208. Dehydrogenation. Part II. The Elimination and Migration of Methyl Groups from Quaternary Carbon Atoms during Catalytic Dehydrogenation.

By R. P. LINSTEAD and S. L. S. THOMAS.

Various hydronaphthalenes containing methyl groups attached to quaternary carbon atoms have been dehydrogenated over metallic catalysts in the vapour phase. The results are summarised below:

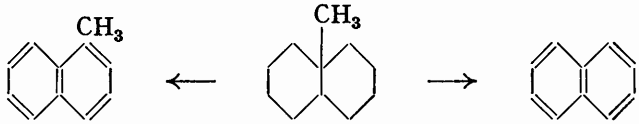
Type.	Compound.	Main product.	Secondary product.
Angular methyl	*cis*-9-Methyldecalin	Naphthalene	1-Methylnaphthalene
	cis-9-Methyloctalin	Naphthalene	1-Methylnaphthalene
	cis-4 : 9-Dimethyloctalin	1-Methylnaphthalene	1 : 5-Dimethylnaphthalene
	cis-1 : 9-Dimethyloctalin	1-Methylnaphthalene	—
gem-Dimethyl	1 : 1-Dimethyltetralin	1-Methylnaphthalene	1 : 2-Dimethylnaphthalene
	1 : 1 : 6-Trimethyltetralin (ionene)	1 : 6-Dimethylnaphthalene	—

Over platinised charcoal the main (and sometimes the exclusive) reaction was dehydrogenation, accompanied by a straightforward *elimination* of methyl from the quaternary atom. When the first three compounds tabulated above were passed over platinised or palladised asbestos, this normal reaction was accompanied by one involving the *migration* of methyl to an adjacent carbon atom. This migration was of minor importance in the case of the two compounds in which the quaternary atom carried a *gem*-dimethyl group.

The catalytic dehydrogenation of various alkyltetralins in the liquid phase has also been examined. Those without a quaternary carbon atom were rapidly and quantitatively dehydrogenated. Those with such an atom were practically unaffected.

PART I (Linstead, Millidge, Thomas, and Walpole, J., 1937, 1146) described, among other matters, the action of metallic catalysts on various octahydronaphthalenes at the boiling point. These substances normally yielded their aromatic counterparts by a process of disproportionation, followed by dehydrogenation; but when a quaternary carbon atom was present no reaction occurred. A number of methyltetralins have now been examined under the same conditions. Two of these, 1 : 1-dimethyltetralin and ionene (1 : 1 : 6-trimethyltetralin), contain quaternary carbon atoms carrying *gem*-dimethyl groups. We find that 6-methyl- and 1 : 6-dimethyl-tetralin give, as expected, almost quantitative yields of hydrogen and the corresponding methylnaphthalenes. 1 : 1-Dimethyltetralin and ionene, however, give only traces of hydrogen and of 1-methyl- and 1 : 6-dimethyl-naphthalene respectively. Thus, under the conditions of these liquid-phase experiments, at 200—250°, there is little tendency for the breaking of carbon-to-carbon bonds. This confirms the belief that the liquid-phase method provides a useful supplementary tool for the determination of the structure of hydroaromatic compounds, providing they contain at least one double bond. In a separate paper (Part IV) are recorded some results of the application of the method to terpenes.

Under more drastic conditions, in the vapour phase at 300—330°, the catalytic dehydrogenation of substances containing a quaternary carbon atom can be effected without difficulty, but the reaction can take two courses. In Part I, it was shown that the angular methyl group of 9-methyldecalin (I) or 9-methyloctalin either was eliminated with the formation of methane and naphthalene, or migrated to the α-position :



(I.)

