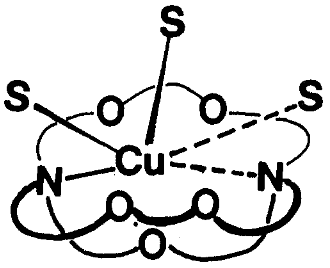
ion dissociates under the circumstances. The oxygen atoms in the bridges are able to rotate outward from the cavity, and this may form the basis of the initial interaction of the cation in the cavity with the solvent. Usually the dissociation of cryptates proceeds through two parallel paths, as already shown previously:[24] the acid-assisted path and the solvent path (i.e., acid-independent path). In $Me_2SO$, which is the most basic solvent, the solvent path prevails. Since the transition state for the dissociation reaction should be the same as for the formation reaction, it follows that the reactions would occur only through the (i,i) form. It is in the most plausible transition state **1** that one of the Cu–N bonds in the intermediate, i.e., the solvated copper(II) ion binding to two nitrogens atoms of the cryptand, is dissociated by the solvent attack. Thus, the process in which the second nitrogen atom binds to the copper(II) ion to form the solvated copper(II) binding to the two nitrogen atoms is the rate-determining step for the cryptate formation.[49]



**1**

We speculate that the complex formation and dissociation occur not through the smaller 15-membered ring of the cryptand but through the larger 18-membered ring, judging from both the ring size of the cryptand and the ionic radius of the metal ion.

The small values of the activation volume imply that, in the transition state, a volume increment caused by opening the cage is almost compensated for by a volume decrement due to electrostriction. The molal volume of the transition state for copper(II) cryptate is expected to be smaller in comparison to that of sodium(I) cryptate because there is no strong interaction between the sodium ion and the two nitrogen atoms. This is consistent with the fact that $\Delta V_f^{\ddagger}$ for $Cu^{2+}$ in $Me_2SO$ is smaller than that for $Na^+$ (see Table IV).

In conclusion, the results of the dynamics of the conformational change (i,o) $\rightleftharpoons$ (i,i) of cryptand 221 have shown that the main conformation of 221 is (i,i) in $Me_2SO$, DMF, and $CH_3CN$. The complexation of copper(II) ion with 221 proceeds via the Eigen–Winkler mechanism. Small values of the activation volume obtained by the first high-pressure study on the cryptate formation support the proposed mechanism.

**Acknowledgment.** The present work was supported by Grant-in-Aid for Scientific Research (No. 62470041) and for Scientific Research on Priority Area (No. 02245106) from the Ministry of Education, Science and Culture, Japan. We thank Professor H. Nomura (Nagoya University), Professor S. Yamada (Shizuoka University), and Dr. S. Kato (Nagoya University) for their generous advice for measurement of ultrasonic absorption spectra.

**Supplementary Material Available:** $\alpha/f^2$ values for cryptand 221 as a function of $f$ under various conditions (Table SI), rate constants for cryptate formation (Tables SII–SIV), and rate constants for cryptate dissociation (Table SV) (13 pages). Ordering information is given on any current masthead page.

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(48) Kauffmann, E.; Lehn, J.-M.; Sauvage, J.-P. *Helv. Chim. Acta* **1976**, *59*, 1099–1111.

(49) The proposed mechanisms for the cryptate formation are restricted to the solvent studied. The mechanisms in protic solvents are probably very different due to the interaction of the protic solvent with the nitrogen atoms of cryptands.

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# Photochemistry of 3-Methyl- and 4-Methyl-1,2-dihydronaphthalene in Solution[1]

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

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

**Abstract:** Photolysis of 3-methyl-1,2-dihydronaphthalene (3-MDHN) in hexane solution with 254-nm light produces one major product, 5-methylbenzobicyclo[3.1.0]hex-2-ene (5-MBBH; $\phi = 4.7 \times 10^{-4}$). Photolysis in hexane in the presence of trifluoroacetic acid produces exclusively 2-methylene-1,2,3,4-tetrahydronaphthalene (2-MTHN). The 254-nm photolysis of 4-methyl-1,2-dihydronaphthalene (4-MDHN) in hexane produces 2-(*o*-tolyl)-1,3-butadiene (T13B; $\phi = 2.2 \times 10^{-3}$), 1-methylbenzobicyclo[3.1.0]hex-2-ene (1-MBBH; $\phi = 1.4 \times 10^{-3}$), 1-methyl-1,4-dihydronaphthalene (1-M-1,4-DHN; $\phi = 8.7 \times 10^{-3}$), 1-methyltetralin (1-MT; $\phi = 1.5 \times 10^{-3}$), and 1-methylnaphthalene (1-MN; $\phi = 2.7 \times 10^{-3}$). Triplet sensitization of 4-MDHN produces only 1-MN in small amounts, suggesting that the direct photolyses proceed via singlet chemistry. The products appear to derive from a combination of electrocyclic opening of the cyclohexadienyl ring to generate an *o*-quinodimethane intermediate, disproportionation leading to net oxidation–reduction and, in 4-MDHN, a [1,3] hydrogen shift to form 1-M-1,4-DHN. The *o*-quinodimethane intermediates further react to form benzobicyclo[3.1.0]hex-2-ene derivatives (via a photochemical [4 + 2] cycloaddition; Scheme VI) and, in the case of 4-MDHN, the 1,3-butadiene T13B (via a thermal [1,5] hydrogen shift; Scheme VII).

Some time ago we reported the photoinduced alkyl migration reaction of alkylindenes in hexane solution via a C1/C2 transposition of the indenyl five-membered ring (Scheme I).[2] More recently, we reported[3] that the photolysis of alkylindenes in the gas phase also produces alkyl (as well as hydrogen) migration products, but deuterium and $^{13}C$ labeling[3,4] studies demonstrate

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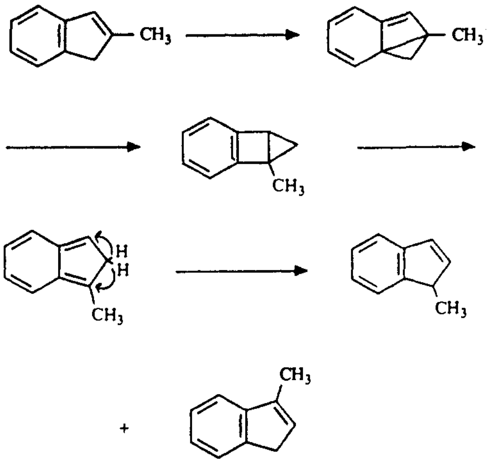
(1) *Organic Photochemistry*, Part 87. Part 86: Farrow, S. J.; Mohammad, T.; Baird, W. M.; Morrison, H. *Chem.-Biol. Interact.* **1990**, *75*, 105–113. Part 85: Nash, J. J.; Morrison, H. *J. Org. Chem.* **1990**, *55*, 1141–1143. Abstracted, in part, from the Doctoral Dissertation of Robert Duguid, Purdue University, Dec 1989.

