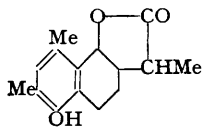
361. *The Constitution of ψ-Santonin. Part VII. Some Dimethylethylnaphthols.*

By Wesley Cocker, B. E. Cross, A. K. Fateen, Cyril Lipman, E. R. Stuart, W. H. Thompson, and D. R. A. Whyte.

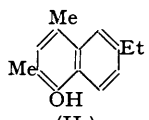
Dehydrogenation of desmotropo-ψ-santonin with palladised charcoal yields a dimethylethylnaphthol. Spectroscopic studies suggest that it is 2 : 4-dimethyl-6-ethyl-1-naphthol (II). Several new dimethylethylnaphthols are described.

Clemo and Cocker (*J.*, 1946, 30) showed that deoxy-ψ-santonin is dehydrogenated with selenium to 1-methyl-7-ethylnaphthalene and that desmotropo-ψ-santonin yields 2 : 4-dimethyl-1-naphthol on fusion with sodium hydroxide. On the basis of this evidence the structure (I) was assigned to desmotropo-ψ-santonin. We have now found conditions whereby desmotropo-ψ-santonin is dehydrogenated, with palladised charcoal (cf. Cocker *et al.*, *Chem. and Ind.*, 1949, 641) to a dimethylethylnaphthol.

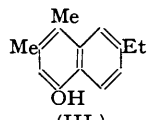
This naphthol fails to couple with diazotised *p*-nitroaniline. It is thus substituted in the *ortho*- and *para*-positions to the phenolic group. Further, ultra-violet and infra-red light-absorption studies suggest that the new naphthol is 2 : 4-dimethyl-6-ethyl-1-naphthol (II), an expected dehydrogenation product of a desmotropo-compound of structure (I). The synthesis of (II) has not yet been accomplished, and further work on this is in progress.



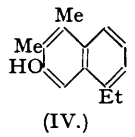
(I.)



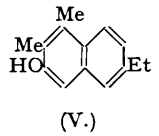
(II.)



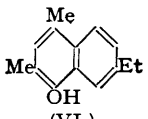
(III.)



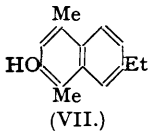
(IV.)



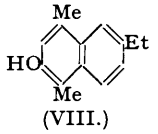
(V.)



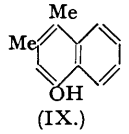
(VI.)



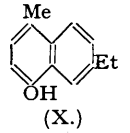
(VII.)



(VIII.)



(IX.)



(X.)

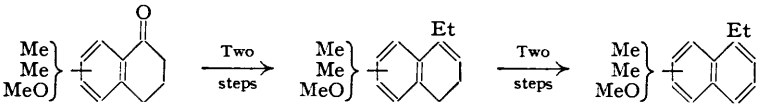
Only one dimethylethylnaphthol has so far been described, namely, 1 : 4-dimethyl-6-ethyl-3-naphthol obtained by the fusion of an artemisic or dihydroartemisic acid with potassium hydroxide (Bertolo, *Gazzetta*, 1926, **56**, 856). It is now shown that this naphthol is also obtained when (−)-α-desmotroposantonin is heated at 240—250° with palladised charcoal, and the identity of the naphthol has been confirmed by synthesis.

We had access to four xylenols, namely *o*-3-, *o*-4-, *m*-4-, and *p*-xylenol, from which we have prepared a number of naphthols possessing an ethyl group in the non-phenolic ring, namely, 3 : 4-dimethyl-6-ethyl-1-naphthol (III), 1 : 2-dimethyl-5- (IV) and -6-ethyl-3-naphthol (V), 2 : 4-dimethyl-7-ethyl-1-naphthol (VI), 1 : 4-dimethyl-6-ethyl-3- (VII) and -2-naphthol (VIII). In addition, 3 : 4-dimethyl-1-naphthol (IX) (cf. Arnold, Buckley, and Richter, *J. Amer. Chem. Soc.*, 1947, **69**, 2323; Kruber and Schade, *Ber.*, 1935, **68**, 11) and 4-methyl-7-ethyl-1-naphthol (X) have been prepared. 3 : 4-Dimethyl-1-naphthol (IX) was obtained by the condensation of succinic anhydride with *o*-4-xylyl methyl ether and *via* the following compounds: β-(2-methoxy-4 : 5-dimethylbenzoyl)propionic acid, γ-(2-methoxy-4 : 5-dimethylphenyl)butyric acid, 1-keto-5-methoxy-7 : 8-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene, and 5-methoxy-7 : 8-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene.

Naphthols substituted by Ethyl in an α-Position in the Non-phenolic Nucleus.—The method followed (cf. Haworth, *J.*, 1932, 1125, 2717; Haworth, Letsky, and Mavin, *ibid.*, p. 1784) involved the reaction of ethylmagnesium iodide with the appropriate tetralone followed by dehydration of the product and dehydrogenation of the unsaturated compound so formed.

The three tetralones employed, namely, 1-keto-5-methoxy-7 : 8-dimethyl-, 1-keto-8-methoxy-5 : 7-dimethyl- (Cocker and Lipman, *J.*, 1947, 53; Cocker, Lipman, and Whyte, preceding paper), and 1-keto-7-methoxy-5 : 6-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene (Cocker, *J.*, 1946, 36), condensed readily with the Grignard reagent and the corresponding dihydro-

naphthalene derivatives were obtained in good yield. These were satisfactorily demethylated with hydriodic acid, but in two cases subsequent attempts to effect dehydrogenation gave



anomalous results. Thus, 4-methoxy-1 : 2-dimethyl-8-ethyl-5 : 6-dihydronaphthalene, obtained from the first-mentioned tetralone, yielded 3 : 4-dimethyl-1-naphthol (IX); and 5-methoxy-6 : 8-dimethyl-4-ethyl-1 : 2-dihydronaphthalene obtained from the second-mentioned tetralone, gave 2 : 4-dimethyl-1-naphthol when heated with selenium at 340° or sulphur at 210°. On the other hand, 1 : 2-dimethyl-5-ethyl-3-naphthol (IV) was directly produced when 3-methoxy-1 : 2-dimethyl-5-ethyl-7 : 8-dihydronaphthalene, obtained from the last of the three tetralones mentioned, was heated with hydriodic acid containing free iodine. However, this reagent did not give satisfactory results with the other dihydro-compounds. Neither chloranil nor *N*-bromosuccinimide was successful as dehydrogenating agent. Catalytic reduction of the dihydro-compounds followed by dehydrogenation also led to the loss of the ethyl group and the production of much tarry material.

Unsatisfactory results were also obtained when 5-hydroxy-7 : 8-dimethyl-4-ethyl-1 : 2 : 3 : 4-tetrahydronaphthalene [obtained from ethyl β-(2-methoxy-4 : 5-dimethylbenzoyl)propionate through the stages 4-(2-methoxy-4 : 5-dimethylphenyl)hex-3-enoic acid *, 4-(2-methoxy-4 : 5-dimethyl)phenylhexanoic acid, and 1-keto-5-hydroxy-7 : 8-dimethyl-4-ethyl-1 : 2 : 3 : 4-tetrahydronaphthalene] or its methyl ether was submitted to dehydrogenation. None of the required 1 : 2-dimethyl-5-ethyl-1-naphthol was obtained.

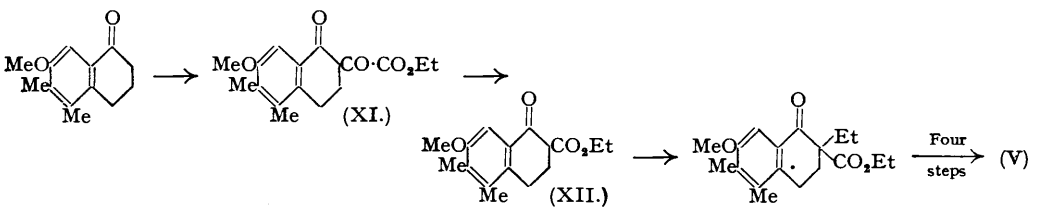
It is significant that, in our experience, loss of alkyl group was experienced only in those compounds where this group was present in an α-position in the reduced ring and where there was another group in the corresponding α-position of the aromatic ring. We propose to investigate this point more fully.

Other workers have met similar dealkylation during dehydrogenation (cf. Ramage, *J.*, 1938, 1853) but amongst the examples of the phenomenon, which we have found in the literature, that mentioned by Ruzicka, Ehmann, and Morgeli (*Helv. Chim. Acta*, 1933, **16**, 314, 325) approaches most closely to those described by us. These workers found that 2 : 7-dimethyl-1-ethyl-3 : 4-dihydronaphthalene is partly converted into 2 : 7-dimethylnaphthalene when heated with selenium at 300°.

When 4-methoxy-1 : 2-dimethyl-8-ethyl-5 : 6-dihydronaphthalene was catalytically reduced and the product was heated with palladised charcoal at 300°, 1 : 2-dimethyl-8-ethylnaphthalene was obtained and characterised as its picrate and its trinitrobenzene and trinitrotoluene adducts. A similar result was obtained when the hydroxy-compounds were dehydrogenated. Ruzicka, Hofmann, and Frei (*Helv. Chim. Acta*, 1936, **19**, 386) recorded that 3-methoxy-2 : 6-dimethylnaphthalene is converted into 2 : 6-dimethylnaphthalene when heated with palladised charcoal. Further investigation of this point is in hand.

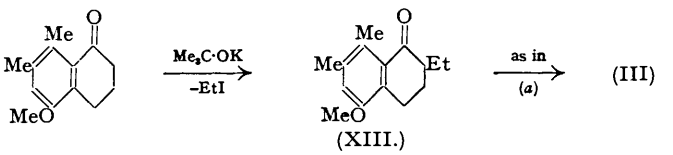
Naphthols substituted by Ethyl in a β-Position in the Non-phenolic Nucleus.—Numerous methods are available for the synthesis of alkylnaphthalenes in which the alkyl group is in a β-position, and many are applicable to the synthesis of the corresponding naphthols. Some of these are illustrated schematically below, using actual examples employed in the present investigation.

(*a*) (cf. Cocker and Lipman, *J.*, 1947, 523):

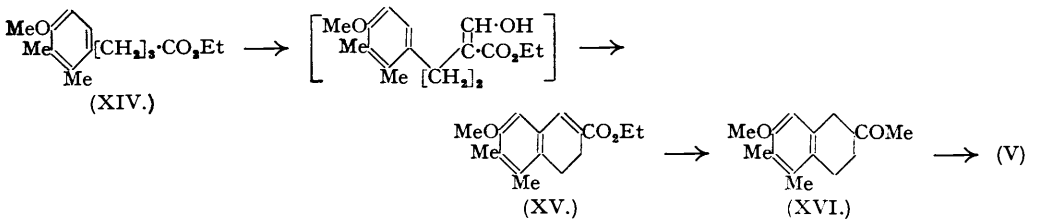


* Geneva nomenclature.

