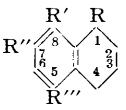
481. *The Elimination of Non-angular Alkyl Groups in Aromatisation Reactions. Part II.**

By Wesley Cocker, Brian E. Cross, J. T. Edward, D. S. Jenkinson, and (Miss) Joan McCormick.

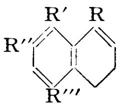
Further examples of the loss of alkyl groups from tetrahydronaphthalenes of type (I; R = R′ = alkyl; or R = alkyl and R′ = OMe), when dehydrogenated with palladised charcoal and selenium, have been encountered (cf. Cocker, Cross, and McCormick, *J.*, 1952, 72). It has been shown that the ethyl group is eliminated as ethyl hydrogen selenide when selenium is the dehydrogenating agent. Two examples of the loss of methyl are described.

In Part I * of this series it was shown that in the reaction of tetralins of type (I; R = Et, R′ = R″ = R‴ = H; R = R′ = R″ = R‴ = Me; R = Et, R′ = H, R″ = R‴ = Me) with sulphur, selenium, or palladised charcoal, normal aromatisation proceeds, yielding compounds of type (III; R = alkyl). In systems such as (I; R = Et, R′ = R″ = R‴ = Me; R = Et, R′ = R‴ = Me, R″ = H; R = Et, R′ = Me, R″ = H, R‴ = OMe), however, dehydrogenation with selenium leads to loss of the ethyl group, and production of compounds of type (III; R = H). Similar results were experienced with the corresponding dihydro-compounds (II). The work has been extended, and the results are summarised in the annexed Table.

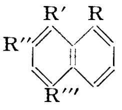
From the Table the following conclusions may be drawn. (*a*) Under normal conditions of use, sulphur is a " safe " catalyst; all alkyl groups are retained. It must be admitted that the number of examples of its use is small. At temperatures above 250°, or if an excess of sulphur is used, intractable products are produced. (*b*) No example of the loss of ethyl was encountered when palladised charcoal was used at 260—280°, but at 330—350° (I; R = Et, R′ = R″ = R‴ = Me) partly loses its ethyl group (cf. Part I, *loc. cit.*), and the *n*-propyl group is partly eliminated from the system (VI) at 260—280°. On the other hand, in (IX; R = Me or Et, R′ = Pr^i), the *iso*propyl group is eliminated from the aromatic ring when palladised charcoal is the catalyst; we were unable to prepare the tetralin (I; R = Pr^i, R′ = Me). This catalyst is also capable of removing methoxyl. Thus, the ether (XVII) yields the hydrocarbon (XVIII), and it has been shown † that the methoxy-compound (XX) yields a mixture of the methoxyl-free compounds (XXI) and (XXII) on dehydrogenation with palladised charcoal at 300° for twenty minutes. Cocker *et al.* (*J.*, 1950, 1781) further have shown that 1-ethyl-1 : 2 : 3 : 4-tetrahydro-5-methoxy-7 : 8-dimethylnaphthalene affords 8-ethyl-1 : 2-dimethylnaphthalene with palladised



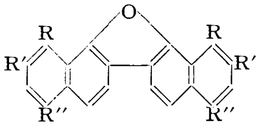
(I)



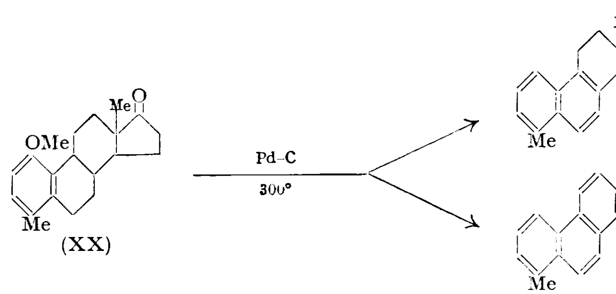
(II)



(III)



(XIX)

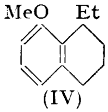
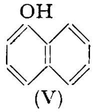
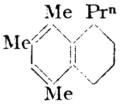
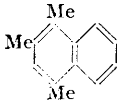
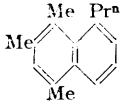
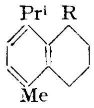
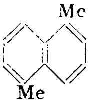
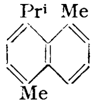
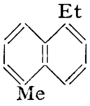
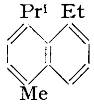
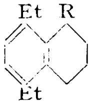
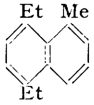
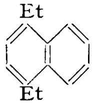
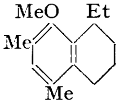
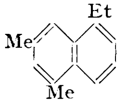


(XX) (XXI) (XXII)

---

* Part I, *J.*, 1952, 72. † Personal communication from Dr. Andre Dreiding, Detroit.

charcoal. (*c*) Selenium removes ethyl or larger groups from $C_{(1)}$ in systems of type (I; R = Et or Pr, R′ = Me). There is insufficient evidence to show whether *iso*propyl is eliminated from $C_{(8)}$ in systems where there is an ethyl group at $C_{(1)}$, although the odour of alkyl selenide indicates loss of alkyl; but in the system where ethyl groups are at $C_{(1)}$ and $C_{(8)}$, it is the 1-ethyl which is eliminated: (XIV; R = Et) ⟶ (XVI).

