945. *Hydrogen Transfer. Part XIX.*[1] *Dehydrogenation of Substituted* 1,2-*Dihydronaphthalenes by Quinones, and the Correlation of Donor Reactivity with the Nature of Substituents.*

By L. M. Jackman and D. T. Thompson.

The stoicheiometry and kinetics of the dehydrogenation of a series of substituted 1,2-dihydronaphthalenes by tetrachloro-1,2-benzoquinone in 1,2-dichlorobenzene have been studied. A charge-transfer complex is formed between the reactants; the significance of this, and the degree of complex formation, are discussed. The rates have been correlated with σ and σ^+, and certain deviations from the straight-line plots have been shown to be due to a change in the principal site of attack in these cases from the 2- to the 1-position. The difference in ease of attack at the 1- and the 2-position of the dihydronaphthalene system has been assessed. The results are discussed in terms of the two-step ionic mechanism postulated in earlier papers. Syntheses of a number of new 1,2-dihydronaphthalenes are described.

It has been shown (Part II [2]) that, in accord with the postulated two-step ionic mechanism, the reactivity of quinones is increased by the presence of electron-attracting

[1] Part XVIII, Braude, Hannah, and Linstead, *J.*, 1960, 3268.
[2] Braude, Jackman, and Linstead, *J.*, 1954, 3548.

substituents, and that there is a linear free-energy relation with oxidation–reduction potentials. In the first section of this paper an investigation into the kinetics of the dehydrogenation of a series of 6- and 7-substituted 1,2-dihydronaphthalenes by tetrachloro-1,2-benzoquinone is described, in which the effect of substituents on the rate of dehydrogenation is established; the second section describes the synthesis of a number of new 1,2-dihydronaphthalenes; and the third section contains the results of preparative dehydrogenations which establish the stoicheiometry of the class of reactions discussed in the first section.

Kinetic Studies.—All kinetic experiments were carried out with 1,2-dichlorobenzene as solvent; the rate of disappearance of quinone was measured by the spectroscopic technique " b " described in Part XI.[3] Each reaction was found to obey the second-order rate equation up to at least 80% completion (70% in the case of 1,2-dihydro-2,2-dimethylnaphthalene). However, it was observed that with many of the dihydronaphthalenes the initial optical density of the reaction system at 5700 Å was higher than that found for a solution of the same concentration of quinone alone in the solvent (Table 1). These results indicate that the quinone and the dihydronaphthalenes form

TABLE 1.

Initial extinction coefficients of 1,2-dihydronaphthalenes (0·0500M) and tetrachloro-1,2-benzoquinone (0·0100M) in 1,2-dichlorobenzene.

Subst. 1,2-dihydronaphthalene	Temp. range	E_0 (5700 Å) range	Subst. 1,2-dihydronaphthalene	Temp. range	E_0 (5700 Å) range
Control (0·01M-quinone) ...	23·0°	0·98	7-Methyl.....	36·8—55·3°	1·28—1·32
Parent compound	48·3—77·2°	0·98—1·03	6-Methyl.....	31·9—56·7	1·25—1·32
1,1-Dimethyl-.....	60·4—82·4	0·97—1·03	6-Acetamido-.....	36·1—61·9	1·17—1·25
2,2-Dimethyl-.....	88·0—114·8	0·94—1·00	7-Chloro-	68·2—90·5	0·94—0·98
7-Methoxy-.....	22·6—39·8	1·40—1·45	6-Chloro-	70·9—93·2	0·94—0·97
7-Methoxy-1,1-dimethyl- ...	27·4—42·4	1·10—1·17	6-Bromo-	71·0—93·1	0·92—0·95
6-Methoxy-	28·0—52·8	1·17—1·24	6-Nitro-	89·2—111·5	0·90—0·91
6-Methoxy-1,1-dimethyl- ...	55·9—73·9	1·05—1·12			

charge-transfer complexes and, as expected, the tendency to do so is most pronounced with the dihydronaphthalenes bearing electron-donating substituents. Complex formation between the reactants was not observed in previous investigations carried out with phenetole as solvent, presumably because the solvent itself forms a complex with the quinone (see below).

The initial formation of a charge-transfer complex between the reactants can be demonstrated by studying the kinetics at varying concentrations of reactants.[4] Second-order rate constants for the 1,2-dihydro-6-methylnaphthalene reaction have been determined at a series of concentrations of hydrocarbon (Fig. 1). Andrews and Keefer [4] have shown that when one of the reactants is present in excess the observed second-order rate constants ($k_{obs.}$) are related to the equilibrium constant (K) for complex formation and the rate constant (k_1 or k_2) of the rate-determining step by equations (3) and (4) (which are written here for an excess of donor), depending on whether the complex undergoes the product-forming reaction (1) or is an unreactive by-product (2), respectively.

$$Q + DHN \underset{\text{(Fast)}}{\overset{K}{\rightleftharpoons}} Q.DHN \xrightarrow[\text{(Slow)}]{k_1} \text{Products} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$Q + DHN \xrightarrow[\text{(Slow)}]{k_2} \text{Products} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$\begin{array}{l} \text{(Fast)}\downarrow\uparrow K \\ Q + DHN \end{array}$$

$$1/k_{obs.} = 1/k_1K + [DHN]/k_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$1/k_{obs.} = 1/k_2 + K[DHN]/k_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

[3] Braude, Jackman, Linstead, and Shannon, *J.*, 1960, 3116.
[4] Andrews and Keefer, *J. Amer. Chem. Soc.*, 1955, **77**, 6284.

K, k_1, and k_2 can be evaluated from the plot of $1/k_{obs.}$ against [DHN] (Fig. 1), which should have a constant slope in the region where the concentration of dihydronaphthalene is much greater than that of the quinone. Thus we have used Fig. 1 to give us the approximate values $k_1 = 0{\cdot}67 \times 10^{-2}$ sec.$^{-1}$ by equation (3), and $k_2 = 1{\cdot}2 \times 10^{-2}$ l. mole^{-1} sec.$^{-1}$ by equation (4); $K = 1{\cdot}8$ l. mole^{-1} by both equations.

Andrews and Keefer [4] also used the variation of initial optical densities with concentration of reactants as an independent means of evaluating the equilibrium constant.

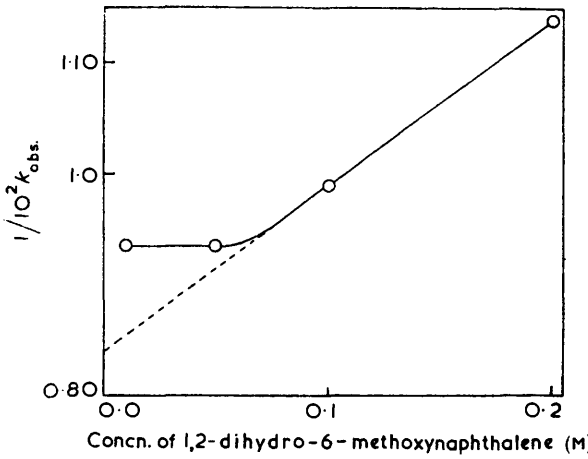


FIG. 1. Plot of $1/k_{obs.}$ against concentration of 1,2-dihydro-6-methylnaphthalene with 0·0100M-tetrachloro-1,2-benzoquinone.

We have used expression (5) (where A_c is the initial absorbance and ε_c the extinction coefficient of the complex) to obtain an approximate value

$$[Q]/A_c = (K\varepsilon_c)^{-1}\,(1/[DHN]) + 1/\varepsilon_c \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

of $K = 2$ l. mole^{-1}. It is seen that the two values of K are in reasonable agreement. It is not possible to distinguish between the paths represented by equations (1) and (2). In principle, values of k_2 (or k_1K) could be determined for the entire series of dihydronaphthalenes but in practice such experiments would require considerable quantities of materials, some of which are difficult to obtain. However, the results obtained for 1,2-dihydro-6-methylnaphthalene indicate that although $k_{obs.}$ determined at 0·05M-concentration of the hydrocarbon is lower than k_2 (or k_1K) the error introduced by equating the two is small. This error will probably be somewhat larger for the methoxy-derivatives but substantially smaller for those derivatives which have electron-withdrawing substituents. We have therefore determined $k_{obs.}$ at 0·05M-concentration for each member of the series and will use these values for comparing the relative reactivities of the dihydronaphthalenes. Table 2 gives values of observed second-order rate constants, $k_{obs.}$, at 25° and the related Arrhenius parameters $\Delta S^{\ddagger}$ and E_A.

The results can now be discussed in terms of the two-step ionic mechanism postulated in earlier papers.[2,3,5-8] If it is assumed that the rate-controlling hydride-ion abstraction occurs at the 2-position of the dihydronaphthalene, 6- and 7-substituents are respectively analogous to *meta*- and *para*-substituents in their electronic effects. Fig. 2 shows the Hammett plot based on $k_{obs.}$ at 25° and Jaffé's [9] σ-values. With the exceptions of 6-acetamido-1,2-dihydronaphthalene and 1,2-dihydro-6-methoxynaphthalene, a reasonable

[5] Braude, Jackman, and Linstead, *J.*, 1954, 3564.
[6] Barnard and Jackman, *J.*, 1960, 3110.
[7] Braude, Jackman, Linstead, and Lowe, *J.*, 1960, 3123.
[8] Braude, Jackman, Linstead, and Lowe, *J.*, 1960, 3133.
[9] Jaffé, *Chem. Rev.*, 1953, **53**, 191.

