625. *Hydrogen Transfer. Part XIII.*[1] *The Kinetics of Dehydrogenation of* 1,1-*Disubstituted* 1,2-*Dihydronaphthalenes and Tetralins by Tetrachloro*-1,2-*benzoquinone.*

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The rates and Arrhenius parameters have been determined for the reaction of tetrachloro-1,2-benzoquinone with tetralin and 1,1-dimethyltetralin. Several 1,1-disubstituted 1,2-dihydronaphthalenes have been synthesised and the stoïcheiometry and kinetics of their dehydrogenation by tetrachloro-1,2-benzoquinone examined. The reaction of diphenylpicrylhydrazyl with 1,1-dimethyl-1,2-dihydronaphthalene is described. The results are discussed in terms of steric and electronic factors and favour the two-step ionic mechanism previously postulated.

The concurrence of Wagner–Meerwein rearrangement and dehydrogenation by quinones of several hydroaromatic systems was described in the preceding paper. Ready rearrangements of this type are usually associated with reactions which may be formally represented as involving carbonium-ion intermediates. In many cases the rearrangement is synchronous and the migration may actually be associated with a lowering of the activation energy of the heterolysis.[2] Radical intermediates, on the other hand, do not appear to rearrange with such ease.[3] There has not been a report of an alkyl migration.[4] Aryl migrations, as in the Urry–Karasch rearrangement, occur after formation of the intermediate and possibly[5] require activation energies of the order of 8 kcal. mole^{-1}. It follows that information regarding the ease of rearrangement accompanying dehydrogenation by quinones might establish more firmly the ionic character of the reaction. Accordingly, we have studied this type of reaction kinetically and the results are presented below.

The first example was dehydrogenation of 1,1-dimethyltetralin. Its initial stage leads to the dihydronaphthalene and is not concerned with rearrangement. Therefore, unless the rearrangement step were rate-controlling, no direct information regarding the rearrangement would be obtained. As in fact the first stage remained rate-controlling further studies in the tetralin series were abandoned in favour of the corresponding 1,2-dihydronaphthalenes in which the rearrangement stage could be examined directly.

1,1-Disubstituted 1,2-dihydronaphthalenes were unknown at the commencement of the investigation, but their synthesis from the tetralins was readily achieved. The tetralins were converted into the 4-bromo-derivatives by *N*-bromosuccinimide. Dehydrobromination with pyridine gave only low yields of hydrocarbons, and use of dimethylaniline and concentrated ethanolic sodium ethoxide resulted solely in substitution. The most satisfactory method was treatment with solid sodium or potassium hydroxide at 145°. In this way the tetralins were converted into the dihydronaphthalenes in overall yields of 50—80%.

The stoicheiometry of the dehydrogenations was checked and found to involve equimolecular amounts of reactants. The kinetic measurements were carried out by a spectrometric technique described previously (method *b* of ref. 6). Phenetole was used as a solvent; it introduced a minor complication in the tetralin experiments in that a correction was needed for the rate at which tetrachloro-1,2-benzoquinone decomposed in it. The correction was almost negligible for most of the dihydronaphthalenes.

In addition to the kinetic study, two other experiments of importance to the subsequent

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[1] Part XII, preceding paper.

[2] See Streitwieser, *Chem. Rev.*, 1956, **56**, 571, for a review.

[3] Henbest, *Ann. Reports*, 1956, **53**, 152.

[4] Leffler, " The Reactive Intermediates of Organic Chemistry," Interscience Publ. Inc., New York, 1956, p. 32.

[5] Seubold, *J. Amer. Chem. Soc.*, 1953, **75**, 2532.

[6] Braude, Jackman, Linstead, and Shannon, *J.*, 3116.

discussion were performed. It was shown that benzocycloheptene was not dehydrogenated by tetrachloro-1,2-benzoquinone in conditions where tetralin reacts completely; also that the stable readical, diphenylpicrylhydrazyl, does not convert 1,2-dihydro-1,1-dimethylnaphthalene into 1,2-dimethylnaphthalene although it readily dehydrogenates 1,2-dihydronaphthalene.[7]

EXPERIMENTAL

For general remarks see Part XII.[1]

Synthesis of 1,1-*Disubstituted* 1,2-*Dihydronaphthalenes.*—The general method is described for 1,2-dihydro-1,1-dimethylnaphthalene.

