

## Thermolysis of Phenyl-substituted 1,2-Dihydronaphthalenes. Evidence for Diphenylbutadienes as Intermediates

Joseph J. M. Lamberts, Theo J. H. M. Cuppen, and Wim H. Laarhoven\*

Department of Organic Chemistry, Catholic University, Toernooiveld, 6525 ED Nijmegen, The Netherlands

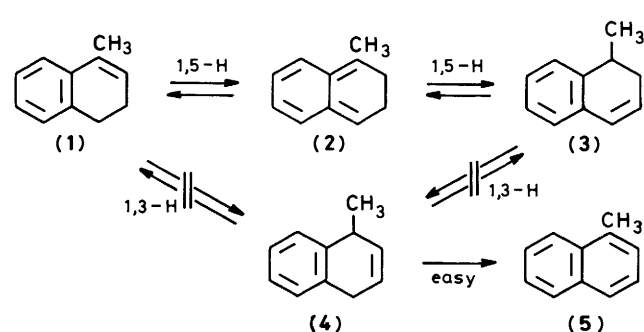
The thermal rearrangements of the four phenyl-substituted 1,2-dihydronaphthalenes (**15**), (**16**), (**19**), and (**20**) have been studied by flash vacuum pyrolysis (FVP).

By using the deuteriated starting compounds  $[3,4\text{-}^2\text{H}_2]$ -(**15**) and  $[3,4\text{-}^2\text{H}_2]$ -(**16**), it has been established that 1- and 4-phenyl-1,2-dihydronaphthalene (**15**) and (**19**) and 2- and 3-phenyl-1,2-dihydronaphthalene (**16**) and (**20**) are interconverted *via* the intermediates 1- and 2-phenyl-2,3-dihydronaphthalene (**17**) and (**18**), respectively, through two consecutive, sigmatropic 1,5-hydrogen shifts. In both processes partial oxidation to the corresponding phenylnaphthalenes (**21**) and (**22**) takes place. The deuterium distribution in the pyrolysis products suggests that in the hot zone diphenylbutadienes are formed, which are reconverted into phenyldihydronaphthalenes upon reaching the cold receiving flask. By FVP of 4-(*p*-tolyl)-1,2-dihydronaphthalene (**34**), 1-phenyl-1-(*p*-tolyl)butadiene (**39**), and 1-phenyl-4-(*p*-tolyl) butadiene (**45**) the latter type of interconversion could be confirmed.

Previously, we described the photolysis of phenyl-substituted 1,2-dihydronaphthalenes.<sup>1,2</sup> This paper concerns the thermolysis of these compounds.

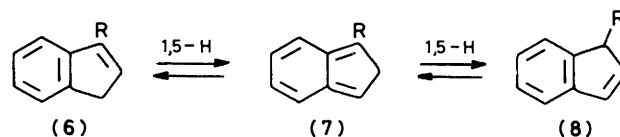
There are several examples in the literature of 1,2-dihydronaphthalenes as end products of thermal reactions in the condensed<sup>3</sup> or vapour phase.<sup>4</sup> At higher temperatures in the condensed phase 1,2-dihydronaphthalenes readily undergo dehydrogenation to naphthalenes and polycyclic aromatic hydrocarbons<sup>5</sup> or disproportion to tetralins and naphthalenes.<sup>6</sup> In one of the rare examples in which the intramolecular rearrangements of 1,2-dihydronaphthalenes have been studied by high-temperature flash vacuum pyrolysis (FVP),<sup>7</sup> 4- and 1-methyl-1,2-dihydronaphthalene [(**1**) and (**3**); Scheme 1] were found to give the same product mixture containing mainly 1- and 2-methylnaphthalene, naphthalene, and smaller quantities of indene, benzofulvene, and dimethylnaphthalenes.<sup>8</sup> The authors concluded that the starting compounds were readily interconverted before other thermal reactions took place. They postulated rearrangement of (**1**) into (**3**) and *vice versa* by consecutive, symmetry-allowed 1,5-hydrogen migrations<sup>9</sup> *via* an intermediate, non-aromatic 2,3-dihydronaphthalene (**2**). An alternative explanation through an intermediate 1,4-dihydronaphthalene (**4**) *via* consecutive 1,3-hydrogen shifts was not considered feasible, since cyclohexa-1,4-dienes are known to undergo quantitative elimination of hydrogen at comparatively low temperatures.<sup>10</sup>

More literature is available on sigmatropic shifts in



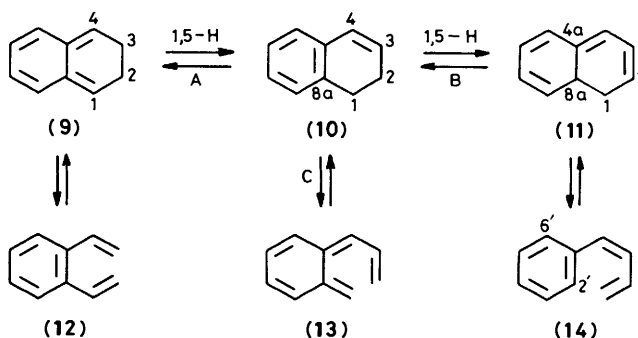
Scheme 1.

indenes<sup>9,11</sup> [(**6**) and (**8**); Scheme 2]. This system is similar to that for 1,2-dihydronaphthalene in that a 1,5-H shift will lead to disruption of the aromatic system to produce an *o*-quinonoid structure (**7**). In both cases the activation energy is found to be high. However, in contrast to the 1,3-dihydronaphthalene skeleton, no special conformational restraint has to be imposed on the indene moiety to bring the migration termini to such a position that the migrating group can interact simultaneously<sup>9,12</sup> with both of them in the transition state. Consequently, the energy of activation for rearrangement in 1,2-dihydronaphthalene is expected to be higher than in indenes.



Scheme 2.

According to the Woodward-Hoffmann rules<sup>13</sup> several thermal reactions are possible in 1,2-dihydronaphthalenes (**10**) (Scheme 3). All of these are expected to require a large activation energy because they all lead to sacrifice of aromaticity. Pathway A involves a 1,5-hydrogen shift from C(1) to C(3) in (**10**) leading to 2,3-dihydronaphthalenes (**9**). In (**9**)



Scheme 3.

**Table 1.** Chemical shifts of the non-aromatic protons in 1,2-dihydronaphthalene (DHN) and its phenyl-substituted derivatives (PDHNs). Compounds (15), (16), and (20) in CDCl<sub>3</sub>; (19) and (10) in CCl<sub>4</sub>

Compound	Name	H(1)	H'(1)	H(2)	H'(2)	H(3)	H(4)
(15)	1-PDHN <sup>a</sup>	4.12	—	2.60	2.65	5.98	6.52
(16)	2-PDHN <sup>a</sup>	2.98	3.10	3.74	—	6.03	6.57
(20)	3-PDHN	2.6—3.1				—	6.84
(19)	4-PDHN <sup>b</sup>	2.69		2.21		5.96	—
(10)	DHN <sup>b</sup>	2.57		2.03		5.90	6.43

<sup>a</sup> J. Lamberts and W. H. Laarhoven, *Recl. Trav. Chim. Pays-Bas*, 1983, **102**, 181. <sup>b</sup> M. J. Cook, A. R. Katritzky, F. C. Pennington, and B. M. Semple, *J. Chem. Soc. B*, 1969, 523.

**Table 2.** Coupling constants (Hz) of the non-aromatic protons in DHN and the PDHNs. Compound (15), (16), and (20) in CDCl<sub>3</sub>; (19) and (10) in CCl<sub>4</sub>

Compound	$J_{1,1'}$	$J_{1,2}$	$J_{1',2}$	$J_{1,2'}$	$J_{1',2'}$	$J_{2,2'}$	$J_{2,3}$	$J_{2',3}$	$J_{2,4}$	$J_{2',4}$	$J_{3,4}$
(15) <sup>a</sup>	—	9.9	—	7.3	—	-17.3	4.2	4.4	-2.2	-1.7	9.7
(16)	-15.5	11.6	7.1	—	—	—	3.5	—	-2.3	—	9.7
(20)	—	—	—	—	—	—	—	—	-1.2		—
(19) <sup>b</sup>	-14.2	9.2	6.4	9.2	6.4	-15.8	4.7		—	—	—
(10) <sup>b</sup>	-15.4	9.4	7.0	9.4	7.0	-16.8	4.3		1.8		9.4

<sup>a,b</sup> References as for Table 1.

