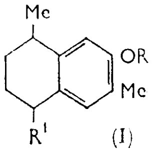
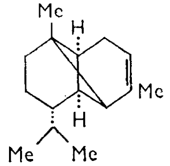
602. *Synthesis of* 1,2,3,4-*Tetrahydro*-7-*hydroxy*-4-*isopropyl*-1,6-*dimethylnaphthalene. A Degradation Product of Copaene*

By Wesley Cocker and D. M. Sainsbury

A racemic form of 1,2,3,4-tetrahydro-7-hydroxy-4-isopropyl-1,6-dimethylnaphthalene (I; R = H, R^1 = Pr^i) has been shown to be identical in gross structure with an optically active form derived from copaene (II).

The structure of copaene has recently been revised[1] and shown to be (II). One of its derivatives was the phenol (I; R = H, R^1 = Pr^i) which has now been shown to be identical in gross structure with a synthetic specimen of a compound of this structure.


(I)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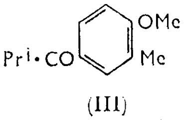
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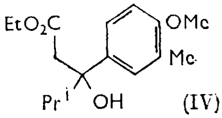
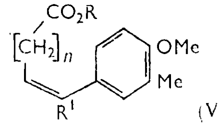
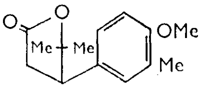
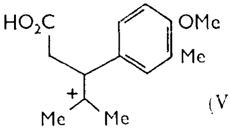

(IV)

Condensation of methyl o-tolyl ether with isobutyryl chloride afforded 4-methoxy-3-methylisobutyrophenone (III), which on reaction with ethyl bromoacetate and zinc gave ethyl 3-hydroxy-3-(4′-methoxy-3′-methylphenyl)-4-methylpentanoate (IV). This was dehydrated, giving ethyl 3-(4′-methoxy-3′-methylphenyl)-4-methylpent-2-enoate (V; R = Et, R^1 = Pr^i, *n* = 0). We found difficulty in reducing this compound. It was therefore hydrolysed with methanolic potassium hydroxide giving a mixture from which the acid (V; R = H, R^1 = Pr^i, *n* = 0) and β-(4-methoxy-3-methylphenyl)-γγ-dimethylbutyrolactone (VI) were isolated by acidification. The identity of the latter was confirmed by its infrared and n.m.r. spectra. Its production involves the carbonium ion (VII).


(V)


(VI)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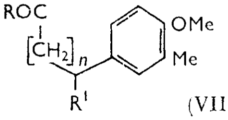
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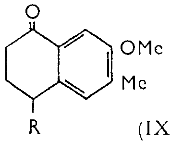
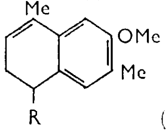

(IX)


(X)

Hydrogenation of the acid (V; R = H, R^1 = Pr^i, *n* = 0) over Adams catalyst gave the acid (VIII; R = OH, R^1 = Pr^i, *n* = 1), the acid chloride of which was converted by the Arndt–Eistert method into the amide (VIII; R = NH_2, R^1 = Pr^i, *n* = 2). The corresponding acid, 4-(4′-methoxy-3′-methylphenyl)-5-methylhexanoic acid (VIII; R = OH, R^1 = Pr^i, *n* = 2), was cyclised through its acid chloride to 1,2,3,4-tetrahydro-4-isopropyl-7-methoxy-6-methyl-1-oxo-naphthalene (IX; R = Pr^i). Reaction of this tetralone with methylmagnesium iodide gave 1,2-dihydro-1-isopropyl-6-methoxy-4,7-dimethylnaphthalene (X; R = Pr^i) which was reduced over platinum to the tetralin (I; R = Me, R^1 = Pr^i). Demethylation of the latter with boron tribromide in methylene chloride[2] gave the required phenol (I; R = H, R^1 = Pr^i), the 3,5-dinitrobenzoate of which had an infrared spectrum identical with that of a specimen prepared from copaene. We

[1] G. Büchi and S. H. Feairheller, P. de Mayo, and R. E. Williams, *Proc. Chem. Soc.*, **1963**, 214.
[2] J. F. W. McOmie and M. L. Watts, *Chem. and Ind.*, 1963, 1658.

are grateful to Professor de Mayo for providing a copy of the infrared spectrum of his 3,5-dinitrobenzoate and for comparing the two 3,5-dinitrobenzoates.

