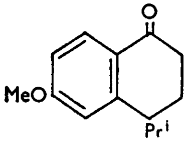
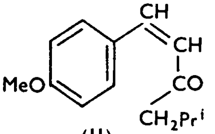
887. *Synthesis of Polycyclic Compounds. Part VI.* The Preparation of* 1 : 2 : 3 : 4-*Tetrahydro*-6-*methoxy*-1-*oxo*-4-iso*propylnaphthalene and Related Compounds.*

By J. C. Bardhan and D. N. Mukherji.

The isomeric alcohols (IV), (VI), and (VII), on cyclodehydration [1] with 85% phosphoric acid, afford mainly 1 : 2 : 3 : 4-tetrahydro-7-methoxy-1-*iso*propylnaphthalene, since on reduction with lithium and ethanol in liquid ammonia [2] this is converted into 2 : 3 : 4 : 5 : 6 : 7 : 8 : 10-octahydro-2-oxo-8-*iso*propylnaphthalene. On oxidation with chromic acid the former product gives a good yield of 1 : 2 : 3 : 4-tetrahydro-6-methoxy-1-oxo-4-*iso*propylnaphthalene, also prepared by the ring closure of 4-*m*-methoxyphenyl-5-methylhexanoic acid which has been synthesised from *m*-methoxybenzaldehyde.

In connection with another investigation we required a supply of 1 : 2 : 3 : 4-tetrahydro-6-methoxy-1-oxo-4-*iso*propylnaphthalene (I), and the present paper reports a satisfactory preparation of it in moderate quantities.


(I)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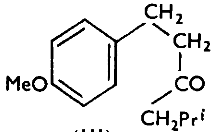
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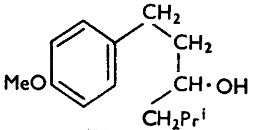
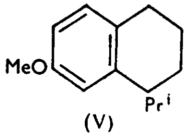

(IV)

*iso*Butyl 4-methoxystyryl ketone (II), prepared by the condensation of *p*-anisaldehyde with *iso*butyl methyl ketone in presence of alkali, on hydrogenation over W-7 Raney nickel [3] gave *iso*butyl *p*-methoxyphenethyl ketone (III), and this on further reduction with lithium aluminium hydride gave an excellent yield of 1-*p*-methoxyphenyl-5-methylhexan-3-ol (IV), which was smoothly cyclised by hot 85% phosphoric acid to 1 : 2 : 3 : 4-tetrahydro-7-methoxy-1-*iso*propylnaphthalene (V). The same hydrocarbon was obtained analogously in an inferior overall yield from the isomeric alcohols [1] (VI) and (VII).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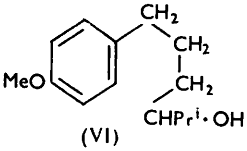
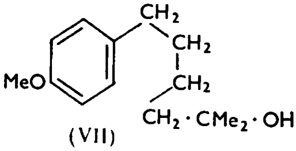

(VI)


(VII)

The structure of the liquid hydrocarbon (V) follows from its reduction by lithium and ethanol in liquid ammonia [2] to the enol-ether (VIII), which on hydrolysis with ethanolic hydrochloric acid furnishes 2 : 3 : 4 : 5 : 6 : 7 : 8 : 10-octahydro-2-oxo-8-*iso*propylnaphthalene (IX). The presence of a conjugated system in this octalone was indicated by its ultraviolet light absorption [4a] and that of its semicarbazone,[4b] and was confirmed by an unequivocal synthesis involving the coupling of 2-hydroxymethylene-6-*iso*propyl*cyclo*hexanone (X) with 4-diethylaminobutan-2-one methiodide according to known procedure.[5]

On oxidation with chromic acid the methoxy*iso*propyltetralin (V) furnishes a good yield

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* Part V, *J.*, 1956, 1809.

[1] Roblin, Davidson, and Bogert, *J. Amer. Chem. Soc.*, 1935, **57**, 151, and other papers.

[2] (*a*) Wilds and Nelson, *J. Amer. Chem. Soc.*, 1953, **75**, 5363; Birch, *J.*, 1944, 434; (*b*) Birch, *J.*, 1946, 597.

