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Beyond the Roger Brown Rearrangement: Long-Range Atom Topomerization in Conjugated Polyynes

John Mabry and Richard P. Johnson*

Contribution from the Department of Chemistry, University of New Hampshire, Durham, New Hampshire 03824

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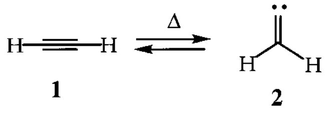
Abstract: Long-range carbon atom topomerization in a 1,3-diyne has been demonstrated for the first time. 1-Phenyl-4-*p*-tolyl-1,3-butadiyne, ^{13}C-enriched at C-1, was synthesized and subjected to flash vacuum pyrolysis. At 800 °C and 0.01 Torr, this resulted in nearly complete ^{13}C label equilibration between C-1 and C-2, as seen by NMR analysis. Pyrolysis at 900 °C further led to ca. 35% of the label migrating about equally to C-3 and C-4. These results demonstrate that both intrabond and interbond atom exchange processes are operative, with the former having a lower activation barrier. DFT and Moller−Plesset calculations support a mechanism that passes through Brown rearrangement (1,2-shift), closure to trialene (bicyclo[1.1.0]-1,3-butadiene), bond-shift isomerization to exchange C-2 and C-3, and ring opening. The resulting vinylidene can rearrange to a butadiyne with the isotopic label at C-3 or C-4. Consistent with earlier calculations, trialene is predicted to have alternating peripheral bonds, with a weak central σ bond and significant diradical character. Trialene is predicted [(B3LYP/6-311+G(2d,p)] to lie 64.6 kcal/mol above butadiyne, with barriers of 2.2 and 4.4 kcal/mol, respectively, for ring opening or bond-shift isomerization. Other potential rearrangement mechanisms which pass through tetrahedrene ($E_{\rm rel}$ = 167.2 kcal/mol) or 1,2,3-cyclobutatriene ($E_{\rm rel}$ = 161.1 kcal/mol) lie at much higher energies.

Introduction

The thermal interconversion of alkynes (**1**) and vinylidenes (**2**), also known as the Roger Brown rearrangement, is a reaction of great mechanistic and synthetic importance.[1] This rearrangement was first demonstrated in 1974 by Roger Brown and coworkers, who observed carbon atom transpositions in isotopically labeled phenylacetylene.[2] An organometallic version of this reaction forms the basis of a common synthesis of alkynes.[3] Vinylidenes clearly represent very shallow energy minima and even the simplest members of this series still pose many unanswered questions.[4]

Our interest in pericyclic routes to highly strained reactive intermediates[5] led us to investigate whether more complex atom transpositions might occur in a 1,3-butadiyne. In conjugated polyynes, the sequential 1,2-shifts of Brown rearrangement provide a straightforward mechanism for *intrabond* atom scrambling, but it is easy to conceive of several mechanisms for *interbond* atom transposition. In principle, a linear diyne might fold like an accordion into a symmetrical cyclic structure and then open with the central atoms having exchanged positions. We present here the first experimental evidence for such a process. Computational studies provide support for a remarkable rearrangement that passes through intermediate alkynylvinylidenes (**4**) and trialenes (**5**).



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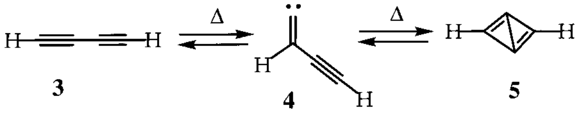

(2)

C$_4$H$_2$ Chemistry. Present knowledge of the C$_4$H$_2$ potential surface is sparse; butadiyne (**3**) is the sole shelf-stable structure[6] and few other isomers have been investigated. Butatrienylidene (**6**) has been studied by computation[7] and generated in the laboratory;[8] the spectroscopic signature of this carbon-rich

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* Corresponding author. E-mail: rpj@cisunix.unh.edu.

(1) Recent examples: (a) Review: Brown, R. F. C. *Eur. J. Org. Chem.* **1999**, 3211. (b) Schulz, K.; Hofmann, J.; Zimmermann, G. *Eur. J. Org. Chem.* **1999**, *12*, 3407. (c) Scott, L. T.; Cheng, P.-C.; Hashemi, M. M.; Bratcher, M. S.; Meyer, D. T.; Warren, H. B. *J. Am. Chem. Soc.* **1997**, *119*, 10963. (d) Scott, L. T.; Necula, A. *Tetrahedron Lett.* **1997**, *38*, 1877. (e) Synthetic applications: Kirmse, W. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1165.