Reactant		Product obtained by using Selenium (330—350°)	Product obtained by using Palladised charcoal (260—280°)	Product obtained by using Sulphur (230—240°)
 (IV)		 (V) After demethylation		
 (VI)		 (VII)	(VII) + (VIII)	 (VIII)
 (IX)	R = Me	Mixture; (XI) isolated	 (X)	 (XI)
	R = Et	Intractable mixture	 (XII)	 (XIII)
 (XIV)	R = Me	 (XV)	(XV)	
	R = Et	 (XVI)	Not aromatised	Not aromatised
 (XVII)			 (XVIII)	
(I; R = Et; R′ = R″ = R‴ = Me)			330—350°. Mixture; (III; R = H; R′ = R″ = R‴ = Me) isolated	

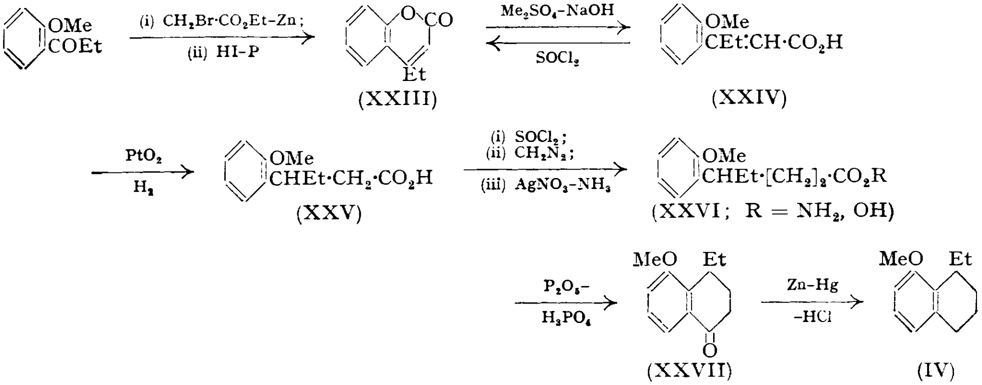
Two examples of loss of non-angular methyl groups have been encountered during dehydrogenation with selenium. Thus, 1 : 2 : 3 : 4-tetrahydro-5 : 8-dimethyl-1-oxonaphthalene affords 5′ : 5″-dimethyldinaphtho(1′ : 2′-2 : 3)(2″ : 1″-4 : 5)furan (XIX; R = R′ = H, R″ = Me), along with the expected 5 : 8-dimethyl-1-naphthol. Under similar conditions 1 : 2 : 3 : 4-tetrahydro-5 : 7 : 8-trimethyl-1-oxonaphthalene yields 5 : 7-dimethyl-1-

naphthol and 5′ : 5″-7′ : 7″ : 8′ : 8″-hexamethyldinaphtho(1′ : 2′-2 : 3)(2″ : 1″-4 : 5)furan (XIX; R = R′ = R″ = Me). The dimethyldinaphthofuran (XIX; R = R′ = H, R″ = Me) has not been synthesised by an unambiguous method but there can be little doubt of its structure. Thus, the analogous tetramethylfuran (XIX; R = H, R′ = R″ = Me) is obtained when 1 : 2 : 3 : 4-tetrahydro-5 : 7-dimethyl-1-oxonaphthalene is heated with selenium, and this furan is the product of dehydrogenation of 5 : 7-dimethyl-1-naphthol with vanadium pentoxide (cf. Clemo, Cockburn, and Spence, *J.*, 1931, 1265). Further, the three furans mentioned, and dinaphtho(1′ : 2′-2 : 3)(2″ : 1″-4 : 5)furan (XIX; R = R′ = R″ = H) (Clemo, Cockburn, and Spence, *loc. cit.*) have similar light-absorption characteristics, with appropriate changes due to the number and position of the alkyl groups. From past experience we have no reason to believe that 5 : 7 : 8-trimethyl-1-naphthol could yield 5 : 7-dimethyl-1-naphthol on dehydrogenation; it is much more likely that bis-5 : 7 : 8-trimethyl-1-naphthyl ether is the precursor of the dimethylnaphthol.

We have investigated the by-products in the aromatisation of (I; R = Et, R′ = R″ = R‴ = Me) with selenium; it has been found that the ethyl group eliminated is converted into ethyl hydrogen selenide in at least 60% of the theoretical quantity; no dialkyl selenide was encountered. Losses in manipulation probably account for the remainder, since although we were unable to analyse the gaseous products for paraffins, no olefin was produced. At least 70% of the theoretical quantity of hydrogen selenide was trapped as its lead salt.

It is difficult to see why the ethyl and *n*-propyl groups should be, in general, eliminated from systems such as (I; R = Et, R′ = R″ = R‴ = Me), whereas in similar systems where R = Me the group is retained. Models show that there is little interference between *n*-alkyl, and even *iso*propyl, groups at $C_{(1)}$ and $C_{(8)}$ in either the tetralin or the naphthalene. It may be that loss of ethyl proceeds via the ethylidene group, which could yield ethyl hydrogen selenide on attack by selenium. At the same time it must be remembered that 1-ethyltetralin (I; R = Et, R′ = R″ = R‴ = H) is unaffected by selenium (Cocker, Cross, and McCormick, *loc. cit.*).

The tetralins of type (I) were made by conventional methods, with the exception of (IV), for which the route shown was employed. A number of interesting points emerge from this synthesis. It was found that the hydroxy-ester obtained in the Reformatsky reaction between *o*-methoxypropiophenone and ethyl bromoacetate could not be dehydrated in the usual way, but with hot hydriodic acid 4-ethylcoumarin (XXIII) was obtained in fair yield. The unsaturated acid (XXIV) did not give an acid chloride with thionyl chloride, but afforded 4-ethylcoumarin instead. An analogy to this is the reaction between benzoyl chloride and phenetole, in which ethyl benzoate is produced. Cyclisation of the acid (XXVI; R = OH) was difficult, as might be expected since ring-closure *meta* to methoxyl is involved (cf. Johnson, "Organic Reactions," John Wiley and Sons, Inc., 1944, Vol. II, p. 120). Of the many reagents employed, in conjunction with either the



acid or its chloride, polyphosphoric acid (cf. Birch, Jaeger, and Robinson, *J.*, **1945**, 582) was the only one to effect cyclisation in resonable yield.