In an earlier approach to the synthesis we started with β-(4-methoxy-3-methylbenzoyl)propionic acid (VIII; $R = OH$, $R^1 = {:}O$, $n = 2$)[3] the ethyl ester of which, condensed with isopropylmagnesium iodide, gave as main product 4-(4′-methoxy-3′-methylphenyl)-5-methylhex-3-enoic acid (V; $R = H$, $R^1 = Pr^i$, $n = 1$). This was reduced over Raney nickel giving the corresponding hexanoic acid which was cyclised with polyphosphoric acid to a mixture of tetralones in which compound (IX; $R = Pr^i$) predominated and from which its pure oxime was isolated. However, gas–liquid chromatography showed the presence of a second component. Reaction of the mixture of tetralones with methylmagnesium iodide gave a mixture of compounds in which compound (X; $R = Pr^i$) predominated. This mixture was reduced to a mixture of tetralins which was resolved by preparative gas–liquid chromatography into the required tetralin (I; $R = Me$, $R^1 = Pr^i$) and 1,2,3,4-tetrahydro-7-methoxy-1,6-dimethylnaphthalene (I; $R = Me$, $R^1 = H$). The presence of the latter compound is a result of anomalous Grignard reaction with the keto-ester (VIII; $R = OEt$, $R^1 = {:}O$, $n = 2$), since gas–liquid chromatography of the unsaturated methyl esters obtained from the reaction products revealed the ester (V; $R = Me$, $R^1 = Pr^i$, $n = 1$) and another component which must be compound (V; $R = Me$, $R^1 = H$, $n = 1$). There is ample precedent for such anomalous reactions.[4] It should be added that the yield of the required acid (V; $R = H$, $R^1 = Pr^i$, $n = 1$) was not increased by the addition of anhydrous magnesium bromide[5] to the mixture of Grignard reagent and ketone.

EXPERIMENTAL

Infrared spectra were measured in Nujol suspensions (N), liquid film (L), and KBr discs.

4-Methoxy-3-methylisobutyrophenone (III).—A solution of aluminium chloride (60 g.) in nitrobenzene (300 c.c.) was slowly added to an ice-cold solution of methyl o-tolyl ether (50 g.) and isobutyryl chloride (46 g.) in nitrobenzene (100 c.c.), and the mixture was set aside overnight. The complex was decomposed with ice and hydrochloric acid, the organic layer was separated and distilled in steam to remove nitrobenzene. Distillation of the residue under reduced pressure afforded the *ketone* (III), b. p. 98—99°/0·4 mm.; $\nu_{\text{max.}}$ (L) 1700 cm.$^{-1}$ (aromatic ketone) (Found: C, 75·05; H, 8·3. $C_{12}H_{16}O_2$ requires C, 75·0; H, 8·4%). Its *semicarbazone* consisted of rhombs (ethyl acetate–light petroleum), m. p. 147° (Found: C, 62·2; H, 7·6. $C_{13}H_{19}N_3O_2$ requires C, 62·6; H, 7·7%).

Ethyl 3-Hydroxy-3-(4′-methoxy-3′-methylphenyl)-4-methylpentanoate (IV).—A mixture of the ketone (III) (50 g.) and ethyl bromoacetate (45·6 g.) in dry benzene (100 c.c.) was added dropwise to a stirred, refluxing mixture of zinc shavings (17·8 g.) and benzene (200 c.c.). Heating and stirring were then continued for 1 hr. longer. The mixture was cooled, poured into an excess of cold 10% sulphuric acid, stirred well, and the benzene layer was collected. It was washed with water, dried, and the solvent removed giving a brown oil (69 g.); $\nu_{\text{max.}}$ (L) 3550 (OH) and 1720 cm.$^{-1}$ (ester). It was not purified further.