1,1-Dimethyltetralin (12 g.), benzoyl peroxide (0·2 g.), *N*-bromosuccinimide (16 g.), and carbon tetrachloride (250 ml.) were heated under reflux for 20 min., then cooled and filtered. Removal of the solvent gave a residue (25 g.) which was heated with finely ground sodium hydroxide (50 g.) for 2 hr. at 140—150°. The cooled mixture was extracted with ether. After removal of the solvent this residue was twice distilled from sodium, to give 1,2-*dihydro*-1,1-*dimethylnaphthalene* (8·2 g., 69%) (Table 1). Other *compounds* prepared by the same method are listed in Table 1.

TABLE 1. 1,1-*Disubstituted* 1,2-*dihydronaphthalenes.*

Subst.	Yield (%)	B. p./mm.	n_D^t	$\lambda_{max.}$ (Å) (ε)		Found (%) C	Found (%) H	Formula	Reqd. (%) C	Reqd. (%) H
Me_2	69	50—51°/0·6	1·5532 ^{21}	2170 (25,000)	2600 (10,000)	91·0	9·1	$C_{12}H_{14}$	91·1	8·9
Et_2	53	84°/1	1·5555 ^{20}	2170 (24,200)	2620 (9,300)	90·1	9·8	$C_{14}H_{18}$	90·3	9·7
Pr^i_2	76	84°/0·3	1·5451 ^{22}	2180 (26,700)	2680 (6,900)	89·6	10·3	$C_{16}H_{22}$	89·7	10·3
MePh	53	125—126°/0·8	1·6150 ^{19}	2150 (24,600)	2620 (8,100)	92·5	7·5	$C_{17}H_{16}$	92·7	7·3
Ph_2	59	M. p. 116°	—	—	2630 (7,300)	93·4	6·5	$C_{22}H_{18}$	93·6	6·4

Dehydrogenation of 1,2-*Dihydro*-1,1-*dimethylnaphthalene.*—The hydrocarbon (0·75 g.), sublimed tetrachloro-1,2-benzoquinone (1·30 g.), and benzene (2·5 ml.) were heated under reflux for 2 hr., diluted with light petroleum (b. p. 40—60°; 30 ml.), stored at 25° for 24 hr., filtered, and passed through an alumina column which was then eluted with benzene. The evaporated eluate (0·69 g., 93%) had $\lambda_{max.}$ 2270 (ε 98,000) and 2800 Å (ε 6100) and was therefore pure 1,2-dimethylnaphthalene; it gave a picrate, m. p. and mixed m. p. 129—130°.

Similar experiments with the other hydrocarbons noted in Table 1 gave the expected products in high yields.

Attempted Dehydrogenation of Benzocycloheptene.—The hydrocarbon [1·65 g.; n_D^{18} 1·5444; $\lambda_{max.}$ 2100 (ε 7300) and 2620 Å (ε 320)], tetrachloro-1,2-benzoquinone (8·0 g.), and benzene (15 ml.) were refluxed for 20 hr., and then treated as above. Elution with light petroleum (b. p. 40—60°) gave starting material (1·40 g.), n_D^{23} 1·5420, $\lambda_{max.}$ 2140 (ε 8500) and 2570 (ε 360), with the correct infrared spectrum.

Reaction of 1,2-*Dihydro*-1,1-*dimethylnaphthalene with* NN-*Diphenylpicrylhydrazyl.*—The hydrocarbon (0·19 g.), *NN*-diphenylpicrylhydrazyl (1·10 g.), and benzene (2·5 ml.) were heated under reflux for 20 hr. The mixture, on dilution with light petroleum (b. p. 40—60°; 25 ml.), consisted of a black tar and an upper layer of solvent. The solvent was decanted and on evaporation gave only a trace of tar. The tarry layer was chromatographed in benzene over alumina, and eluted with benzene. Evaporation of the eluate afforded the starting material (5 mg.), $\lambda_{max.}$ 2150 ($E^{1\%}_{1\,cm.}$ 1360) and 2650 Å ($E^{1\%}_{1\,cm.}$ 640).