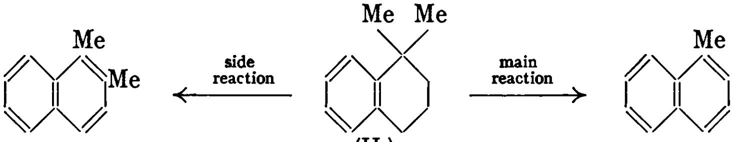
This reaction has now been examined further with a wider range of both materials and catalysts. After preliminary comparisons, we have taken as a standard method for the preparation of catalysts, the reduction of the chlorides of platinum or palladium with alkaline formaldehyde in the presence of a suitable carrier. The effect of various modifications of the preparative methods on the activity of the catalysts need not be given in detail. Our general conclusions are : (1) Very active catalysts are conveniently prepared by the method of Willstätter and Waldschmidt-Leitz (*Ber.*, 1921, **54**, 123), but a slightly higher activity and better reproducibility are obtained by precipitating the metal at higher dilutions than have been used by previous workers. This enables the mixture to be mechanically stirred and gives greater uniformity. (2) Platinum and palladium catalysts made under the same conditions have very similar activities. Palladium has the advantage of cheapness, but seems to have a greater tendency to produce side reactions. (3) The activity of both metals is considerably affected by the carrier, other things being equal. The order of activity is : metal on charcoal > metal on asbestos > metal as " black ". (4) The course of the dehydrogenation of substances containing a quaternary cyclic carbon atom is considerably affected by the nature of the carrier, but not by the choice of metal.

As far as compounds containing the angular methyl group are concerned, the results in general confirmed those of Part I. The catalysts mounted on asbestos produced the greatest amount of methyl migration, but the normal elimination was greater than that observed in the earlier work (probably owing to improvements in the technique of the examination of the product) and was about equal to the amount of migration. With the charcoal catalysts, elimination was by far the most important reaction. The process is very economical and precise. Thus in experiments with less than a gram of 9-methyldecalin, both naphthalene and 1-methylnaphthalene can be separated in good yield from the product, and the methane and hydrogen contents of the evolved gas can be measured.

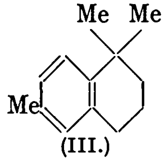
Bogert, Davidson, and Appelbaum (*J. Amer. Chem. Soc.*, 1932, **54**, 959) observed that 1 : 1-dimethyltetralin (II) resisted the action of sulphur at 221°. We found that it was rapidly dehydrogenated over platinised charcoal at 305° to 1-methylnaphthalene, a methyl group being eliminated from the quaternary carbon atom.* Catalysts mounted on asbestos were much less effective but gave the same product. Indications of the formation of a dimethylnaphthalene were obtained in an experiment with palladised charcoal at 315°. To identify the product of the side reaction, a comparatively large amount of the hydrocarbon was continuously circulated over this catalyst in the vapour phase. In addition to the 1-methylnaphthalene which formed the bulk of the product, a small quantity of 1 : 2-

* This is in contrast to the behaviour of the closely related 1 : 1-dimethyl*cyclo*hexane, which is reported to be unaffected by a very active catalyst (Zelinsky, Packendorff, and Chochlova, *Ber.*, 1935, **68**, 98). The reactivity of 1 : 1-dimethyltetralin is probably connected with the fact that it does not contain an intact *cyclo*hexane ring.

dimethylnaphthalene was identified. Again, therefore, the side reaction is one of migration to an adjacent carbon atom.



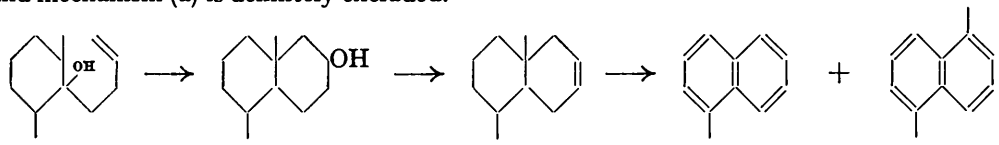
(II.)



(III.)

The hydrocarbon ionene has been proved by Bogert and his collaborators (*loc. cit.*; *J. Amer. Chem. Soc.*, 1931, **53**, 4674) to have the structure (III). Over both platinised asbestos and palladised charcoal, and at 305—330°, it yielded 1 : 6-dimethylnaphthalene, identical with material synthesised by a new and unequivocal method. We were unable to detect the presence of any trimethylnaphthalene, formed by migration. The result falls into line with those obtained by dehydrogenation with sulphur (Ruzicka and Rudolph, *Helv. Chim. Acta*, 1927, **10**, 915) and with selenium (Clemo and Dickenson, J., 1935, 735). It seems that there is much less tendency for the migration of methyl from a *gem*-group than from the angular position in hydronaphthalenes under these conditions.