TABLE 2.

Arrhenius parameters and observed rate constants at 25°.

Subst. 1,2-dihydronaphthalene	$k_{obs.}$ (l. mole^{-1} sec.$^{-1}$)	$\Delta S_{25}^{\ddagger}$ (E.U.)	E_A (kcal. mole^{-1})
Parent compound	$1{\cdot}19 \pm 0{\cdot}08 \times 10^{-3}$	$30{\cdot}2 \pm 1{\cdot}5$	$13{\cdot}2 \pm 0{\cdot}4$
1,1-Dimethyl-	$7{\cdot}36 \pm 0{\cdot}84 \times 10^{-4}$	$31{\cdot}4 \pm 1{\cdot}9$	$14{\cdot}3 \pm 0{\cdot}5$
2,2-Dimethyl-	$3{\cdot}03 \pm 0{\cdot}15 \times 10^{-5}$	$28{\cdot}9 \pm 3{\cdot}5$	$15{\cdot}5 \pm 1{\cdot}0$
7-Methoxy	$2{\cdot}29 \pm 0{\cdot}10 \times 10^{-2}$	$30{\cdot}8 \pm 1{\cdot}4$	$10{\cdot}4 \pm 0{\cdot}4$
7-Methoxy-1,1-dimethyl-	$1{\cdot}43 \pm 0{\cdot}06 \times 10^{-2}$	$31{\cdot}4 \pm 0{\cdot}8$	$11{\cdot}9 \pm 0{\cdot}2$
6-Methoxy-	$9{\cdot}93 \pm 0{\cdot}33 \times 10^{-3}$	$31{\cdot}7 \pm 1{\cdot}4$	$11{\cdot}5 \pm 0{\cdot}4$
6-Methoxy-1,1-dimethyl-	$9{\cdot}73 \pm 0{\cdot}92 \times 10^{-4}$	$24{\cdot}9 \pm 1{\cdot}9$	$14{\cdot}9 \pm 0{\cdot}5$
7-Methyl-	$4{\cdot}47 \pm 0{\cdot}14 \times 10^{-3}$	$31{\cdot}0 \pm 1{\cdot}1$	$12{\cdot}2 \pm 0{\cdot}3$
6-Methyl-	$4{\cdot}06 \pm 0{\cdot}06 \times 10^{-3}$	$29{\cdot}5 \pm 0{\cdot}4$	$12{\cdot}1 \pm 0{\cdot}1$
6-Acetamido-	$3{\cdot}31 \pm 0{\cdot}15 \times 10^{-3}$	$32{\cdot}8 \pm 1{\cdot}1$	$11{\cdot}8 \pm 0{\cdot}3$
7-Chloro-	$4{\cdot}37 \pm 0{\cdot}12 \times 10^{-4}$	$29{\cdot}8 \pm 0{\cdot}6$	$13{\cdot}9 \pm 0{\cdot}1$
6-Chloro-	$2{\cdot}81 \pm 0{\cdot}22 \times 10^{-4}$	$28{\cdot}0 \pm 1{\cdot}2$	$14{\cdot}6 \pm 0{\cdot}3$
6-Bromo-	$2{\cdot}87 \pm 0{\cdot}19 \times 10^{-4}$	$27{\cdot}8 \pm 0{\cdot}8$	$14{\cdot}8 \pm 0{\cdot}2$
6-Nitro-	$5{\cdot}13 \pm 0{\cdot}95 \times 10^{-5}$	$27{\cdot}8 \pm 2{\cdot}0$	$15{\cdot}8 \pm 0{\cdot}5$

correlation is obtained. When the σ^+-values, determined by Brown and Okamoto,[11] are used instead of σ (Fig. 3) the only points falling a significant distance from the plot are those arising from the experiments with compounds having electron-donating

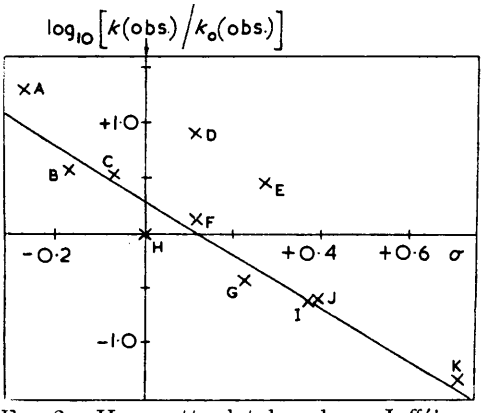


FIG. 2. Hammett plot based on Jaffé's σ-values.[9] (σ for *m*-acetamido was determined by McDaniel and Brown.[10])

A, 7-MeO. B, 7-Me. C, 6-Me. D, 6-MeO. E, 6-NHAc. F, 6-MeO-1,1-Me_2 (corr.). G, 7-Cl. H, Unsubst. I, 6-Cl. J, 6-Br. K, 6-NO_2.

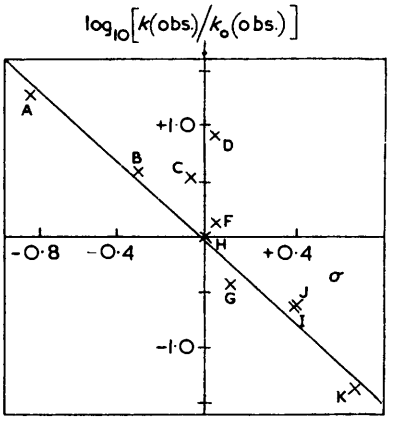


FIG. 3. ρ–σ^+ Correlation based on Brown and Okamoto's σ^+ values.[11] Key as for Fig. 2.

6-substituents (methoxy and methyl). That these deviations are not due to the assumption that $k_{obs.}$ is equal to k_2 (or k_1K) can be demonstrated by the inclusion of points corresponding to the correct value of k_2 (or k_1K) for the 6-methyl compound. Two possible explanations for the observed deviations will now be considered.

If the reaction follows scheme (1), so that $k_{obs.} \simeq k_1K$, either or both steps could determine the relative reactivities used in the σ and σ^+ correlations. If K is the dominant term it may be incorrect to assign *meta*- and *para*-substituent constants to the 6- and the 7-position, respectively. Thus, if complex formation is merely determined by the activation of the aromatic ring, the position of the substituent would be unimportant. If *para*-substituent constants are used for both the 6- and the 7-substituted 1,2-dihydronaphthalenes, there are no longer any deviations as great as those observed for the

[10] McDaniel and Brown, *J. Org. Chem.*, 1958, **23**, 420.
[11] Brown and Okamoto, *J. Amer. Chem. Soc.*, 1958, **80**, 4979.

6-methoxy-substituent in the previous plots (Figs. 2 and 3), but the overall correlations are not as good as those in Figs. 2 and 3.

For the 1,2-dihydro-6-methylnaphthalene reaction, the values of K and E_0 at 40° have been used to afford the magnitude of the molecular extinction coefficient (ε_c) of the complex. This value for ε_c was then used, together with the initial extinction coefficients at various temperatures, in calculating an approximate value of −0·6 kcal. mole^{-1} for the heat of formation of the complex. If anything, the optical density for the 6-nitro-compound decreases with increasing temperature, so that even for this compound the heat of formation of the complex is less than, or equal to, zero. The difference in the heat of formation of $\geqslant$0·6 kcal. mole^{-1} for complexes with the 6-methyl and the 6-nitro-compound is substantially less than that (3·6 kcal. mole^{-1}) between their activation energies for dehydrogenation. The former value is of the same order as that (0—1·5 kcal. mole^{-1}) found for the heats of formation of complexes between tetrachloro-1,4-benzoquinone and a series of *meta*- and *para*-substituted styrenes, ranging from the *p*-methoxy- to the *m*-chloro-derivatives, by Walling *et al.*[12] It is therefore unlikely that complex formation can play a major rôle in determining the sensitivity of the reaction to substituent effects. Further, it is probable that complex-formation involves the isolated double bond rather than the aromatic ring. If initial extinction coefficients (Table 1) can be regarded as an approximate measure of complex formation, it is seen that the 6-methoxy-compound forms a complex less readily than does the 7-derivative, suggesting that the isolated double bond is in fact the site of complex formation and that we were originally correct in using *meta*- and *para*-substituent constants for the 6- and the 7-substituents, respectively. The conclusion regarding the site of complex formation is consistent with Andrews and Keefer's observations[13] that silver cations form a more stable complex with styrene than with anisole.

