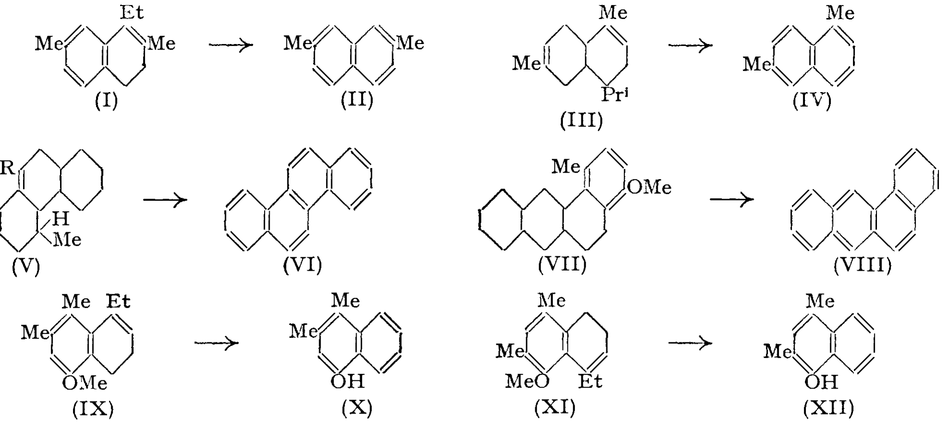
17. *The Elimination of Non-angular Alkyl Groups in Aromatisation Reactions. Part I.*

By Wesley Cocker, Brian E. Cross, and (Miss) Joan McCormick.

Dehydrogenation of a number of di- and tetra-hydronaphthalenes with palladised charcoal, selenium, and sulphur shows that in systems such as (XIII; R = Et, R′ = Me) the ethyl group is eliminated when selenium is the reagent.

Dehydrogenation of cyclic polyhydro-compounds by various reagents such as sulphur, selenium, palladium, and platinum has frequently been used as a means of assessing structure. In such reactions elimination of angular alkyl groups is the rule, but the value of the method for diagnostic purposes is generally based on the fact that, in simple systems at any rate, non-angular alkyl groups are unaffected by the process. Nevertheless, a number of instances are mentioned in the literature in which such alkyl groups are either eliminated or migrate during the aromatisation reaction. Thus, Ruzicka, Ehmann, and Mörgeli (*Helv. Chim. Acta*, 1933, **16**, 325) showed that 1-ethyl-3 : 4-dihydro-2 : 7-dimethylnaphthalene (I) is partly converted into 2 : 7-dimethylnaphthalene (II) by selenium at 300°. Cadinene (III) yields some 1 : 6-dimethylnaphthalene (IV) on being heated with selenium at 320° (Seidel, Müller, and Schinz, *ibid.*, 1944, **27**, 738), or with platinised charcoal at 305° (Linstead, Michaelis, and Thomas, *J.*, 1940, 1139). 1 : 2 : 3 : 4-Tetrahydro-1-*cyclo*pentylnaphthalene yields naphthalene when passed in a current of nitrogen over platinum at 310—315° (Denisenko and Naber, *Chem. Abs.*, 1940, **34**, 7283). Jones and Ramage (*J.*, 1938, 1853) showed that the perhydrochrysene (V; R = H or Me) yielded chrysene (VI) when heated with selenium for 72 hours at 280—300°, and Cook and Robinson (*J.*, 1938, 506) found that the decahydro-1 : 2-benzanthracene (VII) gave a small yield of 1 : 2-benzanthracene (VIII) at a similar temperature. Recently (*J.*, 1950, 1781) it was shown that 8-ethyl-5 : 6-dihydro-4-methoxy-1 : 2-dimethylnaphthalene (IX) yielded 3 : 4-dimethyl-1-naphthol (X) after demethylation and dehydrogenation with selenium at 330°. Similarly, 4-ethyl-1 : 2-dihydro-5-methoxy-6 : 8-dimethylnaphthalene (XI) yielded 2 : 4-dimethyl-1-naphthol (XII).



(I) (II) (III) (IV)

(V) (VI) (VII) (VIII)

(IX) (X) (XI) (XII)

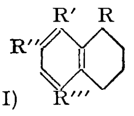
Examples are cited by Plattner (" Newer Methods of Preparative Organic Chemistry," New York, 1948, p. 21) in which migration of groups or change in carbon skeleton takes place during dehydrogenation, but the number of recorded cases where a non-angular alkyl group is eliminated from simple systems such as those mentioned, is relatively few.

