241. *Dehydrogenation. Part I. The Catalytic Dehydrogenation of Hydronaphthalenes with and without an Angular Methyl Group.*

By R. P. Linstead, A. F. Millidge, S. L. S. Thomas, and A. L. Walpole.

Ruzicka has shown the fundamental importance of dehydrogenation as a method for the determination of the structure of natural products containing the hydronaphthalene and similar, more complex, polycyclic groups. Dehydrogenation over noble metals provides a useful auxiliary or alternative method to dehydrogenation by selenium or sulphur, but our knowledge of the behaviour of various types of hydronaphthalenes over such catalysts is incomplete, and to some extent conflicting (for a review, see *Ann. Reports*, 1936, **33**, 305). In the present paper we describe the first stage in a general investigation of this question. The method of attack has been to examine the behaviour of substances of known structure over catalysts in the liquid and the vapour phase with the following practical objects: (1) To find the mildest conditions suitable for the conversion of hydroaromatic compounds into their aromatic counterparts without molecular rearrangements, such as the migration of alkyl groups. (2) To find a reliable test for the presence of an angular methyl (or similar) group, and, if possible, a method capable of giving evidence as to its position.

I. *Substances not containing an Angular Methyl Group.—Tetralins.* When liquid tetralin was boiled (208°) with platinum or palladium, naphthalene was rapidly formed. When the hydrogen evolved was led into a measuring apparatus so that a closed system was formed, far less than the theoretical quantity was evolved, owing without doubt to the reversal of the reaction. When, however, the hydrogen was swept from the reaction vessel in a stream of carbon dioxide, the reaction went smoothly to completion. The hydrogen was freed from carbon dioxide and measured in the apparatus described in the experimental section. The yields of hydrogen and naphthalene were theoretical within the limits of accuracy of the method. The reaction was unimolecular, the plot of $\log (V_\infty - V_t)$ against t being a straight line, where V_t is the volume of gas evolved in time t, and V_∞ the total volume evolved. Actually, an exact correspondence with theory was not to be expected, because the temperature was held at the boiling point, which rose slightly as the reaction proceeded. The results show that the reaction is a direct dehydrogenation and that no disproportionation of hydrogen, with formation of decalin and naphthalene, occurred under these conditions.* Tetralin was also catalytically dehydrogenated at even lower temperatures, but not sufficiently rapidly to be of much practical interest.

At the boiling point, the velocity of dehydrogenation depended on the catalyst. The most active catalysts were platinised charcoal, made by reducing hydrochloroplatinic acid with hydrogen at 135°, following Packendorff and Leder-Packendorff (*Ber.*, 1934, **67**, 1388), and a palladised charcoal made by reduction with formaldehyde in alkaline solution (Zelinski and Turowa-Pollak, *Ber.*, 1925, **58**, 1295). With these, reaction was nearly complete in four hours, with a half-change period of about an hour. This appears to be the best preparative method for obtaining naphthalenes from tetralins, and presumably also from dihydronaphthalenes. Ruzicka and co-workers have recently used palladised charcoal for the dehydrogenation of various derivatives of tetralin in synthetic work (*e.g.*, Ruzicka, Hösli, and Ehmann, *Helv. Chim. Acta*, 1936, **19**, 370).

To test whether polycyclic substances containing the tetralin system were dehydrogenated with similar ease we examined the *s*.-octahydrophenanthrene (I) and *s*.-octahydroanthracene (II) of Schroeter (*Ber.*, 1924, **57**, 1990 ff.). Both substances when boiled with palladium lost the theoretical quantity (4 mols.) of hydrogen in less than an hour, and quantitative yields of phenanthrene and anthracene respectively were isolated.

Decalins. Both *cis*- and *trans*-decalins, on the other hand, were only very slowly

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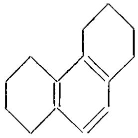
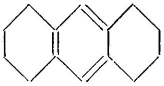
* Zelinski (*Ber.*, 1923, **56**, 1724) states that tetralin yields decalin and naphthalene over platinum at 300°, but gives no experimental details. In view of the results described above, it seems most unlikely that any appreciable amount of decalin would be formed under these conditions. Zelinski's statement that the change is analogous to the disproportionation of *cyclo*hexene is not correct, for the double bond common to both rings in tetralin is part of an aromatic system and would be reduced much less readily than that of *cyclo*hexene.

dehydrogenated over the same catalysts in the liquid phase at the boiling point (*ca.* 190°), and to obtain a satisfactory yield of naphthalene it was necessary to work in the vapour

(I.)





(II.)

phase at 300° (cf. Zelinski, *Ber.*, 1923, **56**, 1723). Under the latter conditions 1-*methyldecalin* readily yielded 1-methylnaphthalene and this appears to be the best practical method for dehydrogenating such saturated hydrocarbons.

Octalins. When *trans*-Δ^2-octalin or $\Delta^{9:10}$-octalin was boiled with palladium, the evolution of hydrogen was at first rapid, being comparable with that from tetralin, but after a few hours almost ceased. At this resting stage the yield of naphthalene was about a third of that calculated for complete dehydrogenation. The yield of hydrogen varied somewhat from experiment to experiment, but was roughly a sixth of that calculated on the same basis. The non-aromatic product was a decalin. These facts can be explained as follows: The octalin rapidly undergoes a disproportionation with the formation of decalin and tetralin in the molecular ratio of 2 : 1. The tetralin is then rapidly dehydrogenated in the normal manner:

$$\text{(i)}\ 3C_{10}H_{16} \longrightarrow 2C_{10}H_{18} + C_{10}H_{12} \qquad \text{(ii)}\ C_{10}H_{12} \longrightarrow C_{10}H_8 + 2H_2$$

The theoretical yields of hydrogen and naphthalene on this basis are $\frac{1}{6}$ and $\frac{1}{3}$ respectively of those required for the complete dehydrogenation: $3C_{10}H_{16} \longrightarrow 3C_{10}H_8 + 12H_2$.

In addition to these main reactions, it is reasonable to expect that there will be a little dehydrogenation of the decalin formed, and probably also some direct dehydrogenation of octalin to tetralin, and thence to naphthalene. In other words, some of the hydrogen liberated by the octalin molecules in their change to tetralin will escape free, without being employed in the reduction of other octalin molecules in the manner indicated by equation (i). The relative tendencies to disproportionation and direct dehydrogenation will be bound up with the ease of reduction of the double bond in the octalin—the more easily this is reduced, the greater the tendency to disproportionation. This was borne out experimentally, for the hydrogen evolution was greater from $\Delta^{9:10}$- than from Δ^2-octalin, which corresponds with the observation of Hückel, Danneel, Schwartz, and Gercke (*Annalen*, 1929, **474**, 121) that the double bond in the latter is hydrogenated much more readily than that in the former.

