*, 1879, 12, 1575; 1880, 13, 1516), obtained from *l*-santonin, and therefore 1 : 3-dimethyl-2-naphthol and 3 : 4-dimethyl-2-naphthol have been prepared. None of these naphthols was identical with that obtained from desmotropo- ψ -santonin, but it was later shown (Clemo and Cocker, *loc. cit.*) that the latter was identical with 2 : 4-dimethyl-1-naphthol (Cornforth, Cornforth, and Robinson, *J.*, 1943, 168).

3 : 4-Dimethyl-1-naphthol was previously known (Kruber and Schade, *Ber.*, 1935, 68, 11), and in order to complete our knowledge of the six possible dimethyl naphthols with all the substituents in the same ring, 2 : 3-dimethyl-1-naphthol has also been prepared.

The general method of preparation has been the condensation of succinic anhydride with the appropriate xylyl methyl ether followed by Clemmensen reduction, ring closure, further reduction of the cyclic ketone, and dehydrogenation.

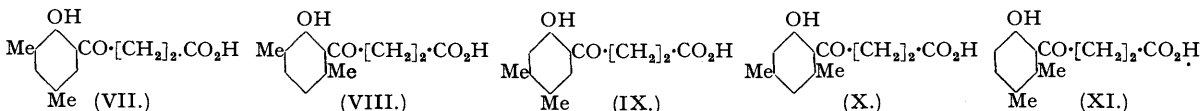
In general, the condensation with succinic anhydride takes place *para* to the methoxy group, and this gives the desired keto acid in the preparation of 1 : 3-dimethyl-2-naphthol and 3 : 4-dimethyl-2-naphthol. In the preparation of 2 : 3-dimethyl-1-naphthol according to the following scheme it is necessary to obtain an *ortho*-hydroxy-keto acid (II).



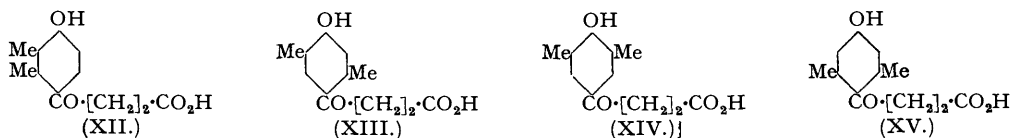
Compound (II) is obtained by making use of the fact that in the Fries rearrangement of phenolic esters the acyl group usually migrates to the *ortho* position when the reaction with aluminium chloride is performed at temperatures of 130—140° (compare Eykmann, *Chem. Weekblad*, 1904, 1, 453; Rosenmund and Schnurr, *Annalen*, 1928, 460, 56). One objection to this method is that aluminium chloride frequently causes the migration of methyl groups (compare Auwers, *Annalen*, 1928, 460, 254; Baddeley, *J.*, 1943, 273, 527), but there is no evidence of this happening in the present instance.

The *o*-xylyl 3-hydrogen succinate readily dissociates on warming, and it is necessary to effect the rearrangement by the reversal of the usual method of adding the aluminium chloride to the heated ester. Consequently, reduced yields are obtained if attempts are made to use more than about 2 g. of ester at a time, but, with this quantity, an acid, concluded to be (II) for reasons stated below, is obtained in 60% yield. It couples with diazotised *p*-nitroaniline.

If migration of methyl groups took place during the Fries rearrangement, one of the following compounds could be produced :



In addition, if the succinoyl group migrated to the *para* position one of the following would be expected :



Compounds (VII) and (XIV) may be excluded, since, under ordinary conditions, these would not couple with diazotised *p*-nitroaniline. Also compounds (VIII), (X), (XI), and (XV) would be unlikely to undergo cyclisation after reduction without loss of a methyl group. Of the remaining possibilities, compounds (IX), (XII), and (XIII) would ultimately lead, respectively, to 3 : 4-dimethyl-1-naphthol, 3 : 4-dimethyl-2-naphthol and 1 : 4-dimethyl-2-naphthol, all of which are different from the dimethyl naphthol obtained. The keto acid, obtained by the Fries rearrangement, could therefore only be (II).