Further work is now described, which had as its objective the elucidation of factors which might be responsible for the loss of alkyl groups. Such factors as the nature of the reagent, and its mode of employment, and also the position of the alkyl groups in the molecule, have been considered. The subject is still under investigation, but the facts which have so far emerged are recorded in the table, which makes it apparent that an

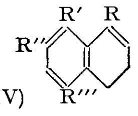
Structure of reactant	Product obtained by using :	
	Selenium (330—350°)	Pd–C (260—280°) and S (230—240°)
XIII; R = Et; R′ = R″ = R‴ = Me	XVI; R = H; R′ = R″ = R‴ = Me	XVI; R = Et; R′ = R″ = R‴ = Me
XIV; ,, ,,	XVI; ,, ,,	XVI; ,, ,,
XIII; R = R′ = R″ = R‴ = Me	XVI; R = R′ = R″ = R‴ = Me	—
XIV; ,, ,,	—	XVI; R = R′ = R″ = R‴ = Me *
XVI; R = Et; R′ = R″ = R‴ = Me	XVI; R = H; R′ = R″ = R‴ = Me	—
XIII; R = Et; R′ = R‴ = Me; R″ = H	XVI; R = R″ = H; R′ = R‴ = Me	XVI; R = Et; R′ = R‴ = Me; R″ = H ‡
XIV; ,, ,,	—	XVI; ,, ,,*
XVI; ,, ,,	XVI; R = Et; R′ = R‴ = Me; R″ = H	—
XIII; R = Et; R′ = H; R″ = R‴ = Me	XVI; R = Et; R′ = H; R″ = R‴ = Me	XVI; R = Et; R′ = H; R″ = R‴ = Me *
XIII; R = Et; R′ = Me; R″ = H; R‴ = OMe	XVI; R = R″ = H; R′ = Me; R‴ = OMe	XVI; R = Et; R′ = Me; R″ = H; R‴ = OMe *
XIII; R = Et; R′ = Me; R″ = H; R‴ = OH	←—— Unsatisfactory results ——→	
XIV; R = Et; R′ = Me; R″ = H; R‴ = OMe	XVI; R = R″ = H; R′ = Me; R‴ = OMe	—
XIII; R = Et; R′ = R″ = R‴ = H	Not dehydrogenated	XVI; R = Et; R′ = R″ = R‴ = H†
XIV; ,, ,,	XVI; R = Et; R′ = R″ = R‴ = H	—

* Pd–C only. † Sulphur only. ‡ Also with Pd–C at 330—350°.

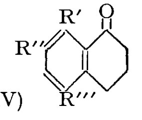
ethyl group (R) attached to carbon atom no. 1 is eliminated, during dehydrogenation with selenium, from di- and tetra-hydronaphthalenes in which a methyl group is located at carbon atom no. 8. The two examples mentioned earlier by us (*J.*, 1950, 1781) also fall into this category. It also emerges that the ethyl group (R) is retained when dehydrogenation is performed with palladised charcoal and sulphur, and that a methyl group at carbon atom no. 1 is retained under all conditions investigated.



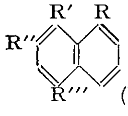
(XIII)



(XIV)



(XV)



(XVI)

We have also found that when 5-ethyl-1 : 4-dimethyl- and 8-ethyl-1 : 2 : 4-trimethylnaphthalene are heated with selenium at 340° only the latter loses its ethyl group.

In contrast to the majority of the results recorded in the literature, the yields of product obtained in this investigation from reactions in which an alkyl group is eliminated are generally very good. Although there is some indication (*e.g.*, colour of picrates) that the dehydrogenated product is a mixture, the de-alkylated naphthalene is always the major constituent and all attempts to isolate the higher homologue have been unsuccessful.

It is too early to reach any final decisions on the mechanism of the loss of an ethyl group from the systems mentioned. We are extending the investigation to compounds in which groups other than methyl and ethyl are located at the 1- and the 8-position in hydrogenated naphthalenes, and to other ring systems.