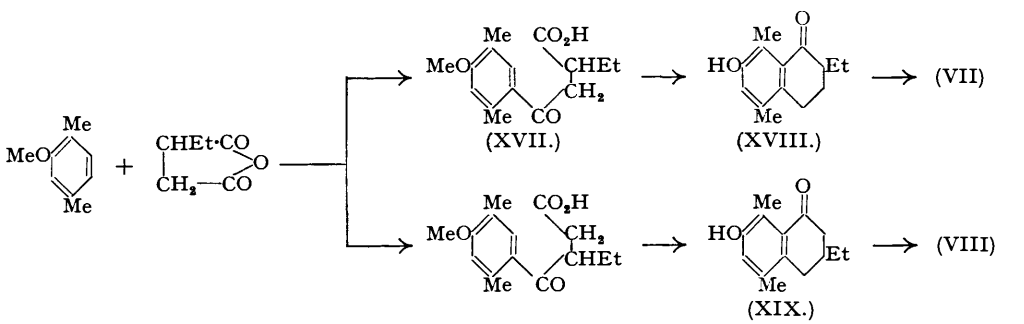
(*b*) (cf. Koebner and Robinson, *J.*, 1941, 573) :



(*c*) (cf. Holmes and Trevoy, *Org. Synth.*, 1946, **26**, 28) :



(*d*) (cf. Haworth, *J.*, 1932, 1128) :



Method (a). By this route ethyl 1-keto-7-methoxy-5 : 6- (XI) and 1-keto-5-methoxy-7 : 8-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene-2-glyoxylate and the corresponding carboxylates were obtained, but only the carboxylate (XII) derived from (XI) was successfully ethylated.

Method (b). 1-Keto-7-methoxy-5 : 6-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene (Cocker, *loc. cit.*) was directly ethylated using potassium *tert.*-butoxide, but apparently *gem*-diethyl compounds were produced, since subsequent Clemmensen reduction was very slow and the reduction product resisted dehydrogenation (as shown by ultra-violet light absorption measurements). This agrees with the experience of Clemo and Dickenson (*J.*, 1937, 255) who showed that 2 : 2-dimethyl- and 2-methyl-2-ethyltetralin resisted the action of selenium. Sen Gupta (*J. pr. Chem.*, 1938, [ii], **151**, 82) asserted that the former yields 2-methylnaphthalene when heated with selenium in a sealed tube but, in our case, this modification also failed.

1-Keto-5-methoxy-7 : 8-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene, however, was directly ethylated to 1-keto-5-methoxy-7 : 8-dimethyl-2-ethyl-1 : 2 : 3 : 4-tetrahydronaphthalene (XIII) which was converted in the usual way into 3 : 4-dimethyl-6-ethyl-1-naphthol (III).

Method (c). From the appropriate butyric esters, ethyl 7-methoxy-5 : 6- (XV) and 8-methoxy-5 : 7-dimethyl-3 : 4-dihydronaphthalene-2-carboxylate were obtained although the yields left much to be desired. These were reduced to the tetrahydro-compounds, hydrolysed, and converted into the acid chlorides, which were not isolated but were treated immediately with dimethylcadmium. No reaction took place, presumably owing to insolubility of the reaction mixture in the solvent but, by the action of methylmagnesium iodide on 7-methoxy-5 : 6-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene-2-carboxyamide a very small quantity of a ketone, probably 7-methoxy-2-acetyl-5 : 6-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene (XVI), was obtained.

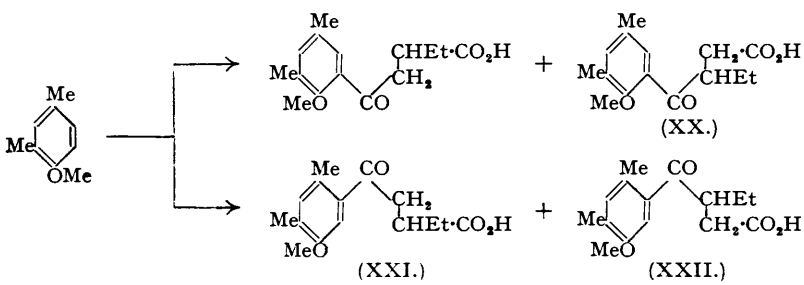
Method (d). This provides a very direct route to the required naphthols. The first stage consists in the condensation of ethylsuccinic anhydride with the appropriate xylyl ether. The

subsequent stages are well known. Using methylsuccinic anhydride, the method has been extensively applied to the synthesis of polycyclic hydrocarbons (cf. Berliner, *Org. Reactions*, 1949, **5**, 242, 275). As shown in the formulæ above, the reaction may yield either an α- or a β-alkyl-β-benzoylpropionic acid. In general, however, the use of an ionising solvent favours the formation of the α-alkyl compound, whereas non-ionising solvents act in the reverse sense (cf. Cocker *et al.*, *loc. cit.*, who review the earlier work on the condensation of unsymmetrical alkylsuccinic anhydrides with aromatic systems). In the condensation of methylsuccinic anhydride (unpublished work) and ethylsuccinic anhydride with phenyl ethers in nitrobenzene, the α-alkyl-β-benzoylpropionic acids generally predominate. With *p*-xylyl methyl ether, however, ethylsuccinic anhydride yields a mixture from which pure β-(4-methoxy-2 : 5-dimethylbenzoyl)-α-ethylpropionic acid (XVII) was isolated, leaving an intractable oil which, on reduction by amalgamated zinc, yielded a product from which pure β-(4-methoxy-2 : 5-dimethylbenzyl)-*n*-valeric acid was isolated; the quantities isolated indicate that the anhydride condensation had proceeded in each direction to about the same extent.

The identity of the two acids mentioned was established by their conversion into the corresponding tetralones (XVIII) and (XIX). The keto-group of (XVIII) is hindered and did not form a semicarbazone, whilst (XIX) readily yielded this derivative.

o-4-Xylyl methyl ether and ethylsuccinic anhydride give a sticky product from which only α-ethyl-β-(2-methoxy-4 : 5-dimethylbenzoyl)propionic acid has so far been isolated in a pure condition. This compound, after reduction to the corresponding butyric acid, was readily cyclised to 1-keto-5-methoxy-7 : 8-dimethyl-2-ethyl-1 : 2 : 3 : 4-tetrahydronaphthalene, which failed to yield a semicarbazone but was converted into 3 : 4-dimethyl-6-ethyl-1-naphthol (III). In our view, failure of a 1-tetralone to yield a semicarbazone indicates the presence of groups in the 2- and the 8-position and can be used for diagnostic purposes (cf. Cagniant and Buu-Hoï, *Bull. Soc. chim.*, 1942, **9**, 841).

Von Auwers and Mauss (*Ber.*, 1928, **61**, 1495) showed that acetyl chloride reacts with *m*-4-xylyl methyl ether in boiling carbon disulphide to yield a mixture of 5-hydroxy-2 : 4- and 2-hydroxy-3 : 5-dimethylacetophenone. The reaction of ethylsuccinic anhydride with the ether could, in a similar fashion, take place both *ortho*- and *meta*- to the methoxy-group to yield a mixture of α- and β-ethylbenzoylpropionic acids in each case, that is four products in all :



When we condensed ethylsuccinic anhydride with *m*-4-xylyl methyl ether in cold nitrobenzene, a mixture was obtained in which α-ethyl-β-(5-methoxy-2 : 4-dimethylbenzoyl)-propionic acid (XXI) predominated. Its identity was established by oxidation to 5-methoxy-2 : 4-dimethylbenzoic acid [obtained from the known 5-methoxy-2 : 4-dimethylacetophenone (von Auwers and Mauss, *loc. cit.*)], and by reduction followed by cyclisation to 1-keto-8-hydroxy-5 : 7-dimethyl-2-ethyl-1 : 2 : 3 : 4-tetrahydronaphthalene. From this ketone, which failed to give a semicarbazone or a piperonylidene derivative, 8-hydroxy-5 : 7-dimethyl-2-ethyl-1 : 2 : 3 : 4-tetrahydronaphthalene (*A*) and thence 2 : 4-dimethyl-7-ethyl-1-naphthol (VI) were obtained.

In addition to the keto-acid already mentioned, we obtained an appreciable quantity of an intractable, oily keto-acid. This yielded a tetralone from which a pure semicarbazone was eventually obtained. The semicarbazone was reduced by the Huang-Minlon modification of the Wolff–Kishner reaction to the foregoing tetralin (*A*), which also gave the naphthol (VI); assuming that no isomeric changes took place during the reduction, it must be concluded that the semicarbazone was derived from 1-keto-5-methoxy-6 : 8-dimethyl-3-ethyl-1 : 2 : 3 : 4-tetrahydronaphthalene which must have originated from β-ethyl-β-(2-methoxy-3 : 5-dimethylbenzoyl)propionic acid (XX). Oxidation of the oily keto-acid yielded an impure sample of

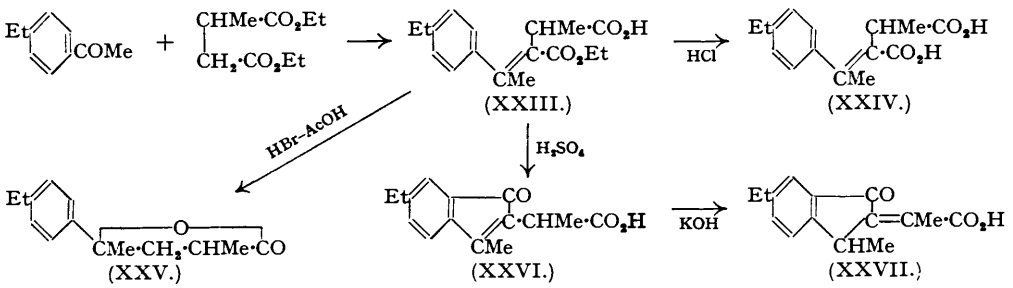
5-methoxy-2 : 4-dimethylbenzoic acid and, thus, it is obvious that the oil also contains (XXI) or the unknown (XXII), or both.

It is of interest that, when we condensed chloroacetyl chloride with *m*-4-xylyl methyl ether in cold nitrobenzene, ω-chloro-5-methoxy-2 : 4-dimethylacetophenone was the sole product isolated. Its identity was established by reduction to 5-methoxy-2 : 4-dimethylacetophenone. In cold carbon disulphide, the same product was isolated in good yield but there was evidence of other products (cf. von Auwers and Mauss, *loc. cit.*).

Amongst other products prepared from *m*-4-xylyl methyl ether was 5-methoxy-2 : 4-dimethylbenzyl alcohol which was obtained in excellent yield by the reduction of 5-methoxy-2 : 4-dimethylbenzoic acid with lithium aluminium hydride in ether. The derived benzyl chloride with ethyl ethylmalonate gave ethyl 5-methoxy-2 : 4-dimethylbenzylethylmalonate, hydrolysed to an oily acid, which was further reduced with lithium aluminium hydride to an alcohol, but attempts to convert the last into the corresponding chloride were not successful. We intend to investigate these reactions further.

The syntheses so far described started with the appropriate xylenol to which a second ring carrying an ethyl group was fused. Attempts were made, starting with ethylbenzene, to fuse on the phenolic nucleus. The first method we employed in this connection was that due to Stobbe (cf. Campbell, *Annual Reports*, 1947, **44**, 136, for many references). Methylsuccinic ester was condensed with *p*-ethylacetophenone to yield a mixture of unsaturated acids from which 3-carbethoxy-4-*p*-ethylphenyl-2-methylpent-3-enoic acid (XXIII) was isolated. Attempted decarboxylation of this half ester with concentrated hydrochloric acid yielded only the corresponding dicarboxylic acid (XXIV or an isomer), m. p. 142°; but in hydrobromic acid in acetic acid the half-ester yielded the lactone of 4-hydroxy-4-*p*-ethylphenyl-2-methylpentanoic acid (XXV). Distillation of the half-ester under reduced pressure yielded a second dicarboxylic acid (m. p. 155°), which on storage was gradually transformed into the lower-melting acid. The relationship of these acids has still to be investigated. Attempted cyclisation of the half-ester with concentrated sulphuric acid yielded a colourless keto-compound, m. p. 83°, which when refluxed with alcoholic potash gave an isomeric yellow compound, m. p. 122°. The former compound is probably α-(1-keto-3-methyl-6-ethyl-2-indenyl)propionic acid (XXVI) (cf. Campbell, *loc. cit.*) and the latter the more highly conjugated α-(1-keto-3-methyl-6-ethyl-2-indanylidene)propionic acid (XXVII).