Attempts to prepare (I; $R = Pr^i$, $R' = R''' = Me$, $R'' = H$) were unsuccessful. When 1 : 2 : 3 : 4-tetrahydro-5 : 8-dimethyl-1-oxonaphthalene (Barnett and Sanders, *J.*, 1933, 434) was condensed with *iso*propylmagnesium bromide in ether, the product consisted of a mixture of unchanged tetralone, and its reduction product, the tetralol. In boiling anisole, the product obtained gave analyses as a mixture of the required *iso*propyl compound (II; $R = Pr^i$, $R' = R''' = Me$, $R'' = H$) and (II; $R = R'' = H$, $R' = R''' = Me$). After hydrogenation, followed by dehydrogenation with selenium, 1 : 4-dimethylnaphthalene was obtained, with only a slight odour of alkyl selenide. Further efforts to prepare the required tetralin involved the following reactions: tetralone $\xrightarrow{LiAlH_4}$ tetralol $\xrightarrow{HBr}$ bromotetralin (I; $R = Br$, $R' = R''' = Me$, $R'' = H$). The last compound formed a Grignard solution, but this failed to react with *iso*propyl bromide.

Two cases of loss of alkyl group were encountered, other than during dehydrogenation. Thus, bromination of 1 : 2 : 3 : 4-tetrahydro-1 : 5-dimethyl-8-*iso*propylnaphthalene gave a tribromo-compound with loss of the *iso*propyl group. Again 2-*tert.*-butyl-5-methylanisole reacted with succinic anhydride and aluminium chloride in methylene chloride to give β-(4-methoxy-2-methylbenzoyl)propionic acid.

EXPERIMENTAL

Unless otherwise stated, the standard conditions for dehydrogenation were as follows: (1) *Palladised charcoal.* Equal weights of catalyst and hydrocarbon were heated together at 260—280° for 4—4·5 hr. (2) *Selenium.* Three parts of this reagent and one part of hydrocarbon were heated together at 330—350° for 4 hr. (3) *Sulphur.* Theoretical quantities of both reagents were heated together at 220—240° for 3 hr. All hydrocarbons were distilled from sodium before analysis.

1 : 2 : 3 : 4-*Tetrahydro*-5 : 7 : 8-*trimethyl*-1-n-*propylnaphthalene* (VI) *and* 1 : 2-*Dihydro*-5 : 6 : 8-*trimethyl*-4-n-*propylnaphthalene*.—The corresponding tetralone (cf. Cocker, Cross, and McCormick, *loc. cit.*) (10·7 g.) in ether (70 c.c.) was added to a Grignard solution from *n*-propyl bromide (31·1 c.c.) and magnesium (8·3 g.) in ether (80 c.c.), and the mixture refluxed for 1 hr. and set aside overnight. After decomposition, the *dihydro*-compound (9·2 g.) was obtained as an oil, b. p. 170—172°/20 mm. (Found: C, 88·0; H, 10·15. $C_{16}H_{22}$ requires C, 89·7; H, 10·3%). The *tetrahydro*-compound (VI) was produced as an oil (4·7 g.), b. p. 170—172°/6 mm., when the preceding compound was reduced in acetic acid (40 c.c.) over palladised charcoal (0·8 g.). The oil slowly solidified, and crystallised from methyl alcohol–ether as plates, m. p. 45—46° (Found: C, 88·6; H, 11·0. $C_{16}H_{24}$ requires C, 88·9; H, 11·1%).

1 : 3 : 4-*Trimethyl*-5-n-*propylnaphthalene* (VIII).—The tetralin (0·9 g.), heated with sulphur, yielded an oil, b. p. 158°/15 mm., which was converted into its *picrate* (0·45 g.), m. p. 76°. This crystallised as dark red needles (from methyl alcohol), m. p. 81—82° (Found: C, 59·2; H, 5·2. $C_{22}H_{23}O_7N_3$ requires C, 59·9; H, 5·2%). 1 : 3 : 4-*Trimethyl*-5-n-*propylnaphthalene* was obtained from the picrate as a pale yellow oil, but there was too little for an accurate b. p. to be taken (Found: C, 90·6; H, 9·5. $C_{16}H_{20}$ requires C, 90·6; H, 9·4%).

1 : 2 : 4-*Trimethylnaphthalene*.—The above tetralin (0·7 g.), heated with selenium, yielded an oil (0·44 g.; b. p. 150—153°/5 mm.). From the oil (0·1 g.), a picrate (0·12 g.), m. p. 146—148° undepressed by authentic 1 : 2 : 4-trimethylnaphthalene (Ruzicka and Ehmann, *Helv. Chim. Acta*, 1932, **15**, 140), was obtained.

1 : 5-*Dimethyl*-4-iso*propylnaphthalene* (XI) *and* 1 : 2 : 3 : 4-*Tetrahydro*-1 : 5-*dimethyl*-8-iso-*propylnaphthalene* (IX; $R = Me$).—β-(2-Methyl-5-*iso*propylbenzoyl)propionic acid (Muhr, *Ber.*, 1895, **28**, 3217; Dev and Guha, *J. Indian Chem. Soc.*, 1948, **25**, 315) was orientated by oxidation with hypochlorite to 2-methyl-5-*iso*propylbenzoic acid (Bogert and Tuttle, *J. Amer. Chem. Soc.*, 1916, **38**, 1353), and characterised as its amide. The required 1 : 2 : 3 : 4-tetrahydro-5-methyl-1-oxo-8-*iso*propylnaphthalene was then prepared as described by Dev and Guha.

