

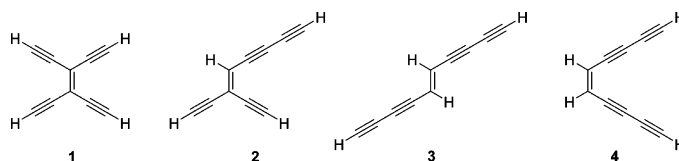
## Enediyne Isomers of Tetraethynylethene

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Three isomers of tetraethynylethene (**1**, C<sub>10</sub>H<sub>4</sub>) have been prepared by palladium-catalyzed Negishi coupling of a trimethylsilylbutadiynyl zinc reagent with a bromoalkene, followed by mild deprotection with potassium carbonate in methanol. The unsubstituted enynes, 3-ethynyl-oct-3-ene-1,5,7-triyne (**2**), *trans*-dec-5-ene-1,3,7,9-tetrayne (**3**), and *cis*-dec-5-ene-1,3,7,9-tetrayne (**4**), exhibit modest stability at -20 °C but decompose rapidly at room temperature. Electronic absorption spectra of **2**, **3**, and **4** reveal a characteristic vibronic progression at 260–320 nm. Spectral features at shorter wavelength discriminate among the isomers, and permit the assignment of **2** and **3** as apparent dimerization products of triplet carbene H–C≡C– $\dot{C}$ –C≡C–H in matrices at low temperature. Computed relative energies of these C<sub>10</sub>H<sub>4</sub> isomers (MP2/6-31G\*) are **1** (14.0 kcal/mol), **2** (6.8 kcal/mol), **3** (0.0 kcal/mol), and **4** (1.0 kcal/mol).

### Introduction

The enediyne functionality appears as an important structural feature in a variety of interesting organic molecules. Natural products containing the enediyne moiety, for instance, are capable of cleaving DNA at room temperature and physiological pH through a Bergman cycloaromatization mechanism.<sup>1–4</sup> The potential therapeutic benefits of these natural products, along with the intriguing mechanism by which they are proposed to function, inspired a great deal of research over recent decades.<sup>1–8</sup> Cycloaromatization reactions of enediynes are also thought to

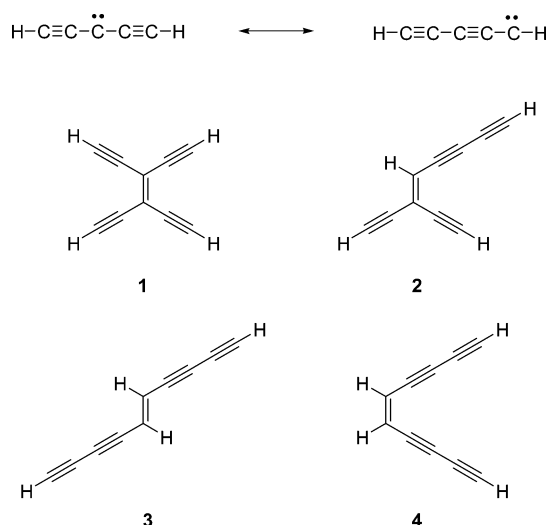
play a role in the formation of aromatic compounds, fullerenes, carbon nanotubes, and soot in combustion processes.<sup>9–11</sup> Enediyne units, in the form of tetraethynylethene and butadiynylethene substructures, represent building blocks for a variety of highly conjugated carbon-rich networks.<sup>12–16</sup>

Our interest in enediynes of the formula C<sub>10</sub>H<sub>4</sub> stems from our studies of C<sub>5</sub>H<sub>2</sub> carbenes, in which we suspected the formation of one or more C<sub>10</sub>H<sub>4</sub> enediynes upon carbene dimerization (Chart 1).<sup>17</sup> We sought to obtain authentic samples of the unsubstituted enediynes **1–4**, but we were surprised to

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## CHART 1



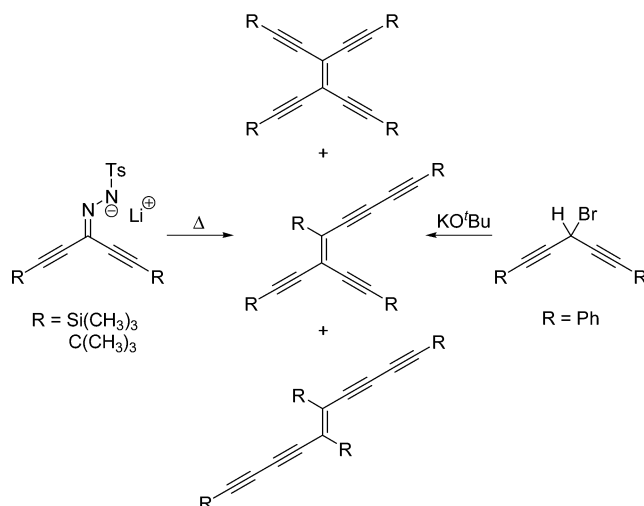
find that procedures for the preparation of compounds 2–4 have not been described in the literature. Substituted derivatives of 2–4 are known, but they have been generated as regioisomeric mixtures via carbene dimerization.<sup>18–20</sup> Needing the unsubstituted compounds, we developed procedures, based on modern synthetic methodology,<sup>21,22</sup> for the synthesis of enediynes 2–4, as well as their trimethylsilyl-substituted derivatives. The TMS derivatives serve as stable, well-behaved precursors for the unsubstituted enediynes and represent potentially useful intermediates in synthetic chemistry. With authentic samples of enediynes 1–4 in hand, careful analysis of their UV/visible spectra enables us to assign the spectroscopic features previously observed in our matrix isolation study of the triplet carbene  $\text{H}-\text{C}\equiv\text{C}-\overset{\cdot\cdot}{\text{C}}-\text{C}\equiv\text{C}-\text{H}$ .