The alternative explanation for the anomalous effect of electron-donating 6-substituents is that the initial assumption of exclusive removal of a hydride ion from the 2-position is incorrect. It is possible that in the presence of such substituents the mechanism changes to one involving predominant attack at the 1-position. In order to test this possibility we have examined the effect of a 6- and a 7-methoxy-substituent on the rate of dehydrogenation of 1,2-dihydro-1,1-dimethylnaphthalene in which attack at the 1-position cannot occur. The results (Table 2) show that the 6-methoxy-substituent is no longer effective in activating the reaction. The rate constant for attack at the 2-position of 1,2-dihydro-7-methoxynaphthalene can be estimated by multiplying the observed rate constant for 1,2-dihydro-7-methoxy-1,1-dimethylnaphthalene by the ratio (1·62 : 1) of the rate constants for 1,2-dihydronaphthalene and 1,2-dihydro-1,1-dimethylnaphthalene. The value thus obtained for 1,2-dihydro-7-methoxynaphthalene is $2{\cdot}32 \times 10^{-2}$ l. mole^{-1} sec.$^{-1}$, in excellent agreement with the observed value ($2{\cdot}29 \times 10^{-2}$ l. mole^{-1} sec.$^{-1}$). A similar calculation gives the rate constant for 1,2-dihydro-6-methoxynaphthalene as $1{\cdot}58 \times 10^{-3}$ l. mole^{-1} sec.$^{-1}$ which is substantially lower than the observed value ($9{\cdot}93 \times 10^{-3}$ l. mole^{-1} sec.$^{-1}$); when assigned σ- and σ^+-values for the *m*-methoxy-substituent these results give points which fall close to the plots (Figs. 2 and 3) obtained from 7-substituents and electron-attracting 6-substituents. There is little doubt, therefore, that the anomalous effect of electron-donating 6-substituents is due to a change from the 2- to the 1-position as the principal site of hydride ion abstraction.

The relative rate constants for attack at the 1- and the 2-position of 1,2-dihydronaphthalene itself can be estimated from the ratio of the rate constants for reaction with 1,2-dihydro-2,2-dimethyl- and 1,2-dihydro-1,1-dimethyl-naphthalene, and it is seen that attack at the 2-position is favoured by a factor of *ca.* 24. This result confirms earlier conclusions[7,8] and reflects the relative stabilities of the 1- and the 2-naphthalenium ion.[6] In the presence of a 6-methoxy-substituent the rate constant for attack at the 2-position is reduced to 0·19 times that for attack at the 1-position.

[12] Walling, Briggs, Wolfstern, and Mayo, *J. Amer. Chem. Soc.*, 1948, **70**, 1537.
[13] Andrews and Keefer, *J. Amer. Chem. Soc.*, 1949, **71**, 3644; 1950, **72**, 3113, 5034.

The ρ-value observed for the reaction represents an upper limit for the sensitivity of hydride ion abstraction to the nature of substituents in the donor, because if mechanism (1) operates the observed value of ρ will be the sum of the ρ-values for the two steps and these will both be negative. Our ρ-value (−2·5) would be consistent with an ionic nature of mechanism (2) as it is of the same magnitude as that (−2·6) found [9] for the solvolysis of triphenylmethyl chlorides,[14] an ionic reaction having comparable activation energy (12·5 kcal. mole^{-1} for the *p*-methyl to 16·7 kcal. mole^{-1} for the *p*-nitro-derivative).

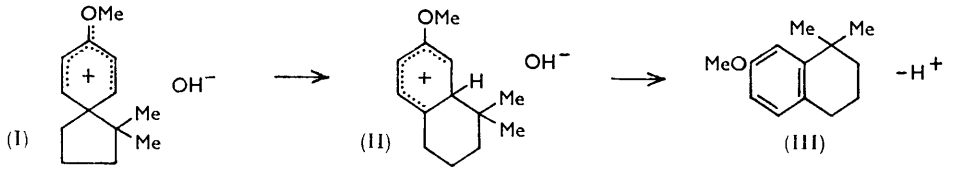
At 77°, the rate constant for the reaction of 1,2-dihydronaphthalene in phenetole [8] is smaller by a factor of 3·1 times that observed here for reaction in 1,2-dichlorobenzene. However, the activation energy of the reaction in phenetole is 2·2 kcal. mole^{-1} greater than that for the reaction in 1,2-dichlorobenzene and the difference is doubtless due to the fact that the quinone forms complexes strongly with the former solvent. The solvent–quinone complex-formation can be clearly demonstrated by light-absorption measurements. At 25°, the optical density at 6050 Å of a 0·01M-solution of the quinone is 0·9 in phenetole compared with 0·2 in 1,2-dichlorobenzene.

The Preparation of 6- *and* 7-*Substituted* 1,2-*Dihydronaphthalenes.*—The most convenient synthetic approach involved preparation of the appropriate 1-tetralone, the majority of which were obtained by cyclisation in anhydrous hydrofluoric acid of the corresponding substituted phenylbutyric acid, or by oxidation of the appropriately substituted tetralin. Schroeter's method [15] was used to prepare 7-nitro-1-tetralone from 1-tetralone. Selective reduction [16] of the nitro-group of this ketone, and acetylation of the product gave 7-acetamido-1-tetralone. The 1-tetralones were reduced with potassium borohydride or aluminium isopropoxide,[17] and the resulting 1-tetralols dehydrated to give the 1,2-dihydronaphthalene.

1,2-Dihydro-1,1-dimethylnaphthalene was prepared by the method described earlier,[7,8] except that we carried out the cyclodehydration of 1,1-dimethyl-4-phenylbutan-1-ol to 1,1-dimethyltetralin very effectively in anhydrous hydrofluoric acid. 6- and 7-Methoxy-1,1-dimethyltetralin were obtained by similar cyclodehydration of 4-*m*- and 4-*p*-methoxyphenyl-1,1-dimethylbutan-1-ol, respectively. These alcohols were obtained from acetone and the Grignard compound formed from the appropriate 1-bromo-3-methoxyphenylpropane. However, neither of these last two cyclodehydrations can be regarded as unambiguous. The *meta*-derivative can in principle cyclise in either the *ortho*- or the *para*-positions by the Ar_2-6 mechanism,[18] although for steric reasons the latter is the more likely. The product appeared to be homogeneous on vapour-phase chromatography and its nuclear magnetic resonance spectrum showed it to be a 1,3,4- rather than a 1,2,3-trisubstituted benzene since one proton resonance did not exhibit an *ortho*-coupling. There can therefore be no doubt that this compound is 6-methoxy-1,1-dimethyltetralin. Cyclisation of the *para*-alcohol probably takes place by an Ar_1-5 mechanism [18] involving the spiro-intermediate (I), rather than direct substitution at the positions *meta* to the methoxy-substituent. The subsequent rearrangement of (I) could yield either 6- or 7-methoxytetralin although preferential migration of the more heavily substituted carbon is expected.[18] Again the product was homogeneous and it had an infrared spectrum different from that for 6-methoxy-1,1-dimethyltetralin; it must therefore be the 7-methoxy-isomer. Support for the assigned structures of these two tetralins was obtained when the conversion of these two isomers into the 1,2-dihydronaphthalenes was attempted. The 6-isomer was converted into the 4-bromo-derivative by *N*-bromosuccinimide,[8] and subsequently dehydrobrominated [8] to 1,2-dihydro-6-methoxy-1,1-dimethylnaphthalene. In contrast, bromination of the 7-methoxy-compound was followed

[14] Nixon and Branch, *J. Amer. Chem. Soc.*, 1936, **58**, 492.
[15] Schroeter, *Ber.*, 1930, **63**, 1308.
[16] Veselý and Stürsa, *Coll. Czech. Chem. Comm.*, 1933, **5**, 170, 174.
[17] Macbeth and Mills, *J.*, 1949, 2646.
[18] Winstein, Heck, Lapporte, and Baird, *Experientia*, 1956, **12**, 138.

by spontaneous dehydrobromination, consistently with the ready loss of bromide ion from a benzylic position *para* to a methoxy-substituent. The desired dihydronaphthalene was obtained by oxidation of the tetralin with chromic–acetic acid, and the product was purified by means of its 2,4-dinitrophenylhydrazone. Reduction of the regenerated ketone and dehydration of the resulting tetralol gave 1,2-dihydro-7-methoxy-1,1-dimethylnaphthalene.



1,2-Dihydro-2,2-dimethylnaphthalene was prepared by a combination of the methods described above. 3-Benzoylpivalic acid was reduced by the Clemmensen method and the resulting αα-dimethyl-γ-phenylbutyric acid cyclised by the hydrofluoric acid method. Clemmensen reduction of the 2,2-dimethyl-1-tetralone gave the corresponding tetralin, oxidation of which as above afforded a mixture of 2,2- and 3,3-dimethyl-1-tetralone. Only the latter readily formed a 2,4-dinitrophenylhydrazone, providing a convenient method of separation. Regeneration of the ketone followed by reduction and dehydration gave 1,2-dihydro-2,2-dimethylnaphthalene.

1,2-Dihydronaphthalene itself was prepared by Straus and Lemmel's method.[19]

Preparative Dehydrogenations.—In order to check the stoicheiometry of the reactions investigated kinetically, preparative dehydrogenations were carried out between each of the 1,2-dihydronaphthalenes and tetrachloro-1,2-benzoquinone. Quantitative recovery of naphthalenes when 1,2-dichlorobenzene was used as a solvent was not feasible and benzene was used instead. The naphthalene was usually obtained in high yield and shown to be of high purity by melting point, mixed melting point, or ultraviolet-light absorption (Table 3), but some cases require comment. With the 7-methyl and the 7-chloro-compound only 50 mg. of the dihydronaphthalenes were available, so that the yields were poor, but the identity and purity of the naphthalenes were established by infrared spectroscopy.

TABLE 3.

Preparative dehydrogenation of 1,2-dihydronaphthalenes by tetrachloro-1,2-benzoquinone.

