2,2′-Dimethyl-, 4,4′-dimethyl-, 3,3′,5,5′-tetramethylstilbene as well as 1,2-di(2-naphthyl)ethylene were isomerized to the trans form by stirring at ambient temperature for 1 h with 20 mol % (counted on total stilbenes) of $TeCl_4$. 4,4′-Dimethoxystilbene was completely isomerized after only 5 min. The isomerizations of very electron-rich stilbenes (4,4′-dimethoxy- and 3,3′,5,5′-tetramethylstilbene) were accompanied by precipitation of small amounts of elemental tellurium.

Acknowledgment. This work was financially supported by the Swedish Natural Science Research Council.

Registry No. **3a**, 3112-88-7; **3b**, 71996-48-0; **3c**, 19523-24-1; **3d**, 91110-67-7; **3e**, 51229-57-3; **3f**, 51229-56-2; **3g**, 91110-68-8; **3h**, 91110-69-9; **3i**, 55539-39-4; **3j**, 17164-88-4; **3k**, 91110-70-2; **4a**, 83600-56-0; **4b**, 91110-71-3; **4c**, 91110-72-4; **4d**, 91110-73-5; **4e**, 91110-74-6; **4f**, 91110-75-7; **4g**, 91110-76-8; **4h**, 91110-77-9; **4i**, 91110-78-0; **4j**, 91110-79-1; **4k**, 91110-80-4; *cis*-**59**, 645-49-8; *trans*-**59**, 103-30-0; *cis*-**56**, 20657-42-5; *trans*-**56**, 36888-18-3; *cis*-**5c**, 2510-76-1; *trans*-5c, 18869-29-9; *cis*-**5d**, 20657-43-6; *trans*-**5d**, 25144-38-1; *cis*-**5e**, 20101-53-5; *trans*-**5e**, 23958-24-9; *cis*-**5f**, 2510-74-9; *trans*-**5f**, 1657-56-3; *cis*-**5g**, 23958-29-4; *trans*-**5g**, 18869-30-2; *cis*-**5h**, 20657-30-1; *trans*-**5h**, 13863-27-9; *cis*-**5i**, 2510-75-0; *trans*-**5i**, 15638-14-9; *cis*-**5j**, 2633-08-1; *trans*-**5j**, 2753-11-9; *cis*-**5k**, 91110-81-5; *trans*-**5k**, 91110-82-6; **6**, 34063-53-1; **7**, 51229-68-6; **8a**, 16823-63-5; **8b**, 3406-03-9; **8c**, 16212-07-0; Te, 13494-80-9; S, 7704-34-9; Se, 7782-49-2; $TeCl_4$, 10026-07-0; *n*-BuLi, 109-72-8.

Products, Radical Intermediates, and Hydrogen Atom Production in the Thermal Decomposition of 1,2-Dihydronaphthalene[1,2]

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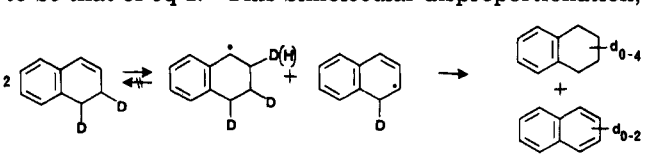
The thermal decomposition of 1,2-dihydronaphthalene (DHN) at 300 °C produces tetralin, naphthalene, hydrogen, and five C_{20} hydrocarbon products (**1**–**5**). The isolation of compounds **1**–**5** from the thermal decomposition of 1,2-dihydronaphthalene-*4-d* revealed compounds **1** and **2** to be formed by the addition of 2-hydronaphthyl (2HN) to DHN followed by intramolecular cyclization and hydrogen abstraction. Compound **3** was formed by addition of 1-tetralyl radical to DHN followed by hydrogen abstraction, and compounds **4** and **5** were formed by a sequence involving initial addition of 2-tetralyl radical to dihydronaphthalene. The thermal decomposition of DHN at 400–450 °C leads to the formation of a hydrogen atom which participates in subsequent hydrocracking reactions of available substituted aromatic structures.

Introduction

The thermal decomposition of 1,2-dihydronaphthalene (DHN) provides an example of the reaction of two closed-shell molecules to produce a pair of free radicals, termed molecule-assisted homolysis.[3] The understanding of this mechanism of atom transfer, as well as related mechanisms of initiation, chain reactions, and hydrogen shuttling pathways is central to the development of a global mechanism of coal liquefaction.[4] In an early study of DHN decomposition,[5] Gill et al. found the rate of disappearance of DHN to follow second-order kinetics and found that radical inhibitors either did not inhibit the reaction or accelerated it. The temperature dependence of the decomposition over a narrow (15 °C) temperature range gave $E_a = 37 \pm 1.2$ kcal/mol and log $(A/M^{-1}\ s^{-1}) = 9.7$. They proposed a concerted scheme for the reaction, but Heesing and Müllers, using stereospecifically deuterium-labeled DHN, demonstrated that the reaction was nonconcerted.[6] These workers also noted the presence of a substantial yield (~25%) of C_{20} products and solvent adducts but did not determine the structures of the C_{20} products. Heesing and Müllers determined, by studying recovered DHN, that stereospecificity of labeling in the recovered starting material was not lost in the reaction, and proposed the principal pathway of the of the reaction to be that of eq 1. This bimolecular disproportionation,



(1)

or molecule-assisted homolysis,[3] must be effectively irreversible, from the observed preservation of label stereospecificity.[6] In the related cyclohexadiene system, Benson

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(2) A preliminary account of a portion of this work has appeared: Franz, James A.; Camaioni, Donald M., Beishline, Robert R.; Dalling, Don *Prepr. Fuel Div., Am. Chem. Soc.* **1983**, *28* (5), 150–153.

(3) Pryor, W. A. In "Organic Free Radicals"; Pryor, W. A., Ed. *ACS Symp. Ser.* **1978**, *69*, 33–62.

(4) Stein, S. E. *ACS Symp. Ser.* **1981**, *169*, 97–129.

(5) Gill, G. B.; Hawkins, S.; Gore, P. H. *J. Chem. Soc., Chem. Commun.* **1974**, *18*, 742.

(6) Heesing, A.; Müllers, W. *Chem. Ber.* **1980**, *113*, 9–18.

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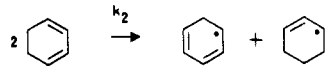
and Shaw[7] proposed bimolecular disproportionation in the thermal decomposition of 1,3-cyclohexadiene (eq 2). They



(2)

found complex kinetics and the involvement of hydrogen atom at 635–694 °K. Later, Demaré, Huybrechts, and Toth[8] examined this reaction at 512–672 °K and reported simple second-order kinetics and found for eq 2 the Arrhenius expression $\log (k_2/M^{-1}\ s^{-1}) = (10 \pm 0.4) - (35.5 \pm 1)/\theta$, $\theta = 2.3RT$ kcal/mol.

Thus, the bulk of available evidence suggests that disproportionation and oxidation reactions of DHN occur by nonconcerted radical pathways in the absence of strong oxidants such as tetracyanoethylene (TCE) and quinones, in which case nonconcerted heterolytic pathways become accessible. Recent work by Virk and co-workers resulted in claims that 1,2- and 1,4-dihydronaphthalene transferred hydrogen to acceptors via concerted H_2 transfer,[9] although other workers dispute this conclusion.[10]

This study was undertaken to deduce additional mechanistic details of the decomposition over the temperature range 300–400 °C. Our approach employed the isolation and identification of C_{20} products by chemical and spectroscopic methods and a study of conditions effecting the formation of H_2, tetralin, naphthalene, and C_{20} products. The results reveal the identities of radical intermediates and permit a detailed formulation of the mechanism.

