Thermal Fragmentation Reactions of Dihydroaromatic Molecules

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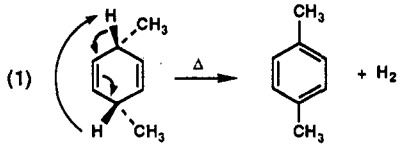
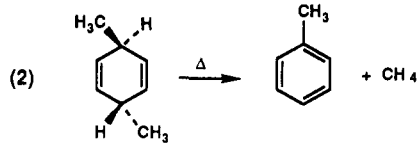
Thermal decompositions of 1,4-dihydrobenzene derivatives (usually at temperatures in the 300–350 °C range) result in elimination of hydrogen, provided the reacting molecules have at least one hydrogen at a diallylic position syn to one at the other diallylic carbon.[1] These fragmentation reactions have been shown to proceed via concerted, intramolecular processes, as in eq 1.[1c] In contrast, elimi-



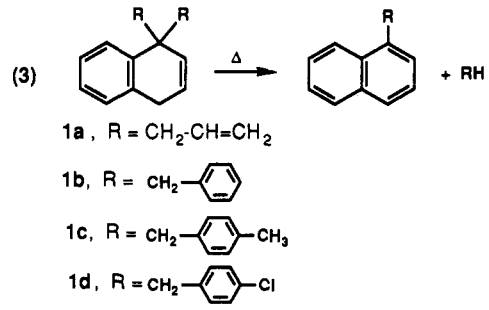
nations of methane (e.g., eq 2) and of ethane require higher temperatures and proceed via free-radical chain mechanisms.[1c]



The different mechanisms for the elimination of hydrogen and of alkanes and the lower temperatures required for elimination of hydrogen (despite the greater strength of carbon–hydrogen bonds compared to carbon–carbon bonds) may be accounted for on the grounds that "sideways" bond formation between the s-orbitals of two hydrogen atoms should be geometrically more favorable than similar reactions between hydrogen atoms and the sp^3 orbitals of carbon. The higher temperatures required for eliminations of alkanes would favor free-radical chain processes, which should have higher entropies of activation.

It seemed to us that if the dissociation energies of bonds linking substituents to saturated carbons of 1,4-dihydroaromatic rings were reduced, the lower temperatures required for fragmentation reactions to occur would minimize the importance of the entropy factor, and concerted mechanisms might prevail. To test this hypothesis, we have studied the thermolysis reactions of 1,1-diallyl-1,4-dihydronaphthalene (**1a**) and of 1,1-dibenzyl-1,4-dihydronaphthalene derivatives **1b–d**. These compounds were all prepared by Shapiro elimination reactions[2] of the tosylhydrazones of the corresponding 1,1-disubstituted 2-tetralones.

The supposition that allyl- and benzyl-substituted 1,4-dihydroaromatic molecules would undergo easy thermal fragmentations was quickly confirmed. Hydrocarbons **1b–d** decomposed rapidly on heating in sealed tubes at 150 °C to yield 1-benzylnaphthalenes and toluene or substituted toluenes, while **1a** fragmented at the same temperature to yield 1-allylnaphthalene (and, presumably, propene, although that product was not identified).



^{1}H NMR analysis showed that neat samples of **1a** were approximately 50% decomposed after 30 min at 150 °C, while **1b** required only about 10 min for a similar degree of decomposition. The remarkable ease with which these fragmentations occur at very low temperatures is shown by the fact that **1b** and **1c** undergo significant decomposition on overnight heating on the steam bath.

Our initial observations suggested that these fragmentations might indeed proceed by concerted mechanisms, since addition of small amounts (up to 3 mol %) of free radical chain inhibitors (including benzoquinone, diphenylamine, galvinoxyl, and phenol) did not significantly affect the rates of decomposition of **1a** or **1b**. However, it was then observed that larger amounts of inhibitors (ranging from 6 to 50 mol % of inhibitor, usually diphenylamine) did effect decreases in decomposition rates. The inhibitory effects of diphenylamine reached a maximum at ca. 30 mol %, and larger amounts of inhibitor did not result in further rate reductions.