(2) Morrison, H.; Giacherio, D.; Palensky, F. J. *J. Org. Chem.* **1982**, *47*, 1051–1058.

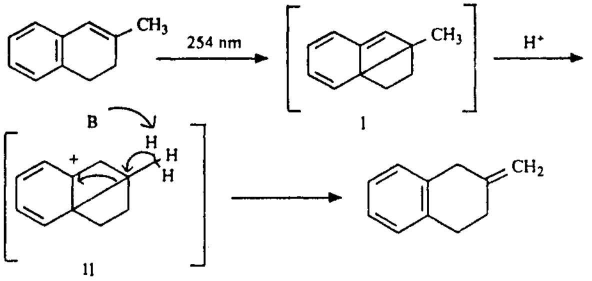
(3) Suarez, M. L.; Duguid, R. J.; Morrison, H. *J. Am. Chem. Soc.* **1989**, *111*, 6384–6391.

0002-7863/91/1513-1265$02.50/0

**Scheme I.** Mechanism for the Solution-Phase Skeletal Rearrangement of Alkylindenes[2]



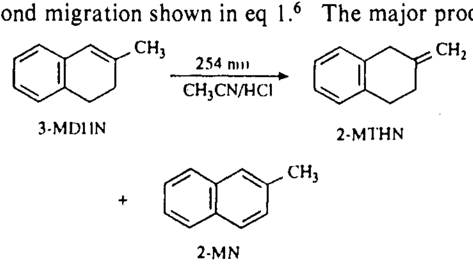
**Scheme II.** Possible Mechanism for the Formation of 2-MTHN upon Photolysis of 3-MDHN in Acidic Media[6]



that the gas-phase rearrangements proceed via a series of stepwise [1,2] alkyl and hydrogen shifts, possibly involving diradical intermediates. The gas-phase chemistry has been attributed[3] to reactions originating in upper electronic and vibrational excited states.

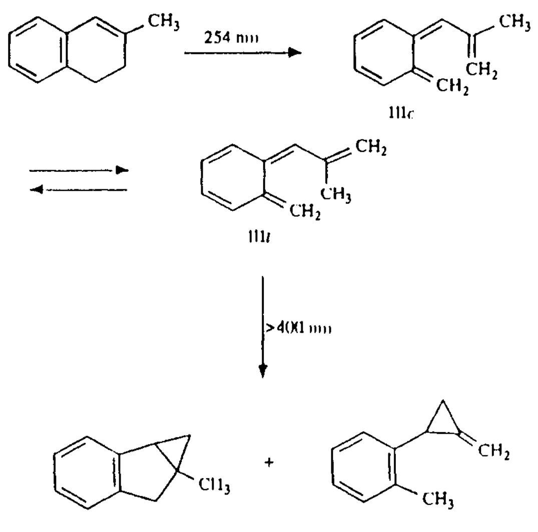
We now report the extension of these studies to the dihydronaphthalene series, specifically 3-methyl- and 4-methyl-1,2-dihydronaphthalene (3-MDHN and 4-MDHN, respectively). These compounds have been photolyzed in solution and in the gas phase, with our observations in solution reported herein and the gas-phase photochemistry discussed in the following companion paper.[5]

We are aware of no prior reports on the solution-phase photochemistry of 4-MDHN, but 3-MDHN has been previously studied by two laboratories.[6,7] We irradiated 3-MDHN in acidic acetonitrile with 254-nm light at room temperature and observed the double-bond migration shown in eq 1.[6] The major product [2-methylene-1,2,3,4-tetrahydronaphthalene (2-MTHN)] was formed with a quantum efficiency ($\phi$) of 0.027 and was accompanied by minor amounts of 2-methylnaphthalene (2-MN). Both acid and light were found to be essential for the reaction. A plausible mechanism was proposed by analogy with a mechanism put forward for a similar reaction seen in the alkylindene series[6] (Scheme II). A simple [1,3] hydrogen shift mechanism was eliminated for the alkylindenes (and by analogy for 3-MDHN) on the basis of the study of appropriately deuterium-labeled indenes.

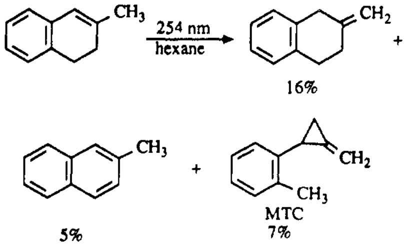


(1)[6]

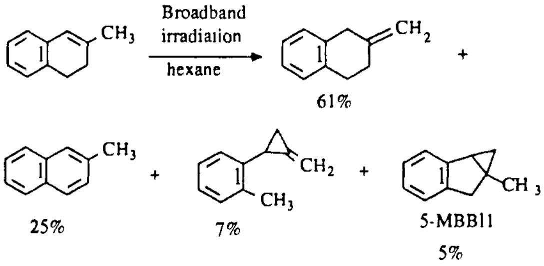
**Scheme III.** Proposed Biphotonic Mechanism for the Formation of MTC and 5-MBBH from 3-MDHN in Hexane[7]



A second study of 3-MDHN was conducted in hexane, using both 254-nm and broadband (i.e., unfiltered medium-pressure mercury lamp) light, with the results shown in eqs 2 and 3.[7] This paper indicates that acid is **not** required for the formation of 2-MTHN, and it is proposed[7] that this product is generated through a concerted photochemical [1,3] hydrogen shift. Both the 1-methylene-2-(*o*-tolyl)-cyclopropane (MTC) and 5-methylbenzobicyclo[3.1.0]hex-2-ene (5-MBBH) photoproducts are rationalized as being derived from an initially generated ring-opened intermediate (IIIt) through the two-photon process shown in Scheme III, thus the absence of 5-MBBH in the monochromatic photolysis. The proposal is by analogy with 1,2-dihydronaphthalene photochemistry (see Discussion) but does not explain why MTC is observed with monochromatic (e.g., 254 nm) light. In addition to the products shown in eq 3, a small amount (2%) of 2-methyl-1,4-dihydronaphthalene (2-M-1,4-DHN) was isolated when the photolysis was conducted at −45 °C and attributed to a retro-di-$\pi$-methane rearrangement of 5-MBBH.