Experimental Section

General Methods. NMR spectra were determined with a Varian FT-80 (^{13}C and ^2H at 20.00 and 12.211 MHz) or with a 300.24-MHz Varian SC-300 (^1H). GCMS spectra were determined with a Hewlett-Packard Model 5885 system. 1,2-Dihydronaphthalene (DHN) was obtained from Aldrich and purified by filtration of a pentane solution through silica gel to give material of typically ≥98% purity, the principal impurities being tetralin and naphthalene. Alternately, DHN was prepared by treatment of 1-tetralone with $LiAlH_4$ or $LiAlD_4$ followed by distillation from $KHSO_4$. This provides, after a second distillation, DHN or 1,2-dihydronaphthalene-*4-d* of 99% purity.

Preparation and Isolation of C_{20} Products. Samples of DHN or DHN-*4-d* were freeze–thaw degassed and sealed in glass or quartz tubes which were placed in type 316 stainless steel tubing reactors (made from $^3/_8$-in. tubing with Swagelok caps) and surrounded with tetralin to counter internal pressure. The tubes were heated in a fluidized sand bath at 300 °C for up to 16 h, and analyzed by GC and GCMS. Isolation of compounds **1–5** was accomplished by preparative GC (20-ft × $^3/_8$-in. aluminum column with 15% OV-101 on 45/60 mesh chromosorb G, 250 °C isothermal, 100 mL/min He flow) followed by filtration of a pentane solution of each product through a short silica gel column to remove GC stationary phase. The ^{13}C and ^1H NMR, mass spectrometric, and melting point data are presented below by compound.

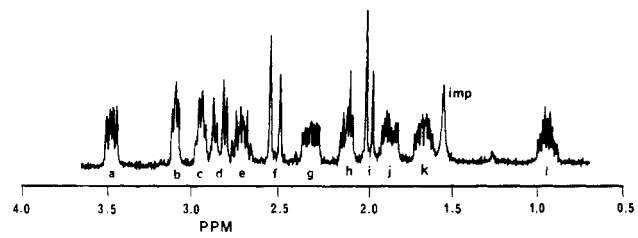


Figure 1. Aliphatic region of 300.24-MHz ^1H NMR spectrum of **1** showing **12** fully resolved resonances. An impurity consisting of GC stationary phase is indicated by imp. The letters correspond to the structure **1** in Figure 2.

***(endo*-2α,7α)-3,4:10,11-Dibenzotricyclo[6.3.1.0^{2,7}]dodecane (1).** The GCMS spectrum for **1** gave (*m/e*, relative intensity) 261 (M + 1, 2), 260 (M^+·, 12) and clusters centered at 130 (100) and 115 (20). The proton decoupled and off-resonance decoupled ^{13}C NMR spectra are presented in Table I. The compound exhibited a melting point of 83–84 °C. The ^{13}C data for **1** prepared from DHN-*4-d* was identical except for resonances at 44.3 and 31.7 ppm which "disappeared" (peak at 44.3 ppm) (due to loss of NOE, ^{13}C–^2H coupling and long T_1) or reappeared (peak at 31.7) as 1:1:1 triplet (δ 31.4, $J(^{13}C$–$^2H) = 20.0$ Hz) (see Figure 3) with small isotope shifts. The 300.24-MHz ^1H NMR spectrum showed the disappearance of proton a (Figure 1) and simplification of coupling patterns involving protons a, d, and f. The ^2H NMR spectrum (12.211 MHz, $CDCl_3$ δ = 7.25 internal standard in $CHCl_3$) displayed two peaks of equal area at 3.49 and 2.51 ppm corresponding to protons a and f_{ax}. Anal. Calcd for $C_{20}H_{17}D_3$: C, 91.20; H + D, 8.80. Found: C, 90.96; H + D, 8.44.

***(exo*-2β,7β)-3,4:10,11-Dibenzotricyclo[6.3.1.0^{2,7}]dodecane (2).** The GCMS spectrum of **2** was nearly identical with that of **1**, with M + 1 at *m/e* 261 (10%) and M^+· at *m/e* 260 (50%). The melting point of **2** was 69–70 °C. The ^{13}C and ^1H NMR spectra of **2** are presented in Table II.

The ^{13}C NMR spectrum of **2** isolated from the reaction of DHN-*4-d* was identical with the product from DHN except for the conversion of the 40.2 ppm methylene to a 1:1:1 protonated triplet and the conversion of the 45.9 ppm methine to a barely detectable 1:1:1 triplet centered at 45 ppm. Anal. Calcd for $C_{20}H_{17}D_3$: C, 91.20; H + D, 8.80. Found: C, 91.43; H + D, 8.26.

Deuteration of 2. To a sample of 1.5 mL of Aldrich dimethyl-d_6 sulfoxide, 99.5% label, and 0.0451 g (0.173 mmol) of **2** in a glove box was added 0.8 g of sodium hydride. The mixture was heated to 130 °C, maintained at 95–100 °C for 30 min, and extracted with pentane. The pentane solution of **2** was washed with water, dried (sodium sulfate), and concentrated to solid **2**, which was shown by ^1H NMR to have deuterium in positions a, b, e, f, and g (see Figure 1). Once-exchanged **2** was subjected to a second exchange, but no additional deuteration occurred. The ^{13}C NMR revealed carbons appearing at 40.2, 45.9, and 29.4 ppm to be deuterated.

Mixture of Diastereomers of 1,2′-Bitetralyl (3). The GCMS spectrum (70 eV) of **3** gave *m/e* 262 (M^+·, 5), 132 (25), 131 (100), 130 (35). ^{13}C NMR ($CDCl_3$) δ 139.6, 139.3, 138.0, 137.8, 137.2, 136.9, 136.7 (2 carbons) (quaternary carbons (eight total) of the two diastereomers), 129.23, 129.05 (2 carbons), 128.96, 128.67 (2 carbons), 128.5, 128.3, 125.48 (3 carbons), 125.3 (3 carbons), 125.2 (2 carbons) (protonated aromatics (16 expected)), 42.17, 41.7 (C-1 methine carbons), 38.7, 37.8 (C-2′ methine carbons), 34.5, 31.3 (C-1′ methylene carbons), 30.1, 29.7 (C-4 methylene carbons), 29.5, 29.5 (C-4′ methylene carbons), 28.1, 25.1 (C-2 methylene carbons), 24.2, 24.0 (C-3′ methylene carbons), 20.8, 20.8 (C-3 methylene carbons). When DHN-*4-d* was used to produce **3**, the ^{13}C resonances at 42.7, 41.7, 34.5, and 31.3 exhibited deuteration. ^1H NMR δ 7.35–7.0 (m, 8 H, aromatic H), 3.0–2.5 (m, 7 H, benzylic H), 2.35–2.25 (m, 1 H), 2.0–1.4 (m, 8 H). The material formed an oil which did not crystallize.

Mixture of *meso*- and *d,l*-2,2′-Bitetralyl (4). The GCMS spectrum (70 eV) gave *m/e* 262 (M^+·, 8), 132 (20), 131 (100), 130 (28). ^{13}C NMR δ 136.94 (2 carbons, aromatic quaternary), 136.86

(7) Benson, S. W.; Shaw; R. *J. Am. Chem. Soc.* **1967**, *89*, 5351.

(8) DeMaré, G. R.; Huybrechts, G.; Toth, M. *J. Chem. Soc., Perkin Trans. 2* **1972** 1256–1258.