**Table 3.** Product composition (%) after FVP of the phenyl-substituted 1,2-dihydronaphthalenes (15), (16), (19), and (20) at various temperatures

Product	Pyrolysis temperatures (°C)						
	600	675	700	750	800	850	900
	FVP of (15)						
(15)	100	90	84	70	47	35	26
(19)	—	10	16	30	42	48	42
(21)	—	—	—	—	11	17	32
	FVP of (16)						
(16)	100	100	94	83	53	32	17
(20)	—	—	6	17	36	42	40
(22)	—	—	—	—	11	26	43
	FVP of (20)						
(16)	—	—	—	—	8	17	29
(20)	100	100	100	100	81	63	40
(22)	—	—	—	—	11	20	31
	FVP of (19)						
(15)	—	—	4	16	23	30	29
(19)	100	100	96	83	69	53	47
(21)	—	—	—	1	8	17	24

there are three options: electrocyclic ring-opening to give 1,2-divinylbenzene (12) and two 1,5-H shifts, *viz.* from C(2) to C(4) and from C(3) to C(1), both leading back to (10). If compound (10) is substituted, the H-migrations result in two different 1,2-dihydronaphthalenes. In pathway B, a 1,5-H shift from C(2) to C(8a) in (10) leads to 1,8a-dihydronaphthalene (11). In (11) there are again three options including 1,5-H shift from C(8a) to C(2) leading back on (10) or a 1,5-H shift from C(1) to C(4a). As the latter migration does not lead to restoration of the aromatic system it is probably not a major pathway. The third possibility

is an electrocyclic ring-opening giving 1-phenylbuta-1,3-diene (14). In compound (14) reclosure can take place on either of the two *ortho* positions (2' and 6') of the phenyl group. This leads again to different 1,2-dihydronaphthalenes when the phenyl group is unsymmetrically substituted. Pathway C involves electrocyclic ring-opening of compound (10) leading to a conjugated pentaene (13). The aromatic system can only be restored by reclosure to (10).

#### Pyrolysis Experiments

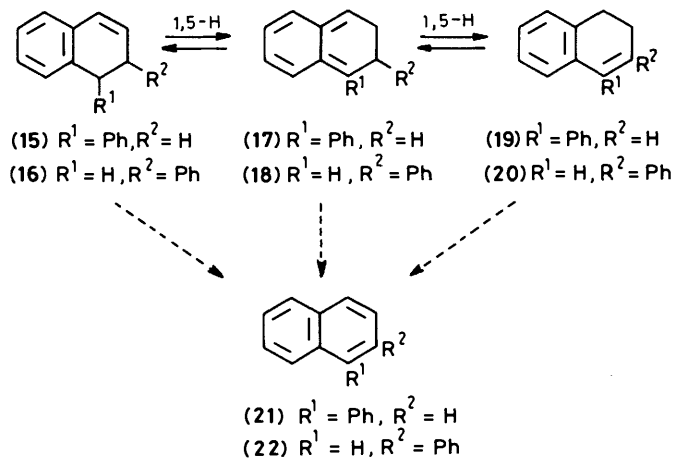
The synthesis of 2-phenyl-1,2-dihydronaphthalene (16) has been described previously.<sup>1</sup> The synthesis of 1-phenyl- and 3-phenyl-1,2-dihydronaphthalene (15) and (20) are given in the Experimental section. For the sake of simplicity reference n.m.r. data for the phenyl-1,2-dihydronaphthalenes are compiled in Tables 1 and 2.

Aliquots of the compounds (*ca.* 50 mg per run) were subjected to FVP at temperatures ranging from 600–900 °C at a pressure of 0.1 Torr. The product mixtures were collected in a cold-finger and analysed. In Table 3 are tabulated the g.l.c. data.

Compound (15) turned out to be stable up to *ca.* 640 °C, compounds (16) and (19) to 685–695 °C, and compound (20) even to 760 °C. The data show that (15) and (19) are interconverted and that the same holds for (16) and (20). Decrease of the concentration of the starting compound and increase of the product concentration are linear with temperature up to 800 °C on FVP of compounds (15), (16), and (19), and on FVP of compound (20) even throughout the whole temperature range studied. Except for compound (20), a deflection of both curves is observed at higher temperatures, pointing to an equilibration tendency of the two phenyl-1,2-dihydronaphthalenes involved. True equilibration is not possible since we are dealing with a flow system in which fresh starting compound is supplied and product is carried off continuously. At temperatures of 740–770 °C dehydrogenation of compounds (16) and (20) to (22), and of compounds (15) and (19) to (21), begins to play an increasingly important role. In FVP of compound (20) dehydrogenation begins even slightly

earlier than does rearrangement to (16). The dehydrogenation of the four compounds shows a linear variation with temperature.

These experimental results can be rationalized most adequately by assuming interconversion of the phenyl-1,2-dihydronaphthalenes by two consecutive sigmatropic 1,5-H shifts leading from (15) to (19) and from (16) to (20) and *vice versa* via 1- and 2-phenyl-2,3-dihydronaphthalene (17) and (18), respectively (Scheme 4).



Scheme 4.

The very high temperatures needed for these 1,5-H shifts reflect the inevitable sacrifice of aromaticity in going from the starting compounds to the intermediates (17) and (18). The start of the rearrangement of (15) at lower temperatures than for the other compounds can be ascribed to the more extensive conjugation in the intermediate (17) than in (18). In compound (19), also leading to (17), more (cross-)conjugation is lost, so that the energy of activation for the primary 1,5-H shift will be lower for (15). The rearrangement of (16) begins at about the same temperature as that for (19); it starts at a higher energy level than (19) but this is apparently compensated for by the higher energy of intermediate (18) compared with that of (17). Compound (20) faces disruption of its extensive, stilbene-like conjugated system and in addition the primary product is the less stable intermediate (18). Consequently, the energy of activation for its rearrangement will be the highest of the four primary 1,5-H shifts. The activation energy for the second rearrangement leading from (17) and (18) to a phenyl-1,2-dihydro-naphthalene is expected to be very small compared with the first step because the aromatic system is restored.

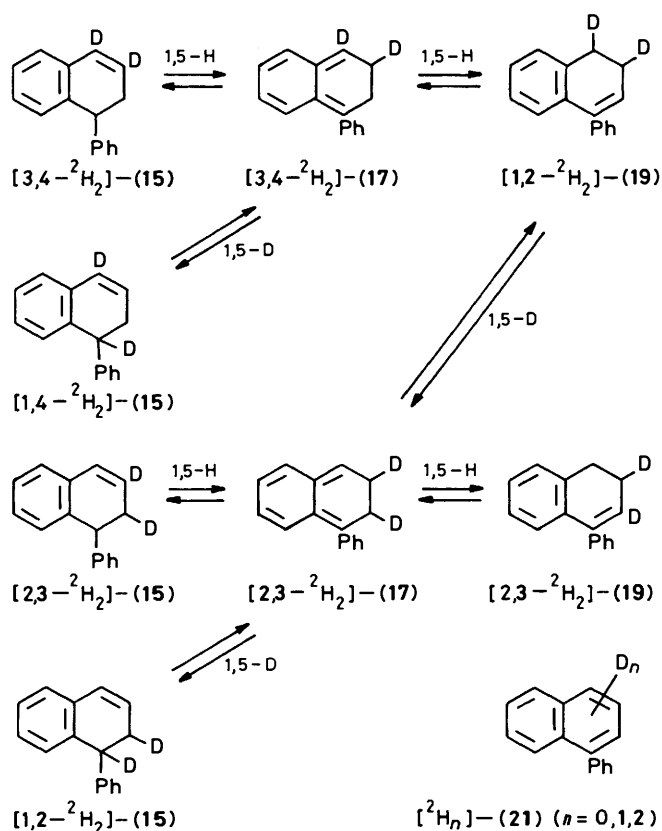
Comparison of the data in Table 3 shows that the dehydrogenation process begins around 750 °C for all four phenyl-1,2-dihydronaphthalenes. Experiments in which the quartz pyrolysis tube was filled with a packing of quartz wool or quartz beads led to almost complete dehydrogenation at 800 °C, suggesting that the dehydrogenation is a surface reaction.