The hydrocarbons of structure (XIII) were prepared by reaction of the appropriate Grignard reagent with the tetralones (XV), followed by dehydration and hydrogenation. The tetralones were prepared by conventional methods :

Aromatic hydrocarbon + succinic anhydride $\xrightarrow{AlCl_3}$ substituted β-benzoylpropionic acid $\xrightarrow[HCl]{Zn-Hg}$ substituted γ-phenylbutyric acid $\xrightarrow{\textit{via}\text{ acid chloride or }H_2SO_4}$ tetralone.

Attempts were made to prepare 1 : 2 : 3 : 4-tetrahydro-1-keto-5 : 8-dimethoxynaphthalene (XV; R′ = R‴ = OMe, R″ = H). γ-(2 : 5-Dimethoxyphenyl)butyric acid (Fieser, Gates, and Kilmer, *J. Amer. Chem. Soc.*, 1940, **62**, 2966) gave only a tar, with either concentrated or 80% sulphuric acid, presumably as a result of demethylation and subsequent oxidation. Attempted cyclisation of the acid chloride with aluminium chloride or bromide gave a small amount of the desired product, characterised by its semicarbazone. On use of a solution of boron trifluoride in ether as catalyst, a tetralone was obtained having the composition of a hydroxymethoxytetralone. It gave a semicarbazone and a dark green ferric reaction, the product being soluble in ether; but it could not be methylated. From these properties it seems probable that the tetralone is 5 : 6 : 7 : 8-tetrahydro-8-keto-4-methoxy-1-naphthol (XV; R′ = OH, R″ = H, R‴ = OMe).

EXPERIMENTAL

(Analyses by Drs. Weiler and Strauss.)

Unless otherwise stated, the standard conditions for dehydrogenation were as follows: (1) *Palladised charcoal.* Equal weights of catalyst and hydrocarbon were heated at 260—280° for 4—4½ hours. (2) *Selenium.* The hydrocarbon was heated with three times its weight of reagent at 330—350° for 4—4½ hours. All hydrocarbons were distilled from sodium for analysis.

1 : 2 : 3 : 4-*Tetrahydro*-1-*keto*-5 : 7 : 8-*trimethylnaphthalene* (XV; R′ = R″ = R‴ = Me).—β-(2 : 4 : 5-Trimethylbenzoyl)propionic acid, obtained from ψ-cumene, had m. p. 105—107° (Muhr, *Ber.*, 1895, **28**, 3215, gave m. p. 98°; Claus, *Ber.*, 1887, **20**, 1378, gave m. p. 105°). Its *semicarbazone*, needles (from methyl alcohol), had m. p. 184° (Found: C, 61·0; H, 6·55. $C_{14}H_{19}O_3N_3$ requires C, 60·65; H, 6·85%), and its *methyl* ester, a low-melting solid, had b. p. 197°/15 mm. (Found: C, 71·7; H, 7·8. $C_{14}H_{18}O_3$ requires C, 71·8; H, 7·7%). γ-(2 : 4 : 5-Trimethylphenyl)butyric acid had m. p. 120—121° (Willgerodt and Scholtz, *J. pr. Chem.*, 1910, **81**, 391, give m. p. 71°) (Found: C, 75·35; H, 8·95. Calc. for $C_{13}H_{18}O_2$: C, 75·7; H, 8·75%). The butyric acid (12 g.), heated for 1·3 hours on the water-bath with a mixture of sulphuric acid (38 c.c.) and water (14 c.c.), gave the required *tetralone* (10·9 g.; m. p. 58—62°), which crystallised from methyl alcohol as rhombic plates, m. p. 61—62° (Found: C, 82·9; H, 8·05. $C_{13}H_{16}O$ requires C, 83·0; H, 8·5%) (semicarbazone, m. p. 200—201°). A *dibromo*-compound, made in ether with excess of bromine, crystallised from methyl alcohol as needles, m. p. 102—103° (Found: C, 44·9; H, 4·2. $C_{13}H_{14}OBr_2$ requires C, 45·1; H, 4·1%).

1 : 2 : 3 : 4-*Tetrahydro*-5 : 7 : 8-*trimethylnaphthalene*, obtained by reduction of the tetralone (0·5 g.) with amalgamated zinc and hydrochloric acid, crystallised in leaflets (0·25 g.), m. p. 46—47°, from ether–methyl alcohol (Found: C, 89·2; H, 10·6. $C_{13}H_{18}$ requires C, 89·65; H, 10·35%). This was heated with palladised charcoal, to give the known 1 : 2 : 4-trimethylnaphthalene, m. p. 50—52° (Ruzicka and Ehmann, *Helv. Chim. Acta*, 1932, **15**, 140).