Subst. 1,2-dihydronaphthalene	Recovered * crude naphthalene	Purity of naphthalene (U.V.)	Overall yield (%) of naphthalene
7-Methoxy-	99%		
6-Methoxy-	100	99%	99
7-Methyl-	83		
6-Methyl-	81	95	77
6-Acetamido-	100	89	89
7-Chloro-	52		
6-Chloro-	89	87	78
6-Bromo-	87	91	79
6-Nitro-	99	94	93
7-Methoxy-1,1-dimethyl-	95		
6-Methoxy-1,1-dimethyl-	47		
2,2-Dimethyl-	48		

* When pure naphthalene was put through the same working-up procedure it was recovered in 68% yield.

Dehydrogenation of 1,2-dihydro-6-methoxy-1,1-dimethylnaphthalene gave a crude product, whose ultraviolet absorption was consistent with what can be predicted from the

[19] Straus and Lemmel, *Ber.*, 1921, **54**, *B*, 25.

spectra of naphthalene,[20] 1,2-dimethylnaphthalene,[8] and 2-methoxynaphthalene for the unknown 6-methoxy-1,2-dimethylnaphthalene. Similarly, the 1,2-dihydro-7-methoxy-1,1-dimethylnaphthalene gave a crude product containing naphthalenoid material.

Dehydrogenation of 1,2-dihydro-2,2-dimethylnaphthalene gave a poor recovery of hydrocarbon which contained some 1,2-dimethylnaphthalene but was mainly unchanged dihydronaphthalene.

Dehydrogenation of 1,2-dihydronaphthalene [8] and 1,2-dihydro-1,1-dimethylnaphthalene [8] has been described previously.

In one case (1,2-dihydro-6-methylnaphthalene) tetrachlorocatechol was isolated.

Experimental

Microanalyses were carried out in the Microanalytical Laboratory (Miss J. Cuckney), and ultraviolet and infrared spectra were measured in the Spectrographic Laboratory (Mrs. A. I. Boston and Dr. R. L. Erskine) of this Department. Ultraviolet spectra refer to ethanol solutions. Nuclear magnetic resonance data, quoted as τ values,[21] were obtained with a Varian Associates V-4300 spectrometer and a 56·445 Mc/sec. oscillator at 21°. Spectra were calibrated by the side-band technique.

Kinetic Experiments.—Materials. Pure 1,2-dichlorobenzene was distilled from sodium and had b. p. 177—178°/746 mm., n_D^{25} 1·5480. Tetrachloro-1,2-benzoquinone,[22] supplied by Messrs. Hopkin and Williams Ltd., was purified by sublimation.

Reaction rates. The rates were determined by following spectrometrically the disappearance of the quinone. E_0 values were determined by graphical extrapolation to zero time. The experimental method was method " b " described in Part XI.[3] Values of $k_{obs.}$ were calculated from the normal second-order rate equation. The Arrhenius parameters were computed by the method of least squares, and their precision (standard deviations) by the equations set out in a previous paper.[3] Values of $k_{obs.}$ at 25° were obtained by least-squares extrapolation and the method of least squares was also used to obtain the ρ values:

For Fig. 2, $\rho = -2{\cdot}5 \pm 0{\cdot}2$, y intercept $= 0{\cdot}3 \pm 0{\cdot}1$.

Fig. 3, $\rho = -1{\cdot}8 \pm 0{\cdot}1$, y intercept $= 0{\cdot}04 \pm 0{\cdot}05$.

Individual runs. Two representative runs are recorded in full. Following these is a summary of rate constants for all the runs. Unless otherwise stated, the initial concentration of quinone was 0·0100M, and that of the 1,2-dihydronaphthalene 0·0500M. 1,2-Dichlorobenzene was the only solvent used.

(1) (a) *Stability of tetrachloro-1,2-benzoquinone in 1,2-dichlorobenzene at* 117°.

t (min.)	0	80	140	200	335
E (5700 Å)	0·767	0·764	0·761	0·759	0·755

(b) *Variation of quinone absorbance with temperature.*

Temp.	22°	36·2°	50·3°	74·8°	97·1°
E (5700 Å)	0·98	0·96	0·93	0·86	0·81

(2) 1,2-*Dihydro-6-methoxynaphthalene at* 47·3°.

t (min.)	0	8	9	10	11	12	13	14	15
E (5700 Å)	1·23	0·499	0·448	0·407	0·363	0·328	0·297	0·268	0·241
$10^2 k_{obs.}$ (l. mole^{-1} sec.$^{-1}$)	—	4·03	4·06	4·00	4·06	4·03	4·03	4·03	4·04

(3) 1,2-*Dihydro-6-nitronaphthalene at* 108°.

t (min.)	0	12	15	17	19	20	24	25	28	31	32
E (5700 Å)	0·90	0·496	0·430	0·399	0·367	0·350	0·298	0·287	0·251	0·222	0·211
$10^2 k_{obs.}$ (l. mole^{-1} sec.$^{-1}$)	—	1·74	1·75	1·70	1·70	1·70	1·67	1·67	1·67	1·66	1·67

[20] Friedel and Orchin, " Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, 1951.
[21] Tiers, *J. Phys. Chem.*, 1958, **62**, 1151.
[22] Braude, Brook, and Linstead, *J.*, 1954, 3569.

Summary of rate constants.

(The units for rate constants are l. mole^{-1} sec.$^{-1}$.)

1,2-Dihydronaphthalene						
Temp.	48·3°	53·5°	57·8°	62·7°	67·5°	77·2°
$10^2k_{obs.}$	0·610	0·780	1·09	1·42	1·98	3·21

1,2-Dihydro-7-methoxynaphthalene						
Temp.	22·0°	23·4°	23·6°	28·5°	32·0°	34·8°	39·8°
$10^2k_{obs.}$	1·97	2·07	2·10	2·77	3·27	3·92	5·46

1,2-Dihydro-6-methoxynaphthalene						
Temp.	28·0°	34·2°	38·5°	43·4°	47·3°	52·8°
$10^2k_{obs.}$	1·18	1·77	2·30	3·07	4·04	4·96

1,2-Dihydro-7-methylnaphthalene						
Temp.	36·8°	42·4°	45·2°	50·6°	54·6°	55·3°
$10^2k_{obs.}$	0·981	1·39	1·61	2·27	2·81	3·06

1,2-Dihydro-6-methylnaphthalene						
Temp.	31·9°	35·6°	41·4°	45·9°	51·8°	56·7°
$10^2k_{obs.}$	0·643	0·816	1·20	1·53	2·23	2·86

6-Acetamido-1,2-dihydronaphthalene						
Temp.	36·1°	41·3°	45·8°	51·7°	56·0°	61·5°	61·9°
$10^2k_{obs.}$	0·667	0·955	1·24	1·63	2·13	2·84	3·14

7-Chloro-1,2-dihydronaphthalene						
Temp.	68·2°	72·7°	79·5°	82·5°	89·2°	90·5°
$10^2k_{obs.}$	0·847	1·12	1·64	1·94	2·77	3·03

6-Chloro-1,2-dihydronaphthalene						
Temp.	70·9°	75·3°	79·0°	83·9°	88·9°	93·2°
$10^2k_{obs.}$	0·761	0·987	1·23	1·60	2·16	2·84

6-Bromo-1,2-dihydronaphthalene						
Temp.	71·0°	75·6°	79·7°	84·1°	89·4°	93·1°
$10^2k_{obs.}$	0·816	1·09	1·37	1·74	2·42	3·05

1,2-Dihydro-6-nitronaphthalene						
Temp.	89·2°	93·7°	96·9°	102·2°	108°	111·5°
$10^2k_{obs.}$	0·597	0·704	0·897	1·22	1·69	2·04

1,2-Dihydro-1,1-dimethylnaphthalene						
Temp.	60·4°	64·4°	67·4°	73·2°	77·4°	82·4°
$10^2k_{obs.}$	0·960	1·19	1·52	2·11	2·56	3·74

1,2-Dihydro-2,2-dimethylnaphthalene						
Temp.	88·0°	92·8°	97·9°	104·5°	109·2°	114·8°
$10^2k_{obs.}$	0·260	0·420	0·545	0·779	0·945	1·23

1,2-Dihydro-7-methoxy-1,1-dimethylnaphthalene				
Temp.	27·4°	34·1°	37·5°	42·4°
$10^2k_{obs.}$	1·49	2·44	2·80	3·90

1,2-Dihydro-6-methoxy-1,1-dimethylnaphthalene						
Temp.	55·9°	57·1°	60·5°	64·5°	69·6°	73·9°
$10^2k_{obs.}$	1·06	1·17	1·44	1·83	2·59	3·31

Determination of the Heat of Formation of the Complex with 1,2-*Dihydro*-6-*methylnaphthalene.* The initial concentration of hydrocarbon (DHN) was varied as indicated below. Kinetic runs were carried out at two temperatures in each case and $k_{obs.}$ at 40° was evaluated by interpolation of the Arrhenius plots. The initial concentration of quinone was always 0·0100M.