## Background

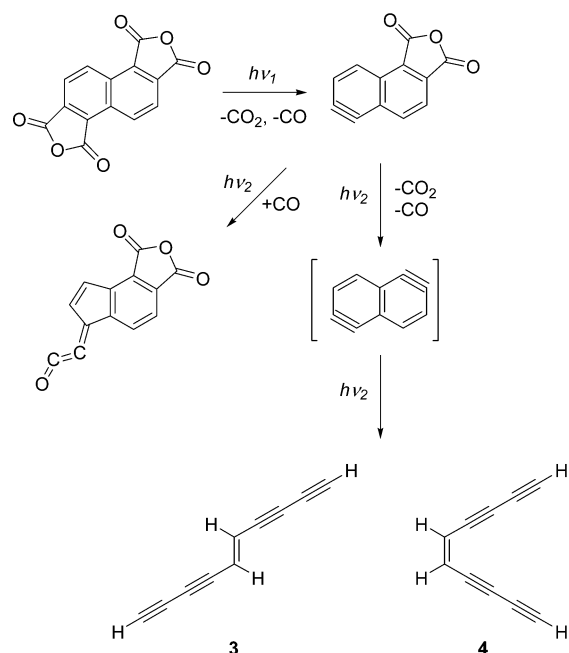
Tetraethynylethene (1) is the only isomer of the four enediynes (Chart 1) that has been generated by conventional synthetic means.<sup>23,24</sup> Both the tetrakis-TMS protected species and the unsubstituted species were characterized in solution by using infrared and UV/vis spectroscopy.<sup>23</sup> It was, in fact, the striking similarities between the published electronic spectrum of tetraethynylethene (1) and certain features observed in the spectrum of diethynyl carbene ( $\text{H}-\text{C}\equiv\text{C}-\overset{\cdot\cdot}{\text{C}}-\text{C}\equiv\text{C}-\text{H}$ )<sup>17</sup> that drew our attention to these  $\text{C}_{10}\text{H}_4$  isomers.

Previous studies of dialkynyl carbenes, and their formal dimers, involved substituted derivatives (Scheme 1). Hori and co-workers obtained a mixture of three phenyl-substituted dimers upon  $\alpha$ -elimination of 1,5-diphenyl-3-bromo-1,4-pentadiyne

## SCHEME 1



## SCHEME 2



with potassium *tert*-butoxide.<sup>18</sup> Hauptmann obtained a similar mixture of trimethylsilyl- or *tert*-butyl-substituted dimers upon thermolysis of lithium salts of tosylhydrazone precursors.<sup>25</sup> The unsubstituted enediynes 3 and/or 4 (stereochemistry not determined) have been generated under matrix isolation conditions upon photolysis of 1,2,5,6-naphthalenetetracarboxylic dianhydride (Scheme 2).<sup>26,27</sup> The UV/visible spectrum attributed to 3 and/or 4 qualitatively resembles those of tetraethynylethene (1)<sup>23</sup> and the unassigned features in our spectrum of the triplet carbene  $\text{H}-\text{C}\equiv\text{C}-\overset{\cdot\cdot}{\text{C}}-\text{C}\equiv\text{C}-\text{H}$ .<sup>17</sup>

## Results and Discussion

**Synthesis of Enynes.** Although Hauptmann's procedure provides a route to the tetrakis(trimethylsilyl) derivatives of the

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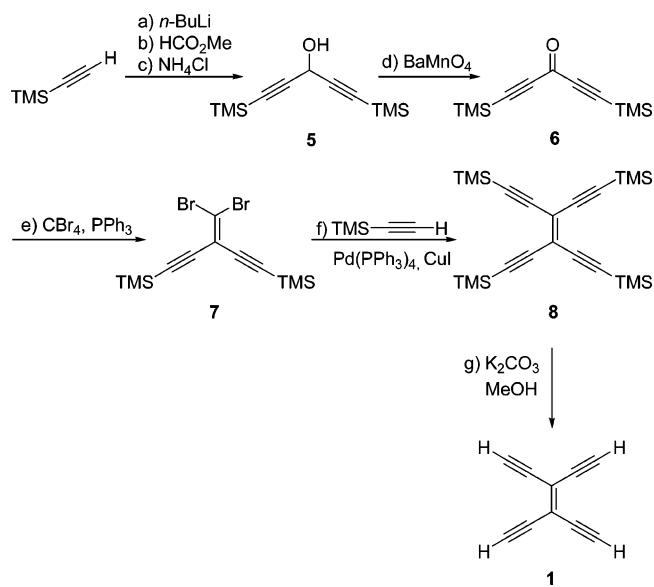
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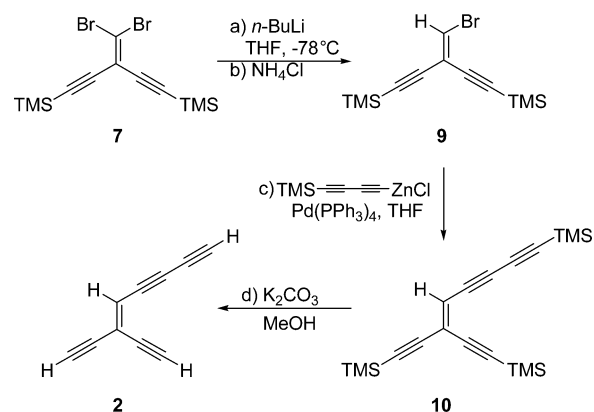
SCHEME 3<sup>a</sup>

<sup>a</sup> Reagents and conditions: (a) (Me)<sub>3</sub>SiC≡CH (2 equiv), *n*-BuLi (2 equiv) (solution in hexane), THF, 0 °C, 15 min; (b) HCO<sub>2</sub>Me (1 equiv), Δ (near reflux), ~5 min; (c) saturated aqueous NH<sub>4</sub>Cl, EtOAc, rt, 90% yield; (d) BaMnO<sub>4</sub>, CH<sub>2</sub>Cl<sub>2</sub>, rt, 2 h, 89% yield; (e) 6 added to CBr<sub>4</sub>, PPh<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, rt, 1 h, 71% yield; (f) (Me)<sub>3</sub>SiC≡CH, Pd(PPh<sub>3</sub>)<sub>4</sub>, CuI, *n*-BuNH<sub>2</sub>, benzene, rt, 12 h, 55% yield; (g) K<sub>2</sub>CO<sub>3</sub>, MeOH, 15 min, rt.

desired enediynes (Scheme 1),<sup>25</sup> we found this procedure to be an unsatisfactory preparative method because of low yields, formation of several byproducts, and difficult separation and purification. In addition, we were concerned about the inability to deprotect the vinyl trimethylsilyl moiety in the precursor to enediyne 2 using the mild conditions employed to deprotect the alkynyl trimethylsilyl groups in the synthesis of tetraethynylethene (1).<sup>23</sup> In light of these problems, we felt that a strategy that allowed regiochemical control in the preparation of enediynes 1–4 would afford superior results.

