(C1 or C4), 116.9 (C1 or C4), 19.6 ($CH_3$); high-resolution MS (*m/e*) calcd 144.0939, found 144.0940.

**1-Methylbenzobicyclo[3.1.0]hex-2-ene (1-MBBH; 9.0 min).** The method of Simmons and Smith[25] was employed to prepare the title compound from 3-methylindene. A zinc-copper couple was prepared by successively washing zinc powder with 1.0 N HCl (4×), $H_2O$ (5×), $CuSO_4$ solution (2×), $H_2O$ (5×), ethanol (3×), and ether (4×) and drying in a vacuum desiccator containing phosphorus pentoxide. A three-neck round-bottom flask equipped with a magnetic stir bar, a condenser with nitrogen inlet tube, and an addition funnel was flame dried under a stream of nitrogen. The zinc-copper couple (1.10 g; 16.8 mol of zinc) was placed in the flask with 15 mL of ether. A crystal of iodine was added to the slurry, and the mixture was stirred until the brown color had dissipated (approximately 5 min). 3-Methylindene (2.01 g; 15.5 mmol) and diiodomethane (4.70 g; 17.5 mmol) were added to the addition funnel, the mixture was added to the flask in one portion, and the reaction mixture was heated to reflux. The reaction progress was monitored by GLC on column C at 160 °C (retention times: $CH_2I_2$ = 18.8 min; 3-MI = 28.1 min; 1-MBBH = 22.3 min) with ether and Zn-Cu couple periodically added to the flask (the former to keep the volume constant and the latter to enhance the conversion). The diiodomethane was completely consumed after 44 h of reflux. The ether solution was filtered and washed with saturated $NH_4Cl$ solution, saturated $NaHCO_3$ solution, and water. The ether solution was dried ($MgSO_4$) and the ether evaporated under vacuum to afford 1.65 g of crude product (74% yield). The product was purified by preparative GLC on column C at 160 °C ramped to 200 °C: FT-IR analysis (neat) 3022, 2986, 2946, 2910, 2866, 2840, 1480, 1462, 1444, 1022, 756, 722 $cm^{-1}$; $^1H$ NMR analysis ($CDCl_3$, 300 MHz) $\delta$ 7.04-7.24 (m, aromatic, 4 H), 3.16 (dd, $J_{44'}$ = 16.9 Hz, $J_{45}$ = 6.5 Hz, C4 diastereotopic proton, 1 H), 2.85 (d, $J_{4'4}$ = 16.9 Hz, C4 diastereotopic proton, 1 H), 1.58-1.64 (m, C5 methine, 1 H), 1.53 (s, methyl, 3 H), 0.92 (dd, $J_{6exo,6endo}$ = 3.3 Hz, $J_{6exo,5}$ = 8.1 Hz, C6 exo proton, 1 H), 0.18 (dd overlapping, $J_{6endo,6exo}$ = 3.4 Hz, $J_{6endo,5}$ = 3.9 Hz, C6 endo proton, 1 H); $^{13}C$ and APT analysis ($CDCl_3$, 75.6 MHz) $\delta$ 149.7 (aromatic C), 141.9 (aromatic C), 125.8 (aromatic CH), 125.2 (aromatic CH), 121.9 (aromatic CH), 35.2 (C4 methylene), 29.9 (C1 quaternary), 23.7 (C5 methine), 23.1 (C6 methylene), 18.0 (methyl); low-resolution MS (*m/e*) EI $M^+$ = 144, M − $CH_3$ = 129, CI M + H = 145; high-resolution MS (*m/e*) calcd for $C_{11}H_{12}$ 144.0939, found 144.0940.

A time course study was conducted by photolyzing eight quartz tubes, each containing 4 mL of hexane 5.08 mM in 4-MDHN which had been deoxygenated with argon, with 254-nm light in the Rayonet reactor equipped with four lamps. The progress of the photolysis was monitored by GLC on column A at 140 °C, with octadecane as the internal standard. The sum of the products accounted for 46-65% of the total mass of 4-MDHN lost; the data are plotted in Figure 1. The photolysis of 4-MDHN was also studied by using 300-nm lamps. A 6.14 mM solution of 4-MDHN in hexane was prepared, and 2 mL of the solution was placed in each of two Pyrex photolysis tubes. The solutions were deoxygenated by argon bubbling and were photolyzed at 300 nm (15 lamps) in the Rayonet reactor for 2 h. The total conversion of 4-MDHN was 32.0%, and the results are compared to the 254-nm photolysis in Table I. No reaction was observed in a dark control.

**Fluorene-Sensitized Photolysis of 4-MDHN in Hexane.** Two-milliliter aliquots of a hexane solution of 4-MDHN (2.72 mM) and fluorene (74.7 mM) were added to each of four Pyrex photolysis tubes. The solutions were deoxygenated by argon bubbling and were photolyzed at 300 nm (16 lamps) in the Rayonet reactor for 4 h. The fluorene adsorbed approximately 92% of the incident 300-nm light. One tube was used as a dark control, and the reaction progress was monitored by GLC on column D at 100 °C, ramped to 150 °C, using octadecane as the internal standard. Approximately 65% of the 4-MDHN was consumed in the photolysis, of which 22% could be accounted for as 1-MN.

**Acknowledgment.** We are grateful to the National Science Foundation (Grant CHE-8700333) for support of this research.

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(25) Smith, R. D.; Simmons, H. E. *Org. Synth.* **1964**, *41*, 72-75.

# Photochemistry of 3-Methyl- and 4-Methyl-1,2-dihydronaphthalene in the Gas Phase[1]

**Robert J. Duguid and Harry Morrison***

*Contribution from the Department of Chemistry, Purdue University, West Lafayette, Indiana 47907.* *Received June 7, 1990*

**Abstract:** The photochemistry of 3-methyl-1,2-dihydronaphthalene (3-MDHN) and 4-methyl-1,2-dihydronaphthalene (4-MDHN) has been studied in the gas phase. Photolysis of 3-MDHN with 254-nm light produces 2-methyl-1,2-dihydronaphthalene (2-MDHN) as the major primary product. Naphthalene is also formed, apparently as a secondary photoproduct from 2-MDHN. Addition of butane to the photolysis mixture quenches the formation of 2-MDHN while producing a new photoproduct, 1-isopropenylbenzocyclobutene (IBCB). This product is also formed when light centered at 300 nm is used for the photolysis. Photolysis of 4-MDHN vapor with 254-nm light gives three products unique to the gas phase: 1-isopropenyl-2-vinylbenzene (IVB), 3-(*o*-tolyl)-1,2-butadiene (T12B), and 1-methyl-1,2-dihydronaphthalene (1-MDHN). An apparent alkyl shift product, 3-methyl-1,2-dihydronaphthalene (3-MDHN), and naphthalene are also formed, apparently as secondary photolysis products from 1-MDHN. In addition, several photoproducts common to both the solution and gas phase are detected: 2-(*o*-tolyl)-1,3-butadiene (T13B), 1-methylbenzobicyclo[3.1.0]hex-2-ene (1-MBBH), 1-methyl-1,4-dihydronaphthalene (1-M-1,4-DHN), 1-methyltetralin (1-MT), and 1-methylnaphthalene (1-MN). Again, the presence of butane during the 254-nm photolysis, or the use of longer wavelength light, gives rise to a new photoproduct, 1-methyl-1-vinylbenzocyclobutene (MVBCB). The fluorescence excitation spectrum for 4-MDHN confirms that 254-nm excitation into $S_2$ leads to minimal population of the emissive vibrational levels of $S_1$. Two pathways appear to dominate the photochemistry: retro [4 + 2] cycloaddition to give *o*-quinodimethane intermediates and sequential hydrogen shifts. These pathways derive from $S_2$ and/or upper vibrational levels of $S_1$ ($S_1^{vib}$) as indicated by the characteristic responses of their ultimate products to the presence of buffer gas. The benzocyclobutenes are unique; they are postulated to arise through a 2 + 2 closure of a vibrationally relaxed precursor *o*-quinodimethane or via a [1,3] sigmatropic shift in a uniquely populated set of $S_1^{vib}$ levels.

Despite a long and fruitful history, the photochemistry of organic compounds in the gas phase is an area that has been relatively unexploited in recent years. The novelty of gas-phase photochemistry derives from the ability to access upper electronic and vibrational excited states of molecules that are inaccessible in solution photolyses due to rapid radiationless decay. These upper excited states can provide reaction pathways not observed in solution, as exemplified by reports some time ago concerning the photochemistry of the nonconjugated aryl olefin 1-phenyl-2-butene. In solution, initial excitation of the aryl chromophore leads to *E/Z* isomerization through the intermediacy of $T_1$,[2] while in

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(1) *Organic Photochemistry*, Part 88. Part 87: Duguid, R. J.; Morrison, H. *J. Am. Chem. Soc.* **1991**, preceding paper in this issue. Abstracted from the Doctoral Dissertation of Robert Duguid, Purdue University, 1989.

(2) Morrison, H.; Peiffer, R. *J. Am. Chem. Soc.* **1968**, *90*, 3428-3432.

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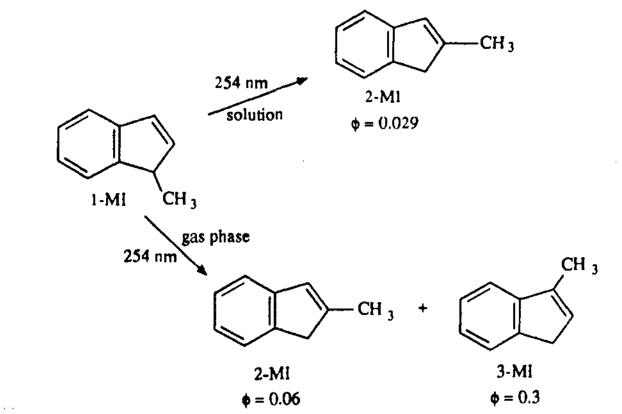
**Scheme I.** Photochemistry of 1-Methylindene (1-MI) in Solution and in the Gas Phase



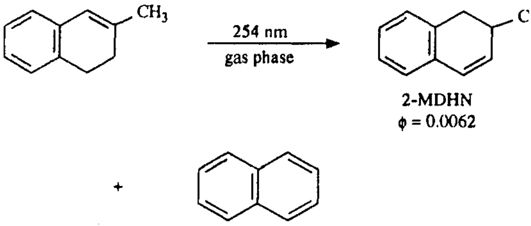
the gas phase isomerization is accompanied by the formation of 1-methyl-2-phenylcyclopropane, a di-$\pi$-methane rearrangement product attributed to reaction from excited vibrational levels of $T_2$.[3]

A more recent illustration of the divergence of solution- and gas-phase photochemistry is provided by the alkylindenes. For example, in solution the photolysis of 1-methylindene (1-MI) cleanly yields the rearrangement product 2-methylindene (2-MI),[4] while in the gas phase photolysis produces 2-MI and the formal hydrogen shift product 3-methylindene (3-MI) (see Scheme I).[5] Similar results are obtained with 2-MI, 3-MI, and 1,1-dimethylindene (1,1-DMI), each of which form hydrogen- and methyl-shift products unique, for these compounds, to the gas phase.[5] The solution-phase rearrangement originates from $S_1$ and involves a C1/C2 transposition of the indenyl skeleton,[4,6] while wavelength dependence, buffer gas quenching, and sensitization studies of the gas-phase photochemistry indicate that products are formed from the upper vibrational levels of $S_1$ ($S_1^{vib}$).[5] We have probed the mechanism of the gas-phase chemistry through detailed studies of deuterium- and $^{13}C$-labeled methylindenes[5,7] and have concluded that a combination of concerted [1,3] and/or [1,5] hydrogen shifts, plus the skeletal rearrangement observed in solution, does not adequately explain the statistical distributions of label in the photoproducts. We have therefore proposed that photoproducts derived from $S_1^{vib}$ are formed via multiple, sequential [1,2] hydrogen and methyl migrations which occur while the excited methylindene explores an excited energy surface that is high above the potential energy barriers for hydrogen and methyl migration, a reaction sequence best viewed in structural terms as involving diradical intermediates.[5]

In this paper we extend our observations of methylindene gas-phase photochemistry to the 1,2-dihydronaphthalene homologues 3-methyl-1,2-dihydronaphthalene (3-MDHN) and 4-methyl-1,2-dihydronaphthalene (4-MDHN). As reported in the preceding paper,[6] the solution photochemistry of 3-MDHN and 4-MDHN is dominated by ring opening in $S_1$ to form *o*-quinodimethane intermediates, which further rearrange to benzobicyclo[3.1.0]hex-2-enes and, in the case of 4-MDHN, 2-(*o*-tolyl)-1,3-butadiene. A hydrogen-shift product and oxidation–reduction chemistry are also observed in the solution photolyses of these compounds. We now report that the photochemistry of 3-MDHN and 4-MDHN in the gas phase involves new and extensive hydrogen-shift chemistry similar to that observed for the methylindenes, additional products attributable to the *o*-quinodimethane intermediates, and novel benzocyclobutenes seen only during gas-phase photolyses in the presence of a buffer gas.