[DHN]	0·0100M	0·0100M	0·100M	0·100M	0·200M	0·200M
Temp.	36·7°	47·0°	36·8°	46·2°	36·4°	43·1°
$10^2k_{obs.}$ (l. mole^{-1} sec.$^{-1}$)	0·852	1·65	0·817	1·48	0·694	1·07

At 0·05M-hydrocarbon, E_0 (31·9°) = 1·32, E_0 (56·7°) = 1·25, and (by interpolation) E_0 (40°) = 1·29. ε_Q can be calculated at each temperature from (1b) above.

$$K = [Q \,.\, DHN]/[Q][DHN] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$$[Q] = 0{\cdot}01 - [Q \,.\, DHN] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

$$E = \varepsilon_Q[Q] + \varepsilon_C[Q \,.\, DHN] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

$$(\ln K_2 - \ln K_1) = -\Delta H/\boldsymbol{R}(1/T_1 - 1/T_2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

The value $K = 1{\cdot}8$ l. mole^{-1} found above, together with equations (6) and (7) can be used to give the initial concentration of complex as 8×10^{-4}M at 40°. Substitution in equation (7) gives $\varepsilon_c = 520$. If it is assumed that ε_c is independent of temperature (ΔH will be numerically smaller if a correction for solvent expansion is applied), equations (6) and (8) give $K_{31\cdot9} = 1{\cdot}84$ and $K_{56\cdot7} = 1{\cdot}70$ l. mole^{-1}, and by equation (9) $\Delta H = 0{\cdot}6$ kcal. mole^{-1}.

Preparation of 6- *and* 7-*Substituted* 1-*Tetralones.*—7-Methoxy-,[23] 7-chloro-,[24] and 7-bromo-1-tetralone [25] were prepared by recorded methods.

γ-*p*-Tolylbutyric acid [26] in anhydrous hydrofluoric acid (200 ml.) was left in a Polythene

[23] Haworth and Sheldrick, *J.*, 1934, 1950.
[24] Koo, *J. Amer. Chem. Soc.*, 1953, **75**, 1891.
[25] Fieser and Seligman, *J. Amer. Chem. Soc.*, 1938, **60**, 170.
[26] Fieser and Dunn, *J. Amer. Chem. Soc.*, 1936, **58**, 572.

beaker for 46 hr., then poured into an excess of dilute aqueous sodium carbonate and extracted with ether. This gave 7-methyl-1-tetralone (19·2 g., 70%) as prisms, m. p. 31—33° (lit.,[27] m. p. 31—33°).

Similar treatment of γ-phenylbutyric acid [28] (38·5 g.) with anhydrous hydrofluoric acid (250 ml.) for 40 hr. furnished 1-tetralone (34 g., 99%), n_D^{20} 1·5713 (lit.,[29] n_D^{20} 1·5693).

7-Nitro-1-tetralone was prepared by a modification of Schroeter's method.[15] The reaction was conducted at the lowest temperature at which the mixture remained liquid. Crystallisation of the product from light petroleum (b. p. 60—80°) afforded 7-nitro-1-tetralone (31%) as needles, m. p. 105—106° (lit.,[15] m. p. 106°).

7-Amino-1-tetralone [16] with acetic anhydride gave 7-acetamido-1-tetralone, prisms, m. p. 164—166°.

1,2-Dihydro-6-methylnaphthalene (6·3 g.; see below), ethanol (10 ml.), and Adams platinum oxide (28 mg.) were shaken in hydrogen at 21°/758·5 mm. until no more hydrogen was taken up (45 min.) (1026 ml. absorbed; theor. 1055 ml.). Filtration and removal of the solvent afforded 6-methyltetralin (6·1 g., 96%), $n_D^{22·5}$ 1·5366 (lit.,[30] n_D^{20} 1·5357).

6-Methoxy- [31] and 6-chloro-tetralin [32] were prepared by known methods.

6-Methoxy-, 6-methyl-, and 6-chloro-1-tetralone were prepared by the general method here described for 6-methyl-1-tetralone:

Chromium trioxide (6·7 g.) in water (3 ml.) and acetic acid (19 ml.) was added dropwise at 5—11° with stirring to 6-methyltetralin (6·1 g.) in acetic aid (38 ml.) during 1 hr. The solution was stirred at 0—5° for a further 3 hr. and left at room temperature for 3 days, then diluted with water (1 l.) and extracted with pentane (5 × 100 ml.). The combined extracts were washed with 2N-sodium carbonate (150 ml.). Removal of solvent from the dried ($MgSO_4$) extracts and distillation through a short Vigreux column gave impure 6-methyltetralin (2·1 g., 34%), b. p. 64—80°/1·2 mm., $n_D^{22·5}$ 1·5365—1·5453, and impure 6-methyl-1-tetralone (2·5 g., 33%), b. p. 98—104°/1·2 mm., $n_D^{22·5}$ 1·5619—1·5677. The crude ketone was treated with semicarbazide hydrochloride (5 g.) and sodium acetate (7·5 g.) in aqueous ethanol, and the *6-methyl-1-tetralone-semicarbazone* recrystallised from ethanol and from methanol, giving prisms (1·0 g., 30%), m. p. 238—239° (Found: C, 66·0; H, 7·0; N, 19·4. $C_{12}H_{15}N_3O$ requires C, 66·3; H, 7·0; N, 19·3%). A suspension of the semicarbazone (0·9 g.) and phthalic anhydride (2·5 g.) in water (50 ml.) was steam-distilled and 6-methyl-1-tetralone, n_D^{22} 1·557, was isolated by ether extraction of the distillate. This ketone was used in the next stage.

Oxidation of 6-methoxytetralin gave a crude solid product, m. p. 62—73°, recrystallisation (seven times from aqueous ethanol) of which afforded pure 6-methoxy-1-tetralone as needles, m. p. 75—78° (lit.,[31] m. p. 77·5°).

6-Chloro-1-tetralone semicarbazone was obtained as plates, m. p. 231—232° (Found: C, 55·6; H, 5·3; Cl, 14·6; N, 17·6. $C_{11}H_{12}ClN_3O$ requires C, 55·6; H, 5·1; Cl, 14·9; N, 17·7%).

Preparation of 6- and 7-Substituted 1,2-Dihydronaphthalenes.—Preparations of the 6- and the 7-methoxy-compounds were carried out by the method here described for the 6-methoxy-isomer.

The 6- [33] and the 7-methyl compound were prepared similarly except that the tetralols were dehydrated at 190° with potassium hydrogen sulphate.

Potassium borohydride (1·5 g.), 7-methoxy-1-tetralone (3·0 g.), and methanol (50 ml.) were refluxed for 3 hr. After cooling, the mixture was treated with concentrated hydrochloric acid (25 ml.). The resulting suspension was filtered and the methanol removed from the filtrate. The residue was extracted with ether (3 × 25 ml.), and the combined extracts were washed successively with 2N-sodium carbonate (30 ml.) and water (30 ml.). Removal of ether from the dried ($MgSO_4$) solution gave an oil which on distillation afforded 1,2-dihydro-6-methoxynaphthalene (1·8 g., 64%).

Potassium borohydride (2·5 g.), 7-acetamido-1-tetralone (3·3 g.), and methanol (50 ml.) were refluxed for 3 hr. On cooling, concentrated hydrochloric acid was added, and the resulting suspension filtered. Removal of the methanol left a brown solution, which was diluted with

[27] Newman, *J. Amer. Chem. Soc.*, 1940, **62**, 1683.
[28] Martin, *Org. Synth.*, Coll. Vol. II, p. 499.
[29] Linstead and Michaelis, *J.*, 1940, 1134.
[30] Mair and Streiff, *J. Res. Nat. Bur. Stand.*, 1941, **27**, 343.
[31] Burnop, Elliot, and Linstead, *J.*, 1940, 727.
[32] Schroeter, *Ber.*, 1938, **71**, 1040.
[33] Wenham and Whitehurst, *J.*, 1957, 4037.

water (200 ml.). Acetic anhydride (3·0 ml.) was added with stirring to this brown solution of 6-amino-1,2-dihydronaphthalene hydrochloride. As soon as the mixture became homogeneous, sodium acetate (100 g.) in water (100 ml.) was added, and stirring continued for 15 min. The product was extracted with ether (100 ml., 2 × 25 ml.). The combined ether extracts were washed with 2N-sodium carbonate (75 ml.) and with water (50 ml.). Removal of ether from the dried ($MgSO_4$) extracts afforded a residue (3·0 g., 100%), m. p. 65—72°, which on recrystallisation from light petroleum (b. p. 60—80°) gave 6-acetamido-1,2-dihydronaphthalene as needles.

The 7-chloro-, 6-chloro-, 6-bromo-, and 6-nitro-compounds were prepared by the method here described for the 6-bromo-compound, except that the 6-nitro-compound was obtained from its tetralol by another method.

7-Bromo-1-tetralone (2·4 g.) in absolute propan-2-ol (25 ml.) was added dropwise during 2 hr. to aluminium isopropoxide (2·4 g.; b. p. 110—125°/1·5 mm.) in boiling absolute propan-2-ol (30 ml.) in a flask fitted with a 6″ Stedman column attached to a total condensation, variable-take-off distillation head. The 7-bromo-1-tetralone solution was warmed with a hot-air blower to prevent crystallisation, and the bath around the reaction vessel was maintained at *ca.* 140° so that the acetone formed passed immediately into the Stedman column. Propan-2-ol was removed slowly through the column and tested periodically for acetone. The volume of the solution was kept constant by the addition of more propan-2-ol. After 4 hr. the acetone test was negative, and the mixture was refluxed for 30 min. The propanol was removed under reduced pressure, the residue was cooled in ice-water, and ice-cold 2N-hydrochloric acid (50 ml.) was added. The liberated oil was extracted with ether and the combined extracts (100 ml.) were washed successively with water (30 ml.), N-hydrochloric acid (2 × 12·5 ml.), sodium hydrogen sulphite solution (2 g. in 10 ml.), and water (25 ml.). Removal of ether from the dried ($MgSO_4$) extracts left crude 7-bromo-1-tetralol which readily decomposed on distillation from potassium hydrogen sulphate into 6-bromo-1,2-dihydronaphthalene (1·71 g., 77%) and water.

