209. *Dehydrogenation. Part III. The Formation of Naphthols from Alcohols and Ketones of the Hydronaphthalene Group.*

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The dehydrogenation of the following substances in the liquid phase over a palladium catalyst has been studied: α-Tetralone, *ar*- and *ac*-β-tetralols, *trans*-α-decalone, *cis*- and *trans*-β-decalones, *cis*- and *trans*-β-decalols. All these substances yield mixtures of the appropriate naphthol (α- or β-) and naphthalene; *trans*-β-decalone also yields some ββ′-dinaphthyl. Comparatively drastic conditions are necessary to dehydrogenate the substances furthest removed from the aromatic type, and there is then a greater tendency for the elimination of the oxygen atom. An improvement can be effected in many cases by the addition of a diluent, but the mixture must be kept in a state of ebullition.

Tetralin is readily dehydrogenated in the liquid phase only when it is actually boiling. There is a rapid catalytic dehydrogenation when the liquid is made to boil at 185° by reduction in pressure or addition of a diluent, but none in the tranquil liquid at 200°.

This paper describes a study of the dehydrogenation of hydroaromatic alcohols and ketones containing the functional group directly attached to a six-membered ring. The particular object of the work was the conversion of these compounds into the corresponding phenols without elimination of oxygen. A method capable of accomplishing this would be of obvious value in the investigation of oxygen-containing compounds of the terpene and steroid groups.

There has been little systematic study of this subject, although there is a considerable scattered literature (see *Ann. Reports*, 1936, **33**, 294). The published data show that there is, in general, a difficulty in bringing about dehydrogenation without simultaneous removal of the oxygen atom. Since the above review was written, Mosettig and Duval have succeeded in obtaining good yields of 1- and 4-phenanthrols by catalytic dehydrogenation of the corresponding ketotetrahydrophenanthrenes (*J. Amer. Chem. Soc.*, 1937, **59**, 367). These ketones, in their enolic forms, are dihydrophenanthrols and undoubtedly the removal of the last two hydrogen atoms which separate them from the aromatic state is particularly easily accomplished (cf. also Ruzicka and Mörgeli's preparation of 7-methyl-1-naphthol from the corresponding tetralone; *Helv. Chim. Acta*, 1936, **19**, 377). It has generally been found that the dehydrogenation, by any method, of more highly hydrogenated substances is considerably more difficult and the danger of loss of oxygen, and other side-reactions, is increased.

We have made a study of the catalytic dehydrogenation of alcohols and ketones of the hydronaphthalene series, both of the tetrahydro- and the decahydro-type and containing the oxygen atom in the α- and the β-position. The catalyst most generally useful has been palladised charcoal prepared in dilute solution. The results of some isolated experiments with Adams's catalyst are given, but we have not sufficient data to generalise on its usefulness for the present purpose. The most favourable results are summarised in the table. The total yield of isolated aromatic compounds ranged from 50 to 97%. The product was invariably composed of a mixture of naphthalene and the appropriate naphthol. The yield of naphthol varied from 12 to 60%. There was no evidence whatever of the migration of a hydroxyl group.

TABLE I.

Compound.	% Yield of total aromatic material.	% Yield of naphthol.
α-Tetralone	81	46 α-
ar-β-Tetralol	97	55 β-
ac-β-Tetralol	96	60 β-
trans-α-Decalone	97	19 α-
trans-β-Decalone	61	41 β-; ββ′-dinaphthyl also formed
cis-β-Decalone	69	28 β-
trans-β-Decalol	51	17 β-
cis-β-Decalol	56	12 β-

These figures show that, as the compound becomes more removed from the aromatic type, it is less easily dehydrogenated, and, as a corollary, the yield of the phenolic product falls.