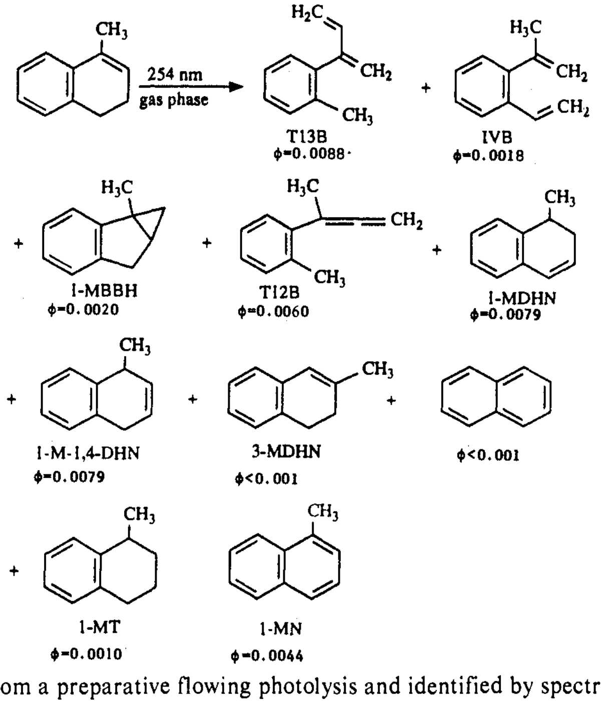
## Results

**Photolysis of 3-MDHN Vapor.** A GLC-purified sample of 3-MDHN was photolyzed with 254-nm light in the gas phase under "flowing" conditions (see the Experimental Section for descriptions of the several different conditions used for the gas-phase studies) and found to lead to two products detectable by GLC, in a ratio of 1.0:1.5. The products were isolated from a preparative photolysis under "low flow rate" conditions, analyzed by $^1H$ NMR and capillary GC/mass spectrometry, and assigned as 2-methyl-1,2-dihydronaphthalene (2-MDHN) and naphthalene by spectral comparison with authentic samples. The quantum efficiency for 2-MDHN formation was determined under "static" photolysis conditions (where 2-MDHN is the major product) using (*E*)-1-phenyl-2-butene as the gas-phase actinometer,[3] and these results are summarized in eq 1.



(1)

**Photolysis of 4-MDHN Vapor.** GLC-puriified 4-MDHN was photolyzed at 254 nm under flowing conditions to give 10 products detectable by capillary GLC (cf. eq 2). The products were isolated



(2)

from a preparative flowing photolysis and identified by spectral comparison with authentic samples of 2-(*o*-tolyl)-1,3-butadiene (T13B), 1-isopropenyl-2-vinylbenzene (IVB), 1-methylbenzobicyclo[3.1.0]hex-2-ene (1-MBBH), 3-(*o*-tolyl)-1,2-butadiene (T12B), 1-methyl-1,2-dihydronaphthalene (1-MDHN), 1-methyl-1,4-dihydronaphthalene (1-M-1,4-DHN), naphthalene, and 1-methylnaphthalene. Two minor photoproducts were identified by their GC retention times as 1-methyltetralin and 3-MDHN. The quantum efficiencies for photoproduct formation were determined under static photolysis conditions using (*E*)-1-phenyl-2-butene actinometry, and these results are also reported in eq 2.[8]

**Time Course Studies.** Time course plots for the 254-nm-initiated gas-phase photochemical reactions of 3-MDHN and 4-MDHN

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[3] Comtet, M. *J. Am. Chem. Soc.* **1970**, *92*, 5308–5312.

[4] Morrison, H.; Giacherio, D.; Palensky, F. J. *J. Org. Chem.* **1982**, *47*, 1051–1058.

[5] Suarez, M. L.; Duguid, R. J.; Morrison, H. *J. Am. Chem. Soc.* **1989**, *111*, 6384–6391.

[6] Duguid, R. J.; Morrison, H. *J. Am. Chem. Soc.* **1991**, preceding paper in this issue. The mechanism of the solution-phase rearrangement is summarized in this paper.

[7] Duguid, R. J. Doctoral Dissertation, Purdue University, 1989. Duguid, R. J.; Morrison, H. *J. Am. Chem. Soc.* **1991**, in press.

[8] Though the 4-MDHN vapor was only photolyzed for 30 s in the quantum efficiency experiment, the total loss of 4-MDHN in this static photolysis was ca. 62%, a probable source of the differences between the quantum yield ratio and the GLC ratio determined in the flowing experiment.

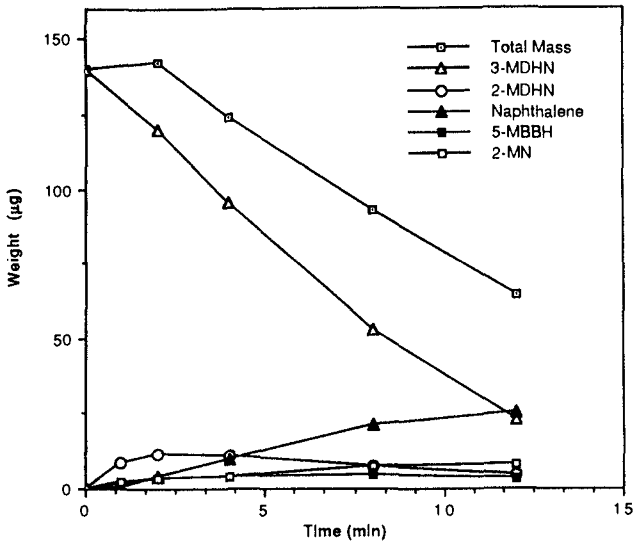


**Figure 1.** Time course study of the photolysis of 3-MDHN.

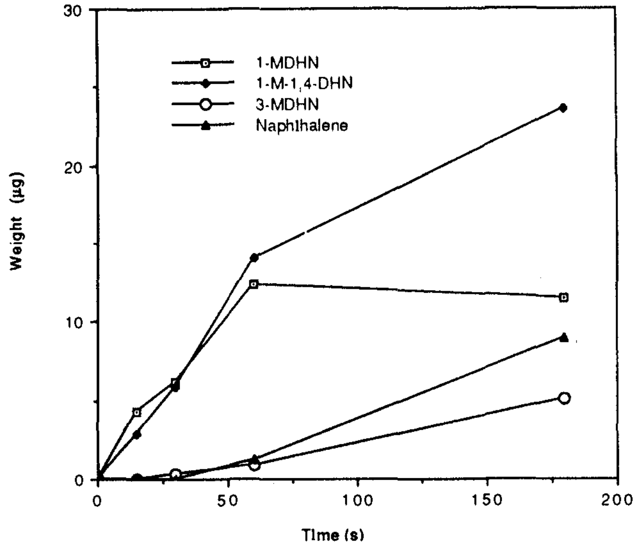


**Figure 2.** Time course study for the formation of hydrogen- and methyl-shift products, and naphthalene, from 4-MDHN.

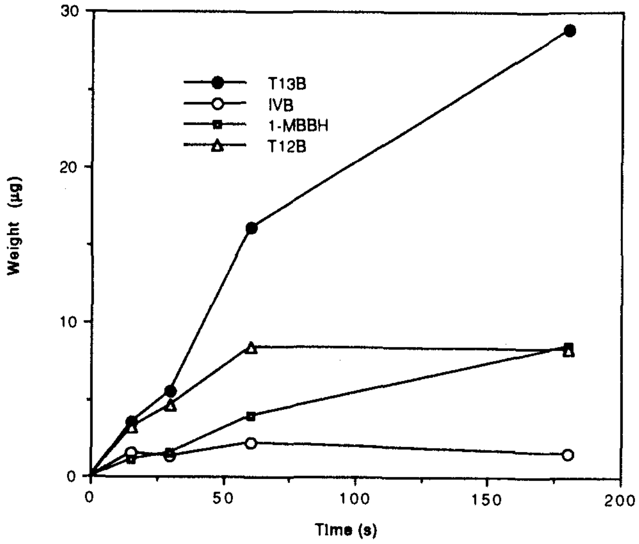


**Figure 3.** Time course study for the formation of products derived from initial ring cleavage of 4-MDHN.

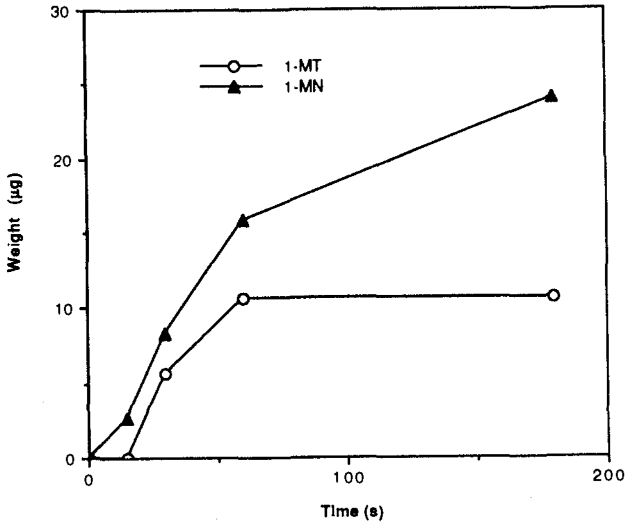
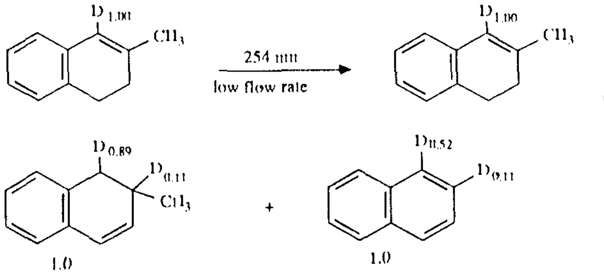


**Figure 4.** Time course study for the formation of 1-MN and 1-MT from 4-MDHN.

were determined by using static photolysis conditions and are shown in Figures 1–4. Under these static conditions, the photolysis of 3-MDHN (Figure 1) led to the formation of small amounts of 5-methylbenzobicyclo[3.1.0]hex-2-ene (5-MBBH) and 2-methylnaphthalene (2-MN), both products seen in solution,[6] in addition to those products (2-MDHN and naphthalene) found under flowing conditions. Note that 2-MDHN is the predominant product at short irradiation times, it diminishes with time, and there appears to be an induction period for formation of naphthalene. The amount of 5-MBBH remains relatively constant throughout the photolysis, while the quantity of 2-MN increases slightly at longer irradiation times.