This tetralone (8·8 g.) with methylmagnesium iodide gave 1 : 2-*dihydro*-4 : 8-*dimethyl*-5-iso*propylnaphthalene* as an oil (6·6 g.), b. p. 129·5—132·5°/10 mm. (Found: C, 89·8; H, 10·2. $C_{15}H_{20}$ requires C, 90·0; H, 10·0%).

1 : 2 : 3 : 4-*Tetrahydro*-1 : 5-*dimethyl*-8-iso*propylnaphthalene* (IX; $R = Me$) was obtained as an oil (3·2 g.), b. p. 131—135°/8 mm. (Found: C, 88·95; H, 10·9. $C_{15}H_{22}$ requires C, 89·1; H, 10·9%), when the previous compound (5·3 g.) was reduced in acetic acid over Adams catalyst.

It gave, with loss of the *iso*propyl group, a *tribromo*-compound (not orientated), m. p. 104° (leaflets from alcohol) (Found: C, 36·4, 36·7; H, 3·0, 3·3; Br, 60·0. $C_{12}H_{13}Br_3$ requires C, 36·3; H, 3·3; Br, 60·45%).

The tetrahydro-compound (0·6 g.), dehydrogenated with sulphur, gave an oil (0·4 g.), b. p. 110—114°/6 mm., which was converted into its *picrate*. This separated from methyl alcohol in orange needles, m. p. 132—133° (Found: C, 59·3; H, 4·9. $C_{21}H_{21}O_7N_3$ requires C, 59·0; H, 4·9%). Decomposition of the picrate with ammonia yielded 1 : 5-*dimethyl*-4-iso*propylnaphthalene* (XI), b. p. 95°/6 mm. (Found: C, 90·8; H, 8·9. $C_{15}H_{18}$ requires C, 90·9; H, 9·1%).

Dehydrogenation of the tetrahydro-compound (2·5 g.) with palladised charcoal gave an oil (1·53 g.), b. p. 115—120°/5 mm., which slowly solidified. Crystallisation from methyl alcohol-ether yielded 1 : 5-dimethylnaphthalene (X; 0·5 g.), m. p. 80—82° (cf. "Elsevier's Encyclopaedia of Organic Chemistry," 1948, Vol. XIIB, p. 136), characterised as its picrate, m. p. 138—139° (Elsevier, *op. cit.*), and its *styphnate* (yellow needles from methyl alcohol), m. p. 156—158° (Found: C, 54·0; H, 3·75. $C_{18}H_{15}O_8N_3$ requires C, 53·9; H, 3·75%).

4-*Ethyl*-1 : 2-*dihydro*-8-*methyl*-5-iso*propylnaphthalene*.—1 : 2 : 3 : 4-Tetrahydro-5-methyl-1-oxo-8-*iso*propylnaphthalene (6·72 g.), reacting with ethylmagnesium iodide from magnesium (4·85 g.) and ethyl iodide (16 c.c.), yielded the required *dihydro*-compound (6 g.), b. p. 130—135°/6 mm. (Found: C, 89·5; H, 10·3. $C_{16}H_{22}$ requires C, 89·7; H, 10·3%).

1-*Ethyl*-1 : 2 : 3 : 4-*tetrahydro*-5-*methyl*-8-iso*propylnaphthalene* (IX; R = Et).—The dihydro-compound (3·36 g.), reduced in acetic acid (20 c.c.) over Adams's catalyst (100 mg.), yielded the *tetralin* (2·42 g.), b. p. 130—135°/7 mm. (Found: C, 88·3; H, 10·8. $C_{16}H_{24}$ requires C, 88·9; H, 11·1%).

Picrate of 1-*Ethyl*-5-*methylnaphthalene* (XII).—The preceding compound (0·7 g.), heated with palladised charcoal, gave an oil (0·6 g.), which was converted into its picrate (0·9 g.; m. p. 64—80°). Crystallised thrice from methyl alcohol, it had m. p. 97—98° (Harvey, Heilbron, and Wilkinson, *J.*, 1930, 423, give m. p. 97°), depressed by picrates of 1-methyl-4-*iso*propyl- (Ruzicka and Mingazzini, *Helv. Chim. Acta*, 1922, **5**, 710), and 5-ethyl-1-methyl-4-*iso*propylnaphthalene (XIII).

5-*Ethyl*-1-*methyl*-4-iso*propylnaphthalene* (XIII).—The tetralin (IX; R = Et) (0·5 g.), dehydrogenated with sulphur, afforded an oil (0·25 g.) from which the *picrate* of (XIII), m. p. 92—93° (orange-red needles from methyl alcohol), was obtained (Found: C, 59·8; H, 5·55. $C_{22}H_{23}O_7N_3$ requires C, 59·9; H, 5·2%).

1 : 4-*Diethyl*-5-*methylnaphthalene* (XV) *and* β-(2 : 5-*Diethylbenzoyl*)*propionic Acid*.—*p*-Diethylbenzene (45·4 g.), condensed in methylene chloride (150 c.c.) with succinic anhydride (43·5 g.) and aluminium chloride (90 g.), gave, after two crystallisations from ligroin, the required *acid* (43 g.; m. p. 67—70°), sufficiently pure for further work. Crystallised from light petroleum it was obtained as rosettes of needles, m. p. 73—74° (Found: C, 71·7; H, 7·95. $C_{14}H_{18}O_3$ requires C, 71·8; H, 7·7%).

γ-(2 : 5-*Diethylphenyl*)*butyric Acid*.—This was obtained as an oil (32·5 g.), b. p. 208—210°/6—7 mm., when the keto-acid (43 g.) was reduced under Clemmensen conditions. Its p-*nitrobenzylthiuronium* salt (felted needles from dilute alcohol) had m. p. 129° (Found: C, 61·4; H, 6·7. $C_{22}H_{29}O_4N_3S$ requires C, 61·25; H, 6·7%).