Ethyl 3-(4′-Methoxy-3′-methylphenyl)-4-methylpent-2-enoate (V; $R = Et$, $R^1 = Pr^i$, $n = 0$).—The hydroxy-ester was heated for 2 hr. at 140—150° with fused sodium hydrogen sulphate (69 g.). The mixture was diluted with water and extracted with ether giving an oil which on distillation afforded the required *ester* (38 g.), b. p. 115°/0·3 mm.; $\nu_{\text{max.}}$ (L) 1733 cm.$^{-1}$ (CO_2Et) (Found: C, 73·1; H, 8·7. $C_{16}H_{22}O_3$ requires C, 73·25; H, 8·45%). It resisted hydrogenation over Adams catalyst and over Raney nickel.

Hydrolysis of the Ester.—The ester (38 g.) was refluxed for 5 hr. with 5% methanolic potassium hydroxide (300 c.c.). Solvent was removed, water (200 c.c.) was added, and the mixture was extracted with ether. The aqueous phase was acidified and extracted with ether (3 × 70 c.c.), the extract was washed with water, and the solvent removed, giving a gum (29 g.). Trituration of this with light petroleum afforded a solid (10 g.), m. p. 85—90°, the

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[3] R. D. Desai and M. A. Wali, *Proc. Indian Acad. Sci.*, 1937, 144.

[4] J. Miller, G. Gregoriou, and H. S. Mosher, *J. Amer. Chem. Soc.*, 1961, **83**, 3966; D. O. Cowan and H. S. Mosher, *J. Org. Chem.*, 1962, **27**, 1; cf. W. Cocker, B. E. Cross, J. T. Edward, D. H. Jenkinson, and J. McCormick, *J.*, 1953, 2355.

[5] C. G. Swain and H. B. Boyles, *J. Amer. Chem. Soc.*, 1951, **73**, 870.

infrared spectrum of which showed the presence of acid and lactone. It was washed with 4% ammonia giving a solid which on crystallisation from ligroin (b. p. 60—80°) afforded β-(4-*methoxy-3-methylphenyl)-γγ-dimethylbutyrolactone* (VI) as needles, m. p. 114°; $\nu_{max.}$ (KBr) 1776 (CO), 1392, 1378, 1170, and 1145 cm.$^{-1}$ (CMe_2). Its n.m.r. spectrum showed two unsplit methyl groups, τ 8·45 and 8·93 (Found: C, 71·75, 71·6; H, 7·7, 7·8. $C_{14}H_{18}O_3$ requires C, 71·8; H, 7·7%).

The petroleum mother-liquors were extracted with 4% ammonia and the extract was combined with the ammonia extract mentioned above. Acidification with acetic acid at 0° gave an acidic gum (20·5 g.); $\nu_{max.}$ (L) 1710 cm.$^{-1}$ (CO_2H), which could not be crystallised. It was probably a mixture of *cis*- and *trans*-isomers.

3-(4'-*Methoxy*-3'-*methylphenyl*)-4-*methylpentanoic Acid* (VIII; $R = OH, R^1 = Pr^i, n = 1$).—The gum (20·5 g.) in acetic acid (50 c.c.) was stirred with Adams platinic oxide catalyst (500 mg.) in an atmosphere of hydrogen. The product was a gum (20 g.) which on trituration with light petroleum gave a solid (10 g.), m. p. 80°. It crystallised from light petroleum giving the required *acid* as rhombs, m. p. 94°; $\nu_{max.}$ (N) 1700 cm.$^{-1}$ (CO_2H) (Found: C, 71·4; H, 8·4. $C_{14}H_{20}O_3$ requires C, 71·2; H, 8·5%). Its *acid chloride* (VIII; $R = Cl, R^1 = Pr^i, n = 1$) (7 g.) was obtained as a golden oil, b. p. 116—118°/0·3 mm., $\nu_{max.}$ (L) 1810 cm.$^{-1}$ (COCl), when the acid (7·5 g.) was refluxed for 1 hr. with thionyl chloride (15 g.).