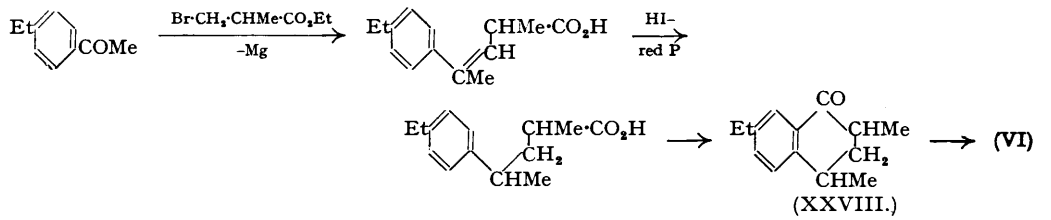
All attempts to obtain the required 2 : 4-dimethyl-7-ethyl-1-naphthol or its 3-carboxylic acid were unsuccessful.



The following method was then employed. *p*-Ethylacetophenone was condensed, in boiling xylene, with ethyl β-bromo*iso*butyrate in presence of magnesium. The magnesium dissolved fairly rapidly under these conditions and the product was hydrolysed, yielding an oil, probably a mixture of the required 4-*p*-ethylphenyl-2-methylpent-3-enoic acids. Attempted ring-closure of this oil with phosphorus trichloride (cf. Borsche, *Annalen*, 1936, **526**, 1) yielded the lactone (XXV), and treatment of the lactone with concentrated sulphuric acid gave a product which possessed the odour of a naphthol but proved intractable.

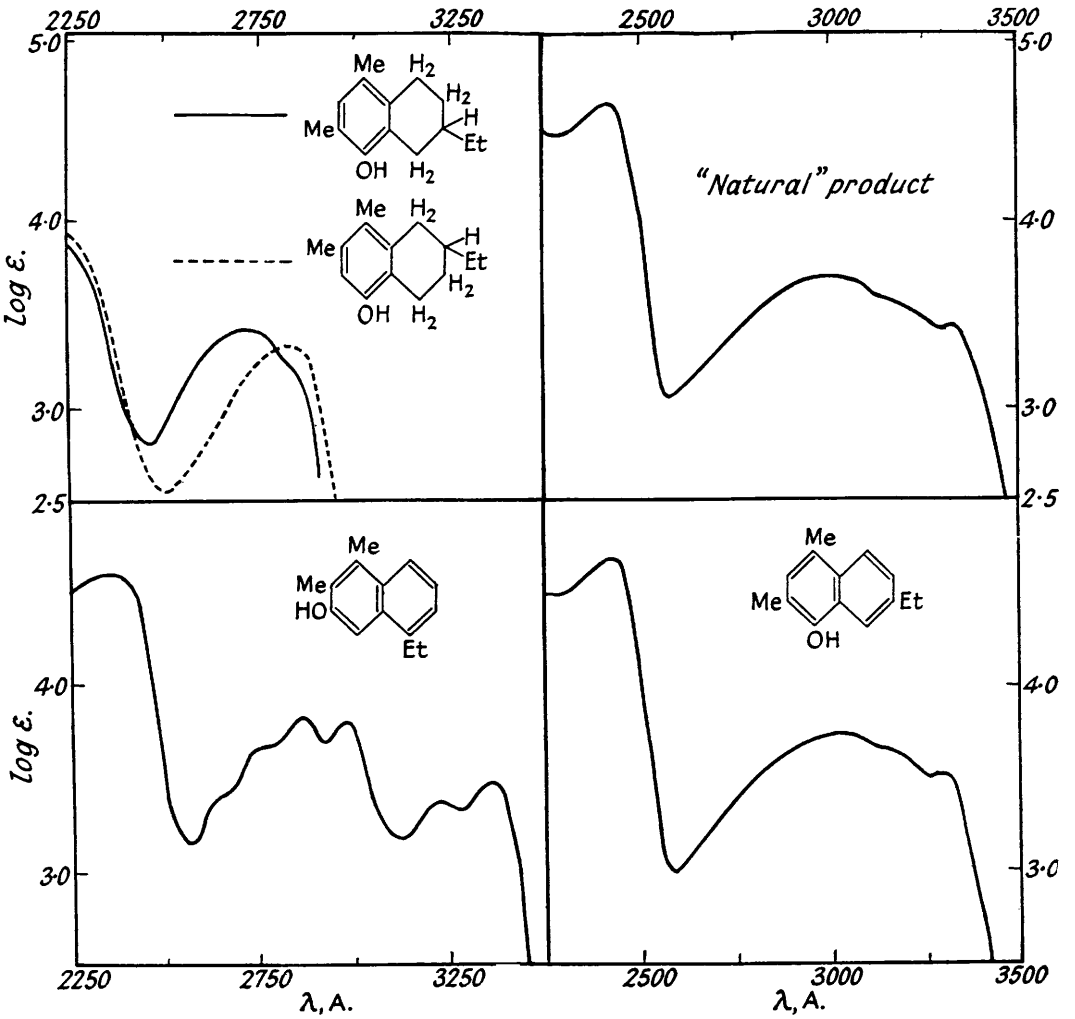
In a further experiment, designed as a model, methyl β-*p*-ethylbenzoylpropionate was treated with methylmagnesium iodide yielding 4-*p*-ethylphenylpent-3-enoic acid, but efforts to cyclise this to 4-methyl-7-ethyl-1-naphthol with phosphorus trichloride (Borsche, *loc. cit.*), acetic anhydride, or sulphuric acid gave either the acid chloride or intractable material. The acid chloride could not be cyclised and it would appear that, in spite of the work of Borsche, these unsaturated acids are not suitable for cyclisation to phenolic

compounds (cf. also Fieser and Fieser, " Natural Products Related to Phenanthrene," New York, 1949, p. 87).



However, when the mixture of 4-(*p*-ethylphenyl)-2-methylpent-3-enoic acids was reduced with hydriodic acid and red phosphorus, a product was obtained which was cyclised in sulphuric acid to 1-keto-2 : 4-dimethyl-7-ethyl-1 : 2 : 3 : 4-tetrahydronaphthalene (XXVIII). Bromin-

FIG. 1.



ation in ether and dehydrobromination with dimethylaniline yielded the required 2 : 4-dimethyl-7-ethyl-1-naphthol (VI) which did not depress the melting point of the compound prepared by the route already described.

By a similar process, 4-*p*-ethylphenylpent-3-enoic acid gave 1-keto-4-methyl-7-ethyl-1 : 2 : 3 : 4-tetrahydronaphthalene and thence 4-methyl-7-ethyl-1-naphthol (X).

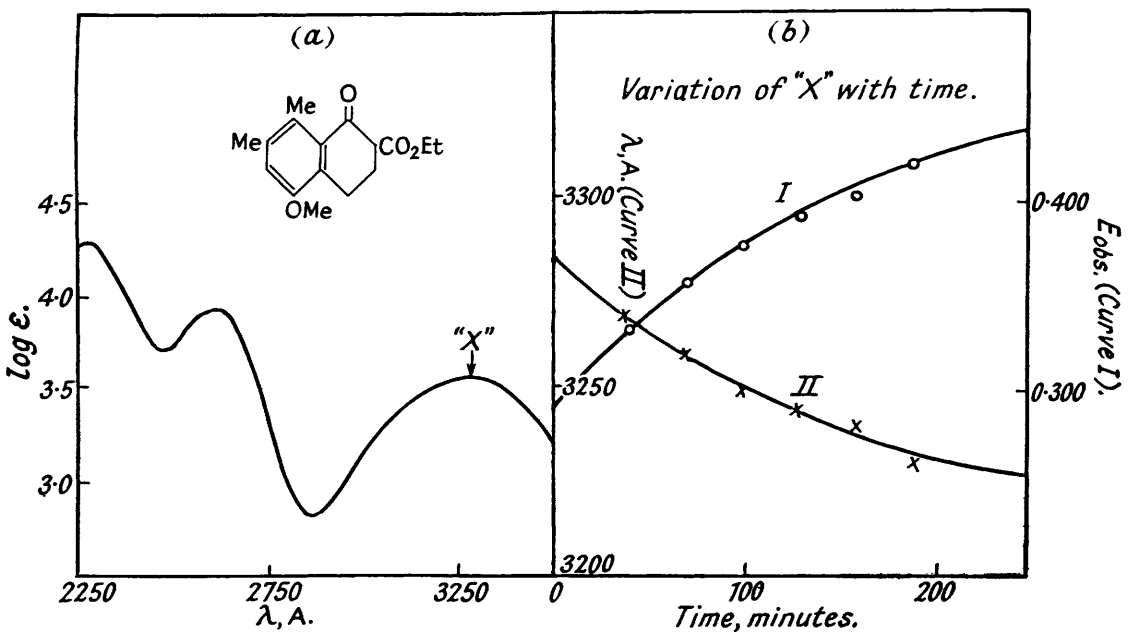
Few examples of the use of β-bromo-esters in the Reformatsky reaction are to be found in the literature. In the case in point, the reaction did not proceed in presence of zinc under any conditions employed. Magnesium reacted slowly in boiling benzene, but very rapidly in boiling xylene, and the yields of the product were of the order of 45%. Bromination of the tetralone followed by dehydrobromination was very smooth and this method appears to us to be of considerable preparative value.

Absorption Spectra.—The absorption spectra of the various naphthols and some related compounds were measured (see Experimental section) and Fig. 1 shows typical examples.

The 1- may be clearly distinguished from the 2-naphthols, particularly by the " triplet " and " doublet " bands of the latter, and here the degree of resolution in the " triplets " and " doublets " varies with the position of the substituent alkyl groups.

The carbethoxy-tetralones showed an interesting phenomenon. One of the peaks (denoted by X in Fig. 2*a*) alters with time in respect to position and also intensity. Measurement of this

FIG. 2*a*. FIG. 2*b*.



change is illustrated in Fig. 2*b*. However, there was no simultaneous change in the peak at 2290 A. and only a slight fall in $E_{obs.}$ for the peak at 2610 A. Further studies of this problem are in hand, but the phenomenon is likely to be associated with the equilibrium shown below :

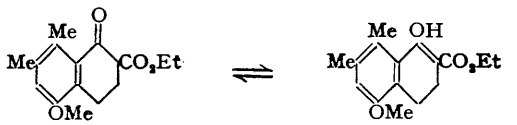


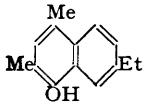
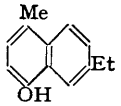
Fig. 1 shows conclusively that the " natural " naphthol from desmotropo-ψ-santonin is a 1-naphthol. Furthermore, its ultra-violet light absorption shows such a close resemblance to that of 2 : 4-dimethyl-7-ethyl-1-naphthol that it probably differs from the latter only in the possession of a 6- in place of a 7-ethyl group.

The infra-red absorption spectra of 4-methyl- and 2 : 4-dimethyl-7-ethyl-1-naphthol and the " natural " naphthol have been examined (see table) by Messrs. Imperial Chemical Industries Limited, Billingham Division, who report that the " natural " naphthol and 2 : 4-dimethyl-7-ethyl-1-naphthol have spectra of the same clear, well-defined type, but that there are many

differences in detail which are consistent with a shift in the position of the ethyl group from the 7- to the 6-position, but that they are inconsistent with a shift to the 5- or the 8-position.

Infra-Red Absorption.

The numerals give the band frequencies (cm.$^{-1}$), the letters the band strength (W = weak, M = medium, S = strong).