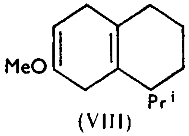
[3] *Org. Synth.*, 1949, **29**, 28; Adkins and Billica, *J. Amer. Chem. Soc.*, 1948, **70**, 697.

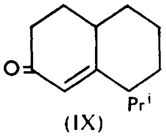
[4] (*a*) Woodward, *J. Amer. Chem. Soc.*, 1941, **63**, 1123; 1942, **64**, 76; (*b*) Evans and Gillam, *J.*, 1941, 815; 1943, 565.

[5] Shunk and Wilds, *J. Amer. Chem. Soc.*, 1949, **71**, 3948; 1950, **72**, 2392; Woodward, Sondheimer, Taub, Heusler, and McLamore, *ibid.*, 1952, **74**, 4223.

of a ketone (semicarbazone, 2 : 4-dinitrophenylhydrazone, and piperonylidene derivative) which is regarded as (I), since several instances of such selective oxidation [6] are on record. Nevertheless, it seemed desirable to prove structure (I) by a more obvious synthesis. Derivatives of tetrahydronaphthalene such as this are, however, peculiarly difficult to prepare [7] but after several unsuccessful attempts we devised the following method.

m-Methoxybenzaldehyde and *iso*propylmagnesium bromide gave 1-*m*-methoxyphenyl-2-methylpropan-1-ol which was converted into the bromide in the usual way, and then treated with ethyl sodiomalonate, affording the ester (XI). Hydrolysis and elimination of carbon dioxide gave the acid (XII). Reduction of the corresponding ethyl ester by Bouveault's method afforded the alcohol (XIII), which was successively converted through the bromide and nitrile into the acid (XIV). Ring closure with phosphoric oxide dissolved in orthophosphoric acid [8] then gave the tetralone (I), identical with the product described above. Moreover, the synthetic ketone on reduction by Clemmensen's method gave a hydrocarbon identical with that obtained by the cyclisation of the alcohols (IV), (VI), and (VII).


(VIII)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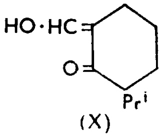
(X)

(XI) $\mathrm{R{\cdot}CHPr^{i}{\cdot}CH(CO_2Et)_2}$ $\mathrm{R{\cdot}CHPr^{i}{\cdot}CH_2{\cdot}CO_2H}$ (XII)

(XIII) $\mathrm{R{\cdot}CHPr^{i}{\cdot}[CH_2]_2{\cdot}OH}$ $\mathrm{R{\cdot}CHPr^{i}{\cdot}[CH_2]_2{\cdot}CO_2H}$ (XIV)

($\mathrm{R} = m\text{-}\mathrm{MeO{\cdot}C_6H_4}$)

By the action of an excess of methylmagnesium iodide on the tetralone (I) an unstable alcohol was obtained which when heated with potassium hydrogen sulphate yielded 3 : 4-dihydro-6-methoxy-1-methyl-4-*iso*propylnaphthalene, hydrogenated over palladium to 1 : 2 : 3 : 4-tetrahydro-6-methoxy-1-methyl-4-*iso*propylnaphthalene. This was readily reduced by lithium and ethanol in liquid ammonia [2] to 1 : 2 : 3 : 4 : 5 : 8-hexahydro-6-methoxy-1-methyl-4-*iso*propylnaphthalene.

EXPERIMENTAL

1 : 2 : 3 : 4-*Tetrahydro-7-methoxy-1-*iso*propylnaphthalene* (V).—(a) iso*Butyl 4-methoxystyryl ketone* (II) was prepared by shaking a mixture of *p*-anisaldehyde (30·2 g.), *iso*butyl methyl ketone (22·2 g.), ethanol (85 ml.), water (29 ml.), and 10% aqueous sodium hydroxide (22 ml.) for 15 hr. at room temperature. The unsaturated *ketone* was isolated with benzene and on distillation formed a pale yellow oil (43 g.), b. p. 168—169°/4 mm., 192°/12 mm., m. p. 46—47° (from aqueous methanol) (Found : C, 76·4; H, 8·6. $C_{14}H_{18}O_2$ requires C, 77·0; H, 8·3%).