In the presence of ca. 30–50 mol % of diphenylamine, **1b**, **1c**, and **1d** decomposed with half-lives of ca. 3 h, 2 h, and 6 h, respectively, at 150 °C. Thus, the rates of fragmentation followed an order paralleling the relative bond energies of the carbon–carbon bonds being broken. This result is consistent with either free-radical or concerted mechanisms. The fact that each alkene continued to undergo fragmentation at a consistent rate even in the presence of very large amounts of radical chain inhibitors appeared to support the possibility that the residual fragmentations were the results of concerted processes.

To distinguish between concerted (intramolecular) and radical chain (intermolecular) fragmentation processes, we decided to determine whether crossover products were formed from decomposition of a mixture of dihydroaromatic molecules. 1,4-Dihydro-1,1-bis(4-methylbenzyl)-naphthalene-*4,4-d*$_2$ (**1c**-d_2) was prepared as described in the Experimental Section. In the presence of ca. 40% of diphenylamine, **1c**-d_2 decomposed at 150 °C with a half life of ca. 10 h. Since this rate was closer to the rate of decomposition of **1d** than of **1a** or **1b**, an approximately equimolar mixture of **1c**-d_2, **1d**, and diphenylamine was heated in a sealed tube at 150 °C for 24 h.

Mass spectroscopic analysis of the volatile products of the reaction showed it to consist of a *p*-xylene fraction containing ca. 23% of *p*-xylene-d_1 and a *p*-chlorotoluene fraction containing ca. 28% of *p*-chlorotoluene-d_1. Thus, fragmentations of **1c** and **1d** occur largely, if not entirely, by intermolecular (presumably radical chain) mechanisms,

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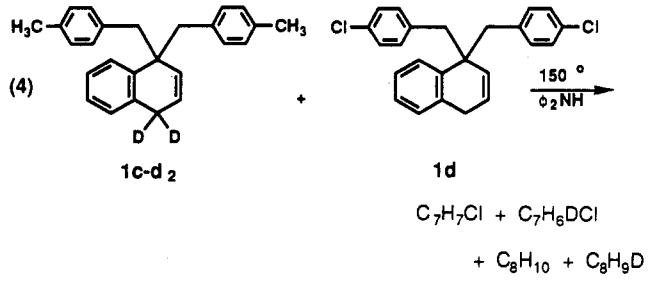
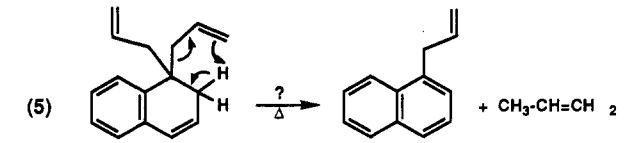


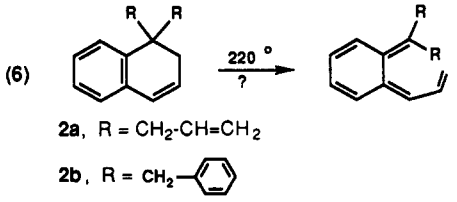
even in the presence of very large amounts of a radical chain inhibitor.

A study of the thermolyses of 1,2-dihydronaphthalene derivatives also appeared to be of interest, since it seemed likely that retro-ene reactions of allyl-substituted derivatives (eq 5), and possibly even of their benzyl analogs,



might take place at relatively low temperatures. On the basis of kinetic studies, it has been suggested that retro-ene reactions may occur (at temperatures above ca. 400 °C) as minor processes accompanying the predominant free-radical chain reactions leading to fragmentations of alkenes.[3] However, at lower temperatures, retro-ene reactions in all-carbon systems occur only with highly strained cycloalkenes (such as trans-cyclooctene)[4] or when the process involves opening of a cyclopropane ring.[5]

1,1-Diallyl-1,2-dihydronaphthalene (**2a**) was prepared from its unconjugated isomer **1a** by refluxing with potassium *tert*-butoxide in 2-methyl-2-propanol, in a manner similar to the preparation of **2b** from **1b**.[6] In contrast to **1a** and **1b**, both **2a** and **2b** proved to be relatively stable on heating. Neither hydrocarbon decomposed rapidly at temperatures below ca. 180 °C. Both compounds were essentially completely decomposed after 5 h at 220 °C, but neither 1-allylnaphthalene or 1-benzylnaphthalene was formed in these reactions. Instead, both reactions yielded only viscous, high molecular weight products. We believe these products were formed by electrocyclic ring openings (eq 6), followed by dimerization or polymerization of the resulting *o*-quinone dimethides.