The conversion of the acid (III) to the cyclic *ketone* (IV) by concentrated sulphuric acid at 60° gives very poor yields due to sulphonation, only to be expected of a xylenol having an unsubstituted *para* position to the hydroxy group. The cyclisation is, however, efficiently performed by the use of 80% sulphuric acid at the water-bath temperature. From the above evidence and the fact that the dimethyl naphthol obtained from (IV) couples with diazotised *p*-nitroaniline to give an azo dye, it is concluded that compound (VI) has the structure indicated.

Attempts to nitrate 6 : 7-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene so as to afford a more direct method to 2 : 3-dimethyl-1-naphthol were discouraging. Nitration in acetic anhydride gave an oil having a constant boiling point, but it was obviously a mixture of a nitro compound and the original dimethyl tetralin, since reduction gave only a trace of amine, presumably 5-amino-6 : 7-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene mixed with the original dimethyl tetralin. Nitration in sulphuric acid gave a charred mass from which a very small quantity of a dinitro compound, presumably 5 : 8-dinitro-6 : 7-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene, was isolated. The method was therefore abandoned.

EXPERIMENTAL.

1 : 3-Dimethyl-2-naphthol.— β -(4-Methoxy-3 : 5-dimethyl)benzoylpropionic acid. Technical 1 : 3 : 2-xylenol (2 : 6-dimethylphenol) was distilled in a vacuum and collected at 92°/17 mm. It had m. p. 44—45° (Noelting, *Ber.*, 1888, 21, 2829, gives m. p. 47—48°), but it was considered to be pure enough for further work. It was methylated by methyl sulphate in sodium hydroxide and the methyl ether collected at 180—183°.

A mixture of 1 : 3 : 2-xylyl methyl ether (13.4 g.), succinic anhydride (10 g.), and dry benzene (25 c.c.) at 10° was stirred vigorously and treated with finely powdered aluminium chloride (13.4 g.). The mixture was then shaken for 24 hours, decomposed with ice and hydrochloric acid and the crystalline solid was collected. It was washed with dilute hydrochloric acid, then with water and freed from residual benzene. It was dissolved in cold 10% sodium carbonate solution, filtered (charcoal) and reprecipitated with hydrochloric acid. The precipitate after washing and drying weighed 8.2 g., m. p. 112°. This was sufficiently pure for the subsequent stages of the reaction. When crystallised from a large volume of hot water it yielded colourless prisms, m. p. 114—115° (Found : C, 66.2; H, 7.0. $C_{13}H_{16}O_4$ requires C, 66.1; H, 6.8%). The *p*-nitrobenzylthiouronium salt crystallised from 50% alcohol as silvery needles, m. p. 142° (Found : C, 54.8; H, 6.0. $C_{21}H_{25}O_8N_3S_2H_2O$ requires C, 54.2; H, 5.8%).

γ -(4-Methoxy-3 : 5-dimethyl)-phenylbutyric acid. A mixture of the above keto acid (5.8 g.), amalgamated zinc (40 g.), hydrochloric acid (60 c.c.), and water (10 c.c.) was refluxed for 18 hours, cooled, and extracted with ether. After removal of the solvent, the residue was shaken with dimethyl sulphate (5 c.c.) and sodium hydroxide and then acidified. The oil quickly solidified; it was washed with water and dried yielding 5.0 g. of the required material, m. p. 65—66°, sufficiently pure for the next stage. When crystallised from ligroin, it was obtained as colourless prisms, m. p. 72° (Found : C, 70.3; H, 8.2. $C_{13}H_{18}O_3$ requires C, 70.3; H, 8.1%). Its *p*-nitrobenzylthiouronium salt crystallised from dilute alcohol as colourless needles, m. p. 131—132° (Found : C, 58.3; H, 6.1. $C_{21}H_{27}O_8N_3S$ requires C, 58.2, H, 6.2%).