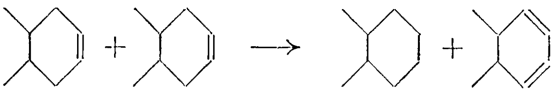
At lower temperatures the disproportionation was accompanied by very little dehydrogenation. When *trans*-Δ^2-octalin was heated with palladium at 140° or 170°, tetralin could be isolated in good yield [on the basis of equation (i)] in the form of its β-sulphonanilide. This disproportionation is similar to that observed in the *cyclo*hexene series by Knoevenagel, Zelinski, Boëseken, and others (for references, see *Ann. Reports*, 1936, **33**, 307); also Wieland (*Ber.*, 1912, **45**, 486) found that dihydronaphthalene yielded naphthalene and tetralin when heated over palladium.

1-*Methyloctalin* and *trans*-2-methyloctalin, prepared by dehydrating the corresponding tertiary alcohols, behaved similarly. The former gave the greater amount of hydrogen (28%), possibly because some $\Delta^{9:10}$-isomeride was present. The latter was essentially free from the $\Delta^{9:10}$-form, as it gave a white *nitrosochloride.* With palladium it yielded 2-methylnaphthalene, 2-*methyldecalin*, and 20% of hydrogen.

In the vapour phase over platinum and palladium at 300—350°, octalin and its 1- and 2-methyl derivatives gave the corresponding aromatic hydrocarbons in good yield. There was no evidence of the migration or elimination of the 1- or the 2-methyl group; *e.g.*, when 2-methyloctalin was passed over platinised asbestos at as high a temperature as 355°, 2-methylnaphthalene (m. p. 32°) solidified at the cool end of the tube.

No experiments have yet been carried out on di- and hexa-hydronaphthalenes, but on the basis of the above results it may be anticipated that at the boiling point in the liquid phase these will undergo disproportionation, followed by complete and partial dehydrogenation respectively.

II. *Substances containing an Angular Methyl Group.*—9-Methyldecalin, made by reducing pure 9-methyl-2-decalone, and 9-methyloctalin, made by dehydrating solid 9-methyldecalol (Linstead, Millidge, and Walpole, this vol., p. 1145), will be considered first. When these substances were boiled with palladium in the liquid phase (at *ca.* 200°), no significant quantity of hydrogen was evolved. The 9-methyloctalin was recovered unchanged, in striking contrast to the behaviour of 2-methyloctalin. Both dehydrogenation and disproportionation are therefore stopped under these conditions, which are not sufficiently drastic to break the link holding the methyl group to the 9-carbon atom. It is interesting that 9-methyloctalin is recovered and not a mixture of the corresponding diene and decalin. If the disproportionation of an octalin (or a *cyclo*hexene) took place in two steps, there is no formal reason why the first of these, shown below, should not proceed even when an angular methyl group is present:

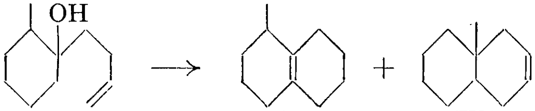


There is, however, no evidence that this occurs, perhaps because the reaction is reversible with an equilibrium on the left-hand side.

Very interesting results were obtained from experiments in the vapour phase at 300—330°. Dehydrogenation occurred, although rather more slowly than with compounds not containing the angular group. The fate of the methyl group depended upon the nature of the catalyst. With the platinum and palladium catalysts described above, the main product was naphthalene, the methyl group being eliminated, and some α-methylnaphthalene was formed by a secondary reaction. Over platinum prepared by Loew's method (*Ber.*, 1890, **23**, 289) the migration of the methyl group became the main reaction, α-methylnaphthalene being obtained, either alone or contaminated with only a trace of naphthalene. These surprising results have been repeated a number of times and there can be no doubt as to their authenticity. In parallel experiments, using different catalysts, we have obtained almost complete elimination and migration severally from one and the same sample of hydrocarbon. 9-Methyl-octalin and -decalin appeared to be essentially equivalent under the conditions of reaction. The formation of naphthalene was in itself a proof of the presence of the angular group, as direct experimental comparison showed that 1- and 2-methyl groups were not eliminated over the same catalyst under the same conditions.

Clemo and Dickenson (J., 1935, 735) report a failure to dehydrogenate a 9-methyldecalin over a platinum catalyst. The hydrocarbon was prepared by Clemmensen reduction of 2 : 4-diketo-9-methyldecalin (Ruzicka, Koolhaas, and Wind, *Helv. Chim. Acta*, 1931, **14**, 1154), a method which is not altogether reliable for the preparation of a pure compound owing to the danger of molecular rearrangement (cf. Dey and Linstead, J., 1935, 1063). Their result may, however, have been due to a lower catalyst activity. It is remarkable that Zelinski, Packendorff, and Chocklova (*Ber.*, 1935, **68**, 98; cf. Zelinski, *Ber.*, 1923, **56**, 1716) found that 1 : 1-dimethyl*cyclo*hexane was unaffected by a catalyst which we find capable of eliminating the angular methyl group from 9-methyldecalin. On the other hand, Ruzicka and Waldmann (*Helv. Chim. Acta*, 1933, **16**, 842; 1935, **18**, 611) have observed an almost quantitative elimination of angular methyl groups over palladium. The simple migration to the α-position now established is without precedent, although many examples are known of migration accompanying the elimination of a neighbouring substituent.

The dehydrogenation of the methyloctalins obtained by direct cyclisation of methylbutenyl*cyclo*hexanols may now be considered. The methyl group in the hydrocarbon obtained by dehydrating 1-methyl-2-butenyl*cyclo*hexanol (Hibbit and Linstead, J., 1936, 470) appears to be almost entirely in the 9-position, because the hydrocarbon gave off very little hydrogen when boiled with palladium. That obtained from the isomeric 2-methyl-1-butenyl*cyclo*hexanol (Hibbit, Linstead, and Millidge, J., 1936, 476), on the other hand, evolved hydrogen fairly readily. The aromatic product was α-methylnaphthalene, the non-aromatic was mainly a methyldecalin. Hence the methyloctalin made in this way contains material with the methyl group in the 1- and not the angular position. This is formed by a " reversed " cyclisation away from the methyl group, a possibility suggested in the earlier paper. From the results of Linstead, Wang, Williams, and Errington (this vol., p. 1136) the hydrocarbon (III) with a $\Delta^{9:10}$-double bond is probably present. At the same time the presence of 9-methyloctalin (such as IV) in the material is also certain from the results of oxidation and the fact that vapour-phase dehydrogenation over palladium yields a considerable amount of naphthalene.



(III.) (IV.)

When these octalins or the decalins prepared from them were dehydrogenated over Loew platinum at 330°, they yielded almost exclusively α-methylnaphthalene, whereas over palladium at this temperature a mixture of naphthalene and α-methylnaphthalene was obtained, consisting mainly of the former.* These results therefore fall into line with those from the homogeneous 9-methyl hydrocarbons.