Experiments bearing on Mechanism.—In Part I it was pointed out that there were three ways in which the methyl group might migrate from the angular to the α-position during the dehydrogenation of 9-methyldecalin : (a) One ring might break at the 1—9 bond, and then re-form at C_5; (b) the angular group might form an intermediate three-membered ring involving C_1; (c) there might be migration of an actual hydrocarbon fragment. The first possibility was held to be excluded by the fact that 4 : 9-dimethyloctalin (IV) and 4 : 9-dimethyldecalin both yielded 1-methylnaphthalene and 1 : 5-dimethylnaphthalene on catalytic dehydrogenation. It was thought advisable to confirm these results, because the dimethyloctalin used in the early work was obtained by direct cyclisation of dimethylbutenyl*cyclo*hexanol (V) (Linstead, Millidge, and Walpole, J., 1937, 1143) without purification through a crystalline compound. A vague possibility therefore existed that it might contain some 1 : 5-dimethyloctalin formed by a rearrangement during the cyclisation, although it is not easy to see how this could occur. To exclude any such possibility, the monocyclic alcohol (V) was cyclised to cis-4 : 9-*dimethyldecalol* (VI) by the method of Linstead, Millidge, and Walpole (*loc. cit.*). The decalol was obtained as a crystalline solid, and was dehydrated under mild conditions to *cis*-4 : 9-dimethyloctalin (IV). (The hydrocarbon has the skeleton structure shown, although some double-bond isomerides may be present.) Dehydrogenation of this hydrocarbon over platinised charcoal gave mainly 1-methylnaphthalene, whereas over platinised asbestos the main product was 1 : 5-dimethylnaphthalene. The earlier results are thus confirmed, the argument given above is valid, and mechanism (a) is definitely excluded.



m. p. 93°. m. p. 77°.

(V.) (VI.) (IV.)

This series of changes, in which both the initial and the final products are crystalline solids of different skeletal structure, supplies the most clear-cut evidence of this kind of migration.

The hypothesis of intermediate ring-formation (b) would account for the experimental fact that in the observed migrations the methyl group only passes to an adjacent carbon atom. It seemed possible to obtain some further evidence from a study of 1 : 9-dimethyloctalin. If an intermediate ring were formed, it might be a *cyclo*butane ring involving C_1 and C_9 or a *cyclo*propane ring involving C_8 and C_9. These would lead to 1-ethylnaphthalene and 1 : 8-dimethylnaphthalene respectively as final products of dehydrogenation. Direct migration of methyl groups might be expected to lead to 1 : 8-, 1 : 5-, or 1 : 4-dimethylnaphthalenes.

cis-1 : 9-*Dimethyloctalin* was prepared by the dehydration of cis-1 : 9-*dimethyldecalol* with oxalic acid, the alcohol being obtained from *cis*-9-methyl-1-decalone (Elliott and Linstead, J., 1938, 660) by a Grignard reaction. 1 : 9-Dimethyloctalin was practically unaffected by platinised asbestos at 335°, but over platinised charcoal it yielded 1-methylnaphthalene by straightforward elimination of the angular methyl group. No higher homologue could be isolated and hence no evidence bearing on the question of mechanism was obtained.

To obtain a reasonable degree of dehydrogenation of the more resistant hydrocarbons containing quaternary carbon atoms, we frequently used catalysts mounted on charcoal at, or slightly above, 325°. Although this led to a copious evolution of gas and a satisfactory conversion into aromatic structures, there appeared to be some disintegration of the molecule into small hydrocarbon fragments. The total recovery of liquid material would sometimes fall to about 70%. With the catalysts mounted on asbestos the total recovery was always excellent, although the amount of conversion into aromatic material was considerably lower.