In the pyrolysis experiments with compounds (16) and (20) at 800 and 900 °C an additional product was observed. Its only visible signal in the n.m.r. spectra of the product mixtures was a singlet at  $\delta$  8.40, so that the product is expected to have an extensive and highly symmetrical aromatic system. With regard to the symmetry, it is assumed that the singlet corresponds to at least two protons; the concentration of this product would amount to less than 2% at 800 °C and less than 5% at 900 °C on FVP of both compounds (16) and (20). No attempt was made to isolate the compound.

*Pyrolysis of Deuteriated Starting Compounds; Elucidation of the Mechanism.*—With the aid of 3,4-dideuterio-1-phenyl-1,2-dihydronaphthalene [3,4- $^2\text{H}_2$ ]-**(15)** and 3,4-dideuterio-2-phenyl-1,2-dihydronaphthalene [3,4- $^2\text{H}_2$ ]-**(16)**<sup>1</sup> an attempt was made to establish more firmly the nature of the rearrangement by which compounds (15) and (19) on the one hand and compounds (16) and (20) on the other hand are interconverted. The compounds [3,4- $^2\text{H}_2$ ]-**(15)** and [3,4- $^2\text{H}_2$ ]-**(16)** were pyrolysed at 800 °C in the usual way. This temperature was chosen because according to the data from Table 3 it causes substantial rearrangement whereas dehydrogenation does not become too extensive.

*Pyrolysis of Compound [3,4- $^2\text{H}_2$ ]-**(15)**.*—Table 4 shows the main characteristics of the various signals in the 90 MHz  $^1\text{H}$  n.m.r. spectra of compounds (15), (19), and [3,4- $^3\text{H}_2$ ]-**(15)**, and of the last compound pyrolysed at 800 °C. The most intense signals of the last spectrum are italicized. Coupling constants are not mentioned, but they are unchanged in comparison with the reference compounds. It is clear that the main [ $^2\text{H}_2$ ]-**(15)** species after FVP is still [3,4- $^2\text{H}_2$ ]-**(15)**. Some intensity is observed at the normal positions of H(3) and H(4) of (15): a doublet of doublets at  $\delta$  6.52 together with a broad singlet in between. The doublet of doublets is present as a doublet of triplets in the n.m.r. spectrum of unlabelled compound (15). It denotes a compound in which one of the protons responsible for the allylic coupling to H(4), *viz.* one of the protons at C(2), has been replaced by D. The large coupling to H(3) is still present. These data point to a [ $^2\text{H}_2$ ]-**(15)** species having D at C(2) and at C(1) {[1,2- $^2\text{H}_2$ ]-**(15)**}. The broad singlet at  $\delta$  6.52 corresponds to H(4) of a [ $^2\text{H}_2$ ]-species with D at C(3) since the large coupling with H(3) has disappeared. The position of the other D atom in this product cannot be determined unequivocally; it must be either at C(1) or C(2) {[1,3- $^2\text{H}_2$ ]-**(15)** or [2,3- $^2\text{H}_2$ ]-**(15)**}. Between the signals of the triplet at  $\delta$  4.12 corresponding to H(1) of [3,4- $^2\text{H}_2$ ]-**(15)** a doublet is just visible. Apparently there is a [ $^2\text{H}_2$ ]-**(15)** species having one D atom at C(2) together with H at C(1) {[2,3- $^2\text{H}_2$ ]-**(15)** or [2,4- $^2\text{H}_2$ ]-**(15)**}. The signals at  $\delta$  5.98 of [ $^2\text{H}_2$ ]-**(15)** are obscured by those of [ $^2\text{H}_2$ ]-**(19)** and the signal at  $\delta$  2.5–2.8 of the allylic protons is largely the same as in the spectrum of [3,4- $^2\text{H}_2$ ]-**(15)**. An analysis of all species that might arise from 1,5-H and 1,5-D shifts in [3,4- $^2\text{H}_2$ ]-**(15)** is given in Scheme 5. The scheme is arranged in such a way that 1,5-H shifts are represented by horizontal and 1,5-D shifts by slanting arrows. The left column contains the four possible [ $^2\text{H}_2$ ]-**(15)** products, the middle column the intermediates, and the right column the two [ $^2\text{H}_2$ ]-**(19)** products. Analysis of the n.m.r. data belonging to [ $^2\text{H}_2$ ]-**(15)** species is in accord with Scheme 5 when in the two cases where assignment of n.m.r. signals was not unequivocal, one of the solutions is rejected {[1,3- $^2\text{H}_2$ ]-**(15)** and [2,4- $^2\text{H}_2$ ]-**(15)**}; the observed species is then the same in both cases, *viz.* [2,3- $^2\text{H}_2$ ]-**(15)**, and three of the four [ $^2\text{H}_2$ ]-**(15)** species expected from Scheme 5 are identified in the n.m.r. spectrum of the [3,4- $^2\text{H}_2$ ]-**(15)** sample pyrolysed at 800 °C, *viz.* [3,4- $^2\text{H}_2$ ]-**(15)**, [1,2- $^2\text{H}_2$ ]-**(15)**, and [2,3- $^2\text{H}_2$ ]-**(15)**. It should be noted that small amounts of [1,4- $^2\text{H}_2$ ]-**(15)**, if present, should not easily be detected in the n.m.r. spectrum of the FVP mixture, because its H(3) signal should be obscured and its H(2) signal should coincide largely with the H(2) signal of the main compound [3,4- $^2\text{H}_2$ ]-**(15)**.

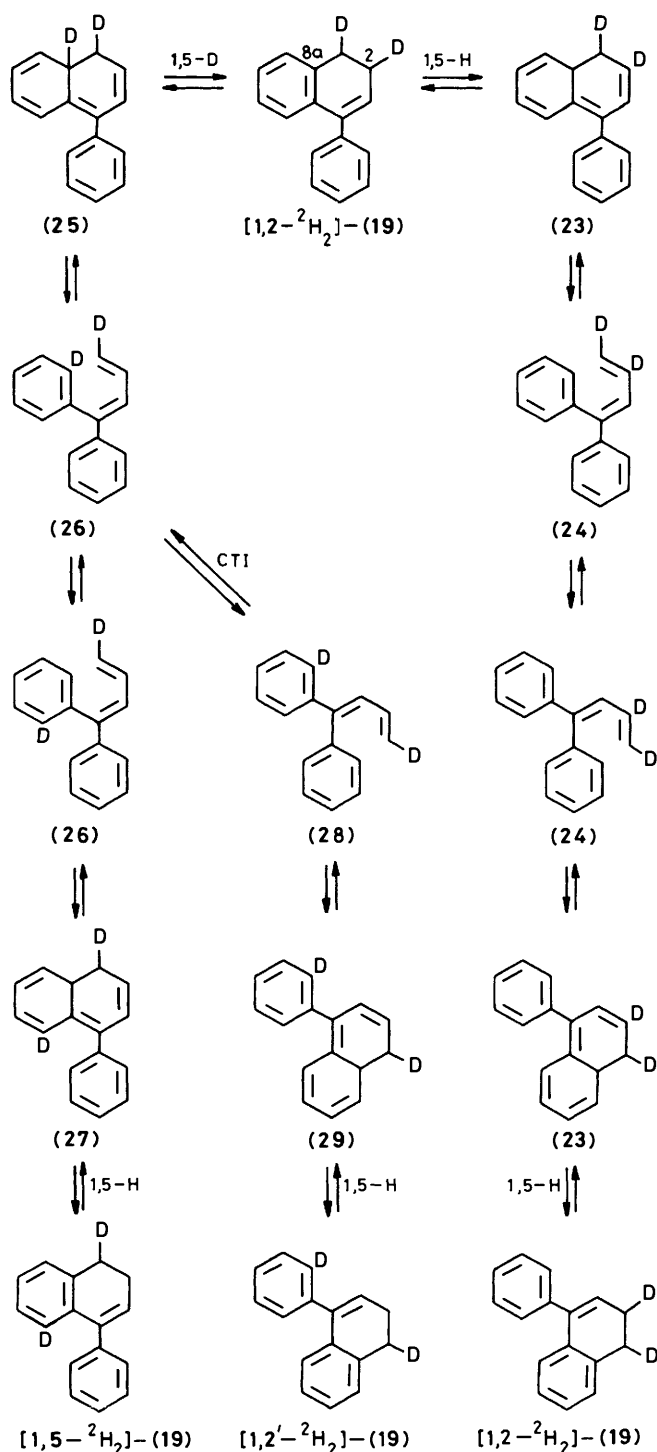
For the expected [ $^2\text{H}_2$ ]-**(19)** compounds a doublet with  $J_{2,3}$  4.7 Hz is found at  $\delta$  6.06 where a triplet with the same coupling constant is observed in the n.m.r. spectrum of unlabelled (19). This means that one of the protons at C(2) has been replaced by D. Consequently, the other D atom must be at C(1) {[1,2- $^2\text{H}_2$ ]-**(19)**}. Apparently, the main [ $^2\text{H}_2$ ]-**(19)** species is that arising from [3,4- $^2\text{H}_2$ ]-**(15)**: *via* two 1,5-H shifts. When [1,2- $^2\text{H}_2$ ]-**(19)**