"Natural" naphthol	773 W	826 S	880 S	931 M	987 W	1030 W	1049 W	1108 M	1162 M	1193 W	1225 W	1244 W	1276 W	1309 M	
	815 S	847 M	870 M	889 M	940 W	1002 W	1033 W	1055 W	1071 W	1101 M	1162 M	1195 M	1238 M	1306 M	1337 W
	825 S	888 M	918 W	1035 W	1051 S	1144 M	1162 W	1196 M	1220 W	1253 W	1274 W				

Experimental.

(Analyses are by Drs. Weiler and Strauss, Oxford.)

Absorption spectra were measured with a Beckman Quartz Spectrophotometer, Model D.U., using silica cells of thickness 1·000 ± 0·001 cm. Spectra were measured in alcohol and the initial concentrations were of the order of 20 mg./l., with ten-fold dilution when necessary to bring the high intensity peaks within the range of the instrument.

All the Friedel–Crafts reactions were performed in nitrobenzene. The description given under *A* below is typical of all the experiments in this category.

A. Experiments with o-4-*Xylenol.*

3 : 4-*Dimethyl*-1-*naphthol* (IX).—*β*-(2-*Methoxy*-4 : 5-*dimethylbenzoyl*)*propionic acid.* A mixture of *o*-4-xylyl methyl ether (26·8 g.), succinic anhydride (22 g.), and dry nitrobenzene (100 c.c.) was slowly treated with a solution of aluminium chloride (25 g.) in nitrobenzene (200 c.c.) at 15—20°, and the mixture was set aside overnight. It was then poured into ice and hydrochloric acid, and the nitrobenzene layer was separated, washed successively with hydrochloric acid and water, and extracted several times with 20% aqueous ammonia. The extract was washed with ether, filtered, and acidified, yielding the *keto-acid* (26·5 g.; m. p. 155°), which crystallised from dilute alcohol as needles, m. p. 161° (Found: C, 66·1; H, 7·1. $C_{13}H_{16}O_4$ requires C, 66·1; H, 6·8%). Its *methyl* ester crystallised from light petroleum (b. p. 40—60°) as stout rods, m. p. 58° (Found: C, 66·8; H, 7·15. $C_{14}H_{18}O_4$ requires C, 67·2; H, 7·2%). Its *ethyl* ester consisted of needles (from light petroleum), m. p. 73—74° (Found: C, 67·9; H, 7·9. $C_{15}H_{20}O_4$ requires C, 68·2; H, 7·6%).

The identity of the keto-acid was shown by oxidation with sodium hypochlorite to 2-*methoxy*-4 : 5-*dimethylbenzoic acid*, which crystallised from dilute alcohol as needles, m. p. 141—142° (Found: C, 66·8; H, 6·7. $C_{10}H_{12}O_3$ requires C, 66·7; H, 6·7%), and was also obtained from 2-methoxy-4 : 5-dimethylacetophenone (von Auwers, Bundesmann, and Wieners, *Annalen*, 1926, **447**, 176) by oxidation with sodium hypochlorite.

γ-(2-*Methoxy*-4 : 5-*dimethylphenyl*)*butyric acid.*—The keto-acid (14·4 g.), refluxed for 24 hours with amalgamated zinc (50 g.), concentrated hydrochloric acid (50 c.c.) and water (30 c.c.), yielded the *butyric acid* (12·6 g.) which crystallised from light petroleum (b. p. 40—60°) as needles, m. p. 78—79° (Found: C, 69·9; H, 8·1. $C_{13}H_{18}O_3$ requires C, 70·3; H, 8·1%).

1-*Keto*-5-*methoxy*-7 : 8-*dimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene.* The butyric acid (12·5 g.) was heated for 10 minutes at 65—70° with concentrated sulphuric acid (60 c.c.), cooled, and poured on crushed ice, and the *ketone* was collected (11·6 g.). It was washed successively with sodium carbonate and water and crystallised from light petroleum (b. p. 60—80°) as colourless needles, m. p. 76° (Found: C, 76·5; H, 8·0. $C_{13}H_{16}O_2$ requires C, 76·5; H, 7·8%). Its *semicarbazone* crystallised from dilute alcohol as silvery plates, m. p. 205—206° (Found: C, 63·7; H, 7·0. $C_{14}H_{19}O_2N_3$ requires C, 64·4; H, 7·3%).

5-*Hydroxy*-1-*keto*-7 : 8-*dimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* was obtained when the butyric acid was heated with 80% sulphuric acid on the water-bath for 2 hours. It crystallised from dilute alcohol as prisms, m. p. 193—194° (Found: C, 75·6; H, 7·3. $C_{12}H_{14}O_2$ requires C, 75·8; H, 7·4%).

5-*Methoxy*-7 : 8-*dimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene.* 1-Keto-5-methoxy-7 : 8-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene (17·2 g.) was reduced during 24 hours with a mixture of concentrated hydrochloric acid (140 c.c.), water (100 c.c.), and amalgamated zinc (140 g.), and the product was extracted with ether. The required *methoxytetralin* was obtained as a colourless oil (9·3 g.), b. p. 152°/6 mm. (Found: C, 81·6; H, 9·2. $C_{13}H_{18}O$ requires C, 82·1; H, 9·5%).

5-*Hydroxy*-7 : 8-*dimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene.* The last-mentioned methoxy-compound (9·0 g.) was refluxed for 90 minutes with hydriodic acid (*d* 1·7; 45 c.c.). The *product* (4·7 g.) crystallised from light petroleum (b. p. 60—80°) as felted needles, m. p. 116—117° (Found: C, 81·6; H, 8·7. $C_{12}H_{16}O$ requires C, 81·8; H, 9·1%). Its *carbanilate* crystallised from dilute alcohol as prisms, m. p. 145—146° (Found: C, 76·8; H, 7·0. $C_{19}H_{21}O_2N$ requires C, 77·3; H, 7·1%).

3 : 4-*Dimethyl*-1-*naphthol* (IX). The preceding compound (1 g.) was heated with selenium (3 g.) for

2·25 hours at 330—340° and the product was extracted with benzene (charcoal) and distilled in steam. The distillate yielded the naphthol (0·2 g.) which crystallised from light petroleum (b. p. 60—80°) as prisms, m. p. 121·5° (Arnold, Buckley, and Richter, *loc. cit.*, give m. p. 121—122°, and Kruber and Schade, *loc. cit.*, give m. p. 114—115°) (Found: C, 83·4; H, 7·0. Calc. for $C_{13}H_{12}O$. C, 83·7; H, 7·0%). Light absorption: Maxima, 2420, 3060 (3160), and 3300 A.; log ε = 4·43, 3·89 (3·85), and 3·73, respectively. Its *picrate* crystallised from benzene as scarlet needles, m. p. 168° (Found: C, 53·9, 53·7; H, 4·0, 3·9. $C_{18}H_{15}O_8N_3$ requires C, 53·9; H, 3·7%). Its 3:5-*dinitrobenzoate* crystallised from benzene–light petroleum as needles, m. p. 222—224° (Found: C, 61·6; H, 2·9. $C_{19}H_{14}O_6N_2$ requires C, 62·3; H, 3·8%).

3:4-*Dimethyl*-6-*ethyl*-1-*naphthol* (III).—*Ethyl* 1-*keto*-5-*methoxy*-7:8-*dimethyl*-1:2:3:4-*tetrahydronaphthalene*-2-*glyoxylate*. 1-Keto-5-methoxy-7:8-dimethyl-1:2:3:4-tetrahydronaphthalene (30·6 g.) in freshly distilled ethyl oxalate (21·3 g.) and absolute alcohol (150 c.c.) was cooled to −5° and a solution of sodium (3·45 g.) in alcohol (60 c.c.) was added at −5°. Next morning the solution was poured into a mixture of ice and concentrated hydrochloric acid. The *glyoxylate* which separated crystallised from alcohol as golden needles (25 g.), m. p. 90—91° (Found: C, 67·1; H, 6·5. $C_{17}H_{20}O_5$ requires C, 67·1; H, 6·6%).

Ethyl 1-*keto*-5-*methoxy*-7:8-*dimethyl*-1:2:3:4-*tetrahydronaphthalene*-2-*carboxylate*. The preceding compound (21·5 g.) was heated with powdered glass (30 g.) at 190—200° until evolution of carbon monoxide ceased. The product was collected (b. p. 200—208°/10 mm.) and crystallised from light petroleum (b. p. 40—60°) as silky needles (12·5 g.), m. p. 62·5—63·5° (Found: C, 70·1; H, 6·9. $C_{16}H_{20}O_4$ requires C, 69·6; H, 7·2%).

α-*Ethyl*-β-(2-*methoxy*-4:5-*dimethylbenzoyl*)*propionic acid*. A mixture of *o*-4-xylyl methyl ether (22 g.), ethylsuccinic anhydride (cf. Wren and Crawford, *J.*, 1937, 230) (22 g.), and nitrobenzene (30 c.c.), treated with aluminium chloride (50 g.) in nitrobenzene (100 c.c.), yielded a *keto-acid* (21 g.) which crystallised from dilute alcohol as tufts of needles, m. p. 138—142° (Found: C, 68·4; H, 7·7. $C_{15}H_{20}O_4$ requires C, 68·2; H, 7·6%). Its identity was confirmed by oxidation to 2-methoxy-4:5-dimethylbenzoic acid.

γ-(2-*Methoxy*-4:5-*dimethylphenyl*)-α-*ethylbutyric acid*. The foregoing keto-acid (21 g.) was reduced under Clemmensen conditions to an oil which failed to solidify.

1-*Keto*-5-*methoxy*-7:8-*dimethyl*-2-*ethyl*-1:2:3:4-*tetrahydronaphthalene* (XIII) was obtained (3·6 g.) as an oil, b. p. 168°/10 mm., when the above oil (5 g.) was heated with concentrated sulphuric acid (25 c.c.) for 10 minutes at 65—70° (Found: C, 77·6; H, 8·7. $C_{15}H_{20}O_2$ requires C, 77·6; H, 8·6%). It failed to yield a semicarbazone. This compound was also obtained when 1-keto-5-methoxy-7:8-dimethyl-1:2:3:4-tetrahydronaphthalene (5 g.), dissolved in a stirred solution of potassium (16 g.) in *tert.*-butyl alcohol (382 c.c.), was slowly treated with ethyl iodide (100 c.c.), and the mixture refluxed for 2 hours. Removal of solvent and addition of water yielded an oil (5·3 g.) which was extracted with ether, washed with sulphurous acid, dried, and distilled (Found: C, 77·7; H, 8·5%).

5-*Hydroxy*-7:8-*dimethyl*-2-*ethyl*-1:2:3:4-*tetrahydronaphthalene*. The foregoing oily ketone (9 g.) was reduced under Clemmensen conditions and the product was refluxed for 2·5 hours with hydriodic acid (25 c.c.) and glacial acetic acid (10 c.c.). The *hydroxy*-compound, which was extracted with ether, crystallised from light petroleum (b. p. 40—60°) as lustrous needles (6 g.), m. p. 97—98° (Found: C, 82·3; H, 10·1. $C_{14}H_{20}O$ requires C, 82·4; H, 9·8%). Light absorption: Maxima, 2200 A., log ε = 3·96; 2850 A., log ε = 3·32. This compound (Found: C, 82·2; H, 9·8%) was also obtained from the 1-keto-5-methoxy-7:8-dimethyl-2-ethyl-1:2:3:4-tetrahydronaphthalene obtained by direct ethylation.

3:4-*Dimethyl*-6-*ethyl*-1-*naphthol* (III). The preceding compound (0·8 g.) was dehydrogenated with selenium (2·4 g.) at 340—360° for 2·5 hours. The *product* (0·48 g.) crystallised from light petroleum (b. p. 40—60°) as needles, m. p. 76—77° (Found: C, 84·4; H, 8·0. $C_{14}H_{16}O$ requires C, 84·0; H, 8·0%). Its *picrate* crystallised from benzene–light petroleum (b. p. 40—60°) as scarlet needles, m. p. 135—136° (Found: C, 55·3; H, 4·4. $C_{20}H_{19}O_8N_3$ requires C, 55·9; H, 4·4%). Light absorption: Maxima, 2450 (2920) and 3050 (3100) A.; log ε = 4·67 (3·64) and 3·64 (3·71) respectively.