5 : 8-*Diethyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*oxonaphthalene*.—The preceding acid (30 g.) was treated with thionyl chloride (40 c.c.), giving the acid chloride (25 g.), b. p. 167—168°/5—6 mm. This was added to aluminium chloride (30 g.), in methylene chloride (150 c.c.), and set aside overnight. The *tetralone* (17 g.), isolated in the usual way, consisted of an oil, b. p. 164°/5 mm. (Found: C, 83·2; H, 8·9. $C_{14}H_{18}O$ requires C, 83·2; H, 8·9%).

5 : 8-*Diethyl*-1 : 2-*dihydro*-4-*methylnaphthalene*.—The tetralone (7 g.), treated with methylmagnesium iodide, from magnesium (5·1 g.), gave the *dihydro*-compound as an oil (5·8 g.), b. p. 131—135°/7 mm. (Found: C, 90·0; H, 10·2. $C_{15}H_{20}$ requires C, 90·0; H, 10·0%).

5 : 8-*Diethyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*methylnaphthalene* (XIV; R = Me) was obtained from the preceding compound by reduction over Adams's catalyst in acetic acid. It distilled at 126—129°/10 mm. (Found: C, 89·1; H, 10·9. $C_{15}H_{22}$ requires C, 89·1; H, 10·9%).

1 : 4-*Diethyl*-5-*methylnaphthalene* (XV).—The tetrahydro-compound (1 g.), dehydrogenated with either palladised charcoal or selenium, afforded 1 : 4-*diethyl*-5-*methylnaphthalene* (XV) (0·7—0·8 g.), b. p. 129—132°/10 mm. (Found: C, 90·8; H, 9·2. $C_{15}H_{18}$ requires C, 90·9; H, 9·1%). Its *picrate* (orange-red needles from methyl alcohol) had m. p. 105—106° (Found: C, 59·8; H, 4·7. $C_{21}H_{25}O_7N_3$ requires C, 59·0; H, 4·9%).

4 : 5 : 8-*Triethyl*-1 : 2-*dihydronaphthalene*.—5 : 8-Diethyl-1 : 2 : 3 : 4-tetrahydro-1-oxo-

naphthalene (9·3 g.), reacting with ethylmagnesium iodide, from magnesium (6·7 g.), gave the required *dihydro*-compound (8·1 g.) as an oil, b. p. 143—145°/11 mm. (Found: C, 89·1; H, 10·1. $C_{18}H_{22}$ requires C, 89·7; H, 10·3%).

1 : 5 : 8-*Triethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (XIV; R = Et) was quantitatively obtained from the preceding compound by reduction over Adams's catalyst, and was collected at 160—164°/5—6 mm. (Found: C, 88·4; H, 11·3. $C_{16}H_{24}$ requires C, 88·9; H, 11·1%).

1 : 4-Diethylnaphthalene (XVI) was obtained (0·76 g.; b. p. 124—127°/5 mm.) when the preceding compound (1 g.) was dehydrogenated with selenium. It was characterised as its picrate, m. p. and mixed m. p. with authentic material, 91—92° (cf. Arnold and Barnes, *J. Amer. Chem. Soc.*, 1944, **66**, 960). Authentic 1 : 4-diethylnaphthalene was prepared by conventional methods from 5 : 8-diethyl-1 : 2 : 3 : 4-tetrahydro-1-oxonaphthalene, and further characterised as its *trinitrotoluene* adduct (yellow prisms from methyl alcohol), m. p. 67—69° (Found: C, 61·7; H, 5·2. $C_{21}H_{21}O_6N_3$ requires C, 61·3; H, 5·1%).

5 : 8-*Dimethyl*-1-*naphthol*.—1 : 2 : 3 : 4-Tetrahydro-5 : 8-dimethyl-1-oxonaphthalene (1·3 g.) (Barnett and Sanders, *J.*, 1933, 434) in ether (5 c.c.) was treated with bromine (0·6 c.c.) in ether (10 c.c.). The crude product, after removal of ether, was refluxed for 45 min. with diethylaniline (4 c.c.), and the product was added to sulphuric acid (50%; 25 c.c.) and distilled in steam. The required *naphthol* (0·22 g.), collected from the distillate, crystallised from light petroleum as radiating needles, m. p. 76° (Found: C, 83·7; H, 6·9. $C_{12}H_{12}O$ requires C, 83·7; H, 7·0%). Its *picrate* (red needles from benzene) had m. p. 179—181° (Found: C, 54·3; H, 3·7. $C_{18}H_{15}O_8N_3$ requires C, 53·9; H, 3·7%). Its *styphnate* (brick-red rods from benzene) had m. p. 165—166° (Found: C, 52·2; H, 3·7. $C_{18}H_{15}O_9N_3$ requires C, 51·8; H, 3·6%).

1 : 2 : 3 : 4-*Tetrahydro*-5 : 8-*dimethyl*-1-*naphthol* (I; R = OH, R″ = H, R′ = R‴ = Me).—The corresponding tetralone (Barnett and Sanders, *loc. cit.*) (7·7 g. in ether, 40 c.c.) was slowly added to lithium aluminium hydride (0·84 g. in ether, 50 c.c.), and the mixture then refluxed for 30 min. The *alcohol* (6·7 g.; m. p. 89—91°), isolated in the usual way, crystallised from light petroleum as prisms, m. p. 90—91° (Found: C, 81·7; H, 9·0. $C_{12}H_{16}O$ requires C, 81·8; H, 9·1%).