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(3) Eisler, S.; Tykwinski, R. R. *J. Am. Chem. Soc.* **2000**, *122*, 10736 and references therein.

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structure has been observed in interstellar gas clouds.[9] The geometry and spectroscopic properties of cyclopropenylidenemethylene (**7**) have been predicted,[7b,10] but this interesting carbene remains unknown. Bicyclo[1.1.0]buta-1,3-diene (**5**), more commonly known as trialene or propalene, presents an unusual π bond topology that has invited a variety of theoretical studies,[11] beginning with Hückel theory.[11a,b] Trialene was used as an example in the classic 1961 HMO text by J. D. Roberts.[11a] Nevertheless, its existence and involvement in C_4H_2 chemistry have received almost no serious consideration. Baird and Dewar first used the semiempirical MNDO method to predict a C_{2h} symmetric trialene structure, with alternating single and double bonds.[11c] These authors further suggested that trialene might be made by matrix photolysis of **3**. Schleyer and co-workers later predicted[11g] that **5** should easily convert to ethynylvinylidene (**4**), itself lying in a shallow energy minimum.[11g,h,12] Simkin predicted that bond shift isomerization in **5** will have a low barrier, proceeding through a D_{2h} structure.[11h]


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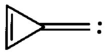
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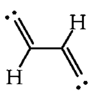
8a **8b**


9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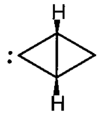
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Several higher energy C_4H_2 structures are relevant to the present work; these include 1,2,3-cyclobutatriene or cyclobutenyne (**8a** or **8b**), tetrahedrene (**9**), and 1,3-butadiene-1,4-diylidene (**10**).[7a] All of these substances are unknown. In principle, **7** and **8** might interconvert by a 1,2-shift pathway, which is similar to that predicted for cyclobutyne.[13] Structures **8a** and **8b** represent the smallest homologues in the cyclic butatriene or cyclic enyne series.[14] Sauer and Harris very recently described calculations on **9** and the related biscarbene **11**; these are predicted to be high-energy species.[15]

Scheme 1. Synthesis and Pyrolysis of Labeled 1-Phenyl-4-*p*-tolyl-1,3-butadiyne

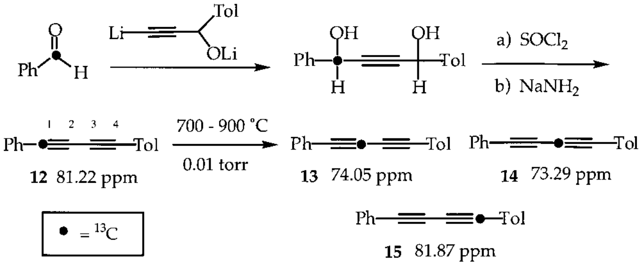

Table 1. ^{13}C Label Distributions from NMR Integration

	carbon no. (δ ppm)			
	C-1 (δ 81.22)	C-2 (δ 74.05)	C-3 (δ 73.29)	C-4 (δ 81.87)
unreacted **12**	20.8	0.72	0.88	1.40
pyrolysis at 800 °C	11.6	7.37	1.16	0.89
pyrolysis at 900 °C	8.79	8.76	3.99	3.01

Results and Discussion: Experimental Studies

We investigated butadiyne thermal rearrangements through preparation and pyrolysis (Scheme 1) of ^{13}C-labeled 1-phenyl-4-*p*-tolyl-1,3-butadiyne.[16] This substance was chosen because the aryl groups differentiate the sp carbons and also serve as end-caps. This should allow C_4 chain chemistry to occur, without the fragmentations that are generally observed for alkyl-substituted alkynes.[17] The four sp hybridized carbons of this diyne were found to be well-resolved in ^{13}C NMR. Control experiments demonstrated its thermal stability in flash pyrolysis up to 950 °C. Diphenylbutadiyne rearranges to give polycyclic aromatics above 1100 °C.[18]

The results of our experimental studies, including label distributions and chemical shifts for sp-hybridized carbons, are summarized in Scheme 1 and Table 1. A sample of diyne that was ca. 20% ^{13}C enriched at C-1 (isotopomer **12**) was synthesized from ^{13}C-labeled benzaldehyde as shown. This level of isotopic substitution was chosen so that all the sp carbons could readily be observed and integrated in each spectrum. Measurement of quantitative ^{13}C spectra for the sp resonances was facilitated by addition of chromium acetonylacetonate to the sample.[19]

Flash vapor pyrolysis of ^{13}C-labeled diyne **12** at 800 °C/0.01 Torr led to nearly complete exchange between C-1 and C-2, as shown by NMR integration (Table 1), but with good recovery of starting material. Lower temperature reaction resulted only in partial equilibration. Pyrolysis of samples at 900 °C similarly exchanged C-1 and C-2 but also reproducibly resulted in ca.