4 : 9(1 : 10)-Dimethyloctalin, prepared from 2 : 6-dimethylbutenyl*cyclo*hexanol (preceding paper), gave very little hydrogen when boiled with palladium in a current of carbon dioxide, and even after 23 hours the octalin was recovered unchanged. Hence the compound is essentially of the angular methyl class. A little 1 : 5-dimethylnaphthalene was, however, obtained from the product, but in view of what follows this may well have been formed by migration during dehydrogenation (and not by dehydrogenation from already-formed 1 : 5-material). In the vapour phase at 330° over palladium 4 : 9-dimethyl-octalin and -decalin both yielded mainly α-methylnaphthalene, and 1 : 5-dimethylnaphthalene as by-product. Over Loew platinum at the same temperature no α-methylnaphthalene could be isolated, the main product being 1 : 5-dimethylnaphthalene, contaminated with an isomeride which has not yet been identified. Hence the main reactions over palladium and platinum at this temperature are elimination and migration of the methyl group respectively, as with the lower homologues.

For comparison with the unknown dimethylnaphthalene, 1 : 2-, 1 : 4-, and 1 : 8-dimethylnaphthalenes were synthesised, the last by a new and unequivocal method. None of these was identical with the dehydrogenation by-product, and it is possible that this is an inseparable mixture of isomerides. The identity of the 1 : 5-dimethylnaphthalene obtained by dehydrogenation was, however, established by comparison with synthetic material. The properties of these substances and of their derivatives are summarised in Table I.

TABLE I.

Substance.	Free hydrocarbon.	Picrate.	Styphnate.
x : *x*-Dimethylnaphthalene, dehydrogenation	Liquid	Orange-red, m. p. 134°	Yellow, m. p. 145°
1 : 2- ,, synthetic	,,	Orange, 131°	Chrome-yellow, 141°
1 : 4- ,, synthetic	,,	Orange-red, 142°	Orange, 125°
1 : 8- ,, synthetic	M. p. 63°*	Orange-yellow, 148°*	Orange-yellow, 160°
1 : 5- ,, dehydrogenation	77°	Yellow, 137°	—
1 : 5- ,, synthetic	79°	Yellow, 137°	—

* 1 : 8-Dimethylnaphthalene is described by Veselý and Štursa (*Coll. Czech. Chem. Comm.*, 1931, **3**, 430) as an oil (picrate, m. p. 143°).

Any proposed mechanism for the migration of the methyl group must allow for the fact that the α-methylnaphthalene obtained from 9-methyl-decalin and -octalin contained no

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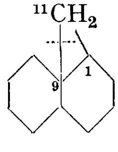
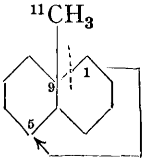
* In 1933, Dr. D. C. Hibbit obtained naphthalene by dehydrogenating 9-methyloctalin (prepared from 1-methyl-2-butenyl*cyclo*hexanol) over Loew platinum (thus showing the presence of the angular methyl group), but we have not since had a Loew catalyst capable of eliminating the angular group in this way. This illustrates the dependence of catalyst activity on minor variations in the method of preparation.

detectable amount of the β-isomeride, and also that migration was independent of the presence of a double bond. Two essentially different explanations may be considered : (*a*) The bond connecting the methyl group to C_9 is broken, but the hydrocarbon fragment remains adsorbed on the catalyst and is able to recombine with the hydronaphthalene residue at some stage during its dehydrogenation. There is evidence that catalysts can adsorb hydrocarbon fragments, *e.g.*, in the work of Taylor and co-workers (*J. Amer. Chem. Soc.*, 1935, **57**, 592). Alternatively, (*b*) the methyl group does not part from C_9 until it combines with C_1. In other words the first stage * is dehydrogenation with the formation of a three-membered ring (V). This would be extremely unstable, for both the 1 : 11- and the 9 : 11-bond would tend to break with addition of hydrogen. The former would merely reverse the reaction, but the latter would subsequently enable dehydrogenation to go to completion and would therefore be the effective process. There is no analogy for the formation of such a *cyclo*propane compound, although Haworth, Mavin, and Sheldrick have suggested the formation of an intermediate 5-membered ring to explain the migration of methyl from C_4 to C_1 during the selenium dehydrogenation of certain hydrophenanthrenes (J., 1934, 454). The reductive fission of the *cyclo*propane ring over dehydrogenating catalysts is, however, well established (Zelinski and Levina, *Annalen*, 1929, **476**, 60). Models indicate that the strain in the 3-membered ring of (V) is not substantially greater than that in an isolated *cyclo*propane ring. An alternative explanation which at first appeared attractive is illustrated by formula (VI), the suggestion being that the 1 : 9-bond breaks and the 4-carbon side-chain then cyclises on to C_5, subsequent dehydrogenation leaving the methyl group in the α-position. This explanation, however, fails to account for the formation of 1 : 5-dimethylnaphthalene from 4 : 9-dimethyloctalin.

(V.)





(VI.)

We hope to be able to decide between these possibilities by further study of migration reactions. At present, the hypothesis of an intermediate ring seems more acceptable, as otherwise it is difficult to explain the preference for migration to the α-position.

The *elimination* of the methyl group involves the fission, probably the reductive fission, of a carbon-to-carbon bond. Of the four bonds of the quaternary carbon atom, C_9, there is no *prima facie* reason why that holding the methyl group should alone be broken. Hence it might be anticipated that, under conditions leading to elimination of an alkyl group, the total yield of naphthalene derivatives might be lowered by ring fission. On the whole this appears to be true in our experiments, but it is not universally correct, for Ruzicka and Waldmann obtained excellent yields of retene from abietic acid and fichtelite (*loc. cit.*).

The investigation is being extended to other synthetic compounds and to natural products, and a further examination of catalysts is being made.

EXPERIMENTAL.

I. *Materials.*—Tetralin was purified by fractional distillation, sulphonation, and hydrolysis of the sulphonate, following Schroeter (*Annalen*, 1922, **426**, 111).

trans-Decalin was prepared by fractionation of commercial decalin. *cis*-Decalin was obtained as a by-product in the preparation of *cis*-β-decalol from *ac*-β-tetralol (we are indebted to Mr. D. A. H. Parsons for this material). *trans*-Δ^2-Octalin was prepared by dehydrating *trans*-β-decalol with potassium hydrogen sulphate and refluxing the product over potassium. $\Delta^{9:10}$-Octalin (principally this isomeride) was prepared by dehydrating *trans*-β-decalol with phosphoric acid (Linstead, Wang, Williams, and Errington, *loc. cit.*) and as follows : A mixture of 100 g. of *trans*-β-decalol and 240 g. of crystalline oxalic acid was refluxed for 9 hours at about 160°, and the product distilled in steam. The hydrocarbon was dried and fractionally distilled, finally over

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* *I.e.*, the first stage in the migration; the loss of hydrogen from other parts of the molecule may occur earlier.

sodium. It was a mixture of octalins, the main fraction (31 g.) boiling at 84—86°/22 mm. and yielding the blue nitrosochloride of the $\Delta^{9:10}$-isomeride, m. p. 91—92° (cf. Hückel, Danneel, Schwartz, and Gercke, *loc. cit.*).