4-(4'-*Methoxy*-3'-*methylphenyl*)-5-*methylhexanoic Acid Amide* (VIII; $R = NH_2, R^1 = Pr^i, n = 2$).—The acid chloride (7 g.) in ether (50 c.c.) was added dropwise to a stirred, ice-cold solution of diazomethane (3·45 g.) in ether (135 c.c.) and the mixture was set aside overnight. Ether was removed under reduced pressure, the residue was dissolved in dioxan (100 c.c.), ammonia (30%, 80 c.c.), and silver nitrate solution (10%, 30 c.c.) were added and the mixture was refluxed for 2 hr. The mixture was filtered, dioxan and water were removed under reduced pressure, the residue was dissolved in ether, the solution was washed and dried, and the solvent was removed giving a brown gum (5·5 g.). Trituration with light petroleum followed by crystallisation from ligroin gave the required *amide* as needles, m. p. 80°; $\nu_{max.}$ (KBr) 3370 and 3200 (NH), 1650 (CO), and 1610 cm.$^{-1}$ (amide and/or aromatic) (Found: C, 72·5, 72·4; H, 9·3, 9·4. $C_{15}H_{23}NO_2$ requires C, 72·25; H, 9·3%).

4-(4'-*Methoxy*-3'-*methylphenyl*)-5-*methylhexanoic Acid* (VIII; $R = OH, R^1 = Pr^i, n = 2$).—The amide (2·3 g.) was heated under reflux with 15% aqueous potassium hydroxide for 16 hr. The mixture was acidified and extracted with ether (3 × 30 c.c.) giving the required *acid* as an oil (1·9 g.), b. p. 160°/0·3 mm.; $\nu_{max.}$ (L) 1705 cm.$^{-1}$ (CO_2H) (Found: C, 72·3; H, 8·9. $C_{15}H_{22}O_3$ requires C, 72·0; H, 8·9%).

1,2,3,4-*Tetrahydro*-4-*isopropyl*-7-*methoxy*-6-*methyl*-1-*oxonaphthalene* (IX; $R = Pr^i$).—The acid (1·9 g.) was refluxed for 1 hr. with thionyl chloride (5 c.c.), and excess of this reagent was removed by distillation giving the acid chloride as a pale brown oil. A solution of this in tetrachloroethane (20 c.c.) was cooled to −10°, stirred, slowly treated with a suspension of aluminium chloride (1·14 g.) in tetrachloroethane (15 c.c.), and set aside at room temperature for 16 hr. The mixture was poured on to a stirred mixture of ice and hydrochloric acid, the organic layer was separated, and the solvent was removed by distillation. The residue, in ether (100 c.c.), was washed with 5% sodium carbonate solution (2 × 30 c.c.), then with water (3 × 30 c.c.), and dried. Distillation gave the *tetralone* as an oil (700 mg.), b. p. 115°/0·2 mm.; $\nu_{max.}$ (L) 1680 cm.$^{-1}$ (aromatic ketone) (Found: C, 77·6; H, 8·6. $C_{15}H_{20}O_2$ requires C, 77·55; H, 8·7%). Its *oxime* consisted of rhombs (methanol), m. p. 158° (Found: C, 73·0; H, 8·5. $C_{15}H_{21}NO_2$ requires C, 72·8; H, 8·6%).