We prepared tetrakis(trimethylsilyl)ethynylethene (8) and tetraethynylethene (1) using the procedure of Diederich and co-workers (Scheme 3).<sup>23,24</sup> Lithiation of 2 equiv of trimethylsilylacetylene followed by nucleophilic addition to methyl formate yields the symmetrical alcohol 5 upon acidic workup. Oxidation of alcohol 5 with BaMnO<sub>4</sub> gives the symmetrical ketone 6 in high yield. Ketone 6 is readily converted to 7 through a high-yielding dibromoolefination reaction. Sonogashira coupling of trimethylsilylacetylene with dibromoolefin 7 yields tetrakis(trimethylsilyl)ethynylethene (8). The tetrakis-TMS derivative (8) is quite robust and can be manipulated at room temperature under atmospheric conditions. Enyne 8 is efficiently deprotected in the presence of a small amount of potassium carbonate in methanol. Tetraethynylethene (1) is modestly stable in solution at room temperature, allowing characterization via <sup>1</sup>H NMR, UV/vis, and IR spectroscopy. Samples in CDCl<sub>3</sub> persist for weeks at –20 °C. As an isolated solid (under a N<sub>2</sub> atmosphere), enediyne 1 decomposes rapidly at room temperature. At –15 °C, decomposition occurs over several minutes, while at –41 °C, enediyne 1 can be maintained for up to an hour with very little discoloration.

The tetrakis-TMS derivative of enediyne 2 has been prepared in low yield by Hauptmann<sup>25</sup> and, more recently, by de Meijere and co-workers.<sup>28</sup> We do not consider the tetrakis-TMS deriva-

SCHEME 4<sup>a</sup>

<sup>a</sup> Reagents and conditions: (a) *n*-BuLi (1 equiv) (solution in hexane), THF, –78 °C, 1 h; (b) NH<sub>4</sub>Cl at –78 °C, then saturated aqueous NH<sub>4</sub>Cl upon warming, 59%; (c) (Me)<sub>3</sub>SiC≡C–C≡CZnCl, Pd(PPh<sub>3</sub>)<sub>4</sub>, THF, 0 °C then rt, 68% yield; (d) K<sub>2</sub>CO<sub>3</sub>, MeOH, 15 min, rt.

tive to be a good precursor to the unsubstituted enediyne 2, however, because deprotection of a vinyl trimethylsilyl moiety requires reaction conditions that are incompatible with our experimental constraints for workup and isolation.<sup>29,30</sup> We therefore approached the preparation of enediyne 2 via the tris-TMS derivative 10 (Scheme 4). Tykwinski and co-workers established that dibromoalkene 7 can be selectively reduced to monobromoalkene 9 by monolithiation (–78 °C, THF), followed by protonolysis.<sup>31</sup> Negishi coupling of bromoalkene 9 with the zinc adduct of trimethylsilylbutadiyne, which is readily obtained upon treatment of 1,4-bis(trimethylsilyl)-1,3-butadiyne with 1 equiv of MeLi·LiBr complex followed by ZnCl<sub>2</sub>,<sup>32,33</sup> yields the tris(trimethylsilyl) enyne 10. Deprotection of 10 with potassium carbonate in methanol provides 2 as a white solid at –41 °C. The stabilities of 10 and 2 are comparable to those of 8 and 1, respectively. Tris-TMS enyne 10 is stable as a neat oil at room temperature for hours and at –20 °C for months. Neat enyne 2 shows only slow decomposition at –41 °C, while solutions in CDCl<sub>3</sub> show no sign of decomposition over several days at –20 °C.

Encouraged by the successful Negishi coupling involving the TMS-butadiynyl zinc reagent in the preparation of enyne 10, we employed this strategy in the synthesis of enynes 11 and 12 (Scheme 5). Indeed, Negishi coupling of the zinc reagent with 1,2-dibromoethylene, which is commercially available as a 2:1 mixture of *trans*:*cis* isomers, yields a mixture of TMS-enynes 11 and 12. Separation is realized with consecutive applications of flash chromatography. Deprotection of each species is uneventful, yielding the enynes 3 and 4 as white solids at –41 °C. The stabilities of these compounds (11, 12, 3, and 4) are quite similar to those of the other isomers in this series. The TMS derivatives (11 and 12) are stable for months as solids at

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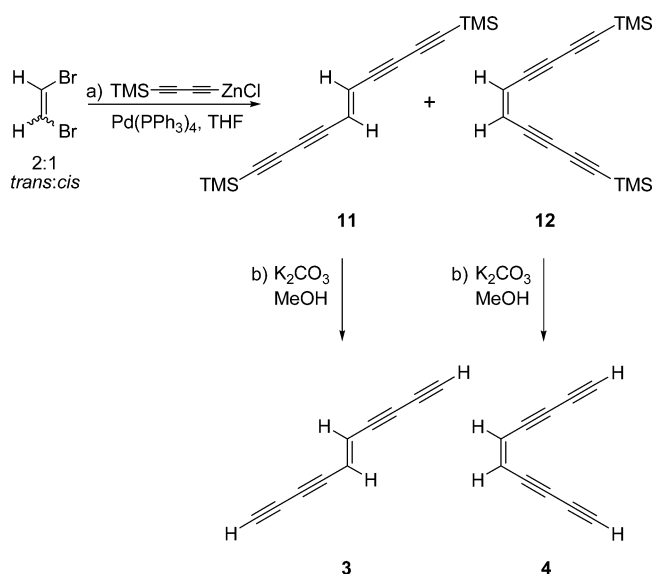
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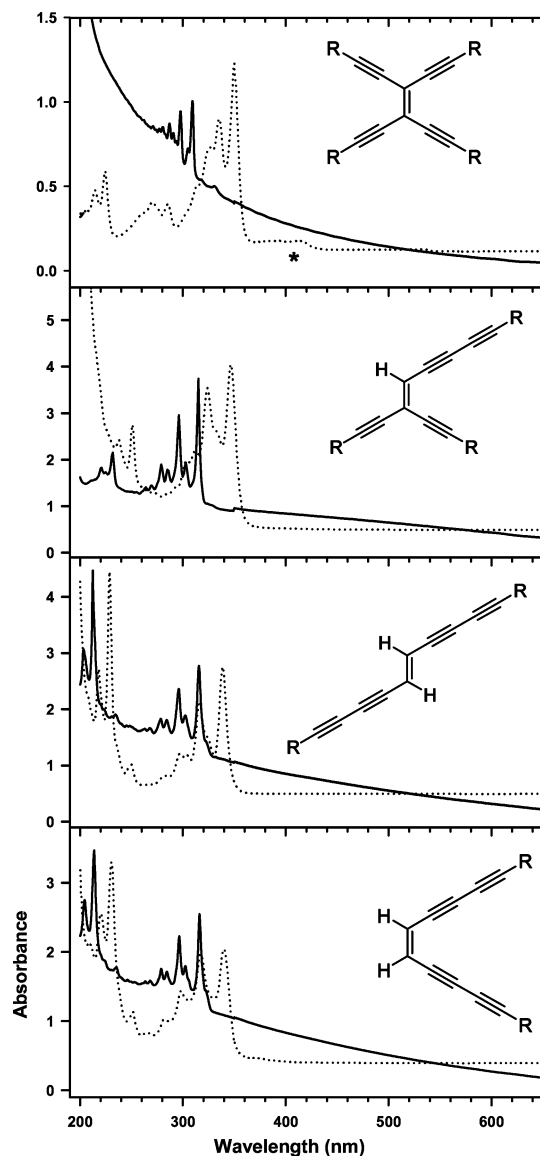
SCHEME 5<sup>a</sup>