1-*Methyl-octalin and -decalin. ar*-α-Tetralol was reduced in acetic acid solution over Adams's catalyst. The resulting α-decalol was oxidised to α-decalone, following Hückel and Brinkmann (*Annalen*, **1925**, **441**, 28). The ketone was only partly solid in ice and hence was the *cis*-isomeride, not quite pure. The ketone (9·5 g.) was converted into 1-*methyl*-1-*decalol* by treatment with methylmagnesium iodide. The carbinol (9 g., b. p. 112—113°/10 mm.) appeared from the analysis to be slightly dehydrated (Found : C, 79·5; H, 12·2. $C_{11}H_{20}O$ requires C, 78·5; H, 12·0%). It was heated for 2 hours at 130—140° with an equal weight of anhydrous oxalic acid, and the 1-*methyloctalin* isolated by means of ether and distilled over sodium. Yield, almost theoretical; b. p. 81—83°/10 mm. (Found : C, 88·05; H, 12·1. $C_{11}H_{18}$ requires C, 87·9; H, 12·1%). It rapidly absorbed the theoretical quantity of hydrogen over Adams's catalyst in acetic acid solution. The 1-*methyldecalin* (mainly *cis*-), after purification by treatment with potassium permanganate and distillation over sodium, boiled at 80—81°/12 mm. (Found : C, 86·75; H, 13·2. $C_{11}H_{20}$ requires C, 86·75; H, 13·25%).

trans-2-Methyloctalin was prepared by dehydrating *trans*-2-methyl-2-decalol (Ruzicka, Koolhaas, and Wind, *Helv. Chim. Acta*, **1931**, **14**, 1163) with oxalic acid. It had b. p. 80°/11 mm., and with amyl nitrite and concentrated hydrochloric acid gave a white *nitrosochloride*, which formed plates from ether, m. p. 138°, contaminated with only a trace of greenish-blue material (Found : Cl, 16·7. $C_{11}H_{18}ONCl$ requires Cl, 16·5%).

The 9-methyl- and 4 : 9-dimethyl-octalins and -decalins were prepared as described in the preceding papers and in J., **1936**, 470, 476. Octahydrophenanthrene, m. p. 17°, and octahydroanthracene, m. p. 73—74°, were prepared from tetralin and purified essentially by Schroeter's methods (*loc. cit.*, 1924).

The physical properties of these hydrocarbons are tabulated below to facilitate comparison with the corresponding values for the dehydrogenation products.

TABLE II.

Hydrocarbon.	B. p./mm.	$n_D^{t^\circ}$.	$d_{4^\circ}^{t^\circ}$.	*t*.	Exaltation of $[R]_D$.
trans-Δ^2-Octalin	70°/12	1·4859	0·8956	17·0°	+0·07
$\Delta^{9:10}$-Octalin (oxalic acid)	85/22	1·4992	0·9256	16·5	−0·36
1-Methyloctalin (mainly *cis*-)	82/10	1·5006	0·9155	12·0	+0·17
trans-2-Methyloctalin	80/11	1·4865	0·8893	17·3	+0·47
cis-9-Methyloctalin (from solid alcohol)	79/12	1·4916	0·9074	16·2	−0·17
1-Methyldecalin (mainly *cis*-)	81/12	1·4813	0·8905	12·5	−0·03
cis-9-Methyldecalin (from ketone)	79/11	1·4844	0·8994	12·5	−0·15
4 : 9-Dimethyloctalin	88/10	1·4924	0·9020	15·0	+0·09
4 : 9-Dimethyldecalin	85/10	1·4787	0·8847	16·0	+0·01

II. *Catalysts.*—The following were the most useful catalysts : *Platinum* (1). Platinised asbestos containing 32% of metal, made by Zelinski and Borisoff's modification (*Ber.*, 1924, **57**, 150) of Loew's method (*loc. cit.*), washed free from alkali with water, and dried at 100°.

Platinum (2). Aqueous hydrochloroplatinic acid from 2·25 g. of platinum was absorbed on 7 g. of charcoal (supernorit, first warmed with 5% nitric acid, washed with hot water, and dried at 120°). The reagent (24% platinum) was dried at 100° and reduced with purified hydrogen, first at 100°, then for 7 hours at 135°, and finally for 2 hours at about 300° (compare Packendorff and Leder-Packendorff, *loc. cit.*).

Palladium (1). Palladised charcoal (supernorit) containing 30% of metal, made following Zelinski and Turowa-Pollak (*loc. cit.*), washed with hot water until the washings were no longer alkaline, and dried at 150°.

Palladium (2). Made similarly in 25% strength, but washed with hot water, dilute acetic acid, and then again with water. It was slightly more active than palladium (1).

These catalysts were cooled and stored in a desiccator. For vapour-phase experiments the catalysts mounted on charcoal were mixed with an equal weight of purified asbestos, to prevent movement in the tube. The metal was recovered from spent catalysts by exhaustive extraction with aqua regia, the extracts evaporated to dryness, and the platinum precipitated from a solution in hydrochloric acid by means of formaldehyde and alkali. The metal was then redissolved and used afresh for the preparation of catalyst. The activity of the catalyst so obtained was tested quantitatively for the dehydrogenation of tetralin and found to be equal to that from fresh metal. Palladised silica gel (formaldehyde reduction) and palladium made by reducing the diamminochloride with hydrogen (Keiser and Breed, *Amer. Chem. J.*, 1894, **16**, 20) were also tested against tetralin and found to be considerably less active than palladium (1).

III. *Liquid Phase Dehydrogenations.*—(i) *No Measurement of hydrogen.* In the first series of experiments the hydrocarbon was boiled with the catalyst in a flask fitted with a vertical condenser open to the air. After a suitable time, the product was separated from the catalyst by distillation or by extraction with ether, filtration and removal of the solvent under a column. The aromatic hydrocarbons were isolated either as such or as picrates. The yields given below refer to hydrocarbon dried on a porous tile or are calculated from the weight of recrystallised picrate.

Tetralin. After 5 c.c. (4·85 g.) of tetralin had been boiled for 22 hours with 0·5 g. of palladium (1), the catalyst was quite dry and the naphthalene had sublimed up the tube. Yield, 97%; m. p. and mixed m. p. 81°.