(9) The $\Delta H_{f,298(g)}°$ values in eq 3 for DHN are from ref 10. The value for 1T uses a value of $\Delta H_{f,298(g)}° = 7.3$ for tetralin (ref 11) and DH° of 83.3 kcal/mol (ref 12). This value of DH° may be low by 1–2 kcal/mol. Stein (ref 13) prefers a value of 85 kcal/mol. Values for 1HN and 2HN are derived by using Herndon's structure count method (ref 14): thus, the difference in resonance energy, ΔRE, is given by ΔRE = RE(1HN or 2HN) – RE(DHN). D*H*° for DHN → 1HN + H is given by D*H*° = 94.5 kcal/mol – ΔRE, where 94.5 is Benson's value (ref 12) for secondary D*H*° values. For 1HN, ΔRE = 36.1 – 19.4 = 16.7; for 2HN, ΔRE = 31.8 – 19.4 = 12.4 assuming that the styrene-like olefin contributes neglibigly to the resonance energy of 2HN. Thus, D*H*° (DHN → 1HN + H) = 77.8 and D*H*° (DHN → 2HN + H) = 82.1. If Tsang's value for a secondary hydrocarbon D*H*° value of 97–100 kcal/mol (ref 15) were used, this would raise $\Delta H_{f,298}°$ values of 1HN and 2HN by several kcal/mole. For consistency, $\Delta H_{f,298(g)}°$ values used here are Benson values or experimental values. For simplicity, Δ*H*° calculations are at 298 °K since small relative differences in heat capacities are expected as a function of temperature. See also ref 16 for a pertinent review of $\Delta H_f°$ values for hydrocarbon radicals.

(10) Benson, S. W.; Cruikshank, F. R., Golden, D. M., Hanger; G. R.; O'Neal; H. B., Rodgers, A. S.; Walsh, R. *Chem. Rev.* **1969**, *69*, 125.

(2 carbons, aromatic quaternary), 129.28 (2 carbons, aromatic methine), 128.77 (2 carbons, aromatic methine). 125.51 (4 carbons, aromatic methines), 39.12, 39.00 (C-2 and C-2′ aliphatic methines) 33.52, 33.25 (C-1 and C-1′ benzylic methylene carbons), 29.68, 29.60 (C-4 and C-4′ benzylic methylenes), 26.67 (2 carbons, C-3 and C-3′ methylenes); ^{1}H NMR δ 7.15 (s, 8 H, aromatic H), 3.0–2.75 (m, 3 H, leq, 4eq, and 4ax H), 2.72–2.60 (m, 1 H, 1_{ax} H), 2.1–2.0 (m, 1 H, 3eq H), 1.72–1.60 (m, 1 H, 3ax H), 1.6–1.4 (m, 1 H, 2ax H). The ^{13}C NMR of 4 prepared from DHN-*4-d* revealed the carbons at 33.52 and 33.25 ppm to be selectively deuterated.

The ^{2}H NMR spectrum of deuterated 4 gave an absorption consisting of 2 fused peaks at 2.9 and 2.7 ppm. About 50% of the diastereomeric mixture melted at 70–73 °C with the remaining material melting at 96–100 °C with a clear melt at 101 °C.

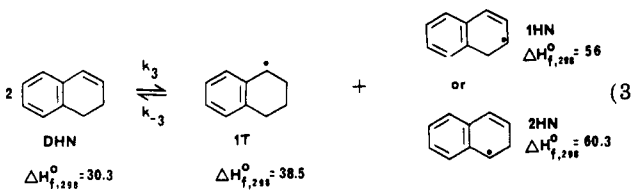
2-(2′-Tetralyl)naphthalene (5). The GCMS spectrum of **5** (70 eV) gave *m/e* 259 (M + 1, 18%), 258 (M$^{+\cdot}$, 77.3), 154 (27), 130 (79.1), 129 (24), 128 (37.7), 104 (100). ^{13}C NMR δ 144.09 (C-2′) 136.63, 136.32 (C-4a and C-8a), 133.68, 132.31 (C-4′a, C-8′a) 129.07, 128.99 (C-5 and C-8), 128.07 (C-4′), 127.63 (2 unresolved carbons, C-5′ and C-8′), 125.95, 125.91 (C-6′ and C-7′), 125.81, 125.69 (C-6 and C-7), 125.29 (C-1′) 124.83 (C-3′), 40.88 (C-2), 37.64 (C-1), 30.43 (C-3), 29.81 (C-4). The ^{13}C NMR of **5** produced from DHN-*4-d* showed selective deuteration of the carbon at 37.64 ppm. ^{1}H NMR δ 7.9–7.8 (m, 3 H, 4-, 5-, and 8′ hydrogens), 7.77 (s, 1 H, 1′ hydrogen), 7.57–7.45 (m, 3 H, 3′, 6′ and 7′ hydrogens), 7.25–7.10 (m 4 H, 5, 6, 7, and 8 hydrogens), 3.25–2.95 (m, 5 H, leq, 1ax, 2ax, 4eq, and 4ax hydrogens), 2.3–2.2 (m 1 H, 3eq), 2.13–1.95 (m, 1 H, 3ax). The material exhibited a melting point of 97–99 °C.

Decomposition of DHN in Tetralin-*1,1-d*$_2$ at 427 °C. Samples of DHN in tetralin-*1,1-d*$_2$ (10% by weight) were freeze–thaw degassed and sealed in glass tubes and heated for 10 min at 427 °C. Conversions of 95% based on DHN were observed. The products were naphthalene (75–88% based on DHN), H_2 (26%), trace yields of C_{20} products, 5% 1-methylindan, and 10% *n*-butylbenzene. The isotopic distribution of products was determined by capillary GCMS at 10 eV ionization voltage. The label distribution of the products are shown in Table IV.

Results and Discussion

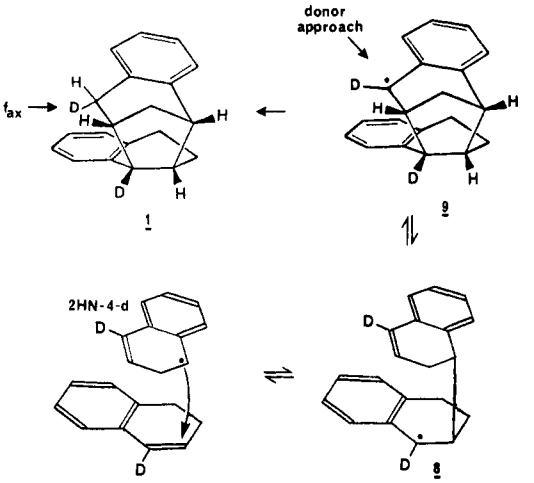
Decomposition of DHN at 300 °C. When DHN is thermolyzed at 300 °C for 16 h the following products with typical yields are formed: tetralin (15%), recovered DHN (45%), 1,4-dihydronaphthalene (0.9%), naphthalene (19%), and the compounds 1 (4.4%), 2 (6.4%), 3 (2 diastereomers, 2.9% and 2.8%), 4 (1.5%), and 5 (1.0%). Analysis of products 1–5 by GCMS showed them to be C_{20} compounds. The compounds and their deuterium substituted analogues prepared by thermolysis of 1,2-dihydronaphthalene-*4-d* (DHN-*4-d*) were isolated by preparative GC and subjected to analysis by proton and ^{13}C NMR spectroscopy. In addition, compound **2** was subjected to deuterium exchange with sodium dimsylate-d_5 in dimethyl-d_6 sulfoxide in order to simplify the ^{1}H NMR spectra and facilitate ^{13}C peak assignments. Thus, the structures and mechanism of formation of 1–5 were deduced from the spectral data and the pattern of deuterium substitution resulting from DHN-*4-d* experiments. In the following sections we present a discussion of the thermochemistry of the reactions and data supporting the structural assignments of 1–5 which require their formation by Scheme I, III, and IV.