Experimental Section

Mp's and bp's are corrected. ^{1}H NMR spectra were taken in deuteriochloroform solutions unless otherwise noted, on Varian XL-200 or Hitachi R-1200 instruments. IR spectra were taken on a Perkin-Elmer 1600 FTIR spectrometer. Mass spectra were taken on a Hewlett-Packard Model 5985B mass spectrometer. Elemental analyses were performed by the University of Massachusetts Microanalytical Laboratory.

1,1-Diallyl-3,4-dihydro-2(1*H*)-naphthalenone *p*-Toluenesulfonylhydrazone. A mixture of 1,1-diallyl-3,4-dihydro-2(1*H*)-naphthalenone[7] (3.2 g, 14.15 mmol), *p*-toluenesulfonylhydrazine (4.2 g, 22.60 mmol), and 0.5 mL of concd hydrochloric acid in 25 mL of methanol was heated under reflux for 16 h. The solution was then cooled in ice and scratched. The resulting white precipitate was filtered off and recrystallized from ethanol to yield the title compound (4.3 g, 11.20 mmol, 79%) as white cubic crystals, mp 128.5–129.5 °C. ^{1}H NMR: δ 2.44 (s), superimposed on a multiplet from 2.35 to 2.63, totalling 7 H, 2.68–2.81 (m, 4 H), 4.53–4.69 (m, 4 H), 4.85–5.27 (m, 2 H), 7.03–7.26 (m, 6 H), 7.28 (d, J = 8.08 Hz, 2 H), 8.04 (d, J = 8.08 Hz, 2 H). IR (KBr): ν_{max} 3184, 1636, 1599, 1487, 1432, 1400, 1328, 1165, 1091, 1032, 994, 959, 911, 813, 762, 716, 589, 537 cm^{-1}. Anal. Calcd for $C_{23}H_{26}N_2O_2S$: C, 70.02; H, 6.64; N, 7.10. Found: C, 70.22; H, 6.51; N, 7.24.

1,1-Diallyl-1,4-dihydronaphthalene (1a). A suspension of 1,1-diallyl-3,4-dihydro-2(1*H*)-naphthalenone *p*-toluenesulfonylhydrazone (4.1 g, 10.67 mmol) in 35 mL of anhydrous ether was stirred and cooled in ice under a slow stream of nitrogen. A 1.5 M solution of methyllithium in ether (15 mL, 22.50 mmol) was added slowly. After completion of the addition (ca. 20 min) stirring was continued for an additional 30 min, and water then added carefully. The ether layer was washed with water and dried over anhydrous calcium chloride. Evaporation of the solvent left a pale yellow oil, which was chromatographed on alumina, eluting with pentanes, to yields **1a** (1.98 g, 9.43 mmol, 88%) as an almost colorless oil. ^{1}H NMR: δ 2.2–2.7 (m, 4 H), 3.32 (bs, 2 H), 4.7–5.1 (m, 4 H), 5.3–6.2 (m, 4 H), 7.1–7.5 (m, 4 H). IR (neat): ν_{max} 1639, 1492, 1445, 993, 912, 749 cm^{-1}. Anal. Calcd for $C_{16}H_{18}$: C, 91.37; H, 8.63. Found: C, 91.15; H, 8.87.