iso*Butyl* p-*methoxyphenethyl ketone* (III). The ketone (II) (72 g.) in ethanol (80 ml.) was shaken with W-7 Raney nickel catalyst [3] (6 g.) in hydrogen at the room temperature; the calculated amount (8·1 l.) was absorbed in 2·5 hr. After removal of catalyst and solvent the *ketone* distilled as a colourless liquid (71 g.), b. p. 165—167°/11 mm. (Found : C, 76·3; H, 9·3. $C_{14}H_{20}O_2$ requires C, 76·4; H, 9·1%). The *semicarbazone* formed prisms, m. p. 113° (from ethanol) (Found : C, 65·1; H, 8·1. $C_{15}H_{23}O_2N_3$ requires C, 65·0; H, 8·3%).

1-p-*Methoxyphenyl-5-methylhexan-3-ol* (IV). The foregoing ketone (44 g.) in ether (120 ml.) was introduced during 45 min. into a stirred solution of lithium aluminium hydride (4 g.) in ether (50 ml.) at room temperature. As soon as the vigorous reaction was over, the mixture was gently refluxed for 0·5 hr., cooled in ice, and treated with water (10 ml.), followed by dilute sulphuric acid. The ethereal layer was separated and the aqueous solution repeatedly extracted with ether. The combined ether solutions were washed with water, dried (Na_2SO_4),

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[6] Goertz, Diss., Berlin, 1924, p. 17; Burnop, Elliot, and Linstead, *J.*, 1940, 731; Martin and Robinson, *J.*, 1943, 493; Johnson, Anderson, and Shelberg, *J. Amer. Chem. Soc.*, 1944, **66**, 219; Schwenk and Papa, *ibid.*, 1945, **67**, 1432; Stork, *ibid.*, 1947, **69**, 579.

[7] Cf. Cocker, Cross, Edward, Jenkinson, and McCormick, *J.*, 1953, 2358.

[8] Koebner and Robinson, *J.*, 1938, 1995; Birch, Jaeger, and Robinson, *J.*, 1945, 582; Bachmann and Horton, *J. Amer. Chem. Soc.*, 1947, **69**, 58; Gilmore and Horton, *ibid.*, 1951, **73**, 1411.

and distilled, the *alcohol* (IV) (42·5 g.) being obtained as a colourless, somewhat viscous liquid, b. p. 173°/12 mm. (Found: C, 75·8; H, 9·8. $C_{14}H_{22}O_2$ requires C, 75·7; H, 9·9%). The alcohol (25 g.) and phosphoric acid (50 ml.; *d* 1·7) were heated in an oil-bath at 175—180° under reflux with stirring for 12 hr. After cooling, water was added and the oil extracted with ether. The ethereal solution was washed with a solution of sodium carbonate and with water, dried ($CaCl_2$), and evaporated. The residual liquid (22 g.) was heated in an oil-bath at 150—160° with sodium (1 g.) for 5 hr. and then distilled. 1 : 2 : 3 : 4-*Tetrahydro*-7-*methoxy*-1-iso*propylnaphthalene* (V) formed a colourless oil (19·8 g.), b. p. 145°/13 mm., $n_D^{19.5}$ 1·5330 (Found: C, 82·3; H, 9·7. $C_{14}H_{20}O$ requires C, 82·3; H, 9·9%).

(b) 3-p-*Methoxyphenylpropyl alcohol*.[9] Ethyl 4-methoxycinnamate[10] (b. p. 162—165°/4 mm.) (40 g.) was reduced with sodium (40 g.) and calcium-dried ethanol (350 ml.). The resulting alcohol (21 g.) had b. p. 133—134°/4 mm. (Found: C, 72·1; H, 8·3. Calc. for $C_{10}H_{14}O_2$: C, 72·3; H, 8·4%).

The alcohol (20 g.), dimethylaniline (28 ml.), and dry chloroform (28 ml.) were cooled in ice and gradually mixed with thionyl chloride (22·5 g.) in dry chloroform (28 ml.), and the mixture was heated on the steam-bath for 45 min. The *chloride* (20 g.) boiled constantly at 130°/5 mm. (Found: Cl, 19·5. $C_{10}H_{13}OCl$ requires Cl, 19·2%).