Effect of Temperature and of Boiling.—A high temperature of dehydrogenation obviously favours loss of oxygen by dehydration of the alcohols or of the ketones (in their enolic forms). Previous work (Part I, J., 1937, 1146) made it seem possible that at temperatures of the order of 200° dehydrogenation might occur and dehydration be largely suppressed. We first examined the behaviour of tetralin. At the boiling point (207°), under standard conditions, rather more than one-third of the material was dehydrogenated in ½ hour, as measured by the yield both of hydrogen and of naphthalene. At a temperature just below the boiling point (200°), no dehydrogenation whatever occurred in the same time. This result suggested that the act of boiling was of fundamental importance. We therefore examined the action of palladised charcoal on tetralin at 185° both at atmospheric pressure and under conditions where free ebullition was made possible, either by diminution of the pressure, or by the addition of a suitable amount of a low-boiling diluent (mesitylene). Under tranquil conditions there was no appreciable dehydrogenation, but the boiling liquid was converted into naphthalene to the extent of about one-third in 2 hours. In the experiment with mesitylene it was proved that this involved straightforward dehydrogenation and not a transfer of hydrogen to the diluent, for the mesitylene was recovered in the pure state from the product and the measured elimination of hydrogen corresponded with the formation of naphthalene.

It is thus clear that for tetralin to be dehydrogenated in the liquid phase at about 200°, it is necessary for the hydrogen to be eliminated from the system by the act of boiling. It appears that the tetralin molecules adsorbed on the catalyst surface suffer fission of the carbon–hydrogen bond but the hydrogen does not at once become free. Under tranquil conditions the reaction is reversible and the point of equilibrium is far on the tetralin side. The mechanical disturbance of boiling upsets this equilibrium by detaching hydrogen molecules, and enables dehydrogenation to proceed.

The convenient technique of the reduction of the boiling temperature by the addition of a diluent (which was also used by Mosettig and Duval) was next applied to the dehydrogenation of alcohols and ketones. Considerable improvements were effected in several cases. For instance, *ac*-β-tetralol, when boiled (263°) under atmospheric pressure with palladised charcoal, yielded almost equivalent amounts of naphthalene and β-naphthol; when the dehydrogenation was carried out in a boiling solution in mesitylene (at 185°), the yield of naphthol was almost twice that of naphthalene. Similarly α-tetralone gave a 46% yield of α-naphthol from a boiling solution in *p*-cymene, but only 9% when the diluent was omitted. In the latter case naphthalene was obtained in an excellent yield. The main reaction then becomes a *dehydration*, $C_{10}H_{10}O \longrightarrow C_{10}H_8 + H_2O$, accompanied or followed by a transfer of hydrogen. This result suggests a convenient simplification of the synthesis of aromatic hydrocarbons through α-ketones. The two middle stages in the usual procedure, α-tetralone type ⟶ α-tetralol ⟶ dihydro-aromatic hydrocarbon ⟶ aromatic hydrocarbon, should be unnecessary.

In the dehydrogenation of *trans*-β-decalone both alone and in diluents, the best yield of β-naphthol (41%) was obtained at 205°. This is a considerable improvement on the results obtained with sulphur and selenium (Ruzicka, *Helv. Chim. Acta*, 1936, **19**, 419). When *trans*-β-decalone was boiled with the catalyst at 242° without a diluent, a small yield of ββ′-dinaphthyl was obtained. It was identified by comparison with material made by the action of lithium on β-bromonaphthalene (Veselý and Štursa, *Coll. Czech. Chem. Comm.*, 1932, **4**, 139). No dinaphthyl was isolated from the dehydrogenation of any of the other substances under discussion.

The following table gives a rough indication of the initial velocity of dehydrogenation of five hydro-derivatives of β-naphthol. The figures given are the % dehydrogenation after one hour's boiling over the same catalyst. The results fall into line with those given in Table I and show the facilitating influence of an aromatic ring already present and the more ready dehydrogenation of ketones compared with alcohols. There is also an indication that *cis*-compounds are more readily dehydrogenated than *trans*-, as has been observed among hydrocarbons.