(2)[7]



(3)[7]

The apparent contradiction in the observations of the two laboratories with regard to 2-MTHN was thus an additional source of our interest in the solution-phase photochemistry of 3-MDHN.

## Results

**Photolysis of 3-MDHN in Hexane.** Photolysis of an argon-degassed 1.1 mM solution of 3-MDHN in spectrograde hexane

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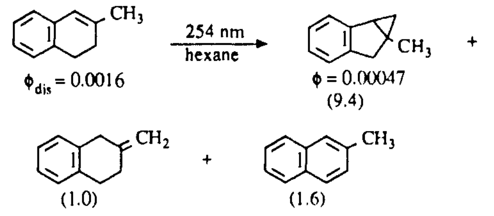
(4) Duguid, R. J. Doctoral Dissertation, Purdue University, 1989.

(5) Duguid, R. J.; Morrison, H. *J. Am. Chem. Soc.* **1991**, following paper in this issue.

(6) Morrison, H.; Giacherio, D. *J. Org. Chem.* **1982**, *47*, 1058–1063. Doctoral Dissertation of David Giacherio, Purdue University, Aug 1980.

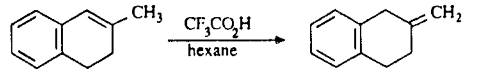
(7) Laarhoven, W. H.; Berendsen, N. *Recl. Trav. Chim. Pays-Bas* **1986**, *105*, 367–371.

at 254 nm (low-pressure mercury lamp) for 6 h produced one product that was later determined to be 5-methylbenzobicyclo-[3.1.0]hex-2-ene (5-MBBH). This product was isolated from a 24-h preparative photolysis and was identified by its $^1$H NMR spectrum (cf. Experimental Section). Two minor products were also detected in the preparative photolysis and were identified as 2-MTHN and 2-MN by their GLC retention times. No MTC was detected. The results of the preparative experiment are summarized in eq 4, together with quantum efficiencies for the disappearance of 3-MDHN and the formation of 5-MBBH.



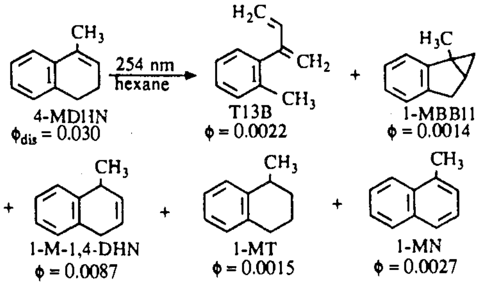
(4)

**Photolysis of 3-MDHN in Hexane and Trifluoroacetic Acid.** Hexane solutions containing 3-MDHN (1.1 mM) and several concentrations of trifluoroacetic acid (0.5, 1.0, 10 mM) were photolyzed at 254 nm for 6 h. The photolyses with 0.5 and 1.0 mM acid produced 2-MTHN exclusively (the photolysis with 10 mM acid completely consumed the 3-MDHN, but no photoproducts were observed) (eq 5). Control studies with 1.0 mM acid showed that neither 3-MDHN nor 5-MBBH is reactive in the dark.[8]



(5)

**Photolysis of 4-MDHN in Hexane.** A 9.88 mM argon-degassed solution of 4-MDHN in hexane was photolyzed at 254 nm for 11.67 h at room temperature. A total of five products were formed, as determined by GLC, at an overall conversion of starting material of 38.4%. The products were isolated and identified by comparison of their $^1$H NMR spectra to those of authentic samples or of data found with data in the literature (see eq 6). Quantum efficiencies for the formation of these products and for the disappearance of 4-MDHN are also reported in eq 6.



(6)

**Time Course Study for the Photolysis of 4-MDHN in Hexane.** An argon-degassed 5.08 mM hexane solution of 4-MDHN was irradiated at 254 nm for 90 min at room temperature while the reaction was monitored periodically by GLC. The time course of the reaction is plotted in Figure 1. The formation of each of the products, as well as the loss of 4-MDHN, was found to be linear with time.

**Photolysis of 4-MDHN in Hexane Using 300-nm Excitation.** A 6.14 mM solution of 4-MDHN in hexane was photolyzed at 300 nm for 2 h, at which time the total conversion of 4-MDHN to product was 32.0%. The five products observed by GLC were identical with those formed with 254-nm excitation, though in a slightly different ratio (cf. Table I).