1-*Bromo*-1 : 2 : 3 : 4-*tetrahydro*-5 : 8-*dimethylnaphthalene* (I; R = Br, R″ = H, R′ = R‴ = Me).—The above alcohol (6·3 g.) was mixed with constant-boiling hydrobromic acid (19·2 g.) and concentrated sulphuric acid (5·5 g.), set aside overnight, and then heated on the water-bath for 30 min. The cooled mixture was extracted with ether, from which the *bromo*-compound (7·2 g.; m. p. 32—38°) was obtained. It crystallised from light petroleum as prisms, m. p. 60—61° (Found: C, 60·4; H, 6·5. $C_{12}H_{15}Br$ requires C, 60·3; H, 6·3%). It rapidly decomposed on being warmed.

Action of Selenium on 1 : 2 : 3 : 4-*Tetrahydro*-5 : 8-*dimethyl*-1-*oxonaphthalene*. 5′ : 5″-*Dimethyldinaphtho*(1′ : 2′-2 : 3)(2″ : 1″-4 : 5)*furan* (XIX; R = R′ = H, R″ = Me).—The tetralone (4·2 g.) was heated under standard conditions with selenium, and the mixture extracted with benzene. The extract, washed with sodium hydroxide, yielded (*a*) 5 : 8-dimethyl-1-naphthol (0·15 g.), m. p. 76°, characterised as its picrate, m. p. 179—180°, undepressed by authentic material, prepared as above; and (*b*) the *furan* (0·55 g.), m. p. 178°, raised to 181—182° (felted needles), by crystallisation from benzene–light petroleum (Found: C, 88·8; H, 6·2. $C_{22}H_{16}O$ requires C, 89·2; H, 5·4%). Light absorption: Maxima, 2620, 2770, (3000), 3200, 3350, 3500 Å; log ε = 4·84, 4·69, (4·11), 4·03, 4·22, 4·12 respectively. Its *picrate* (red needles from benzene) had m. p. 188—189° (Found: C, 63·7; H, 4·4. $C_{22}H_{16}O,C_6H_3O_7N_3$ requires C, 64·0; H, 3·6%). Its *trinitrobenzene* adduct (orange needles from benzene) had m. p. 208° (Found: C, 66·0; H, 3·8. $C_{22}H_{16}O,C_6H_3O_6N_3$ requires C, 66·0; H, 3·7%).

5 : 7-*Dimethyl*-1-*naphthol and* 2-*Bromo*-1 : 2 : 3 : 4-*tetrahydro*-5 : 7-*dimethyl*-1-*oxonaphthalene*.—1 : 2 : 3 : 4-Tetrahydro-5 : 7-dimethyl-1-oxonaphthalene (Heilbron and Wilkinson, *J.*, 1930, 2537) (1 g.) was treated in ether (5 c.c.) with bromine (0·4 c.c.) in ether (10 c.c.), and set aside for 1 hr. After washing with sodium hydrogen sulphite solution and removal of the ether, the required *bromo*-compound (1·6 g.), m. p. 68—70°, was obtained and crystallised from light petroleum as tufts of needles, m. p. 84° (Found: C, 56·9; H, 4·9. $C_{12}H_{13}OBr$ requires C, 56·9; H, 5·1%).

5 : 7-*Dimethyl*-1-*naphthol*.—The above bromo-compound (0·7 g.), dehydrobrominated as described for its isomer, gave the *naphthol* (0·15 g.) which crystallised from light petroleum as needles, m. p. 79—80° (Found: C, 83·5; H, 7·2. $C_{12}H_{12}O$ requires C, 83·7; H, 7·0%). Light absorption: Maxima (in *cyclo*hexane), 2300, 2970, (3140), 3280 Å; log ε = 4·48, 3·66, (3·40), and 3·12 respectively. It gave a green ferric reaction. Its *picrate* (brick-red needles from

methyl alcohol) had m. p. 164—165° (Found : C, 53·6; H, 3·7. $C_{18}H_{15}O_8N_3$ requires C, 53·9; H, 3·7%). Its *trinitrotoluene* adduct (yellow needles from methyl alcohol) had m. p. 102—104° (Found : C, 56·9; H, 4·3. $C_{19}H_{17}O_7N_3$ requires C, 57·1; H, 4·3%).

Action of *Selenium on* 1 : 2 : 3 : 4-*Tetrahydro*-5 : 7-*dimethyl*-1-*oxonaphthalene and* 5′ : 5″- 7′ : 7″-*Tetramethyldinaphtho*(1′ : 2′-2 : 3)(2″ : 1″-4 : 5)*furan* (XIX; R = H, R′ = R″ = Me).—The tetralone (4 g.), heated with selenium under standard conditions, gave a product which was extracted with aqueous sodium hydroxide. From the extract a *monohydrate* of 5 : 7-dimethyl-1-naphthol (0·5 g.; needles from light petroleum), m. p. 58—59°, was obtained (Found : C, 75·5; H, 7·0. $C_{12}H_{12}O,H_2O$ requires C, 75·8; H, 7·4%). Light absorption : Maxima (in *cyclo*hexane), 2300, 2940, 3140, 3280 Å; log ε = 4·79, 3·89, 3·52, 3·45 respectively.