In 1 and 6 hours under the same conditions, the yields were 37% and 87% respectively. With platinum (1) under similar conditions for 21 hours, the yield of naphthalene was 78%. When tetralin was heated with palladium (1) for 4 weeks at about 90°, or boiled with the same catalyst under a pressure of about 20 mm., in a stream of carbon dioxide for 18 hours, very small yields of naphthalene were obtained.

trans-*Decalin.* 10 C.c. (8·79 g.) in 21 hours' boiling with 1 g. of platinum (1) and palladium (1) gave 2·15 g. and 1·15 g. respectively of naphthalene picrate (12 and 6·5% yields).

$\Delta^{9:10}$-Octalin (10 c.c., 9·2 g.), made from *trans*-β-decalol and phosphoric acid, after 23 hours' boiling with 1 g. of palladium (1) yielded in two experiments 33·5 and 33% of naphthalene, isolated as picrate. Octalin, made by oxalic acid dehydration, similarly gave a 30, 36% yield. To estimate approximately the loss involved in the isolation of naphthalene picrate, naphthalene contaminated by twice its weight of decalin was converted into picrate. The yield was 90%. Hence the true yield of naphthalene in these dehydrogenations is about 37%, *i.e.*, rather more than the 33% calculated from equations (i) and (ii) (p. 1147).

Disproportionation of octalins. (a) 5 C.c. of octalin (oxalic acid method) were boiled for 6 hours with 0·5 g. of palladium (1). The product was cooled to − 16°, and the naphthalene filtered off by means of a filter-stick and dried (0·31 g.). The filtrate yielded 0·61 g. of naphthalene picrate (m. p. 151°). The residue was taken up in ether, and the excess of picric acid removed with ammonia. After removal of the solvent, the residual hydrocarbon was warmed for 30 minutes with 100% sulphuric acid to sulphonate the tetralin present. The product was diluted, extracted with ether, washed with aqueous ammonia and water, dried, and distilled. It gave 2·2 g. of decalin, b. p. 65—67°/12 mm., and 0·39 g. of a fraction, b. p. 81—82°/12 mm., probably a mixture of tetralin and unchanged octalin. The decalin had $n_D^{16\cdot8^\circ}$ 1·4806 and $d_{4^\circ}^{16\cdot8^\circ}$ 0·8861 (Found: C, 87·2; H, 12·6. Calc.: C, 87·0; H, 13·0%). It was therefore a mixture of the *cis*- and the *trans*-form. The yields of naphthalene and decalin were 12% and 47% respectively. Allowance being made for the loss involved in the isolation of the decalin, which is appreciably volatile in ether, these yields indicate that disproportionation is complete but dehydrogenation incomplete under these experimental conditions.

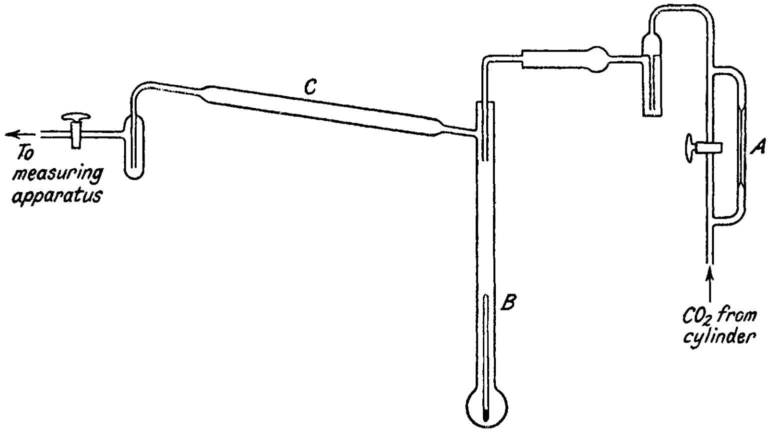
(b) 5 G. of Δ^2-octalin (potassium hydrogen sulphate) and 0·4 g. of palladium (2) were heated for 4 hours at 170°. After separation of picrate, corresponding to 0·3 g. of naphthalene, and removal of the excess of picric acid, the residual oil (4·3 g.) was sulphonated for 3 hours with 1·7 c.c. of concentrated sulphuric acid on the steam-bath. Saturated brine was then added (10 c.c.), which precipitated 2·0 g. of sodium tetralin-β-sulphonate. This was dried and heated with phosphorus pentachloride (1·0 g.) for 3 hours, the melt poured on ice, and the acid chloride extracted with ether. The ethereal solution was evaporated three times with a slight excess of aniline, and the β-sulphonanilide crystallised from alcohol. Yield, 0·75 g.; m. p. 152° (cf. Schroeter, *loc. cit.*, 1922). In a control experiment pure tetralin (2·2 g.), mixed with an equal weight of decalin, was converted similarly into 3·2 g. of sodium salt and 1·3 g. of the same sulphonanilide. On this basis the corrected yield of tetralin formed by disproportionation of the octalin was about 1·3 g., which, together with the naphthalene formed by dehydrogenation, corresponds approximately to the 33% yield required by theory.

5·3 G. of *trans*-Δ^2-octalin were heated for 10 hours with 0·5 g. of palladium (2) in a boiling xylene bath. The product yielded (i) 1·3 g. of recrystallised naphthalene picrate, corresponding to 0·47 g. of naphthalene; (ii) 2 g. of sodium tetralin-β-sulphonate, and thence the sulphonanilide; (iii) a residual oil (2·5 g.), which on fractionation gave a little unchanged octalin and mainly *trans*-decalin, the latter having physical constants almost identical with those given by Hückel.

Methyloctalins. 5·2 G. of 1-methyloctalin were boiled with 0·5 g. of palladium (1) for 23 hours. Distillation yielded 3·5 g. of product with $n_D^{15·5°}$ 1·5302, $d_{4°}^{15·5°}$ 0·9366 and hence containing much aromatic material. This gave 3·8 g. of α-methylnaphthalene picrate, m. p. 141° (29%).

15·2 G. of *trans*-2-methyloctalin were boiled for 6 hours with 1·5 g. of palladium (1). Distillation under 12 mm. yielded 14·6 g. of product with $n_D^{14·5°}$ 1·501, $d_{4°}^{14·5°}$ 0·8991, which gave 7·2 g. of β-methylnaphthalene picrate, m. p. 117° (19%). The residue was purified by successive treatment with ammonia, sulphuric acid and water, dried, refluxed over potassium, and distilled at 70—76°/12 mm. (7·8 g., 51%). On refractionation *trans*-2-methyldecalin was obtained, b. p. 74—76°/12 mm., $n_D^{20°}$ 1·4700, $d_{4°}^{20°}$ 0·8640, $[R_L]_D$ 49·05, exaltation + 0·45. These physical constants are close to those observed by Ruzicka, Koolhaas, and Wind (*loc. cit.*) (Found: C, 86·7; H, 13·1. Calc. for $C_{11}H_{20}$: C, 86·7; H, 13·3%). Under Rosenmund and Kuhnhenn's conditions the hydrocarbon only reacted with 0·3% of the theoretical quantity of bromine required for one double bond, which confirmed the fact that it was saturated.