The 10 photoproducts from 4-MDHN have been classified into three categories: hydrogen and methyl rearrangement products (1-MDHN, 1-M-1,4-DHN, 3-MDHN, naphthalene), products attributable to initial ring cleavage (T13B, IVB, 1-MBBH, T12B), and oxidation–reduction products (1-MT, 1-MN). The time courses for their formation are plotted in Figures 2, 3, and 4, respectively. The diminution of 4-MDHN was approximately monotonic with time, and the mass balance deteriorated from ca. 86% early in the photolysis to 53% toward the end of the study (analogous to that which was found for 3-MDHN; cf. Figure 1). Several products exhibit marked induction periods, specifically 3-MDHN, naphthalene (as also seen from 3-MDHN), and, to a lesser extent, 1-MN. The other products appear to be primary, with four (1-MDHN, IVB, T12B, 1-MT) exhibiting decreases at long photolysis times, presumably a consequence of secondary photochemistry.

**Photolysis of 4-d-3-MDHN Vapor.** A sample of GLC-purified 4-d-3-MDHN was photolyzed at 254 nm under "low flow rate" conditions to give a product mixture in which the naphthalene to 2-MDHN ratio was equal to 1.0:1.0. These products, as well as the starting material, were isolated by preparative GLC and analyzed by $^1$H NMR; the naphthalene was also analyzed by mass spectrometry. The results are reported in eq 3. Analysis of the



(3)

recovered starting material and the naphthalene was straightforward. In particular, mass spectral analysis of the naphthalene indicated the presence of 63.5% monodeuterated species, with the $^1$H NMR spectrum providing the specific distributions for the $\alpha$ and $\beta$ protons. NMR analysis of 2-MDHN was more problematic because the C2 methine and one of the C1 diastereotopic protons

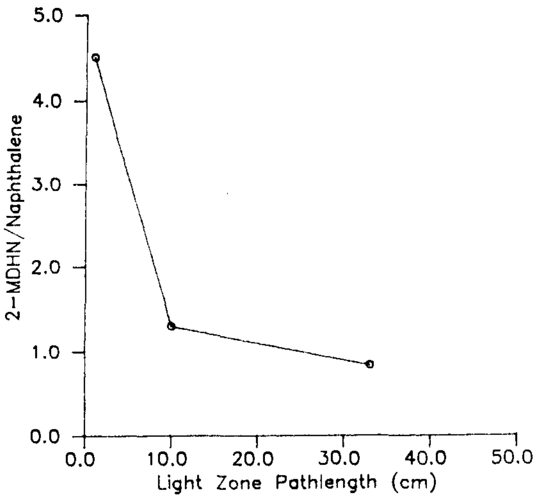
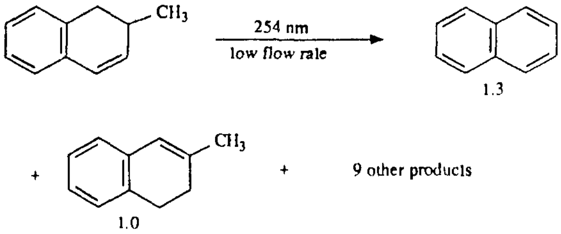


**Figure 5.** Effect of light zone path length on the photolysis of 3-MDHN.

overlap. There was clearly no deuterium at C3 or C4, and it was evident that C1 was >50% deuterated. The specific distribution shown in eq 3 is based on the assumption that 2-MDHN is the sole source of the naphthalene (through secondary photochemistry, cf. Discussion) and that this occurs with no further deuterium scrambling (i.e., C2 is 11% deuterated).

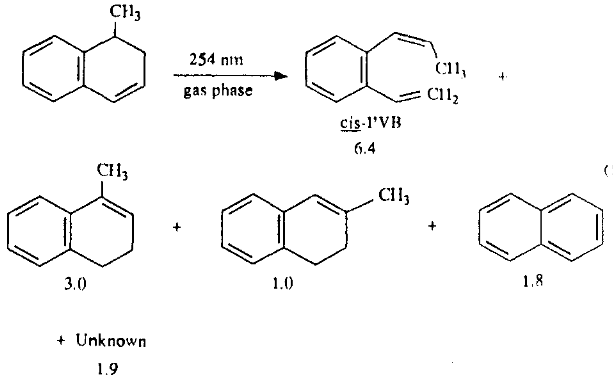
**Photolysis of 3-MDHN Vapor with Varied Light Zone Path Lengths.** Several photolyses of 3-MDHN were performed under low flow rate conditions with the light zone varied so as to assess the role of secondary photochemistry. The ratio of 2-MDHN to naphthalene formed is plotted as a function of light zone pathlength in Figure 5, and it is evident that the relative amount of naphthalene decreases as the light zone path length (and thus opportunity for secondary photochemistry) decreases.

**Photolysis of 2-MDHN Vapor.** GLC-purified 2-MDHN was photolyzed at 254 nm under low flow rate conditions, with 11 products detectable by GLC. The two major products, formed in a ratio of 1.3:1.0, were identified by their retention times and by $^1$H NMR spectroscopy as naphthalene and 3-MDHN, respectively (cf. eq 4). The other products were not identified.



(4)

**Photolysis of 1-MDHN Vapor.** GLC-purified 1-MDHN was photolyzed at 254 nm under flowing conditions and found to afford five major products. Four of the five products were identified by their GLC retention times or by $^1$H NMR spectral analysis and assigned as *cis*-1-propenyl-2-vinylbenzene (*cis*-PVB, 3-MDHN, 4-MDHN, and naphthalene; the fifth product was not identified (cf. eq 5). When 1-MDHN was photolyzed under static conditions for 1 min, to a total loss of 1-MDHN of 36.3%, the distribution of products was as follows: *cis*-PVB, 10.1%, 3-MDHN, 3.1%; 4-MDHN, 2.8%; naphthalene, 1.5%. A second static photolysis was carried out to 98.7% loss of 1-MDHN, at which point no *cis*-PVB was detected, a new product, 1-M-1,4-DHN, was observed (1.0%), and 3-MDHN, naphthalene, and 4-MDHN were present in 6.4, 5.4, and 1.8%, respectively. Further photolysis of 1-M-1,4-DHN under static conditions showed loss of starting material but no detectable volatile products.



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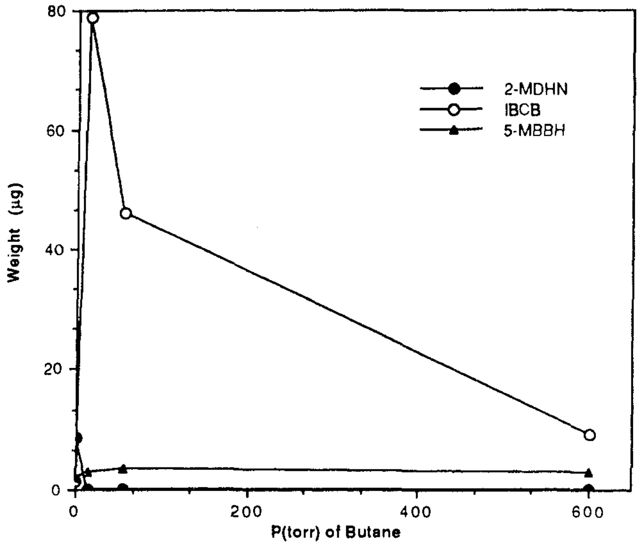


**Figure 6.** Photolysis of 3-MDHN as a function of added butane.

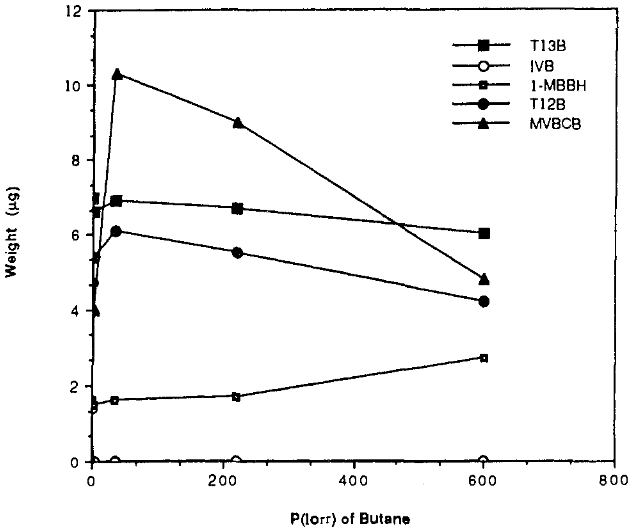


**Figure 7.** Effect of added butane on the products derived from initial ring cleavage of 4-MDHN.

**Effect of Quencher Gases on the Gas-Phase Photochemistry of 3-MDHN and 4-MDHN.** Both substrates were photolyzed with 254-nm light under static conditions in the presence of varying pressures of *n*-butane. The results are plotted in Figures 6–9.

For 3-MDHN (Figure 6), the formation of 2-MDHN (as well as naphthalene and 2-MN) was completely quenched by the addition of as little as 15 Torr of butane, whereas the product also seen from solution photolysis, 5-MBBH, is relatively unaffected by the quencher gas. The most striking result, however, is the formation of large amounts of a product, 1-isopropenylbenzocyclobutene (IBCB), that is not observed in the absence of butane. This product was isolated from a series of preparative photolyses of 3-MDHN in the presence of 15 Torr of butane, and its assignment follows from an analysis of its $^1$H NMR and mass spectra (see Experimental Section). A comparison of IBCB formation with 15 Torr of butane, relative to the formation of 2-MDHN

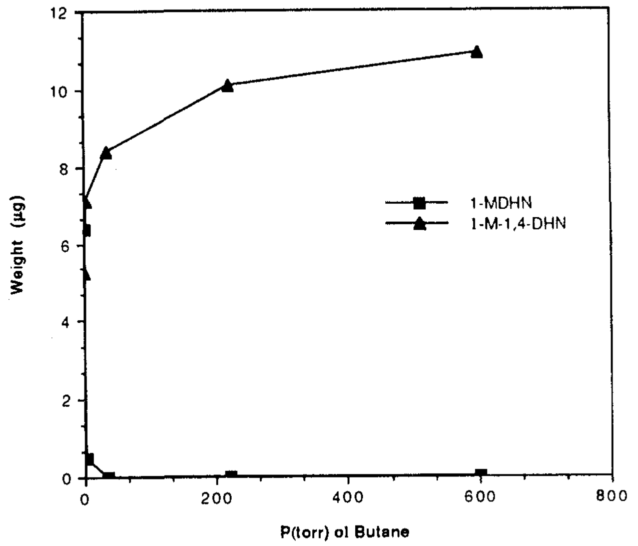


Figure 8. Effect of added butane on the hydrogen-shift products from 4-MDHN.