The non-acidic fraction of the above product yielded the *furan* (0·4 g.), which crystallised from benzene–light petroleum as pale yellow needles, m. p. 201—202° (Found : C, 88·2; H, 6·0. $C_{24}H_{20}O$ requires C, 88·9; H, 6·2%). Light absorption : Maxima (in *cyclo*hexane), 2540, 2660, 2760, 2980, 3100, 3280, 3420, 3560 Å; log ε = 4·66, 4·62, 4·65, 4·41, 4·36, 4·36, 4·54, 4·40 respectively. It gave a green colour with cold concentrated sulphuric acid, changing to deep red on warming. Its *picrate* (brick-red needles from benzene) had m. p. 211° (Found : C, 65·4; H, 4·2. $C_{24}H_{20}O,C_6H_3O_7N_3$ requires C, 65·1; H, 4·2%). Its *styphnate* (deep orange needles from benzene) had m. p. 209—210° (Found : C, 63·8; H, 4·2. $C_{24}H_{20}O,C_6H_3O_8N_3$ requires C, 63·3; H, 4·0%).

Action of Selenium on α-*Naphthol.*—When α-naphthol (10 g.) was heated under standard conditions with selenium it yielded dinaphtho(1′ : 2′-2 : 3)(2″ : 1″-4 : 5)furan (Clemo, Cockburn, and Spence, *loc. cit.*) (1·3 g.), m. p. and mixed m. p. 181—183°. This gave a *styphnate* (brown needles from benzene), m. p. 187—188° (Found : C, 50·7; H, 2·2. $C_{20}H_{12}O,2C_6H_3O_8N_3$ requires C, 50·7; H, 2·4%).

Action of Selenium on 1 : 2 : 3 : 4-*Tetrahydro*-5 : 7 : 8-*trimethyl*-1-*oxonaphthalene* (Cocker, Cross, and McCormick, *loc. cit.*).—Tetralone (5 g.) gave a mixture from which the following were separated : (*a*) 5′ : 5″ : 7′ : 7″ : 8′ : 8″-*hexamethyldinaphtho*(1′ : 2′-2 : 3)(2″ : 1″-4 : 5)*furan* (0·4 g.) (XIX; R = R′ = R″ = Me), m. p. 269—270° (needles from benzene) (Found : C, 88·2; H, 6·9. $C_{26}H_{24}O$ requires C, 88·6; H, 6·8%), which gave a green colour with cold concentrated sulphuric acid, changing to violet on warming. Its *picrate* (deep red prisms; readily dissociated on warming with benzene) had m. p. 228° (Found : C, 65·8; H, 4·7. $C_{26}H_{24}O,C_6H_3O_7N_3$ requires C, 66·1; H, 4·6%). (*b*) The monohydrate of 5 : 7-dimethyl-1-naphthol (m. p. and mixed m. p.) [picrate, m. p. 163°, undepressed by the picrate of authentic 5 : 7-dimethyl-1-naphthol (see above)].

4-*Ethyl*-1 : 2 : 3 : 4-*tetrahydro*-5-*methoxynaphthalene* (IV) *and* 4-*Ethylcoumarin* (XXIII).—*o*-Methoxypropiophenone (152 g.), ethyl bromoacetate (155 g.), and zinc (61 g.) condensed in boiling benzene (200 c.c.) gave a mixed product (222 g.), b. p. 155—163°/7 mm., of hydroxy- and unsaturated esters. A fraction of b. p. 159°/7 mm. was analysed (Found : C, 68·4; H, 7·8. Calc. for $C_{14}H_{20}O_4$: C, 66·7; H, 7·9. Calc. for $C_{14}H_{18}O_3$: C, 71·8; H, 7·7%). The mixture was refluxed for 10 hr. with hydriodic acid (300 c.c.; *d* 1·7) and red phosphorus (200 g.), then diluted with water, and the oily layer was washed with sodium hydrogen sulphite solution. The colourless oil was fractionated, affording (*a*) *o*-hydroxypropiophenone (55 g.), and (*b*) 4-*ethylcoumarin* (48 g.; b. p. 170—185°/15 mm.). The lactone solidified and then crystallised from light petroleum as needles, m. p. 70° (Found : C, 75·8; H, 5·5. $C_{11}H_{10}O_2$ requires C, 75·9; H, 5·7%).

3-o-*Methoxyphenylpent*-2-*enoic acid* (XXIV) (19 g.), obtained from the lactone (33 g.) by hydrolysis with 10% alcoholic potash, followed by methylation with methyl sulphate, crystallised from dilute alcohol as prisms, m. p. 114° (Found : C, 69·3; H, 6·4. $C_{12}H_{14}O_3$ requires C, 69·9; H, 6·8%).

3-o-*Methoxyphenylpentanoic acid* (XXV).—The preceding acid (10 g.) reduced in ethyl acetate with Adams's catalyst gave the saturated *acid* (10 g.) as rhombs (light petroleum), m. p. 63° (Found : C, 68·6; H, 7·4. $C_{12}H_{16}O_3$ requires C, 69·2; H, 7·7%). Its *amide* (needles from benzene) had m. p. 81·5° (Found : C, 69·9; H, 8·1. $C_{12}H_{17}O_2N$ requires C, 69·6; H, 8·2%).

4-o-*Methoxyphenylhexanamide and the Acid* (XXVI; R = NH_2 and OH respectively).—The acid chloride (6 g.) of (XXV) in ether (20 c.c.) was treated at 0° with diazomethane (2·9 g.) in ether (140 c.c.), and the mixture set aside overnight. The oily diazo-ketone (6·1 g.) was treated in dioxan (60 c.c.), at 50°, with a mixture of 20% ammonia (25 c.c.) and 10% aqueous silver nitrate (4 c.c.), and then heated for 2 hr. on the water bath. The dioxan was removed in a vacuum, and the residue was extracted with ether from which the *amide* (XXVI; R = NH_2)

(4·6 g.; needles from benzene) was obtained, having m. p. 89·5° (Found: C, 70·3; H, 8·6. $C_{13}H_{19}O_2N$ requires C, 70·6; H, 8·6%). The *acid* (XXVI; R = OH) (5·9 g.), m. p. 55—56° (prisms from light petroleum), was obtained by hydrolysis of the amide (6·0 g.) for 3 hr. with a solution of potassium hydroxide (5 g.) in water (30 c.c.) (Found: C, 70·8; H, 8·0. $C_{13}H_{18}O_3$ requires C, 70·3; H, 8·1%).