Kinetic Experiments.—*Materials.* Pure tetralin was distilled from sodium before use and had n_D^{26} 1·5374. 1,1-Dimethyltetralin, n_D^{20} 1·5278, was prepared as previously described.[1] Tetrachloro-1,2-benzoquinone, supplied by Messrs. Hopkin and Williams, was sublimed. Phenetole was refluxed over sodium and distilled; the pure solvent had b. p. 170—171°, $n_D^{21\cdot5}$ 1·5071.

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.[6]

To take account of concurrent decomposition of the quinone in the solvent the following analysis was employed.

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[7] Braude, Brook, and Linstead, *J.*, 1954, 3574.

Let a be the molarity of the quinone and b that of the hydrocarbon. Let the concentration of quinone at time t be $(a - x)$, and let k_2 and k_1 be the rate constants for the dehydrogenation and decomposition respectively. Then, provided $k_2 > k_1$ and $b > a$ to a substantial extent, $(b - x)$ will be a good approximation to the concentration of hydrocarbon at time t. Therefore, for the systems under examination and for relative concentrations employed, we may write:

$$\mathrm{d}(a - x)/\mathrm{d}t = -k_2(a - x)(b - x) - k_1(a - x) \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The integrated form of (1) is:

$$k_2 = [\{\ln\{a[k_2(b - x) + k_1]/(a - x)(k_2 b - k_1)\}\}/(b - a)t] - k_1/(b - a) \quad . \quad . \quad (2)$$

For experiments with the dihydronaphthalenes, in which $a = 0{\cdot}01\text{M}$ and $b = 0{\cdot}05\text{M}$, equation (2) expressed in terms of observed extinctions becomes:

$$k_2 = -25k_1 + 25t^{-1}\{\ln[0{\cdot}01k_2(E + 4E_0) + k_1E_0]/E(0{\cdot}05k_2 + k_1)\} \quad . \quad . \quad . \quad (3)$$

Equation (3) could be solved by successive approximation, and for the dihydronaphthalenes, when trial values of k_2 were those calculated by the normal second-order rate equation, the solution was reached at the second approximation. In fact, the correction was negligible for the faster systems. In the experiments with the tetralins it was more convenient to solve equation (1) directly by determining $[\mathrm{d}(a - x)/\mathrm{d}t]_{x=0}$ graphically.

The values of k_1 at various temperatures were found by direct experiment.

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.[6]

RESULTS

Individual Runs.—Representative examples for each hydrocarbon are recorded. Unless otherwise stated, the concentration of quinone was 0·0100M, that of the tetralins 1·00M, and of the 1,2-dihydronaphthalene 0·0500M. Phenetole was the only solvent used.

(i) *Decomposition of tetrachloro*-1,2-*benzoquinone in phenetole at* 116·3°.

t (min.)	0	90	120	150	180	210
E (6050 Å)	0·620	0·423	0·357	0·307	0·267	0·217
10^3k_1 (min.$^{-1}$)	—	4·59	4·85	4·91	4·85	5·17

(ii) *Dehydrogenation of tetralin at* 84·8°.

t (min.)	0	2	4	6	8	10	14	20	28
E (6050 Å)	0·650	0·490	0·400	0·348	0·310	0·281	0·242	0·203	0·169

$k_2 = 0{\cdot}159$ l. mole^{-1} min.$^{-1}$.

(iii) *Dehydrogenation of tetralin* (0·800M) *by quinone* (0·005M) *at* 90·9°.

t (min.)	0	2	4	6	8	12	20	25	30
E (6050 Å)	0·650	0·500	0·433	0·380	0·335	0·284	0·223	0·210	0·176

$k_2 = 0{\cdot}200$ l. mole^{-1} min.$^{-1}$. This value may be compared with the value 0·221 obtained from a plot of k_2 against $1/t$ for experiments with 1·000M-tetralin and 0·0100M-quinone. Similarly, an experiment carried out at 90·5° with 0·500M-tetralin and 0·005M-quinone gave $k_2 = 0{\cdot}205$ l. mole^{-1} min.$^{-1}$.