Thermochemistry of DHN Decomposition. The activation barrier to bimolecular disproportionation of DHN forming 1-tetralyl (1T) and 1- or 2-hydronaphthyl (1HN and 2HN) (eq 3) can be estimated from thermo-

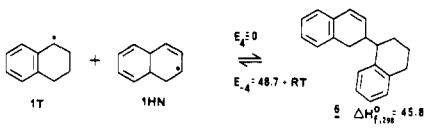


(3)

Scheme I. Mechanism for the Formation of 1



chemical calculations.[9-16] Making the usual assumption that the back reaction occurs with no activation barrier, we arrive at $\Delta H_3^{\ddagger} = \Delta H_3^\circ = 33.9$ kcal/mol for 1 HN formation and $E_3 = 33.9 + RT = 35$ kcal/mol, in agreement with experiment[5] (37 ± 1.2 kcal/mol) within the errors of the estimate, ±3 kcal/mol. Since 2HN is 4.3 kcal/mol less stable than 1HN, formation of 1HN is predicted to be favored over 2HN by a factor of 44 at 300 °C. Combination of 1T and 1HN or 2HN to form **6** (eq 4) or **7** (eq 5)



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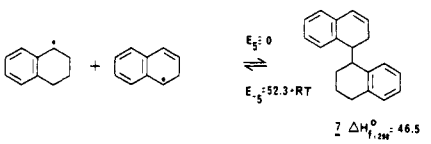


(5)

is expected to be favored over disproportionation to tetralin and naphthalene by factors ranging from 12:1 to 1:1.[13] If **6** and **7** were not consumed by back reactions (k_{-4} and k_{-5}), **6** would be converted to 1,2′-bitetralyl and **7** would be ultimately converted to 1,1′-bitetralyl or the naphthyl–tetralyl analogues under these reaction conditions. 1,1-′Bitetralyl was detected only in minute yields. By assigning A factors for unimolecular decomposition[12,15] of 10^{16} s^{-1}, **6** will exhibit a half-life of 6.8 × 10^2 s and **7** will exhibit a half-life of 1.6 × 10^4 s at 300 °C. Thus, **6** will

(11) Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: New York, 1970; pp 170–171.
(12) Benson, S. W.; "Thermochemical Kinetics. Methods for the Estimation of Thermochemical Data and Rate Parameters"; 2nd ed.; John Wiley & Sons: New York, 1976. For a discussion of the 4-pentenyl to cyclopentyl interconversion, see p 133.
(13) Stein, Stephen S., and Manka, Michael J., have determined that diphenylmethyl radical abstracts hydrogen from tetralin at a rate given by log (k/M^{-1} s^{-1}) = 8.2 − 15.7/θ, θ = 2.3RT kcal/mol. They have also determined disproportionation/combination ratios for radicals: tetralyl, 0.08; indenyl, 0.122; hydroanthracenyl, 0.054; hydrophenanthrenyl, 1.34. Stein suggests a value of 85 kcal/mol for DH° of tetralin (private communication).
(14) Herndon, W. C. *J. Org. Chem.* **1981**, *46*, 2119. See also Miller, R. E.; Stein, S. E. *J. Phys. Chem.* **1981**, *85*, 580.
(15) Tsang, W. In "Shock Waves in Chemistry"; Lifshitz, Assa, Ed.; Marcel Dekker, Inc.: New York, 1981; pp 59–129 and references therein.
(16) McMillen, Donald F.; Golden, David M. *Ann. Rev. Phys. Chem.* **1982**, *33*, 493–532.

Table I. ^1H and ^{13}C NMR Data for 1

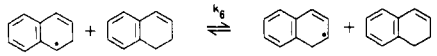
^1H resonances[a]	chem shift[b]	multiplicity	geminal pair	obsd couplings
a	3.48	2 of 2	none	c, e
b	3.10	2 of 2[c]	none	e, h
c	2.96	2 of 3[c]	none	a, d, h
d_{eq}	2.87	2 of 2	f	c, f
e	2.72	complex	none	a, b, k, l
f_{ax}	2.52	2	d	d
g_{eq}	2.31	2 of 2 of 2[c]	j	j, k, l
h	2.10	2 of 3	i	b, c, i
i	1.97	2	h	h
j_{ax}	1.85	2 of 2 of 2	g	g, k, l
k_{eq}	1.66	complex	l	e, g, j, l
l_{ax}	0.93	complex	k	e, g, j, k

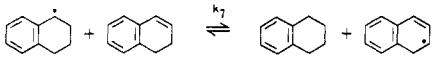
^{13}C Resonances

142.8, 139.7, 138.0, 135.1 (quaternary aromatic); 129.1, 128.6, 128.3, 127.7, 125.9, 125.6, and 124.8 (2 unresolved carbons) (aromatic methines[d]); 45.6, 44.3[e] (C-7), 43.1, and 38.9 (C-1, C-2, C-8 unassigned) (aliphatic methines[d]); 35.8 (C-4) 31.7[e] (C-12), 28.9, and 25.6 (C-3 and C-9, unassigned) (aliphatic methylenes[d])

[a] See Figure 1 for proton and carbon numbering scheme (eq = pseudoequatorial, ax = pseudoaxial). [b] In ppm from internal Me_4Si without correction for second order effects. [c] Partially overlapping multiplet. [d] Quaternary, methine, and methylene functionality determined from off-resonance decoupled spectrum. [e] Exhibited deuterium labeling when 1 was produced from DHN-*4-d*.

probably not accumulate to produce 1,2′-bitetralyl, but **7** might be expected to persist and produce 1,1′-bitetralyl. The failure to observe more than trace yields of 1,1′-bitetralyl indicates that **7** must be produced in only very small quantities from several possible causes: (1) 2HN is produced in only 2–3% of initiating reactions in the solvent cage with 1T. (2) The ratio of cage recombination to cage disproportionation of 2HN at 1T could be as low as 1.[17] (3) The cage lifetime could be quite low leading to low total cage yields of **6** or **7**. These combined effects could reduce the cage yield of **7** to 0.1% per initiating reaction. The noncage formation of **7** is not expected to compete with the much more rapid[18] diversion of 2HN and 1T to 1HN (eq 6 and 7). However, evidence for the noncage partic-


(6)


(7)

ipation of 2-hydronaphthyl is plainly evident from the structures of **1** and **2** resulting from 2HN produced in the primary initiation step or produced at low steady-state levels from equilibria such as eq 6.

Structures of 1 and 2. From mass spectra and ^{13}C NMR spectra, **1** and **2** are formed by two bridges between two tetralin molecules (see Experimental Section and Tables I and II). From ^{13}C NMR symmetry constraints (four nonequivalent alkyl methine and 4 alkyl methylene carbons), geometric constraints, and ^1H homonuclear coupling patterns of the four types of possible double

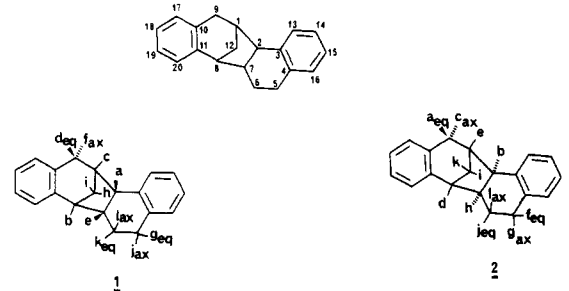


Figure 2. Numbering key for proton assignments for **1** and **2** in Tables I and II. Subscripts ax and eq refer to pseudoaxial or pseudoequatorial protons.