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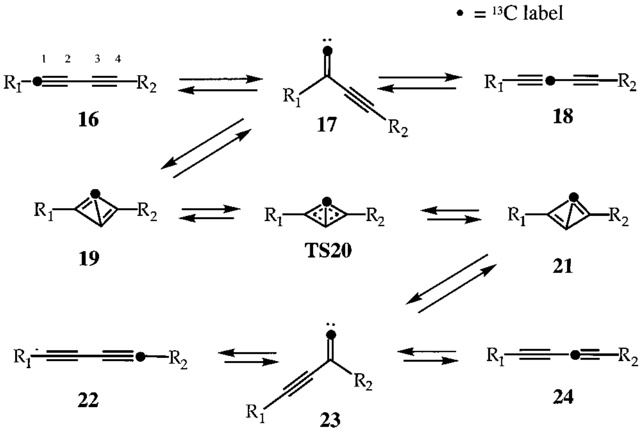
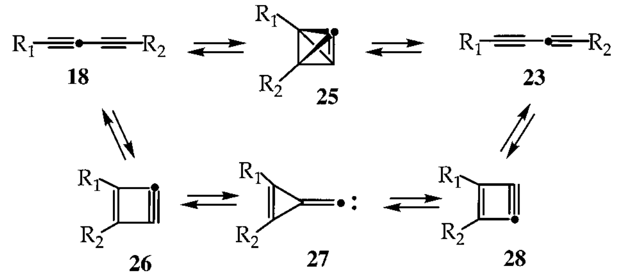
Scheme 2. Potential Reaction Mechanism



Scheme 3. Alternate Reaction Mechanisms



35% of the label migrating to C-3 and C-4, as indicated by formation of isotopomers **14** and **15** in nearly equal proportions. Minor amounts of other products were observed at the higher temperature. Pyrolysis at 1000 °C resulted in more complex mixtures, consistent with Brown's previous studies on diphenylbutadiyne.[18]

The isotopic distributions observed from pyrolyses at 800 or 900 °C demonstrate that both *intrabond* and *interbond* exchange process are operative, with the former passing through a lower activation barrier.

Potential Reaction Mechanisms. Scheme 2 presents a potential mechanism that passes through alkynylvinylidenes and trialenes. Initial 1,2-shift can lead to carbene **17**; a second shift of the *opposite* σ bond then affords **18**. This Roger Brown rearrangement[1,2] easily explains the intrabond atom transposition that is observed from pyrolysis of **12** at 800 °C. Alternatively, higher temperature closure of the carbene to trialene **19** might be followed by bond-shift isomerization (**19** → **21**) via transition state **TS20** and subsequent reopening to carbene **23**. This intermediate will rearrange to either **22** or **24**, thus accomplishing full transit across the four-carbon chain. This process is nearly complete after pyrolysis at 900 °C. In general, 1,2-shifts should result only in alkyne *intrabond* atom interconversions, while trialene provides a simple, if somewhat exotic, mechanism for *interbond* atom rearrangement.

Among alternative mechanisms, structures **3** and **5** might interconvert directly through a synchronous accordion-like [π2s + π2a] mechanism that by-passes the carbene. Entirely different routes pass through other high-energy structures (Scheme 3) in which the central sp carbons of the diyne become structurally equivalent. Tetrahedrene **25** and cyclobutenyne **26** both possess the requisite symmetry for interbond atom transposition. Either structure might be formed directly from the diyne through an electrocyclic process. Reversible interconversion of **25** with vinylidenecyclopropene **27** might be expected if their energetics are favorable. Alternatively, a biscarbene such as **10** might result from two sequential shifts or a dyotropic process.

