

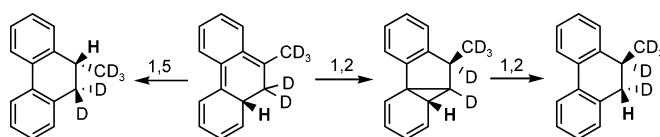
Competitive 1,2- and 1,5-Hydrogen Shifts Following 2-Vinylbiphenyl Photocyclization

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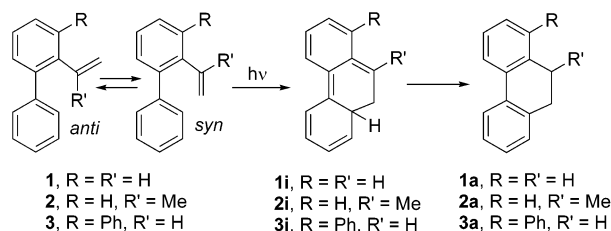


The photocyclization of 2-vinylbiphenyl and its derivatives has been proposed to occur via a two-step mechanism: photocyclization to form an unstable 8a,9-dihydro-phenanthrene intermediate, followed by exothermic unimolecular isomerization to a 9,10-dihydrophenanthrene. The mechanism of the hydrogen shift process has been investigated using deuterated derivatives of 2-isopropenylbiphenyl and 2,6-diphenylstyrene. ¹H NMR analysis of the photoproducts indicates that the thermally allowed 1,5-hydrogen or deuterium shift is a minor product-forming pathway and that an unusual double 1,2-hydrogen or deuterium shift is the major product-forming pathway. The potential energy surface for photocyclization and hydrogen shift processes has been explored computationally. The calculated barrier for the 1,5-shift is predicted to be significantly lower than that for the 1,2-shift. Alternative mechanisms for the occurrence of 1,2-hydrogen or deuterium migration are presented.

Introduction

The thermal sigmatropic 1,5-hydrogen shift reactions of cyclic dienes provide textbook examples of pericyclic reactions.¹ In contrast to the extensively documented reactions of cyclopentadienes, the analogous reactions of 1,3-cyclohexadienes have received relatively little attention. An investigation of the rearrangement of 1,4-*d*₂-cyclohexadiene provided a value of *E*_a = 41 kcal/mol,² substantially higher than that for cyclohexadiene, 24.3 kcal/mol.³ Density functional calculations have reproduced the higher experimental barrier for cyclohexadiene, which is attributed to added strain in the transition state, which has both a larger H⋯C⋯H angle and longer C₁–C₅ distance when compared to the transition state for cyclopentadiene.^{4,5}

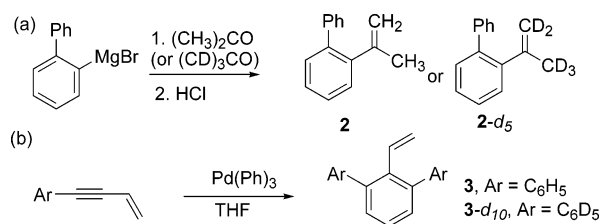
SCHEME 1



Our interest in the thermal rearrangement of cyclohexadienes was stimulated by recent studies of the photochemical reactions of 2-vinylbiphenyls.^{6,7} The photochemical conversion of 2-vinylbiphenyl **1** to 9,10-dihydrophenanthrene **1a** (Scheme 1) was initially described by Horgan et al.⁸ They proposed a two-stage

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SCHEME 2



mechanism for product formation: photocyclization to yield the unstable 8a,9-dihydrophenanthrene **1i** followed by a thermal intramolecular hydrogen shift to yield **1a**. As a consequence of the gain in aromaticity, the 1,5-hydrogen shift is highly exothermic. Alabugin et al. have calculated values of $\Delta H_{\text{rxn}} = -54$ kcal/mol and $E_a = 17$ kcal/mol for the 1,5-hydrogen shift of **1i**.⁵