1,2-*Dihydro*-1-*isopropyl*-6-*methoxy*-4,7-*dimethylnaphthalene* (X; $R = Pr^i$).—The tetralone (700 mg.) in ether (10 c.c.) was added dropwise to an ice-cold solution of methylmagnesium iodide (from magnesium, 0·145 g., and methyl iodide, 0·855 g.) in ether (20 c.c.), and the mixture was refluxed for $\frac{3}{4}$ hr. The complex was decomposed with ice and hydrochloric acid, the ether layer was separated, and the residue was further extracted with ether (3 × 20 c.c.). The combined extracts were washed with water, sodium bisulphite solution, and water. The dried extract afforded an oil the infrared spectrum of which showed contamination with tetralone. The oil, in light petroleum, was chromatographed on neutral alumina and eluted with the same solvent. The required *dihydronaphthalene* (420 mg.) distilled as a colourless oil, b. p. 102°/0·35 mm.; $\nu_{max.}$ (L) 1603 (C=C and aromatic) and 1555 (aromatic), 1380, 1368, 1175, and 1142 (CMe_2), 1271 and 1095 cm.$^{-1}$ (aromatic ether) (Found: C, 83·3; H, 9·7. $C_{16}H_{22}O$ requires C, 83·4; H, 9·6%).

1,2,3,4-*Tetrahydro-4-isopropyl-7-methoxy-1,6-dimethylnaphthalene* (I; $R = Me$, $R^1 = Pr^i$).—A solution of the dihydronaphthalene (420 mg.) in ethanol (15 c.c.) was stirred for 2 hr. in an atmosphere of hydrogen with Adams catalyst (50 mg.). The mixture was filtered and distilled giving the required *tetralin* (313 mg.) as a colourless oil, b. p. 97°/0·2 mm.; $\nu_{max.}$ (L) 1608 and 1570 (aromatic), 1380, 1368, 1175, and 1142 (CMe_2), 1271 and 1095 cm.$^{-1}$ (aromatic ether) (Found: C, 82·6, 82·9; H, 10·1, 10·4. $C_{16}H_{24}O$ requires C, 82·7; H, 10·4%). Gas–liquid chromatography under the following conditions showed a very high degree of purity. Column: 5 ft. × $\frac{1}{8}$ in. packed with S.A.I.B. on 60—80 mesh Chromosorb W; temp. 176°; N_2 flow 33 c.c./min.; H_2 flow 27 c.c./min.; chart speed 20 in./hr.; retention time 17·6 min.; retention volume 580 c.c.

1,2,3,4-*Tetrahydro-7-hydroxy-4-isopropyl-1,6-dimethylnaphthalene* (I; $R = H$, $R^1 = Pr^i$).—Boron tribromide in methylene chloride (10 c.c.) was added dropwise with stirring to a solution of the methoxy-compound (300 mg.) in methylene chloride (10 c.c.) at −35°. The mixture was allowed to warm to room temperature and kept for 12 hr. Water (15 c.c.) was carefully added, the methylene chloride layer was separated, and the aqueous layer was extracted with more methylene chloride. The required phenol was obtained as an oil (150 mg.), b. p. 104°/0·25 mm., $\nu_{max.}$ (L) 3300 cm.$^{-1}$ (OH), identical with the product obtained by the alternative method described below.