was the only  $[^2\text{H}_2]$ -(19) species present, the integrals of the doublet at  $\delta$  2.2 and each of the multiplets at  $\delta$  2.2–2.5 and 2.7–3.0 that correspond to the allylic and benzylic protons of  $[^2\text{H}_2]$ -(19), respectively, should be equal. The latter integrals, however, are each twice as large as that of the doublet of H(3). According to Scheme 5 the only other  $[^2\text{H}_2]$ -(19) species that can be present is  $[2,3\text{-}^2\text{H}_2]$ -(19). The n.m.r. signals of the hydrogen atoms at C(1) and C(2) of this species that would have to make up for the relatively large intensity at  $\delta$  2.2–2.5 and 2.7–3.0 would show unequal intensities. Therefore, we have to conclude that there is still another mechanism operating, which generates  $[^2\text{H}_2]$ -(19) species, that can allow for the equality of the peak areas in the positions mentioned.

For this reason we propose the mechanism shown in Scheme 6 for  $[1,2\text{-}^2\text{H}_2]$ -(19) (cf. path B, Scheme 3) as a second rearrangement mode. It consists of a 1,5-H or a 1,5-D shift from C(2) to C(8a) [to give intermediates (23) and (25)] followed by an electrocyclic ring-opening to give a 1,1-diphenyl-1,3-butadiene (24) or (26). After *cis-trans* (*E-Z*) isomerization (CTI) to give (28) from (26) reclosure can take place on the other benzene ring to give (23) and (29). A final 1,5-H shift leads then back to the starting compound when the first step was a 1,5-H shift (right part of Scheme 6), but to  $[1,2'\text{-}^2\text{H}_2]$ -(19) when the reaction sequence started with a 1,5-D shift (middle part of the Scheme); compound  $[1,5\text{-}^2\text{H}_2]$ -(19) will be the product when the deuteriated phenyl substituent in the butadiene (26) undergoes a rotation and recloses [to (23)] in the unlabelled 2'-position leaving a D atom in the aromatic nucleus of the 1,2-dihydronaphthalene (left part of Scheme 6).

This mechanism provides two new  $[^2\text{H}_2]$ -(19) species having only one D atom in the cyclohexadiene moiety, viz.  $[1,2\text{-}^2\text{H}_2]$ -(19) and  $[1,5\text{-}^2\text{H}_2]$ -(19). When it is assumed that the sum of the concentrations of these compounds is nearly equal to the



concentration of  $[2,3\text{-}^2\text{H}_2]$ -(19) the peak areas observed for the benzylic and allylic protons can be explained. Application of mechanism B to the starting compound  $[3,4\text{-}^2\text{H}_2]$ -(15) leads to  $[1,2\text{-}^2\text{H}_2]$ -(19) via an intermediate 1,4-diphenyl-1,3-butadiene (31) as shown in Scheme 7.

This mechanism has been described previously in the literature<sup>4</sup> to explain formation of compound (15) in the FVP of 1,4-diphenylbuta-1,3-diene. When mechanisms A and B operate with comparable rates extensive scrambling of D in the phenyl-(dihydro)naphthalene skeleton has to be expected since every

**Table 4.** Comparison of the 90 MHz  $^1\text{H}$  n.m.r. spectra ( $\text{CDCl}_3$ ) before and after FVP of  $[3,4\text{-}^2\text{H}_2]\text{-(15)}$  at  $800^\circ\text{C}$ . Compounds (15) and (19) are added for reference (see also Tables 1 and 2)

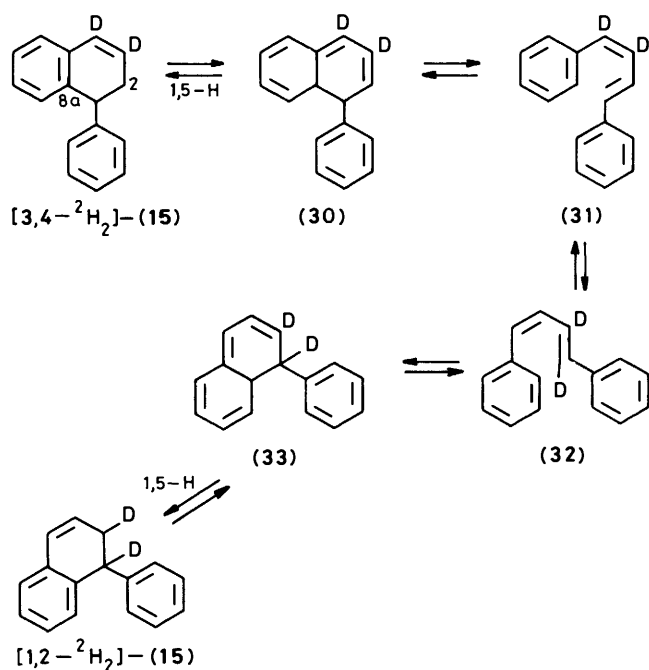
Compound	(15)	(19)	(15)	(15)	(19)	(15)	(19)
	Proton	H(4)	H(3)	H(3)	H(1)	H(1), H'(1)	H(2), H'(2)
$\delta$	6.52	6.06	5.98	4.12	3.0–2.7	2.8–2.5	2.5–2.2
Multiplicity	(15) dt	(19) —	(15) dt	(15) t	(19) —	(15) m	(19) —
[3,4- $^2\text{H}_2$ ]- <b>(15)</b>	—	—	—	t	—	d	—
FVP ( $800^\circ\text{C}$ ) of [3,4- $^2\text{H}_2$ ]- <b>(15)</b>	dd + br s	d	obs*	<i>t</i> + d	m	<i>d</i>	m

\* obs = obscured. For the meaning of italicized multiplicities, see text.

**Table 5.** Product composition (%) measured by g.l.c. of FVP products (at  $800^\circ\text{C}$ ) of compounds (34), (39), and (45)

Product	(34)	(36)	(37)	(41)	(42)	(43)	(47)	(48)	(49)
Retention time (min)	8.48	8.22	8.72	9.28	8.99	9.56	8.04	8.36	8.50
(34)	55	31	9	0.1		1.2	2.7	0.4	<i>b</i>
(34) + DDQ			90			2.0			5.5
(39)	61	24	3	8.4	3				
(39) + DDQ			89			11			
(45) <sup>a</sup>	11	10	4.5				5.7	3.2	
(45) + DDQ			26.5						11

<sup>a</sup> A large amount of the starting compound remained (*R*, 9.75). <sup>b</sup> Probably obscured by the large peak of compound (34) (*R*, 8.48).