<sup>a</sup> Reagents and conditions: (a)  $(\text{Me}_3\text{SiC}\equiv\text{C}-\text{C}\equiv\text{CZnCl})$ ,  $\text{Pd(PPh}_3)_4$ , THF, 0 °C then rt, 51% yield; (b)  $\text{K}_2\text{CO}_3$ , MeOH, 15 min, rt.

−20 °C. The neat enynes **3** and **4** show only slow decomposition at −41 °C, while solutions in  $\text{CDCl}_3$  show no sign of decomposition over several days at −20 °C.

<sup>1</sup>H NMR and mass spectra of enynes **1–4** provide no evidence of partially deprotected species. Thin-layer chromatography reveals the formation of only one product in each of the deprotection reactions. IR spectra of enynes **1–4**, obtained under matrix isolation conditions ( $\text{N}_2$ , 10 K), exhibit reasonable agreement with computed spectra (B3LYP/6-31G\*).<sup>34</sup> The experimental spectra exhibit absorptions near  $1200\text{ cm}^{-1}$ ; although these absorptions are not predicted in the calculation of harmonic vibrational frequencies, they are readily attributed to combination bands.<sup>35</sup> The IR spectra of **3** and **4** provide the basis for a secure assignment as *trans* and *cis* isomers, respectively. (These isomers are nearly indistinguishable by NMR spectroscopy.) Comparison of the authentic IR spectra of enynes **1–4** with the IR spectrum obtained during the spectroscopic characterization of triplet carbene  $\text{HC}_5\text{H}$  reveals no coincidences, thereby supporting the conclusion that the “dimers” (enynes **1–4**) are not major constituents in the matrix containing  $\text{HC}_5\text{H}$ .<sup>17</sup> IR spectra of the TMS-protected precursors (**8** and **10–12**;  $\text{N}_2$ , 10 K) display characteristic features of the trimethylsilyl moiety (C–H stretching absorption at  $2900\text{--}3000\text{ cm}^{-1}$ ; sharp absorptions at  $1200\text{--}1300\text{ cm}^{-1}$ ; strong, broad absorptions at  $800\text{--}900\text{ cm}^{-1}$ ).<sup>34,36</sup> The absence of unassigned bands at  $2900\text{--}3000$  and  $800\text{--}900\text{ cm}^{-1}$  in the IR spectra of enynes **1–4** confirms that these species are completely desilylated.

**UV/Visible Absorption Spectroscopy.** The electronic absorption spectra of the  $\text{C}_{10}\text{H}_4$  isomers exhibit  $\pi\text{--}\pi^*$  transitions of moderate intensity ( $\epsilon \approx 20\,000\text{ M}^{-1}\text{ cm}^{-1}$ ) at  $300\text{--}350\text{ nm}$  (ca. 80 kcal/mol) with extensive vibronic coupling (Figure 1). The spectra of the TMS-protected precursors (**8** and **10–12**; MeOH, 298 K) show a significant red shift compared to their



**FIGURE 1.** Solid lines: UV/visible spectra of unsubstituted enynes **1–4** ( $\text{R} = \text{H}$ ;  $\text{N}_2$ , 10 K). Dotted lines: UV/visible spectra of substituted enynes **8**, **10**, **11**, **12** ( $\text{R} = \text{TMS}$ ; MeOH, 298 K). \* = impurity.

deprotected counterparts (**1–4**;  $\text{N}_2$ , 10 K). The magnitude of the red shift increases with the number of TMS groups: **1** vs **8** ( $\Delta = 41\text{ nm}$ ;  $3791\text{ cm}^{-1}$ ; four TMS), **2** vs **10** ( $\Delta = 32\text{ nm}$ ;  $2928\text{ cm}^{-1}$ ; three TMS), **3** vs **11** ( $\Delta = 23\text{ nm}$ ;  $2147\text{ cm}^{-1}$ ; two TMS), and **4** vs **12** ( $\Delta = 24\text{ nm}$ ;  $2234\text{ cm}^{-1}$ ; two TMS). Despite the red shift, the vibronic features of the unsubstituted vs TMS-substituted enynes display strong similarities.