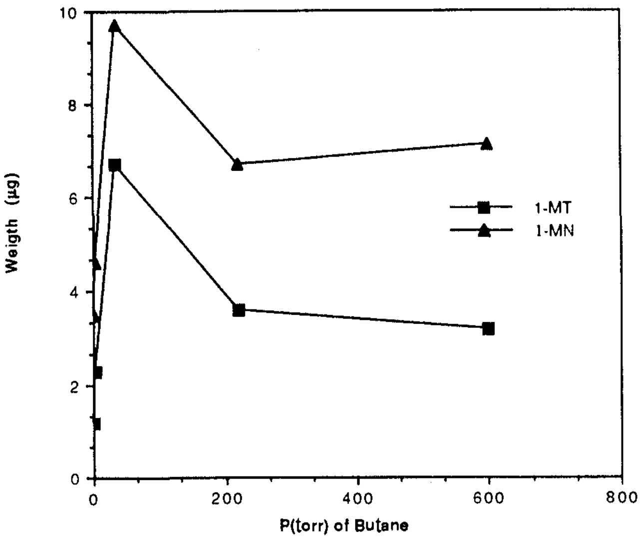
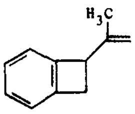
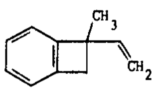


Figure 9. Effect of added butane on the formation of 1-MN and 1-MT from 4-MDHN.

in the absence of butane, provided a quantum efficiency for IBCB formation of ca. 0.036.



IBCB



MVBCB

The presence of butane during the photolysis of 4-MDHN also produced a new product in high yield, identified by its $^1$H NMR and mass spectra as 1-methyl-1-vinylbenzocyclobutene (MVBCB; cf. Figure 7). This product is formed in greatest amount at low butane pressures and is quenched at higher pressures. The effects of butane on other "ring cleavage" products are included in Figure 7, and one notes that one of the products unique to the gas phase, T12B, is also initially enhanced by the addition of butane and then slowly quenched. Another product characteristic of the gas phase, IVB, is completely eliminated by the addition of small amounts of butane. Butane has little effect on T13B and 1-MBBH, products that are also seen in the solution-phase photolysis of 4-MDHN, and, in fact, slightly enhances the formation of 1-MBBH.

Figure 8 displays the data for the hydrogen-shift products, and one notes that the product common to both the solution and the gas phase, 1-M-1,4-DHN, is enhanced by butane while the gas-phase product, 1-MDHN, is rapidly quenched by the quencher gas. No data are shown for the methyl-shift product, 3-MDHN, since none of this product is detectable in the presence of butane. Likewise, the methane cleavage product, naphthalene, is not observed in the presence of butane. In Figure 9 we note that both 1-MN and 1-MT show an enhancement in the presence of small amounts of butane and are then partially quenched at higher pressures.

**Table I.** Relative Product Distributions from the Photolyses of 4-MDHN with 254- and 300-nm Light[a]

| | 254 nm | 300 nm |
|---|---|---|
| T13B | 3.0 | 19.6 |
| IVB | 2.0 | 0.4 |
| 1-MBBH | 3.0 | 24.2 |
| T12B | 6.0 | 15.8 |
| MVBCB | - | 12.1 |
| 1-MDHN | 21.0 | 1.2 |
| 1-M-1,4-DHN | 9.0 | 6.5 |
| 3-MDHN | 1.0 | 1.0 |
| naphthalene | 3.0 | - |
| 1-MT | 6.0 | 1.7 |
| 1-MN | 1.0 | 8.5 |

[a] Data are normalized to 3-MDHN for each wavelength; since the fluxes of the two light sources are different, no comparison of the absolute values of the data in the two columns can be made.

**Table II.** Fluorescence Quantum Yields for 4-MDHN Vapor in the Presence of Butane

| butane press., Torr | $\phi_f$ | butane press., Torr | $\phi_f$ |
|---|---|---|---|
| 0.0 | 0.0 | 200.0 | 0.0036 |
| 65.0 | 0.0022 | 550.0 | 0.0043 |

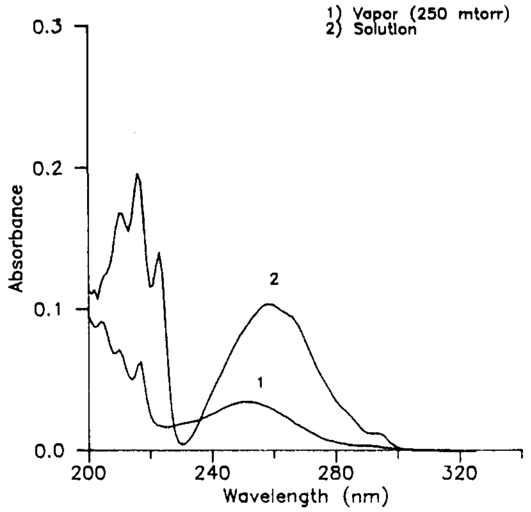


Figure 10. Ultraviolet absorption spectra of 4-MDHN as a gas and in solution.

Photolyses of 3-MDHN and 4-MDHN were also performed in the presence of *cis*-piperylene, and the response curves for the various photoproducts were generally equivalent to that seen with butane. The exceptions occur at high pressures of the diene at which the yields of several products decrease sharply. However, new products with long GLC retention times are observed from the photolyses with high *cis*-piperylene pressures, a possible indication that in such cases there is an onset of quenching due to new chemical reactions involving the quencher gas.

**Wavelength Effects on the Gas-Phase Photochemistry of 3-MDHN and 4-MDHN.** Only IBCB could be detected during the photolysis of 3-MDHN with broadband light centered at 300 nm under static conditions. Several consequences of a shift to longer wavelength light for irradiation of 4-MDHN are noteworthy: (1) naphthalene is not observed; (2) MVBCB is formed, whereas it is observed with 254-nm excitation only in the presence of butane; and (3) long-wavelength light produces an enhanced amount of

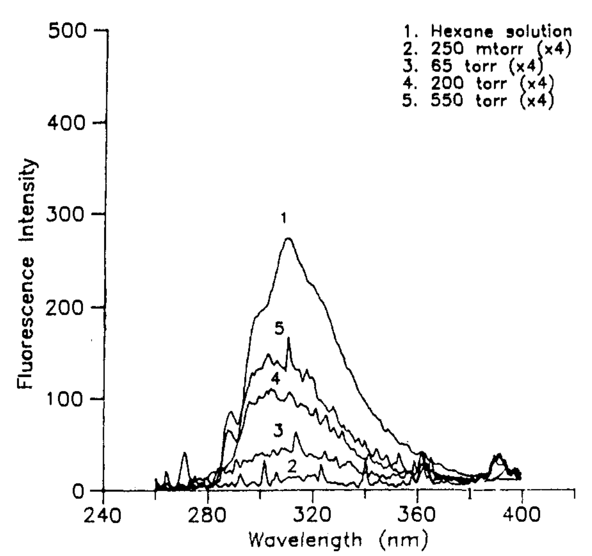


**Figure 11.** Corrected fluorescence spectra of 4-MDHN in the gas phase and in solution; excitation at 254 nm.

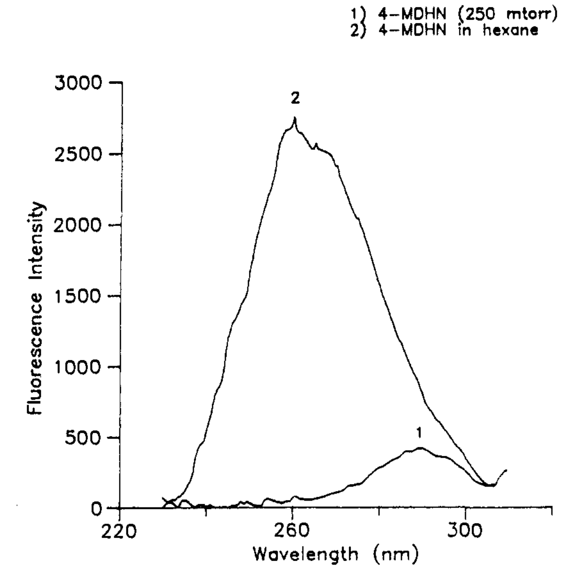


**Figure 12.** Corrected excitation spectra for 4-MDHN in the gas phase and in solution.

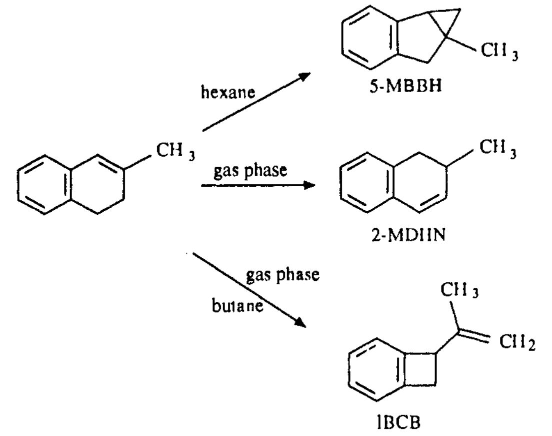
products attributable to initial ring cleavage while virtually eliminating the major 254-nm product, 1-MDHN (cf. Table I).

**Photophysics of 4-MDHN.** The absorption spectra of 4-MDHN in hexane ($1.11 \times 10^{-5}$ M) and in the gas phase (250 mTorr) are shown in Figure 10, and the fluorescence spectra for a ca. $10^{-5}$ M solution in hexane and the gaseous 4-MDHN in the presence of butane are shown in Figure 11. Corrected excitation spectra for the solution (hexane, ca. $10^{-5}$ M) and the vapor (250 mTorr) are shown in Figure 12. The fluorescence quantum efficiencies for 4-MDHN in the presence of varying amounts of butane are presented in Table II.

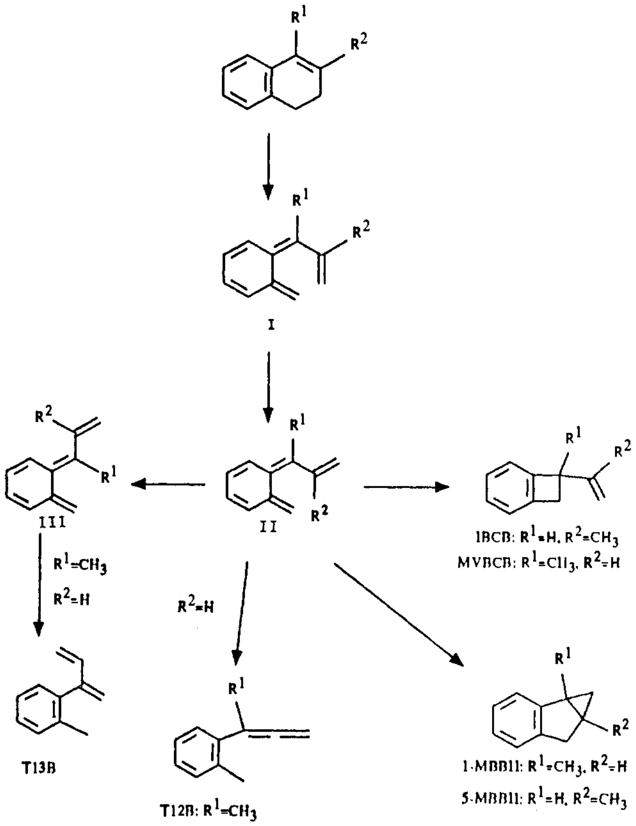
## Discussion

**Comparison of Solution- and Gas-Phase Photochemistry. Ring Cleavage Photochemistry.** The principal photoproducts formed from 3-MDHN in solution,[6] in the gas phase (eq 1), and in the gas phase in the presence of butane are shown in Scheme II.[9] The novel benzocyclobutene product, IBCB, is also formed in the vapor phase in the absence of buffer gas when longer wavelength (300 nm) light is employed. 2-MDHN is clearly the consequence of a series of hydrogen shifts, while 5-MBBH and IBCB result from initial ring fission.