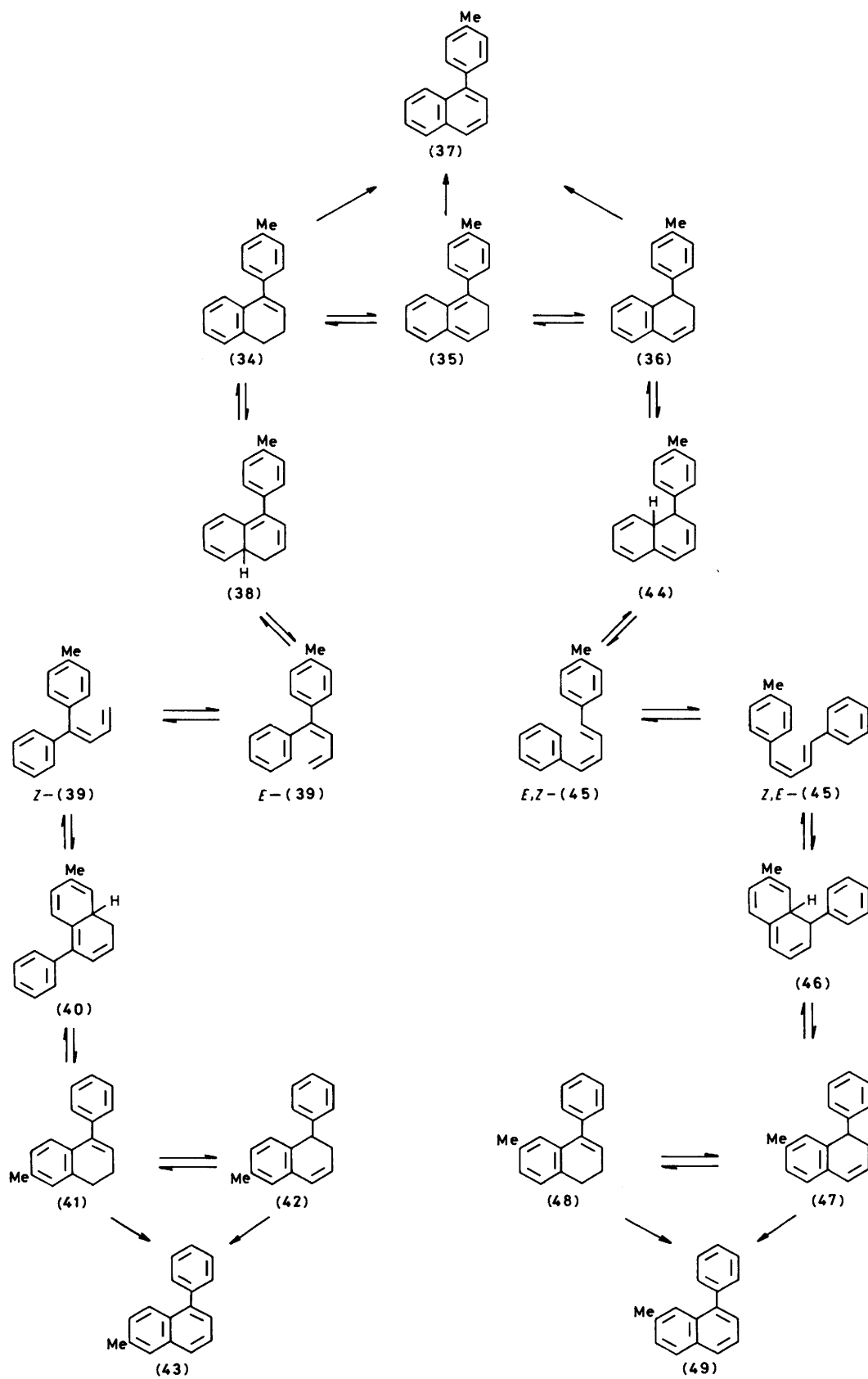
new species generated in mechanism A leads to a number of different products in mechanism B and *vice versa*. This might lead to misinterpretation of the n.m.r. spectrum of the pyrolysed  $[3,4\text{-}^2\text{H}_2]\text{-(15)}$ . In the following experiment it will become clear, however, that the interconversion  $(15) \rightleftharpoons (19)$  according to mechanism A is a much more important process than the D-scrambling in the individual compounds according to mechanism B. The estimated product composition after FVP of  $[3,4\text{-}^2\text{H}_2]\text{-(15)}$  is given in Table 7 (Experimental section).

**Pyrolysis of 4-(*p*-Tolyl)-1,2-dihydronaphthalene (34).**—The pyrolysis of this *p*-methyl derivative of compound (19) was

examined in order to consolidate the supposition that diphenylbutadienes like (24), (26), and (28) (Scheme 6) are formed on pyrolysis of  $[1,2\text{-}^2\text{H}_2]\text{-(19)}$ . If the supposition were correct, pyrolysis of compound (34) would lead to products having the methyl group in the naphthalene moiety. Scheme 8 presents a survey of possible products which can be expected from pyrolysis of compound (34) when pathway A as well as B is operating; compound (34) should lead, *via* 1-phenyl-1-(*p*-tolyl)butadiene (39), to compounds (41) and (42); compound (36) originating, *via* intermediate (35), from the thermal isomerization (A) of (34) should yield, *via* 1-phenyl-4-(*p*-tolyl)butadiene (45), the products (47) and (48). Moreover, small amounts of the naphthalene derivatives (37) [from (34) and (36)], (43) [from (41) and (42)], and (49) [from (47) and (48)] should arise by oxidation. These naphthalene derivatives should become the only products when the pyrolysis mixture is treated with dichlorodicyanobenzoquinone (DDQ) before analysis.

In Table 5 the product compositions (g.l.c.) of the pyrolysis mixture of compound (34) both without and after DDQ treatment are given and compared with those of mixtures obtained from the independently prepared diarylbutadienes (39) and (45) under the same conditions.

The presence of the compounds (41)—(43) and (47)—(49) in the pyrolysis mixtures studied confirms that the butadienes (39) and (45) are formed on pyrolysis of compound (34). The interconversion  $(34) \rightleftharpoons (36)$  is, however, the main reaction, because isomers (34) and (36) are the main products and the naphthalene (37) is formed in at least 90% yield on oxidation of the pyrolysis mixture. The ring closure on pyrolysis of the butadienes proceeds more to the phenyl than to the tolyl ring, as (39) and (45) give mainly a mixture of the *p*-tolyl derivatives (34) and (36) and only small amounts of the phenyl derivatives (41) and (42), or (47) and (48), respectively. The preference for formation of compounds (34) and (36) is especially clear in the pyrolysis of compound (39), which was used as a 1:1 *E/Z* mixture. The low product yield in the pyrolysis of (45) may be ascribed to the application of *E,E*-(45) as the starting compound. As expected, in all experiments the amounts of compounds (42) and (48) are lower than those of their precursors (41) and (47), respectively.

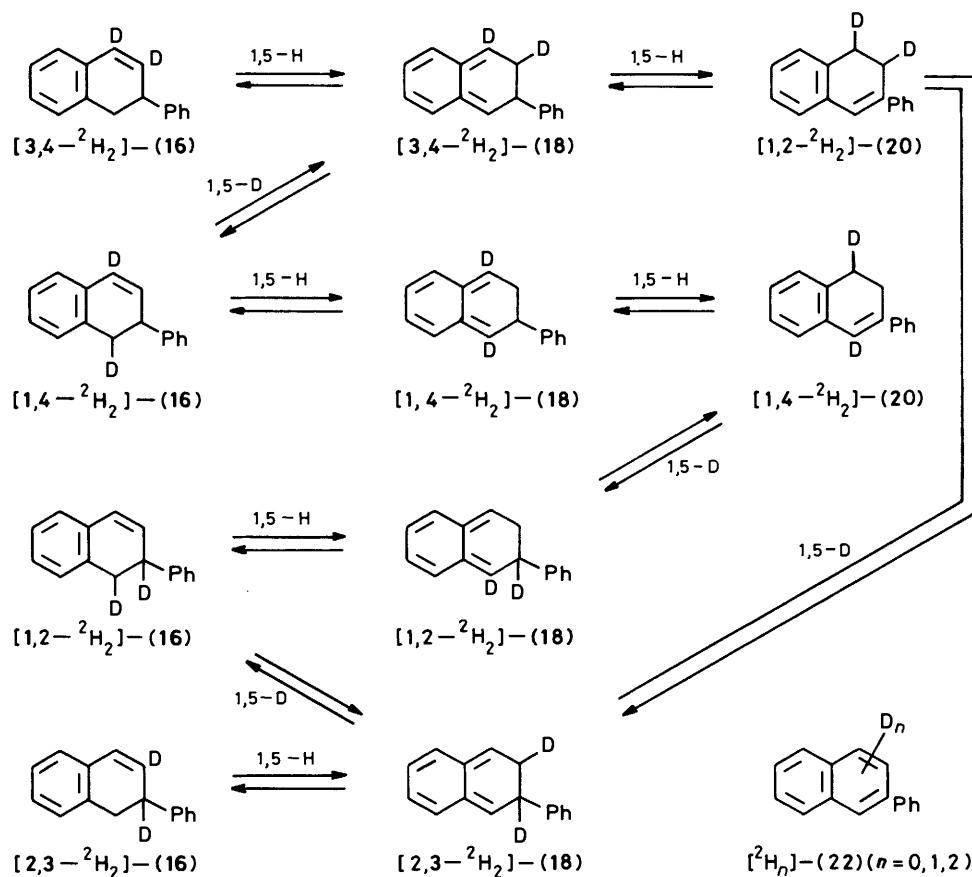


Scheme 8.