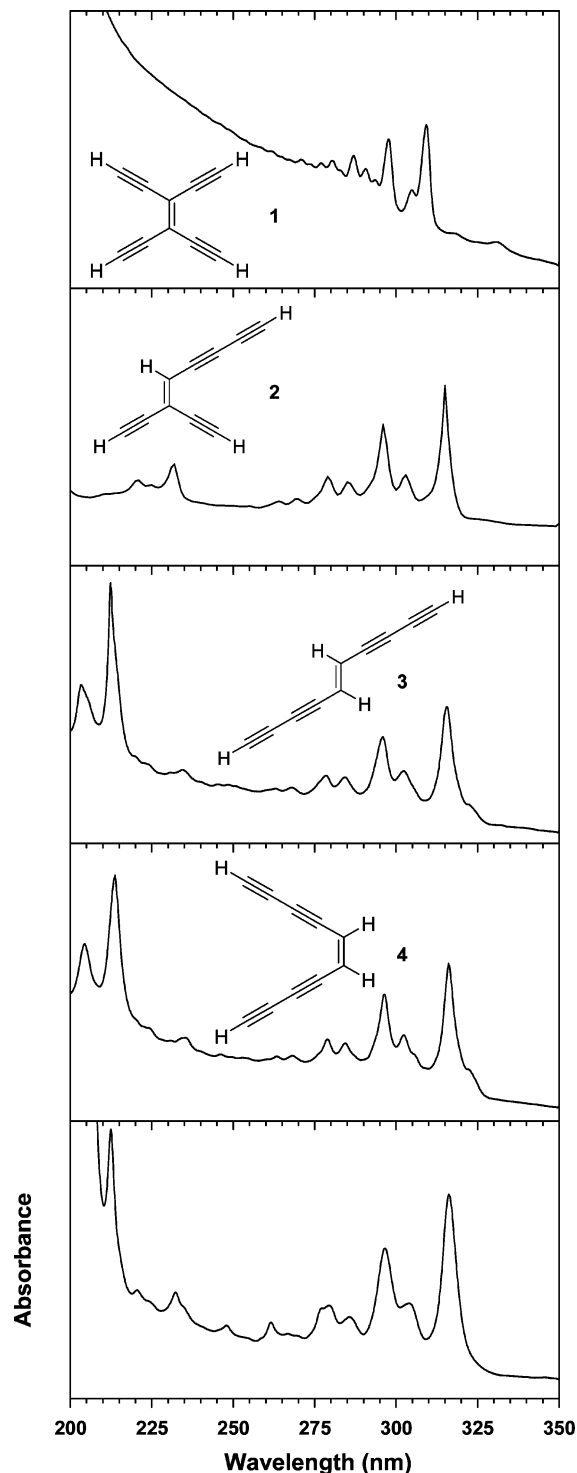
The most striking feature of the electronic spectra of enynes **2–4** is the great similarity of the vibronic features in the region  $250\text{--}350\text{ nm}$  (Figure 2), which undoubtedly reflects a common structural feature. The dissimilarity of the UV/vis spectrum of enyne **1** provides insight that this feature must, in fact, involve the butadiene units of **2–4**.

The UV/vis absorption spectra of enynes **1–4** are crucial to the proper interpretation of UV/vis spectra obtained in the course of our characterization of the carbene  $\text{H-C}\equiv\text{C}-\dot{\text{C}}-\text{C}\equiv\text{C-H}$ .<sup>17</sup> In our matrix studies, photolysis ( $\lambda > 444\text{ nm}$ ) of 1-diazo-2,4-pentadiyne affords an electronic spectrum that contains two distinct vibronic progressions (Figure 3). The feature at  $340\text{--}$

(34) Details available as Supporting Information.

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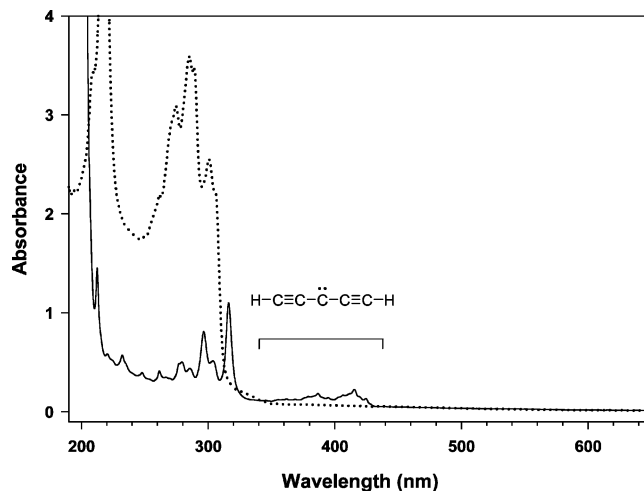
**FIGURE 2.** UV spectra of enynes **1–4** ( $N_2$ , 10 K). Bottom: Spectrum obtained upon irradiation ( $\lambda > 444$  nm) of 1-diazo-2,4-pentadiyne ( $N_2$ , 10 K).

440 nm represents the lowest energy electronic transition ( $A^3\Sigma_u^- \leftarrow X^3\Sigma_g^-$ ) of triplet carbene  $HC_5H$ .<sup>17,37–39</sup> The features at 200–320 nm, however, are not consistent with theoretical predictions for allowed electronic transitions of  $HC_5H$ .<sup>38,39</sup> In

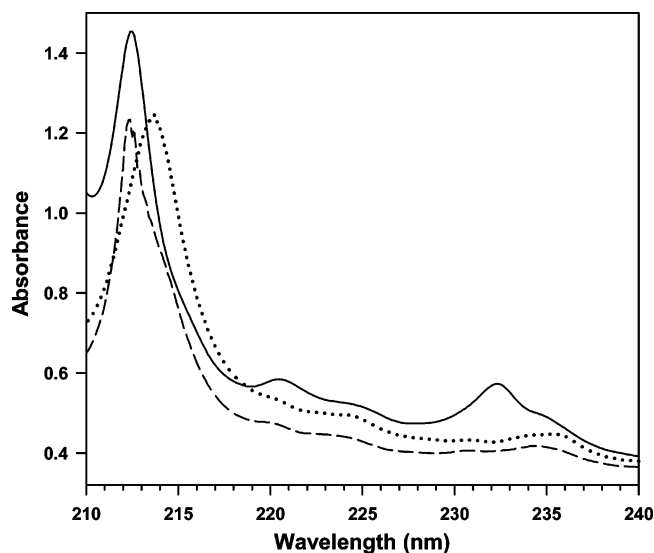
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**FIGURE 3.** Dotted line: UV/visible spectrum of 1-diazo-2,4-pentadiyne ( $N_2$ , 10 K) prior to irradiation. Solid line: Spectrum obtained upon irradiation ( $\lambda > 444$  nm; 1.7 h).