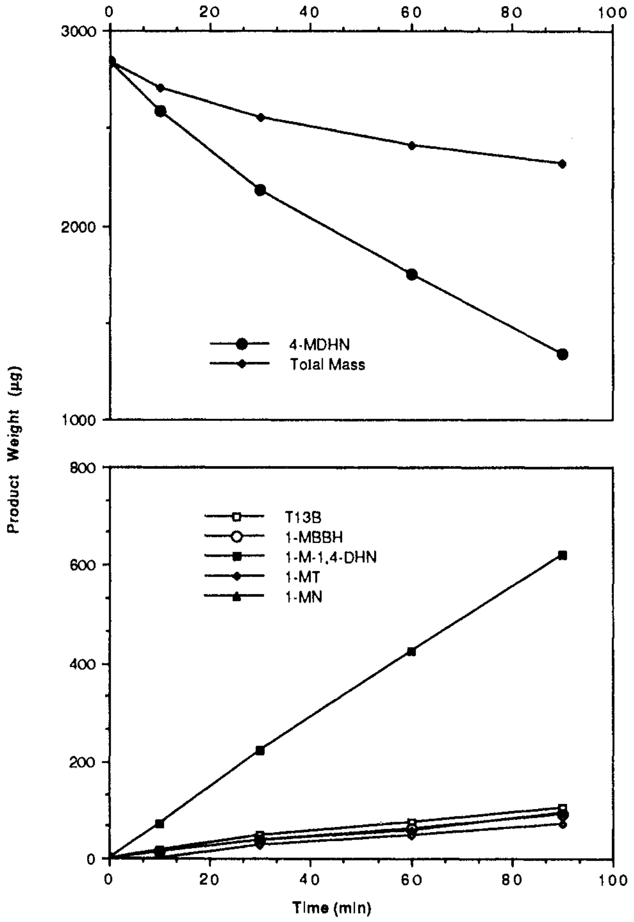


**Figure 1.** Time course plot for the photolysis of 4-MDHN in hexane.

**Table I.** Relative Photoproduct Formation for the Photolysis of 4-MDHN in Hexane at 254 and 300 nm

| compd | rel % product formation[a] 254 nm | rel % product formation[a] 300 nm |
|---|---|---|
| T13B | 11.1 | 2.8 |
| 1-MBBH | 9.3 | 6.3 |
| 1-M-1,4-DHN | 64.1 | 63.5 |
| 1-MT | 7.0 | 9.7 |
| 1-MN | 8.5 | 17.6 |

[a] Product percentages calculated relative to total amount of product formed.

**Fluorene Sensitization of 4-MDHN.** Fluorene ($E_T$ = 68 kcal/mol[9]) should be capable of triplet sensitization of 4-MDHN, if one assumes that the triplet energy for the latter is comparable to that of indene ($E_T$ = 63 kcal/mol[10]) and styrene ($E_T$ = 61.7[9]). A hexane solution of 4-MDHN (2.72 mM) and fluorene (74.7 mM) was thus prepared and irradiated at 300 nm, at which wavelength the fluorene absorbed approximately 92% of the incident light. Approximately 65% of the 4-MDHN was consumed after 4 h, but 1-MN was the only product observed (it accounted for 22% of the 4-MDHN lost). Since none of the other products from the direct photolysis were observed, we conclude that the direct photolysis of 4-MDHN (and, by analogy, 3-MDHN) proceeds primarily through the excited singlet state.

**Fluorescence and Excitation Spectra.** The corrected fluorescence excitation and emission spectra of 4-MDHN in hexane ($\simeq 10^{-5}$ M) are depicted in Figure 2. The fluorescence quantum efficiency was determined to be 0.018 by using biphenyl as the fluorescence standard ($\phi_f$ = 0.15).[9] The fluorescence quantum

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[8] A photolysis of 3-MDHN in the absence of acid, and further with added acid, indicates that 5-MBBH is photoreactive with acid. We cannot say what the products of this reaction are at this time. It is possible that 5-MBBH forms 2-MTHN under such conditions, but acid would have to also greatly accelerate the photoconversion of 3-MDHN to 5-MBBH to explain the much greater rate of formation of 2-MTHN in acid relative to the formation of 5-MBBH in neutral hexane.

[9] Murov, S. L. *Handbook of Photochemistry*; Dekker: New York, 1973; p 3.

[10] Harrigan, E. T.; Hirota, N. *Chem. Phys. Lett.* **1973**, *22*, 29–32.

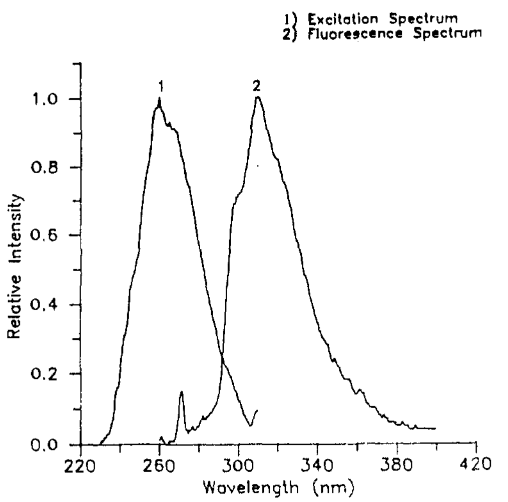
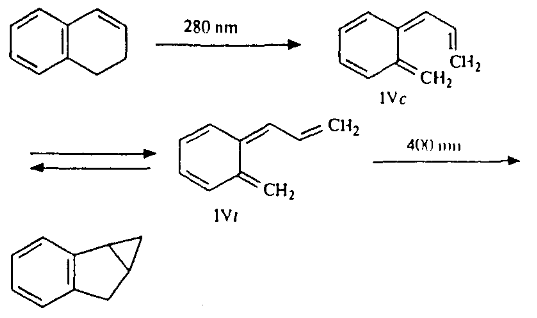


Figure 2. Excitation and fluorescence spectra for 4-MDHN in hexane solution.

**Scheme IV.** Proposed Biphotonic Mechanism for the Formation of Benzobicyclo[3.1.0]hex-2-ene from 1,2-Dihydronaphthalene[11]



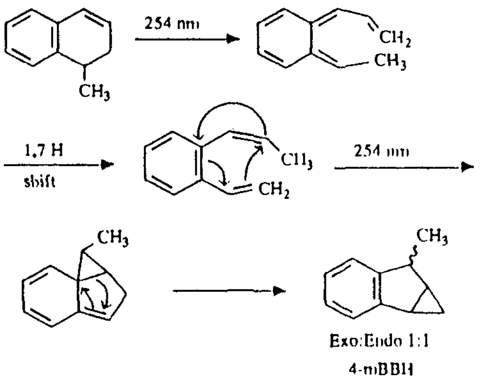
efficiency of 3-MDHN in hexane (2.2 × $10^{-5}$ M) was determined to be 0.0034.