Table II. ^1H and ^{13}C NMR Data for 2

^1H resonance[a]	chem shift[b]	multiplicity	geminal pair	obsd couplings
a_{eq}	3.24	2 of 2	c	c, e
b	3.05	2	none	h
c_{ax}	2.98	2	a	a
d	2.88	2	none	i
e	2.75[c]	complex	none	a, i
f_{eq}	2.71[c]	2 of 3	g	g, j, l
g_{ax}	2.52[c]	3 of 2	f	f, j, l
h	2.48[c]	complex	none	b, j, l
i	2.02[c]	complex	k	d, e, k
j_{eq}	1.93[c]	complex	l	f, g, h, l
k	1.61	2	i	i
l_{ax}	1.52	4 of 2	j	f, g, h, j

^{13}C Resonances

145.1, 140.4, 138.3, 134.3 (quaternary[d] aromatic carbons); 129.46, 129.26, 128.17, 126.89, 126.09, 125.60 (2 unresolved carbons) (aromatic methines[d]); 49.9, 48.2, 45.9[e,f] (C-7), 44.9 (aliphatic methines[d]; 40.2[e,d] (C-12), 31.6 (C-9?), 29.4[f] (C-4), 28.1 (C-3?) (aliphatic methylenes[d])

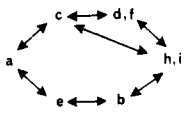
[a] See Figure 1 for proton and carbon numbering scheme (eq = pseudoequatorial, ax = pseudoaxial). [b] In ppm from Me_4Si without correction for second-order effects. [c] Partially overlapping resonance. [d] Quaternary, methine, and methylene functionality determined from an off-resonance decoupled spectrum. [e] Carbons exhibiting deuterium labeling when **2** was produced from DHN-*4-d*. [f] Carbons exhibit deuterium labeling after Me_2SO-d_6/dimsylate-d_5 exchange.

bridges (1,2:1′,3′; 1,2:1′,4′; 1,3:1′,4′ and 2,3:1′,3′), all but 1,2:1′,3′ bridging are unambiguously ruled out. There remain eight possible diastereomers with 1,2:1′,3′ bridging. Compound **1** is unique in that all 12 aliphatic protons were fully resolved at 300 MHz (Figure 1). Homonuclear coupling revealed all of the coupling relationships (Table I and Figure 2). The geminal pairs, with coupling constants of about 11 Hz,[19] are d,f, g,j, h,i, and k,l leaving a, b, c, and e as the bridgehead signals. The eight possible diastereomers are divided into a group of four isomers of **1** (Scheme I) which differ by the stereochemistry about carbons 2 and 7 (Figure 2) and four isomers of **10** (Scheme II) also differing from each other by the stereochemistry about carbons 2 and 7. For each set there is one methine hydrogen (a) which is coupled only to two other methines (c and e). This leads to two sets of coupling relationships determined by which proton, b or c, is coupled to members of both geminal pairs d,f and h,i and is *also* coupled to a. In fact, only the four diastereomers of **1** (formed by inverting one or both of carbons 2 and 7 to which protons a and e are attached) are possible from the observed vicinal coupling relationship (Table I). The coupling constant between a and e (11 Hz), indicates a syn relationship, eliminating the two anti diastereomers, which models show

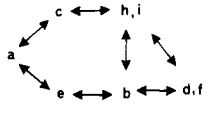
(17) Koenig, T.; Fischer, H. In "Free Radical"; Kochi, Jay K., Ed. Wiley-Interscience: New York, 1973; Vol. I, pp 157–189.

(18) By using the rate of initiation of ref 5, assuming 100% cage escape, and equating it to the termination rate, $2 \times 10^{8.5}[rad]^2$, where [rad] is the total radical concentration, the maximum radical concentration with 5.4 M DHN is 2.66×10^{-6} M. From recent rates of benzylic abstraction reactions, we can choose k_6 or k_7 to be given by $10^{8.3\pm0.5}$ exp $(-16\,000 \pm 1500/RT)$. The relative rate of all termination reactions of 1T or 2HN to abstraction from DHN is then given roughly by $10^{8.3}$ (exp $(-16\,000/RT)$)[21.6 M]/$(10^{8.5} \times 2.66 \times 10^{-6}) \approx 10^5$. Since the radical concentration is decreased further by the cage yield, this relative rate may approach 10^6.

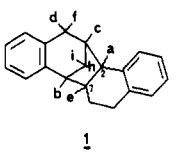
(19) Karplus, M. J. *Chem. Phys.* **1959**, *30*, 11.



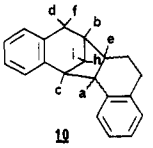
Coupling for Isomers of 1



Coupling for Isomers of 10



1



10

to be rather highly strained. The coupling constants for bridgehead pairs a,c and b,e are large for 1, demanding a cis–syn–cis relationship. A model of 1 shows that a,c and b,e bridgehead pairs are almost eclipsed. This leads to the structure of 1 in Figure 2.

The proposed structure of 1 is strongly supported by the isolation of 1 from the decomposition of DHN-*4-d*. Scheme I shows the addition of 2HN-*4-d* in an endo fashion to DHN-*4-d*, followed by the intramolecular cyclization of 8 to 9 and hydrogen abstraction by 9 to give 1. The product would have deuterium at one aliphatic methylene and at one methine. In the conversion of 9 to 1, the donor may only approach from the topside as shown in Scheme I. Thus the deuterium atom is stereospecifically placed in the f_{ax} position. If, however, compound 1 had been produced from the addition of 1HN to DHN, as depicted in Scheme II, the product would have had one benzo substituent displaced by one carbon and it would be one of the four diastereomers ruled out from homonuclear decoupling experiments. Furthermore, the product (10) would have deuterium at two adjacent aliphatic methines (Scheme II).

The result shown in Figure 3 clearly supports Scheme I and not Scheme II. Furthermore, a proton-decoupled ^2H NMR spectrum of 1 prepared from DHN-*4-d* shows two resonances at δ 3.49 and 2.51 (relative to internal $CDCl_3$ at δ 7.25) corresponding to protons a and f_{ax} but not d_{eq} at δ 2.87. This further confirms the endo conformation of 1 and the stereospecific approach of the hydrogen donor. It should be noted that the conversion of 8 to 9 in Scheme I is a direct analogue of the 5-hexenyl → cyclopentylmethyl rearrangement,[20] in which the primary radical center enjoys nearly optimal approach to the π^* orbital of the olefin[21] and cyclizes with a barrier of 6.87 kcal/mol,[22] whereas in Scheme II, the cyclization of 11 to 12 is the analogue of a 4-pentenyl → cyclopentyl cyclization, which can only occur by nearly rupturing the π-bond of the olefin, and as a result proceeds with a much higher barrier, 20 kcal/mol.[12]

The structure of compound 2 was more difficult to determine directly by 300.24-MHz ^1H NMR due to several overlapping peaks (e,f, g,h, and i,j) in the ^1H NMR spectrum. The ^{13}C NMR indicated four methine aliphatic carbons and four methylene carbons with 1,2-substituents on one tetralin moeity and 1′,3′-substituents on the attached tetralin moeity. Deuteration of 2 was carried out taking advantage of the higher acidity of benzylic hydrogens[23] to specifically introduce label at these positions.