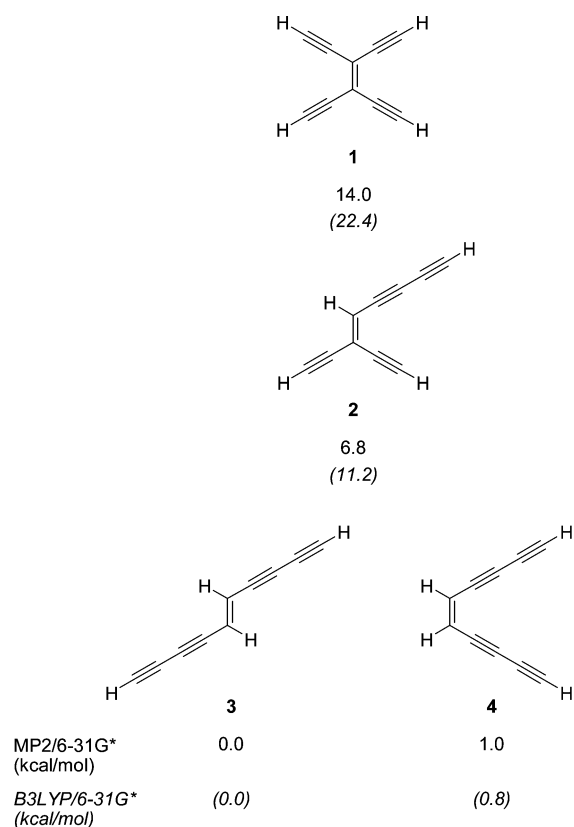


**FIGURE 4.** Solid line: UV spectrum obtained upon irradiation ( $\lambda > 444$  nm) of 1-diazo-2,4-pentadiyne ( $N_2$ , 10 K). Dashed line: UV spectrum of an authentic sample of *trans*-enyne **3** ( $N_2$ , 10 K). Dotted line: UV spectrum of an authentic sample of *cis*-enyne **4** ( $N_2$ , 10 K).

considering possible side-products or impurities that might be responsible for these spectral features, our attention turned to the enynes **1–4**, since they represent formal dimers of carbene  $HC_5H$ . The authentic spectra of enynes **2–4**, in fact, each exhibit striking agreement with the vibronic progression at 260–320 nm (Figure 2). Consideration of the absorption features at shorter wavelength provides a basis for discriminating between isomers **2**, **3**, and **4**. Absorptions at 220, 224, and 232 nm correlate with those in the authentic spectrum of enyne **2**. The absorption at 212 nm correlates slightly better with the peak in the authentic spectrum of *trans*-enyne **3** than with that of *cis*-enyne **4** (Figure 4). Thus, we conclude that the features observed in the UV/vis spectrum obtained upon photolysis of 1-diazo-2,4-pentadiyne arise from a mixture of enynes **2** and **3**. It is not possible to exclude the presence of enyne **4**, but it is possible to exclude the presence of tetraethynylethene (**1**).

**Implications for  $HC_5H$  Dimerization.** The observation of  $C_{10}H_4$  isomers **2** and **3**, but not **1**, in a matrix containing carbene

CHART 2



HC<sub>5</sub>H was surprising to us. Chemical trapping of HC<sub>5</sub>H with molecular oxygen at low temperature (30 K) occurs selectively at the central carbon (C3),<sup>17</sup> and we anticipated that the analogous dimerization of **1** would also occur predominantly at C3. Computational studies of the enyne isomers, however, provided an interesting perspective on thermodynamic considerations. Tetraethynylethene (**1**) is the highest energy isomer of the four enynes, lying 14 kcal/mol higher than **3** (MP2/6-31G\*; Chart 2).<sup>40–43</sup> To the extent that the carbene dimerization reaction is controlled by the thermodynamic stabilities of the products, little of enyne **1** would be expected, relative to **3** (or **4**). Because the carbene dimerization reaction is substantially exothermic, initially formed enyne **1** may possess sufficient internal energy to allow intramolecular isomerization, possibly through a Bergman cycloaromatization pathway. Dimerization of HC<sub>5</sub>H via coupling at carbons C3 and C1' would afford enyne **2**, which could persist as a detectable product since a Bergman cyclization pathway leads to a degenerate rearrangement (automerization). Further investigations of the isomerizations and rearrangements of enynes **1–4** are currently underway. While UV/vis spectra support an interpretation that annealing of matrix-isolated carbene HC<sub>5</sub>H produces enynes **2** and **3**,<sup>44</sup> we cannot exclude the possible involvement of either diazo compound +

(40) DFT methods overestimate bond delocalization, which is a serious issue in computing structures and energies for the types of highly unsaturated molecules encountered in the current investigation. For closed-shell systems such as enynes **1–4**, MP2 energies are likely to be more reliable than DFT energies.

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carbene, or diazo compound dimerization, in the formation of enynes **2** and **3** under photochemical conditions.

## Summary

TMS-protected enynes **10**, **11**, and **12** have been prepared by the palladium-catalyzed Negishi coupling of a TMS-butadiynyl zinc reagent with a bromoalkene. Deprotection under mild conditions (K<sub>2</sub>CO<sub>3</sub>/MeOH) affords the corresponding unsubstituted enynes **2**, **3**, and **4**. Electronic absorption spectra of these C<sub>10</sub>H<sub>4</sub> isomers permit the identification of **2** and **3** as components in a matrix-isolated sample of triplet carbene H–C≡C–C̈–C≡C–H.<sup>17</sup> The symmetrical dimer, tetraethynylethene (**1**), is not observed. MP2 calculations indicate that isomer **1** is ca. 14 kcal/mol higher in energy than **3** or **4**. Dimerization of carbene HC<sub>5</sub>H may afford enyne **1** with sufficient internal energy to undergo isomerization to enynes **3** or **4**.

## Experimental Section

**Matrix Isolation Spectroscopy.** The matrix isolation technique and apparatus have been described previously.<sup>45,46</sup> Infrared spectra were recorded on a FTIR spectrometer equipped with a DTGS detector with a resolution of 2 cm<sup>-1</sup>. UV/vis spectra were recorded on a UV/vis/NIR spectrophotometer utilizing a spectral bandwidth of 1.0 nm.

**Computational Methods.** Optimized geometries and harmonic vibrational frequencies were calculated for each of the four C<sub>10</sub>H<sub>4</sub> isomers by using density functional theory. MP2 calculations were used for geometry optimizations, although harmonic vibrational frequencies were not obtained. DFT calculations were performed with the hybrid three-parameter functional of Becke<sup>47</sup> and the correlation functional of Lee, Yang, and Parr<sup>48</sup> (B3LYP), and ab initio calculations were performed with second-order Møller–Plesset perturbation theory (MP2), each with the 6-31G\* basis set, as implemented in the Gaussian 98 package.<sup>49</sup>

**Synthesis.** 1,5-Bis(trimethylsilyl)-1,4-pentadiyn-3-ol (**5**),<sup>50</sup> 1,5-bis(trimethylsilyl)-1,4-pentadiyn-3-one (**6**),<sup>50</sup> 3-(dibromomethylidene)-1,5-bis(trimethylsilyl)penta-1,4-diyne (**7**),<sup>24</sup> 1,6-bis(trimethylsilyl)-3,4-bis[(trimethylsilyl)ethynyl]hex-3-ene-1,5-diyne (**8**),<sup>24</sup> and 3-(bromomethylidene)-1,5-bis(trimethylsilyl)penta-1,4-diyne (**9**)<sup>31</sup> were prepared by literature methods. <sup>1</sup>H NMR spectra (300 MHz) and <sup>13</sup>C NMR spectra (75.4 MHz) were obtained in CDCl<sub>3</sub> and referenced to internal SiMe<sub>4</sub>.