(iv) *Dehydrogenation of* 1,1-*dimethyltetralin at* 95·1°.

t (min.)	0	2	4	6	10	20	30	40	50	70
E (6050 Å)	0·730	0·709	0·688	0·673	0·636	0·560	0·484	0·415	0·349	0·246

$k_2 = 0{\cdot}0127$ l. mole^{-1} min.$^{-1}$.

(v) 1,2-*Dihydronaphthalene at* 94·5°.

t (min.)	0	8	12	16	20	27	30
E (6050 Å)	1·000	0·490	0·370	0·269	0·186	0·120	0·095
k_2 (l. mole^{-1} min.$^{-1}$)	—	1·87	1·76	1·78	1·85	1·76	1·77

(vi) 1,2-*Dihydro*-1,1-*dimethylnaphthalene at* 80·7°.

t (min.)	0	15	21	27	35	45	55	60
E (6050 Å)	0·700	0·462	0·398	0·337	0·284	0·223	0·169	0·148
k_2 (l. mole^{-1} min.$^{-1}$)	—	0·566	0·557	0·565	0·546	0·543	0·560	0·565

(vii) 1,1-*Diethyl*-1,2-*dihydronaphthalene at* 89·6°.

t (min.)	0	16	18	20	22	24	26
E (6050 Å)	0·820	0·208	0·175	0·149	0·128	0·108	0·094
k_2 (l. mole^{-1} min.$^{-1}$)	—	1·871	1·887	1·888	1·880	1·893	1·875

(viii) 1,2-*Dihydro*-1,1-*di-isopropylnaphthalene at* 88·6°.

t (min.)	0	10	12	14	18	22	26
E (6050 Å)	0·800	0·428	0·378	0·335	0·271	0·216	0·168
k_2 (l. mole^{-1} min.$^{-1}$)	—	1·302	1·311	1·315	1·288	1·291	1·317

(ix) 1,2-*Dihydro*-1-*methyl*-1-*phenylnaphthalene at* 88·8°.

t (min.)	0	16	20	25	30	40	50
E (6050 Å)	700	0·440	0·394	0·347	0·302	0·232	0·180
k_2 (l. mole^{-1} min.$^{-1}$)	—	0·586	0·586	0·577	0·581	0·582	0·580

(x) 1,2-*Dihydro*-1,1-*diphenylnaphthalene at* 100·4°.

t (min.)	0	25	40	50	60	70	80
E (6050 Å)	0·830	0·642	0·554	0·508	0·462	0·420	0·385
k_2 (l. mole^{-1} min.$^{-1}$)	—	0·173	0·172	0·167	0·168	0·168	0·166

Summary of rate constants.

Decomposition of tetrachloro-1,2-benzoquinone in phenetole.

T°	116·3	105·4	100·9	79·9
10^5k_1 (sec.$^{-1}$)	8·00	4·17	2·67	0·767

The units for the following rates are l. mole^{-1} sec.$^{-1}$.