1-Keto-7-methoxy-6 : 8-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene. The above butyric acid (3 g.) was stirred into concentrated sulphuric acid (15 c.c.) and the mixture maintained at 65—70° for 10 minutes. When cold, it was poured

on to ice and extracted with chloroform. The extract was washed thrice with 5% sodium carbonate, dried and fractionated. The required ketone (1.7 g.) was collected at 141–142°/1 mm. (Found: C, 76.3; H, 7.9. $C_{13}H_{16}O_2$ requires C, 76.5; H, 7.8%). The compound solidified and was crystallised from ligroin as colourless plates, m. p. 40°. Its 2:4-dinitrophenylhydrazone crystallised from benzene as orange needles with a violet reflex, m. p. 246–247° (decomp.) (Found: C, 59.2; H, 5.25. $C_{19}H_{20}O_2N_4$ requires C, 59.4; H, 5.2%).

7-Methoxy-6:8-dimethyl-1:2:3:4-tetrahydronaphthalene. The above ketone (5 g.) was reduced during 14 hours with a mixture of conc. hydrochloric acid (40 c.c.), water (10 c.c.), alcohol (70 c.c.), and amalgamated zinc (40 g.). Alcohol was removed and the residue shaken with dimethyl sulphate (5 c.c.) and 2N-sodium hydroxide, cooled and extracted with ether. The extract was dried, fractionated, and the compound collected (3.5 g.), at 109°/0.2 mm. (Found: C, 81.9; H, 10.0. $C_{13}H_{18}O$ requires C, 82.1; H, 9.5%).

7-Hydroxy-6:8-dimethyl-1:2:3:4-tetrahydronaphthalene. The above methyl ether (3.7 g.) was gently refluxed with hydriodic acid (*d* 1.7, 15 c.c.) for 90 minutes. The mixture was cooled, the solid separated and washed first with dilute sodium bisulphite, then with water and dried, yielding 3.3 g. of the required compound, m. p. 91–92°. It was crystallised from dilute alcohol as long, colourless needles, m. p. 97.5–98° (Found: C, 81.9; H, 9.1. $C_{12}H_{16}O$ requires C, 81.8; H, 9.1%). It was sparingly soluble in dilute sodium hydroxide, but dissolved in 20% sodium hydroxide. Its carbanilate crystallised from aqueous alcohol as colourless prisms, m. p. 181.5–182.5° (Found: C, 77.0; H, 7.1. $C_{18}H_{21}O_2N$ requires C, 77.3; H, 7.1%).

1:3-Dimethyl-2-naphthol. The above tetrahydro compound (0.2 g.) was heated with selenium (0.5 g.) at 330–340° for 2–3 hours. The cooled product was extracted with methyl alcohol, distilled in steam, and crystallised from dilute alcohol as felted needles (0.12 g.), m. p. 89–90° (Found: C, 83.5; H, 7.1. $C_{12}H_{12}O$ requires C, 83.7; H, 7.0%). Its picrate crystallised from ligroin (b. p. 80–100°) as scarlet needles, m. p. 132–133° (Found: C, 54.0; H, 4.0. $C_{12}H_{12}O_6N_3$ requires C, 53.9; H, 3.7%). Its *p*-toluenesulphonate crystallised from ligroin as colourless prisms, m. p. 85–86° (Found: C, 69.6; H, 5.6. $C_{18}H_{18}O_3S$ requires C, 69.9; H, 5.5%). Its carbanilate crystallised from alcohol as silvery plates, m. p. 197° (Found: C, 77.9; H, 5.9. $C_{19}H_{19}O_2N$ requires C, 78.3; H, 5.9%).

3:4-Dimethyl-2-naphthol.—*o*-3-Xylenol. Technical *o*-xylene (50 g.) was nitrated as described by Emerson and Smith (*J. Amer. Chem. Soc.*, 1940, **62**, 141), the product was first steam distilled, then fractionated, the fraction, b. p. 130–140°/30 mm., being collected. This was again fractionated and collected (60–62 g.) at 127–130°/15 mm. The product, consisting largely of 3-nitro-*o*-xylene, was then reduced in methanol (60 c.c.) with Raney nickel (1 g.) at 100–110°/100 atm., yielding *o*-3-xylylene (43 g.), b. p. 222–224°.