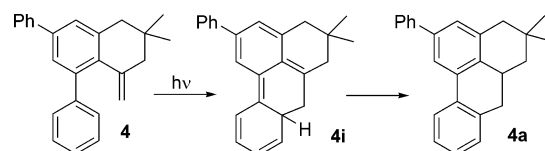
The photocyclization of **1** and other vinylbiphenyls is subject to ground state conformational control, cyclization occurring from the minor conformer *syn*-**1** but not from the major conformer *anti*-**1** (Scheme 1).⁷ Since the singlet *anti* conformer is unreactive, the quantum yield for the formation of **1a** is low (<0.01), even though the preparative yield is quantitative. An increase in the ground-state population of *syn*-**2** is accompanied by an increase in the quantum yield for cyclization. 2-Vinyl-1,3-terphenyl **3** undergoes photocyclization to yield **3a** in high quantum yield upon irradiation in fluid solution, as a consequence of symmetry-enforced conformational control.⁶ Irradiation of **3** at 77 K in a methylcyclohexane glass results in the formation of a dark purple product assigned to the intermediate **3i**. However, upon warming the glass to 120 K, the color disappears within a few seconds, indicative of a thermal barrier much lower than the value calculated for **1i**.⁹

To obtain further information about the rearrangement mechanism, we have investigated the photochemical behavior of deuterated derivatives of **2** and **3**. ¹H NMR spectral analysis of the photocyclization products obtained from these derivatives indicates that a double 1,2-hydrogen shift is the major pathway for product formation at room temperature. Barriers for the 1,5- and 1,2-hydrogen shifts and ring-opening isomerization of **2i** have been calculated at the B3LYP/6-311G**//B3LYP/6-31G** level and provide the basis for discussion of the isomerization mechanism.

Results and Discussion

Synthesis and Photochemical Behavior. The syntheses of **2** and **3** and their deuterated analogues **2-d₅** and **3-d₁₀** are outlined in Scheme 2. Reaction of 2-biphenyl-magnesium bromide and acetone or acetone-*d*₆, followed by acid-catalyzed dehydration, affords **2** and **2-d₅**, respectively. The synthesis of **3** via the palladium-catalyzed homodimerization of 1-(but-3-en-1-ynyl)benzene has been reported.¹⁰ Reaction of the *d*₅-phenyl analogue provided **3-d₁₀**. Synthetic procedures and product characterization are described in Experimental Section.

SCHEME 3



The photochemical behavior of **1–3** has been reported.^{6,7} Irradiation at 298 K in cyclohexane solution results in quantitative conversion to the cyclized isomers **1a–3a** (Scheme 1). The quantum yields for formation of **3a** and **3a-d₁₀** at 298 K are identical. Irradiation of **3** at 77 K in a methylcyclohexane (MC) glass results in the formation of a 535 nm absorption band assigned to the intermediate **3i**.⁶ No long-wavelength absorption band is observed upon irradiation of **1** in a MC glass at 77 K, and a very weak band is observed for **2**, in accord with the low populations of their reactive *syn* rotamers at low temperature.⁷ The 535 nm band assigned to **3i** disappears rapidly upon warming of the glass, and it is not observed when either **3** or **3-d₁₀** are irradiated at 90 K in liquid propane.

We have also attempted to study the formation and decay of **3i** by means of femtosecond time-resolved pump–probe spectroscopy of **3** at room temperature. A weak transient with an absorption maximum at 510 nm is formed within the ca. 1 ps rise time of the exciting 267 nm laser pulse and decays with a lifetime longer than the 100 ps probe period. This result is consistent with an earlier report by Fournier de Violet et al. of the observation of a 510 nm intermediate with a decay time of ca. 1 ms upon laser flash photolysis of a 2-vinylbiphenyl derivative.¹¹

A long wavelength intermediate is observed upon irradiation of the conformationally constrained 2-vinylbiphenyl derivative **4** in liquid propane at low temperatures (Scheme 3). The first-order kinetics for thermal bleaching of the absorption band assigned to **4i** over the temperature range 90–130 K provides values of $E_a = 2.5$ kcal/mol and $\log A = 3.3$, which are consistent with a tunneling mechanism.¹²

Deuterium Labeling Studies. The upfield region of the ¹H NMR spectra of the products obtained following irradiation of **2** and **2-d₅** in cyclohexane solution are shown in Figure 1. The spectrum of **2a** has been assigned by Harvey et al. and is consistent with the chemical shifts and coupling constants.¹³ Comparison of the spectrum of the product obtained from **2-d₅** with that from **2** indicates that aromatization of the putative intermediate **2i** occurs predominantly via a 1,2-hydrogen migration rather than a 1,5-hydrogen migration (Scheme 4a). A ratio of ca. 90:10 for 1,2- vs 1,5-migration products can be calculated from the integrated peak areas for **2a-d₅**.