1,1-Bis(4-chlorobenzyl)-3,4-dihydro-2(1*H*)-naphthalenone. 2-Tetralone (5.0 g, 34.3 mmol) was added in portions to a stirred solution of potassium *tert*-butoxide (8.60 g, 76.8 mmol) which was cooled in an ice bath. 4-Chlorobenzyl chloride (11.61 g, 72.1 mmol) was then added to the cooled, stirred solution over a period of 30 min. Stirring was continued with cooling for another 30 min and then at room temperature for 12 h. The mixture was diluted with water and extracted with dichloromethane. The organic layer was washed several times with water, dried over magnesium sulfate, filtered, and evaporated to yield a pale brown oil which crystallized on standing. Recrystallization from 95% ethanol yielded the title compound (11.01 g, 27.8 mmol, 81%) as white crystals, mp 135.0–135.5 °C. ^{1}H NMR: δ 1.89 (m, 4 H), 3.27 (d, J = 12.9 Hz, 2 H), 3.57 (d, J = 12.9 Hz, 2 H), 5.63 (d, J = 9.98 Hz, 1 H), 5.75 (dt, J = 9.98, 3.5 Hz, 1H), 6.76 (d, J = 8.1 Hz, 2 H), 7.02 (d, J = 8.1 Hz, 2 H), 6.8–7.55 (m, ca. 3 H), 7.70 (dd, J = 7.8, 2.2 Hz, 2 H). IR ($CDCl_3$): μ_{max} 1712, 1489, 1444, 1410, 1092, 1014, 840, 812, 767, 737, 640, 528, 516 cm^{-1}. Anal. Calcd for $C_{24}H_{20}Cl_2O$: C, 72.91; H, 5.06; Cl, 17.98. Found: C, 73.08; H, 5.20; Cl, 17.73.

1,1-Bis(4-chlorobenzyl)-3,4-dihydro-2(1*H*)-naphthalenone *p*-Toluenesulfonylhydrazone. A suspension of 1,1-bis-(4-chlorobenzyl)-3,4-dihydro-2(1*H*)-naphthalenone (9.80 g, 24.8 mmol), *p*-toluenesulfonylhydrazine, (13.20 g, 71.0 mmol), and 1 mL of concd HCl in 200 mL of methanol was heated under reflux for 60 h. (Reaction was slow due to the insolubility of the ketone.) The reaction mixture was then allowed to cool to room temperature and filtered. The resulting white solid was washed with a 3:2 mixture of dichloromethane and pentane to remove unreacted ketone. The remaining solid was recrystallized from absolute ethanol to yield the title compound (7.7 g, 13.6 mmol, 55%) as white crystals, mp 202.5–203.0 °C dec. ^{1}H NMR (1:1 $CDCl_3$ and DMSO-d_6): δ 1.64 (m, 4 H), 2.42 (s, 3 H), 3.20 (d, J = 12.6 Hz, 2 H), 3.16 (d, J = 12.6 Hz, 2 H), 6.28 (d, J = 7.2 Hz, 4 H), 6.80 (d, J = 7.2 Hz, 4 H), ca. 6.9–7.8 (m), 7.48 (d, J = 8.1 Hz, 2 H, superimposed on multiplet), 8.08 (d, J = 8.1 Hz, 2 H). Anal. Calcd for $C_{31}H_{28}Cl_2N_2O_2S$: C, 66.08; H, 4.97; Cl, 12.61; N, 4.97; S, 5.69. Found: C, 66.01; H, 4.80; Cl, 12.40; N, 4.94; S, 5.84.

1,1-Bis(4-chlorobenzyl)-1,4-dihydronaphthalene (1d). A suspension of 1,1-bis(4-chlorobenzyl)-3,4-dihydro-2(1*H*)-naph-

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(4) For references, see: Hoffmann, H. M. R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 556.
(5) For references, see: Oppolzer, W.; Snieckus, V. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 476.
(6) Miller, B.; Shi, X. *J. Org. Chem.* **1992**, *57*, 1677.
(7) Jonczyk, A.; Pytlewski, T. *Rocz. Chem.* **1975**, *49*, 1425.