7-Nitro-1-tetralol, formed in 99% yield by the above method, recrystallised from light petroleum (b. p. 60—80°) as needles, m. p. 109° (lit.,[34] m. p. 109°).

7-Nitro-1-tetralol, toluene-*p*-sulphonic acid (0·5 g.), and glacial acetic acid (60 ml.) were refluxed for 4½ hr., then diluted with water (1·5 l.) and extracted with ether (150 ml., 5 × 100 ml.). The combined ether extracts were washed with 2N-sodium carbonate (100 ml.) and with water (100 ml.). After removal of ether from the dried ($MgSO_4$) extracts, the residue was twice distilled, to give 1,2-dihydro-6-nitronaphthalene (1·8 g., 67%), m. p. 36°.

Synthesis of 1,2-*Dihydro*-1,1-*dimethylnaphthalene*.—(i) 1,1-*Dimethyltetralin*. Anhydrous hydrofluoric acid (100 ml.) was added to 1,1-dimethyl-4-phenylbutan-1-ol [7] (12·8 g.) and the resulting deep-red solution left for 3 days in a closed Polythene bottle. The solution was poured into a Polythene beaker and most of the acid allowed to evaporate. The residue was poured into an excess of aqueous sodium carbonate, and the product extracted with ether (300 ml.). This gave 1,1-dimethyltetralin (7·2 g., 62%), b. p. 56—62°/0·8 mm., n_D^{17} 1·5275 (lit.,[7] b. p. 40°/0·04 mm., n_D^{22} 1·5270).

(ii) 1,2-*Dihydro*-1,1-*dimethylnaphthalene*. This compound was prepared by the method described in Part XIII.[8]

Synthesis of 1,2-*Dihydro*-2,2-*dimethylnaphthalene*.—(i) 2,2-*Dimethyl*-1-*tetralone*. Cyclisation of γ-phenyl-αα-dimethylbutyric acid [35] by the hydrofluoric acid method furnished the tetralone, $n_D^{20·5}$ 1·5428 (lit.,[36] n_D^{25} 1·5414), in theoretical yield. When this ketone was treated with Brady's reagent, no precipitation occurred until 60 min. had elapsed.

(ii) 2,2-*Dimethyltetralin*. Amalgamated zinc (from 120 g. of zinc wool), water (70 ml.), concentrated hydrochloric acid (180 ml.), 2,2-dimethyl-1-tetralone (13·5 g.), and toluene (70 ml.) were refluxed for 15 hr. A further quantity (140 ml.) of concentrated hydrochloric acid was added and the mixture refluxed for an additional 5 hr. The aqueous layer was removed, diluted with water and extracted with ether (4 × 100 ml.). The combined organic layers were washed with saturated aqueous sodium hydrogen carbonate solution (100 ml.) and dried ($MgSO_4$). Removal of solvents afforded a residue which on distillation gave impure 2,2-dimethyltetralin (6·9 g., 55%), b. p. 38—44°/0·15—0·45 mm., n_D^{20} 1·5203—1·5243 (lit.,[35] b. p.

[34] Asahina and Momose, *J. Pharm. Soc. Japan*, 1944, **64**, 153.
[35] Clemo and Dickenson, *J.*, 1937, 255.
[36] Sengupta, *J. prakt. Chem.*, 1938, **151**, 82.

104°/12 mm.), and impure 2,2-dimethyl-1-tetralone (1·16 g., 9%), b. p. 48—62°/0·10—0·15 mm., n_D^{20} 1·5328—1·5418.

(iii) 3,3-*Dimethyl*-1-*tetralone*. The impure 2,2-dimethyltetralin (6·5 g.) was oxidised by chromic–acetic acid. Distillation of the product gave unchanged 2,2-dimethyltetralin (2·6 g., 40%), b. p. 44—48°/0·4—0·45 mm., $n_D^{20·5}$ 1·5190—1·5218, and a mixture of 2,2- and 3-3-dimethyl-1-tetralones (3·0 g., 42%; b. p. 68—80°/0·4—0·85 mm., $n_D^{20·5}$ 1·5312—1·5405). Brady's reagent (from 4·0 g. of 2,4-dinitrophenylhydrazine in 25 ml. of methanol) was added to the mixed tetralones (2·9 g.) in methanol (20 ml.). The orange precipitate, which was formed after 1 min., was removed after 15 min., washed with methanol, and recrystallised from chloroform–ethanol to give pure 3,3-*dimethyl*-1-*tetralone* 2,4-*dinitrophenylhydrazone* (2·3 g., 39%) as bright-orange needles, m. p. 193—194° (Found: C, 61·0; H, 5·5; N, 15·5. $C_{18}H_{18}N_4O_4$ requires C, 61·0; H, 5·1; N, 15·8%). The ketone was regenerated from this derivative by Demaecker and Martin's method,[37] and redistillation of the crude product gave 3,3-dimethyl-1-tetralone (0·56 g., 64%), b. p. 70—84°/0·2—0·3 mm., n_D^{21} 1·5386—1·5405, which was used without furher purification in the next stage.

(iv) 1,2-*Dihydro*-2,2-*dimethylnaphthalene*. Reduction of 3,3-dimethyl-1-tetralone (0·50 g.) by potassium borohydride as described for 1,2-dihydro-6-methylnaphthalene gave 1,2-dihydro-2,2-dimethylnaphthalene (0·36 g., 79%).

Synthesis of 1,2-*Dihydro*-6-*methoxy*-1,1-*dimethylnaphthalene*.—(i) 1-*Bromo*-3-m-*methoxyphenylpropane*. Reaction of phosphorus tribromide with 3-*m*-methoxyphenylpropan-1-ol [38] (26 g.) by Newman and Wotiz's procedure [39] furnished 1-bromo-3-*m*-methoxyphenylpropane (25 g., 66%), b. p. 85—86°/0·15 mm., n_D^{21} 1·5471 (lit.,[40] b. p. 85—86°/1·1 mm.) (Found: C, 52·4; H, 6·0; Br, 35·3. Calc. for $C_{10}H_{13}BrO$: C, 52·4; H, 5·7; Br, 34·9%).

(ii) 4-m-*Methoxyphenyl*-1,1-*dimethylbutan*-1-*ol*. "AnalaR" acetone (16·5 ml.) in ether (30 ml.) was added slowly with stirring to a solution of the Grignard reagent from 1-bromo-3-*m*-methoxyphenylpropane (25 g.) in ether (120 ml.) during ½ hr. The stirred mixture was refluxed for a further 5 hr., treated with saturated aqueous ammonium chloride solution (200 ml.), and extracted with ether. Removal of the ether from the dried ($MgSO_4$) extract and distillation of the residue gave a low-boiling substance (5·4 g.), b. p. 38—120°/0·7—0·9 mm., $n_D^{22·5}$ 1·4560—1·4810 and crude 4-*m*-methoxyphenyl-1,1-dimethylbutan-1-ol (16·1 g., 68%), b. p. 120—127°/0·5—1·0 mm., $n_D^{22·5}$ 1·5117—1·5180.

(iii) 6-*Methoxy*-1,1-*dimethyltetralin*. Cyclodehydration of 4-*m*-methoxyphenyl-1,1-dimethylbutan-1-ol (5·3 g.) by hydrofluoric acid furnished 6-*methoxy*-1,1-*dimethyltetralin* (3·8 g., 80%), b. p. 77—81°/0·3 mm., n_D^{21} 1·5324, τ 8·78, 8·36, 7·30, 6·31, 3·54, 3·37, 2·97, 2·80 (Found: C, 82·0; H, 9·5. $C_{13}H_{18}O$ requires C, 82·1; H, 9·5%).

(iv) 1,2-*Dihydro*-6-*methoxy*-1,1-*dimethylnaphthalene*. Treatment of 6-methoxy-1,1-dimethyltetralin with *N*-bromosuccinimide and dehydrobromination of the product by the methods described in Part XIII [8] gave 1,2-dihydro-6-methoxy-1,1-dimethylnaphthalene.

Synthesis of 1,2-*Dihydro*-7-*methoxy*-1,1-*dimethylnaphthalene*.—(i) 4-*p*-Methoxyphenyl-1,1-dimethylbutan-1-ol was prepared in 54% yield from 1-bromo-3-*p*-methoxyphenylpropane [41] as described above for the *m*-isomer and had b. p. 118—122°/0·1 mm., n_D^{21} 1·5138—1·5143.

(ii) 7-*Methoxy*-1,1-*dimethyltetralin*. Cyclodehydration of the 4-*p*-methoxyphenyl-1,1-dimethylbutan-1-ol (5·3 g.) by hydrofluoric acid furnished 7-*methoxy*-1,1-*dimethyltetralin* (3·3 g., 68%), b. p. 76—81°/0·1—0·2 mm., n_D^{20} 1·5325 (Found: C, 82·3; H, 9·8%).