Attempts to prepare 3:4-*Dimethyl*-5-*ethyl*-1-*naphthol*.—4-*Methoxy*-1:2-*dimethyl*-8-*ethyl*-5:6-*dihydronaphthalene*. 1-Keto-5-methoxy-7:8-dimethyl-1:2:3:4-tetrahydronaphthalene (5·3 g.) in dry ether (75 c.c.) was slowly added to a solution of ethylmagnesium iodide, from ethyl iodide (10 c.c.) in ether (75 c.c.). The reaction was completed by 1 hour's refluxing and the mixture was decomposed with ice and hydrochloric acid and extracted with ether from which the unsaturated *compound* was obtained as an oil (4·9 g.), b. p. 156—159°/8 mm. (Found: C, 82·7; H, 9·0. $C_{15}H_{20}O$ requires C, 83·3; H, 9·3%).

When this product (6 g.) was refluxed with hydriodic acid (16 c.c.) for 2 hours and the product heated with selenium (8 g.) at 330—340° for 3·5 hours, the mixture yielded much tarry material and 3:4-dimethyl-1-naphthol (0·5 g.), m. p. 121·5°. A similar result was obtained when the product of the Grignard reaction was directly heated with selenium and then demethylated with hydrogen iodide.

1:2-*Dimethyl*-8-*ethylnaphthalene* (Found: C, 91·4; H, 8·6. $C_{14}H_{16}$ requires C, 91·3; H, 8·7%) was obtained (0·45 g.) as a colourless oil, b. p. 145—146°/10 mm., when the above unsaturated compound (0·6 g.) was reduced in acetic acid with palladised charcoal and the product was heated with palladised charcoal (0·5 g.) for 2 hours at 300—320°. Light absorption: Maxima, 2280, 2610, 2880, and 3210 A.; log ε = 4·72, 3·59, 3·69, and 2·81, respectively. Its *picrate* crystallised from methyl alcohol as orange-red needles, m. p. 91° (Found: C, 59·0; H, 4·35. $C_{20}H_{19}O_7N_3$ requires C, 58·1; H, 4·6%). Its *trinitrobenzene* derivative crystallised from methanol as dark yellow needles, m. p. 109° (Found: C, 60·5; H, 4·5. $C_{20}H_{19}O_6N_3$ requires C, 60·45; H, 4·8%). Its *trinitrotoluene* derivative crystallised from methanol as dark yellow needles, m. p. 82° (Found: C, 61·1; H, 4·9. $C_{21}H_{21}O_6N_3$ requires C, 61·3; H, 5·2%).

2-*Hydroxy*-4:5-*dimethylstyryl ethyl ketone*. 2-Hydroxy-4:5-dimethylbenzaldehyde (2·55 g.), prepared by the modification of the Gattermann reaction described by Adams and Levine (*J. Amer. Chem. Soc.*, 1923, **45**, 2373; Adams and Montgomery, *ibid.*, 1924, **46**, 1518), in 10% sodium hydroxide (35 c.c.) was treated with methyl ethyl ketone (10 c.c.) in water (80 c.c.). The solution was then refluxed for 3 days, acidified, and extracted with ether, from which the *ketone* was obtained as a brown oil. It quickly solidified and was thrice recrystallised from benzene–light petroleum (b. p. 60—80°) and obtained (0·5 g.)

as pale yellow needles, m. p. 143° (Found: C, 76·3; H, 7·9. $C_{13}H_{16}O_2$ requires C, 76·5; H, 7·8%). It yielded a 2 : 4-dinitrophenylhydrazone, m. p. 239—240°.

Attempts to obtain 1 : 2-*Dimethyl*-5-*ethyl*-4-*naphthol*.—4-(2-*Methoxy*-4 : 5-*dimethylphenyl*)*hex*-3-*enoic acid*. Ethyl β-(2-methoxy-4 : 5-dimethylbenzoyl)propionate (18 g.) in ether (250 c.c.) was added at 0° to a Grignard solution from ethyl iodide (15 g.). After being stirred for 2 hours in the cold the mixture was refluxed for 1 hour and decomposed with ammonium chloride. The ethereal layer was separated and extracted 3 times with 10% sodium carbonate, from which an oily mixture of isomeric acids (9·5 g.) was obtained. On rubbing with light petroleum (b. p. 40—60°) one of the required *acids* solidified and was crystallised from light petroleum as tablets, m. p. 82·5° (Found: C, 72·3; H, 8·2. $C_{15}H_{20}O_3$ requires C, 72·6; H, 8·1%).

4-(2-*Methoxy*-4 : 5-*dimethylphenyl*)*hexanoic acid*. Hydrogenation of either the mixture of acids or the pure acid mentioned above in presence of platinic oxide in ethyl acetate gave a quantitative yield of the saturated *acid*. It crystallised from light petroleum as sheaves of needles, m. p. 82—83°, depressed to 70° by its precursor (Found: C, 72·1; H, 8·5. $C_{15}H_{22}O_3$ requires C, 72·0; H, 8·8%).

The *lactone* of 4-hydroxy-4-(2-methoxy-4 : 5-dimethylphenyl)hexanoic acid was obtained when the above unsaturated acid was heated with potassium hydrogen sulphate at 160°. It crystallised from ligroin as prisms, m. p. 98—99° (Found: C, 72·7; H, 7·9. $C_{15}H_{20}O_3$ requires C, 72·6; H, 8·1%).

5-*Hydroxy*-1-*keto*-7 : 8-*dimethyl*-4-*ethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*. The hexanoic acid (7 g.), heated with 80% sulphuric acid (40 c.c.) at 100° for 3·5 hours, gave a mixture of the required *hydroxyketone* (2·5 g.), which crystallised from ligroin as fine needles, m. p. 156—157° (Found: C, 76·6; H, 8·4. $C_{14}H_{18}O_2$ requires C, 77·1; H, 8·2%), and its *methyl ether*, b. p. 160—163°/10 mm. (Found: C, 77·9; H, 9·3. $C_{15}H_{20}O_2$ requires C, 77·6; H, 8·6%).

5-*Hydroxy*-7 : 8-*dimethyl*-4-*ethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene and its methyl ether*. The preceding compounds were reduced under Clemmensen conditions, yielding the required *hydroxytetralins* as colourless oils, b. p. 158—160°/10 mm. (Found: C, 82·3; H, 10·1. $C_{14}H_{20}O$ requires C, 82·3; H, 9·8%) and 140—142°/10 mm. (Found: C, 82·5; H, 10·3. $C_{15}H_{22}O$ requires C, 82·6; H, 10·1%), respectively. Efforts to dehydrogenate these compounds were unsuccessful.

B. Experiments with o-3-*Xylenol.*

1 : 2-*Dimethyl*-5-*ethyl*-3-*naphthol* (IV).—3-*Methoxy*-1 : 2-*dimethyl*-5-*ethyl*-7 : 8-*dihydronaphthalene*. 1-Keto-7-methoxy-5 : 6-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene (Cocker, *J.*, 1946, 36) (5·7 g.), allowed to react in the usual way with ethylmagnesium iodide [prepared from ethyl iodide (9·2 c.c.)], yielded an oil (6·1 g.) which was heated at 160° with potassium hydrogen sulphate (6·0 g.). The mixture was extracted with ether, yielding the required *ether* (2·8 g.), which crystallised from methanol as prisms, m. p. 82·5° (Found: C, 84·0; H, 8·5. $C_{15}H_{20}O$ requires C, 83·3; H, 9·3%).

1 : 2-*Dimethyl*-5-*ethyl*-3-*naphthol* (IV). The foregoing dihydro-compound (0·7 g.) was simultaneously demethylated and dehydrogenated when refluxed for 2 hours with hydriodic acid containing iodine (4 c.c.). The product was first sublimed and was then crystallised from light petroleum (b. p. 60—80°), yielding the *naphthol* as feathery needles (0·5 g.), m. p. 121° (Found: C, 83·5, 83·8; H, 7·9, 8·0. $C_{14}H_{16}O$ requires C, 84·0; H, 8·0%). Light absorption: Maxima, 2380, 2760, 2860, 2970, 3230, and 3370 A.; log ε = 4·62, 3·68, 3·85, 3·82, 3·39, and 3·49, respectively. Its *picrate* crystallised from benzene–light petroleum (b. p. 80—100°) as deep-red needles, m. p. 118—119° (Found: C, 55·5; H, 4·4. $C_{20}H_{19}O_8N_3$ requires C, 55·9; H, 4·4%).

1 : 2-*Dimethyl*-6-*ethyl*-3-*naphthol* (V).—*Ethyl* γ-(4-*methoxy*-2 : 3-*dimethylphenyl*)*butyrate* was obtained as an oil, b. p. 166—168°/2—3 mm., when the corresponding acid (Cocker, *J.*, 1946, 36) was refluxed for 4 hours with alcohol and sulphuric acid (Found: C, 72·1; H, 8·8. $C_{15}H_{22}O_3$ requires C, 72·0; H, 8·8%).

Ethyl 7-*methoxy*-5 : 6-*dimethyl*-3 : 4-*dihydronaphthalene*-2-*carboxylate*. Absolute alcohol (8 c.c.) was slowly added to powdered sodium (3·14 g.) in dry ether (65 c.c.), and the mixture was refluxed until the sodium had dissolved. The solution was cooled to −15° and a mixture of the above ester (15·7 g.), ethyl formate (9·5 c.c.), and ether (50 c.c.) was added dropwise with stirring during 1 hour. The mixture was set aside at room temperature for 72 hours, powdered ice was added, and the ethereal layer containing unchanged butyric ester (8·5 g.) was separated. The aqueous layer was acidified and the crude formyl compound (3·8 g.) which separated was collected with ether and dried. The solvent was removed and the residue was added at −10° to a well-stirred mixture of 90% phosphoric acid (15·5 c.c.) and concentrated sulphuric acid (3·3 c.c.). The mixture, allowed to warm to 10° during 2 hours, was poured on ice and extracted with ether. The aqueous solution was nearly neutralised with sodium hydroxide and again extracted with ether. The combined extracts, washed first with sodium hydrogen carbonate and then with water and dried, yielded the required *ester* (3·35 g.) which crystallised from dilute alcohol as needles, m. p. 65—68° (Found: C, 73·7; H, 7·8. $C_{16}H_{20}O_3$ requires C, 73·8; H, 7·7%). Light absorption: Maxima, 2440, 3020, and 3350 A.; log ε = 4·25, 4·13, and 3·88, respectively.

7-*Methoxy*-5 : 6-*dimethyl*-3 : 4-*dihydronaphthalene*-2-*carboxylic acid* separated from alcohol as prisms, m. p. 232° (Found: C, 72·0; H, 7·1. $C_{14}H_{16}O_3$ requires C, 72·4; H, 6·9%). Light absorption: Maxima, 2430, 3020, and 3330 A.; log ε = 4·25, 4·1, and 3·84, respectively.

7-*Methoxy*-5 : 6-*dimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-2-*carboxylic acid* was obtained (1·3 g.) when the preceding compound (1·35 g.) was reduced in ethyl acetate (100 c.c.) using palladised charcoal (0·1 g.). The saturated acid crystallised from dilute alcohol as prisms, m. p. 190° (Found: C, 71·8; H, 7·65. $C_{14}H_{18}O_3$ requires C, 71·8; H, 7·7%). Its *amide*, prepared from the crude acid chloride, crystallised from dilute alcohol as needles, m. p. 216° (Found: C, 71·9; H, 7·8. $C_{14}H_{19}O_2N$ requires C, 72·1; H, 8·2%).