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**1,8-Bis(trimethylsilyl)-3-(trimethylsilyl)ethynyl-oct-3-ene-1,5,7-triayne (10).** To a solution of 300 mg (1.54 mmol) of 1,4-bis(trimethylsilyl)-1,3-butadiyne in 15 mL of THF was added 1.03 mL of MeLi·LiBr complex (1.5 M) in ether. This mixture was stirred for 3.5 h at room temperature. The mixture was cooled to  $-30\text{ }^{\circ}\text{C}$  and a  $\text{ZnCl}_2$  (0.21 g, 1.54 mmol) suspension in 2 mL of THF was added. The reaction mixture was allowed to slowly warm to  $0\text{ }^{\circ}\text{C}$ . At this temperature, a solution of the monobromo species **9** (150 mg) in 2.0 mL of THF was added along with 0.035 g of  $\text{Pd}(\text{PPh}_3)_4$  (0.03 mmol). The mixture was stirred for 18 h at room temperature. The reaction mixture was rinsed into a separatory funnel with 30 mL of ether and the organic layer was washed once with a saturated aqueous  $\text{NH}_4\text{Cl}$  solution. The organic phase was dried with  $\text{MgSO}_4$ , filtered, and concentrated to reveal a dark, oily solid. This oil was purified via flash chromatography yielding **10** (0.116 g) as a colorless oil (0.34 mmol, 68% yield).  $^1\text{H NMR}$   $\delta$  6.13 (s, 1 H), 0.25 (s, 9 H), 0.214 (s, 9 H), 0.206 (s, 9 H).  $^{13}\text{C NMR}$   $\delta$  124.1, 119.3, 103.0, 101.5, 100.5, 100.4, 96.4, 87.8, 86.5, 74.5,  $-0.12$ ,  $-0.15$ ,  $-0.28$ . EIMS (70 eV)  $m/z$   $\text{M}^+$  340 (36), 325 (11), 285 (15), 268 (18), 253 (16), 73 (33). UV/vis  $\lambda_{\text{max}}$  ( $\epsilon$ ,  $\text{M}^{-1}\text{cm}^{-1}$ ) (MeOH) 346.7 (20 542), 332.0 (12 219), 323.8 (17,531), 312.1 (9740), 303.5 (8500), 250.8 (12 927), 237.7 (11 156) nm. IR (rel intensity) 2962 (26), 2901 (9), 2190 (3), 2150 (4), 2090 (12), 1326 (11), 1252 (68), 1188 (31), 910 (57), 875 (60), 846 (100)  $\text{cm}^{-1}$ .

**1,10-Bis(trimethylsilyl)dec-5-ene-1,3,7,9-tetrayne (trans-11 and cis-12).** To a solution of 1.0 g (5.14 mmol) of 1,4-bis(trimethylsilyl)-1,3-butadiyne in 35 mL of THF was added 3.43 mL of MeLi·LiBr complex (1.5 M) in ether. This mixture was stirred at room temperature for 3.5 h. The reaction mixture was cooled to  $-30\text{ }^{\circ}\text{C}$  and a  $\text{ZnCl}_2$  (0.700 g, 5.14 mmol) suspension in 5 mL of dry THF was added. Upon slowly warming to  $0\text{ }^{\circ}\text{C}$ , 0.083 mL (1.0 mmol, 2:1 *trans:cis*) of dibromoethylene was added along with 0.173 g (0.15 mmol) of  $\text{Pd}(\text{PPh}_3)_4$ . After being stirred for 24 h at room temperature, the mixture was rinsed into a separatory funnel with 30 mL of ether. The organic mixture was washed once with a saturated aqueous  $\text{NH}_4\text{Cl}$  solution, and the layers were separated. The organic phase was dried with  $\text{MgSO}_4$ , filtered, and concentrated to reveal a black, oily solid. Flash chromatography (pentane) afforded modest separation of *trans* (**11**) and *cis* (**12**) isomers, with *trans* eluting first. A total mass of 136 mg was recovered after 2–3 consecutive chromatographic separations (0.506 mmol, 51% yield, 2:1 *trans:cis*).

**trans-1,10-Bis(trimethylsilyl)dec-5-ene-1,3,7,9-tetrayne (11).**  $^1\text{H NMR}$   $\delta$  6.12 (s, 2 H), 0.22 (s, 18 H).  $^{13}\text{C NMR}$   $\delta$  123.2, 95.0, 87.5, 81.4, 74.8,  $-0.29$ . EIMS (70 eV)  $m/z$   $\text{M}^+$  268 (26), 253 (24), 73 (19). UV/vis  $\lambda_{\text{max}}$  ( $\epsilon$ ,  $\text{M}^{-1}\text{cm}^{-1}$ ) (MeOH) 338.6 (24 038), 323.2 (10 868), 316.1 (17 389), 303.1 (7544), 296.5 (7544), 285.1 (3580), 279.1 (2941), 249.9 (5498), 228.7 (42 067), 218.1 (23 654) nm. IR (rel intensity) 3036 (13), 2962 (44), 2901 (17), 2202 (13), 2099 (56), 1252 (67), 1222 (33), 928 (33), 885 (61), 858 (100), 846 (100)  $\text{cm}^{-1}$ .

**cis-1,10-Bis(trimethylsilyl)dec-5-ene-1,3,7,9-tetrayne (12).**  $^1\text{H NMR}$   $\delta$  5.97 (s, 2 H), 0.22 (s, 18 H).  $^{13}\text{C NMR}$   $\delta$  121.6, 95.1, 87.8, 83.0, 73.8,  $-0.27$ . EIMS (70 eV)  $m/z$   $\text{M}^+$  268 (75), 253 (52), 196 (41), 181 (100), 73 (76). UV/vis  $\lambda_{\text{max}}$  ( $\epsilon$ ,  $\text{M}^{-1}\text{cm}^{-1}$ ) (MeOH) 339.8 (15,216), 317.2 (14,768), 298.2 (9845), 281.5 (5818), 264.8 (4028), 251.2 (6713), 230.7 (26 851), 220.4 (19 691), 209.2 (16 111) nm. IR (rel intensity) 2959 (41), 2926 (33), 2901 (24), 2871 (16), 2855 (17), 2203 (8), 2098 (35), 1252 (62), 1142 (8), 885 (54), 845 (100), 760 (47), 742 (21)  $\text{cm}^{-1}$ .