The method of purification suggested by Emerson and Smith (*loc. cit.*) making use of a difference in solubility of the sulphates of the *o*-3- and *o*-4-xylylenes was rejected in favour of a purification through the acetyl derivatives, but in the later experiments it was found that the purification could best be performed after diazotisation. Diazotisation was carried out in the following manner. The above xylylene mixture (66 g.) in dilute hydrochloric acid (190 c.c. concentrated acid, 190 c.c. water) and finely powdered ice (500 g.) was cooled to –10° and sodium nitrite (41.3 g.) dissolved in the minimum quantity of water slowly added. Diazotisation was completed by further stirring for 30 minutes at 0° to –10°. This solution was then added to a boiling solution of copper sulphate (12 g.) in 50% sulphuric acid (55 c.c.), the xylylene being removed by steam as it was produced. The semi-solid mass collected from the distillate was distilled and collected at 212–224°. The distillate solidified, was pressed on porous plate, and crystallised from ligroin as colourless plates (12 g.), m. p. 72°.

β -4-Methoxy-2:3-dimethylbenzoylpropionic acid. *o*-Xylenol-3-methyl ether (6.7 g.) was condensed with succinic anhydride (5 g.) in benzene (20 c.c.) with aluminium chloride (6.7 g.). The mixture was stirred for 6 hours at room temperature and the required product isolated as previously described. The yield of practically pure material was 5.8 g., m. p. 172–173°. When crystallised from alcohol it formed long prisms, m. p. 174° (Found: C, 66.05; H, 6.6. $C_{18}H_{16}O_4$ requires C, 66.1; H, 6.8%). Its *p*-nitrobenzylthiouonium salt crystallised from dilute alcohol as colourless needles, m. p. 153° (decomp.) (Found: C, 56.0; H, 5.6. $C_{21}H_{25}O_6N_3S$ requires C, 56.4; H, 5.6%).

γ -(4-Methoxy-2:3-dimethyl)-phenylbutyric acid was obtained (4.3 g.), m. p. 113–114°, by the Clemmensen reduction of the above keto acid (5 g.) with amalgamated zinc (40 g.) and concentrated hydrochloric acid (40 c.c.). It was not found necessary to remethylate the compound before isolation. A portion was crystallised from dilute alcohol as silvery plates, m. p. 119–120° (Found: C, 70.2; H, 7.8. $C_{15}H_{18}O_3$ requires C, 70.3; H, 8.1%).

Its *p*-nitrobenzylthiouonium salt crystallised from dilute alcohol as pale yellow prisms, m. p. 148–149° (decomp.) (Found: C, 58.6; H, 6.3. $C_{21}H_{27}O_5N_3S$ requires C, 58.2; H, 6.2%).

1-Keto-7-methoxy-5:6-dimethyl-1:2:3:4-tetrahydronaphthalene. The above butyric acid (8 g.) was treated in the usual way with conc. sulphuric acid (40 c.c.) yielding 5.2 g. of the required ketone, m. p. 77–78°. It crystallised from ligroin as colourless needles, m. p. 78–79° (Found: C, 76.2; H, 7.6. $C_{13}H_{16}O_2$ requires C, 76.5; H, 7.8%). Its semicarbazone crystallised from alcohol as needles, m. p. 258–259° (Found: C, 64.6; H, 7.3. $C_{14}H_{19}O_2N_3$ requires C, 64.4; H, 7.3%).

7-Methoxy-5:6-dimethyl-1:2:3:4-tetrahydronaphthalene was prepared by the Clemmensen reduction of the above ketone (6 g.) yielding colourless needles (5 g.), m. p. 65°, after purification by sublimation under reduced pressure (Found: C, 82.7; H, 9.4. $C_{13}H_{18}O$ requires C, 82.1; H, 9.5%).

7-Hydroxy-5:6-dimethyl-1:2:3:4-tetrahydronaphthalene, purified by sublimation, consisted of long prisms, m. p. 114–115° (Found: C, 81.2; H, 8.8. $C_{12}H_{16}O$ requires C, 81.8; H, 9.1%). Its carbanilate crystallised from alcohol as needles, m. p. 174–175° (Found: C, 77.0; H, 7.1. $C_{18}H_{21}O_2N$ requires C, 77.3; H, 7.1%). Its *p*-toluenesulphonate crystallised from ligroin as needles, m. p. 108–109° (Found: C, 69.0; H, 6.5. $C_{19}H_{22}O_3S$ requires C, 69.1; H, 6.7%).