7-*Methoxy*-2-*acetyl*-5 : 6-*dimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*. A suspension of the above amide (0·5 g.) in anisole (50 c.c.) was added to a Grignard solution prepared from magnesium (0·7 g.) and ethyl iodide (4·2 g.) in anisole (25 c.c.), and the mixture was refluxed in an atmosphere of nitrogen for 50 hours. The mixture was worked up in the usual way and the product (50 mg.) was crystallised from alcohol, from

which the required *ketone* separated as clusters of needles, m. p. 120—122° (Found : C, 76·8; H, 8·3. $C_{15}H_{20}O_2$ requires C, 77·6; H, 8·6%). It yielded a 2 : 4-dinitrophenylhydrazone.

Ethyl 1-*keto*-7-*methoxy*-5 : 6-*dimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-2-*glyoxylate* (XI). 1-Keto-7-methoxy-5 : 6-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene (Cocker, *loc. cit.*) (10 g.) was condensed in the usual way with ethyl oxalate in presence of potassium ethoxide. The *glyoxylate* (7·5 g.; m. p. 94—95°) crystallised from alcohol as scarlet prisms, m. p. 95—96° (Found : C, 66·7; H, 6·7. $C_{17}H_{20}O_5$ requires C, 67·1; H, 6·6%). Light absorption : Maxima, 3250 A.; log ε = 4·01; 3750 A.; log ε = 4·02.

Ethyl 1-*keto*-7-*methoxy*-5 : 6-*dimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-2-*carboxylate* (XII) was obtained (1·8 g.) when the glyoxylate (2 g.) was heated for 1 hour with powdered glass (3 g.). It crystallised from alcohol as needles, m. p. 99·5° (Found : C, 69·1; H, 7·7. $C_{16}H_{20}O_4$ requires C, 69·6; H, 7·2%). Light absorption : Maxima, 2240, 2710, 3100, and 3290 A.; log ε = 4·26, 4·1, 3·63, and 3·70, respectively.

1-*Keto*-7-*methoxy*-5 : 6-*dimethyl*-2-*ethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*. A solution of the preceding compound (3·7 g.) in *tert.*-butyl alcohol (40 c.c.) was added to potassium *tert.*-butoxide [from potassium (2·0 g.) and *tert.*-butyl alcohol (60 c.c.)]. Ethyl iodide (15 c.c.) was then slowly added, with stirring, in the cold, and the mixture was refluxed for 3 hours and set aside overnight. The alcohol was removed, the residue was diluted with water and extracted with ether and the extract was washed several times with cold 40% sodium hydroxide solution. The dried extract was distilled, yielding an oil (1·7 g.), b. p. 174—180°/5 mm., which was refluxed for 2 hours with potassium hydroxide (0·5 g.) in methyl alcohol (10 c.c.). The solid product was crystallised several times from light petroleum (b. p. 40—60°), from which the required *ketone* separated as prisms (0·5 g.), m. p. 66° (Found : C, 77·4; H, 8·5. $C_{15}H_{20}O_2$ requires C, 77·6; H, 8·6%).

7-*Hydroxy*-5 : 6-*dimethyl*-2-*ethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*. The preceding compound (0·4 g.) was reduced under Clemmensen conditions and gave an oil which was refluxed for 1·5 hours with hydriodic acid (4 c.c.) and acetic acid (10 c.c.). The required *hydroxytetralin* (0·3 g.) crystallised from light petroleum (b. p. 60—80°) as prisms, m. p. 93° (Found : C, 82·0; H, 9·5. $C_{14}H_{20}O$ requires C, 82·4; H, 9·8%). Light absorption : Maxima, 2200 A., log ε = 3·94; 2870 A., log ε = 3·41.

α-*Ethyl*-β-(4-*methoxy*-2 : 3-*dimethylbenzoyl*)*propionic acid*. *o*-3-Xylyl methyl ether (16 g.) was condensed with ethylsuccinic anhydride (16 g.) and aluminium chloride (26 g.). The product was crystallised several times from benzene–light petroleum (b. p. 100—120°), from which the required *acid* (18 g.) separated as needles, m. p. 135° (Found : C, 67·7; H, 7·5. $C_{15}H_{20}O_4$ requires C, 68·2; H, 7·6%).

α-*Ethyl*-γ-(4-*methoxy*-2 : 3-*dimethylphenyl*)*butyric acid*. The above keto-acid (12·2 g.), reduced under Clemmensen conditions, yielded a solid which, after 3 crystallisations from light petroleum (b. p. 40—60°), yielded the required *acid* (12·2 g.) as radiating needles, m. p. 78° (Found : C, 71·7; H, 8·7. $C_{15}H_{22}O_3$ requires C, 72·0; H, 8·8%). Heated for 10 minutes at 65—70° with concentrated sulphuric acid (10 c.c.), this (2·7 g.) yielded 1-keto-7-methoxy-5 : 6-dimethyl-2-ethyl-1 : 2 : 3 : 4-tetrahydronaphthalene (2·0 g.), m. p. 66°, undepressed by the ketone prepared as described above. It yielded 7-hydroxy-5 : 6-dimethyl-2-ethyl-1 : 2 : 3 : 4-tetrahydronaphthalene after reduction and demethylation.

1 : 2-*Dimethyl*-6-*ethyl*-3-*naphthol* (V). 7-Hydroxy-5 : 6-dimethyl-2-ethyl-1 : 2 : 3 : 4-tetrahydronaphthalene (0·4 g.) was heated with powdered selenium (1·2 g.) for 2·5 hours at 340—360°. The product was crystallised from benzene–light petroleum (b. p. 40—60°) from which the required *naphthol* (0·15 g.) separated as long needles, m. p. 102—102·5° (Found : C, 84·4; H, 8·2. $C_{14}H_{16}O$ requires C, 84·0; H, 8·0%). Light absorption : Maxima, 2370 (2740), 2860 (2960), 3190, and 3330 A.; log ε = 4·81 (3·55), 3·64 (3·54), 3·22, and 3·34, respectively.

Direct Ethylation of 1-*Keto*-7-*methoxy*-5 : 6-*dimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*.—This ketone (3 g.) was added to a solution of potassium (9·6 g.) in *tert.*-butyl alcohol (180 c.c.), and the mixture stirred for 1 hour with ethyl iodide (60 c.c.) and then refluxed for 2 hours. The product, an oil (2·9 g.), b. p. 185°/5 mm., solidified and was then crystallised from light petroleum (b. p. 40—60°) from which it separated as prisms, m. p. 52—53° (Found : C, 78·0, 78·6; H, 8·8, 9·2. $C_{17}H_{24}O_3$ requires C, 78·5; H, 9·2%). The product was probably 1-*keto*-7-*methoxy*-5 : 6-*dimethyl*-2 : 2-*diethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*. Complete reduction of this ketone (3 g.) under Clemmensen conditions took about 72 hours, the supposed 7-*methoxy*-5 : 6-*dimethyl*-2 : 2-*diethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* being obtained as an oil (1·7 g.), b. p. 166°/1—2 mm. (Found : C, 82·2; H, 10·5. $C_{17}H_{26}O$ requires C, 82·9; H, 10·6%).

When the ketone (1 g.) was heated for 1 hour with hydriodic acid (5 c.c.) it yielded a glass which solidified on being rubbed with light petroleum (b. p. 40—60°). On crystallisation from this solvent the supposed 7-*hydroxy*-1-*keto*-5 : 6-*dimethyl*-2 : 2-*diethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* separated as needles, m. p. 149° (Found : C, 77·7; H, 8·6. $C_{16}H_{22}O_2$ requires C, 78·0; H, 8·9%).

C. Experiments with m-4-*Xylenol*.

Attempts to prepare 1 : 3-*Dimethyl*-5-*ethyl*-4-*naphthol*.—1-Keto-8-methoxy-5 : 7-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene (5 g.) (cf. Cocker and Lipman, and Cocker, Lipman, and Whyte, *locc. cit.*) and ethylmagnesium iodide [from ethyl iodide (4 c.c.)] gave 5-*methoxy*-6 : 8-*dimethyl*-4-*ethyl*-1 : 2-*dihydronaphthalene* as an oil (2·9 g.), b. p. 135°/10 mm. (Found : C, 82·9; H, 9·1. $C_{15}H_{20}O$ requires C, 83·3; H, 9·2%). When this compound (3·4 g.) was heated with sulphur (1·2 g.) at 205—210° for 4 hours and the product demethylated, 2 : 4-dimethyl-1-naphthol was produced.

Ethyl γ-(5-*methoxy*-2 : 4-*dimethylphenyl*)*butyrate*, prepared from the corresponding acid (Cocker and Lipman, *loc. cit.*), distilled at 157°/3 mm. (Found : C, 72·0; H, 8·8. $C_{15}H_{22}O_3$ requires C, 72·0; H, 8·8%).

Ethyl 5-*methoxy*-6 : 8-*dimethyl*-1 : 2-*dihydronaphthalene*-3-*carboxylate* was obtained (2·3 g.) as a yellow oil from the above ester (10 g.) by condensation with ethyl formate (see above). It was refluxed for 4 hours with 10% methyl-alcoholic potash (40 c.c.), yielding 5-methoxy-6 : 8-dimethyl-1 : 2-dihydronaphthalene-3-carboxylic acid (1·9 g.), which separated from dilute alcohol in needles, m. p. 212—213° (Found : C, 71·7, 72·0; H, 6·9. $C_{14}H_{16}O_3$ requires C, 72·4; H, 6·9%).

5-*Methoxy*-6 : 8-*dimethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-3-*carboxylic Acid*.—The preceding compound was quantitatively reduced in ethyl acetate over palladised charcoal, yielding the required saturated *acid* which separated from alcohol as prisms, m. p. 158° (Found : C, 71·9; H, 7·45. $C_{14}H_{18}O_3$

requires C, 71·8; H, 7·7%). Its *amide* separated from dilute alcohol as needles, m. p. 199—200° (Found: C, 71·8; H, 8·3. $C_{14}H_{19}O_2N$ requires C, 72·1; H, 8·2%).

2 : 4-*Dimethyl*-7-*ethyl*-1-*naphthol* (VI).—*α-Ethyl-β-*(5-*methoxy*-2 : 4-*dimethylbenzoyl*)*propionic acid* (XXI). *m*-4-Xylyl methyl ether (31 g.) condensed with ethylsuccinic anhydride (30 g.) and aluminium chloride (25 g.) to yield a sticky product which solidified when rubbed with benzene–light petroleum (b. p. 60—80°). After several crystallisations from this mixture the required *acid* was obtained as colourless needles (11 g.), m. p. 64° * (Found: C, 68·1; H, 7·65. $C_{15}H_{20}O_4$ requires C, 68·2; H, 7·6%). Its *semicarbazone* separated from alcohol as needles, m. p. 165—166° (Found: C, 59·6; H, 7·0. $C_{16}H_{23}O_4N_3$ requires C, 59·8; H, 7·2%). Oxidation of the keto-acid with sodium hypochlorite yielded 5-*methoxy*-2 : 4-*dimethylbenzoic acid* which separated from dilute alcohol as needles, m. p. 164° (Found: C, 66·7; H, 6·6. $C_{10}H_{12}O_3$ requires C, 66·7; H, 6·7%). It was demethylated with hydriodic acid in acetic acid to 5-hydroxy-2 : 4-dimethylbenzoic acid, which crystallised from dilute alcohol as plates, m. p. 185—186° (Meisenheimer, Hanssen, and Wachterowitz, *J. pr. Chem.*, 1928, [ii], **119**, 315, give m. p. 185—186°). 5-Methoxy-2 : 4-dimethylbenzoic acid was also obtained by the oxidation of the known 5-methoxy-2 : 4-dimethylacetophenone (von Auwers and Mauss, *loc. cit.*) with sodium hypochlorite.