**Scheme II.** Composite of the Major Photoproducts from 3-MDHN in Solution, in the Gas Phase, and in the Gas Phase in the Presence of Butane



**Scheme III.** Mechanistic Scheme for the Formation of Products Derived from the Initial Ring Cleavage of 3-MDHN and 4-MDHN



The photochemistry of 4-MDHN is much more complex, but among the plethora of products formed in the gas phase (eq 2), two of the ring cleavage products (T13B and 1-MBBH), one of the hydrogen-shift products (1-M-1,4-DHN), and the disproportionation products 1-MT and 1-MN are common to the solution phase.[6] The other five products in eq 2 are only found in the gas phase. As with 3-MDHN, a benzocyclobutene (MVBCB) is uniquely generated by the presence of butane in the 254 nm vapor phase photolysis or by the use of longer wavelength light without buffer gas.

With one exception (the formation of IVB from 4-MDHN), a comprehensive picture of the ring cleavage chemistry for both 3-MDHN and 4-MDHN can be compiled as shown in Scheme III. These products can be classified on the basis of their responses to added butane vapor (cf. Figures 6 and 7). Several (5-MBBH from 3-MDHN; 1-MBBH and T13B from 4-MDHN) are rela-

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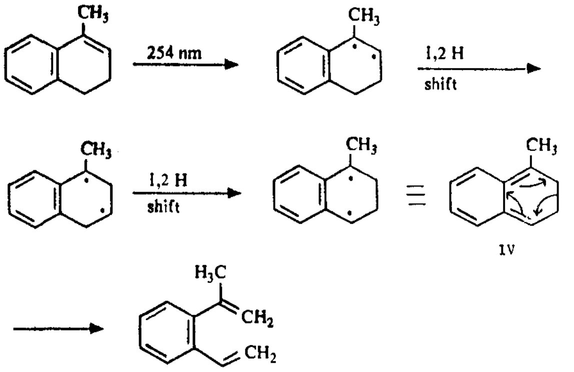
[9] As noted under Results, gas-phase photolysis under static conditions also leads to the formation of small amounts of 5-MBBH.

**Scheme IV.** Proposed Mechanism for the Formation of IVB from 4-MDHN



tively unaffected, perhaps slightly enhanced, by the buffer gas. These are products also formed in solution. Others (IBCB from 3-MDHN; MVBCB and T12B from 4-MDHN) are gas-phase products only, are much more dramatically enhanced by the presence of the butane, and are ultimately quenched at higher pressures.

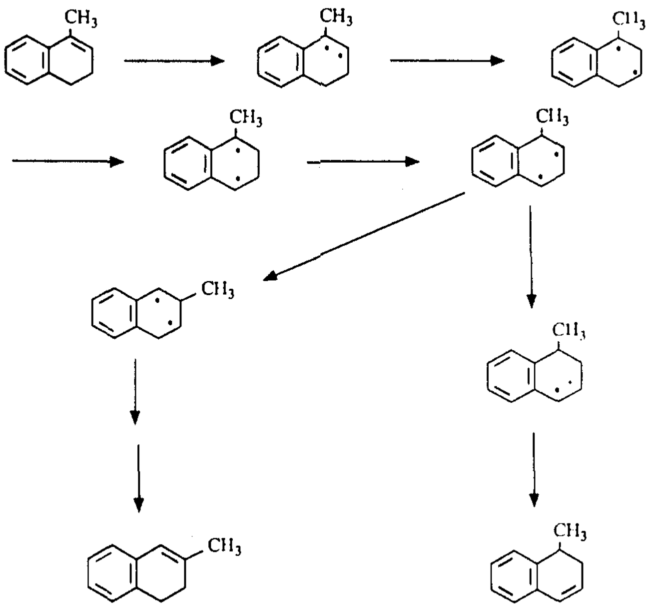
As proposed in Scheme III, both substrates undergo an initial retro [4 + 2] cycloaddition to form *o*-quinodimethane intermediates (I)[10] which, after bond rotation to II, have a number of options. One of these is an intramolecular [2 + 2] cycloaddition to generate the benzocyclobutenes. *Because the addition of butane to a 254-nm photolysis is absolutely essential for the detection and isolation of these products, one must argue that in the gas phase the o-quinodimethane intermediates convey so much vibrational energy to IBCB and MVBCB that they revert back to the quinodimethane species.* In this view, the diminished vibrational energy provided by 300-nm light accomplishes the same ends.

An alternative mechanism would be the direct conversion of the dihydronaphthalenes to the benzocyclobutenes through a [1,3] sigmatropic shift. *The buffer gas and wavelength effects could then be explained by arguing that the reactive species is* $S_1^{vib}$, *generated either with 300-nm light directly or by deactivation of* $S_2$, *the species formed by 254-nm excitation (see below).* Whichever of these mechanisms is valid, the absence of the benzocyclobutenes in solution and the marked quenching of these products at higher pressures of butane indicate that their precursor must have some vibrational excitation.

The other ring cleavage product that is uniquely formed in the gas phase is the allene T12B. Allenes have been observed as products from the photolysis of 1-alkyl-dihydronaphthalenes[11] and from the gas-phase photolysis of 1,3,5-hexatriene.[12] The genesis of T12B can be readily rationalized as the consequence of a [1,5] hydrogen shift in II ($R^2$ = H). As noted above, its response to the presence of butane shows a pattern similar to, but less dramatic than, that of the benzocyclobutenes. A thermal process involving a modestly vibrationally excited II and a photochemical conversion of the hexatriene to the allene are both plausible; the response of this product to the presence of the buffer gas leads us to favor the former.

By contrast, formation of the benzobicyclohexenes appears to be less dependent on the pressures and the thermal energy of the intermediates. This observation is consistent with our proposal[6] that the conversion of II to these products is a photochemical process. The similarly mild response of T13B to added butane also implicates secondary photochemistry for the conversion of II to III and possibly III to T13B.[13]

**Scheme V.** Possible Mechanisms for the Formation of 3-MDHN and 1-MDHN from 4-MDHN



There is one ring cleavage product, IVB, which is formed from 4-MDHN, that is only observed in the gas phase and is rapidly and completely quenched upon the addition of butane (Figure 7). This product is unique in that it formally derives from the cleavage of the C2–C3 bond of 4-MDHN, as opposed to cleavage of the C1–C2 bond. A logical precursor is the *o*-xylylene IV (Scheme IV), a species that could be formed from multiple [1,2] hydrogen shifts of the excited 1,2-dihydronaphthalene. The observations that the hydrogen-shift product from 4-MDHN, 1-MDHN, is also efficiently quenched by butane and that the relative amounts of both 1-MDHN and IVB are reduced when 300-nm excitation is used (Table I) are consistent with a common mechanism for their formation [as well as suggesting that these products are formed from an upper excited state (see below)].

**Hydrogen- and Methyl-Shift Photochemistry.** The major gas-phase photoproducts from 3-MDHN and 4-MDHN under flowing conditions are the hydrogen-shift products 2-MDHN and 1-MDHN, respectively. Neither of these products is seen in the solution-phase photochemistry,[6] they are virtually eliminated when longer (i.e., 300 nm) light is used, and they are both immediately quenched upon the addition of butane (the sensitivity of gas-phase hydrogen-shift products to buffer gas was noted in the methylindene series[5,7]). All of the above observations are consistent with the hydrogen rearrangements involving $S_2$ and/or upper levels of $S_1^{vib}$. The gas-phase photolysis of 4-MDHN also gives rise to a methyl-shift product, 3-MDHN (cf. eqs 1 and 2). A mechanism for these rearrangements, analogous to that which we have proposed[6] for hydrogen and methyl shifts observed in the gas-phase photochemistry of methylindenes, is presented for 4-MDHN in Scheme V.

Deuterium-labeling studies in the indene series confirmed the existence of multiple, sequential hydrogen (and alkyl) shifts, with the diradical valence bond picture representative of highly energetic excited species which explore the energy surfaces for migration at levels well above their potential energy barriers, until collisions funnel the rearranged molecules back to the ground state. A similar picture for these dihydronaphthalenes is supported by the observation of deuterium label at C2 as well as at C1 in the deuterated 2-MDHN recovered from the photolysis of 4-d-3-MDHN (eq 3). Neither concerted [1,3] nor [1,5] hydrogen shifts in the 4-d-3-MDHN would give rise to label at C2.

The inclusion of alkyl shifts in Scheme V has precedent in our earlier observations in the alkylindene series.[5] However, there is an induction period evident in the time course plot for the

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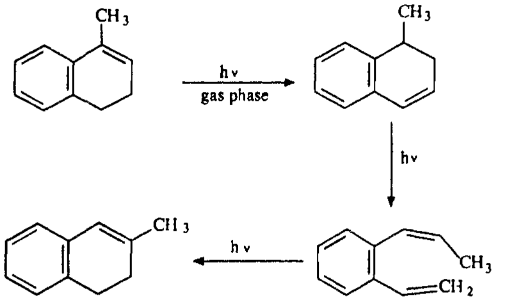
[10] Drawn as the fully bonded singlet ground-state species. There is no evidence from this, or our prior study,[5] for the involvement of a triplet, i.e., diradical, species. See: Wintgens, V.; Netto-Ferreira, J. C.; Casal, H. L.; Scaiano, J. C. *J. Am. Chem. Soc.* **1990**, *112*, 2363–2367, for a discussion of this point.

[11] Heimgartner, N.; Ulrich, L.; Hansen, H. J.; Schmid, H. *Helv. Chim. Acta* **1971**, *54*, 2313–1354.

[12] Srinivasan, R. *J. Am. Chem. Soc.* **1961**, *83*, 2806–2808. Crowley, K. J. *Proc. Chem. Soc.* **1964**, 17.

[13] See Wintgens et al.[10] and references cited therein.

**Scheme VI.** Possible Mechanism for the Formation of 3-MDHN from 4-MDHN Involving the Secondary Photolysis of 1-MDHN



formation of 3-MDHN (Figure 2) which suggests that this may be a secondary photoproduct. One such secondary route to 3-MDHN is from 1-MDHN, a primary photoproduct from 4-MDHN that we have shown does generate the 3-methyl product (cf. eq 5). This may occur through the intermediacy of *cis*-PVB, also a photoproduct of 1-MDHN (eq 5). Photolytic closure of *cis*-PVB to an *o*-xylylene, followed by a [1,5] hydrogen shift, would give 3-MDHN. Consistent with this mechanism is the fact that the amount of 1-MDHN detected from 4-MDHN actually falls off with time (Figure 2) as 3-MDHN grows in. This proposal is outlined in Scheme VI.[14]

In addition to the hydrogen-shift products noted above, there is a [1,3] hydrogen shift product formed from 4-MDHN, 1-M-1,4-DHN, which is seen both in solution and in the vapor phase. Interestingly, the formation of 1-M-1,4-DHN from 4-MDHN vapor is *enhanced* by the addition of butane (Figure 8), consistent with the fact that this product is also a solution-phase photoproduct. These observations are suggestive of a mechanism for this rearrangement which is different from that proposed for the other hydrogen-shift products, such as a concerted [1,3] hydrogen shift.[6]

**Oxidation-Reduction Chemistry.** The formation of 1-methylnaphthalene (1-MN) and 1-methyltetralin (1-MT) from 4-MDHN mirrors that which we have observed in solution; both disproportionation and oxidation due to adventitious oxygen were considered as potential sources of these products.[6] The lack of quenching of either of these products by butane (Figure 9) is consistent with the fact that they are common to both the solution and the gas phase (in fact, these products are *enhanced* by low butane pressures and then modestly quenched, suggestive of optimal reactivity from $S_1^{vib}$). There is evidence from the time course study (Figure 4) that 1-MT may in part derive from a secondary photolysis.