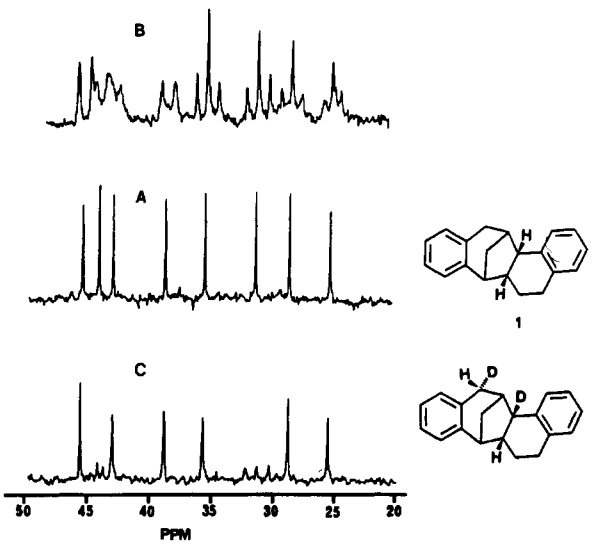
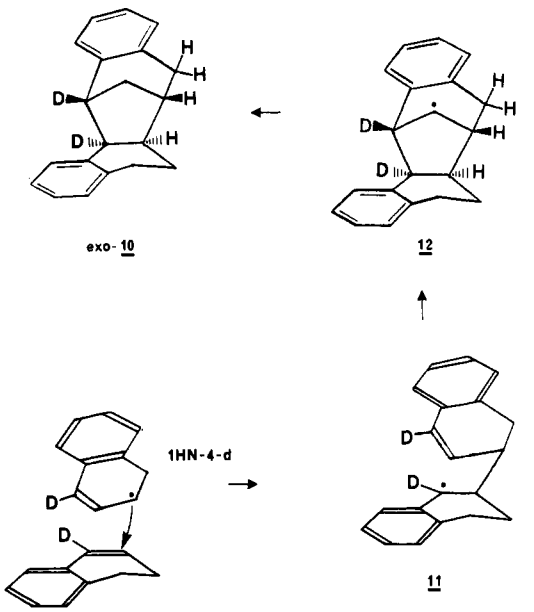


Figure 3. (a) Proton-decoupled ^{13}C NMR of 1 (aliphatic region). (b) Off-resonance decoupled ^{13}C NMR of 1 showing four doublets (methines) and four triplets (methylenes). (c) Proton-decoupled ^{13}C NMR spectrum of 1 prepared from DHN-*4-d* showing deuterium label at one methine and one methylene.

Scheme II. Hypothetical Product of Exo Addition of 1HN to DHN-*4-d*



Protons a, b, c, f, and g, but not d, were exchanged (Figure 4). This greatly simplified the ^1H NMR spectrum and all coupling relationships were determined (Table II). The large coupling constant $J_{b,h}$ for 2 demanded, as for 1, that protons b and h have a syn relationship, but the almost nonexistent couplings between b,e and d,h pairs of 2 indicate trans relationships, and a molecular model shows that the b,e and d,h dihedral angles are approximately 90°. The molecular model of 2 also shows that proton d lies in the nodal plane of the aryl rings, and the incipient anion cannot be stabilized by resonance with the aryl ring, explaining why it failed to undergo deuterium exchange. When 2 was isolated from a reaction of DHN-*4-d*, it was again found that an aliphatic methine and a methylene were selectively deuterated (Figure 4). Scheme III shows the pathway that this label pattern demands. As in the formation of 1, a mechanism involving the addition of 1HN is ruled out since it would give an isomer with the benzo substituent displaced by one carbon on the aliphatic ring

(20) Beckwith, A. L. J.; Ingold, K. U. In "Rearrangements in Ground and Excited sites"; Academic Press: New York, 1980; Chapter 4, Vol. 1, pp 170–172.
(21) Dewar, M. J. S.; Olivella, S. *J. Am. Chem. Soc.* **1978**, *100*, 5290–5295.
(22) Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 7739.
(23) Lowry, Thomas H.; Richardson, Kathleen Schueller, "Mechanism and Theory in Organic Chemistry"; Harper & Row: New York, 1981; pp 259–262 and references therein.

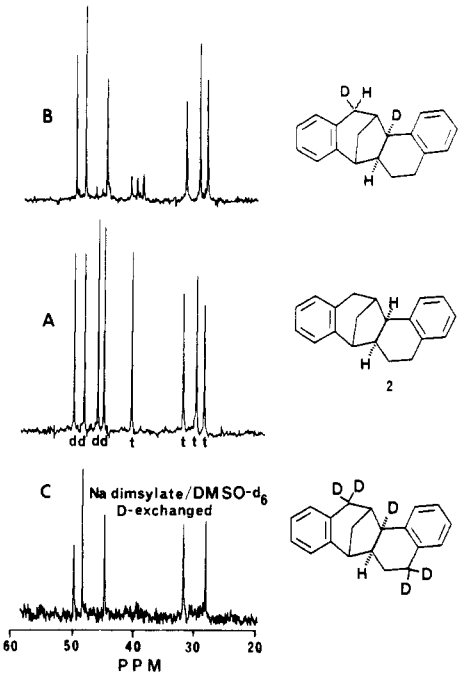
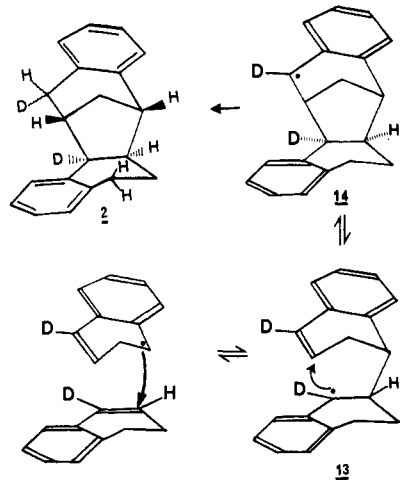


Figure 4. (a) Proton-decoupled ^{13}C NMR of **2** (aliphatic carbons) with off-resonance decoupled multiplicities indicated by d (doublet, methine carbon) or t (triplet, methylene carbon). (b) The proton-decoupled ^{13}C NMR of **2** prepared from DHN-*4-d* showing deuteration of one methine and one methylene. (c) Proton-decoupled ^{13}C NMR spectrum of **2** after sodium dimsylate-d_5/Me_2SO-d_6 exchange showing labeling of two methylenes but only one benzylic methine, due to its location in the nodal plane of the aromatic ring.

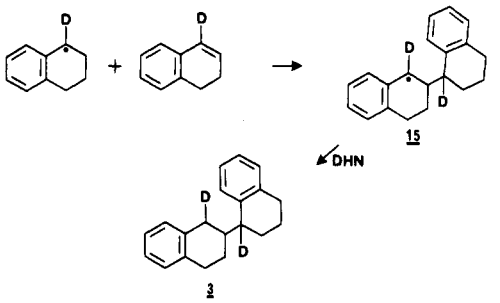
Scheme III. Formation of 2 by Exo Addition of 2HN to DHN-*4-d*. The Intramolecular Cyclization is the Favored 5-Hexenyl-Like Cyclization and Results in Labeling of an Aliphatic Methylene and an Aliphatic Methine



from where it is in **2**, and it would result in the aliphatic deuterium atoms residing on two adjacent methine carbons. It would also require the disfavored 4-pentenyl → cyclopentyl-type cyclization. Thus, the experimental data for **2** again demands the intermediacy of 2HN. Mechanisms of Schemes I and III differ only in the exo or endo mode of addition of 2HN to DHN.

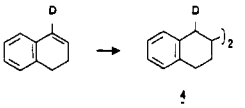
Formation of a Diastereomeric Mixture of 1,2′-Bitetralyl (3). In previous work[24] we described the isolation of 1,1′-bitetralyl as a pair of *d,l* and meso diastereomers. The capillary GC columns used in that study and the columns used here resolved 1,1′-bitetralyl most readily, and 1,2′-bitetralyl less readily into 1:1 pairs of diastereomers. The structure of **3** was immediately apparent from the molecular ion in the mass spectrum (262) and the ^{13}C NMR spectrum, which displayed two C-1 benzylic methines at 42.17 and 41.7 ppm, revealing **3** to be a 1:1 mixture of diastereomers. This data and ^1H NMR integral ratios permitted unambiguous assignment of the structure of **3**. The deuteration of the 1′-tetralyl methine carbons at 34.5 and 31.3 ppm and the benzylic methines at 42.17 and 41.7 ppm when DHN-*4-d* was substituted for DHN indicates that **3** is formed by the addition of 1-tetralyl radical to DHN as shown in Scheme IV.