α-Ethyl-β-(5-*hydroxy*-2 : 4-*dimethylbenzoyl*)*propionic acid* obtained by heating the methoxy-acid with hydriodic acid separated from ethyl acetate–light petroleum as needles, m. p. 144° (Found: C, 67·0; H, 7·2. $C_{14}H_{18}O_4$ requires C, 67·2; H, 7·2%).

8-*Hydroxy*-1-*keto*-5 : 7-*dimethyl*-2-*ethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*.—The methoxy-acid (XXI) (7·5 g.) was reduced under Clemmensen conditions to an oil (7 g.) which was heated with 80% sulphuric acid (40 c.c.) for 2 hours on the water-bath and afforded 8-*hydroxy*-1-*keto*-5 : 7-*dimethyl*-2-*ethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (4 g.), b. p. 163°/10 mm., which solidified and then crystallised from dilute alcohol as needles, m. p. 28° (Found: C, 76·9; H, 8·1. $C_{14}H_{18}O_2$ requires C, 77·1; H, 8·3%).

8-*Hydroxy*-5 : 7-*dimethyl*-2-*ethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*.—The preceding compound (3·5 g.) was reduced (Clemmensen); the *product* (3 g.) separated from light petroleum (b. p. 40—60°) as needles, m. p. 80° (Found: C, 82·8; H, 10·5. $C_{14}H_{20}O$ requires C, 82·4; H, 9·8%). Light absorption: Maxima, 2200 A., log ε = 4·05; 2720 A., log ε = 3·42.

2 : 4-*Dimethyl*-7-*ethyl*-1-*naphthol* (VI).—The foregoing hydroxytetralin (0·5 g.) was heated at 340—360° for 2·5 hours with selenium (1·5 g.), and the product was crystallised from light petroleum (b. p. 40—60°) from which the *naphthol* separated as needles m. p. 110° (Found: C, 83·3, 83·5; H, 8·1, 7·8. $C_{14}H_{16}O$ requires C, 84·0; H, 8·0%). Light absorption: Maxima, 2400, 3030 (3160), and 3400 A.; log ε = 4·62, 3·72 (3·64), and 3·50, respectively. Its *carbanilate* separated from aqueous alcohol as needles, m. p. 144° (Found: C, 79·2; H, 6·5. $C_{21}H_{21}O_2N$ requires C, 79·0; H, 6·6%). Its *picrate* separated from benzene as scarlet needles, m. p. 123—124° (Found: C, 55·4; H, 4·6. $C_{20}H_{19}O_8N_3$ requires C, 55·9; H, 4·4%).

The mother-liquors from the crystallisation of the methoxy-keto-acid described yielded an oily acid. This (8 g.) was reduced (Clemmensen) and cyclised with concentrated sulphuric acid to a mixture of methoxytetralones (3·6 g.), b. p. 168°/3 mm. (Found: C, 77·4; H, 8·4. Calc. for $C_{15}H_{20}O_2$: C, 77·6; H, 8·6%), which yielded a *semicarbazone* (1·2 g.), m. p. 190—191° (Found: C, 65·7; H, 8·2. $C_{16}H_{23}O_2N_3$ requires C, 66·4; H, 8·0%). This was probably the semicarbazone of 1-*keto*-5-*methoxy*-6 : 8-*dimethyl*-3-*ethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* since on reduction by the Huang-Minlon modification of the Wolff–Kishner reaction and then demethylation it (1·2 g.) afforded 8-hydroxy-5 : 7-dimethyl-2-ethyl-1 : 2 : 3 : 4-tetrahydronaphthalene (0·5 g.).

3-*Carbethoxy*-4-(p-*ethylphenyl*)-2-*methylpent*-3-*enoic Acid* (XXIII).—A mixture of *p*-ethylacetophenone (10·4 g.), ethyl methylsuccinate (21·2 g.), and *tert.*-butyl alcohol (15 c.c.) was added to a solution of potassium (1·32 g.) in *tert.*-butyl alcohol (60 c.c.), and the mixture was refluxed for 40 minutes. After cooling, the mixture was rendered faintly acid and the solvent was removed under reduced pressure. The residue was extracted with ether which was washed with water and then shaken several times with saturated sodium carbonate. The filtered alkaline extracts were acidified, yielding a mixture of half-esters as an orange oil (20 g.) which partly solidified. The solid half-*ester* (2 g.) was collected and crystallised from light petroleum (b. p. 40—60°) from which it separated as needles, m. p. 112—113° (Found: C, 70·0; H, 7·4. $C_{17}H_{22}O_4$ requires C, 70·4; H, 7·6%). The half-ester was refluxed with 15% hydrochloric acid, yielding 3-*carboxy*-4-(p-*ethylphenyl*)-2-*methylpent*-3-*enoic acid* which separated from water as needles, m. p. 142° (Found: C, 68·3; H, 6·9. $C_{15}H_{18}O_4$ requires C, 68·7; H, 6·9%). On distillation, the oily half-ester yielded a *dicarboxylic acid*, m. p. 155° (Found: C, 68·2; H, 6·9%). On storage, the latter dicarboxylic acid was transformed into the former, m. p. 142°.

Lactone of 4-*Hydroxy*-4-(p-*ethylphenyl*)-2-*methylpentanoic acid* (XXV).—The oily half-ester (5 g.) was refluxed for several hours with a mixture of glacial acetic acid (15 c.c.) and 48% hydrobromic acid (20 c.c.), and the oily *lactone* (2·5 g.) was collected, having b. p. 182—184°/10 mm. (Found: C, 76·9; H, 8·2. $C_{14}H_{18}O_2$ requires C, 77·1; H, 8·3%).

α-(1-*Keto*-3-*methyl*-6-*ethyl*-2-*indenyl*)*propionic Acid* (XXVI).—The oily half-ester (1 g.) was heated at 65—70° for 10 minutes with concentrated sulphuric acid (5 g.). The *product* (0·3 g.) crystallised from benzene–light petroleum (b. p. 60—80°) as white needles, m. p. 83° (Found: C, 73·7; H, 6·6. $C_{15}H_{16}O_3$ requires C, 73·8; H, 6·6%). Its *semicarbazone* separated from benzene–light petroleum as needles, m. p. 190° (Found: C, 63·7; H, 6·3. $C_{16}H_{19}O_3N_3$ requires C, 63·8; H, 6·3%). *α-*(1-*Keto*-3-*methyl*-6-*ethyl*-2-*indanylidene*)*propionic acid* (XXVII) was obtained as yellow needles (from alcohol), m. p. 122°, when its isomer was heated with alcoholic potash (Found: C, 73·1; H, 6·1%).

1-*Keto*-2 : 4-*dimethyl*-7-*ethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (XXVIII).—A mixture of methyl β-bromo*iso*butyrate (58 g.) (Pickard and Lochte, *J. Amer. Chem. Soc.*, 1947, **69**, 15), *p*-ethylacetophenone (47·2 g.), and xylene (50 c.c.) was added to a boiling mixture of magnesium (8·4 g.) and xylene (50 c.c.) to which a crystal of iodine had been added. After 3 hours' refluxing and stirring, all the magnesium had dissolved; the mixture was then treated with dilute sulphuric acid and ice, and the dried xylene layer was distilled, yielding a viscous yellow oil (46·5 g.). This was refluxed for 2 hours with potassium

* Another modification of this acid melted at 83°. Crystallisation of the latter from dilute alcohol gave the form of m. p. 64°. Both gave the same benzoic acid on oxidation and on demethylation.

hydrogen sulphate (90 g.), and the unsaturated esters (34·6 g.) were collected at 170—220°/10 mm. Hydrolysis with alcoholic potash gave a liquid mixture of acids which when shaken with 70% sulphuric acid yielded the lactone of 4-hydroxy-4-(*p*-ethylphenyl)-2-methylpentanoic acid (Found : C, 77·4; H, 8·4%).

The mixture of unsaturated acids (3·0 g.) was refluxed with hydriodic acid (15 c.c.) and red phosphorus (3 g.) for 5 hours, yielding an oil which no longer decolorised bromine. The oil was heated on the water-bath for 1 hour with a mixture of concentrated sulphuric acid (7 c.c.) and water (1·5 c.c.), and 1-*keto*-2 : 4-*dimethyl*-7-*ethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (XXVIII) was obtained as an oil (1·0 g.), b. p. 136°/10 mm. (Found : C, 83·2; H, 8·9. $C_{14}H_{18}O$ requires C, 83·2; H, 8·9%). Its *semicarbazone* separated as silvery plates (from dilute alcohol), m. p. 202—203° (Found : C, 68·9; H, 7·95. $C_{15}H_{21}ON_3$ requires C, 69·5; H, 8·1%).

2 : 4-*Dimethyl*-7-*ethyl*-1-*naphthol* (VI).—The ketone (XXVIII) (0·6 g.) in anhydrous ether (8 c.c.) was slowly treated at room temperature with bromine (0·15 c.c.) in ether (5 c.c.). After 15 minutes, the solution was washed with aqueous sodium hydrogen carbonate, and a colourless oil was obtained. This was refluxed with dimethylaniline (2·5 c.c.) for 50 minutes and the solution was then added to excess of dilute sulphuric acid and distilled in steam. The filtered distillate yielded the required naphthol which crystallised from light petroleum (b. p. 40—60°) as needles, m. p. 110—111°, which gave no depression with the naphthol already described (Found : C, 83·7; H, 7·95%). Its picrate and carbanilate (Found : C, 78·7; H, 6·6%) gave no depression in m. p. with the compounds prepared by the alternative method described above.

ω-*Chloro*-5-*methoxy*-2 : 4-*dimethylacetophenone*.—A solution of aluminium chloride (42 g.) in nitrobenzene (100 c.c.) was added to a stirred mixture of *m*-4-xylyl methyl ether (29·5 g.) and chloroacetyl chloride (25 g.), and the solution was set aside overnight. It was treated in the usual way and the product was extracted with chloroform and distilled. The oil (22 g.) which collected at 160—170°/2—3 mm. solidified (m. p. 82—84°) and crystallised from benzene–light petroleum as plates, m. p. 85—86° (Found : C, 61·8; H, 6·0. $C_{11}H_{13}O_2Cl$ requires C, 62·1; H, 6·1%).

5-*Methoxy*-2 : 4-*dimethylbenzyl Alcohol*.—5-Methoxy-2 : 4-dimethylbenzoic acid (2·5 g.) in dry ether (175 c.c.) was added slowly to a stirred suspension of lithium aluminium hydride (1 g.) in dry ether (200 c.c.) at such a rate as to maintain gentle reflux. The mixture was then gently refluxed for a further 30 minutes, cooled, and slowly treated with water and then with dilute sulphuric acid, and the ethereal layer separated. It was washed several times with dilute sodium carbonate solution and dried and the solvent removed, yielding the required *alcohol* (2·35 g.) which separated from light petroleum (b. p. 40—60°) as needles, m. p. 56—57° (Found : C, 71·8; H, 8·9. $C_{10}H_{14}O_2$ requires C, 72·3; H, 8·4%).

5-*Methoxy*-2 : 4-*dimethylbenzyl Chloride*.—The above alcohol (10·7 g.) was slowly treated in the cold with thionyl chloride (7·7 g.). A further, equal quantity of thionyl chloride was then added and the mixture set aside overnight, whereafter it was gently refluxed for 30 minutes. Excess of thionyl chloride was removed, and the residue was washed with aqueous sodium carbonate, dried in ether, and distilled, yielding the *chloro*-compound as an oil (8·5 g.), b. p. 122°/3 mm. (Found : C, 64·9; H, 6·5. $C_{10}H_{13}OCl$ requires C, 65·0; H, 7·1%).