8-*Ethyl*-5 : 6-*dihydro*-1 : 2 : 4-*trimethylnaphthalene*.—The above tetralone (7·5 g.) in ether (75 c.c.) was added to ethylmagnesium iodide, from ethyl iodide (33·9 c.c.) and magnesium (21·4 g.) in ether (125 c.c.), and the mixture refluxed for 1 hour and set aside overnight. After decomposition, the *dihydro*-compound (5·8 g.) distilled as a colourless oil, b. p. 145—146°/10 mm. (Found: C, 89·9; H, 10·1. $C_{15}H_{20}$ requires C, 90·0; H, 10·0%).

1-*Ethyl*-1 : 2 : 3 : 4-*tetrahydro*-5 : 7 : 8-*trimethylnaphthalene*.—The previous compound (3·5 g.) in ethyl acetate (75 c.c.) was quantitatively reduced over Adams's platinic oxide catalyst (420 mg.). The *tetrahydro*-compound obtained (3·2 g.; m. p. 48—50°) recrystallised from methyl alcohol–ether in rhombic plates, m. p. 58·5—59·5° (Found: C, 88·8; H, 10·8. $C_{15}H_{22}$ requires C, 89·1; H, 10·9%).

8-*Ethyl*-1 : 2 : 4-*trimethylnaphthalene* (XVI; R = Et, R′ = R″ = R‴ = Me).—The previous compound (0·3 g.) was dehydrogenated with palladised charcoal, and the product was extracted with methyl alcohol and distilled twice. The *hydrocarbon* was converted into its picrate, from which it was regenerated as an oil (0·17 g.), b. p. 144—145°/8 mm. (Found: C, 90·8; H, 8·9. $C_{15}H_{18}$ requires C, 90·9; H, 9·1%). Its *picrate*, dark red needles, m. p. 97—99° (Found: C, 58·4; H, 5·2. $C_{21}H_{21}O_7N_3$ requires C, 59·0; H, 4·9%), *trinitrobenzene* adduct, long, slender, orange needles, m. p. 124—125° (Found: C, 61·1; H, 5·2. $C_{21}H_{21}O_6N_3$ requires C, 61·3; H, 5·1%), and *trinitrotoluene* adduct, orange needles, m. p. 42—43° (Found: C, 62·1; H, 5·35. $C_{22}H_{23}O_6N_3$ requires C, 62·1; H, 5·4%), were all recrystallised from methyl alcohol.

This naphthalene (0·77 g.) was also obtained when its dihydro-compound (1·0 g.) was dehydrogenated with palladised charcoal.

Dehydrogenation of the tetrahydro-compound (1·6 g.) and of the dihydro-compound (1·5 g.) with the calculated quantities of sulphur, during 3 hours at 220—240°, also yielded (XVI; R = Et, R′ = R″ = R‴ = Me) (1·3 g. and 1·1 g., respectively).

Dehydrogenation of the Tetrahydro-compound with Selenium.—The pure tetralin (0·55 g.) yielded a product, strongly smelling of alkyl selenide. It was extracted with ether and distilled (0·39 g.), giving an oil, b. p. 129—135°/5 mm. Its picrate, after two crystallisations from methyl alcohol, formed orange needles, m. p. 147—148°, undepressed by the picrate of authentic 1 : 2 : 4-trimethylnaphthalene (see above; Ruzicka and Ehmann, *loc. cit.*). It was also characterised through its trinitrobenzene adduct, m. p. 165° (*idem, ibid.*). Its *trinitrotoluene* adduct crystallised as lemon-yellow needles (from methyl alcohol), m. p. 94° (Found: C, 60·2; H, 4·7. $C_{20}H_{19}O_6N_3$ requires C, 60·5; H, 4·8%).

Dehydrogenation of the dihydro-compound (2·9 g.) with selenium (8·7 g.) under the above conditions similarly yielded 1 : 2 : 4-trimethylnaphthalene (1·54 g.).

Action of Selenium on 8-*Ethyl*-1 : 2 : 4-*trimethylnaphthalene.*—The naphthalene (0·6 g.), heated with selenium (1·8 g.) under the above conditions, gave 1 : 2 : 4-trimethylnaphthalene (0·23 g.) and a strong smell of alkyl selenide. The product gave a picrate, m. p. 126—132°, raised to 147° by three crystallisations from methyl alcohol.