thalenone *p*-toluenesulfonylhydrazone (10.6 g, 18.8 mmol) in anhydrous ether was stirred under a stream of nitrogen and cooled to 0 °C. A solution of 1.4 M methyllithium in ether (25.0 mL, 35.8 mmol) was added slowly over a 30-min period. Stirring was continued for an additional hour at 0 °C and then for 1 h as the temperature rose to 23 °C. Water was added, and the layers were separated. The organic layer was washed with water and dried over magnesium sulfate, and the solvent evaporated to yield 7.4 g of a pale yellow oil, which was crystallized from a 1:1 (vol/vol) mixture of methanol and pentane at −2 °C. Compound **1d** (4.52 g, 11.9 mmol, 63%) was obtained as a white powder, mp 73.5–74.0 °C. ^{1}H NMR: δ 2.62 (m, 2 H), 2.90 (d, J = 13.3 Hz, 2 H), 3.27 (d, J = 13.3 Hz, 2 H), ca. 5.6 (m, 2 H), a pair of doublets (6.73 and 6.98, J = 8.1 Hz) superimposed on a multiplet, totalling ca. 11 H, 7.55 (dd, J = 7.9 Hz, 1.6 Hz, 1 H). IR (KBr): ν_{max} 1491, 1450, 1408, 1094, 1017, 838, 825, 800, 752, 647 cm^{-1}. Anal. Calcd for $C_{24}H_{20}Cl_2$: C, 75.99; H, 5.28; Cl, 18.73. Found: C, 75.45; H, 5.41; Cl, 18.00.

3,4-Dihydro-1,1-bis(4-methylbenzyl)-2(1*H*)-naphthalenone *p*-Toluenesulfonylhydrazone. 3,4-Dihydro-1,1-bis(4-methylbenzyl)-2(1*H*)-naphthalenone was prepared in a similar manner to its 4-chlorobenzyl analog. From 5.00 g of 2-tetralone 11.3 g of product was obtained. Its ^{1}H NMR spectrum [δ 1.82 (m, 4 H), 2.14 (s, 6 H), 3.14 (d, J = 13.0 Hz, 2 H), 3.50 (d, J = 13.0 Hz, 2 H), 6.60 (d, J = 8.0 Hz, 2 H), 6.82 (d, J = 8.0 Hz, 2 H), 7.5–6.9 (m, 3 H), 7.70 (dd, J = 8.1, 2.0 Hz, 1 H)] appeared to be that of the desired disubstituted naphthalenone. The product (11.0 g, 31.1 mmol) was dissolved in 100 mL of methanol, and *p*-toluenesulfonylhydrazine (17.38 g, 83.2 mmol) and 1 mL of concd hydrochloric acid were added. The mixture was heated under reflux for 12 h and allowed to cool to room temperature. A white solid (8.4 g) was obtained on filtration. *p*-Toluenesulfonylhydrazine (4.0 g, 21.5 mmol) was added to the mother liquors, and the mixture heated under reflux for 24 h. The solid product obtained on cooling and filtration was combined with the previous solid product, and the combined solid recrystallized from 95% ethanol to yield the title compound (12.5 g, 23.9 mmol, 70% based on 2-tetralone) as white needles, mp 202–203 °C dec. ^{1}H NMR: δ 1.58 (m, 4 H), 2.13 (s, 6 H), 2.43 (s, 3 H), 3.24 (d, J = 13.0 Hz, 2 H), 3.31 (d, J = 13.0 Hz, 2 H), 6.20 (d, J = 8.0 Hz, 4 H), 6.70 (d, J = 8.0 Hz, 4 H), ca. 6.8–7.8 (m, ca. 5 H), 8.08 (d, J = 8.3 Hz, 2 H). IR (KBr): ν_{max} 3210, 1512, 1397, 1339, 1164, 1093, 1045, 925, 810, 690, 667, 548 cm^{-1}. Anal. Calcd for $C_{33}H_{34}N_2O_2S$: C, 75.86; H, 6.51; N, 5.36; S, 6.13. Found: C, 75.98; H, 6.68; N, 5.25, S, 6.29.