Tetralin

T°	89·7	84·8	79·0	75·7	71·3
10^3k_2	3·52	2·65	1·77	1·38	1·15

1,2-Dihydronaphthalene

T°	94·5	90·6	84·1	80·5	76·8
10^2k_2	3·00	2·45	1·62	1·33	1·03

1,1-Diethyl-1,2-dihydronaphthalene

T°	89·6	85·4	80·5	76·1	70·7
10^2k_2	3·13	2·43	1·78	1·32	0·917

1,2-Dihydro-1-methyl-1-phenylnaphthalene

T°	94·0	88·8	84·5	78·9	76·1
10^2k_2	1·35	0·967	0·750	0·533	0·450

1,1-Dimethyltetralin

t°	109·8	105·4	100·9	95·1	88·1
10^4k_2	5·05	3·75	3·27	2·12	1·40

1,2-Dihydro-1,1-dimethylnaphthalene

t°	94·5	89·8	85·0	80·7	75·8
10^2k_2	2·13	1·60	1·18	0·933	0·683

1,2-Dihydro-1,1-di-isopropylnaphthalene

t°	88·6	84·0	79·8	76·1	70·4
10^2k_2	2·17	1·60	1·28	1·05	0·700

1,2-Dihydro-1,1-diphenylnaphthalene

t°	100·4	95·3	90·8	84·0	80·4
10^3k_2	2·82	2·13	1·65	1·03	0·833

Arrhenius Parameters.—The values for the decomposition reaction are $E_A = 17{\cdot}8 \pm 1{\cdot}1$ kcal./mole and $\Delta S^{\ddagger}_{100°} = -34 \pm 3$ E.U. $k_{1(100°)} = 2{\cdot}7\ (\pm 1{\cdot}5) \times 10^{-5}$ sec.$^{-1}$.

The data for the dehydrogenation of the tetralins and 1,2-dihydronaphthalenes are recorded in Table 2.

TABLE 2. *Arrhenius parameters and rate constants at* 100°.

Compound	10^3k_2 (l. mole^{-1} sec.$^{-1}$)	$S^{\ddagger}_{100°}$ (E.U.)	E_A (kcal. mole^{-1})
Tetralin	5·86 ± 0·45	29·0 ± 2·3	15·6 ± 0·8
1,1-Dimethyltetralin	0·290 ± 0·009	33·7 ± 2·2	16·2 ± 0·5
1,2-Dihydronaphthalene [a]	41·1 ± 0·7	25·7 ± 0·8	15·4 ± 0·3
1,2-Dihydro-1,1-dimethylnaphthalene	28·7 ± 0·5	26·2 ± 0·9	15·5 ± 0·03
1,1-Diethyl-1,2-dihydronaphthalene	57·8 ± 0·5	23·4 ± 0·3	16·1 ± 0·1
1,2-Dihydro-1,1-di-isopropylnaphthalene	40·8 ± 1·3	26·5 ± 1·2	15·1 ± 0·4
1,2-Dihydro-1-methyl-1-phenylnaphthalene	18·7 ± 0·1	26·2 ± 0·5	15·9 ± 0·2
1,2-Dihydro-1,1-diphenylnaphthalene	2·77 ± 0·03	29·1 ± 0·9	16·3 ± 0·3

[a] These values are in excellent agreement with those reported in Part XI.[6]

DISCUSSION

The dehydrogenation of tetralin with tetrachloro-1,2-benzoquinone exhibits overall second-order kinetics, being of first order with respect to each reactant. The results for tetralin and 1,2-dihydronaphthalene show that the rate of dehydrogenation of tetralin measured under pseudo-unimolecular conditions with the hydrocarbon in excess is certainly the rate of its conversion into dihydronaphthalene; the same is true for dehydrogenation of 1,1-dimethyltetralin. The observed ratio of 20 : 1 for the rates of reaction of tetralin and 1,1-dimethyltetralin therefore corresponds to a ratio of 10 : 1 for the rates of attack at the 1(and 4)-position of tetralin and the 4-position of the dimethyl derivative. It is difficult to ascribe such a large ratio to electronic effects associated with the change of substitution. In effect, this change is equivalent to passing from an ethyl- to a t-butyl-substituted benzene, and in reactions known to involve carbonium ions such a change results in only a two-fold diminution in rate. Thus the ratio of rates of solvolysis [8] in aqueous formic acid of *p*-ethyl- and *p*-t-butyl-diphenylmethyl bromide is 2 : 1 and for the solvolysis of *p*-alkyldiphenylmethyl chlorides the value is even less.[9] It is likely, therefore, that in the present case an additional factor operates. We believe that this factor is steric in origin and consists of a buttressing effect of the *gem*-dimethyl group. Removal of the hydride ion from the 1-position in tetralin requires that this carbon atom should adopt an sp^2-configuration, coplanar with the benzene ring. For this it is necessary to distort the remaining three methylene groups from their half-chair conformation towards a less favourable conformation in which the pairs of hydrogen atoms are opposed. If one pair of hydrogen atoms is replaced by a pair of methyl groups the process becomes more difficult because the difference in energy of the staggered and the opposed conformation of isobutane (3·87 kcal. mole^{-1}) is substantially greater than that for ethane (2·75 kcal. mole^{-1}).[10] Thus the presence of the *gem*-dimethyl group will retard the rate of dehydrogenation. This form of conformational control is similar to that exhibited in the ethanolysis of benzocycloalkenyl chlorides studied by Baddeley and Chadwick,[11] where alteration of ring size has a profound effect on the rate of reaction. These workers found that 1-chlorotetralin was solvolysed 26 times more rapidly than 3-chlorobenzocycloheptene, which in turn reacted 9 times faster than 1-phenylethyl chloride. The fact that benzocycloheptene did not react under conditions where tetralin was smoothly dehydrogenated is consistent with these results, and the failure of acyclic systems to undergo rearrangement, noted in the previous paper, presumably has its origins in a similar conformational effect.