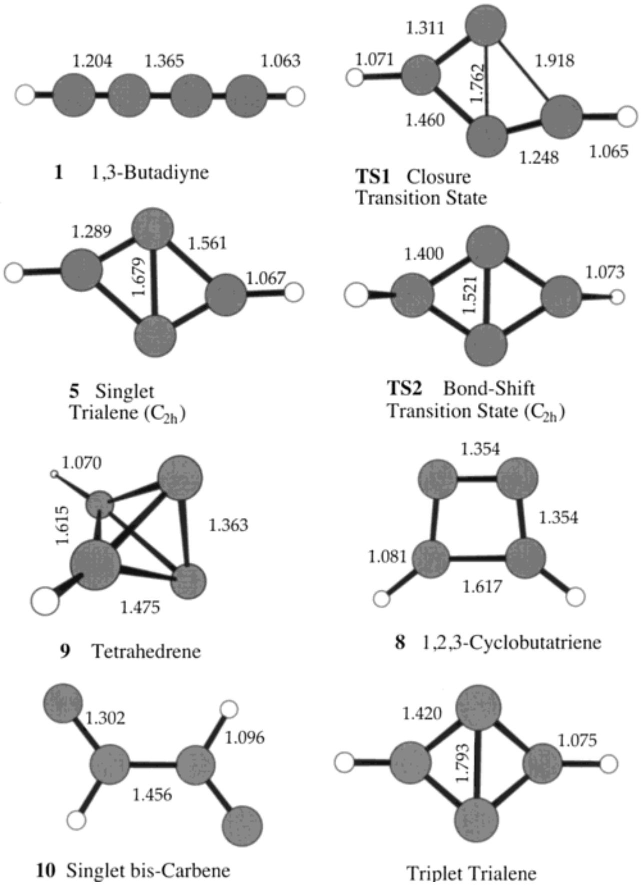


Figure 1. B3LYP/6-311+G(2d,p) stationary points.

Results and Discussion: Computational Studies

We employed a variety of wave functions to assess the energetics of potential C_4H_2 reaction mechanisms. Figure 1 shows structures for selected B3LYP/6-311+G(2d,p) stationary points, while the energetics from B3LYP and MP4//MP2 levels of theory are summarized in Table 2. In general, these two methods provided very similar structures and relative energetics. Selected CASSCF(8,8)/6-31G* calculations also were performed. **TS1** connects **4** and **5** while **TS2** describes bond-shift isomerization in **5**. Relative energies are summarized in Figure 2.

As with parent vinylidene[4] (**2**), theory provides equivocal predictions on the existence of ethynylvinylidene (**4**); as a consequence, the surface for 1,2-shifts is quite dependent on the computational level. Calculations with HF, TCSCF, CASSCF, and B3LYP/6-31G(d) theories all located a minimum for the carbene structure **4**.[11,12] We observe that MP2 and larger basis set B3LYP calculations did not; in these cases, the optimization proceeded steeply downhill to **3**, even with analytical calculation of the gradient at each point. Thus it is unclear if ethynylvinylidene represents a true stationary point. In the present work, it suffices to know that the energy of **4** should lie slightly below the transition state (**TS1**) for closure to trialene.

Consistent with previous lower level calculations,[11] trialene is predicted at *all* levels of theory to have alternating peripheral

Table 2. Summary of Computational Results[e]

structure	B3LYP[a]	E_{rel}	NIMAG[b]	MP4//MP2[c]	E_{rel}	NIMAG[b]
1,3-butadiyne (**3**)	−153.534 12	0.00	0	−153.140 16	0.00	0
ethynylvinylidene (**4**)	−153.450 87[d]	52.2	0			
closure TS (**TS1**)	−153.427 69	66.8	1	−153.037 39	64.5	1
singlet trialene (**5**)	−153.431 13	64.6	0	−153.042 95	61.0	0
bond-switch TS (**TS2**)	−153.424 10	69.0	1	−153.032 46	67.6	1
tetrahedrene (**9**)	−153.267 62	167.2	0	-152.814 56	204.3	0
1,2,3-cyclobutatriene (**8**)	−153.277 41	161.1	1	−152.909 07	145.0	0
cyclopropenylidene (**7**)	−153.419 68	71.8	0	−153.020 43	75.1	0
butatrienylidene (**6**)	−153.468 68	41.0	0	−153.063 94	47.8	0
triplet trialene	−153.403 69	81.8	0			
biscarbene (**10**)	−153.375 97	99.2	0	−152.976 63	102.6	1
bicyclic biscarbene (**11**)	−153.414 30	75.2	0	−153.018 82	76.1	0

[a] B3LYP = B3LYP/6-311+G(2d,p)//B3LYP/6-311+G(2d,p). [b] NIMAG = number of imaginary vibrational modes from B3LYP or MP2 calculation. [c] MP4SDTQ/6-311+G(2d,p)//MP2(FC)/6-311+G(2d,p). [d] At B3LYP/6-31G* optimized geometry. See text. [e] Relative energies in kcal/mol, uncorrected for zero-point differences.