**Table 6.** Comparison of the 90 MHz  $^1\text{H}$  n.m.r. spectra ( $\text{CDCl}_3$ ), before and after FVP of  $[3,4\text{-}^2\text{H}_2]\text{-}(16)$  at  $800^\circ\text{C}$ . Compounds  $(16)$  and  $(20)$  were added for reference (see also Tables 1 and 3).

Compound	(20)	(16)	(16)	(16)	(16)	(20)
	Proton	H(4)	H(4)	H(3)	H(2)	H(1), H'(1); H(2), H'(2)
$\delta$	6.84	6.57	6.03	3.74	3.3–2.7	3.1–2.6
Multiplicity	(16) (20)	— t	— —	— —	— —	— —
	$[3,4\text{-}^2\text{H}_2]\text{-}(16)$	—	—	—	—	—
	{FVP ( $800^\circ\text{C}$ ) of $[3,4\text{-}^2\text{H}_2]\text{-}(16)$ }	d + s	d	m	dd	m

See the text for significance of italicized multiplicities.

**Scheme 9.**

**Pyrolysis of  $[3,4\text{-}^2\text{H}_2]\text{-}(16)$ .**—In Table 6 the main features of the 90 MHz  $^1\text{H}$  n.m.r. spectra of compounds  $(16)$ ,  $(20)$ ,  $[3,4\text{-}^2\text{H}_2]\text{-}(16)$ , and of the latter compound pyrolysed at  $800^\circ\text{C}$  are given. The main  $[^2\text{H}_2]\text{-}(16)$  species after pyrolysis is still  $[3,4\text{-}^2\text{H}_2]\text{-}(16)$ . Some intensity is observed at  $\delta$  6.03 which suggests a  $[^2\text{H}_2]\text{-}(16)$  species having an H atom at C(3). No  $J_{3,4}$  coupling is visible, so there must be a D atom at C(4), and, because the H(3) signal is not a singlet, there must be an H atom at C(2). This implies that the second D atom is at C(1), *i.e.*  $[1,4\text{-}^2\text{H}_2]\text{-}(16)$ . Very little intensity is observed at  $\delta$  6.57 corresponding to H(4). A doublet with  $J$  9.7 Hz and a singlet between the two signals of the doublet can just be recognized. The doublet suggests the presence of a species without the allylic coupling  $J_{2,4}$  but with  $J_{3,4}$  coupling still present. This corresponds to a  $[^2\text{H}_2]\text{-}(16)$  species having D at C(2) and H at both C(3) and C(4). The second D atom must then be at C(1), *i.e.*  $[1,2\text{-}^2\text{H}_2]\text{-}(16)$ .

$(16)$ . The singlet suggests a species having H at C(4) and D at C(3) and, since  $J_{2,4}$  is absent, D at C(2), *i.e.*  $[2,3\text{-}^2\text{H}_2]\text{-}(16)$ . The four species observed in the n.m.r. spectrum,  $[3,4\text{-}^2\text{H}_2]\text{-}(16)$ ,  $[1,4\text{-}^2\text{H}_2]\text{-}(16)$ ,  $[1,2\text{-}^2\text{H}_2]\text{-}(16)$ , and  $[2,3\text{-}^2\text{H}_2]\text{-}(16)$ , are those expected according to the mechanism given in Scheme 9 (*cf.* Scheme 3, mechanism A).

Concerning the  $[^2\text{H}_2]\text{-}(20)$  compounds, a doublet with  $J$  1.2 Hz is observed for H(4) at  $\delta$  6.84, suggesting that one of the hydrogen atoms at C(2) has been replaced by a D. This leaves C(1) as the only possible position for the other D atom, *i.e.*  $[1,2\text{-}^2\text{H}_2]\text{-}(20)$ . Since the n.m.r. spectrum of compound  $(20)$  has no characteristic signals apart from that at  $\delta$  6.84, no other  $[^2\text{H}_2]\text{-}(20)$  species can be observed individually. According to Scheme 9 only one other species,  $[1,4\text{-}^2\text{H}_2]\text{-}(20)$  can be expected.

Application of mechanism B to  $[3,4\text{-}^2\text{H}_2]\text{-}(16)$  does not lead to any new product as no D is present at C(2). Compound  $[1,2\text{-}^2\text{H}_2]\text{-}(16)$

$^2\text{H}_2$ ]-**(20)** might arrange to [1,4- $^2\text{H}_2$ ]-**(20)** via mechanism B, but in this case indications for such scrambling cannot be derived from the n.m.r. spectrum. An estimate of the product composition after FVP of [3,4- $^2\text{H}_2$ ]-**(16)** is given in Table 7 (Experimental section).

**Conclusion.**—This study of the thermal rearrangements of phenyl-substituted 1,2-dihydronaphthalenes, two deuteriated analogues, and 4-tolyl-1,2-dihydronaphthalene has clearly established that consecutive sigmatropic 1,5-H migrations constitute the major mechanism for the interconversion of substituted 1,2-dihydronaphthalenes. Careful analysis of the n.m.r. spectra of FVP-product mixtures of the deuteriated compounds leads to the supposition that in the hot zone diphenylbuta-1,3-dienes are produced. This was confirmed in the experiment with the tolyl derivative.

In this way the occurrence of two of the three primary reactions (A and B) presented in Scheme 3 has been demonstrated experimentally. The occurrence of the third pathway C cannot be demonstrated in this way, because it does not lead to new products. It may be assumed, however, that this electrocyclic reaction takes place too, because its activation energy is probably lower than that for pathways A and B. The conversion **(10)**  $\rightleftharpoons$  **(13)** proceeds with very little atomic displacement, whereas the 1,5-H shifts in mechanisms A and B are rather unfavourable in this respect.

### Experimental

$^1\text{H}$  N.m.r. spectra were recorded on a Bruker WH-90 or WH-500 spectrometer in  $\text{CDCl}_3$ .  $\delta$  Values are reported relative to  $\text{SiMe}_4$  as internal standard. Mass spectra were recorded on a Varian MAT SM-2B or a Finnigan 2000 quadrupole mass spectrometer, and u.v. spectra on a Perkin-Elmer 555 instrument. M.p.s were determined using a Leitz melting-point microscope and are uncorrected. Gas-liquid chromatography (g.l.c.) was performed using either a Varian aerograph, series 1200, or a Hewlett-Packard 5710 A instrument fitted with a 10% w/w SE-30 column on Chromosorb WHP and a flame-ionization detector.

4-Phenyl-1,2-dihydronaphthalene (**19**) was purchased from Aldrich Europe and used without further purification.