9-Methyloctalin * (3·6 g.) was boiled with 0·4 g. of palladium (1) for 23 hours. The product, after distillation from the catalyst, yielded no picrate. After removal of the picric acid and distillation, the methyloctalin (1·6 g.) was recovered unchanged, b. p. 79—80°/10 mm., $n_D^{16°}$ 1·4954, $d_{4°}^{16°}$ 0·9088, values almost identical with those of the starting material (see Table II) (Found: C, 87·8; H, 12·3. Calc. for $C_{11}H_{18}$: C, 87·9; H, 12·1%).



1 : 10(4 : 9)-Dimethyloctalin (5·2 g.) was boiled with 0·5 g. of palladium (1) for 23 hours. and the product distilled (4·1 g.). On cooling in ice–salt, 1 : 5-dimethylnaphthalene separated and was collected by means of a filter-stick and identified by m. p. and mixed m. p. (0·4 g.). The filtrate was freed from a trace of residual aromatic hydrocarbon with picric acid and after distillation had b. p. 90°/10 mm., $n_D^{18°}$ 1·4905, $d_{4°}^{18°}$ 0·8988 (Found: C, 87·5; H, 12·3. Calc. for $C_{12}H_{20}$: C, 87·7; H, 12·3%). These figures show that the recovered octalin was practically free from decalin.

(ii) *Measurement of hydrogen.* The apparatus in its final form is shown diagrammatically in the figure. Carbon dioxide from a cylinder was led at a steady rate, controlled by the capillary by-pass, *A*, through a water bubbler and potassium carbonate drying-tube to the vertical reaction vessel, *B*. This contained known weights of the hydrocarbon and catalyst and a thermometer immersed in the liquid. It was heated electrically. The gas then passed through a straight inclined tube of sofnolite, *C*, and a micro-bubbler containing aqueous potassium hydroxide, to a graduated receiving apparatus, also containing potash. The main features aimed at were a small dead space and an absence of pockets in which hydrogen could collect, and escape being swept out by the carbon dioxide. The apparatus was assembled, and the air displaced as far as possible by carbon dioxide. The reaction vessel was then heated so as to keep the hydrocarbon boiling vigorously, a steady stream of carbon dioxide was maintained, and the evolution of gas measured at suitable intervals. When no more gas passed through the micro-bubbler, the apparatus was swept out with carbon dioxide and the final volume of hydrogen measured. Two small corrections were necessary: (*a*) for the permanent gas present as im-

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* The 9-methyloctalin used in the experiments described in this and the following (vapour-phase) section was the pure material prepared by dehydration of solid 9-methyl-2-decalol; and the 9-methyldecalin, by reduction of regenerated 9-methyl-2-decalone. Dehydrogenation experiments with methyloctalins of less certain purity, prepared by phosphoric acid dehydrations, are described in section V.

purity in the carbon dioxide, which was determined in blank experiments. (*b*) At the beginning of a run the sofnolite tube (and micro-bubbler) contained air, at the end hydrogen, except for the part containing spent sofnolite, which contained carbon dioxide. This " exhausted " part of the tube was greater at the end of an experiment and the volume of hydrogen was therefore slightly too large, and a small correction had to be applied. The accuracy of the method is estimated at about 5%. As an example of the results obtained, an experiment with tetralin is given below in detail; other experiments are summarised.

TABLE III.

0·91 G. of tetralin, 0·1 g. of Pd(1) at b. p. Gas measured at 768 mm. and 14°. Theo. evolution of hydrogen, 326 c.c.

Time (mins.) ...	10	20	30	40	61	80	103	120	165	189	210	240	270
C.c. of gas	8	20	60	89	131	162	195	217	255	273	284	297	307
,, ,, (corr.)	13	24	64	92	132	161	192	213	247	263	272	283	291
% Theo.	4	7	20	28	40·5	49	59	65	76	81	83	87	89
k (unimolecular) × 10^3	—	—	7·3	8·3	8·5	8·5	8·6	8·8	8·6	8·7	8·6	8·4	8·3

After 360 and 390 mins. the corrected volume of hydrogen was 300 c.c. (92%).
Mean $k = 8·5 \times 10^{-3}$ (t in mins.).

Other catalysts gave the following evolutions of hydrogen from tetralin, expressed as % of the theoretical quantity for complete dehydrogenation.

TABLE IV.

Time (mins.)	20	40	60	80	100	120	210	300	Final
Reaction with Pd(1)	21	36	—	—	64	69	87	94	95
,, ,, Pd(2) *	26	—	47	59	—	72	91	—	91
,, ,, Pd(2)	21	40	—	68	73	—	—	—	96
,, ,, Pt(2)	25	43	59	66	81	83	89	90	90

* Catalyst made from recovered palladium.

The corresponding approximate velocity constants are: palladium (1) 10·6; palladium (2) 10·7, 13·0; platinum (2) 14·4 (all × 10^{-3}, t in mins.).

TABLE V.

% Evolution of hydrogen from octahydroanthracene and octahydrophenanthrene at b. p. (0·85 g. of hydrocarbon + 0·19 g. of catalyst).

Time (mins.)	3	8	10	15	21	32	37·5	Final
Octahydroanthracene + Pd(1)............	7	36	44	63	79	89	95	97·5
,, + Pt(2)............	10	34	44	63	79	93	97	103
Octahydrophenanthrene + Pd(1)	8	31	—	63	84	99	—	103

The anthracene from the dehydrogenation of octahydroanthracene had sublimed up the reaction vessel. It was extracted with benzene and crystallised from acetic acid; m. p. and mixed m. p. 211°; yield, theoretical. The phenanthrene from the octahydrophenanthrene was extracted with ether and identified by its m. p. (99°) and picrate, m. p. 143°; yield, theoretical. Dehydrogenation of octahydroanthracene by palladium (1) at a bath temperature of 240—250° gave about 50% evolution of hydrogen in 10 hours.

In the same apparatus *cis*-decalin at the b. p. over palladium (2) gave 4% of hydrogen in 100 minutes, and 8% in 28 hours. The evolution of hydrogen from *trans*-decalin was even slower.

TABLE VI.

% Evolution (corrected) of hydrogen from octalins and methyloctalins at the b. p. over 10% of palladium (1). For convenience in tabulation many of these figures were obtained by interpolation between the experimental values. The gas evolution is expressed as the percentage of that obtainable in complete dehydrogenation to naphthalenes.