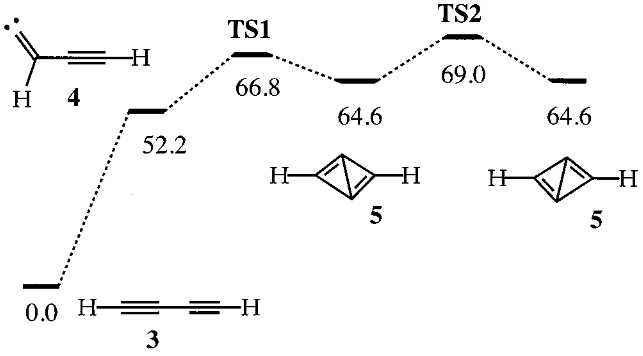
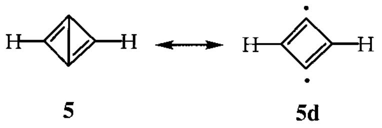


Figure 2. B3LYP energetics along the trialene pathway.

ring bonds with an elongated central bond. The central σ bond length in **5** is sensitive to the level of theory, presumably because of the strong contribution from resonance structure **5d**, but calculations indicate it is *not* a true diradical. In the CASSCF-(8,8)/6-31G* wave function, the σ bonding and antibonding orbitals which describe the transannular bond have occupation numbers of 1.88 and 0.126, respectively; for a pure diradical these values would be equal.



Other spectroscopic properties for trialene are of inherent interest. Using the GIAO method[20] and a B3LYP wave function, we calculate a ^{1}H NMR chemical shift of 3.79 ppm, perhaps consistent with a modest degree of antiariomaticity, and ^{13}C chemical shifts of 87.9 (C-2 methine carbon) and 150.18 ppm. RTD-B3LYP/6-311+G(2d,p) calculations[21] predict the lowest electronic excitation to occur at 3.41 eV (363 nm) with a modest oscillator strength. Triplet trialene is predicted (Table 2) to lie 17 kcal/mol higher in energy and thus should not play a role in this chemistry.

Our calculations predict trialene (**5**) to lie in a shallow minimum 61−65 kcal/mol above butadiyne. Low-energy paths exist for both ring opening of **5** to **4** via transition state **TS1** or for bond-switch isomerization through **TS2**. **TS2** is predicted to be nonplanar, with C_{2h} symmetry and equal C−C bond lengths around the ring. Efforts to locate a synchronous transition state directly connecting **3** and **5** afforded much higher barriers and no true stationary points.

Butatrienylidene (**6**) is the second lowest energy C_4H_2 structure but there seems to be no facile connection with its isomers. The other exotic intermediates shown in Scheme 3 offer more tempting alternative mechanisms. In principle, **3** might undergo pericyclic closure to **8**, followed by rearrangement through cyclopropenylidenemethylene (**7**). At ca. 70 kcal/mol above **3**, carbene **7** might be accessible energetically, especially if it could derive from 1,2-shifts in **8**. The optimized structure for **8** displays one imaginary mode with B3LYP/6-311+G(2d,p) theory but none at MP2/6-311+G(2d,p). However, in either case, the energy of this structure still is >70 kcal/mol above that of carbene **7**; this places **8** out of consideration as an explanation for our experimental results. Interestingly, B3LYP bond lengths in **8** support its characterization as a cyclic cumulene rather than an enyne. As recently noted by Sauers,[15] and observed independently by us, both DFT and MP2 theories predict the highly pyramidalized tetrahedrene (**9**) to be an energy minimum. While **9** presumably has a low barrier for rearrangement to butadiyne, this structure lies >100 kcal/mol above **5**, which excludes it as a likely intermediate.

Several biscarbenes represent high-energy stationary points on the C_4H_2 surface. According to our DFT calculations, biscarbene **10** is planar and lies about 30 kcal/mol above **5**. Once again, this seems too high for serious consideration. MP2 optimization on this same structure led to the transition state for 1,2-migration of both hydrogens. Sauers has recently described calculations on the interesting biscarbene **11**.[15] This structure is predicted to lie at very high energy relative to butadiyne. In neither case is it clear how C-2 to C-3 atom transposition might occur.