3:4-Dimethyl-2-naphthol. The above tetrahydro compound (0.2 g.) was heated for 4 hours at 330–340° with selenium (0.5 g.). The cooled product was distilled in steam, yielding a white solid which crystallised first from dilute alcohol and then from ligroin as long prisms (0.1 g.), m. p. 113°, and depressed on admixture with the tetrahydro compound (Found: C, 83.9; H, 7.0. $C_{12}H_{12}O$ requires C, 83.7; H, 7.0%). Its *p*-toluenesulphonate crystallised from ligroin as colourless needles, m. p. 128° (Found: C, 69.7; H, 5.6. $C_{18}H_{18}O_3S$ requires C, 69.9; H, 5.5%).

2:3-Dimethyl-1-naphthol.—Nitration of 6:7-dimethyl-1:2:3:4-tetrahydronaphthalene. This compound (Barnett and Sanders, *J.*, 1933, 435) (12 g.) in acetic anhydride (10 c.c.) was stirred at 0° to –5° and fuming nitric acid (*d* 1.515, 3.15 c.c.) in acetic anhydride (3 c.c.) was added. Considerable heat was developed if the addition was made too rapidly, and in order to keep the temperature within the prescribed limits the addition took 90 minutes, after which stirring was continued for 1 hour. The mixture was poured on to ice, extracted with ether, the extract was washed with dilute sodium hydroxide and then fractionated. About 7 g. of the starting material was first collected and then a pale yellow liquid was collected at 140–153°/1 mm. This was redistilled and collected (6.9 g.) at 142–143°/1–2 mm. Although this liquid was fractionated several times, a pure mononitro compound was not obtained (Found: C, 76.2; H, 7.6. $C_{12}H_{15}O_2N$ requires C, 70.2; H, 7.3%). The mixture was reduced by iron powder in alcohol yielding 0.2 g. of the required 5-amino-6:7-dimethyl-1:2:3:4-tetrahydronaphthalene, b. p. 130°/1 mm. It was characterised as its acetyl compound, which crystallised from dilute alcohol as fine colourless needles, m. p. 201° (Found: C, 77.1; H, 8.9. $C_{14}H_{19}ON$ requires C, 77.4; H, 8.8%). Its chloroplatinate crystallised from hot water as pale yellow prisms, m. p. 224–225°

(decomp.), but appeared to be hydrolysed on being heated in water (Found : C, 38.5; H, 4.8; Pt (as residue), 24.6. $C_{24}H_{36}N_6Cl_6Pt$ requires C, 37.9; H, 4.73; Pt, 25.65%).

Nitration in sulphuric acid. The dimethyltetralin (1 g.) stirred with concentrated sulphuric acid (5 g.) was cooled to -10° and slowly treated with a mixture of nitric acid (d 1.42, 0.5 g.) and concentrated sulphuric acid (3 c.c.). Stirring was continued for 15 minutes and the mixture was then poured into water (50 c.c.). The dark-green solid was collected, washed with sodium carbonate, then with water, and dried. It was extracted with alcohol (charcoal) from which a yellow crystalline compound was isolated. On crystallisation from benzene-ligroin it was deposited as colourless flat prisms (0.05 g.), m. p. 203° (Found : C, 57.8; H, 5.6. $C_{12}H_{14}O_4N_2$ requires C, 57.6; H, 5.6%).

β -(6-Hydroxy-4 : 5-dimethyl)-benzoylpropionic Acid.—*o*-Xylol 3-hydrogen succinate. A mixture of *o*-3-xylol (10 g.) and succinic anhydride (10 g.) was heated at 130° for half an hour and then cooled. The solid product was finely powdered, suspended in water (100 c.c.) and sodium carbonate added until just alkaline to phenolphthalein. The mixture was then diluted to 300 c.c.; excess *o*-3-xylol (0.5—1.0 g.) then separated and was collected. The filtrate was treated with charcoal and again filtered and, on acidification, a colourless oil was produced. This solidified on scratching and was collected, washed, and dried in a desiccator yielding the required ester (12.7 g.), m. p. $67-69^\circ$. When crystallised from benzene-ligroin, it was obtained as colourless flat prisms, m. p. $72-73^\circ$ depressed on admixture with the original xylol (Found : C, 65.4; H, 6.5. $C_{12}H_{14}O_4$ requires C, 64.9; H, 6.3%). The ester readily dissociated on heating and was hydrolysed even on warming with dilute ammonia.