5 : 6-*Dihydro*-1 : 2 : 4 : 8-*tetramethylnaphthalene*, prepared from the tetralone (XV; R′ = R″ = R‴ = Me) (6 g.) and methylmagnesium iodide (from methyl iodide, 20 c.c.), was obtained as a colourless oil (2·9 g.), b. p. 140—148°/9—12 mm. (Found: C, 90·4; H, 9·5. $C_{14}H_{18}$ requires C, 90·35; H, 9·65%). The corresponding tetrahydro-compound was obtained by quantitative reduction of the preceding compound over palladised charcoal in ethyl acetate. The tetrahydro-compound was not analysed.

Dehydrogenation. The tetrahydro-compound (0·7 g.) was heated with selenium, yielding 1 : 2 : 4 : 8-tetramethylnaphthalene (0·55 g.), m. p. 56—57° (Found: C, 91·3; H, 8·8. Calc. for $C_{14}H_{16}$: C, 91·3; H, 8·7%) (Ruzicka, Ehmann, and Mörgeli, *Helv. Chim. Acta*, 1933, **16**, 314, describe this compound as an oil), depressed by authentic 1 : 2 : 4-trimethylnaphthalene, m. p. 54—55°. Its picrate had m. p. 149—149·5° (Ruzicka, Ehmann, and Mörgeli, *loc. cit.*, give m. p. 145·5°) (Found: C, 58·0; H, 4·9. Calc. for $C_{20}H_{19}O_7N_3$: C, 58·1; H, 4·6%). Its *trinitrobenzene* adduct crystallised from methyl alcohol as deep yellow rods, m. p. 167° (Found: C, 60·2; H, 4·6. $C_{20}H_{19}O_6N_3$ requires C, 60·4; H, 4·8%). Its *trinitrotoluene* adduct formed yellow needles, m. p. 88° (Found: C, 61·1; H, 4·75. $C_{21}H_{21}O_6N_3$ requires C, 61·3; H, 5·1%).

Dehydrogenation of the corresponding dihydro-compound (0·5 g.) with palladised charcoal under conditions mentioned above again gave 1 : 2 : 4 : 8-tetramethylnaphthalene (0·26 g.).

(With Dr. D. R. A. WHYTE). 1 : 2 : 3 : 4-*Tetrahydro*-1-*keto*-5-*methoxy*-8-*methylnaphthalene* (cf. Cocker, Lipman, and Whyte, *Chem. and Ind.*, 1950, 237).—β-(2-Methoxy-5-methylbenzoyl)-propionic acid, m. p. 114—115·5°, obtained from methyl *p*-tolyl ether and succinic anhydride in nitrobenzene, was reduced under Clemmensen conditions to γ-(2-methoxy-5-methylphenyl)butyric acid, b. p. 180—185°/4 mm., m. p. 63·5—64·5°. The butyric acid (11 g.) and pure thionyl chloride (60 c.c.) were warmed until molten, set aside for 30 minutes, and then refluxed for 10 minutes. The excess of thionyl chloride was removed at the pump. The residue was cooled in ice, dissolved in carbon disulphide (50 c.c.), and treated with powdered aluminium chloride (10 g.) in one portion. After refluxing for 10 minutes, the mixture was cooled and poured on ice and hydrochloric acid. From the organic layer, the required *tetralone* * was obtained as an oil (7·9 g.), b. p. 157—158°/9 mm., which solidified on storage and had m. p. 31—33° (Found: C, 76·1; H, 7·7. $C_{12}H_{14}O_2$ requires C, 75·8; H, 7·4%); the *semicarbazone* * (rosettes of needles from aqueous alcohol) melted at 233—234° (Found: C, 63·2; H, 6·6. $C_{13}H_{17}O_2N_3$ requires C, 63·2; H, 6·9%).

1 : 2 : 3 : 4-*Tetrahydro*-5-*methoxy*-8-*methylnaphthalene.*—The above tetralone (2·5 g.) was reduced with amalgamated zinc (50 g.), hydrochloric acid (75 c.c.), and water (32 c.c.) for

---

* These compounds were described by Cocker, Lipman, and Whyte (*loc. cit.*, where refs. are given; see also Herran *et al.*, *J. Org. Chem.*, 1951, **16**, 899) without preparative details and analyses.