β-(4-*Methoxy-3-methylbenzoyl)propionic Acid* (VIII; $R = OH$, $R^1 = {:}O$, $n = 2$).—A mixture of methyl o-tolyl ether (100 g.) and succinic anhydride in dry nitrobenzene (200 c.c.) was slowly treated at 0° with aluminium chloride (215 g.) in dry nitrobenzene (400 c.c.), and the mixture was set aside overnight. It was poured on ice and hydrochloric acid, and the keto-acid was collected and crystallised from aqueous ethanol, forming needles (144 g.), m. p. 150° (lit.,[3] 150°), $\lambda_{max.}$ (EtOH) 2700—2760 Å (log ε 4·13); $\nu_{max.}$ (N) 1710 (CO_2H) and 1680 cm.$^{-1}$ (ArCO). This acid (140 g.) was refluxed for 6 hr. with ethanol (300 c.c.) containing sulphuric acid (30 c.c.) giving *ethyl* β-(4-*methoxy-3-methylbenzoyl)propionate* (VIII; $R = OEt$, $R' = {:}O$, $n = 2$) (127 g.) as silvery plates (light petroleum), m. p. 55°; $\nu_{max.}$ (N) 1750 (CO_2Et) and 1680 cm.$^{-1}$ (ArCO) (Found: C, 67·7; H, 7·35. $C_{14}H_{18}O_4$ requires C, 67·2; H, 7·25%). The *ester semicarbazone* consisted of needles (ethanol), m. p. 134°, $\lambda_{max.}$ (EtOH) 2140 and 2850 Å (log ε 4·26 and 4·32) (Found: C, 59·1; H, 6·8. $C_{15}H_{21}N_3O_4$ requires C, 58·6; H, 6·9%).

Reaction of the Keto-ester with Isopropylmagnesium Iodide.—The keto-ester in dry ether (200 c.c.) was slowly treated, with stirring, at 0° with a solution of isopropylmagnesium iodide prepared from isopropyl iodide (46·75 g.) and magnesium (6·75 g.) in ether (100 c.c.). The mixture was then set aside for 30 min. after which toluene (200 c.c.) was added and the ether was removed by distillation. The residue was heated at 100° for 6 hr. and the product was poured into ice–hydrochloric acid, stirred, and extracted with ether (3 × 200 c.c.). The extract was washed with 10% ammonia (3 × 100 c.c.) and the washings were acidified and extracted with ether from which an acid (27 g.) was obtained. This was not purified. It was refluxed for 6 hr. with methanol (100 c.c.) and sulphuric acid (10 c.c.) giving a mixture of esters (18 g.), b. p. 123—125°/0·15 mm.; $\nu_{max.}$ (L) 1603 (Ar), 1634 (C=C), 1639 cm.$^{-1}$ (CO_2Me) (Found: C, 72·8; H, 8·4. Calc. for $C_{16}H_{22}O_3$: C, 73·25; H, 8·45%); in which compound (V; $R = Me$, $R^1 = Pr^i$, $n = 2$) predominated.

Reduction of the Unsaturated Esters.—The mixture of esters (11·5 g.) in methanol (50 c.c.) was hydrogenated over Raney nickel (1·5 g.), for 6 hr. at 90 atm. and 120°. The product was refluxed for 5 hr. with 5% methanolic potassium hydroxide giving a mixture of acids (11 g.), b. p. 155—160°/0·3—0·5 mm., $\nu_{max.}$ 1715 cm.$^{-1}$ (Found: C, 71·3; H, 8·1. Calc. for $C_{15}H_{22}O_3$: C, 72·0; H, 8·9%) in which compound (VIII; $R = OH$, $R^1 = Pr^i$, $n = 2$) predominated. S-*Benzylisothiouronium* 4-(4′-*methoxy*-3′-*methylphenyl*)-5-*methylhexanoate* consisted of silvery plates (aqueous ethanol), m. p. 134—135° (Found: C, 66·9; H, 7·2. $C_{23}H_{32}N_2O_3S$ requires C, 66·3; H, 7·7%).

Cyclisation of the Mixture of Saturated Acids.—This mixture (12 g.) was added to polyphosphoric acid, prepared by heating 90% phosphoric acid (30 c.c.) with phosphorus pentoxide (31·1 g.) at 165° for 1 hr., and the whole was heated with vigorous stirring at this temperature for 5 min. The product was cooled, poured into water, and extracted with ether (3 × 75 c.c.). The extract was washed with 10% sodium carbonate and with water, dried, and distilled giving a mixture of tetralones (5 g.), b. p. 115—120°/0·2—0·3 mm., $\nu_{max.}$ (L) 1680 cm.$^{-1}$ (Found: C, 77·1; H, 8·2. Calc. for $C_{15}H_{20}O_2$: C, 77·55; H, 8·7%). This mixture afforded the oxime of compound (IX; $R = Pr^i$) which consisted of rhombs (methanol), m. p. 158° undepressed by a specimen prepared by the first method, $\nu_{max.}$ (KBr) 1645 cm.$^{-1}$ (C = N) (Found: C, 73·0; H, 8·5. Calc. for $C_{15}H_{21}NO_2$: C, 72·8; H, 8·6%).