## Discussion

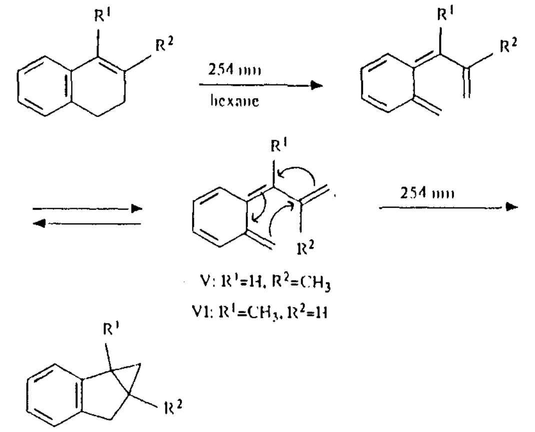
**Formation of Benzobicyclohexenes.** There are several anomalies in what we have observed by comparison with what has been reported in the literature. One is our observation of 5-MBBH upon photolysis of 3-MDHN (eq 4), whereas Laarhoven and Berendsen specifically report[7] that 5-MBBH is *not* formed from the 254-nm photolysis of 3-MDHN. They only observed the formation of 5-MBBH when 3-MDHN was irradiated with a broadband high-pressure mercury lamp (eq 3). Furthermore, they report the formation of MTC with 254-nm photolysis, a product we do not observe in any event. It is noteworthy that we also observe a benzobicyclohexene product (1-MBBH) from the 254-nm photolysis of 4-MDHN (eq 6).

The Laarhoven and Berendsen report that broadband light is needed for 5-MBBH formation appears to be consistent with the observation[11] that in the parent 1,2-dihydronaphthalene the formation of benzobicyclo[3.1.0]hex-2-ene requires a two-photon process; i.e., the "two-color" photolysis of 1,2-dihydronaphthalene, using 280- and 400-nm sources at right angles, results in the formation of benzobicyclo[3.1.0]hex-2-ene, while the removal of either beam eliminates this reaction. The proposed mechanism (Scheme IV) involves an initial photochemically allowed six-electron conrotatory ring opening to an *o*-quinodimethane intermediate (IVc), followed by bond rotation to form the more stable *s*-trans conformer (IVt). A second, **long-wavelength** photon then initiates a [4 + 2] closure to form the benzobicyclo[3.1.0]hex-2-ene product.[12]

**Scheme V.** Proposed Biphotonic Mechanism for the Formation of 4-MBBH from 1-Methyl-1,2-dihydronaphthalene[14]



**Scheme VI.** Proposed Biphotonic Mechanism for the Formation of 5-MBBH and 1-MBBH from 3-MDHN and 4-MDHN, Respectively



However, monochromatic 254-nm photolysis **is** reported to convert several 1-methyl- and 2-methyl-substituted 1,2-dihydronaphthalenes into benzobicyclo[3.1.0]hex-2-ene derivatives.[14] A two-photon process has still been invoked to explain these observations, with the postulate that the benzobicyclo[3.1.0]hex-2-ene derivatives are produced via the secondary photolysis of divinylbenzenes. This is illustrated in Scheme V for the conversion of 1-methyl-1,2-dihydronaphthalene into 4-methylbenzobicyclo[3.1.0]hex-2-ene (4-MBBH).[14] Critical to this mechanism is the proposal of a rapid, thermal [1,7] hydrogen shift in the initially formed *o*-quinodimethane, to generate *cis*-1-propenyl-2-vinylbenzene, which then undergoes a photoinitiated [4 + 2] closure followed by a vinyl cyclopropane rearrangement to 4-MBBH. (Divinylbenzenes are known to undergo photocyclization to benzobicyclo[3.1.0]hex-2-ene derivatives upon 254-nm photolysis.)[15] Clearly, a methyl group is needed in the 1- or 2-position of the 1,2-dihydronaphthalene to give an *o*-quinodimethane intermediate capable of the requisite [1,7] hydrogen shift. Since both 3-MDHN and 4-MDHN lack such a methyl group, the mechanism outlined in Scheme V cannot be applicable to these cases.

How, then, do we explain our observation in the formation of 5-MBBH and 1-MBBH using monochromatic radiation? We are forced to conclude that it is possible for 254-nm light to initiate a [4 + 2] reaction of the *o*-quinodimethane intermediate to form these benzobicyclohexene products (cf. Scheme VI).

Certainly, there should be no problem in achieving the requisite absorption of a 254-nm photon for the intramolecular cycloaddition since the absorption spectrum of the parent *o*-quinodimethane, *o*-xylylene, has been obtained in a rigid glass and shows an extinction coefficient at 254 nm of ca. 2000.[16] Furthermore, our

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[11] Salisbury, K. *Tetrahedron Lett.* **1971**, 737–739.

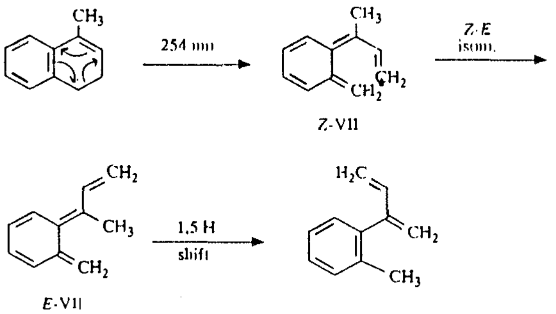
[12] There is evidence to suggest that an analogous [4 + 2] closure of a homologous *o*-quinodimethane is **not** a thermal reaction.[13] The formation of 4-*exo*-methyl-6-*exo*-benzobicyclo[3.1.0]hex-2-ene from *trans*-1,2-dimethyl-1,2-dihydronaphthalene, upon broadband irradiation with a corex filtered medium-pressure lamp, is enhanced from 20% at 20 °C to 50% at −70°C at the same total conversion of starting material.

[13] Seeley, D. A. *J. Am. Chem. Soc.* **1972**, *94*, 4378–4380.

[14] Heimgartner, H.; Ulrich, L.; Hansen, H. J.; Schmid, H. *Helv. Chim. Acta* **1971**, *54*, 2313–2354.

[15] Laarhoven, W. H. *Org. Photochem.* **1989**, *10*, 163–308.

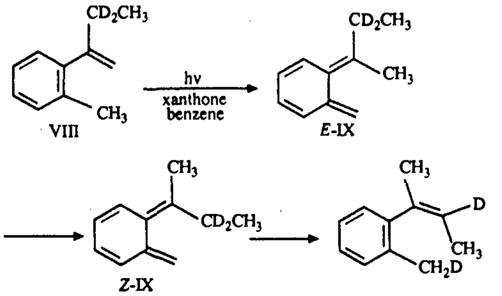
**Scheme VII.** Proposed Mechanism for the Formation of T13B from 4-MDHN



proposal has precedent in the reported photochemical conversion of 4-phenyl-1,2-dihydronaphthalene into 1-phenylbenzobicyclo-[3.1.0]hex-2-ene using 254-nm light.[17] The reaction has been attributed to the secondary 254-nm photolysis of an initially formed *o*-quinodimethane.[17,18] [Note that 300-nm light also is capable of generating 1-MBBH (see below).]