**Formation of Naphthalene.** Naphthalene is formed with a pronounced induction period from both 3-MDHN and 4-MDHN (Figures 1 and 2) but becomes a dominant product with extended irradiation times. In each case the naphthalene grows in as the hydrogen-shift products, 2-MDHN and 1-MDHN, decline. This suggests that these products are the source of the naphthalene, a proposal supported by the diminution in the naphthalene to 2-MDHN ratio observed in the reduced light zone photolysis of 3-MDHN (Figure 5). We also observed that the photolysis of 4-d-3-MDHN gave naphthalene with partially scrambled deuterium (eq 6), indicative of a [1,2] deuterium shift prior to the elimination of methane. Finally, both 2-MDHN and 1-MDHN do indeed produce naphthalene as a major product upon photolysis (eqs 4 and 5).

**Photophysical Characteristics and the Nature of the Reactive Excited States.** The 1,2-dihydronaphthalene moiety has two absorption bands above 220 nm, as exemplified in the absorption spectra for 4-MDHN (Figure 11). An analogous intense transition at 250–260 nm has been assigned[15] as an $S_2$ transition (or A band) in acyclic styrene derivatives, associated with the transition from the highest occupied $\pi$ MO to the lowest unoccupied $\pi^*$MO and very dependent on the conjugation of the olefinic and aryl moieties. A weaker band at 280–300 nm can just barely be discerned in the solution-phase spectrum and has been assigned as an $S_1$ transition ($\alpha$ band) associated with the transition to an unoccupied MO localized on the aryl group. Thus, the 254-nm excitation used in this work initially populates the $S_2$ state, while excitation at 300 nm initially populates the $S_1$ state. The fact that the triplet quencher *cis*-piperylene is no more effective than the collisional buffer gas butane in these studies suggests that the photochemistry reported herein is derived from one or both of these singlet states.

**Scheme VII.** Mechanistic Scheme for the Photophysical and Photochemical Consequences of Excitation of 4-MDHN into $S_2$

$$S_0 \xrightarrow{254\ \text{nm}} S_2$$

$$S_2 \xrightarrow{k_{nr1}} S_1$$

$$S_2 \xrightarrow{k_{nr2}} S_0,\ T,\ \text{or } P$$

$$S_2 + B \xrightarrow{k_q} S_1$$

$$S_1 \xrightarrow{k_f} S_0 + h\nu$$

$$S_1 \xrightarrow{k_{nr3}} S_0,\ T,\ \text{or } P$$

Both 4-MDHN and 3-MDHN show modest fluorescence in solution when excited into $S_2$ ($\phi = 0.018$ and 0.0034, respectively).[6] However, the $S_2$ state is nonemissive in the gas phase and only becomes so upon the addition of a neutral buffer gas (cf. Figure 11). A similar observation has been made in the alkylindene series.[5] *This lack of "communication" between $S_2$ and emissive levels of $S_1$ is vividly illustrated by the excitation spectra of 4-MDHN (Figure 12), which show that the initial population of $S_2$ in the gas phase does not lead to significant $S_1$ emission.*

These observations mirror those reported for several acyclic and cyclic styrene derivatives in the gas phase.[16] While excitation of *cis*- and *trans*-1-phenylpropene at 275–290 nm into $S_1$ causes observable fluorescence ($\phi_{cis} \simeq 0.07$; $\phi_{trans} \simeq 0.2$), excitation into $S_2$ with 250-nm light produces very weak emission.[16a] It could be demonstrated, by measuring the wavelength dependence of the excited-state lifetimes, that a large increase in the nonradiative rate constant at short wavelengths is the cause of the drop in fluorescence efficiency (the nonradiative rate constant, $k_{nr}$, for the $S_2$ state of *trans*-1-phenylpropene was found to be $1.2 \times 10^9$ s$^{-1}$). The gas-phase excited-state decay characteristics of the $S_2$ states of styrene, *trans*-1-phenylpropene, 1-phenylcyclobutene, 2-phenylbut-2-ene, and indene have also been studied by fluorescence decay and gated emission spectroscopy.[16b–d] Excitation at 257 nm gave nonexponential fluorescence decay in all cases, with a double-exponential decay observed for *trans*-1-phenylpropene. For the latter compound, the short-lived component ($\simeq$2 ns) produced a strong longer wavelength emission and the long-lived component ($\simeq$45 ns) produced a weak shorter wavelength spectrum. The short-lived emission was attributed to upper vibrational levels of $S_1$ which have been populated by $S_2$ to $S_1$ internal conversion, whereas the higher energy long-lived component was assigned to a singlet state of twisted $\pi$ bond character derived from the initially populated Franck–Condon

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[14] 1-MDHN is reported[11] to form 4-methylbenzobicyclo[3.1.0]hex-2-ene upon 254-nm photolysis in solution, a reaction attributed to the secondary photolysis of *cis*-PVB; see also: Laarhoven, W. H. *Org. Photochem.* **1989**, *10*, 163–308.

[15] Suzuki, H. *Electronic Absorption Spectra and Geometry of Organic Molecules*; Academic Press: New York, 1967; Chapter 13.

[16] (a) Rockley, M. G.; Salisbury, K. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1582–1585. (b) Steer, R. P.; Swords, M. D.; Crosby, P. M.; Phillips, D.; Salisbury, K. *Chem. Phys. Lett.* **1976**, *43*, 461–464. (c) Ghiggino, K. P.; Phillips, D.; Salisbury, K.; Swords, M. D. *J. Photochem.* **1977**, *7*, 141–146. (d) Ghiggino, K. P.; Hara, K.; Mant, G. R.; Phillips, D.; Salisbury, K.; Steer, P.; Swords, M. D. *J. Chem. Soc., Perkin Trans. 2* **1978**, 88–91.

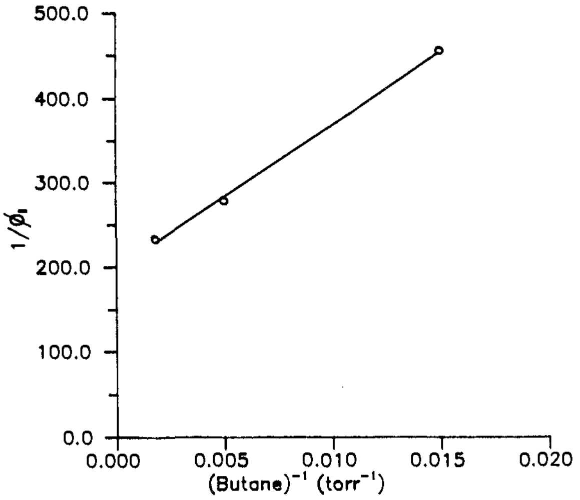

**Figure 13.** Stern-Volmer analysis of the butane enhancement of 4-MDHN fluorescence.

$S_2$ state. The long-lived component was even observed for compounds with a large degree of ring strain such as 1-phenylcyclobutene but not for 1-phenylnorbornene. *It is reasonable to consider that these long-lived twisted singlet states, derived from the $S_2$ states of ring-constrained styrene derivatives, may be equivalent to the diradical intermediates we have suggested as the precursors to the hydrogen- and alkyl-shift photoproducts from the alkylindenes and the dihydronaphthalenes (cf. Schemes IV and V and ref 5).*

An estimate of the lifetime of the 4-MDHN $S_2$ state can be obtained from a Stern–Volmer-type analysis of the fluorescence enhancement of 4-MDHN vapor in the presence of butane (Figure 11). The mechanistic scheme is outlined in Scheme VII (B = butane). The mechanism assumes that $S_2$ does not fluoresce and that butane does not enhance internal conversion of $S_1$ to $S_0$.[17]

Using the steady-state approximation for the concentrations of the $S_2$ and $S_1$ states, assuming $k_q[B]$ is greater than $k_{nr1}$ (since fluorescence is only observed in the presence of butane), and with $\phi_f^\circ$ defined as the fluorescence quantum efficiency at infinite butane pressure, one can express the reciprocal of the fluorescence quantum efficiency of 4-MDHN vapor

$$\frac{1}{\phi_f} = \frac{1}{\phi_f^\circ} + \frac{k_{nr2}}{\phi_f^\circ k_q[B]} \tag{6}$$

In this expression, the rate constant for quenching, $k_q$, should be limited by the rate of collision of molecules in the gas phase, i.e., from the collision theory of reaction kinetics, and for a mixture of butane and 4-MDHN, ca. $3.1 \times 10^{11}$ $M^{-1}$ $s^{-1}$ ($1.7 \times 10^7$ $Torr^{-1}$ $s^{-1}$). A plot of the reciprocal of the 4-MDHN fluorescence quantum efficiencies vs the reciprocal of the butane pressure is presented in Figure 13. The slope ($1.70 \times 10^4$ Torr; $r = 0.999$) and the $y$ intercept (198.0) provide a value of $k_{nr2}$ of $1.5 \times 10^9$ $s^{-1}$, which corresponds to a lifetime of 0.7 ns for $S_2$. This value matches quite well with the $S_2$ nonradiative decay rate constant of $1.2 \times 10^9$ $s^{-1}$ reported for *trans*-1-phenylpropene vapor excited at 255 nm.[16a]

## Conclusions

Photolysis of 3-MDHN and 4-MDHN in the gas phase gives rise to products common to the solution-phase photochemistry but also involves reaction pathways unique to the vapor phase. Principal among the latter are hydrogen rearrangements which dominate the product mixtures when 254-nm light is used, a wavelength which initially populates $S_2$. We attribute this chemistry to multiple [1,2] hydrogen shifts via diradical-like intermediates (as has been previously proposed for the hydrogen/methyl-shift photochemistry in the methylindene series). Such intermediates could be relaxed forms of $S_2$ or upper vibrational levels of $S_1$ ($S_1^{vib}$). These hydrogen-shift products are virtually eliminated by the use of broadband light centered at 300 nm, excitation that directly populates lower levels of vibrationally excited $S_1$.

The use of such long-wavelength light produces predominantly cyclohexadienyl ring cleavage chemistry from both substrates. *o*-Quinodimethane intermediates are formed which then give rise to a variety of products by either subsequent thermal or photochemical processes.

The presence of a buffer gas during 254-nm excitation, or the use of long-wavelength light, also gives rise to benzocyclobutenes from both 3-MDHN and 4-MDHN which are unique to these gas-phase conditions and must involve thermally relaxed precursors that are otherwise inaccessible in either the gas or solution phase. The formation of naphthalene from 3-MDHN and 4-MDHN appears to be due to secondary photoreactions of 2-MDHN and 1-MDHN, respectively.

## Experimental Section

The detailed experimental procedures for this work may be found in the doctoral dissertation of R.J.D. The salient features are summarized below.