The mixture of tetralones (5 g.), reacted with methylmagnesium iodide as described above, afforded a mixture of dihydronaphthalenes (3·5 g.), b. p. 105°/0·6—0·7 mm., $\lambda_{max.}$ (EtOH) 2660 and 3040 Å (log ε 3·87 and 3·7), $\nu_{max.}$ 1616 and 1556 cm.$^{-1}$ (aromatic) (Found: C, 83·6; H, 9·2. Calc. for $C_{16}H_{22}O$: C, 83·4; H, 9·6%).

Reduction of the mixture of dihydronaphthalenes (5 g.) gave an oil (5 g.) which was separated into two fractions by preparative gas chromatography using an Aerograph Autoprep A 700 instrument (Wilkens Instrument and Research Inc.). The following conditions were used. Column: 10 ft. × $\frac{3}{8}$ in. packed with Apiezon L on 60—80 Chromosorb W treated with hexamethyldisilazane; temp. 160°; N_2 flow 200 c.c./min.; chart speed 10 in./hr. Fractions 1 and 2 had, respectively, the following retention distances, times, and volumes: 2·5 in., 5·5 in.; 15 min., 33 min.; 3 l., 6·6 l. Fraction 1, consisting of 1,2,3,4-*tetrahydro*-7-*methoxy*-1,6-*dimethylnaphthalene* (I; R = Me, R^1 = H) had $\lambda_{max.}$ (ethanol) 2830 Å, log ε 3·6, $\nu_{max.}$ (L) 1610 and 1575 cm.$^{-1}$ (aromatic) (Found: C, 82·15; H, 9·6. $C_{13}H_{18}O$ requires C, 82·1; H, 9·5%). Fraction 2, the required *compound* (I; R = Me, R^1 = Pr^i), had $\lambda_{max.}$ 2820 Å (log ε 3·5); $\nu_{max.}$ (L) 1610, 1575 (aromatic) 1380, 1370, 1175, and 1150 cm.$^{-1}$ (CMe_2) (Found: C, 82·3; H, 10·2. $C_{16}H_{24}O$ requires C, 82·7; H, 10·4%).

1,2,3,4-*Tetrahydro*-7-*hydroxy*-4-*isopropyl*-1,6-*dimethylnaphthalene* (I; R = H, R^1 = Pr^i).—Fraction 2 (450 mg.) was refluxed with hydriodic acid (5 c.c.) and red phosphorus for 5 hr. The mixture was poured into water (20 c.c.) and extracted with ether (3 × 20 c.c.) from which a thick oil (440 mg.) was recovered. Distillation gave the desired phenol, b. p. 120°/0·3 mm., $\lambda_{max.}$ (ethanol) 2830 Å, log ε 3·6, $\nu_{max.}$ (L) 3400 cm.$^{-1}$ (Found: C, 83·1; H, 10·4. $C_{15}H_{22}O$ requires C, 82·5; H, 10·2%). Its 3,5-*dinitrobenzoate*, prepared in pyridine, crystallised from ethanol as needles, m. p. 146° undepressed by a sample (m. p. 146°), obtained from phenol prepared by the first method; $\nu_{max.}$ (KBr) 1742 (CO_2R), 1629, 1590 (aromatic), 1545, 730, and 716 cm.$^{-1}$ (NO_2) (Found: C, 64·3; H, 6·0. $C_{22}H_{24}N_2O_6$ requires C, 64·1; H, 5·9%).

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