**Formation of 2-(*o*-Tolyl)-1,3-butadiene (T13B) from 4-MDHN.** A mechanism for the formation of T13B is outlined in Scheme VII. Initial photochemical opening of 4-MDHN generates the *o*-quinodimethane *Z*-VII, which then undergoes *Z*/*E* isomerization to (*E*)-VII. A [1,5] hydrogen shift generates the observed 1,3-butadiene product.

The *Z*/*E* isomerization of the *o*-quinodimethane intermediates has precedent in the literature, although it is not well understood.[19] Triplet-sensitized photolysis of 2-(*o*-tolyl)-3,3-dideuterio-1-butene (VIII) generates an *o*-quinodimethane derivative [(*E*)-IX], which then undergoes geometric isomerization to (*Z*)-IX followed by a [1,5] deuterium shift to form the observed product (cf. eq 7).[20]



(7)

The [1,5] hydrogen shift of the (*E*)-VII in Scheme VII intermediate also has precedent in the literature.[21a] Such a [1,5] hydrogen shift is photochemically allowed in an antarafacial mode, a process that is favored when steric constraints force the *o*-quinodimethane to be nonplanar. There is recent evidence that a photochemically driven, presumably antarafacial, [1,5] hydrogen shift is 10 orders of magnitude faster than the corresponding thermal process.[21b] However, since (*E*)-VII is not sterically congested, and would be expected to be relatively planar, we cannot rule out a hydrogen shift in this case via a thermal, suprafacial process.

An interesting wavelength effect was observed for the formation of T13B. Photolysis of 4-MDHN in hexane at 300 nm led to a 4-fold reduction in the relative formation of T13B by comparison with that seen in the 254-nm photolysis (see Table I). This is in part due to less effective ring scission with 300-nm irradiation since the sum of T13B and 1-MBBH is reduced at 300 nm relative to the total of the oxidation and reduction products. However, the ratio of T13B to 1-MBBH is 1.2 at 254 nm and 0.44 at 300 nm; i.e., once ring opening has occurred, the relative formation of T13B is substantially reduced when longer wavelength light is employed (consistent with a photolytic *Z*/*E* isomerization step in Scheme VII).[20]

**Hydrogen-Shift Photochemistry.** It was noted at the outset of the Discussion that there are several anomalies resulting from a comparison of this work with reports in the literature. These include the report[7] that the double-bond shift product, 2-MTHN, is the major photoproduct of 3-MDHN, with 2-MN and MTC appearing as minor products (eq 2). By contrast, we find that 2-MTHN is only formed upon extended irradiation (possibly as a secondary photoproduct of 5-MBBH; see below) or **when acid has intentionally been added to the photolysis solution** (compare eqs 4 and 5).[8] Since Laarhoven and Berendsen observe 2-MTHN as the major product at a modest (28%) conversion of 3-MDHN, the discrepancy between their work and ours cannot be attributed to overirradiation. We are forced to conclude that the hexane solvent used by these workers was contaminated by acidic impurities.

However, there is a hydrogen-shift product, 1-methyl-1,4-dihydronaphthalene (1-M-1,4-DHN), that indeed constitutes the major photoproduct from 4-MDHN. It has been reported[11] that 1,2-dihydronaphthalene generates 1,4-dihydronaphthalene upon irradiation at 280 nm in solution and that photolysis of 4-phenyl-1,2-dihydronaphthalene at 254 nm in solution produces 1-phenyl-1,4-dihydronaphthalene.[17] The mechanism of the first reaction is not discussed, and the second was attributed to a secondary photolysis of initially formed 1-phenylbenzobicyclo-[3.1.0]hex-2-ene. The photolysis of 4-phenyl-1,2-dihydronaphthalene at 300 nm gave no 1-phenyl-1,4-dihydronaphthalene (attributed to a lack of absorption of 300-nm light by 1-phenylbenzobicyclo[3.1.0]hex-2-ene),[17] and the direct photolysis of the bicyclic intermediate at 254 nm has been shown to produce 1-phenyl-1,4-dihydronaphthalene.[22]

We find no evidence that 1-M-1,4-DHN is a secondary photoproduct (see Figure 1) and the formation of 1-M-1,4-DHN at 300 nm occurs with the same relative efficiency as at 254 nm (Table I). We thus favor a photochemically allowed suprafacial [1,3] hydrogen shift as the source of 4-MDHN in the photolysis of 1-MBBH.

**Oxidation-Reduction Photochemistry.** The photolysis of 3-MDHN produces the oxidation product 2-methylnaphthalene (2-MN) at long irradiation times, while the photolysis of 4-MDHN produces both the oxidation product 1-methylnaphthalene (1-MN) and the reduction product 1-methyltetralin (1-MT). Though the formation of 1-MN and 1-MT from 4-MDHN could be rationalized as a disproportionation involving two molecules of 4-MDHN, the fact that the quantum efficiency for 1-MN formation ($\phi = 0.0027$) is approximately twice that for 1-MT ($\phi = 0.0015$) indicates that the photolytic redox reaction involves an oxidant other than just 4-MDHN. This conclusion is supported by the fact that no reduction product is observed for 3-MDHN. A similar quandry was faced by Laarhoven and Berendsen[7] (eq 2), and we can only assume that a trace amount of oxygen in the solution, due to inefficient deoxygenation, is the other oxidant.

## Conclusions

Several, apparently singlet states derived, reaction pathways are available to 3-MDHN and 4-MDHN upon photolysis in solution, i.e., electrocyclic opening of the cyclohexadienyl ring to generate an *o*-quinodimethane intermediate, disproportionation leading to net oxidation-reduction, and a [1,3] hydrogen shift in 4-MDHN to form 1-methyl-1,4-dihydronaphthalene (1-M-1,4-

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(16) Flynn, C. R.; Michl, J. *J. Am. Chem. Soc.* **1974**, *96*, 3280-3288.