During two vapour-phase dehydrogenations of 1 : 1-dimethyltetralin over platinised charcoal at about 320°, small quantities of naphthalene were isolated. This was evolved during the early stages of the reaction, and appears to correspond to the presence in the catalyst of some centres of transitory and abnormally high activity. A little naphthalene was also formed during the dehydrogenation of 1 : 9-dimethyloctalin. This may have been due to the same cause or to the presence of a trace of 9-methyloctalin as impurity in the starting material. This would have come from 9-methyldecalol formed by the reducing action of the Grignard reagent. On the other hand, the 1 : 9-dimethyloctalin gave correct analytical figures.

EXPERIMENTAL.

Catalysts (with K. A. O. MICHAELIS).—Norit charcoal was heated on a steam-bath for 24 hours with 10% nitric acid, washed free from acid, and dried at 100°. It was then heated at 340° in a flask which was slowly evacuated to 4 mm., left for an hour under these conditions, and allowed to cool. Gooch asbestos (tremolite, not chrysolite variety) was boiled with concentrated nitric acid, washed free from acid, and dried at 100°. All the catalysts used in the experiments described in this and the following papers were prepared by the following standard procedure, with variations only in the nature of the metal and carrier and in the concentration of the solution of metallic chloride. Catalysts prepared in more concentrated solutions (approximately the same as those of Willstätter and Waldschmidt-Leitz) will in future be designated by the suffix -*c*; those made in dilute solutions by the suffix -*d*.

Catalyst-*d*. A solution of the chloride (free from nitrate) from 5·0 g. of platinum or palladium in 50 c.c. of water and 5 c.c. of concentrated hydrochloric acid was cooled in a freezing mixture and treated with 50 c.c. of 40% formaldehyde and 11 g. of carrier (asbestos or charcoal). The mixture was stirred mechanically during the slow addition of a solution of 50 g. of potassium hydroxide in 50 c.c. of water. The temperature was kept below 5° during the addition, and finally raised to 60° for 15 minutes. The catalyst was washed thoroughly by decantation with water and finally with dilute acetic acid, collected on a filter, and washed with hot water until the washings gave no reaction for chloride, alkali or reducing material. It was dried at 100° and stored in a desiccator.

Catalyst-*c*. The same procedure was used, but the volumes of solution for 5 g. of metal were : dilute acid, 25 c.c.; formaldehyde, 35 c.c.; potassium hydroxide, 32 g. in 32 c.c. of water.

Metal was recovered from spent catalyst and purified by the methods described in Part I, or, for platinum, by Baldeschwieler and Mikeska's method (*J. Amer. Chem. Soc.*, 1935, **57**, 977), and, for palladium, by Keiser and Breed's method (*Amer. Chem. J.*, 1894, **16**, 20). The fact that recovered metal has an unimpaired activity, and the reproducibility of the catalyst, are shown by the following figures, which give the percentage elimination of hydrogen from boiling tetralin in the presence of two samples of palladised charcoal-*d* :

Time, mins.	5	10	20	30	40	50	60	
Catalyst from pure palladium	10	23	40	52	62	68	78	% Hydrogen
Catalyst from recovered palladium	10	23	35	46	62	69	79	

Materials.—*cis*-9-Methyloctalin was prepared by dehydrating pure *cis*-9-methyl-2-decalol, m. p. 72°, with potassium bisulphate (Linstead, Millidge, and Walpole, *loc. cit.*). The *cis*-9-

methyldecalin was kindly supplied by Dr. A. L. Walpole. It had been made by reduction of the corresponding 2-ketone. 6(7)-Methyltetralin was prepared by Clemmensen reduction of a sample of 7-methyl-1-tetralone, kindly given by Dr. G. A. R. Kon. 1 : 1-Dimethyltetralin (II), b. p. 100°/13 mm., was prepared by the method of Bogert, Davidson, and Apfelbaum (*loc. cit.*). 1 : 6-Dimethyltetralin was synthesised as follows :

β-*p*-Toluoylpropionic acid (Barnett and Sanders, J., 1933, 436) was converted into the ethyl ester, m. p. 43·5°, and from this γ-*p*-tolylvaleric acid was made by the method of Rupe and Steinbach (*Ber.*, 1911, **44**, 584). The chloride of this acid was cyclised by means of stannic chloride to 4 : 7-dimethyltetralone (4·3 g., b. p. 148°/14 mm., from 5·6 g. of tolylvaleric acid), which on reduction by the Clemmensen method yielded 1 : 6-dimethyltetralin (2·5 g., b. p. 107°/12 mm.).