The syntheses of 2-phenyl-1,2-dihydronaphthalene (**16**) and its 3,4-dideuterio analogue [3,4- $^2\text{H}_2$ ]-**(16)** have been described previously.<sup>1</sup>

**1-Phenyl-1,2-dihydronaphthalene (15).**—4-Phenyl-1-oxotetrahydronaphthalene was synthesized from 1-naphthol and benzene in the presence of  $\text{AlCl}_3$  using a method described in the literature.<sup>14</sup> The procedure was modified by an additional extraction of residual 1-naphthol from the organic layer with 0.01M-NaOH solution prior to drying and distillation. Crystallization from methanol afforded 4-phenyl-1-oxotetrahydronaphthalene (83%) as white crystals, m.p. 76–78.5 °C (lit.,<sup>14</sup> 79–80 °C). 4-Phenyl-1-oxotetrahydronaphthalene (14.4 g, 0.065 mol) was reduced with  $\text{NaBH}_4$  (1.3 g, 0.034 mol) in absolute ethanol (145 ml).<sup>15</sup> After being stirred for 30 min the mixture was evaporated to dryness and the residue was taken up in water and extracted with ether. The ether layer was dried ( $\text{Na}_2\text{SO}_4$ ), filtered, and evaporated under reduced pressure. Without further purification the residue (13 g, 0.058 mol) was dissolved in toluene (150 ml), toluene-*p*-sulphonic acid (0.5 g) was added, and water was removed by azeotropic distillation.<sup>16</sup> The reaction mixture was then washed with saturated aqueous solutions of  $\text{NaHCO}_3$  and  $\text{NaCl}$ , and dried ( $\text{CaCl}_2$ ). After filtration and evaporation of the solvent, the resulting oil was purified on silica with hexane as eluant. In this way 1-phenyl-

1,3-dihydronaphthalene (**15**) (10.8 g, 0.052 mol) was obtained as a clear oil which solidified spontaneously into a white solid, m.p. 59–61 °C, yield 81% (based on a 4-phenyl-1-oxotetrahydronaphthalene).  $^1\text{H}$  N.m.r. data (500 MHz;  $\text{CDCl}_3$ ) are given in Tables 1 and 2, except for  $\delta$  6.82 [1 H, d, H(8)] and 6.9–7.3 (8 H, m, arom) (cf. ref. 17);  $\lambda_{\text{max}}$  (MeOH) (log  $\epsilon$ ) 259 (3.72) and 220 nm (4.08);  $\lambda_{\text{min}}$  (MeOH) 239 nm (3.46);  $m/z$  206 ( $M^+$ , 14%), 128 (32), 115 (14), and 91 (50) (Found: C, 93.1; H, 6.9. Calc. for  $\text{C}_{16}\text{H}_{14}$ : C, 93.16; H, 6.84%).

**3,4-Dideuterio-1-phenyl-1,2-dihydronaphthalene [3,4- $^2\text{H}_2$ ]-**(15)**.**—This compound was synthesized in an analogous way as described previously for [3,4- $^2\text{H}_2$ ]-**(16)**.<sup>1</sup>

**3-Phenyl-1,2-dihydronaphthalene (20).**—2-Oxotetrahydronaphthalene was prepared by passage of a stream of ethylene through a well stirred, cold solution of phenylacetyl chloride (37 g, 0.24 mol) in  $\text{CH}_2\text{Cl}_2$  (1 l) in the presence of  $\text{AlCl}_3$  (40 g, 0.30 mol).<sup>18,19</sup> After work-up, fractional distillation yielded 2-oxotetrahydronaphthalene (26.9 g, 77%) as a clear oil.

3-Phenyl-1,2-dihydronaphthalene (**20**) was synthesized by a Grignard reaction of phenylmagnesium bromide, prepared from Mg (5 g) and phenyl bromide (34.5 g, 0.22 mol), and 2-oxotetrahydronaphthalene (26.9 g, 0.184 mol) in dry ether (100 ml). After work-up the resulting alcohol was dissolved in toluene (150 ml), toluene-*p*-sulphonic acid (1 g) was added, and the alcohol was dehydrated as described in the preparation of compound (**15**). The reaction mixture was washed with saturated aqueous solutions of  $\text{NaHCO}_3$  and  $\text{NaCl}$  and dried ( $\text{CaCl}_2$ ). After filtration and evaporation of the solvent under reduced pressure the residue was purified on silica with hexane as eluant. A mixture of 2- and 3-phenyl-1,4-dihydronaphthalene was isolated which could be separated by careful chromatography on alumina. Crystallization from methanol afforded a pure compound of (**20**) (5.7 g, 15%) as a white powder, m.p. 65–66 °C (lit.,<sup>20</sup> 64–66 °C; lit.,<sup>21</sup> 62.5–64.5 °C);  $\delta$  ( $\text{CDCl}_3$ ) 2.6–3.1 [4 H, m, H(1) and H(2)], 6.84 (1 H, t,  $J_{2,4} = 1.2$  Hz), H(4)], 7.13 (5 H, s, arom), and 7.2–7.6 (4 H, m, arom);  $\lambda_{\text{max}}$  (MeOH) (log  $\epsilon$ ) 302 nm (4.28), 230 (4.19), and 206 nm (4.15);  $\lambda_{\text{min}}$  (MeOH) (log  $\epsilon$ ) 254 (3.38) and 214 nm (4.07);  $m/z$  206 ( $M^+$ , 100%), 191 (10), 178 (5), 165 (5), 128 (13), 115 (6), and 91 (17);  $M^+$ , 206.111  $\pm$  0.003. Calc. for  $\text{C}_{16}\text{H}_{24}$ :  $M$ , 206.110 (Found: C, 93.1; H, 6.9. Calc. for  $\text{C}_{16}\text{H}_{14}$ : C, 93.16; H, 6.84%).

**4-(*p*-Tolyl)-1,2-dihydronaphthalene (34).**—This was synthesized from *p*-methylbenzylmagnesium bromide and 1-oxotetrahydronaphthalene followed by dehydration, according to the method of von Braun.<sup>22</sup>

**1-Phenyl-4-(*p*-tolyl)buta-1,3-diene (45).**—This was prepared in accordance with the procedure of McDonald.<sup>23</sup>

**1-Phenyl-1-(*p*-tolyl)butadiene (39).**—To a solution of allylmagnesium bromide, prepared from Mg (1.2 g) and allyl bromide (6 g, 0.05 mol) in ether (10 ml) was added a solution of 4-methylbenzophenone (2 g, 0.01 mol) in ether (10 ml) dropwise. After being boiled for 3 h the solution was cooled, saturated aqueous ammonium chloride was added, and the organic layer was separated. The water layer was extracted with ether and the ether solutions were combined and dried ( $\text{MgSO}_4$ ). Evaporation gave crude 1-phenyl-1-(*p*-tolyl)but-3-enol (cf. ref. 24).

The carbinol was dehydrogenated by treatment with formic acid at room temperature. The solution became turbid and, after 3 h, was extracted with hexane. The hexane solution was concentrated by distillation and chromatographed over silica gel with carbon tetrachloride as eluant. The yield of the mixture of *Z*- and *E*-**(39)** was 1.3 g (53%);  $\delta$  ( $\text{CDCl}_3$ ) 7.03–7.40 (9 H, m), 6.33–6.75 (2 H, m), 5.03–5.44 (2 H, m), and 2.38 (s) and 2.32 (s)



**Table 7.** Estimated product composition (%) after FVP of [3,4-<sup>2</sup>H<sub>2</sub>]-**(15)** and [3,4-<sup>2</sup>H<sub>2</sub>]-**(16)** at 800 °C

FVP of [3,4- <sup>2</sup> H <sub>2</sub> ]- <b>(15)</b> Product		FVP of [3,4- <sup>2</sup> H <sub>2</sub> ]- <b>(16)</b> Product	
[3,4- <sup>2</sup> H <sub>2</sub> ]- <b>(15)</b>	18	[3,4- <sup>2</sup> H <sub>2</sub> ]- <b>(16)</b>	23
[2,3- <sup>2</sup> H <sub>2</sub> ]- <b>(15)</b>	5	[1,4- <sup>2</sup> H <sub>2</sub> ]- <b>(16)</b>	8
[1,2- <sup>2</sup> H <sub>2</sub> ]- <b>(15)</b>	9	[1,2- <sup>2</sup> H <sub>2</sub> ]- <b>(16)</b>	3
[1,4- <sup>2</sup> H <sub>2</sub> ]- <b>(15)</b>	7	[2,3- <sup>2</sup> H <sub>2</sub> ]- <b>(16)</b>	2
Total <b>(15)</b>	39	Total <b>(16)</b>	35
[1,2- <sup>2</sup> H <sub>2</sub> ]- <b>(19)</b>	35	[1,2- <sup>2</sup> H <sub>2</sub> ]- <b>(20)</b>	40
[2,3- <sup>2</sup> H <sub>2</sub> ]- <b>(19)</b>	14	[1,5- <sup>2</sup> H <sub>2</sub> ]- <b>(20)</b> <sup>+</sup>	9
[1,5- <sup>2</sup> H <sub>2</sub> ]- <b>(19)</b> <sup>+</sup>	14	[1,4- <sup>2</sup> H <sub>2</sub> ]- <b>(20)</b>	
[1,2- <sup>2</sup> H <sub>2</sub> ]- <b>(19)</b>		Total <b>(20)</b>	49
Total <b>(19)</b>	53	[ <sup>2</sup> H <sub>n</sub> ]- <b>(22)</b>	14
[ <sup>2</sup> H <sub>n</sub> ]- <b>(21)</b>	8	Unknown	2

(together 3 H), ratio *Z/E* 43/57; *m/z* 220 (*M*<sup>+</sup>, 100%), 205 (95), 204 (30), 203 (25), 202 (21), 128 (22), and 105 (23).