(17) Lamberts, J. J. M.; Laarhoven, W. H. *Recl. Trav. Chim. Pays-Bas* **1984**, *103*, 131-135.

(18) The quantum efficiencies for formation of 5-MBBH from 3-MDHN and 1-MBBH from 4-MDHN are 0.00047 and 0.0014, respectively. The greater reactivity of the 4-methyl isomer may be due to the steric requirements of the methyl group in the *s-trans-o*-quinodimethane intermediate, V, derived from 3-MDHN. This may destabilize the *s*-trans conformer relative to *s*-cis; retrocycloaddition of the latter would lead back to starting material.

(19) Hornback, J. M.; Barrows, R. D. *J. Org. Chem.* **1982**, *47*, 4285-4291.

(20) It is unclear as to whether the reported information is thermal or photochemical. However, it appears from data presented in the following paper[5] that the isomerization is a photochemical reaction.

(21) (a) McCullough, J. J. *Acc. Chem. Res.* **1980**, *13*, 270-276. (b) Wintgens, V.; Netto-Ferreira, J. C.; Casal, H. L.; Scaiano, J. C. *J. Am. Chem. Soc.* **1990**, *112*, 2363-2367.

(22) Lamberts, J. J. M.; Laarhoven, W. H. *J. Org. Chem.* **1983**, *48*, 2202-2206.

DHN). In our hands, a net [1,3] hydrogen shift of 3-MDHN is at best a minor, and possibly secondary, reaction, except in the presence of acid, whereupon the product may be formed via deprotonation and ring opening of an initially formed intramolecular [2 + 2] cycloadduct (Scheme II). The *o*-quinodimethane intermediates further react to form benzobicyclo[3.1.0]hex-2-ene derivatives (via a photochemical [4 + 2] cycloaddition; Scheme VI) and, in the case of 4-MDHN, the 1,3-butadiene T13B (via a thermal [1,5] hydrogen shift; Scheme VII).

## 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), trifluoroacetic acid (MCB), and fluorene (MCB) were stored at room temperature and were used as received. (*E*)-1-Phenyl-2-butene (Pfaltz and Bauer) was vacuum distilled and was purified by GLC (column E at 140 °C) prior to use. Hexane used in the photochemical and spectroscopic studies was of spectroquality grade from Burdick and Jackson. 3-Methyl-1,2-dihydronaphthalene (3-MDHN) was prepared by either (1) LAH reduction of 2-methyl-1-tetralone (Aldrich) followed by dehydration or (2) addition of $CH_3MgI$ to β-tetralone (Aldrich) followed by dehydration. 4-Methyl-1,2-dihydronaphthalene (4-MDHN) was prepared by $CH_3MgI$ addition to α-tetralone (Aldrich) followed by dehydration.

**Chromatography.** Analytical GLC analyses were performed on a Hewlett-Packard Model 5710A gas chromatograph equipped with a capillary injector or on a Varian Model 3700 capillary gas chromatograph (both with flame ionization detectors). The chromatograms were integrated with a Hewlett-Packard Model 3390A integrator. The following columns were used in all the analytical work: (A) 30 m × 0.25 mm i.d. DB-Wax capillary column (J&W Scientific) with a 0.50-μm film thickness; (B) 30 m × 0.25 mm i.d. RSL-150 capillary column (Alltech) with a 0.25-μm film thickness; (C) 30 m × 0.25 mm i.d. Superox capillary column (Alltech) with a 0.25-μm film thickness; (D) 50 × 0.25 mm i.d. GB-20M capillary column (Foxboro) with a 0.25-μm film thickness. Preparative GLC separations were performed on a Varian Model 3300 gas chromatograph, modified to accommodate 0.25-in. columns, and were investigated by either Hewlett-Packard 3390A or 3393A integrators. The following columns were used for the preparative GLC work: (E) 16 ft × 0.25 in. 25% XF-1150 on 60/80 AW Chromasorb P at 50–60 mL of He/min; (F) 10 ft × 0.25 in. 10% Carbowax 20M on 60/80 AW-DMCS Chromasorb W at 60 mL of He/min.

**Spectroscopy.** Qualitative and quantitative $^1H$ and $^{13}C$ NMR spectra were obtained with a General Electric QE-300 300-MHz NMR spectrometer. Mass spectra were obtained on a Finnigan 4000 mass spectrometer interfaced to a gas chromatograph containing an OV-17 or OV-101 packed column or a DB-1 capillary column. The mass spectrometer was operated at a source temperature of 250 °C. Electron impact (EI) spectra were obtained at an ionization energy of 70 eV, and chemical ionization (CI) spectra were also obtained at 70 eV by using isobutane at a pressure of 0.30 Torr. Ultraviolet spectra were recorded on either a Hewlett-Packard Model 8451A diode array spectrophotometer equipped with a Hewlett-Packard Model 98155 data handling system, a Cary Model 17D spectrophotometer, or a Perkin-Elmer Model Lambda 3B spectrophotometer that was interfaced to a Zenith Z157 microcomputer controlled by Perkin-Elmer Computerized Spectroscopy Software (PECSS). Single-wavelength measurements were recorded on the Perkin-Elmer Lambda 3B or on a Gilford modified Beckman DU instrument. Fluorescence excitation spectra were obtained on a component fluorometer.[3]

**Photolyses.** Photolyses were performed in quartz tubes in a turntable reactor equipped with a Hanovia Model 688A-45 low-pressure mercury resonance lamp or in a Rayonet reactor (Model RPR-100; Southern New England Ultraviolet Co.). The Rayonet reactor was equipped with sockets for 16 lamps (either 2357- or 3000-Å lamps were used), a merry-go-round turntable, and a cooling fan. Some preparative photolyses were performed in a quartz immersion well which held approximately 150 mL of solution. A Hanovia low-pressure mercury lamp was placed in a quartz insert inside the immersion well, and the lamp was maintained at ambient temperature by cooling with a stream of air. Actinometry was performed by using the *E*/*Z* isomerization of (*E*)-1-phenyl-2-butene, for which the quantum efficiency for formation of *Z* has been determined to be 0.20.[23] One actinometer solution was irradiated at the beginning of the photolysis and the other at the end of the photolysis to provide a time average of the photon flux over the course of the photolysis. The amount of the *Z* isomer formed was determined by GLC on column A at 110 °C; the retention times of the two isomers were 9.9 and 10.88 min for the *E* and *Z* isomers, respectively. Conversions to the *Z* isomer were corrected for back reaction.