*iso*Butyraldehyde (5 g.) in ether (10 ml.) was added dropwise with constant shaking to an ice-cold ethereal solution of the Grignard reagent from 3-*p*-methoxyphenylpropyl chloride (11 g.), magnesium (1·5 g.), and dry ether (30 ml.). After 12 hr. at room temperature the mixture was decomposed with ice and ammonium chloride, giving 6-p-*methoxyphenyl*-2-*methylhexan*-3-*ol* (VI) (8 g.), b. p. 156—158°/5 mm. (Found: C, 75·4; H, 10·1. $C_{14}H_{22}O_2$ requires C, 75·7; H, 9·9%). On cyclisation with phosphoric acid (8 ml.) as described above, it (4 g.) gave the tetralin (V) (2·5 g.), b. p. 132°/4 mm. (Found: C, 82·1; H, 9·7%).

(c) δ-*p*-Methoxyphenyl-δ-oxovaleric acid[11] (50 g.), potassium hydroxide (35 g.), hydrazine hydrate (25 ml.), and trimethylene glycol (250 ml.) were heated under reflux[12] provided with a continuous water-separator until no more water collected (1·5 hr.). The temperature was allowed to rise to 195° and refluxing continued for 4 hr. more. The crude 5-*p*-methoxyphenylpentanoic acid[13] (46 g.), isolated in the usual way, was converted into the *ethyl ester*, b. p. 159°/4 mm. (Found: C, 71·1; H, 8·6. $C_{14}H_{20}O_3$ requires C, 71·2; H, 8·5%).

The ester (20 g.) was allowed to react with methylmagnesium iodide (magnesium, 4·5 g.; methyl iodide, 27 g.; dry ether, 50 ml.) in the usual way, giving 6-p-*methoxyphenyl*-2-*methylhexan*-2-*ol* (VII) (15 g.), b. p. 150—151°/9 mm. (Found: C, 75·4; H, 9·8. $C_{14}H_{22}O_2$ requires C, 75·7; H, 9·9%), which (5 g.) on treatment with phosphoric acid (10 ml.) followed by distillation over sodium gave the tetralin (V) (3 g.), b. p. 127—128°/3 mm. (Found: C, 82·5; H, 9·7%).

2 : 3 : 4 : 5 : 6 : 7 : 8 : 10-*Octahydro*-2-*oxo*-8-iso*propylnaphthalene* (IX).—Lithium (1·2 g.) was rapidly added to a stirred solution of the tetralin (V) (5 g.) in ether (25 ml.) and liquid ammonia (70 ml.) at −80°. After 20 min. ethanol (20 ml.) was introduced slowly and stirring continued until the mixture became colourless.[2] The excess of ammonia was then allowed to evaporate, the residue dissolved in water, and the liquid repeatedly extracted with ether. The ethereal solutions were washed with a solution of sodium chloride, dried (Na_2SO_4), and distilled. 1 : 2 : 3 : 4 : 5 : 8-*Hexahydro*-7-*methoxy*-1-iso*propylnaphthalene* (VIII) (4·2 g.) had b. p. 132—138°/11 mm. This was heated in ethanol (56 ml.) at 80—90° for 0·5 hr. with 2N-hydrochloric acid (50 ml.), giving the iso*propyloctalone* (IX) (2·8 g.), b. p. 150°/12 mm. (Found: C, 81·2; H, 10·4. $C_{13}H_{20}O$ requires C, 81·3; H, 10·5%), $\lambda_{max.}$ 240 mμ (ε 12,040 in EtOH). The *semicarbazone* separated from methanol as prisms, m. p. 192—193° (Found: C, 67·7; H, 9·4. $C_{14}H_{23}ON_3$ requires C, 67·5; H, 9·2%), $\lambda_{max.}$ 268 mμ (ε 23,300 in EtOH).