(iii) 6-*Methoxy*-4,4-*dimethyl*-1-*tetralone*. 7-Methoxy-1,1-dimethyltetralin (2·1 g.) was oxidised by chromic–acetic acid to an oil (1·7 g.), n_D^{21} 1·5586, which was converted into 6-*methoxy*-4,4-*dimethyl*-1-*tetralone* 2,4-*dinitrophenylhydrazone* (1·2 g., 43%), orange-red prisms, m. p. 272° (Found: C, 58·8; H, 5·2; N, 14·2. $C_{19}H_{20}N_4O_5$ requires C, 59·4; H, 5·2; N, 14·6%). This derivative was decomposed by Demaecker and Martin's method [37] to an oil, n_D^{20} 1·5607, which was used without further purification in the next stage.

(iv) 1,2-*Dihydro*-7-*methoxy*-1,1-*dimethylnaphthalene*. 6-Methoxy-4,4-dimethyl-1-tetralone (0·6 g.) in anhydrous ether (20 ml.) was added to a stirred suspension of lithium aluminium hydride (0·2 g.) in ether (20 ml.) during 10 min. The mixture was worked up in the usual way

[37] Demaecker and Martin, *Nature*, 1954, **173**, 266.
[38] Robinson and Schlittler, *J.*, 1935, 1288.
[39] Newman and Wotiz, *J. Amer. Chem. Soc.*, 1949, **71**, 1292.
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TABLE 4.

Principal peaks in the ultraviolet spectra of 1-tetralones.

Subst.	$\lambda_{max.}$ (Å)	ε	$\lambda_{max.}$ (Å)	ε	$\lambda_{max.}$ (Å)	ε	$\lambda_{max.}$ (Å)	ε
Parent			2480	12,600			2920	1780
2,2-Me_2			2450	9800			2920	940
3,3-Me_2	2120	22,500	2610	6600	2700	5500	3020	2130
6-MeO	2250	12,300	2740	15,100				
6-MeO-1,1-Me_2	2250	14,200	2760	15,400				
6-Me			2550	14,400			2860	2160
6-Cl			2550	16,200			2860	2170
7-MeO	2250	19,350	2520	10,200			3200	2290
7-Me			2500	12,650			3030	1920
7-NHAc	2380	34,500					3200	2030
7-Cl			2450	10,100			3020	1890
7-Br			2450	8350			3020	1465
7-NO_2	2350	21,800	2700	8650				

TABLE 5.

Principal peaks in the ultraviolet spectra of 1,2-dihydronaphthalenes.

Subst.	$\lambda_{max.}$ (Å)	ε	$\lambda_{max.}$ (Å)	ε	$\lambda_{max.}$ (Å)	ε	$\lambda_{max.}$ (Å)	ε	$\lambda_{max.}$ (Å)	ε	$\lambda_{max.}$ (Å)	ε
Parent			2120	25,400			2600	9300				
1,1-Me_2	2110	21,500	2160	22,200	2230	15,800	2590i	10,100	2640	10,200		
2,2-Me_2	2110	29,100	2160	41,000	2230	18,200	2590	10,700	2640	10,800	2960	660
7-MeO			2150	16,800			2700	12,800				
7-MeO-1,1-Me_2			2120	21,200			2700	14,800				
7-Me			2220	15,900			2650	11,500				
7-Cl	2130	16,450	2180	17,300			2650	9700				
6-MeO			2220	28,800			2600	7350			3020	2880
6-MeO-1,1-Me_2			2200	27,500			2610	7500	2700	6000	3020	2450
6-Me			2180	24,200			2620	9070			3020	960
6-NHAc			2410	46,800							3020	1400
6-Cl			2200	28,600			2620	8050				
6-Br			2200	30,900			2620	8150			2930	1340
6-NO_2			2570	31,500							3350	2100

i = inflexion.

TABLE 6.

Principal peaks ($cm.^{-1}$) in the infrared spectra of 1,2-dihydronaphthalenes.

Parent: 1629w, 1600w, 1570w, 1482s, 1035m. 1024m, 1007m, 954w, 937m, 882m, 867w, 804w, 781s 746s, 692s, 682m.

1,1-Me_2: 1642w, 1600w, 1567w, 1479s, 993m, 968w, 938w, 872m, 785s, 754s, 689s, 678w.

2,2-Me_2: 1637w, 1600w, 1570w, 1484m, 972w, 938w, 881w, 805m, 778s, 755w, 736m, 704s.

7-MeO: 1626m, 1608s, 1569s, 1495s, 1250s, 1039s, 1013m, 967w, 943w, 891w, 876m, 849m, 817s, 780w, 754w, 713w, 688m.

7-MeO-1,1-Me_2: 1634w, 1608s, 1563s, 1497s, 1241s, 1046s, 1014w, 993m, 970w, 872m, 85?w, 834s, 821m, 811m, 766w, 698m, 679m.

7-Me: 1639w, 1608m, 1563w, 1496m, 1029w, 1014m, 955w, 946w, 891w, 876m, 824s, 783m, 754w, 713w, 689m.

7-Cl: 1631w, 1592m, 1560w, 1479s, 1027w, 1012m, 958w, 935w, 887w, 876m, 842m, 826s, 798w, 779w, 751w, 683m.

6-MeO: 1629w, 1603s, 1571s, 1494s, 1261s, 1041s, 1027m, 1010w, 944w, 876m, 854m, 813m, 779m, 751w, 725w, 695m, 684w.

6-MeO-1,1-Me_2: 1642w, 1605s, 1563s, 1490s, 1252s, 1038s, 995w, 926m, 917w, 871m, 857m, 846w, 818m, 798m, 764m, 702s.

6-Me: 1626w, 1606m, 1569m, 1490s, 1025w, 1009m, 951w, 944w, 877s, 811s, 784s, 750w, 716w, 692s, 676s.

6-NHAc: 1658s, 1614s, 1559s, 1533m, 1495m, 1019w, 1012w, 986w, 887s, 874w. 831m, 792w, 759w, 724m, 696m.

6-Cl: 1627w, 1595s, 1558m, 1482s, 1026m, 1008m, 955w, 935s, 878s, 851s, 813s, 778s, 746m, 702s, 685s.

6-Br: 1629w, 1590m, 1555w, 1476s, 1026w, 1009w, 956w, 934w, 878m, 836s, 810s, 776s, 745w, 698w, 683s.

6-NO_2: 1626w, 1610s, 1585s, 1516s, 1482s, 1341s, 1032w, 1010m, 953w, 937m, 905s, 883w, 861w, 843m, 826s, 805s, 776s, 741s, 702w, 684s.

to give crude 6-methoxy-4,4-dimethyl-1-tetralol (0·6 g., 99%), n_D^{21} 1·547. This was heated to 160° with freshly fused potassium hydrogen sulphate, cooled, and distilled to give 1,2-dihydro-7-methoxy-1,1-dimethylnaphthalene.

Ultraviolet-light absorption data for the 1-tetralones and 1,2-dihydronaphthalenes are recorded in Tables 4 and 5. Infrared absorption data for 1,2-dihydronaphthalenes are given in Table 6.

Physical constants and analytical data of the 1,2-*dihydronaphthalenes*, prepared as indicated above, are listed in Table 7.

Preparative Dehydrogenations.—General method. A solution of the dihydronaphthalene and tetrachloro-1,2-benzoquinone in benzene was refluxed under pure, dry nitrogen for several hours. The resulting solution was passed down an alumina column (to remove quinol and any unchanged quinone), and eluted with benzene. Removal of the benzene from the eluate afforded material which was examined as indicated below for the presence of the appropriate naphthalene.

(a) 1,2-*Dihydro*-7-*methoxynaphthalene*. The dihydronaphthalene (39 mg.), the quinone (60 mg.), and benzene (10 ml.) were refluxed for 2 hr. The evaporated eluate (38 mg., 99%) had m. p. 63—69°: (2-methoxynaphthalene [42] has m. p. 72°).

(b) 1,2-*Dihydro*-6-*methoxynaphthalene*. The dihydronaphthalene (0·76 g.), the quinone (1·15 g.), and benzene (10 ml.) were refluxed for 2 hr. The evaporated eluate (0·76 g., 100%) had m. p. and mixed m. p. 70—72°, $\lambda_{max.}$ 2260 (ε 75,000), 2610 (ε 3550), 2710 (ε 4820), 2820 (ε 3320), 3130 (ε 1580), 3200 (ε 1360), 3280 Å (ε 2120). 2-Methoxynaphthalene [43] had m. p. 71·5—72·5°, and $\lambda_{max.}$ 2260 (ε 72,700), 2610 (ε 4270), 2710 (ε 4740), 2820 (ε 3320), 3130 (ε 1550), 3200 (ε 1330), 3270 Å (ε 2130).

TABLE 7.

Substituted 1,2-dihydronaphthalenes.