Time (mins.)	20	40	60	80	100	200	300	400
$\Delta^{9:10}$-Octalin	7	11	14	16	18	22	24	24
Δ^{2}-Octalin	5	6	7	8	9	12	13	13
1-Methyloctalin	14	20	25	27	27	28	27	27
2- ,, ...	10	14	16	18	19	20	19	19

The dehydrogenation of the methyloctalins was more rapid on account of the higher b. p. The product from 1-methyloctalin was extracted with ether and yielded α-methylnaphthalene picrate, m. p. 141° (0·68 g., 26%).

cis-9-Methyloctalin yielded 3% of hydrogen after 19 hours at the b. p. over the same catalyst, and the residue gave a trace (*ca.* 1%) of a picrate (m. p. 147°) which appeared to be a mixture of naphthalene and α-methylnaphthalene derivatives. 4 : 9-Dimethyloctalin yielded 5% and 6% of hydrogen in two experiments for 5 hours under the same conditions. A little 1 : 5-dimethylnaphthalene picrate was isolated from the product. Hence a small amount of dehydrogenation of angular methyl compounds appears to occur under these conditions.

IV. *Vapour Phase Dehydrogenations.*—The reaction tube of Pyrex glass, inclined at about 15° to the horizontal, was connected by ground joints to an apparatus for dropping in the substance to be dehydrogenated and for admission of hydrogen, and at the lower end to a receiver and measuring apparatus. The tube, packed with catalyst, was swept out by a current of hydrogen, purified by means of solutions of acid permanganate, copper sulphate, silver nitrate, sodium plumbite, and dried with calcium chloride. The tube was then heated electrically to the desired temperature in a slow current of hydrogen, the gas stream was stopped, and the apparatus tested for leaks. A weighed quantity of hydrocarbon (generally about 1 g.) was then added at the rate of about 0·3 g. per hour, a slight suction (*ca.* 2 feet of water) being maintained in the measuring apparatus. The volume of gas evolved was noted, and the catalyst tube swept out with hydrogen until no more dehydrogenated product was collected. In some experiments the material was recirculated over the catalyst. This is specially referred to in the account of the individual experiments; where no reference is made, the material was only passed over the catalyst once. The product was cooled in a freezing mixture, any solid hydrocarbon separated, and the remaining aromatic material isolated as picrate. The % yields of gas are calculated on the basis of complete dehydrogenation.

cis-Decalin gave a 95% yield of naphthalene over platinum (1) at 330° (m. p. 81°; picrate, m. p. 149°). *trans*-Δ^2-Octalin over palladium (1) at 300° gave 82% of gas and a product containing 73% of solid naphthalene (m. p. 80—81°) and a little decalin or unchanged octalin.

1-Methyloctalin over platinum (1) at 330° gave 80% of hydrogen. The product yielded α-methylnaphthalene picrate, m. p. 140°. 1-Methyldecalin behaved in an almost identical manner. 2-Methyloctalin over platinum (1) at 300° gave only 50% of hydrogen in two passages, but at 355° gave 70% in one passage. The product from each experiment solidified in ice and yielded β-methylnaphthalene picrate, m. p. 115°. Over palladium (1) at 300°, 2-methyloctalin yielded 80% of hydrogen in one passage, and the same product.

9-*Methyl derivatives* (see also Section V). 9-Methyldecalin (1·07 g.) over platinum (2) at 330° yielded 95% of gas and a product which was separated into 0·4 g. of solid naphthalene (m. p. 80°) and a trace (*ca.* 0·03 g.) of α-methylnaphthalene, identified as picrate, m. p. 141—142°. 9-Methyldecalin (1·2 g.) over palladium (1) at 320° yielded 70% of gas and 0·56 g. of product, mainly solid naphthalene; the liquid yielded 0·3 g. of a picrate, m. p. 143—145°, a mixture of naphthalene and α-methylnaphthalene derivatives. 9-Methyldecalin (1·2 g.) in two passages over platinum (1) at 300° yielded 70% of gas and 1·03 g. of an oil depositing no solid in ice and salt. After treatment with picric acid and fractional crystallisation it yielded 0·9 g. of α-methylnaphthalene picrate, m. p. 141—142°, and no detectable amount of naphthalene picrate. In one passage over the same catalyst at 340° there were obtained 50% of gas, a trace of naphthalene by freezing the product, and the main product was again α-methylnaphthalene (picrate, m. p. 140°. Found : C, 54·9; H, 3·6. Calc. for $C_{17}H_{13}O_7N_3$: C, 55·0; H, 3·5. Calc. for $C_{16}H_{11}O_7N_3$: C, 53·8; H, 3·1%).

9-Methyloctalin (potassium hydrogen sulphate product) over palladium (1) at 330° gave a product which partly solidified in ice; it was separated as before into naphthalene (m. p. 80°; picrate, m. p. 151°) and α-methylnaphthalene (picrate, m. p. 141·5—142·5°. Found : C, 55·0; H, 3·4%).

After two passages over platinum (1) at 330°, the product from 9-methyloctalin failed to solidify in ice, and the only aromatic hydrocarbon present was α-methylnaphthalene (picrate, m. p. 138—140°. Found : C, 54·8; H, 3·5%).

4 : 9-Dimethyloctalin after three passages over platinum (1) at 330° gave 40% of gas and a product which, when cooled in ice and salt, deposited 1 : 5-dimethylnaphthalene, m. p. 77°, not depressed by authentic material, but depressed by admixture with naphthalene (Found : C, 92·2; H, 7·9. Calc. for $C_{12}H_{12}$: C, 92·25; H, 7·75%). It gave a yellow picrate, m. p. 137° (Found : C, 55·7; H, 4·0. Calc. for $C_{18}H_{15}O_7N_3$: C, 56·1; H, 3·9%). The liquid, after the

removal of the 1 : 5-dimethylnaphthalene, yielded a dimethylnaphthalene picrate which crystallised from alcohol in long orange-red needles, m. p. 133—134°. After several crystallisations the m. p. rose to 134—134·5°, but not further (Found : C, 55·7; H, 3·9%). This orange picrate yielded a liquid hydrocarbon on regeneration with ammonia. The corresponding styphnate was yellow, m. p. 145°.

4 : 9-Dimethyloctalin after one passage over palladium (1) at 330° gave 70% of gas, and a product depositing no solid in ice and salt. The main product was α-methylnaphthalene, isolated as the picrate. This had m. p. 138°, and appeared to contain a little dimethylnaphthalene picrate, which could not be separated by crystallisation (Found : C, 55·4; H, 3·9%). A little of the orange (dimethylnaphthalene) picrate, m. p. 134°, was also isolated.