Condensation of 2-*Hydroxymethylene*-6-iso*propyl*cyclo*hexanone* (X) *with* 4-*Diethylaminobutan*-2-*one Methiodide*.—2-*Hydroxymethylene*-6-iso*propyl*cyclo*hexanone* (X). A mixture of 2-*iso*propyl*cyclo*hexanone[14] (b. p. 73·5°/12 mm.; 22·5 g.) and purified ethyl formate (25 g.) was added slowly with shaking to a suspension of finely divided sodium[15] (3·8 g.) in benzene (75 ml.), cooled in ice. After 12 hr. the solid sodio-salt was worked up in the usual way, giving the *hydroxymethylene ketone* (X) (20·1 g.), b. p. 106°/12 mm. (Found: C, 71·1; H, 9·5. $C_{10}H_{16}O_2$

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[9] Ramart-Lucus and Amagat, *Compt. rend.*, 1929, **188**, 640.

[10] Auwers, *Annalen*, 1917, **413**, 268; Vorlander, *ibid.*, 1897, **294**, 295.

[11] Cf. Berliner, " Organic Reactions," John Wiley, New York, 1949, Vol. V, p. 263.

[12] Huang-Minlon, *J. Amer. Chem. Soc.*, 1946, **68**, 2487.

[13] Papa, Schwenk, and Hankin, *J. Amer. Chem. Soc.*, 1947, **69**, 3021; Pratt, Hoppe, and Archer, *J. Org. Chem.*, 1948, **13**, 578.

[14] Kotz and Michels, *Annalen*, 1906, **356**, 204.

[15] Cf. Bardhan, *J.*, 1936, 1851.

requires C, 71·4; H, 9·5%). It had a characteristic smell and gave an intense violet colour with ethanolic ferric chloride.

The compound (X) (8·4 g.) was added to a solution from sodium (1·15 g.) in absolute ethanol (20 ml.), and to the solid sodio-salt, cooled in ice, 4-diethylaminobutan-2-one methiodide (from 7·2 g. of ketone and 4 ml. of methyl iodide) in a little absolute ethanol was added all at once.[5] After 2 days at the room temperature the product was warmed at 40° for 1 hr., cooled, and mixed with a solution of potassium hydroxide (8 g.) in water (500 ml.). The clear solution gradually deposited an oil, and after 12 hr. was saturated with salt and extracted with ether. The product (3 g.) had b. p. 148—149°/10 mm. and was identical with the unsaturated ketone (IX) described above (Found: C, 80·9; H, 10·4%). The semicarbazone had m. p. 191—192° and mixed m. p. 192—193° (from methanol) (Found: C, 67·6; H, 9·3%), $\lambda_{max.}$ 268 mμ (ε 21,730 in EtOH).

1 : 2 : 3 : 4-*Tetrahydro*-6-*methoxy*-1-*oxo*-4-iso*propylnaphthalene* (I).—Chromic acid (19 g.) in water (9·5 g.) and acetic acid (55 ml.) was added during 2 hr. to 7-methoxy-1-*iso*propyltetralin (V) (20 g.) in acetic acid (120 ml.) at 5—10°. The liquid was stirred in the cold for 5 hr. more and then allowed to attain room temperature overnight.[6] Methanol (10 ml.) was added, the excess of acetic acid distilled off at the water-pump, the residue diluted with water, a little hydrochloric acid was added, and the whole extracted with ether in a continuous-extraction apparatus for 24 hr. After the usual washing and drying, the ethereal extract was distilled, giving the *tetralone* (I) as a pale yellow oil (16·5 g.), b. p. 181—185°/10 mm., 116°/0·05 mm. (Found: C, 76·5; H, 8·1. $C_{14}H_{18}O_2$ requires C, 77·0; H, 8·3%). It readily yielded a *semicarbazone* as prisms, m. p. 185—186° (from ethanol) (Found: C, 65·4; H, 7·6. $C_{15}H_{21}O_2N_3$ requires C, 65·4; H, 7·6%), a 2 : 4-*dinitrophenylhydrazone* (from acetic acid), brick red plates, m. p. 187° (Found: C, 60·2; H, 5·5. $C_{20}H_{22}O_5N_4$ requires C, 60·3; H, 5·5%), and a *piperonylidene derivative* (prepared in ethanolic sodium hydroxide), pale yellow prisms (from ethanol), m. p. 127—128° (Found: C, 74·9; H, 6·6. $C_{22}H_{22}O_4$ requires C, 75·4; H, 6·3%).