cis-4 : 9-Dimethyloctalin (IV) was prepared from the 2 : 6-dimethyl-1-Δ^{γ}-butenyl*cyclo*hexanol (V) of Linstead, Millidge, and Walpole as follows : 55 G. of the alcohol were cyclised by means of 5 vols. of a reagent made from 10 vols. of acetic acid, 1·5 vols. of acetic anhydride, and 1 vol. of sulphuric acid. The product was worked up as described for the lower homologue (J., 1937, 1143) and, after hydrolysis, yielded a crude dimethyldecalol of b. p. 132—142°/13 mm. When cooled in a freezing mixture, this fraction solidified. The solid was pressed on a porous tile and crystallised to constant m. p. from light petroleum. Yield of pure cis-4 : 9-*dimethyldecalol*, 9·3 g.; m. p. 93° (Found : 78·7, 78·6; H, 12·0, 11·9. $C_{12}H_{22}O$ requires C, 79·0; H, 12·2%). Dehydration of 9 g. of this with potassium bisulphate (195°, 3 hours) yielded 4 : 9-dimethyloctalin, which was refluxed with potassium and twice distilled; b. p. 86°, yield 6·7 g.

1 : 9-Dimethyloctalin was made from *cis*-9-methyl-1-decalone as follows : the ketone (8·7 g.), regenerated from the pure semicarbazone (13·4 g., m. p. 224°; Elliott and Linstead, *loc. cit.*), was treated with methylmagnesium iodide (30% excess). The product distilled over a range and failed to solidify. Analysis showed that it was 1 : 9-*dimethyl*-1-*decalol* contaminated with a little hydrocarbon (Found : C, 79·7; H, 11·9. $C_{12}H_{22}O$ requires C, 79·0; H, 12·2%). Dehydration through the xanthate was unsatisfactory and the decalol (6 g.) was accordingly heated gently with 10 g. of crystalline oxalic acid. Dimethyloctalin and water slowly distilled, and after 2 hours the bath temperature was raised to 180° and there maintained for a further 2 hours. The distillation was completed by reducing the pressure and the cis-1 : 9-*dimethyloctalin* was extracted with purified light petroleum and distilled from sodium; b. p. 87°/8—9 mm., yield 5 g. (Found : C, 87·6; H, 12·2. $C_{12}H_{20}$ requires C, 87·7; H, 12·3%).

Ionene (1 : 1 : 6-trimethyltetralin) was prepared by the cyclodehydration of β-ionone, following Bogert and Fourman (*J. Amer. Chem. Soc.*, 1933, **55**, 4674); b. p. 113—114°/12 mm.

The physical constants of these hydrocarbons are tabulated below :

TABLE I.

Hydrocarbon.	$n_D^{t°}$.	$d_{4°}^{t°}$.	*t*.	$[R_L]_D$. Found.	$[R_L]_D$. Exaltation over calc.
6-Methyltetralin	1·5351	0·9526	21°	47·71	+0·51
1 : 6-Dimethyltetralin	1·527	0·9403	18·5	52·34	+0·52
1 : 1-Dimethyltetralin	1·5291	0·9470	21	52·10	+0·28
1 : 1 : 6-Trimethyltetralin	1·5253	0·9359	17	56·98	+0·54
cis-9-Methyloctalin	1·4913	0·9098	15	47·82	−0·31
cis-1 : 9-Dimethyloctalin	1·4954	0·9075	20	52·74	−0·01
cis-4 : 9-Dimethyloctalin	1·4905	0·9055	15	52·48	−0·27

Dehydrogenation of Methyltetralins in the Liquid Phase.—The reactions were carried out in a current of carbon dioxide in the apparatus illustrated in Part I (J., 1937, 1153), the various substances being boiled with 10% palladised charcoal-*c*.

Results with tetralin are added, some values being interpolated for ease in comparison.

TABLE II.