Scheme IV. Formation of 3 from the Addition of 1T to 2HN



By contrast, the formation of **3** from combination of 1-tetralyl and 1HN would have given **3** with deuterium at the 1- and 4′ positions. If **3** had arisen from the initial addition of 2HN to DHN the 1-tetralyl methine would not have been deuterated.

Formation of Diastereomeric 4 and 5. Whereas diastereomers of 1,1′- and 1,2′-bitetralyls are resolvable by GC, the 2,2′-bitetralyls were not resolved. However, the ^{13}C NMR clearly demonstrated the compound to be a pair of diastereomers with two benzylic methylenes, one secondary methylene and one methine bridge. This arrangement dictates the structure of the M_r 262 compound to be 2,2′-bitetralyl. When DHN-*4-d* was used, deuterium appears selectively in the 1- and 1′-positions (eq 8). This



(8)

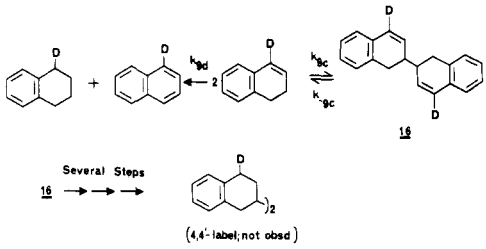
label pattern rules out the termination of 1HN radicals[25] which would have lead to deuterium in the 4 and 4′ positions.

Since 1HN is probably the radical persisting at highest concentration in this reaction, it is the only radical in this system likely to participate in termination reactions (k_{9d}, disproportionation, and k_{9c}, combination) with itself. From the estimated enthalpy of formation of **16**, 71.8 kcal/mol, the half-life of **16** for reaction k_{-8} to regenerate 1HN is only 0.4 s at 300 °C. The result is that **16** is formed in a facile equilibrium with 1HN which is depleted (k_{9d}, eq 9) to form tetralin and naphthalene, and the reactions of eq 9 forming 2,2′-bitetralyl-*4,4′*-d_2 are not observed.

(24) Franz, James A.; Camaioni, D. M. *J. Org. Chem.* **1980**, *45*, 5247–5255.

(25) In a preliminary account of this work (ref 2) the production of **4** was wrongly attributed to 1HN termination. This was due to an early misassignment of carbons 1 and 4 to be 4 and 1.

(26) The ring correction in the 1,2-dihydronaphthalene compounds (e.g., **6**, **7**, **16**) is 2.5 kcal/mol following the discussion in ref 10, p 293. This has been a matter of confusion. See: King, Hsiang-Hui; Stock, Leon M. *Fuel* **1981**, *60*, 748–749, footnote on p 749. see Shaw, Robert; Golden, David M.; Benson, Sidney W. *J. Phys. Chem.* **1977**, *81*, 1716–1729.



(9)

Thus, to account for the pattern of deuterium labeling in **4**, a mechanism is required for the generation of 2-tetralyl radical. In Scheme V, a mechanism is suggested in which the addition of 2HN to DHN leads ultimately to 2-tetralyl. This step involves the same intermediate, **8**, of Scheme I and II, which abstracts hydrogen atom to provide the intermediate **17**, which undergoes subsequent hydrogen abstraction and β-scission to form 2-tetralyl. 2T then adds to DHN to form **4**. The key step is the β-scission reaction of **18** to form naphthalene and 2-tetralyl. From energy barriers for addition of methyl radical to naphthalene and related data[27-29] the barrier to addition of the secondary tetralyl radical is estimated to be 7–10 kcal/mol.

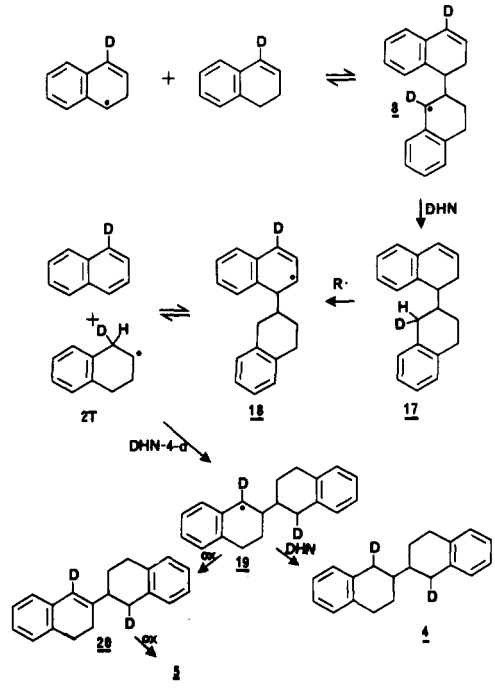
Combining this with $\Delta H°$ for β-scission of **18** of 14 kcal/mol, E_a for β-scission is ≈24 kcal/mol or less. Choosing a typical β-scission A factor[12] of 10^{14} s^{-1} yields a rate constant of β-scission of $\gtrsim 1.6 \times 10^6$ s^{-1} at 300 °C. The competing reaction of trapping of **18** by hydrogen abstraction should occur at a rate given by $\log (k/M^{-1} s^{-1}) = (8 \pm 1) - (16 \pm 1.5)/\Theta$, $\Theta = 2.3RT$, by consideration of $\Delta H°$ for the reaction and comparison with rates of similar abstractions.[13] At 12 M abstractable hydrogen concentration a rate of 8×10^3 $M^{-1} s^{-1}$ is expected for abstraction by **18** from DHN, about 10^3 times slower than β-scission of **18**. Thus, 2-tetralyl may be expected to form as shown in Scheme V. The key step is the conversion of **17** to **18**. The abstracting radical which could accomplish this would be 1HN.

Compound **5** probably forms from the further oxidation of **20** through disproportionation with DHN. Deuterium labeling occurs at the 1-position of **5** in the thermal decomposition of DHN-*4-d*. The unimolecular lifetime of **19** is sufficiently long to allow subsequent abstraction reactions to form **20** as well as **4**.

^{13}C Chemical Shifts in the Bitetralyls. With the isolation of **3** and **4**, along with data from the previously described[24] 1,1′-bitetralyl, a comparison of the effects of bulky substituents on tetralin is possible. Table III presents chemical shifts for the alkyl carbons of the bitetralyls, 2-naphthyl-2-tetralyl, and data of Morin et al.[30] for tetralin and 1-methyl- and 2-methyltetralin.

The chemical shifts for the bulky tetralyl and naphthyl substituents on tetralin generally reflect trends in the methylated tetralins.[30] Several features are apparent from Table III: (1) A 1-substituent causes an upfield shift of C-4 by ~1 ppm. (2) A 2-substituent has no effect on the shift of C-4. (3) A tetralyl substituent at C-1 causes a 13 ppm shift. (4) A tetralyl substituent at C-2 causes a 15 ppm shift. (5) A tetralyl substituent at C-2 causes an upfield shift at C-1 of 3.5 ppm and at C-3 of 3 ppm. The increased chemical shift at C-1 with a tetralyl substituent

Scheme V



is the expected effect of β-branching in an alkane. Thus, the resonances of 1,1′-bitetralyl and 2,2′-bitetralyl are assigned, although the closely spaced resonances of the meso and *d,l* pairs are ambiguous. For 1,2′-bitetralyl, the situation is more complex. Carbons 1 and 2′ are readily identified. Carbons 4 and 4′ can be chosen from the resonances at 30.1, 29.7, 29.5, and 29.5. From the effect of a 1-substituent on C-4 of tetralin, the peak at 30.1 is most probably that of C-4. The peak at 29.7 is probably also at C-4, but is insufficiently displaced downfield to allow unambiguous assignment. Likewise, the 3 and 3′ carbons of **3** are at 20.8, 20.8, 24.2, and 24.0 ppm. Since axial substitution at the 1-position of tetralin causes steric compression at the 3-position[30] and an upfield shift of C-3 (compare 1-methyltetralin), we can assign the 20.8 peaks to C-3 of **3**, and the 24.2 and 24.0 peaks to C-3′ of **3**. The C-3′ carbons should be expected to exhibit a downfield β-equatorial shift.[30] The effect is smaller than expected. The remaining carbons at C-2 and C-1′ are assigned directly based on downfield shift effects of β-branching. In compound **5**, the β-substituent effect of naphthyl is more pronounced: C-1 is shifted 8 ppm and C-3 is shifted 6.8 ppm downfield compared with 3–4 ppm shifts caused by the tetralyl substituent. C-4 in **5** is unaffected by the presumably equatorial 2-naphthyl substituent. This pattern is reminiscent of 2-methyltetralin. Although the close spacing of many of the diastereomeric carbon pairs indicates similar environments for the members of a pair, subtle effects at C-2 of 1,1′-bitetralyl and C-2 and C-1′ of **3** must reflect distinct conformational preferences about the linkages.