The upfield region of the ¹H NMR spectra of solutions of **3** and **3-d₁₀** obtained following irradiation in cyclohexane solution are shown in Figure 2. ¹H NMR assignments for the two methylene multiplets of **3a** proved essential to the interpretation of the deuterium labeling studies.

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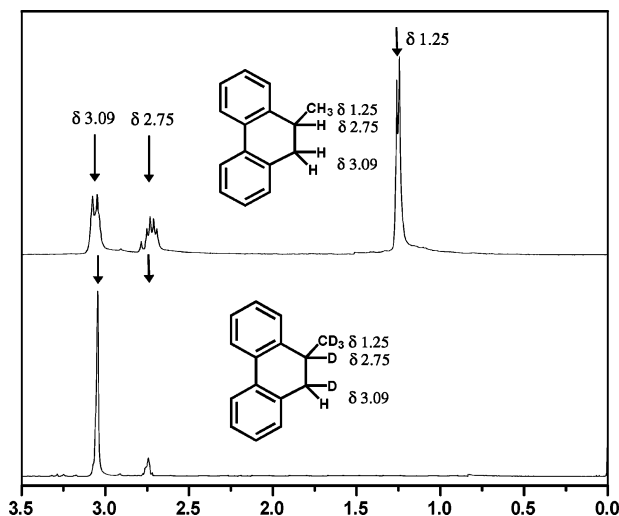
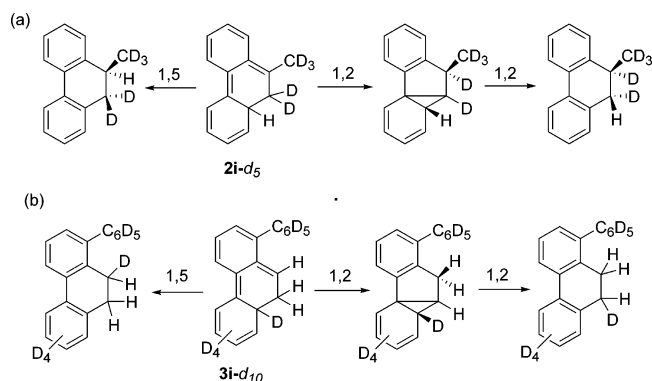


FIGURE 1. ^1H NMR spectra (CDCl_3) of the products **2a** and **2a-d₅** obtained from irradiation of **2** and **2-d₅**, respectively, in cyclohexane solution at room temperature.

SCHEME 4



Assignment of the upfield multiplet to the methylene protons proximal to the phenyl substituent is consistent with the expected shielding effect of the twisted 1-phenyl substituent and is supported by analysis of the NOESY spectra of **3a**. Comparison of spectrum of **3a-d₁₀** with that of **3a** indicates that aromatization of the putative intermediate **3i** occurs predominantly via 1,2-deuterium migration rather than 1,5-deuterium migration. A 85:15 ratio for 1,2- vs 1,5-deuterium migration can be calculated from the integrated 2.78 and 2.81 ppm peak areas (Scheme 4b). The same ratio was obtained following room-temperature irradiation of a glassy solid film supported on a quartz plate. The NMR spectra of solutions of **3-d₁₀** irradiated at 195 and 95 K (see Experimental Section) provide ratios of 75:25 and 55:45 for the multiplets at 2.78 and 2.81 ppm. The quantum yields for cyclization of **3** and **3-d₁₀** at 298 K are identical.

Competitive 1,2- vs 1,5-Shifts. The mechanisms outlined in Scheme 4 are formulated on the assumption that both 1,2- and 1,5-hydrogen shift products are formed via the ground state 8a,9-dihydrophenanthrene intermediates **2i** and **3i**. The 1,5-shift can occur via a concerted symmetry allowed processes, whereas the 1,2-shift product requires two sequential 1,2-shifts. The intermediate formed in the first 1,2-shift is shown in Scheme 4 as a cyclopropane rather than a 1,3-biradical, based on its calculated structure (vide infra). Competitive sequential