Ethyl (5-*Methoxy*-2 : 4-*dimethylbenzyl*)*ethylmalonate*.—A mixture of sodium ethoxide [from sodium (1·74 g.) and absolute alcohol (45 c.c.)], ethyl ethylmalonate (14·3 g.), and sodium iodide (1 g.) was slowly treated with the above chloride (8·5 g.). Stirring was continued for 30 minutes and the mixture was refluxed for 6 hours. It was processed in the usual way and the required *ester* was obtained as an oil (13 g.), b. p. 182°/1 mm. (Found : C, 68·5; H, 8·3. $C_{19}H_{28}O_5$ requires C, 67·9; H, 8·3%).

D. Experiments with p-*Xylenol.*

1 : 4-*Dimethyl*-6-*ethyl*-3-*naphthol* (VII).—α-*Ethyl*-β-(4-*methoxy*-2 : 5-*dimethylbenzoyl*)*propionic acid* (XVII). *p*-Xylyl methyl ether (9 g.) was condensed with ethylsuccinic anhydride (8·7 g.), by use of aluminium chloride (22·5 g.). The crude product (13·5 g.; m. p. 96—104°) was crystallised several times from ligroin (b. p. 120°), from which the required *acid* was obtained as radiating rods (4·05 g.), m. p. 123—124° (Found : C, 68·0; H, 7·4. $C_{15}H_{20}O_4$ requires C, 68·2; H, 7·6%). Its *semicarbazone* crystallised from methanol as needles, m. p. 184° (decomp.) (Found : C, 59·7; H, 7·2. $C_{16}H_{23}O_4N_3$ requires C, 59·8; H, 7·2%). The mother-liquors from the crystallisation of the acid yielded a solid, m. p. 97—107° (see below).

α-*Ethyl*-γ-(4-*methoxy*-2 : 5-*dimethylphenyl*)*butyric acid*. The keto-acid (XVII) (3·9 g.) was reduced by amalgamated zinc (40 g.) to the required *butyric acid*, which crystallised from light petroleum (b. p. 40—60°) as colourless rods (3·3 g.), m. p. 55—56° (Found : C, 71·9; H, 9·1. $C_{15}H_{22}O_3$ requires C, 72·0; H, 8·8%).

7-*Hydroxy*-1-*keto*-5 : 8-*dimethyl*-2-*ethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (XVIII). The preceding compound (3·2 g.), heated with 80% sulphuric acid (15·5 c.c.) at 100° for 2 hours, yielded the *ketone* which crystallised from light petroleum (b. p. 40—60°) as radiating plates (1·45 g.), m. p. 78—79° (Found : C, 77·3; H, 8·6. $C_{14}H_{18}O_2$ requires C, 77·1; H, 8·3%). It did not yield a semicarbazone.

7-*Hydroxy*-5 : 8-*dimethyl*-2-*ethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*. The foregoing ketone (1·1 g.) was reduced with amalgamated zinc, and the required *hydroxytetralin* was crystallised from light petroleum (b. p. 40—60°), from which it was deposited as prisms (0·66 g.), m. p. 75° (Found : C, 82·2; H, 9·6. $C_{14}H_{20}O$ requires C, 82·35; H, 9·8%).

1 : 4-*Dimethyl*-6-*ethyl*-3-*naphthol* (VII). The hydroxytetralin (0·45 g.) was dehydrogenated with selenium (1·5 g.) at 340—350° for 2 hours. The required naphthol was extracted with methyl alcohol and crystallised from light petroleum (b. p. 60—80°) as fine needles (0·2 g.), m. p. 123° (Found : C, 83·9; H, 8·0. Calc. for $C_{14}H_{16}O$: C, 84·0; H, 8·0%). Light absorption : Maxima, 2380 (2780), 2890, 3000, 3300, and 3390 A.; log ε = 4·83 (3·61), 3·73, 3·68, 3·38, and 3·41, respectively. Its *carbanilate* crystallised from alcohol as slender rods, m. p. 138—139° (Found : C, 78·4; H, 6·7. $C_{21}H_{21}O_2N$ requires C, 79·0; H, 6·6%). Its *picrate* crystallised from benzene as red needles, m. p. 130—131° (Found : C, 55·8; H, 4·45. $C_{20}H_{19}O_8N_3$ requires C, 55·9; H, 4·4%).

When the crude α-ethyl-β-(4-methoxy-3 : 5-dimethylbenzoyl)propionic acid (XVII), m. p. 97—107° (6·5 g.), was reduced by amalgamated zinc, the second butyric acid, *β-ethyl-γ-(4-methoxy-2 : 5-dimethylphenyl)butyric acid* was obtained which crystallised from light petroleum (b. p. 40—60°) as prisms (2·1 g.), m. p. 86—87° (Found : C, 71·7; H, 8·6. $C_{15}H_{22}O_3$ requires C, 72·0; H, 8·8%). On treatment with 80% sulphuric acid on the boiling water-bath, the preceding compound (2·0 g.) yielded *7-hydroxy-1-keto-5 : 8-dimethyl-3-ethyl-1 : 2 : 3 : 4-tetrahydronaphthalene* (XIX), which crystallised from 90% alcohol (charcoal) as fine needles (1·3 g.), m. p. 185—186° (Found : C, 76·9; H, 8·2. $C_{14}H_{18}O_2$ requires C, 77·1; H, 8·3%). Its *semicarbazone* crystallised from alcohol as prisms, m. p. 230—231° (Found : C, 65·1; H, 7·5. $C_{15}H_{21}O_2N_3$ requires C, 65·45; H, 7·6%).

The compound (XIX) (0·7 g.) was reduced with amalgamated zinc (20 g.) and concentrated hydrochloric acid (20 c.c.). An oil (0·65 g.) was obtained which was dehydrogenated with selenium (1·8 g.) in the usual way, and the product distilled in steam. The solid obtained was sublimed in a vacuum and crystallised from light petroleum (b. p. 40—60°), yielding 1 : *4-dimethyl-6-ethyl-2-naphthol* (VIII) as radiating needles (0·13 g.), m. p. 92·5° (Found : C, 84·3; H, 7·9. $C_{14}H_{16}O$ requires C, 84·0; H, 8·0%). Light absorption : Maxima, 2380 (2740), 2840, 2940, and 3360 A.; log ε = 4·85 (3·62), 3·73, 3·65, and 3·46, respectively. Its *carbanilate* crystallised from alcohol as fine needles, m. p. 186—187° (Found : C, 78·6; H, 6·6. $C_{21}H_{21}O_2N$ requires C, 79·0; H, 6·6%).

4-Methyl-7-ethyl-1-naphthol (X).—*Methyl β-(4-ethylbenzoyl)propionate*, obtained from its acid (cf. Levy, *Ann. Chim.*, 1938, **9**, 59), consisted of an oil, b. p. 187—188°/10 mm. (Found : C, 71·1; H, 7·3. $C_{13}H_{16}O_3$ requires C, 70·9; H, 7·3%). Its constitution was confirmed by oxidation with alkaline hypochlorite to *p*-ethylbenzoic acid.

4-(p-Ethylphenyl)pent-3-enoic acid. A Grignard solution from magnesium (2·3 g.), methyl iodide (12·8 g.), and ether (70 c.c.) was added at 0° to the preceding ester (18 g.), and the mixture was refluxed for 2 hours. After decomposition of the product, the ethereal solution was extracted several times with 12% sodium carbonate solution from which the required *acid* (4·5 g.), m. p. 56—57°, was obtained as silvery plates (from light petroleum) (Found : C, 76·4; H, 7·9. $C_{13}H_{16}O_2$ requires C, 76·5; H, 7·8%).

1-Keto-4-methyl-7-ethyl-1 : 2 : 3 : 4-tetrahydronaphthalene. The above unsaturated acid (1·0 g.) was heated with hydriodic acid (7 c.c.) and red phosphorus (1·0 g.) for 6 hours and the product (0·5 g.) heated on the water-bath for 2 hours with a mixture of sulphuric acid (2·5 c.c.) and water (0·5 c.c.). The required tetralone was obtained as an oil (0·2 g.), b. p. 138—139°/1 mm. Its *semicarbazone* separated from alcohol as needles, m. p. 188—189° (Found : C, 68·4; H, 7·5. $C_{14}H_{19}ON_3$ requires C, 68·6; H, 7·8%).

4-Methyl-7-ethyl-1-naphthol (X). The above tetralone (1·0 g.) was brominated and dehydrobrominated as described above, yielding the required *naphthol*, which crystallised from light petroleum (b. p. 40—60°) as sheaves of needles (80 mg.), m. p. 75° (Found : C, 83·8; H, 7·5. $C_{13}H_{14}O$ requires C, 83·9; H, 7·5%). Light absorption : Maxima, 2420, 3040 (3160), and 3310 A.; log ε = 4·57, 3·76 (3·69), and 3·56, respectively. Its *picrate* consisted of scarlet needles (from benzene), m. p. 132—133° (Found : C, 54·95; H, 3·9. $C_{19}H_{17}O_8N_3$ requires C, 54·9; H, 4·1%).

Dehydrogenation of Desmotropo-ψ-santonin.—(+)-β-Desmotropo-ψ-santonin (1 g.) was heated with palladised charcoal (1·25 g.) at 250—280° for 55 hours in a sealed tube. The mixture was then extracted several times with methyl alcohol, and the extract was distilled in steam, yielding a *solid* (II ?) (0·23 g.), m. p. 110—111°. This was sublimed in a vacuum and then crystallised from light petroleum (b. p. 40—60°) as needles, m. p. 113° (Found : C, 84·3, 83·9; H, 7·9, 8·3. $C_{14}H_{16}O$ requires C, 84·0; H, 8·0%). Light absorption : Maxima, 2420, 3020 (3170), and 3330 A.; log ε = 4·63, 3·69 (3·57), and 3·45, respectively. It formed a *carbanilate*, minute needles, m. p. 150—151° (from dilute alcohol) (Found : C, 78·3; H, 6·8. $C_{21}H_{21}O_2N$ requires C, 79·0; H, 6·6%), *picrate*, dark red needles (from benzene), m. p. 143—144° (Found : C, 55·3; H, 4·3. $C_{20}H_{19}O_8N_3$ requires C, 55·9; H, 4·4%), and *trinitrobenzene* adduct, orange needles (from benzene), m. p. 150—151° (Found : C, 57·8; H, 4·6. $C_{20}H_{19}O_7N_3$ requires C, 58·1; H, 4·6%).

Dehydrogenation of Desmotroposantonin.—(−)-α-Desmotroposantonin (1 g.; m. p. 190°), heated for 40 hours at 240—250° with palladised charcoal (1 g.), yielded 1 : 4-dimethyl-6-ethyl-3-naphthol (50 mg.) which crystallised from light petroleum (b. p. 120°) as needles, m. p. 123° (compare Bertolo, *loc. cit.*, who gives m. p. 126°) undepressed by the specimen described above.

1 : 4-Dimethyl-2-naphthol obtained by potash fusion of desmotroposantonin (Bertolo, *Gazzetta*, 1902, II, **32**, 374) gave the following light absorption : Maxima, 2360 (2740), 2860, 2970, 3260, and 3380 A.; log ε = 4·75 (3·53), 3·68, 3·65, 3·35, and 3·42, respectively.

The authors thank Imperial Chemical Industries Limited, Billingham Division, for the infra-red light absorption studies and for gifts of xylenols, Messrs. T. and H. Smith, Ltd., for gifts of the santonins, the Medical Research Council of Ireland for a maintenance grant (D. R. A. W.), and the Egyptian Government for a grant (A. K. F.).

TRINITY COLLEGE, DUBLIN. [*Received, March 22nd*, 1950.]