1,4-Dihydro-1,1-bis(4-methylbenzyl)naphthalene (1c). 3,4-Dihydro-1,1-bis(4-methylbenzyl)-2(1*H*)-naphthalenone *p*-toluenesulfonylhydrazone (12.5 g, 23.9 mmol) was reacted with methyllithium as described for the preparation of **1d**. The viscous yellow oil obtained from the reaction crystallized on trituration with cold methanol. Recrystallization from methanol gave **1c** (5.0 g, 14.7 mmol, 62%) as a white powder, mp 75.0–75.5 °C. ^{1}H NMR: δ 2.21 (s, 6 H), 2.67 (m, 2 H), 2.92 (d, J = 13.4, 2 H), 3.21 (d, J = 13.4 Hz, 2 H), 5.60 (d, J = 10.6 Hz, 1 H), 5.72 (dt, J = 10.6, 3.6 Hz, 1 H), 6.81 (d, J = 7.9 Hz, 4 H), 6.87 (d, J = 7.9 Hz, 4 H), 7.0–7.5 (m, 3 H), 7.56 (dd, J = 8.0, 2.1 Hz, 1 H). IR ($CDCl_3$) ν_{max} 1709, 1513, 1446, 808, 741, 613 cm^{-1}. Anal. Calcd for $C_{26}H_{26}$: C, 92.31; H, 7.69. Found: C, 92.41; H, 7.67.

Thermolysis of 1d. Compound **1d** (0.41 g, 1.08 mmol) was placed in the bend nearer the open end of the "S"-shaped, 300- × 8-mm glass tube sealed at one end, with the open end kept in a vertical position. The tube was flushed with nitrogen and sealed. The bend of the tube containing **1d** was placed in an oil bath maintained at 150 °C, while the arm of the tube outside the oil bath was kept in ice. Heating was continued for 17 h. The tube was then removed from the heating bath and cooled in ice. The arm of the tube which had not been in the heating bath was cut away from the remainder of the tube, and its contents were dissolved in ether. Evaporation of the ether left *p*-chlorotoluene (0.072 g, 0.42 mmol, 50%). The contents of the remainder of the reaction tube were dissolved in $CDCl_3$. The ^{1}H NMR spectrum of the solution showed (in addition to aromatic peaks) a singlet at δ 4.4, as well as small peaks attributable to **1d** and *p*-chlorotoluene. The product was chromatographed on alumina, eluting with 10% dichloromethane in pentane, to give 1-(4-chlorobenzyl)-naphthalene (0.37 g, 0.70 mmol, 66%) as a colorless solid, mp 73–74 °C. ^{1}H NMR: δ 4.40 (s, 2 H), 6.8–7.4 (m, with large peaks at 7.08 and 7.11 superimposed on much smaller signals, ca. 8 H), 7.6–7.95 (m, 3 H). IR (mineral oil): 1490, 1090, 1014, 791 cm^{-1}. Anal. Calcd for $C_{17}H_{11}Cl$: C, 70.85; H, 4.55; Cl, 24.60. Found: C, 70.61; H, 4.81.

Thermolyses of 1a–1c were carried out following the same procedure, with **1a** yielding 1-allylnaphthalene,[8] **1b** yielding 1-benzylnaphthalene[6] and toluene, and **1c** yielding 1-(4-methylbenzyl)naphthalene[9] and *p*-xylene.

Preparation of 1c-*d*$_2$. Phenylacetic acid-*2,2-d*$_2$[10] (24.4 g, 0.18 mol) was reacted with lithium aluminum hydride[11] to yield **2-phenylethanol-*d*$_2$**, which was converted to **1-bromo-2-phenylethane-*2,2-d*$_2$** by reaction with phosphorus tribromide.[12] The bromide was reacted with a solution of diethyl malonate and sodium ethoxide in ethanol[13] to form **diethyl 2-(2-phenylethyl-*2,2-d*$_2$)malonate**, which on refluxing with aqueous potassium hydroxide solution[12] yielded **2-(2-phenylethyl-2,2-*d*$_2$)malonic acid**, which was decarboxylated on heating[12] to form **4-phenylbutanoic acid-*d*$_2$** (7.90 g, 0.048 mol, 27%), mp 51–52 °C (reported, [undeuterated] mp 51 °C).[12]