22 hours. The *tetrahydro*-compound (1·14 g.) had b. p. 60—114°/8 mm. and rapidly solidified. It crystallised from aqueous alcohol as white needles or plates, m. p. 43—43·5° (Found : C, 81·4; H, 8·9. $C_{12}H_{16}O$ requires C, 81·8; H, 9·1%).

5-*Ethyl*-5 : 6 : 7 : 8-*tetrahydro*-4-*methyl*-1-*naphthol*.—1 : 2 : 3 : 4-Tetrahydro-1-keto-5-methoxy-8-methylnaphthalene (7·9 g.), on reaction with ethylmagnesium iodide (from ethyl iodide, 35 c.c.), yielded 1-*ethyl*-3 : 4-*dihydro*-5-*methoxy*-8-*methylnaphthalene* as an oil (4·2 g.), b. p. 142—150°/9—10 mm. (Found : C, 81·7; H, 8·9. $C_{14}H_{18}O$ requires C, 83·2; H, 8·9%). When this compound (7·3 g.) was hydrogenated over Raney nickel, and the product heated for 3 hours with hydriodic acid (29·5 c.c.) and acetic acid (29·5 c.c.), it afforded the *tetrahydronaphthol*; this distilled as an oil (3·3 g.; b. p. 160—170°/16 mm.), which solidified and crystallised from light petroleum as needles, m. p. 58—59° (Found : C, 82·4; H, 9·8. $C_{13}H_{18}O$ requires C, 82·1; H, 9·5%); the *carbanilate* (needles from methyl alcohol) had m. p. 156—157° (Found : C, 77·6; H, 7·9. $C_{20}H_{23}O_2N$ requires C, 77·7; H, 7·4%).

Dehydrogenation of the tetrahydronaphthol gave unsatisfactory results, but its methyl ether was smoothly dehydrogenated both with palladised charcoal and with selenium, as follows.

(1) *With palladised charcoal.* The ether (1·5 g.) gave a product which after demethylation yielded 5-ethyl-4-methyl-1-naphthol (0·7 g.), b. p. 126—148°/9 mm. It was not further purified. Its *picrate* crystallised from methyl alcohol as orange-red needles, m. p. 96—97° (Found : C, 55·3; H, 4·0. $C_{19}H_{17}O_8N_3$ requires C, 54·9; H, 4·1%). Its *trinitrobenzene* adduct, golden needles, m. p. 103—104° (Found : C, 56·55; H, 4·3. $C_{19}H_{17}O_7N_3$ requires C, 57·15; H, 4·3%), *trinitrotoluene* adduct, yellow needles, m. p. 54—55° (Found: C, 55·9; H, 4·6. $C_{13}H_{14}O + 1{\cdot}25C_7H_5O_6N_3$ requires C, 55·55; H, 4·3%), and *styphnate*, deep yellow needles, m. p. 131—132° (Found : C, 53·0; H, 3·7. $C_{19}H_{17}O_9N_3$ requires C, 52·9; H, 3·9%), were all crystallised from methyl alcohol.

(2) *With selenium.* The ether (1·5 g.) was dehydrogenated and demethylated, yielding an oily product (0·6 g.) consisting largely of 4-methyl-1-naphthol. Its *picrate* crystallised from methyl alcohol as brick-red needles, m. p. 174—175° (Found : C, 53·0; H, 3·7. $C_{17}H_{13}O_8N_3$ requires C, 52·7; H, 3·3%). Its *trinitrobenzene* adduct crystallised from benzene as orange needles, m. p. 173—174° (decomp.) (Found : C, 54·8; H, 3·4. $C_{17}H_{13}O_7N_3$ requires C, 55·0; H, 3·5%); its *trinitrotoluene* adduct crystallised from benzene–light petroleum as golden needles, m. p. 121—122° (Found: C, 55·8; H, 4·0. $C_{18}H_{15}O_7N_3$ requires C, 56·1; H, 3·9%); its *styphnate* (red needles from methyl alcohol) had m. p. 169° (Found : C, 50·4; H, 3·4. $C_{17}H_{13}O_9N_3$ requires C, 50·6; H, 3·2%). Dehydrogenation of 1-ethyl-3 : 4-dihydro-5-methoxy-8-methylnaphthalene (2·4 g.) with selenium, followed by demethylation, also yielded 4-methyl-1-naphthol (0·6 g.).