Compound.	Temp.	Products.
cis-β-Decalone	249°	31% Naphthalene, 29% β-naphthol
trans-β-Decalone	243	4% ,, 13% ,,
cis-β-Decalol	244	10% ,, 12% ,,
trans-β-Decalol	245	0% ,, 10% ,,
ac-β-Tetralol	263	29% ,, 32% ,,

For direct comparison with the work of Mosettig and Duval (*loc. cit.*) we also examined the dehydrogenation of 4-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene. The results are tabulated below, together with the best result recorded by Mosettig and Duval:

Catalyst.	Conditions.	Products.
3·3% of palladium on charcoal-*d*	75 Mins. at 315°	46% 4-Phenanthrol, 43% phenanthrene
,, ,, ,, ,,	450 Mins. at 240°	62% ,, 32% ,,
(M. & D.) 10% of palladium as black	24 Hrs. in boiling xylene	57% 4-Phenanthrol

The experiment at 240° was performed in a boiling mixture with *p*-cymene. Dehydrogenation was practically complete in less than 8 hours, but some loss of oxygen had occurred. Under the still milder conditions of Mosettig and Duval no loss of oxygen seems to have been observed. It is possible that the loss of oxygen is due to the carrier present in our catalyst. We hope to examine this point further, and to study the dehydrogenation of oxygenated compounds containing quaternary carbon atoms.

EXPERIMENTAL.

Catalyst.—Palladised charcoal-*d* (see preceding paper) was used throughout, except where mentioned.

Materials.—Tetralin was washed repeatedly with concentrated sulphuric acid, then with alkali and water, dried over calcium chloride and phosphoric oxide, refluxed over potassium, and fractionated from potassium. *ac*-β-Tetralol was fractionated and stored in a dark evacuated flask. Even so it tended to darken and was always redistilled before use. B. p. 145°/9 mm., 263°/760 mm., $d_{4^\circ}^{20^\circ}$ 1·0791, $n_D^{20^\circ}$ 1·5583. *ar*-β-Tetralol was prepared from tetralin by

Schroeter's method (we are indebted to Mr. R. H. Hughes of the Imperial College for this material). M. p. 59°, after crystallisation from light petroleum. α-Tetralone was regenerated from the oxime (m. p. 102°; cf. Kipping and Hill, J., 1899, **75**, 151) with hydrochloric acid, distilled in steam, and fractionated under reduced pressure. B. p. 105°/1 mm., 235°/760 mm., $d_{4^\circ}^{20^\circ}$ 1·0995, $n_D^{20^\circ}$ 1·5693. *trans*-α-Decalone, kindly supplied by Dr. A. L. Walpole of the Imperial College, was distilled at atmospheric pressure, following Hückel, to convert the *cis*- into the *trans*-isomeride, and then at 114°/17 mm. The *trans*-ketone was thereafter frozen out in a refrigerator; m. p. 33°, in agreement with Hückel. The two β-decalones and β-decalols were prepared by Hückel's methods (*Annalen*, 1925, **441**, 1), and had the following properties: *trans*-β-decalone, b. p. 80°/1 mm., 243°, $d_{4^\circ}^{20^\circ}$ 0·970, $n_D^{20^\circ}$ 1·4833; *cis*-β-decalone, b. p. 133°/28 mm., 248°, $d_{4^\circ}^{20^\circ}$ 1·000, $n_D^{20^\circ}$ 1·4935; *trans*-β-decalol, b. p. 236°, m. p. 75°; *cis*-β-decalol, b. p. 243°, m. p. 105°. 4-Keto-1 : 2 : 3 : 4-tetrahydrophenanthrene, m. p. 69°, was synthesised by Haworth's method (J. 1932, 1129).