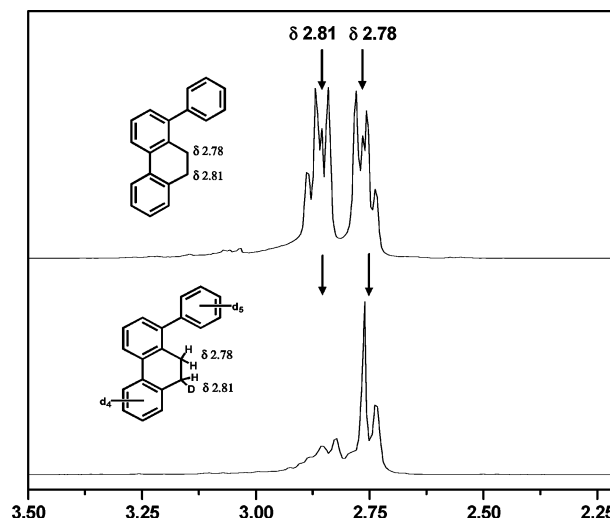


FIGURE 2. ^1H NMR spectra (CDCl_3) of the products **3a** and **3a-d₁₀** obtained from irradiation of **3** and **3-d₁₀**, respectively, in cyclohexane solution at room temperature.

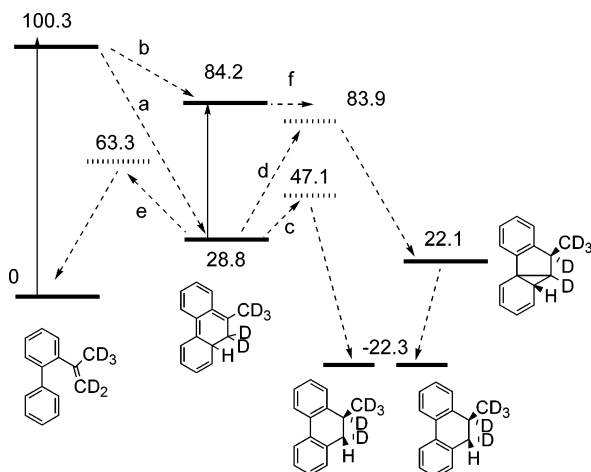
1,2-shifts have previously been proposed by Rodríguez et al. as an alternative to a 1,5-shift for the intramolecular isomerization of isobenzene (1,2,4-cyclohexatriene) to benzene.¹⁴ However there is no experimental evidence for the occurrence of either process.

Barriers for the 1,5-shift of **1i** and **3i** have been calculated by Alabugin et al. at the B3LYP/6-31G** level.⁵ The values they report are 16.6 and 16.2 kcal/mol. The barriers obtained using B3LYP density functional theory are somewhat larger than the experimental values for 1,5-shifts in five-membered rings but are in better agreement with experimental values for six-membered rings.⁵ We have calculated the barriers for the 1,5- and 1,2-shifts and the ring-opening isomerization of **2i** at the B3LYP/6-311G**//B3LYP/6-31G** level using GAUSSIAN 98.¹⁵ The results are shown in Scheme 5 along with the singlet energies of **2** and **2i** obtained from the 0,0 bands of their absorption spectra. The calculated barrier for the 1,5-shift is 18.3 kcal/mol, slightly higher than the value calculated by Alabugin for the 1,5-shift of **1i** using a lower level of theory. The barrier for the 1,2-shift is 55.1 kcal/mol, significantly higher than that for the 1,5-shift, whereas the barrier for ring opening isomerization is 34.5 kcal/mol, intermediate between the calculated values for the 1,5- and 1,2-shift.

The structures of **2i** and the transition states and products of 1,5- and 1,2-hydrogen migration are shown in Scheme 6. Based on the C···H···C bond distances, the

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SCHEME 5. Energies (kcal/mol) Calculated for Nondeuterated 2^a

^a (a) Nonadiabatic photocyclization, (b) adiabatic photocyclization, (c) thermal 1,5-hydrogen shift, (d) thermal 1,2-hydrogen shift, (e) thermal ring-opening isomerization, and (f) excited state 1,2-hydrogen shift.

transition state for 1,5-hydrogen migration is early (1.335 and 1.721 Å), whereas the transition state for 1,2-migration is relatively late (1.473 and 1.228 Å), in accord with the Hammond–Leffler postulate.^{16,17} The bond lengths for the 1,5-shift are in good agreement with those reported for **1i** by Alabugin et al.⁵ The product of the 1,2-shift is best described as a cyclopropane rather than a 1,3-biradical, based on the calculated bond lengths (1.50–1.60 Å for the three cyclopropane bonds).