Expt. No.	Hydrocarbon.	% Evolution of hydrogen in minutes. 40.	120.	140.	320.	Final.
(1)	Tetralin	28	65	72	91	92
(2)	6-Methyltetralin	55	80	86	97	97
(3)	1 : 6-Dimethyltetralin	86	97	—	—	100
(4)	1 : 1-Dimethyltetralin	—	—	5	—	5
(5)	1 : 1 : 6-Trimethyltetralin	—	—	—	5	5

Additional notes.

(2) 770 Mg. of 6-methyltetralin yielded 600 mg. of 2-methylnaphthalene, m. p. and mixed m. p. 32·5°.

(3) 940 Mg. of 1 : 6-dimethyltetralin yielded 870 mg. of aromatic product, which gave 1·97 g. of the yellow picrate of 1 : 6-dimethylnaphthalene, m. p. 111° without crystallisation (lit. 113°), an overall yield of 87%.

(4) The experiment was continued for 50 hours. The product from 1 g. of 1 : 1-dimethyltetralin yielded 0·1 g. of 1-methylnaphthalene picrate, m. p. and mixed m. p. 139°.

(5) The aromatic product from 1 g. of ionene was separated after 50 hours. It was precipitated with an excess of picric acid (following the general technique of Ruzicka), and the mixture of picrate and picric acid dissolved in ether and decomposed with ammonia. 30 Mg. of regenerated hydrocarbon were obtained, which yielded 1 : 6-dimethylnaphthalene picrate, m. p. 109°, mixed m. p. 110°.

Dehydrogenation of 1 : 1-*Dimethyltetralin in the Vapour Phase.*—The apparatus and procedure have been described in Part I. The results are tabulated below. The extent of dehydrogenation given in the last column is calculated from the evolution of gas.

TABLE III.

Catalyst.	Temp.	Quantity used (g.).	% Dehydrogenation.
(1) Platinised charcoal-*c*	320°	1·35	47
(2) Platinised charcoal-*c*	325	1·28	49
(3) Platinised asbestos-*d*	320	1·43	44
(4) Palladised asbestos-*d*	320	1·49	16
(5) Palladised charcoal-*c*	310	1·36	50
(6) Palladised charcoal-*c*	315	1·28	78
(7) Palladised charcoal-*d*	330	0·98	76
(8) Platinised charcoal-*d*	305	1·32	85

Additional notes.

(1) The product (1·18 g.) was separated by means of picric acid into 0·36 g. of aromatic material and 0·69 g. of liquid which formed no picrate. The latter had b. p. 113—114°/21 mm., $n_D^{23^\circ}$ 1·5349, $d_4^{23^\circ}$ 0·9572, and hence was largely unchanged 1 : 1-dimethyltetralin.

(2) In this experiment and in (1) a trace of naphthalene (m. p. and mixed m. p. 81°) collected in the receiver in the early stages. The aromatic product was combined with that from (1); it yielded 1-methylnaphthalene picrate, m. p. and mixed m. p. 139° (Found : C, 55·2; H, 3·8. Calc. for $C_{11}H_{10},C_6H_3O_7N_3$: C, 55·0; H, 3·5%).

(4) The product yielded only 80 mg. of aromatic hydrocarbon from the picrate. This was separated by micro-fractional distillation into 10 mg. portions, which were converted separately into picrates. The first of these melted at 140°, all the others at 141°, alone or mixed with pure 1-methylnaphthalene picrate (m. p. 141°).

(5) The liquid product (0·87 g.) yielded through the picrate 0·58 g. of aromatic hydrocarbon, and thence 1·27 g. of a picrate which softened at 130°, and was evidently a mixture of about equal parts of the derivatives of mono- and di-methylnaphthalenes (Found : C, 55·6, 55·7; H, 3·7, 3·6. Calc. for $C_{11}H_{10},C_6H_3O_7N_3$: C, 55·0; H, 3·5%. Calc. for $C_{12}H_{12},C_6H_3O_7N_3$: C, 56·1; H, 3·9%).