The parity in the rates of dehydrogenation of 1,2-dihydronaphthalene and its 1,1-dialkyl derivatives establishes conclusively that in the unsubstituted compound attack occurs preferentially at the 2-position. This result is in agreement with the calculated stabilities of the 1- and the 2-naphthalenium ion.[12] Introduction of phenyl groups into the 1-position of 1,2-dihydronaphthalene retards the dehydrogenation, but only to an extent compatible with the —*I* effect of this group. Thus the rate enhancements due to synartetic participation, as computed by the method of Winstein *et al.*[13], are 1·3 for 1,2-dihydro-1-methyl-1-phenylnaphthalene and 2·0 for the 1,1-diphenyl compound, and are probably insignificant in view of the assumptions made. Failure to observe participation in the dehydrogenation probably has two causes. First, the carbonium ion involved is one which is well stabilised by resonance, and the activation energy is low compared with that for reactions where significant participation has been observed.[13,14] Secondly, 1,2-dihydronaphthalene differs from cyclohexane or acyclic systems in that the participating and leaving groups cannot adopt the truly diaxial conformation necessary for maximum participation. This second factor is known to be very important [15] and explains why 2,2-dimethylindane reacts with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone to form an unrearranged ether.[1] The five-membered ring of the indane must be almost flat and the methyl groups will lie *ca.* 70° out of the desired plane for maximum participation.

Although there is no kinetic evidence for participation, it has nevertheless been demonstrated that migration, even of alkyl groups, is certainly not rate-controlling. Since there are no authenticated examples of rearrangements of alkyl groups to radical ends [4] and since the much more favourable rearrangement of the phenyl groups has been shown to require activation to the extent of 8 kcal. mole^{-1}, we feel that our results

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[8] Ingold, " Structure and Mechanism in Organic Chemistry," Bell, London, 1953, p. 327.
[9] Hughes, Ingold, and Taher, *J.*, 1940, 949.
[10] Pitzer, *Discuss. Faraday Soc.*, 1951, **10**, 66.
[11] Baddeley and Chadwick, *J.*, 1951, 368.
[12] Barnard and Jackman, *J.*, 3110.
[13] Winstein, Morse, Grunwald, Schreiber, and Corse, *J. Amer. Chem. Soc.*, 1952, **74**, 1113.
[14] Winstein and Heck, *J. Amer. Chem. Soc.*, 1956, **78**, 4801.
[15] Barton and Cookson, *Quart. Rev.*, 1956, **10**, 44.

strongly substantiate the ionic mechanism. The argument is considerably strengthened by the observation that, whereas diphenylpicrylhydrazyl quantitatively converts 1,2-dihydronaphthalene into naphthalene,[7] its reaction with 1,2-dihydro-1,1-dimethylnaphthalene yields no 1,2-dimethylnaphthalene. Apparently rearrangement of the intermediate radical is slow enough to permit intervention of side reactions such as polymerisation or coupling with the reagent.

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