1-*Ethyl*-1 : 2 : 3 : 4-*tetrahydro*-5 : 8-*dimethylnaphthalene*.—1 : 2 : 3 : 4-Tetrahydro-1-keto-5 : 8-dimethylnaphthalene was prepared by the method of Barnett and Sanders (*J.*, 1933, 434) or, preferably, by cyclisation of the acid chloride of γ-(2 : 5-dimethylphenyl)butyric acid, prepared from the acid (26 g.) and thionyl chloride (26 c.c.) which were heated until molten, set aside for 30 minutes, and then warmed for 10 minutes on the water-bath. The acid chloride (19 g.) distilled as a colourless liquid, b. p. 134—142°/2—5 mm. It was dissolved in carbon disulphide (215 c.c.) and treated with aluminium chloride (22·8 g.), added in one portion, with cooling, giving the required tetralone (11·3 g.), b. p. 138—142°/4 mm., m. p. 30—33° (cf. Barnett and Sanders, *loc. cit.*; Ruzicka and Waldman, *Helv. Chim. Acta*, 1932, **15**, 907, 914; Baddeley, *J.*, 1944, 232). From this tetralone (4·7 g.), 1-*ethyl*-3 : 4-*dihydro*-5 : 8-*dimethylnaphthalene* was obtained in the usual manner as a colourless oil (3·8 g.), b. p. 140°/23 mm. (Found : C, 90·3; H, 9·6. $C_{14}H_{18}$ requires C, 90·3; H, 9·7%). When this dihydro-compound (1·7 g.) was reduced in glacial acetic acid over palladised charcoal, it gave 1-*ethyl*-1 : 2 : 3 : 4-*tetrahydro*-5 : 8-*dimethylnaphthalene* as a colourless oil (1·1 g.), b. p. 150°/5 mm., m. p. 35—36·5° (Found : C, 89·1; H, 10·8. $C_{14}H_{20}$ requires C, 89·3; H, 10·6%).

Dehydrogenation. (1) With palladised charcoal. The tetralin (0·4 g.), treated under the standard conditions, yielded 5-*ethyl*-1 : 4-*dimethylnaphthalene* (XVI; R = Et, R′ = R‴ = Me, R″ = H) as an oil which, on regeneration from its picrate, distilled (0·1 g.), b. p. 145—149°/6 mm. (Found : C, 91·3; H, 8·8. $C_{14}H_{16}$ requires C, 91·3; H, 8·7%). Its *picrate* crystallised from methyl alcohol as orange-red needles, m. p. 83° (Found : C, 58·4; H, 4·6. $C_{20}H_{19}O_7N_3$ requires C, 58·1; H, 4·6%), or from benzene–light petroleum with m. p. 78° (Found : C, 61·7; H, 5·0. $C_{20}H_{19}O_7N_3,0{\cdot}5C_6H_6$ requires C, 61·1; H, 4·0%). Its *trinitrobenzene* adduct consisted of golden needles (from methyl alcohol), m. p. 115° (Found : C, 59·8; H, 4·7. $C_{20}H_{19}O_6N_3$ requires C, 60·4; H, 4·8%).

Palladised charcoal at 330—350° and sulphur at 230—250° gave a similar result. 5-Ethyl-

1 : 4-dimethylnaphthalene was also obtained from 1-ethyl-3 : 4-dihydro-5 : 8-dimethylnaphthalene and palladised charcoal under the standard conditions.

(2) With selenium. The tetrahydro-compound (0·7 g.) yielded 1 : 4-dimethylnaphthalene (0·5 g.), b. p. 120—125°/15 mm., which gave a picrate, m. p. 141—142°, and trinitrobenzene adduct, m. p. 164° (Elsevier's Encyclopædia, 1948, **12**, *B*, 136, gives m. p. 143—144° and 165—166°, respectively).

Non-action of Selenium on 5-*Ethyl*-1 : 4-*dimethylnaphthalene*.—The naphthalene was recovered unchanged after being heated with selenium at 330—340°, and very little smell of alkyl selenide was evolved.