4-*Ethyl*-1 : 2 : 3 : 4-*tetrahydro*-5-*methoxy*-1-*oxonaphthalene* (XXVII).—Polyphosphoric acid was made by heating phosphoric acid (10 g.; *d* 1·75) with phosphoric oxide (6·4 g.) at 165° for 1 hr. The hexanoic acid (0·4 g.) was added with vigorous stirring to the polyphosphoric acid (2·4 g.) at 165° (cf. Birch, Jaeger, and Robinson, *J.*, 1945, 582), and the temperature maintained thereat for 5 min. The mixture, worked up in the usual way, yielded the required *ketone* (0·27 g.) as an oil, b. p. 171°/15 mm. (Found: C, 76·4; H, 7·6. $C_{13}H_{16}O_2$ requires C, 76·5; H, 7·8%).

4-*Ethyl*-1 : 2 : 3 : 4-*tetrahydro*-5-*methoxynaphthalene* (IV) was obtained as an oil (0·34 g.), b. p. 139°/15 mm., when the tetralone (0·5 g.) was reduced under Clemmensen conditions (Found: C, 81·9; H, 9·1. $C_{13}H_{18}O$ requires C, 82·1; H, 9·5%). Dehydrogenation of this compound (0·32 g.) with selenium gave an oil (0·22 g.), b. p. 140—144°/15 mm., which on demethylation afforded α-naphthol (m. p. and mixed m. p.).

Dehydrogenation of 1-*Ethyl*-1 : 2 : 3 : 4-*tetrahydro*-8-*methoxy*-5 : 7-*dimethylnaphthalene* (XVII).—The corresponding dihydro-compound (Cocker *et al.*, *J.*, 1950, 1781) was quantitatively reduced over palladised charcoal, giving the tetrahydro-compound (XVII), b. p. 144—151°/20 mm. It was characterised by demethylation and preparation of the *carbanilate*, m. p. 134—135°, of 8-ethyl-5 : 6 : 7 : 8-tetrahydro-2 : 4-dimethyl-1-naphthol (Found: C, 77·7; H, 7·6. $C_{21}H_{25}O_2N$ requires C, 78·0; H, 7·75%). When the methoxy-compound (1·5 g.) was heated with palladised charcoal, 5-ethyl-1 : 3-dimethylnaphthalene (XVIII) (0·94 g.) was obtained, and characterised as its picrate and trinitrotoluene adduct (Cocker, Cross, and McCormick, *loc. cit.*).

Investigation of the By-products produced in the Dehydrogenation of (I; R = Et, R′ = R″ = R‴ = Me) *with Selenium.*—The tetralin (4 g.) was dehydrogenated, in a current of nitrogen, under standard conditions of temperature, time, and quantity of selenium. The reaction was carried out in a long-necked flask (A) (10 c.c.; 17-cm. neck) with side-arm. This was attached to two traps (*B* and *C*), in series, immersed in liquid air; (*C*) was attached to a flask (*D*), similar to (*A*), which was connected to a short water-cooled condenser, leading to a side-arm test-tube (*E*). This test-tube was attached to an absorption train consisting of two lead acetate (1 l.; 10%), one sodium hydroxide (1 l.; 4%), one lead acetate, and two acid permanganate bubblers. Ground-glass joints were used throughout, and the pressure in the system was kept constant by using a mercury manometer attached to (*A*) : (*A*) was heated in an electric furnace.

After 4 hr. the furnace was turned off, and the apparatus was allowed to cool slowly, the stream of nitrogen being adjusted from time to time. After about 1 hr. (*D*) was placed in a freezing mixture (−20°), and the liquid-air containers were removed from (*B*) and (*C*). As these traps reached room temperature, hydrogen selenide was evolved and was collected in the lead acetate train. Finally, (*B*) and (*C*) were warmed in a water-bath, the flask (*D*) being cooled in liquid air, a liquid product thus being collected in (*D*). The liquid was carefully distilled from (*D*) into (*E*) which was cooled in liquid air. The product, ethyl hydrogen selenide (1·02 g.; b. p. 53°), was oxidised with 50% nitric acid (15 c.c.), concentrated, and then treated with concentrated hydrochloric acid, thus affording the hydrochloride of ethylseleninic acid, m. p. 108° (Found: C, 13·6; H, 4·1. Calc. for $C_2H_6SeO_2,HCl$: C, 13·5; H, 3·9%).

The permanganate solutions suffered no reduction, as shown by titration with oxalic acid.

The sodium hydroxide solution was titrated with standard acid, and contained no selenium compound.

The undistilled product remaining in the reaction flask (*A*) yielded pure 1 : 2 : 4-trimethylnaphthalene (0·55 g.) (cf. Part I, *loc. cit.*), and a product (2·0 g.) which by spectroscopy was shown to contain 15—25% of unchanged tetralin (I; R = Et, R′ = R″ = R‴ = Me).

The precipitated lead selenide in the lead acetate bubblers weighed 6·0 g., equivalent to about 70% of 4 H atoms.

The authors thank the Council of the Chemical Society for a grant from the Research Fund, and the Governments of the Republic of Ireland and Northern Ireland and the Medical Research Council of Ireland for maintenance grants. They are also indebted to Imperial Chemical Industries Limited for gifts of materials.

UNIVERSITY CHEMICAL LABORATORIES,
TRINITY COLLEGE, DUBLIN.

[*Received, April 22nd,* 1953.]