Synthesis of 1 : 2 : 3 : 4-*Tetrahydro*-6-*methoxy*-1-*oxo*-4-iso*propylnaphthalene* (I).—(a) 1-m-*Methoxyphenyl*-2-*methylpropan*-1-*ol*. *m*-Methoxybenzaldehyde (15 g.) in dry ether (20 ml.) was added to ethereal *iso*propylmagnesium bromide (magnesium, 3·7 g.; *iso*propyl bromide, 16 g.; ether, 40 ml.) cooled in ice. After being overnight at the room temperature it was worked up as usual. The *alcohol* (13 g.) had b. p. 135—138°/12 mm. (Found: C, 73·0; H, 8·8. $C_{11}H_{16}O_2$ requires C, 73·3; H, 8·9%). The same compound was prepared, in almost equal yield, by the action of *m*-methoxyphenylmagnesium iodide [16] on *iso*butyraldehyde.

(b) The bromide was prepared by adding phosphorus tribromide (9 g.) in carbon tetrachloride (9 ml.) to the above alcohol (13 g.) in carbon tetrachloride (13 ml.) cooled in ice. After storage at the room temperature the mixture was warmed at 70° for 1 hr. The *bromide* distilled as a colourless liquid (13 g.), b. p. 130°/11 mm. (Found: Br, 33·3. $C_{11}H_{15}OBr$ requires Br, 32·9%).

(c) *Ethyl* 2-*ethoxycarbonyl*-3-m-*methoxyphenyl*-4-*methylpentanoate* (XI). The bromide (12 g.) was refluxed with ethyl sodiomalonate (sodium 1·2 g.; absolute ethanol 22 ml.; ethyl malonate, 13 g.) on the steam-bath for 10 hr., giving the *ester* (XI) (12 g.), b. p. 160°/4 mm. (Found: C, 67·2; H, 8·3. $C_{18}H_{26}O_5$ requires C, 67·1; H, 8·0%).

(d) 3-m-*Methoxyphenyl*-4-*methylpentanoic acid* (XII). The ester (XI) (26 g.) was hydrolysed with potassium hydroxide (15 g.) in water (15 ml.) and ethanol (40 ml.) in the usual way. The alkaline solution on acidification yielded an oil which was heated at 160—165° for 3 hr. and then distilled, giving the *acid* (XII) (12 g.), b. p. 168—170°/4 mm. (Found: C, 70·2; H, 8·1. $C_{13}H_{18}O_3$ requires C, 70·3; H, 8·1%). The *ethyl ester* had b. p. 134—136°/5 mm. (Found: C, 71·9; H, 8·7. $C_{15}H_{22}O_3$ requires C, 72·0; H, 8·8%).

(e) 3-m-*Methoxyphenyl*-4-*methylpentan*-1-*ol* (XIII). The ester (XII) (32 g.) was reduced with sodium (32 g.) and absolute ethanol (200 ml.), giving the *alcohol* (XIII) (18 g.), b. p. 172—173°/16 mm. (Found: C, 75·2; H, 9·7. $C_{13}H_{20}O_2$ requires C, 75·0; H, 9·6%). The *bromide*, prepared from the alcohol (15 g.) and phosphorus tribromide (13 g.) in dry carbon tetrachloride as described before, formed a colourless liquid (15 g.), b. p. 145—146°/8 mm. (Found: Br, 29·8. $C_{13}H_{19}OBr$ requires Br, 29·5%). The bromide (9 g.), sodium cyanide (5·5 g.), ethanol (36 ml.), and sodium iodide (1 g.) were refluxed on the steam-bath for 20 hr. The *nitrile* (6·5 g.) had b. p. 152—153°/6 mm. (Found: C, 77·1; H, 8·6. $C_{14}H_{19}ON$ requires C, 77·4; H, 8·7%).