(6) Repetition of the last dehydrogenation over the same catalyst at a slightly higher temperature, however, gave very little migration. The product was separated into 140 mg. of non-aromatic and 770 mg. of aromatic material. The latter on fractionation over sodium yielded 500 mg. of almost pure 1-methylnaphthalene, b. p. 121—124°/22 mm. (Found : C, 93·0; H, 7·3. Calc. : C, 92·9; H, 7·1%), and a little higher-boiling material. The main fraction gave a picrate, m. p. 138°, mixed m. p. 139° (Found : C, 55·1; H, 3·8%). The picrate of the high fraction melted at 131° and was a mixture.

(7) The aromatic product yielded 1·35 g. of 1-methylnaphthalene picrate, m. p. and mixed m. p. 141°.

(8) The picrate of the product melted at 139°, and the styphnate at 133°, mixed m. p. 133·5°.

To identify the dimethylnaphthalene formed under the conditions of experiment (5), an apparatus was used which allowed the vapour of the hydrocarbon to be circulated repeatedly over the catalyst. The apparatus had a vertical catalyst tube and resembled that used by Ruzicka and Stoll (*Helv. Chim. Acta*, 1924, **7**, 84), except that provision was made for gas measurement and the apparatus was used at atmospheric pressure. It was essential to use a carefully dried catalyst and to evacuate the apparatus with the catalyst tube at 320°, before commencing the experiment, to remove traces of moisture. Even so, the apparatus was found difficult to operate continuously for long periods.

6·5 G. of 1 : 1-dimethyltetralin were circulated over palladised charcoal-*c* at 320° during 16 hours. 784 C.c. of gas were evolved. The experiment was then continued with fresh catalyst and a further 153 c.c. of gas were collected during 15 hours. 2·35 G. of aromatic hydrocarbon were separated from the residual liquid by Ruzicka's technique. This was distilled over sodium. It boiled mainly at 123°/20 mm. and this fraction yielded pure 1-methylnaphthalene picrate (yellow needles, m. p. and mised m. p. 141°). About 0·1 g. of a high-boiling fraction was collected which gave the orange-red picrate of 1 : 2-dimethylnaphthalene. After recrystallisation, this melted at 132° alone and at 131·5° in admixture with the authentic picrate prepared by synthesis (m. p. 131°, Part I) (Found : C, 56·2, 56·05; H, 3·8, 3·9. Calc. for $C_{12}H_{12},C_6H_3O_7N_3$: C, 56·1; H, 3·9%).

TABLE IV.

Dehydrogenation of Ionene in the Vapour Phase.

Catalyst.	Temp.	Quantity used (g.).	% Dehydrogenation.
(1) Platinised asbestos-*c*	325°	1·24	37
(2) Platinised asbestos-*c*	305	1·28	16
(3) Palladised charcoal-*c*	330	1·31	86
(4) Palladised charcoal-*c*	310	1·20	89

(1) The liquid product yielded 220 mg. of aromatic hydrocarbon and thence 490 mg. of the picrate of 1 : 6-dimethylnaphthalene melting at 108° (crude) and at 110° after one crystallisation; mixed m. p. 110·5° (Found : C, 56·1; H, 4·0. Calc. for $C_{12}H_{12},C_6H_3O_7N_3$: C, 56·1; H, 3·9%).

(3) 640 Mg. of aromatic hydrocarbon were isolated and thence 1·32 g. of 1 : 6-dimethylnaphthalene picrate (m. p. and mixed m. p. 111°. Found : C 56·3, 56·2; H, 4·0, 4·1%).

Dehydrogenation of cis-*9-Methyl-octalin and -decalin in the Vapour Phase.*—These results supplement those of Part I. The aromatic material from all the experiments was a semi-solid mixture, which was cooled and drained on a porous tile. The residual solid was naphthalene, m. p. 81°. Extraction of the tile yielded 1-methylnaphthalene, identified as the picrate. The last experiment was with 9-methyloctalin, the others with 9-methyldecalin.

TABLE V.