4-Phenylbutanoic acid-d_2 (7.90 g, 0.048 mol) was reacted with thionyl chloride and then aluminum chloride[14] to yield **3,4-dihydro-1(2*H*)-naphthalenone-*4,4-d*$_2$** (6.42 g, 0.043 mol, 90%), bp 105–107 °C/2 Torr (reported [undeuterated], 105–107 °C/2 Torr). The product was dissolved in 50 mL of ethanol, and sodium borohydride (6.0 g, 0.16 mol) was added in portions over a 20-min period. The solution was stirred at room temperature for an additional 2.5 h and water added. The mixture was extracted with ether, the ether layer was washed twice with water, dried over magnesium sulfate, filtered, and the solvent evaporated to yield 4.58 g of **1-hydroxy-1,2,3,4-tetrahydronaphthalene-*4,4-d*$_2$** as a colorless oil.

To a portion of the product (2.80 g, 18.7 mmol) was added finely powdered potassium bisulfate (1.5 g, 11.0 mmol). The mixture was gently stirred under a nitrogen atmosphere and heated in an oil bath. The temperature of the bath was raised over a 10-min period to 150-155 °C and maintained at that range for 9 min. The mixture was then cooled and extracted with ether. The ether solution was washed three times with water and dried and the solvent carefully evaporated on a rotary evaporator, with the bath temperature maintained below 55 °C, to yield 2.1 g of **1,2-dihydronaphthalene-*1,1-d*$_2$**. The product was dissolved in 35 mL of dichloromethane and the solution cooled in a water bath at 23 °C while *m*-chloroperbenzoic acid (3.90 g, 23.6 mmol) was added in portions over a 5-min period. The solution was stirred for an additional 30 min, washed with sodium bisulfite solution, sodium bicarbonate solution, and water, and then dried over magnesium sulfate. The product was filtered and cooled in ice, and boron trifluoride etherate (1.0 g, 7.05 mmol) was added. The mixture was shaken briefly and allowed to stand at room temperature for 5 min. It was then washed with water and with sodium bicarbonate solution, dried over magnesium sulfate, filtered, and the solvent evaporated to yield **3,4-dihydro-2-(1*H*)-naphthalenone-*4,4-d*$_2$** (1.5 g) as a brown oil. This was converted in the manner described for synthesis of **1c** to **1c-*d*$_2$** (1.56 g, 4.56 mmol, 29% based on 1-hydroxy-1,2,3,4-tetrahydronaphthalene-4-d_2), mp 75.0–75.5 °C. Its ^{1}H NMR spectrum showed it to contain 0.08 mol of ^{1}H at C-4.

1,1-Diallyl-1,2-dihydronaphthalene (2a). To a solution of **1a** (0.86 g, 4.09 mmol) in 10 mL of *tert*-butyl alcohol was added potassium *tert*-butoxide (0.71 g, 6.31 mmol). The mixture was heated to reflux under an atmosphere of nitrogen for 18 h and then cooled in ice. Dichloromethane and a brine solution were added, the layers were separated, and the organic layer was washed four times with water to yield a brown oil, which was chromatographed on alumina, eluting with pentanes. Hydrocarbon **2a** (0.49 g, 2.33 mmol, 57%) was obtained as a pale yellow oil. ^{1}H NMR: δ 2.1–2.5 (m, 6 H), 4.6–5.2 (m, 4 H), 5.2–6.0 (m, 3 H), 6.30

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(d, J = 7,8 Hz, 1 H), 7.1 (m, 4 H). IR (neat): ν_{max} 1638, 1484, 1446, 996, 913, 787, 754, 689 cm^{-1}.

Thermolysis of 1c-d_2 and 1d. A mixture of 1c-d_2 (51.3 mg, 0.16 mmol), **1d** (50.5 mg, 0.13 mmol), and diphenylamine (34.7 mg, 0.20 mmol) was heated at 150 °C in an S-shaped tube for 18 h. The tube was cooled in ice and opened, and the volatile products were dissolved in dichloromethane and analyzed by GC–MS. No volatile products other than substituted toluenes were detected.

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