Fries rearrangement. The crude ester (1.0 g.) was slowly added with stirring to finely powdered aluminium chloride (1.0 g.) heated to 130° . The temperature was raised to 140° during 20 minutes and the mixture then cooled. It was finely powdered and added slowly to dilute hydrochloric acid and stirred until all lumps had disappeared. The product was collected, washed with dilute hydrochloric acid, then with water, and extracted with dilute sodium carbonate. From the extract after filtration the required acid was obtained by acidification. It was crystallised from dilute alcohol as long radiating needles (0.6 g.), m. p. $188-189^\circ$ (Found : C, 64.9; H, 6.3. $C_{12}H_{14}O_4$ requires C, 64.9; H, 6.3%).

γ -(6-Hydroxy-4 : 5-dimethyl)-phenylbutyric acid. The above keto acid (4 g.) was reduced with amalgamated zinc (40 g.) and concentrated hydrochloric acid (40 c.c.) for 16 hours. The solid product was collected and crystallised from dilute alcohol as fine needles (2.5 g.), m. p. $109-110^\circ$ (Found : C, 68.9; H, 7.55. $C_{12}H_{16}O_3$ requires C, 69.2; H, 7.7%).

8-Hydroxy-1-keto-6 : 7-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene. The above butyric acid (2.5 g.) was cyclised by heating for $1\frac{1}{2}$ hours on the water-bath with 80% sulphuric acid (25 c.c.) and the product was crystallised from ligroin as clusters of fern-like crystals (1.5 g.), m. p. $153-154^\circ$ (Found : C, 75.4; H, 7.2. $C_{12}H_{14}O_2$ requires C, 75.8; H, 7.4%). Its 2 : 4-dinitrophenylhydrazone crystallised from a large volume of alcohol as scarlet needles, m. p. 290° (Found : C, 58.2; H, 4.9. $C_{18}H_{16}O_5N_4$ requires C, 58.4; H, 4.9%). Its acetate crystallised from ligroin as colourless needles, m. p. 98° (Found : C, 72.1; H, 7.0. $C_{12}H_{16}O_3$ requires C, 72.4; H, 6.9%).

8-Hydroxy-6 : 7-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene. The above ketone (4.5 g.) was reduced with amalgamated zinc (50 g.) and hydrochloric acid (100 c.c.) and the product crystallised from dilute alcohol in colourless needles (3.0 g.), m. p. 83.5° (Found : C, 82.1, H, 9.1. $C_{12}H_{16}O$ requires C, 81.8; H, 9.1%).

2 : 3-Dimethyl-1-naphthol. The tetrahydro compound (1.0 g.) was heated with selenium (3 g.) for 4 hours at $330-340^\circ$ and then the mixture was distilled in steam yielding the required naphthol (0.3 g.), m. p. $77-78^\circ$. It was crystallised twice from dilute alcohol and obtained as rosettes of colourless needles, m. p. 84° , depressed on admixture with the tetrahydro compound and also on admixture with 2 : 4-dimethyl-1-naphthol, which has m. p. $84-85^\circ$ (Found : C, 84.0; H, 7.1. $C_{12}H_{12}O$ requires C, 83.7; H, 7.0%). Its picrate crystallised from benzene-ligroin as scarlet needles, m. p. $143-144^\circ$, depressed on admixture with the picrate of 2 : 4-dimethyl-1-naphthol, which has m. p. $143-144^\circ$ (Cornforth, Cornforth, and Robinson, *loc. cit.*) (Found : C, 54.3; H, 3.9. $C_{12}H_{12}O, C_8H_3O_7N_3$ requires C, 53.9; H, 3.7%). The new naphthol readily coupled with diazotised *p*-nitroaniline giving a deep red azo dye which was crystallised from dilute acetic acid as small deep ruby needles, m. p. $225-226^\circ$ (decomp.) (Found : C, 67.0; H, 4.7. $C_{18}H_{15}O_3N_3$ requires C, 67.3; H, 4.7%).

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