1-*Ethyl*-3 : 4 *dihydro*-5 : 7-*dimethylnaphthalene* was obtained (3·9 g.) as an oil, b. p. 128—134°/8—10 mm. (Found : C, 89·95; H, 9·95. $C_{14}H_{18}$ requires C, 90·3; H, 9·7%), when 1 : 2 : 3 : 4-tetrahydro-1-keto-5 : 7-dimethylnaphthalene (Barnett and Sanders, *loc. cit.*; Forrest, Tucker, and Whalley, *J.*, 1949, 3194) (5·7 g.) was treated with ethylmagnesium iodide (from ethyl iodide, 15·8 c.c.). Reduction (3·1 g.) in methyl alcohol over Raney nickel gave 1-*ethyl*-1 : 2 : 3 : 4-*tetrahydro*-5 : 7-*dimethylnaphthalene* (2·35 g.), b. p. 124—129°/9 mm. (Found : C, 89·4; H, 10·4. $C_{14}H_{20}$ requires C, 89·35; H, 10·65%).

5-*Ethyl*-1 : 3-*dimethylnaphthalene* (XVI; R = Et, R′ = H, R″ = R‴ = Me).—This *hydrocarbon* was obtained (1·0 g.) when the previous compound (1·2 g.) was dehydrogenated under standard conditions with either palladised charcoal or selenium. Regenerated from its picrate, it distilled as an oil, b. p. 131°/9 mm. (Found : C, 91·3; H, 8·7. $C_{14}H_{16}$ requires C, 91·3; H, 8·7%). Its *picrate*, orange-red needles, m. p. 109—110° (Found : C, 58·3; H, 4·9. $C_{20}H_{19}O_7N_3$ requires C, 58·1; H, 4·6%), *trinitrobenzene* adduct, yellow needles, m. p. 118° (Found : C, 60·6; H, 4·7. $C_{20}H_{19}O_6N_3$ requires C, 60·45; H, 4·8%), *styphnate*, orange needles, m. p. 115—116° (Found : C, 55·6; H, 4·5. $C_{20}H_{19}O_8N_3$ requires C, 55·95; H, 4·4%), and *trinitrotoluene* adduct, yellow needles, m. p. 70—71° (Found : C, 61·35; H, 5·0. $C_{21}H_{21}O_6N_3$ requires C, 61·3; H, 5·1%), were all recrystallised from methyl alcohol.

1-*Ethyl*-3 : 4-*dihydronaphthalene*, obtained from 1-tetralone, was an oil, b. p. 96—98°/6 mm. (Found : C, 91·3; H, 8·8. $C_{12}H_{14}$ requires C, 91·1; H, 8·9%).

5 : 6 : 7 : 8-*Tetrahydro*-8-*keto*-4-*methoxy*-1-*naphthol* (XV; R′ = OH, R″ = H, R‴ = OMe).—γ-(2 : 5-Dimethoxyphenyl)butyric acid (Fieser, Gates, and Kilmer, *loc. cit.*) (2·8 g.) in benzene (15 c.c.) was treated with boron trifluoride (48% in ether, 12 c.c.) and set aside overnight. After decomposition in the usual way, the ethereal extract was shaken with methyl sulphate and sodium hydroxide, dried, and distilled, giving the *tetrahydronaphthol* as a thick oil (0·5 g.), b. p. 156—160°/5 mm. It solidified, and crystallised from light petroleum as long, yellow needles, m. p. 95° (Found : C, 68·8; H, 6·5. $C_{11}H_{12}O_3$ requires C, 68·8; H, 6·25%); the *semicarbazone* had m. p. 252—254° (decomp.) (Found : C, 58·2; H, 5·95. $C_{12}H_{15}O_3N_3$ requires C, 57·85; H, 6·0%).

1 : 2 : 3 : 4-*Tetrahydro*-1-*keto*-5 : 8-*dimethoxynaphthalene* (XV; R′ = R‴ = OMe, R″ = H).—Cyclisation of the butyric acid (2·8 g.), through its chloride (by use of 2·9 g. of phosphorus pentachloride in 12 c.c. of benzene) followed by stannic chloride (3 c.c.), yielded a dark red oil (0·5 g.), b. p. 200—240°/5 mm. It formed a *semicarbazone*, m. p. 185·5—186·5° (Found : C, 59·3; H, 6·2. $C_{13}H_{17}O_3N_3$ requires C, 59·3; H, 6·5%).

The authors thank the Council of the Chemical Society for a grant from the Research Fund, Imperial Chemical Industries Limited for gifts of materials, and the Medical Research Council of Ireland for financial assistance.

TRINITY COLLEGE, DUBLIN.

[*Received, September 27th, 1951.*]