On the basis of these calculations, the 1,5-shift should be the predominant reaction pathway for the thermal isomerization of **2i**. Our deuterium labeling results establish that the 1,5-shift is slightly favored over the 1,2-shift upon irradiation of **3-d**₁₀ at 90 K in a MC glass but that the 1,2-shift predominates for both **2-d**₅ and **3-d**₁₀ at 298 K. The occurrence of a 1,2-deuterium shift and 1,2-hydrogen shift as the major process for **2-d**₅ and **3-d**₁₀, respectively, is inconsistent with the high barrier calculated for the 1,2-shift (Scheme 5). In addition, the barriers calculated for the 1,5-shift of **2i** is too high to account for the rapid bleaching of the UV bands of **2i** or **3i** in fluid solution at low temperatures. McCullough and co-workers were successful in detecting the isoindene intermediate **5i** formed upon irradiation of **5** at 203 K (Scheme 7) both by ¹H NMR and chemical trapping, even though the experimentally determined barrier ($E_a = 14.4$ kcal/mol, $A = 20.5$) is smaller than the calculated barrier for **3i**.¹⁸ The formation of **3i** can be observed by means of UV spectroscopy upon irradiation in a frozen methylcyclohexane glass at 77 K but not in liquid propane solution at 90 K. From these observations, we are forced to conclude that *these reactions do not proceed by surmounting the calculated barriers shown in Scheme 5.*

Alternative Mechanisms. Experimental kinetic data is not available for highly exothermic cyclohexadiene 1,5-shift processes, and thus it is possible that DFT calculations substantially overestimate the barriers for such processes. A concerted double 1,2-shift in which the transition state is stabilized by the development of aromaticity provides a possible alternative to the sequential 1,2-shift mechanism. We have been unable to locate a transition state for such a process and are unaware of any literature precedent. It is possible that both the 1,5- and 1,2-shift processes occur via tunneling mechanisms resulting in substantial lowering of the apparent barriers. The activation parameters, namely, the low activation energy and preexponential, obtained for the bleaching of **4i** (Scheme 3) are consistent with a tunneling process. Tunneling is traditionally associated with reactions that occur at low temperature and with large kinetic isotope effects.¹⁷ As an example, Grellmann et al. observed nonlinear Arrhenius plots and large kinetic isotope effects (50–100) at low temperatures for sigmatropic hydrogen shift reactions.¹⁹ However, we note that similar 1,2- and 1,5-shift product ratios are obtained for **2-d**₅ and **3-d**₁₀ even though a deuterium shift leads to the major product for **2-d**₅ and a hydrogen shift leads to the major product for **3-d**₁₀. Peters and Kim have recently pointed out that for highly exothermic proton-transfer reactions tunneling persists at room temperature and can have a negligible isotope effect, a result in accord with the Lee–Hayes tunneling theory.²⁰

Another alternative mechanism for the 1,2-shift would require the presence of a reaction channel for singlet state decay that leads directly to the 1,2-shift products, in competition with formation of the thermally equilibrated intermediates **2i** or **3i**, which lead predominately to the 1,5-shift products. This situation might occur either if the photocyclization processes involves a conical intersection for which the 1,2-shift is the major exit channel at room temperature or if photocyclization occurred via an adiabatic potential energy surface leading to the excited-state intermediates (e.g., **2i**^{*}) that could undergo an allowed 1,2-shift in competition with decay to the ground-state intermediates, **2i**.²¹ Either mechanism would account for the weak 510 nm transient absorption spectrum observed for **3**.

Adiabatic electrocyclic photochemical reactions have been observed in cases where the excited state of the product lies well below that of the reactant.²² Adiabatic isomerization of **2**^{*} to **2i**^{*} is estimated to be exothermic by ca. 16 kcal/mol (Scheme 5, path b) on the basis of the calculated ground-state energies and singlet energies estimated from the 0,0 absorption bands. However, exothermic isomerization is a necessary but not sufficient condition for the occurrence of adiabatic cyclization. Further information about these alternative mechanisms awaits exploration of the excited-state potential energy surfaces.