Procedure.—The compound to be dehydrogenated (1—5 g.), together with 10% of its weight of catalyst and the diluent, if any, were heated in the apparatus described by Linstead, Millidge, Thomas, and Walpole (J., 1937, 1153). When a diluent of comparatively low b. p. was used, it was necessary to cool the upper part of the reaction vessel by a condensing coil. For temperatures below the b. p. the reaction vessel was heated in the vapour of a suitable liquid. The evolution of hydrogen was measured in the usual manner (*loc. cit.*). The product was extracted with ether and freed from catalyst by filtration. The ethereal solution was extracted with 10% aqueous sodium hydroxide (except in experiments with tetralin and ketotetrahydrophenanthrene), and the naphthol precipitated from the alkaline solution by acidification, dried, and weighed. The ethereal solution was freed from solvent under a column, and the naphthalene separated with an excess of picric acid in alcohol. It was regenerated from the picrate and weighed as such. Control experiments on the separation of known mixtures of naphthalene and β-naphthol showed that the manipulative loss involved in the isolation of samples of over 2 g. was negligible, for 1 g. samples was 8%, and for 200 mg. samples was about 17%. A special note is made below of any deviation from the standard procedure. The temperatures of dehydrogenations at the b. p. refer to the initial temperature. This rose as the reaction proceeded.

Results.—

1. *Tetralin: Effect of boiling.*

Catalyst.	Time (mins.).	Conditions.	Yield of products (%).	
			Hydrogen.	Naphthalene.
Palladium black-*c*	415	Boiling at 210°	35	30
Palladium black-*d*	585	,, ,,	76	71
Palladised charcoal-*c*	210	,, ,,	99	96
Palladised charcoal-*d*	180	,, ,,	100	97
,, ,,	30	,, ,,	35	34
,, ,,	60	Tranquil at 197	0	0
,, ,,	115	Tranquil at 186	0	2
,, ,,	115	Boiling at 186 *	—	30
,, ,,	150	Boiling at 185 †	39	36

* Boiling effected by lowering of the pressure.

† Boiling effected by dilution with an equal volume of mesitylene.

2. ac-β-*Tetralol.*

Catalyst.	Time (mins.).	Conditions.	Yield of products * (%).	
			Naphthalene.	β-Naphthol.
Palladised charcoal-*d*	60	Boiling at 235°	29	32
,, ,,	60	,, ,,	—	26
Palladised asbestos-*d*	145	,, ,,	53	26
Palladised charcoal-*d*	365	Boiling at 180 †	36	60
Platinised charcoal-*c*	150	Boiling at 235 ‡	43	52
Adams's PtO_2	75	,, ,,	27	46
Palladised charcoal-*d*	—	Vapour phase at 310°	74	5

* The evolution of hydrogen was measured in most experiments but is not recorded here or in subsequent tables, as it is dependent not only on the amount of dehydrogenation but also on the extent of dehydration and cannot be expressed as a simple percentage yield. In practice, however, the evolution of hydrogen was a useful guide to the progress of the reaction.

† Boiling was effected by dilution of the tetralol with an equal volume of mesitylene.

‡ This experiment was carried out on 12 g. of tetralol. The recovery of aromatic material was excellent.

3. ar-β-*Tetralol.*

Catalyst.	Time (mins.).	Conditions.	Yield of products (%). Naphthalene.	Yield of products (%). β-Naphthol.
Palladised charcoal-*d*	15*	Boiling at 272°	42	55
„ „	30	„ 268	40	55
Palladised asbestos-*d*	125	„ 264	—	56
Adams's PtO_2	155	„ 282	28	67

* The exceptional speed of this dehydrogenation is noteworthy.

4. α-*Tetralone.* (i) 2 G. of α-tetralone were boiled at 235° for 40 minutes with 0·2 g. of palladised charcoal-*d*; very little hydrogen was evolved, only 14% of that required for the straightforward dehydrogenation $C_{10}H_{10}O \longrightarrow C_{10}H_8O + H_2$. The aromatic product was a mixture of naphthalene (77% yield) and α-naphthol (9% yield).

(ii) A mixture of 2·20 g. of α-tetralone, 1 c.c. of *p*-cymene, and 0·2 g. of the same catalyst was boiled under reflux for 15 hours, the internal temperature remaining at *ca.* 201°. There was a copious evolution of hydrogen; yield of naphthalene, 35%; of α-naphthol, 46%.