4 : 9-Dimethyldecalin over platinum (1) at 330° gave 55% of gas in two passages, solid 1 : 5-dimethylnaphthalene (main product), and a little of the orange picrate, m. p. 134°. The same hydrocarbon over palladium (1) at 330° gave 70% of gas, and α-methylnaphthalene (main product), the picrate of which melted at 138°, raised by admixture with an authentic sample (Found : C, 55·3; H, 3·9%). 1 : 5-Dimethylnaphthalene (m. p. and mixed m. p. 76°) and the orange picrate, m. p. 134°, were isolated as by-products. The orange picrate was less soluble in alcohol than that of α-methylnaphthalene.

V. *Dehydrogenation of Methyloctalins obtained by Direct Cyclisation.*—5 G. of methyloctalin, made by dehydration of 1-methyl-2-butenyl*cyclo*hexanol (J., 1936, 470), was dehydrogenated in the vapour phase over palladium (1) at 330°. It yielded 90% of gas in one passage, but only 3·4 g. of liquid product were recovered. This was separated into naphthalene (1·4 g., m. p. 78°) and 1-methylnaphthalene (*ca.* 1·6 g.; picrate, m. p. 140°; styphnate, m. p. 136°). Over platinum (1) at 330° the same hydrocarbon yielded 45% of gas, 1-methylnaphthalene (picrate, m. p. 140°; styphnate, m. p. 136°; mixed m. p.'s the same), and no naphthalene (Found for the picrate: C, 55·1; H, 3·8. Calc. for $C_{17}H_{13}O_7N_3$: C, 55·0; H, 3·5%). Over palladium (1) at the b. p. in the liquid phase this methyloctalin gave only 1% of hydrogen in 210 minutes and hence was essentially a 9-methyl compound.

The following experiment was carried out by Dr. D. C. Hibbit: Methyloctalin from 1-methyl-2-butenyl*cyclo*hexanol, after one passage over freshly prepared platinum (1), gave 51% of solid naphthalene (picrate, m. p. and mixed m. p. 149°).

Methyloctalin, made by dehydration of 2-methyl-1-butenyl*cyclo*hexanol (J., 1936, 476), over palladium (1) at 330° gave 75% of gas, solid naphthalene (m. p. and mixed m. p.), and a little α-methylnaphthalene. After dehydrogenation over platinum (1) at 330° the only isolable product was α-methylnaphthalene (picrate, m. p. 140°. Found : C, 54·95; H, 3·90%). This methyloctalin, when boiled with palladium (1), yielded a maximum of 14% of hydrogen and 20% of α-methylnaphthalene. The residual non-aromatic hydrocarbon was mainly saturated. Hence this methyloctalin was a mixture of the 1- and the 9-methyl compound.

VI. *Synthesis of Dimethylnaphthalenes.*—1 : 5-*Compound.* β-*o*-Tolylethyl alcohol (28 g.), b. p. 113—117°/9 mm., was prepared from the Grignard compound made from 52 g. of *o*-bromotoluene and ethylene oxide. The corresponding bromide, prepared in good yield by the action of phosphorus tribromide in carbon tetrachloride, boiled at 104—106°/9 mm., and on treatment with sodiomalonic ester in toluene yielded ethyl β-*o*-tolylethylmalonate, b. p. 150—155°/1·5 mm. Hydrolysis and distillation yielded γ-*o*-tolylbutyric acid, b. p. 145°/1 mm., m. p. 58°. Harvey, Heilbron, and Wilkinson (J., 1930, 423) give m. p. 60°. The acid was converted, following Harvey, Heilbron, and Wilkinson, successively into 5-methyl-1-tetralone, 1 : 5-dimethyl-3 : 4-dihydronaphthalene, and 1 : 5-dimethylnaphthalene.

1 : 8-*Compound.* *o*-Methylacetophenone (36 g.) was condensed with 70 g. of ethyl bromoacetate and 35 g. of zinc in 250 c.c. of benzene, and the product distilled with a little iodine. The β-*o*-tolylcrotonic ester obtained (45 g., b. p. 144—148°/18 mm.) was reduced in the usual way with 80 g. of sodium in 750 c.c. of calcium-dried alcohol, and the γ-*o*-tolylbutanol isolated by distillation in steam and under reduced pressure (b. p. 140—145°/18 mm.; yield, 23 g.). This was converted through the bromide and nitrile in the usual manner into γ-*o*-tolylvaleric acid (9·9 g.), b. p. 150°/1 mm., which failed to solidify in ice. The chloride of this acid was cyclised by means of aluminium chloride in carbon disulphide to 4 : 5-*dimethyl*-1-*tetralone*, which solidified after distillation (b. p. 154—156°/18 mm.) and was crystallised from methyl alcohol. Yield, 8 g.; m. p. 56° (Found : C, 82·3; H, 8·3. $C_{12}H_{14}O$ requires C, 82·7; H, 8·1%). The ketone (7 g.) was reduced by means of sodium (10 g.) in alcohol (200 c.c.), the solvent removed in steam, and the residue isolated by means of ether. After distillation with a crystal of iodine, 4·5 g. of 1 : 8-dimethyl-1 : 2-dihydronaphthalene were obtained, b. p. 116°/18 mm. This was dehydrogenated with selenium at 300° for 12 hours. The 1 : 8-*dimethylnaphthalene*

solidified after distillation (b. p. 140°/18 mm.) and formed white leaflets from dilute alcohol, m. p. 63° (Found : C, 92·2; H, 7·7. $C_{12}H_{12}$ requires C, 92·25; H, 7·75%).

1 : 2-Dimethylnaphthalene was prepared by the method of Mayer and Sieglitz (*Ber.*, 1922, **55**, 1851), and the 1 : 4-isomeride by the method of Robinson and Thompson (J., 1932, 2015). The properties of these dimethylnaphthalenes and their derivatives are summarised in Table I. The orange-red picrate, m. p. 134°, and the yellow styphnate, m. p. 145°, obtained from the by-product of the dehydrogenation of 4 : 9-dimethyl-octalin and -decalin, resembled the corresponding derivatives of 1 : 2-dimethylnaphthalene. Mixtures of the two picrates and the two styphnates, however, showed considerable depressions of m. p.

SUMMARY.

1. Tetralins and polycyclic compounds containing the tetralin structure are readily and quantitatively dehydrogenated over platinum and palladium at the boiling point; the evolution of hydrogen measures the degree of separation from the aromatic state.

2. Octalins readily disproportionate over these catalysts at the boiling point into the corresponding decalins and tetralins, the latter of which are then dehydrogenated. Octalins can therefore be dehydrogenated at comparatively low temperatures to give moderate yields of naphthalenes. They are dehydrogenated to give good yields of naphthalenes at 300° and above.

3. Decalins are very slowly dehydrogenated at the boiling point, but readily at 300° and above.

4. 1- and 2-Methyl groups remain intact in all these reactions.

5. When an angular methyl group is present, there is no dehydrogenation or disproportionation at about 200°. At about 300° the compound is dehydrogenated; the angular group either is eliminated or migrates to the α-carbon atom, according to the catalyst.

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