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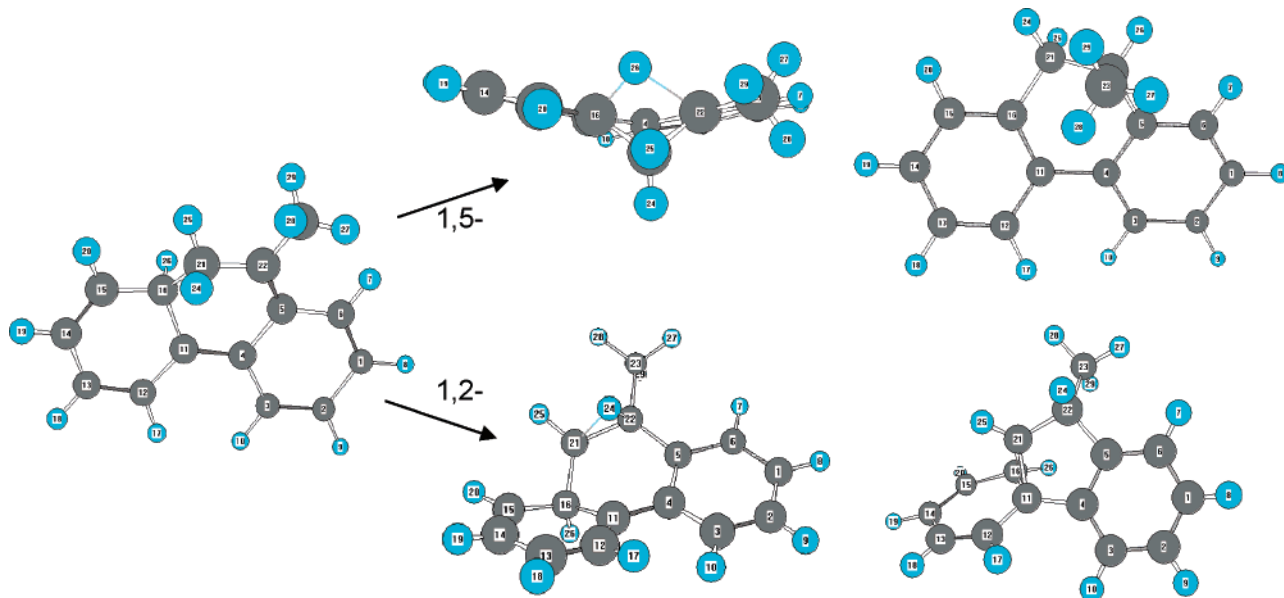
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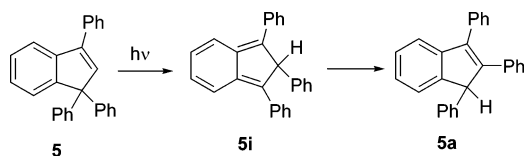
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SCHEME 6



SCHEME 7



Concluding Remarks

The results of deuterium labeling studies of the photochemical rearrangements of the 2-vinylbiphenyl derivatives **2-d₅** and **3-d₁₀** establish that product formation occurs predominantly via 1,2-deuterium and 1,2-hydrogen shifts, respectively. Product formation via 1,5-hydrogen and deuterium shifts account for the minor reaction products at room temperature but increase in importance with decreasing temperature in the case of **3-d₁₀**. Theoretical investigation of the thermal activation barriers for 1,2- and 1,5-shifts are consistent with a significantly lower barrier for the 1,5-shift, as expected for the thermally allowed sigmatropic rearrangement. The preferred formation of the products of 1,2- vs 1,5-hydrogen or deuterium migration appears to be incompatible with competitive ground-state isomerization pathways. Alternative pathways involving direct formation of the 1,2-migration products from excited intermediates need to be considered.

Experimental Section

Syntheses and characterization of the nondeuterated vinylbiphenyls **2** and **3** and their photochemical conversion to the dihydrophenanthrenes **2a** and **3a** have been reported.^{7,23}

2-Isopropenylbiphenyl-d₅ (2-d₅). The deuterium-labeled 2-isopropenylbiphenyl was prepared using a method similar to that for the corresponding protiated derivative **2**.⁷ A solution of MgCl₂ (1.2 g) and potassium metal (1.5 g) was refluxed in 75 mL of dry THF under dry nitrogen for 3 h. To this ash-colored mixture was added 2-bromobiphenyl (2.33 g, 10 mmol) slowly in 20 mL of dry THF. After the addition was complete,