**Photolysis of 3-MDHN in Hexane.** An argon-degassed 1.1 mM solution of 3-MDHN in hexane was photolyzed in the turntable reactor with the low-pressure mercury lamp (254 nm) for 6 h. The irradiated solution gave evidence for one product upon analysis by GLC on column C at 150 °C. For preparative purposes, an 8.73 mM solution of 3-MDHN in hexane (100 mL) was added to a quartz immersion well and degassed by argon bubbling for 30 min prior to photolysis and continuously throughout the photolysis. The solution was photolyzed at 254 nm with a mercury low-pressure lamp for 24 h. The product mixture was analyzed by GLC on column C at 100 °C and showed the following product distribution based on peak integration: 6.9 min, 29.0%; 12.3 min, 3.1%; 26 min, 5%. Three other photoproducts were formed in trace amounts.

The major (6.9 min) product was isolated by preparative GLC on column F at 150 °C and found to have an NMR spectrum identical with that reported for 5-MBBH in the literature.[7] The 3.1% product was found to have the same retention time as a sample of 2-MTHN prepared by the method described by Giacherio.[6] The third product was isolated in a subsequent photolysis of 10 mM 3-MDHN in hexane and identified as 2-MN by its $^1H$ NMR spectrum.

**Photolysis of 3-MDHN in Hexane with Trifluoroacetic Acid.** Aliquots of three hexane solutions, each 1.1 mM in 3-MDHN and also 0.5, 1.0, or 10 mM in trifluoroacetic acid, were photolyzed at 254 nm with the low-pressure mercury lamp for 6 h. After photolysis, the solutions were washed with 5% $NaHCO_3$ solution, dried over $Na_2SO_4$, and analyzed on column C at 150 °C. 2-MTHN was the only product detected in the solutions containing 0.5 and 1.0 mM $CF_3CO_2H$; the solutions containing 10 mM $CF_3CO_2H$ generated no volatile products, though the starting material was completely consumed. 3-MDHN was unchanged in a dark control containing 1.0 mM $CF_3CO_2H$.

**Photolysis of 4-MDHN in Hexane.** Ten quartz tubes, each containing 5 mL of hexane 9.88 mM in 4-MDHN, were deoxygenated with argon and photolyzed for 11.67 h at 254 nm with a mercury low-pressure lamp in the turntable apparatus. Five products were detected by GLC (column B at 90 °C): 5.9 (5.5%), 9.0 (4.6%), 11.5 (28.7%), 12.0 (6.5%), and 18.4 min (2.2%). The solutions were combined, and the products were isolated by preparative GC on column E at 160 °C ramped to 180 °C. Three of the products are known compounds, and their structures were assigned by a consideration of their NMR spectra, i.e., 1-methyl-1,4-dihydronaphthalene (1-M-1,4-DHN; 11.5 min),[24] 1-methyltetralin (1-MT; 12.0 min), and 1-methylnaphthalene (1-MN; 18.4 min). Two products are new compounds; their syntheses are described below.

**2-(*o*-Tolyl)-1,3-butadiene (T13B; 5.9 min).** A three-neck round-bottom flask equipped with a magnetic stir bar, a condenser with nitrogen inlet tube, and an additional funnel was flame dried under a stream of nitrogen. To the flask was added 16 mL of 1.0 M vinylmagnesium bromide (16 mmol) in THF. A solution of 2′-methylacetophenone (2.05 g; 15.3 mmol) in THF (10 mL) was added to the addition funnel. The ketone solution was added dropwise to the Grignard reagent. After stirring for 2 h at room temperature, the reaction mixture was hydrolyzed by adding saturated $NH_4Cl$ solution until neutral pH was reached. The reaction mixture was partitioned between ether and water, and the layers were separated. The aqueous layer was extracted with ether, and the combined ether extracts were washed with water. The ether solution was dried ($MgSO_4$), and the ether was evaporated under vacuum to afford 2.5 g of the crude alcohol (100% yield). The alcohol was analyzed by FT-IR (neat) and showed two major bands at 3418 and 1676 $cm^{-1}$. The alcohol was dehydrated by the addition of 15% aqueous $H_2SO_4$ and the diene product distilled as its $H_2O$ azeotype. The diene/water mixture was extracted with ether (20 mL), and the ether layer was separated and dried ($MgSO_4$). The ether was evaporated under vacuum to produce 1.01 g of the diene (45% yield), which was purified by silica gel chromatography (hexane eluent). Analysis of the purified product by GLC on column D at 90 °C indicated pure T13B: UV [$\lambda_{max}^{hexane}$ (log $\epsilon$)] 215 (4.21), 254 (1.95); FT-IR analysis (neat) 3088, 3062, 3020, 2970, 2924, 1590, 1488, 1456, 1382, 1038, 990, 902, 766, 730 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 300 MHz) $\delta$ 7.06–7.21 (m, aromatic, 4 H), 6.60 [dd, $J_1$ (trans) = 17.3 Hz, $J_2$ = 10.4, C3 vinyl, 1 H], 5.38 [d, $J$ (gem) = 1.1 Hz, C1 vinyl, 1 H], 5.11 [d, $J$ (cis) = 10.4 Hz, C4 vinyl, 1 H], 5.05 (s, C1 vinyl, 1 H), 4.70 [d, $J$ (trans) = 17.4 Hz, C4 vinyl, 1 H], 2.20 (s, methyl, 3 H); $^{13}C$ and APT analysis ($CDCl_3$, 75.6 MHz) $\delta$ 148.5 (Ar C or C2), 139.4 (Ar C or C2), 138.6 (Ar CH or C3), 135.9 (Ar C or C2), 129.7 (Ar CH or C3), 129.5 (Ar CH or C3), 127.2 (Ar CH or C3), 125.4 (Ar CH or C3), 118.1

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*J. Am. Chem. Soc.* **1991**, *113*, 1271-1281

(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.

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

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**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.

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