(f) 4-m-*Methoxyphenyl*-5-*methylhexanoic acid* (XIV). The foregoing nitrile (10·5 g.) was refluxed on the steam-bath with a solution of potassium hydroxide (5·6 g.) in water (5·6 ml.) and

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[16] Bachmann and Thomas, *J. Amer. Chem. Soc.*, 1942, **64**, 95.

ethanol (12 ml.) for 40 hr. The *acid* (XIV), isolated in the usual way, was obtained as a colourless, thick oil (9·2 g.), b. p. 172—173°/4 mm. (Found : C, 71·1; H, 8·6. $C_{14}H_{20}O_3$ requires C, 71·2; H, 8·5%).

(g) 1 : 2 : 3 : 4-*Tetrahydro*-6-*methoxy*-1-*oxo*-4-iso*propylnaphthalene* (I). The preceding acid (3 g.) was added to a stirred mixture of phosphoric acid (9 ml.; *d* 1·7) and phosphoric anhydride (12 g.) at 120°. The temperature was raised to 160° and held there for 30 min. The mixture was allowed to cool and mixed with ice, and the oil extracted with ether. The ethereal solution was washed with a solution of sodium carbonate, then with water, dried ($CaCl_2$), and distilled. The tetralone (I) formed a faint yellow liquid (2·5 g.), b. p. 154°/4 mm. (Found: C, 76·8; H, 8·2%), identical with the product described above. The semicarbazone had m. p. and mixed m. p. 185—186°, and the 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 187°.

(h) *Clemmensen reduction.* The synthetic ketone (3·5 g.), amalgamated zinc (18 g.), water (10 ml.), and concentrated hydrochloric acid (40 ml.) were refluxed for 24 hr. During this period an additional quantity of concentrated hydrochloric acid (40 ml.) was added in small portions. The tetralin (2·2 g.), isolated in the usual way, on distillation over sodium had b. p. 144°/12 mm., $n_D^{20.5}$ 1·5322 (Found : C, 82·3; H, 9·9%), and was identical with the compound described above.

3 : 4-*Dihydro*-7-*methoxy*-1-*methyl*-4-iso*propylnaphthalene*.—The tetralone (I) (9 g.) in dry ether (20 ml.) was added to methylmagnesium iodide (magnesium, 2 g.; methyl iodide, 6 ml.; and dry ether, 30 ml.) at 0°. The mixture was kept overnight and then refluxed for 1 hr. The crude product (8 g.) which contained an appreciable amount of unsaturated material was heated with freshly fused, powdered potassium hydrogen sulphate (16 g.) at 150° for 1 hr. The product was worked up in the usual way and distilled over sodium, giving the pure *ether* (6·5 g.), b. p. 130—134°/4 mm., 155—158°/11 mm. (Found : C, 83·2; H, 9·3. $C_{15}H_{20}O$ requires C, 83·3; H, 9·2%).

1 : 2 : 3 : 4-*Tetrahydro*-7-*methoxy*-1-*methyl*-4-iso*propylnaphthalene*.—A solution of the foregoing ether (6 g.) in ethanol (12 ml.) was mixed with palladous chloride (0·1 g.), gum arabic (0·1 g.), and water (2 ml.) and shaken in hydrogen until a little more than 1 mol. of hydrogen was absorbed. The substituted *tetralin* formed a colourless oil (5·1 g.), b. p. 151°/10 mm. (Found: C, 82·4; H, 10·3. $C_{15}H_{22}O$ requires C, 82·6; H, 10·1%). The above ether (4·5 g.) was reduced in ether (15 ml.) with lithium (1·1 g.) and ethanol (20 ml.) in liquid ammonia (60 ml.), as described in an analogous case, giving the corresponding *derivative* (4 g.), b. p. 140—150°/10 mm. A middle fraction was analysed (Found : C, 81·8; H, 10·9. $C_{15}H_{24}O$ requires C, 81·8; H, 11·0%). This does not, however, give a solid bisulphite compound as was to be expected.[2b] Further work will be necessary to clear up this point.

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UNIVERSITY COLLEGE OF SCIENCE, CALCUTTA.
ORGANISCH-CHEMISCHES LABORATORIUM DER EIDG. TECHNISCHEN HOCHSCHULE, ZURICH.
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