the mixture was stirred for an additional 30 min. Subsequently, acetone-d₆ (700 mg, 10 mmol) was added slowly and mixture was stirred for 24 h. After workup, the crude mixture was chromatographed by column chromatography and elution with hexane gave 1.6 g (73%) of the Grignard product, α,α-dimethyl-2-biphenylmethanol-d₆, along with traces of biphenyl and 2-bromobiphenyl. The α,α-dimethyl-2-biphenylmethanol (500 mg, 2.1 mmol) was dissolved in 50 mL of dry benzene and refluxed with *p*-toluenesulfonic acid (25 mg) for 3 h using a Dean–Stark condenser to remove water. The reaction mixture was filtered through Celite and further purified by silica gel chromatography. Elution with hexane afforded 300 mg (70%) of the product as a colorless oil. ¹H NMR (CDCl₃, 400 MHz): δ 7.31–7.43 (9H, m, aromatic). ¹³C NMR (CDCl₃): δ 127.0, 127.4, 127.4, 128.3, 129.1, 129.4, 130.4, 139.8, 142.3, 143.0, 146.6. Mass spectrum (relative intensity): M⁺ 199 (25), 181 (100), 167 (5), 153 (6), 90 (6).

2-Vinyl-1,3-terphenyl-d₁₀ (3-d₁₀). To a stirred solution of Pd(PPh₃)₄ (720 mg, 2 mol %), CuI (230 mg, 4 mol %), dry piperidine (5 mL), and bromobenzene-d₅ (5.0 g, 30.9 mmol) in anhydrous THF (50 mL) was added dropwise trimethylsilylacetylene (5.25 mL, 37 mmol) at room temperature. The mixture was stirred at 50 °C for 48 h, then quenched with water, extracted (ether), washed (diluted HCl, brine), dried (MgSO₄), filtered through a short column of silica gel, and concentrated. The residue was purified by preparative column chromatography on silica gel (eluent hexane) to obtain 2.8 g (15.8 mmol, 51%) of trimethyl(phenylethynyl)silane-d₅. This was dissolved in methanol (10 mL), and anhydrous K₂CO₃ was added in one portion. The reaction mixture was stirred for 30 min at room temperature, then water was added, and the mixture was extracted with pentane, washed (water, brine), dried (MgSO₄), filtered, and concentrated under ambient pressure. The resulting crude product was added dropwise to a stirred mixture of PdCl₂(PPh₃)₂ (100 mg), CuI (200 mg), dry diethylamine (5 mL), and 1 M solution of vinylbromide in THF (20 mL, 20 mmol). The mixture was stirred at room temperature for 2 h, then poured into ice-cold 5% HCl (150 mL), extracted with ether, washed (water, brine), dried (MgSO₄), filtered, and evaporated in a vacuum from an ice-bath. The residue was purified by preparative column chromatography on silica gel (eluent pentane) to afford 1.5 g (11 mmol, 72%) of but-3-en-1-ylbenzene-d₅. Benzannulation was carried out in two parallel runs. Two 5 mL mini-reactors equipped with mini-inert valves were loaded with but-3-en-1-ylbenzene-d₅ (750 mg, 5.6 mmol), Pd(PPh₃)₄ (200 mg, 0.17 mmol, 3 mol %), and

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anhydrous THF (3 mL). The reaction mixture was stirred at 100 °C for 48 h and then cooled, and the contents of the two reactors were combined. The mixture was filtered through a short column of silica gel (CH₂Cl₂ eluent) and concentrated. The residue was purified by preparative column chromatography on silica gel (hexane/CH₂Cl₂ 10:1 eluent) to afford 2-vinyl-1,3-terphenyl-*d*₁₀. Yield 780 mg (2.9 mmol, 52%). Mp 107–108 °C. ¹H NMR (CDCl₃, 400 MHz): δ 4.60 (1H, d), 5.02 (1H, d), 6.44 (1H, m), 7.26 (2H, m, aromatic), 7.35 (2H, m, aromatic). ¹³C NMR (CDCl₃): δ 121.7, 126.9, 127.4, 127.6, 127.9, 129.9, 134.9, 135.1, 141.8, 142.3. Mass spectrum (relative intensity): M⁺ 266 (100), 259 (5), 248 (7), 184 (10), 170 (5), 123 (5).