5. trans-β-*Decalone.* (i) 2 C.c. of the decalone were boiled for 1 hour at 243° with 10% of palladised charcoal-*d*; 18% of the hydrogen required for complete dehydrogenation to β-naphthol was evolved. The product gave a 4% yield of naphthalene and a 13% yield of β-naphthol. The catalyst was extracted in a Soxhlet apparatus with boiling toluene. The extract yielded 6·5% of crystalline ββ'-dinaphthyl, m. p. 181° after two crystallisations from benzene. For comparison, β-bromonaphthalene (m. p. 58°) was heated in ethereal solution with lithium under nitrogen, following Veselý and Štursa (*loc. cit.*). The product was composed of β-naphthol, a little naphthalene, and ββ'-dinaphthyl, identical with that obtained in the dehydrogenation.

(ii) A similar experiment lasting 5½ hours gave 33% of β-naphthol and 28% of naphthalene.

(iii) A mixture of 2 c.c. of *trans*-β-decalone and 1·33 c.c. of *p*-cymene was boiled with 0·2 g. of catalyst at *ca.* 205° for 59 hours. Yield of β-naphthol, 41%; of naphthalene, 20%. Similar experiments at 194° and 200°, in which mesitylene was used as a diluent, gave much less dehydrogenation (*ca.* 10% of β-naphthol).

6. cis-β-*Decalone.* (i) The ketone was boiled for 1 hour at 249° with 10% of palladised charcoal-*d*. Yield of β-naphthol, 28%; of naphthalene, 41%. The yield of naphthol was not improved by prolonging the reaction for 48 hours.

(ii) A mixture of 2 c.c. of the decalone and 1 c.c. of *p*-cymene was boiled at an initial temperature of 206° for 64 hours. Yield of β-naphthol, 23%; of naphthalene, 29%.

7. trans-α-*Decalone.* (i) The ketone was boiled for 405 minutes at 235° with 10% of palladised charcoal-*d*. Yield of α-naphthol, m. p. 96°, 8%; yield of naphthalene, 21%.

(ii) A similar experiment for 24 hours gave 19% of α-naphthol and 78% of naphthalene. This is an exceptionally good result for the liquid-phase dehydrogenation of a decalin derivative.

8. trans-β-*Decalol.* (i) One hour's boiling at 245° with 10% of palladised charcoal-*d* gave 10% of β-naphthol and no appreciable quantity of naphthalene. A similar experiment prolonged for 46 hours gave a little more naphthol (17%) but 34% of naphthalene.

(ii) A mixture of 2 g. of the decalol and 1 c.c. of *p*-cymene was boiled at 218° with the catalyst for 48 hours. There was a surprisingly high yield of naphthalene (73%) and only 7% of β-naphthol. The *p*-cymene was recovered quantitively in a pure state.

A careful search was made for ββ'-dinaphthyl in these experiments, but none was detected.

9. cis-β-*Decalol.* One hour's boiling at 244° with 10% of palladised charcoal-*d* gave 12% of β-naphthol and 10% of naphthalene. Repetition of this experiment again gave 12% of β-naphthol. Continuation of the boiling to 46 hours raised the yield of naphthalene to 44% without appreciably affecting that of the naphthol.

10. 4-*Keto*-1 : 2 : 3 : 4-*tetrahydrophenanthrene.*—The results of dehydrogenation are tabulated on p. 1136. The experiment at 240° was performed on a boiling mixture of 5 g. of the ketone and 2 c.c. of *p*-cymene. The working up of the product had to be modified in these experiments. The 4-hydroxyphenanthrene was extracted from the ethereal solution of the product with 50% aqueous sodium hydroxide, instead of 10% as with the naphthols. The 4-phenanthrol, isolated by acidification, had m. p. 116°. The phenanthrene, isolated through the picrate, melted at 99°. The spent catalyst on extraction with boiling toluene yielded a solution which deposited a small amount of fluorescent crystals, m. p. 312°. This is presumably a compound

containing two phenanthrene nuclei and possibly also oxygen (cf. Cook and Hewitt, J., **1933**, 404; Mosettig and Duval, *loc. cit.*).

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