**Materials.** Biphenyl (Aldrich), octadecane (Aldrich), lithium aluminum hydride (Alfa), silica gel (EM Science), aluminum chloride (Mallinckrodt), naphthalene (Baker), and *p*-toluenesulfonic acid monohydrate (Baker) were stored at room temperature and were used as received. Iodomethane (EM Science) was stored at −20 °C, and thionyl chloride (EM Science) was distilled prior to use. (*E*)-1-Phenyl-2-butene (Pfaltz and Bauer) was vacuum distilled and was GLC purified prior to use. Diethyl malonate (Baker) and 2-bromo-1-phenylpropane (Aldrich) were vacuum distilled prior to use. *cis*-Piperylene (Chemical Samples) was stored at −20 °C and was used as received. Hexane in the photochemical and spectroscopic studies was of spectroquality grade from Burdick and Jackson. Benzene and ethanol used in synthetic reactions were distilled under nitrogen from sodium, and diethyl ether and tetrahydrofuran used in synthetic reactions were distilled under nitrogen from benzophenone ketyl. Butane (99.5% pure), obtained from Matheson, was used as received. 3-Methyl-1,2-dihydronaphthalene (3-MDHN) was prepared by either (1) $LiAlH_4$ reduction of 2-methyl-1-tetralone (Aldrich) followed by dehydration or (2) $CH_3MgI$ addition to $\beta$-tetralone (Aldrich) followed by dehydration; its NMR spectrum matched that in the literature.[18] 4-d-3-Methyl-1,2-dihydronaphthalene was prepared by $LiAlD_4$ reduction of 2-methyl-1-tetralone followed by dehydration. 4-Methyl-1,2-dihydronaphthalene (4-MDHN) was prepared by $CH_3MgI$ addition to $\alpha$-tetralone (Aldrich) followed by dehydration and had an NMR spectrum identical with that in the literature.[18] 1-Methyl-1,2-dihydronaphthalene (1-MDHN) was prepared by $LiAlH_4$ reduction of 4-methyl-1-tetralone (Aldrich), followed by dehydration, and had an NMR spectrum identical with that in the literature.[11] 2-Methyl-1,2-dihydronaphthalene (2-MDHN) was prepared by $LiAlH_4$ reduction of 3-methyl-1-tetralone, followed by dehydration. The tetralone was synthesized by the base-catalyzed condensation of diethyl malonate with 2-bromo-1-phenylpropane (using the method of Adams and Kamm[19] adapted for malonate ester alkylation), followed by decarboxylation[20] and cyclization.[21] An NMR spectrum matched that in the literature.[11] 1-Methyl-1,4-dihydronaphthalene (1-M-1,4-DHN) was prepared by $Li/NH_3$ reduction of naphthalene followed by quenching by the dropwise addition of iodomethane in THF.[22] The NMR spectrum matched that in the literature.[23]

**Gas Chromatography.** Analytical GLC analyses were performed on a Hewlett-Packard Model 5710A instrument equipped with a capillary injector and on a Varian Model 3700 Capillary GLC. Both chromatographs were equipped with flame ionization detectors and Hewlett-Packard Model 3390A integrators. The following analytical columns were used: (A) 30 m × 0.25 mm i.d., DB-Wax, capillary (J&W Scientific), 0.50-μm film thickness; (B) 30 m × 0.25 mm i.d., RSL-150,

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(17) The latter assumption is discussed in depth in: Suarez, M. L. Ph.D. Thesis, Purdue University, 1987.

(18) Banks, H.; Ziffer, H. *J. Org. Chem.* **1982**, *47*, 3743–3747.

(19) Adams, R.; Kamm, R. M. *Organic Syntheses*; Wiley: New York, 1941; Collect. Vol. 1, pp 250–251.

(20) Reid, E. E.; Ruhoff, J. R. *Organic Syntheses*; Wiley: New York, 1943; Collect. Vol. 11, pp 474–476.

(21) Weidler, A. M.; Bergson, G. *Acta Chem. Scand.* **1964**, *18*, 1484–1486.

(22) Rabideau, P. W.; Harvey, R. G. *Tetrahedron Lett.* **1970**, 4139–4142.

(23) Yasuda, M.; Pac, C.; Sakurai, H. *J. Org. Chem.* **1981**, *46*, 788.

capillary (Alltech), 0.25-μm film thickness; (C) 30 m × 0.25 mm i.d., Superox, capillary (Alltech), 0.25-μm film thickness; (D) 50 m × 0.25 mm i.d., GB-20M, capillary (Foxboro), 0.25-μm film thickness. Preparative GLC separations were performed on a Varian Model 3300 instrument, modified to accommodate 0.25-in. columns and coupled to either a Hewlett-Packard 3390A or 3393A integrator. The columns used were as follows: (E) 16 ft × 0.25 in., 25% XF-1150 on 60/80 AW Chromosorb P, 50–60 mL of He/min; (F) 10 ft × 0.25 in., 10% Carbowax 20M on 60/80 AW-DMCS Chromosorb W, 60 mL of He/min; (G) 10 ft × 0.25 in., 10% SE-30 on 60/80 AW-DMCS Chromosorb W, 60 mL of He/min.

**Spectroscopy.** NMR, mass, ultraviolet, and fluorescence spectra were obtained on the instruments described in the companion paper.[6]

**Photochemical Apparatus.** The gas-phase photolysis apparatus has been described in detail.[5] Photolyses were carried out under flowing, static, and low flow rate conditions. In flowing runs, the sample (5–30 mg) was deoxygenated and photolyzed by allowing the sample vapor to flow through a quartz photolysis vessel inserted through a Rayonet reactor. Typically, the pressure before the collection trap was 0.1 Torr and photolysis was complete in ca. 2–5 min. Preparative runs employed 60–300 mg with a clean vessel inserted after every 20–30 mg. In some cases the photolysis vessel was partially covered with aluminum foil to vary the reaction light zone.

We have found that cooling the sample flask to 0 °C during the photolysis provides increased conversions to products, partly due to the low collision environment at the reduced pressure (typically 0.02 Torr for the methyldihydronaphthalenes) and partly due to the increased (ca. 4-fold) residence time in the reaction vessel.[7] Photolyses under these conditions are referred to in the text as low flow rate, and ca. 2 h was required for the transfer of 20–30 mg of substrate. Static photolyses were carried out by using a cylindrical quartz vessel (length 34 cm × 4.7 cm o.d.) with a constricted neck attached to a Teflon needle valve and an O-ring joint. The volumes of the vessels ranged between 520 and 540 mL. Gaseous samples were distilled into the vessel through a T-joint adapter from a sample reservoir or from a lecture bottle.

Quantum efficiencies for the 3-MDHN and 4-MDHN photoreactions utilized the *E*/*Z* isomerization of (*E*)-1-phenyl-2-butene vapor as the chemical actinometer.[3] The quantum efficiency with 252-nm excitation is reported as 0.075 and was assumed to have the same value at 254 nm.

**Gas-Phase Photolyses of 3-MDHN.** The 3-MDHN was initially photolyzed under flowing conditions at 254 nm with the sample vessel maintained at room temperature (ca. 25 °C) and the flowing pressure at 130 mTorr. Analysis on column C at 130 °C showed two products at 9.5 and 13.9 min (1.5 and 2.3% of the volatiles, respectively). A preparative photolysis, under low flow rate conditions, was performed on 250 mg (GLC purified on column F at 150 °C) with the sample vessel cooled to 0 °C in an ice water bath and the flowing pressure at 20 mTorr. The photolysis cell was changed every 2 h, and a total of 10 2-h photolyses was required for complete transfer. Analysis on column B at 90 °C showed that following product distribution: naphthalene (8.3 min), 10.4%; 2-MDHN (9.5 min), 9.0%; 2-MT (10.0 min), 3.3%; and 2-MN (14.9 min), 2.8%. The naphthalene and 2-MDHN were isolated by GLC on column G at 110 °C and identified by $^1$H NMR; the other two products were identified by coinjection with authentic samples.

**Gas-Phase Photolyses of 4-MDHN.** A sample of 4-MDHN was photolyzed under flowing conditions at 254 nm with the sample vessel maintained at room temperature (ca. 25 °C)) during the photolysis. The product mixture was analyzed by GC on column B at 100 °C ramped to 150 °C and found to consist of 10 major products (9.4% of the isolated reaction mixture on the basis of GLC integration). A 280-mg sample, purified by GLC on column E at 170 °C, was photolyzed at 254 nm under flowing conditions with the sample vessel at room temperature and a flowing pressure of 100 mTorr. The photolysis vessel was changed after the transfer of ca. 20–40 mg (5–15 min), and a total of 12 transfers left 20 mg of starting material in the reaction vessel. The unphotolyzed residue, as well as the product mixture, was analyzed by GLC on column B at 90 °C; the product mixture was 91.6% 4-MDHN and the residue pure starting material. Analysis by capillary GLC/MS on column A at 90 °C gave the following products and retention times: T13B, 5.42 min; IVB, 6.55 min; T12B, 8.44 min; 1-MDHN, 11.13 min; 1-M-1,4-DHN, 11.21 min; 1-MT, 11.46 min. The two hitherto unknown products were isolated by preparative GLC on column E at 160 °C ramped to 180 °C and their $^1$H NMR spectra compared to those of independently synthesized samples.

**1-Isopropenyl-2-vinylbenzene (IVB).** A three-neck round-bottom flask was equipped with a magnetic stir bar, a condenser with a nitrogen inlet tube, and an addition funnel. The apparatus was flame dried, and magnesium (0.69 g; 28.4 mmol) and ether (15 mL) were added to the flask. A solution of 2-bromostyrene (5 g; 27.3 mmol) in ether (15 mL) was placed in the addition funnel and added dropwise; the mixture was stirred for 2 h, but much of the magnesium was still unreacted. Acetone (3 mL; 40.9 mmol) was added dropwise to the Grignard reagent while the flask was cooled in an ice water bath. The mixture was warmed to room temperature, stirred for 1 h, and hydrolyzed by the addition of 40 mL of 1.0 N HCl. The layers were separated, the aqueous layer was extracted with ether, and the combined ether layers were washed with water, saturated $NaHCO_3$ solution, and brine solution. The ether solution was dried ($MgSO_4$) and evaporated to afford 3.47 g of the crude alcohol (48% by GLC analysis on column A at 140 °C). The alcohol was dehydrated in refluxing benzene (100 mL) with catalytic *p*-toluenesulfonic acid (0.20 g; 1.1 mmol). The usual workup provided 3.11 g of crude olefin which was purified by silica gel chromatography (hexane eluent) to give 1.97 g of pure IVB (63.9% yield). This was further purified by preparative GLC on column C at 150 °C for analysis: UV [$\lambda_{max}^{hexane}$ (log $\epsilon$)] 206 (4.31), 246 (4.13); FT-IR (neat) 3084, 3062, 3024, 2970, 2942, 2914, 1628, 1480, 1448, 1434, 1372, 1082, 994, 904, 762 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ 7.13–7.56 (m, aromatic, 4 H), 6.92 [dd, $J_{21}$ (cis) = 11.0 Hz, $J_{21}$ (trans) = 17.6 Hz, $HC{=}CH_2$, 1 H], 5.68 [d, $J_{12}$ (trans) = 17.6 Hz, trans $CH{=}CH_2$, 1 H], 5.20–5.24 (m, cis $CH{=}CH_2$ and $CH_3C{=}CH_2$, 2 H], 4.88 (s, $CH_3C{=}CH_2$, 1 H); 2.05 (d, $J$ = 1.0 Hz, methyl, 3 H); $^{13}$C NMR and APT ($CDCl_3$, 75.6 MHz) 144.8, 142,9, 134.8 (Ar C or vinyl quaternary C), 135.6, 128.0, 127.4 127.0, 125.3 (Ar CH or vinyl CH), 115.9, 114.3 (vinyl $CH_2$), 25.8 ($CH_3$); high-resolution MS (*m*/*e*) calcd 144.0939, found 144.0939.