Photolysis of 2-*d*₅. Room-temperature irradiation was performed in a degassed solution of cyclohexane (30 mg in 100 mL) using a quartz vessel with 254 nm excitation provided by a chamber reactor. The reaction was monitored by GC–MS to the point of complete conversion. The irradiated solution was filtered through silica gel, and the solvent was removed under reduced pressure to afford the photoproduct in quantitative yield. **2a-*d*₅:** ¹H NMR (CDCl₃, 400 MHz): δ 2.75 (corresponding to the methylene proton derived from a 1,5-shift), 3.09 (corresponding to the methylene proton derived from a double 1,2-shift), 7.21–7.76 (8H, m, aromatic). ¹³C NMR (CDCl₃): δ 27.1, 32.7, 123.8, 124.1, 126.9, 127.0, 127.1, 127.4, 127.7, 127.9, 128.3, 129.0, 129.1, 129.3. Mass spectrum (relative intensity): M⁺ 199 (40), 181 (100), 153 (5), 90 (8). Analysis of the integrated NMR spectrum shows that the mixture contains 90% of **2a-*d*₅** derived from a 1,2-shift and 10% from a 1,5-shift.

Photolysis of 3-*d*₁₀. Room-temperature solution irradiation was performed as described for **2-*d*₅**. Irradiation at was also performed on glassy solid film of **3-*d*₁₀** prepared by evaporation of a dichloromethane solution on a quartz plate. Irradiation at 195 K was performed in cyclohexane solution containing added dry ice. Irradiation at ca. 85 K was conducted in liquid propane using a nitrogen-cooled cryostat. To increase solubility of the reactant in propane, a thin layer of the reactant was deposited in a quartz cuvette by evaporation of a dichloromethane solution. To the dried cuvette equipped with a small stir bar, liquid propane was condensed at low temperature and the resulting mixture stirred for about 30 min. This solution was irradiated with constant stirring. The propane was allowed to evaporate and the residue dissolved in cyclohexane. Reactions were monitored to the point of complete conversion by GC–MS analysis. The irradiated solutions were filtered through silica gel, and the solvent was removed under reduced pressure to afford the photoproduct. Room-temperature irradiation of 30 mg of **3-*d*₁₀** in 100 mL cyclohexane afforded **3a-*d*₁₀** in quantitative yield. ¹H NMR (CDCl₃, 400 MHz): δ 2.75 (2H, d), 2.81 (1H, d), 7.26 (1H, d, aromatic), 7.37 (1H, t, aromatic), 7.79 (1H, d, aromatic). ¹³C NMR (CDCl₃): δ 26.6, 29.1, 121.7, 123.6, 126.7, 127.0, 129.4, 129.9, 135.1, 137.6,

141.3. Mass spectrum (relative intensity): M⁺ 266 (60), 259 (10), 248 (25), 184 (100), 155 (8). Ratios of isomeric photoproducts were determined by analysis of the integrated ¹H NMR peak areas for the corresponding aliphatic protons. The product obtained from irradiation at room-temperature either in solution or as a glassy solid contains 85% of **3-*d*₁₀** derived from a 1,2-shift and 15% via a 1,5-shift. The product obtained from irradiation at 195 K contains 75% of **3-*d*₁₀** derived from a 1,2-shift and 25% via a 1,5-shift. The product obtained from irradiation at 85 K contains 45% of **3-*d*₁₀** derived from a 1,2-shift and 55% via a 1,5-shift.

Transient Absorption Spectroscopy. The transient absorption measurements were performed at the Ohio Laboratory for Kinetic Spectroscopy at Bowling Green State University, and the experimental setup has been detailed elsewhere.²⁴ In brief, the output of a Ti:sapphire laser (fwhm = 150 fs) was steered into a third harmonic generator to obtain the 267 nm excitation wavelength. Sample solutions were prepared to have an absorbance of 0.7–1.0 at the excitation wavelength and were used without deaeration. The sample flow-through cell had an optical path of 2 mm and was connected to a solution reservoir and flow system. All measurements were conducted at room temperature, 22 ± 2 °C.

Computational Methods. Ab initio calculations were performed by using the GAUSSIAN 98 program.¹⁵ Geometry optimizations were carried out using B3LYP²⁵ density function with 6-31G** basis set, and energies were calculated at B3LYP/6-311G** level. Transition states were located by using the synchronous transit-guided quasi-newton method²⁶ at B3LYP/6-31G* level. All stationary points were identified as minima or transition states by vibrational analysis. The transition states were characterized by the presence of one negative vibration frequency and confirmed by intrinsic reaction coordination analyses.

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Supporting Information Available: Structures and Cartesian coordinates for reactant, intermediates, and transition states. ¹H NMR and ¹³C NMR spectra of reactants and products. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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