Decomposition of DHN at >400 °C. The decomposition of DHN at >400 °C, by contrast with results at 300 °C, produces insignificant yields of C_{20} products (less than ~2%). Tetralin, naphthalene, H_2, and minor products from hydrocracking reactions are observed. The yield of naphthalene is often 15–30% greater than the tetralin yield. The molecule assisted homolysis, or bimolecular disproportionation, leads initially to 1-tetralyl and 1-hydronaphthyl or 2-hydronaphthyl (eq 1), which readily undergo scission of H atom (eq 10–12). Production of H·

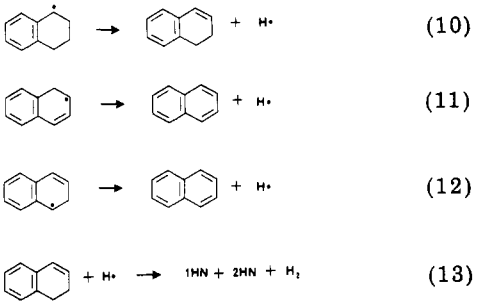
(27) Ingold, Keith U. In "Free Radicals"; Kochi, Jay, Ed. Wiley Interscience: New York, 1973; Vol. I, pp 92–93.
(28) Swarc, M. *Acc. Chem. Res.* **1969**, *2*, 87. Swarc, M. *Prog. Phys. Org. Chem.* **1968**, *6*, 323.
(29) Tedder, John M.; Walton, John C. In "Advances in Physical Organic Chemistry"; Gold, V., Bethel, D., Eds.; Academic Press: New York, 1978; Vol. 16.
(30) Morin, Frederick G; Horton, W. James; Grant, David M; Dalling, Don K.; Pugmire, Ronald J. *J. Am. Chem. Soc.* **1983**, *105*, 3992.

Table III. ^{13}C Assignments for Alkyl Resonances of Bitetralyls[a]

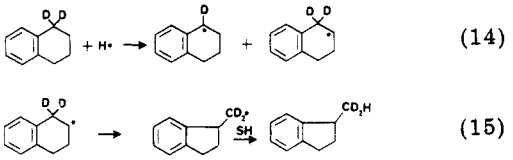
compd	1	2	3	4	1′	2′	3′	4′
1,1′-bitetralyl[b]	43.19	27.57	22.50	30.62				
	41.73	24.44	22.43	30.40				
1,2′-bitetralyl (3)[b]	42.17	28.1	20.8	30.1	34.5	38.7	24.2	29.5
	41.7	25.1	20.8	29.7	31.3	37.8	24.0	29.5
2,2′-bitetralyl (4)[b]	33.52	39.12	26.67	29.68				
	33.25	39.00	26.67	29.60				
2-(2′-tetralyl)naphthalene (5)	37.64	40.88	30.43	29.81				
tetralin	29.6	23.6						
1-methyltetralin	32.7	31.8	20.8	30.2				
2-methyltetralin	38.3	29.4	31.7	29.4				

[a] Chemical shifts are in ppm from Me_4Si in $CDCl_3$ without correction for second order effects. [b] 1:1 mixtures of diastereomers in each case. The assignment of individual carbon resonances at the same carbon position to a diastereomer was not possible. Assignments of resonances differing by less than ~1 ppm are occasionally ambiguous.

atom and abstraction from DHN (eq 13) may lead to the chain decomposition of DHN.

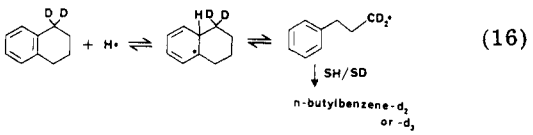


When the decomposition of DHN is carried out in tetralin-*1,1*-d_2, significant yields of 1-methylindan and *n*-butylbenzene are produced. The label distribution in the products (Table IV) shows that 1-methylindan and *n*-butylbenzene are derived from the tetralin-*1,1*-d_2. H atom is sufficiently nonselective in abstraction reactions with tetralin to produce 2-tetralyl radical (eq 14), which may undergo the reverse neophyl-like rearrangement to produce 1-methylindan (eq 15).[24] An alternative to this mechanism



would be the addition of H atom to the 4-position of DHN followed by the 2-tetralyl → 1-indanylmethyl rearrangement. From the deuterium content (mainly d_2 and d_3) of 1-methylindan, this pathway is not important, since it would lead to d_0- or d_1-labeled 1-methylindan.

The production of *n*-butylbenzene must occur by ipso addition of H atom to tetralin, scission of the alkyl group, and hydrogen (deuterium) abstraction (eq 16).



These results directly parallel the results of Benson who found that toluene was demethylated when present during the thermal decomposition of cyclohexadiene.[7] At 300 °C, tetralin and naphthalene yields from DHN decomposition are nearly equal. At 400 °C and higher, naphthalene is produced in greater yields than tetralin, and hydrogen is produced. This supports a hydrogen atom chain (eq 12 and 13) operating at the higher temperature. The results of Benson[7] with cyclohexadiene also suggested a hydrogen atom chain, while at lower temperatures the results of DeMaré suggested a nonchain decomposition.[8]

Table IV. Molecular Ion Abundances of Deuterated Products in the Thermolysis of DHN in Tetralin-*1,1*-d_2[a]

	d_0	d_1	d_2	d_3	d_4	d_5
n-butylbenzene (134)[b]		13.6	100	38.4	3.9	
1-methylindan (132)		31.1	100	68.1	9.4	1.8
tetralin (132)	2	18.8	100	73.3	16.6	
dihydronaphthalene (130)	59	73	100	60	11	
naphthalene (128)	100	53.4	15.7	2.9	0.2	

[a] By capillary GC–MS (Se-54). Mass spectral data collected at 10 eV. Numbers in parentheses are the mass number of the d_0 molecular ion. [b] Values in parentheses are molecular weights of the d_0 compounds.

Conclusions

This study has shown tha the less stable 2-hydronaphthyl and 2-tetralyl radicals as well as hydrogen atom participate to a significant extent in the decomposition of DHN, in addition to 1-tetralyl and 1-hydronaphthyl radicals postulated in an earlier study.[6] This study has demonstrated the role of stepwise formation of reactive radicals and atoms leading to hydrocracking reactions and endothermic, kinetically controlled radical rearrangements and cyclizations.

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Registry No. 1, 91238-66-3; 1-d_2 deriv., 91326-44-2; 2, 91326-45-3; 2-d_2 deriv., 91238-67-4; 2-d_5 deriv., 91238-68-5; 3 (isomer 1), 91238-69-6; 3 (isomer 2), 91238-70-9; *meso*-4, 61716-16-3; *dl*-4, 91238-71-0; 5, 89238-97-1; 1,2-dihydronaphthalene, 447-53-0.