**3-(*o*-Tolyl)-1,2-butadiene (T12B).** A sample of 1,1-dibromo-2-methyl-2-(*o*-tolyl)cyclopropane, prepared by the base-catalyzed addition of bromoform to 2-isopropenyltoluene, was added to a dry three-neck round-bottom flask equipped with a magnetic stir bar and a condenser with a nitrogen inlet tube. Ether (20 mL) was added to the flask, and the flask was cooled to −78 °C in an 2-propanol/dry ice bath. Methyllithium (1.5 M, 22 mL, 33 mmol) was syringed into the flask, and the almost immediate precipitation of lithium bromide was observed. The flask was warmed to room temperature, and the contents were stirred for 1 h, cooled to 0 °C in an ice water bath, and then quenched by 5 mL of $H_2O$. The layers were separated, the aqueous layer was extracted with ether, the combined ether extracts were washed with water, and the ether solution was dried with $MgSO_4$. Evaporation of the solvent under vacuum gave 0.80 g of the crude product, which was purified by preparative GLC on column C at 150 °C: UV [$\lambda_{max}^{hexane}$ (log $\epsilon$)] 239 (3.84); FT-IR (neat) 3070, 3020, 2980, 2960, 2930, 1995, 1490, 1460, 1440, 1425, 1060, 1040, 850, 760, 725, 610 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ 7.14–7.24 (m, aromatic, 4 H), 4.74 (q, $J$ = 3.2 Hz, C1 methylene, 2 H), 2.36 (s, Ar methyl, 3 H), 2.04 (t, $J$ = 3–4 Hz, allenic methyl, 3 H); $^{13}$C NMR and APT 207.6 (C2 allenic quaternary), 137.7, 135.8 (C5 and C6 Ar C), 130.5, 127.5, 126.9, 125.8 (C7, C8, C9, and C10 Ar CH), 98.9 (C3 quaternary vinyl), 74.2 (C1 methylene), 20.4, 20.3 (C4 and C11 methyls); high-resolution MS (*m*/*e*) calcd 144.0939, found 144.0939.

**Gas-Phase Photolyses of 1-MDHN.** A 15-mg sample of GLC-purified 1-MDHN was photolyzed under flowing conditions at 254 nm with the sample vessel maintained at room temperature and a flowing pressure of 160–200 mTorr. The product mixture was analyzed by GLC on column A at 130 °C and found to consist of five major products (19.1% of the total mixture on the basis of GC integration). These were identified as *cis*-1-propenyl-2-vinylbenzene (PVB; 7.0%), 3-MDHN (1.1%), 4-MDHN (3.3%), and naphthalene (2.0%). An unknown was also formed that was 2.1% of the product mixture. PVB was prepared in larger quantity by photolyzing a 100-mg sample of 1-MDHN under flowing conditions (200–250 mTorr) at 254 nm in five portions and isolating the product by GLC on column E at 160 °C, ramped to 200 °C: $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ 7.16–7.56 (m, aromatic, 4 H), 6.89 (dd, $J_{cis}$ = 11.0 Hz, $J_{trans}$ = 17.5 Hz, $HC{=}CH_2$, 1 H), 6.53 (dd, $J_1$ = 1.5 Hz, $J_2$ = 11.4 Hz, $HC{=}CH{-}CH_3$, 1 H), 5.86 (m, $HC{=}CH{-}CH_3$, 1 H), 5.67 (dd, $J_{gem}$ = 1.2 Hz, $J_{trans}$ = 17.6 Hz, $HC{=}CH_2$, 1 H), 5.26 (dd, $J_{gem}$ = 1.1 Hz, $J_{cis}$ = 11.0 Hz, $HC{=}CH_2$, 1 H); 1.69 (dd, $J_{allyl}$ = 1.6 Hz, $J_{gem}$ = 6.9 Hz, $HC{=}CH{-}CH_3$, 1 H).

**Preparative Static Photolysis of 3-MDHN with Butane.** Several static photolyses of 3-MDHN (300 mTorr) and butane (15 Torr) were carried out at 254 nm by filling the static gas-phase photolysis cell with the gases and allowing these to mix for 0.5 h. The mixture was photolyzed for 60 s and the product mixture analyzed by GLC on column D at 130 °C. Each photolysis provided approximately 90 μg of IBCB, and a total of 30 photolyses were performed to provide a combined product mixture containing 24.0% of this product. The mixture was enriched to 29% of IBCB by preparative GLC on column E with 62% of unreacted 3-MDHN also present: $^1$H NMR (ignoring the resonances of residual 3-MDHN) ($CDCl_3$, 300 MHz) $\delta$ 6.94–7.23 (m, aromatic, 4 H). 4.86 (s, vinyl, 1 H), 4.80 (s, vinyl, 1 H), 4.08 (br s, C1 methine, 1 H), 3.42 (dd, $J_{22'}$ = 13.9 Hz, $J_{12cis}$ = 5.6 Hz, C2 diastereotopic proton, 1 H), 2.96 (dd, $J_{2'2}$ = 13.8 Hz, $J_{12trans}$ = 2.8 Hz, C2 diastereotopic proton, 1 H), 1.79 (s, $CH_3$, 3 H); mass spectrum (capillary GLC/MS through column A)

($m/e$) EI $M^+ = 144$, CI $M + H = 145$.

**Preparative Static Photolyses of 4-MDHN at 300 nm.** Static photolyses were performed on 4-MDHN with the following modifications. A 2-L Kimax round-bottom flask was attached to the static gas-phase apparatus (isolated from the main vacuum line via a vacuum valve), placed inside the gas-phase reactor, and filled with 300 mTorr of 4-MDHN. The gas was photolyzed at 300 nm for 2 h, and the products were then pumped into a trap cooled to −196 °C. Analysis by GLC on column D at 100–150 °C, using octadecane as an internal standard, indicated a total conversion of 4-MDHN of 12%. A total of 48 such photolyses (2–5 h each) were performed, the products were combined, and MVBCB was isolated by preparative GLC on column E at 140 °C ramped to 180 °C. Analysis on column D at 100 °C showed 33.3% MVBCB and 65.9% T13B: $^1$H NMR (ignoring the resonances of T13B) ($CDCl_3$, 300 and 600 MHz) $\delta$ 7.06–7.25 (m, aromatic, 4 H), 6.17 (dd, $J_{cis} = 10.5$ Hz, $J_{trans} = 17.2$ Hz, vinyl CH, 1 H), 5.09 (dd, $J_{gem} = 1.7$ Hz, $J_{trans} = 17.1$ Hz, vinyl trans $CH_2$, 1 H), 4.98 (dd, $J_{gem} = 1.6$ Hz, $J_{cis} = 10.3$ Hz, vinyl cis $CH_2$, 1 H), 3.14 (d, $J = 13.7$ Hz, C2 $CH_2$ diastereomeric proton, 1 H), 3.03 (d, $J = 13.7$ Hz, C2 $CH_2$ diastereomeric proton, 1 H), 1.51 (s, $CH_3$, 3 H); mass spectrum (capillary GLC/MS through column A) ($m/e$) EI $M^+ = 144$, CI $M + H = 145$.

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# Diadamantylsilylene and Its Stereochemistry of Addition

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**Abstract:** Lithium-induced dehalogenation assisted by ultrasonic irradiation of diadamantyldiiodosilane in the presence of olefins and alkynes leads to high yields of 1,1-diadamantylsiliranes and 1,1-diadamantylsilirenes, respectively. The siliranes are precursors for the efficient thermal and photochemical generation of diadamantylsilylene ($Ad_2Si$:). The addition of thermally generated $Ad_2Si$: to *cis*- and *trans*-2-butene and -3-hexene is totally stereospecific, implying reaction from a singlet electronic state of the silylene. Photoisomerization of *cis*- and *trans*-1,1-diadamantylsiliranes complicates the study of the stereochemistry of addition of photogenic $Ad_2Si$:, but again a high degree of stereospecificity is observed.

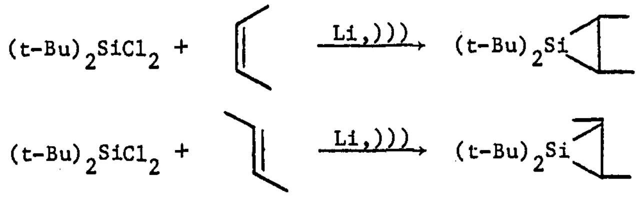
## Introduction

One of the original stimuli for the study of silylenes $R_2Si$:, molecules containing divalent silicon atoms, the silicon analogues of carbenes, was the recognition that silylenes like carbenes should possess several low-lying excited states, each potentially displaying distinctive reactivity.[1] With no verified exceptions, silylenes, unlike carbenes, have singlet ground states. We suggested in 1984[2] that a fruitful approach to triplet ground-state silylenes might be the generation of silylenes with such bulky substituents that the bond angle would be greatly enlarged from the 92° found for $:SiH_2$.[3] In the limit of linearity the nonbonding orbitals should be degenerate, and Hund's rule dictates a triplet ground state.

Ab initio calculations by Gordon predict that for unsubstituted $SiH_2$ the potential energy curves for the lowest singlet and triplet states cross at ca. 129°, with equilibrium bond angles of 93.38° for the singlet and 118.42° for the triplet.[4]

In the last few years, several sterically encumbered silylenes have been studied. Boudjouk and co-workers discovered the synthesis of siliranes via metal-promoted $\alpha$-elimination of dihalosilanes.[5] Treatment of dichloro-di-*tert*-butylsilane in the presence of *cis*- and *trans*-butene under ultrasonic irradiation led to the stereospecific formation of 1,1-di-*tert*-butyl-2,3-dimethylsiliranes (Scheme I).

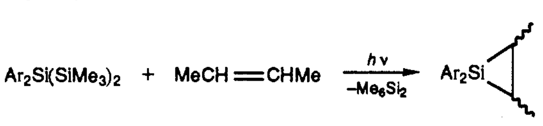
**Scheme I**



The expected product of insertion of $(t\text{-Bu})_2Si$: into the H–Si bond of triethylsilane was obtained upon lithium-promoted dehalogenation of all three dihalosilanes $(t\text{-Bu})_2SiX_2$ examined (X = Cl, Br, I).[5] Since dehalogenation in the absence of a silylene trapping agent did not give the same products from the three dihalosilanes, Boudjouk concluded that a "silylenoid" was the reactive intermediate in at least one of the three cases.[5]

Boudjouk and co-workers made the important discovery that both photolysis and pyrolysis of *cis*- and *trans*-1,1-di-*tert*-butyl-2,3-dimethylsilirane lead to the extrusion of di-*tert*-butylsilylene ($(t\text{-Bu})_2Si$:).[5] The free silylene from silirane dissociation was trapped by insertion into H–Si, H–O, and addition to C≡C bonds. Boudjouk attributed these reactions to a singlet ground-state silylene, although it is not clear that a triplet silylene would give different products from these reactions.

Ando and co-workers have studied the addition of bis(2,4,6-trialkylphenyl)silylenes to *cis*- and *trans*-2-butene:[6]



Ar = mesityl, 2, 4, 6-triisopropylphenyl

While addition of both di(mesityl)- and bis(2,4,6-triisopropylphenyl)silylene to *cis*-butene was nearly stereospecific, addition of both silylenes to *trans*-butene gave mixtures of *cis*- and *trans*-siliranes containing from 23 to 84% of the cis isomer. The largest yields of cis product were found in experiments in which the silylene was generated in a frozen matrix doped with *trans*-butene, and silylene addition was presumed to occur upon

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(1) Gaspar, P. P. *Reactive Intermediates (Wiley)* **1978**, *1*, 229; **1981**, *2*, 335; **1985**, *3*, 333.

(2) Workshop on Organosilicon Reactive Intermediates, Sendai, Japan, Sept 16–18, 1984, discussion following presentation by P. Boudjouk, Ultrasonic Waves and Reactive Organosilanes.

(3) Dubois, I.; Herzberg, G.; Varma, R. D. *J. Chem. Phys.* **1967**, *47*, 4262.

(4) Gordon, M. S. *Chem. Phys. Lett.* **1985**, *114*, 348.

(5) Boudjouk, U.; Samaraweera, R.; Sooriyakumaran, J.; Chrusciel, Anderson, K. R. *Angew. Chem., Int. Ed. Engl.* **1988**, *28*, 1355.

(6) Ando, W.; Fujita, M.; Yoshida, H.; Sekiguchi, A. *J. Am. Chem. Soc.* **1988**, *110*, 3310.

0002-7863/91/1513-1281$02.50/0