#### General Procedure for Deprotection of Alkynyl TMS Groups.

A small quantity of TMS-protected starting material (usually  $\sim 10$  mg) was dissolved in 1–2 mL of MeOH. A small amount of potassium carbonate was added ( $\sim 5$  mg) and the mixture was stirred

at room temperature for 15–30 min. (The deprotection appeared to be instantaneous by TLC.) The mixture was rinsed into a separatory funnel with pentane (5 mL) and water (5 mL). The layers were separated and the organic layer was washed once again with water (5 mL). The organic phase was dried with  $\text{MgSO}_4$  and filtered directly into a dry deposition tube (used for depositing material onto the matrix isolation apparatus). The sample was cooled to  $-41\text{ }^{\circ}\text{C}$  and pentane was removed under reduced pressure to afford the enediyne as a white solid.

**3,4-Diethynylhex-3-ene-1,5-diyne (1).**  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  3.61 (s, 4 H). EIMS  $m/z$   $\text{M}^+$  124 (80), 98 (51), 74 (100), 61 (40), 50 (12). Upon transfer to the matrix isolation apparatus, tetraethynylethene (**1**) was sublimed ( $0\text{ }^{\circ}\text{C}$ , 40 min for IR;  $-19\text{ }^{\circ}\text{C}$ , 20 min for UV/vis;  $10^{-6}$  mmHg) and co-deposited with  $\text{N}_2$  onto an optical window (21 K). Slow decomposition of this sample limits the amount that we are able to deposit onto the matrix window, but a sufficient quantity can be deposited to allow for effective characterization via IR and UV/vis spectroscopy. In  $\text{N}_2$  at 10 K: IR (rel intensity) 3325 (75), 3320 (100), 3312 (88), 3308 (66), 2129 (6), 2112 (38), 1153 (28), 964 (25), 661 (56), 649 (38), 643 (50)  $\text{cm}^{-1}$ . UV/vis  $\lambda_{\text{max}}$  330.5, 317.0, 309.0, 305.0, 298.0, 293.8, 290.9, 287.0, 282.8, 280.4, 277.0, 273.9, 271.0 nm.

**3-Ethynyloct-3-ene-1,5,7-triayne (2).**  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  6.24 (s, 1 H), 3.44 (d,  $J = 0.9$  Hz, 1 H), 3.26 (d,  $J = 0.6$  Hz, 1 H), 2.77 (d,  $J = 1.2$  Hz, 1 H). EIMS  $m/z$   $\text{M}^+$  124 (91), 98 (44), 74 (100), 61 (54), 50 (11). Upon transfer to the matrix isolation apparatus, enyne **2** was sublimed ( $0\text{ }^{\circ}\text{C}$ , 40 min for IR;  $-19\text{ }^{\circ}\text{C}$ , 5 min for UV/vis;  $10^{-6}$  mmHg) and co-deposited with  $\text{N}_2$  onto an optical window (21 K). In  $\text{N}_2$  at 10 K: IR (rel intensity) 3312 (100), 2206 (1), 2122 (3), 1325 (4), 1197 (7), 1162 (14), 853 (4), 770 (4), 759 (3), 670 (23), 648 (21)  $\text{cm}^{-1}$ . UV/vis  $\lambda_{\text{max}}$  315.0, 303.1, 296.0, 285.2, 278.9, 269.4, 263.8, 232.0, 224.7, 220.9, 210.0 nm.

**trans-Dec-5-ene-1,3,7,9-tetrayne (3).**  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  6.15 (s, 2 H), 2.64 (s, 2 H). EIMS  $m/z$   $\text{M}^+$  124 (91), 98 (48), 74 (100), 61 (39), 50 (9). Upon transfer to the matrix isolation apparatus, enyne **3** was sublimed ( $0\text{ }^{\circ}\text{C}$ , 60 min for IR;  $-15\text{ }^{\circ}\text{C}$ , 35 min for UV/vis;  $10^{-6}$  mmHg) and co-deposited with  $\text{N}_2$  onto an optical window (21 K). In  $\text{N}_2$  at 10 K: IR (rel intensity) 3321 (66), 3316 (100), 3310 (66), 3303 (84), 2068 (3), 1255 (32), 1206 (13), 1203 (13), 949 (3), 938 (18), 934 (18), 643 (45), 637 (50), 632 (66)  $\text{cm}^{-1}$ . UV/vis  $\lambda_{\text{max}}$  322.2, 315.5, 302.2, 295.9, 284.2, 278.5, 267.7, 263.2, 234.3, 223.5, 212.6, 212.4, 203.4 nm.

**cis-Dec-5-ene-1,3,7,9-tetrayne (4).**  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  6.00 (s, 2 H), 2.68 (s, 2 H). EIMS  $m/z$   $\text{M}^+$  124 (90), 98 (51), 74 (100), 61 (44), 50 (10). Upon transfer to the matrix isolation apparatus, enyne **4** was sublimed ( $0\text{ }^{\circ}\text{C}$ , 45 min for IR;  $-15\text{ }^{\circ}\text{C}$ , 30 min for UV/vis;  $10^{-6}$  mmHg) and co-deposited with  $\text{N}_2$  onto an optical window (21 K). In  $\text{N}_2$  at 10 K: IR (rel intensity) 3317 (100), 3305 (97), 2193 (3), 2188 (3), 2067 (3), 1685 (7), 1571 (3), 1401 (7), 1258 (17), 1180 (10), 834 (7), 750 (23), 634 (73)  $\text{cm}^{-1}$ . UV/vis  $\lambda_{\text{max}}$  322.9, 316.0, 305.6, 302.4, 296.4, 284.4, 279.0, 268.2, 263.5, 235.5, 223.5, 213.5, 204.5 nm.

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**Supporting Information Available:** Synthetic procedures for compounds **5–9**, NMR spectra for all compounds, IR spectra for unsubstituted enynes **1–4** ( $\text{N}_2$ , 10 K) and TMS-substituted enynes **8, 10–12** ( $\text{CCl}_4$ , 298 K), tabular list of experimental IR and UV/vis absorptions of enynes **1–4**; Cartesian coordinates, absolute energies, harmonic vibrational frequencies, and IR intensities computed for enynes **1–4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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