Conclusions

The Roger Brown rearrangement, which interconverts alkynes and vinylidenes, plays a central role in diverse high-temperature chemistry.[1,2] Our experimental and computational results provide the first evidence for a further link to long-range atom topomerization in a polyyne chain. We observe that carbon atoms can migrate from one end of a 1,3-diyne to the other in a process that clearly passes through sequential stages of intrabond and interbond atom exchange. DFT and Moller−Plesset computations provide consistent predictions for a likely

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reaction mechanism. At lower energy lies a well-precedented Roger Brown rearrangement[1,2] that accounts for intrabond atom transpositions. It is uncertain if ethynylvinylidene (**4**) represents a true energy minimum on this reaction pathway. Along a slightly higher energy pathway, closure to singlet trialene (**5**), followed by bond-switch isomerization, and ring opening (Scheme 2) presents what we believe to be the lowest energy mechanism for interbond carbon scrambling. While our scan of the C_4H_2 potential energy surface is hardly exhaustive, the structural features and energetic similarity of the carbene and trialene mechanisms provide strong argument that they are closely connected. Qualitatively, the predicted reaction energetics are consistent with the temperature required for this rearrangement. Other logical but exotic intermediates such as **8**, **9**, or **10** lie at much higher energy than the trialene mechanism; we believe these can be excluded. Preliminary calculations indicate that the energetics of these processes are little changed in longer polyynes. Thus, in principle, extensive carbon scrambling might occur in an sp carbon chain of any length. One important conclusion is that trialene (**5**) now seems to have evolved from a fictional subject of π electron calculations[11a] to a real reactive intermediate; we speculate that other structures with similar bonding schemes should exist.

Experimental Section

Computational Methods. Structures for reactants and transition states were created initially with Spartan[22] and optimized at the pBP86/DN* level of theory. Further DFT and Moller−Plesset calculations were carried out with GAUSSIAN 98.[23] Both GAMESS[24] and GAUSSIAN were used for CASSCF calculations. Each optimized structure exhibited the expected number of imaginary vibrational modes: i.e., zero for minima and one for saddle points.

Synthesis of ^{13}C-Labeled 1-Phenyl-4-*p*-tolyl-1,3-butadiyne. ^{13}C-enriched benzaldehyde was purchased from Aldrich and diluted to ca. 20% enrichment with unlabeled material. *n*-Butyllithium (31.4 mmol) in hexane was added over 30 min to 1-(4-methylphenyl)-2-propyn-1-ol[25] (2.30 g, 15.7 mol) in THF (17 mL) maintained at −78 °C. The solution was allowed to warm to room temperature and then was recooled to −78 °C. Benzaldehyde (20% ^{13}C enriched; 15.0 mmol) in THF (10 mL) was added over 20 min. After the solution was warmed to room temperature over 3 h, conventional workup and solvent removal afforded 1-phenyl-4-*p*-tolyl-2-butyne-1,4-diol as a viscous oil: 3.24 g (82%). ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.12−7.54 (m, 9H), 5.52 (s, 1H), 5.49 (s, 1H), 2.91 (br s, 2H), 2.36 (s, 3H).

Thionyl chloride (30.0 mmol) in THF (10 mL) was added dropwise over 30 min to a mixture of the diol (2.50 g, 9.91 mmol), pyridine (2.40 mL), and THF (25 mL) at 0 °C. The reaction mixture was allowed to warm to room temperature and crushed ice was added. Conventional workup afforded the dichloride, which was used without further purification.

A solution of the crude dichloride (1.66 g, 5.74 mmol) in THF (10 mL) was added over 5 min to a suspension of freshly prepared sodium amide (17.2 mmol) in liquid ammonia (30 mL) at −78 °C. After 1.5 h, ammonium chloride (2 g) was added and the ammonia and solvent were removed. The residue was extracted with hexanes (50 mL). Concentrated extracts were purified on silica with hexane as eluent to give 0.30 g (20%) of diyne **12**. ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.57−7.15 (m, 9H), 2.39 (s, 3H); mp 107−109 °C (lit.[16a] 110 °C). The ^{13}C NMR spectrum is described in the text.

Pyrolysis Experiments. The apparatus consisted of a 50 cm horizontal quartz tube, packed loosely with quartz chips and held in a tube furnace. Samples of the labeled butadiyne (30−50 mg) were slowly sublimed into the tube at a pressure of 0.01−0.02 Torr. Products were collected in a trap cooled with dry ice. Results are described in the text.

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Supporting Information Available: ^{13}C NMR spectra for samples before and after pyrolysis; Cartesian geometries, energies, and thermodynamic data for B3LYP stationary points (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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