				Found (%)				Required (%)		
Subst.	Yield (%)	B. p./mm.	n_D^t	C	H	Hal or N	Formula	C	H	Hal or N
None *	—	40°/0·8	$1·5822^{21·5}$	92·1	7·9	—	$C_{10}H_{10}$	92·3	7·7	—
7-MeO * ...	26 [a]	105—107°/3·5	$1·5852^{21}$	82·2	7·7	—	$C_{11}H_{12}O$	82·5	7·6	—
6-MeO	64 [a]	82°/1·3	$1·5777^{27}$	82·6	7·6	—	$C_{11}H_{12}O$	82·5	7·6	—
7-Me	43 [a]	68°/1·7	$1·5735^{22}$	91·5	8·7	—	$C_{11}H_{12}$	91·6	8·4	—
6-Me *	71 [a]	103—107°/14	$1·5725^{22·5}$	91·9	8·7	—	$C_{11}H_{12}$	91·6	8·4	—
6-NHAc ...	100 [a, c]	m. p. 70—71°	—	77·0	7·1	7·4	$C_{12}H_{13}NO$	77·0	7·0	7·5
7-Cl	53 [a]	78°/1·3—1·4	$1·5928^{26}$	72·7	5·6	20·6	$C_{10}H_9Cl$	73·0	5·5	21·5
6-Cl	66 [a]	67°/0·1	$1·5941^{21}$	72·9	5·8	21·6	$C_{10}H_9Cl$	73·0	5·5	21·5
6-Br	77 [a]	89—90°/1	$1·6185^{21}$	57·2	4·4	38·1	$C_{10}H_9Br$	57·4	4·3	38·2
6-NO_2	66 [a]	120—124°/1	$1·6166^{24}$	68·3	5·2	8·2	$C_{10}H_9NO_2$	68·6	5·2	8·0
1,1-Me_2 * ...	51 [b]	53—56°/0·6—0·7	$1·5570^{18}$	90·9	9·0	—	$C_{12}H_{14}$	91·1	8·9	—
2,2-Me_2 ...	79 [a]	40—44°/0·4	$1·5451^{22}$	91·3	9·1	—	$C_{12}H_{14}$	91·1	8·9	—
7-MeO-1,1-Me_2	49 [a]	70—82°/0·3	$1·5615^{21}$	83·1	8·6	—	$C_{13}H_{16}O$	82·9	8·6	—
6-MeO-1,1-Me_2	27 [b]	73—75°/0·15	$1·5579^{23}$	83·2	8·7	—	$C_{13}H_{16}O$	82·9	8·6	—

* Known compounds. [a] From ketone. [b] From tetralin. [c] Crude.

(c) 1,2-*Dihydro*-7-*methylnaphthalene*. The hydrocarbon (42 mg.), the quinone (71 mg.), and benzene (10 ml.) were refluxed for 2 hr. The evaporated eluate (35 mg., 83%) had an infrared spectrum identical with that of 2-methylnaphthalene (British Drug Houses Ltd.), m. p. 34—35° (lit.,[44] m. p. 34°).

(d) 1,2-*Dihydro*-6-*methylnaphthalene*. The hydrocarbon (0·69 g.), the quinone (1·16 g.), and benzene (10 ml.) were refluxed for 2 hr., then diluted with light petroleum (b. p. 40—60°), kept at room temperature for 1 hr., and filtered. The precipitate (0·4 g., 34%), m. p. 190—193°, sublimed to give pure tetrachlorocatechol, m. p. 193°, mixed m. p. 190—192° (lit.,[22] m. p. 193°). Chromatography of the filtrate afforded 2-methylnaphthalene (0·55 g., 81%), m. p. 33° and mixed m. p. 33—35°, $\lambda_{max.}$ 2230 (ε 58,300), 2660 (ε 4120), 2760 (ε 4550), 2860 (ε 3120), 3050

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(ε 570), 3130 (ε 360), 3190 Å (ε 570); the pure hydrocarbon had $\lambda_{max.}$ 2230 (ε 67,500), 2650 (ε 4260), 2750 (ε 4690), 2860 (ε 3270), 3050 (ε 570), 3120 (ε 369), 3180 Å (ε 611).

(e) 6-*Acetamido*-1,2-*dihydronaphthalene*. The dihydronaphthalene (190 mg.), the quinone (250 mg.), and benzene (10 ml.) were refluxed for 52 hr. A purple precipitate (3 mg.) was removed and the filtrate chromatographed in the usual manner except that 5% ethanol in benzene was used as eluant. The evaporated eluate (220 mg., 100%) had m. p. 128—130°, $\lambda_{max.}$ 2420 (ε 47,300), 2490 (ε 42,200), 2730 (ε 6660), 2830 (ε 7680), 2940 (ε 7030), 3150 (ε 850), 3300 Å (ε 850) (2-acetamidonaphthalene [45] has m. p. 132°). 2-Acetamidonaphthalene, prepared by acetylation of 2-naphthylamine, m. p. 132—134°, had $\lambda_{max.}$ 2430 (ε 57,000), 2500 (ε 48,000), 2740 (ε 7700) 2840 (ε 8950), 2950 (ε 6450), 3160 (ε 1000), 3320 Å (ε 980).

(f) 7-*Chloro*-1,2-*dihydronaphthalene*. The dihydronaphthalene (48 mg.), the quinone (72 mg.), and 1,2-dichlorobenzene were heated to 90° for 4 hr. The evaporated eluate (25 mg., 52%) had an infrared spectrum which included naphthalenoid peaks.

(g) 6-*Chloro*-1,2-*dihydronaphthalene*. The dihydronaphthalene (184 mg.), the quinone (300 mg.), and benzene (3 ml.) were refluxed for 3 hr. The evaporated eluate (162 mg., 89%) had m. p. 56—57°, $\lambda_{max.}$ 2255 (ε 48,700), 2670 (ε 5030), 2700 (ε 4710), 2770 (ε 5360), 2880 (ε 3570), 3070 (ε 400), 3220 Å (ε 430). 2-Chloronaphthalene [46] has m. p. 56—57°, $\lambda_{max.}$ 2630 (ε 5700), 2700 (ε 5400), 2760 Å (ε 6300).

(h) 6-*Bromo*-1,2-*dihydronaphthalene*. The dihydronaphthalene (500 mg.), the quinone (590 mg.), and benzene (5 ml.) were refluxed for 3 hr. The evaporated eluate (430 mg., 87%) had m. p. 52—54°, $\lambda_{max.}$ 2270 (ε 63,600), 2680 (ε 4540), 2710 (ε 4440), 2780 (ε 4850), 2890 (ε 4050), 3070 (ε 350), 3130 (ε 220), 3220 (ε 260). 2-Bromonaphthalene [47] has m. p. 55—56°. 2-Bromonaphthalene (British Drug Houses Ltd.), m. p. 55°, had $\lambda_{max.}$ 2260 (ε 80,000), 2680 (ε 5000), 2710 (ε 4800), 2780 (ε 5460), 2890 (ε 3630), 3070 (ε 404), 3220 Å (ε 300).

(i) 1,2-*Dihydro*-6-*nitronaphthalene*. The dihydronaphthalene (690 mg.), the quinone (970 mg.), and benzene (10 ml.) were refluxed for 19 hr. The evaporated eluate (670 mg., 99%) had m. p. 70°, $\lambda_{max.}$ 2540 (ε 23,200), 2610 (ε 23,700), 3030 Å (ε 7790) (2-nitronaphthalene [48] has m. p. 79°). Recrystallisation from ethanol gave pure 2-nitronaphthalene, m. p. 77°, $\lambda_{max.}$ 2540 (ε 23,300), 2610 (ε 24,400), 3030 Å (ε 9990).

(j) 1,2-*Dihydro*-2,2-*dimethylnaphthalene*. The hydrocarbon (44 mg.), the quinone (70 mg.), and benzene (2 ml.) were refluxed for 4 hr. The evaporated eluate (21 mg., 48%) had $\lambda_{max.}$ 2170 Å (ε 24,200), $\lambda_{infl.}$ 2270 (ε 18,800), 2550 (ε 2590), 2830 (ε 1380), $\lambda_{max.}$ 2910 (ε 1260), $\lambda_{infl.}$ 3010 (ε 1080), 3070 (ε 820) $\lambda_{max.}$ 3210 Å (ε 156).

(k) 1,2-*Dihydro*-7-*methoxy*-1,1-*dimethylnaphthalene*. The dihydronaphthalene (87 mg.), the quinone (115 mg.), and benzene (3 ml.) were refluxed for 1 hr. The evaporated eluate (82 mg., 95%), n_D^{20} 1·606, had $\lambda_{max.}$ 2330 (ε 17,300), 2800 (ε 2600), $\lambda_{infl.}$ 3150 (ε 705), $\lambda_{max.}$ 3300 Å (ε 630).

(l) 1,2-*Dihydro*-6-*methoxy*-1,1-*dimethylnaphthalene*. The dihydronaphthalene (92 mg.), the quinone (120 mg.), and benzene (2 ml.) were refluxed for 2 hr. The evaporated eluate (43 mg., 47%) had $\lambda_{max.}$ 2270 (ε 55,700), 2560 (ε 4650), 2650 (ε 5390), 2750 (ε 5020), 2870 (ε 3720), 3070 (ε 1880), 3150 (ε 2120), 3220 (ε 2320), 3300 (ε 2120), 3360 Å (ε 2690).

The authors gratefully acknowledge the interest of the late Professor E. A. Braude. This work was carried out during the tenure by one of them (D. T. T.) of a University of London Postgraduate Scholarship.

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[*Received, May 10th*, 1961.]

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