1-(*p*-Tolyl)naphthalene (**37**).—This was prepared by dehydrogenation of compound (**34**) with DDQ. Its physical properties were in accord with those reported.<sup>22</sup>

By irradiation of compound (**45**) in benzene in the presence of iodine as an oxidant with a high-pressure mercury lamp a mixture of equal amounts of compounds (**37**) and (**49**) was formed.<sup>25</sup> The latter compound was identical with 7-methyl-1-phenylnaphthalene, previously synthesized<sup>26</sup> from 7-methyl-1-oxotetrahydronaphthalene.

Irradiation of compound (**39**) under the same conditions gave a mixture of compounds (**37**) and (**43**) in the ratio 1:1. Together with these naphthalene derivatives a product was isolated which has yet to be identified.

*Pyrolyses.*—FVPs were carried out in standard equipment in a horizontal assembly as described in Chapter 2 of ref. 7. The quartz tube (1.6 cm outer diameter) passed for 17.3 cm through the oven and contained no packing material. The receiver used for the collection of products was cooled with an isopropyl alcohol-carbon dioxide mixture, except in case of the FVP of the deuteriated compounds where liquid nitrogen was used. Pressures varying between 0.1 and 0.01 Torr could be obtained. To ensure standard conditions a nitrogen flow was set up such that a stable vacuum of 0.1 Torr was maintained throughout each experiment. Bearing in mind that all compounds used are hydrocarbons of nearly equal molecular weight, it could be assumed that their volatilities are of comparable magnitude so that, in combination with a stable vacuum, the contact time in each experiment could be considered to be about the same. The flask containing the starting compound was preheated at 80 °C and maintained at this temperature to increase the volatility of the starting compound.

For analytical purposes samples of about 50 mg were subjected to FVP. The material was nearly always recovered quantitatively in the receiver. Incidentally some material, insoluble in methylene dichloride, remained behind and may have been produced by polymerization at the preheating temperature. After each run the product mixture was dissolved in ether, the solution was evaporated under reduced pressure, and the residue was analysed by g.l.c. and n.m.r. spectrometry. In g.l.c. analysis the area of each peak was taken as a measure for the relative amount, taking the sum of all peak areas as 100% (Table 3). This procedure is justified since we are dealing only with hydrocarbons of nearly equal molecular weight.

The assignment of each peak was performed by adding one of the pure compounds before running the g.l.c. again. N.m.r. analysis was simplified by the fact that in spectra of the product mixtures containing compounds (**16**), (**20**), and (**22**) the signals corresponding to the olefinic proton H(4) of (**20**) (δ 6.84), proton H(2) of (**15**) (δ 3.74), and proton H(1) of (**22**) (δ 8.0) are present in regions unobscured by other absorptions. In the spectra of product mixtures containing compounds (**15**), (**19**) and (**21**), proton H(1) of (**15**) (δ 4.12) is unobscured. From the added intensities of the nearly coinciding H(3) signals of compounds (**15**) and (**19**) (δ *ca.* 6) their relative amounts could be calculated. A three-proton signal, at the low-field side of the spectrum, belonging to compound (**21**) could be used for the determination of the amount of this compound. The reliability of the product group composition, evaluated from n.m.r. spectra, appeared to be good by comparison with g.l.c. results.

Estimates of the product composition of the deuteriated compounds (**15**) and (**16**) are given in Table 7.

## References

- J. J. M. Lamberts and W. H. Laarhoven, *J. Am. Chem. Soc.* 1984, **106**, 1736.
- J. J. M. Lamberts and W. H. Laarhoven, *Recl. Trav. Chim. Pays-Bas*, 1984, **103**, 131.
- H. Heimgartner, H. J. Hansen, and H. Schmid, *Helv. Chim. Acta*, 1972, **55**, 1385; H. Heimgartner, J. Zsindely, H. J. Hansen, and H. Schmid, *ibid.*, 1973, **56**, 2924; M. R. De Camp, R. H. Levin, and M. Jones jr., *Tetrahedron Lett.*, 1974, 3575; P. Schiess and R. Dinkel, *Helv. Chim. Acta*, 1981, **64**, 801.
- P. B. Valkovich, J. L. Conger, F. A. Castiello, T. D. Brodie, and W. P. Weber, *J. Am. Chem. Soc.*, 1975, **97**, 901.
- G. M. Badger and T. M. Spotswood, *J. Chem. Soc.*, 1959, 1635; T. M. Spotswood, *ibid.*, 1960, 4427.
- A. Heising and W. Mullers, *Chem. Ber.*, 1980, **113**, 9.
- R. F. C. Brown, 'Pyrolytic Methods in Organic Chemistry,' Academic Press, New York, 1980.
- R. F. C. Brown, G. E. Gream, D. E. Peters, and R. K. Solly, *Aust. J. Chem.*, 1968, **21**, 2223.
- C. W. Spangler, *Chem. Rev.*, 1976, **76**, 187.
- R. J. Ellis and H. M. Frey, *J. Chem. Soc. A*, 1966, 553; I. Fleming and E. Wildsmith, *Chem. Commun.*, 1970, 223.
- C. Manning, M. R. McGlory, and J. J. McCullough, *J. Org. Chem.*, 1981, **46**, 919; L. L. Miller and R. F. Boyer, *J. Am. Chem. Soc.*, 1971, **93**, 650.
- J. R. de Dobbelaere, E. L. van Zeeventer, J. W. de Haan, and H. M. Buck, *Theor. Chim. Acta*, 1975, **38**, 241.
- R. B. Woodward and R. Hoffmann, 'The Conservation of Orbital Symmetry,' Verlag Chemie, Weinheim, 1970.
- Houben Weyl, 'Methoden der organischen Chemie,' Georg Thieme Verlag, Stuttgart, 1976, Vol. VII, 2b, p. 1710.
- S. A. Fine and R. L. Stern, *J. Org. Chem.*, 1967, **32**, 4132.
- J. Klein and E. D. Bergmann, *J. Org. Chem.*, 1957, **22**, 1019.
- F. R. Mayo, *J. Am. Chem. Soc.*, 1968, **90**, 1289.
- J. J. Sims, L. H. Selman, and M. Cadogan, *Org. Synth.*, 1971, **51**, 109.
- J. J. Sims, M. Cadogan, and L. H. Selman, *Tetrahedron Lett.*, 1971, 951.
- N. Campbell and D. Kidd, *J. Chem. Soc.*, 1954, 2154.
- J. Jacques and H. B. Kagan, *Bull. Soc. Chim. Fr.*, 1956, 128.
- J. von Braun and E. Anton, *Ber. Dtsch. Chem. Ges.*, 1934, **67**, 1051.
- R. N. McDonald and T. W. Campbell, *Org. Synth.* (1973), Coll. Vol. V, p. 499.
- J. J. Eisch and G. R. Husk, *J. Org. Chem.*, 1966, **31**, 589.
- C. C. Leznoff and R. J. Hayward, *Can. J. Chem.*, 1970, **48**, 1842.
- A. H. A. Tinnemans and W. H. Laarhoven, *J. Am. Chem. Soc.*, 1974, **96**, 4617.

Received 9th October 1984; Paper 4/1741