Catalyst.	Temp.	Hydrocarbon, g.	% Dehydrogenation.	Aromatic product.			
				Total, g.	Naphthalene, g.	1-Methylnaphthalene picrate, g.	1-Methylnaphthalene picrate, m. p.
(1) Palladised asbestos-*d*	320°	0·88	8·5	—	—	—	—
(2) Platinised asbestos-*d*	325	0·90	19	0·25	0·10	0·22	140°
(3) Palladised charcoal-*d*	325	0·83	73	0·58	0·37	0·22	140
(4) Platinised charcoal-*c*	320	0·85	83	0·50	0·39	0·15	140
(5) Platinised asbestos-*c*	330	1·12	32	0·20	0·07	0·16	141

Additional notes.

(2) 0·53 G. of non-aromatic material recovered.

(4) The gas evolved contained 84% of hydrogen and 11% of methane, together with 5% of air from the dead space of the apparatus.

(5) The non-aromatic portion (0·66 g.) was boiled with potassium and distilled. Its physical properties ($n_D^{19·3°}$ 1·4928, $d_{4°}^{19·3°}$ 0·9089) were very close to those of the original 9-methyloctalin (see Table I) and it was unsaturated to bromine in chloroform.

TABLE VI.

Dehydrogenation of cis-*Dimethyloctalins in the Vapour Phase.*

Hydrocarbon.	Catalyst.	Temp.	Quantity used, g.	% Dehydrogenation.	Aromatic products.
(1) 4 : 9-Dimethyl	Pt asbestos-*c*	330°	0·91	10	Mixture of mono- and di-methylnaphthalene
(2) ,,	,,	325	1·42	40	1 : 5-Dimethyl- and some methylnaphthalene
(3) ,,	Pt charcoal-*c*	325	1·30	16	Mainly 1-methylnaphthalene
(4) 1 : 9-Dimethyl	Pt asbestos-*c*	335	1·72	20	
(5) ,,	Pt charcoal-*c*	325	1·13	90	1-Methylnaphthalene and a little naphthalene

Additional notes.

(1) The aromatic product (0·08 g.) failed to solidify on cooling and yielded a mixed picrate, m. p. 136° (Found: C, 55·7, 55·7; H, 3·9, 3·7. Calc. for $C_{11}H_{10},C_6H_3O_7N_3$: C, 55·0; H, 3·5%. Calc. for $C_{12}H_{12},C_6H_3O_7N_3$: C, 56·1; H, 3·9%).

(2) The hydrocarbon was passed twice over the same catalyst. The final product (1·25 g.) yielded 1·00 g. of non-aromatic material which decolorised bromine ($n_D^{20^\circ}$ 1·5081) and 0·21 g. of aromatic material. This deposited 40 mg. of 1 : 5-dimethylnaphthalene, m. p. and mixed m. p. 77°. The liquid portion was fractionally distilled. It yielded mainly 1 : 5-dimethylnaphthalene, together with some lower-boiling material, presumably 1-methylnaphthalene. The yellow picrate of the main fraction had m. p. 135°, or 135·5° when mixed with 1 : 5-dimethylnaphthalene picrate, m. p. 137° (Found: C, 56·3; H, 4·1%).

(3) The aromatic fraction (0·35 g.) did not solidify on cooling. It yielded a picrate, m. p. 137°, or at 138° in admixture with 1-methylnaphthalene picrate. Analysis showed it was the latter, contaminated with a little of the dimethyl derivative (Found: C, 55·3, 55·5; H, 3·5, 3·5%).

In these experiments the orange picrate, m. p. 134°, isolated in Part I (p. 1156), was not encountered.

(4) 1·64 G. of hydrocarbon were recovered, which were separated into 1·40 g. of non-aromatic and 0·06 g. of aromatic material.

(5) 0·60 G. of liquid hydrocarbon and 0·11 g. of crude solid naphthalene were isolated. The liquid product was purified in the usual way through the picrate and the aromatic portion (0·53 g.) was freed from a little more solid by cooling to −20°. The liquid product gave a picrate, m. p. 138°, and a styphnate, m. p. 132°. In admixture with the corresponding derivatives of 1-methylnaphthalene the m. p.'s were 139° and 134° respectively. The styphnate had C, 53·1; H, 3·5% (Calc. for $C_{11}H_{10},C_6H_3O_8N_3$: C, 52·7; H, 3·4%).

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