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Dehydropericyclic Reactions: Symmetry-Controlled Routes to Strained Reactive Intermediates

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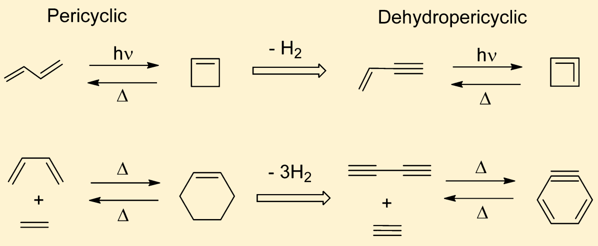
Ⓢ *Supporting Information*



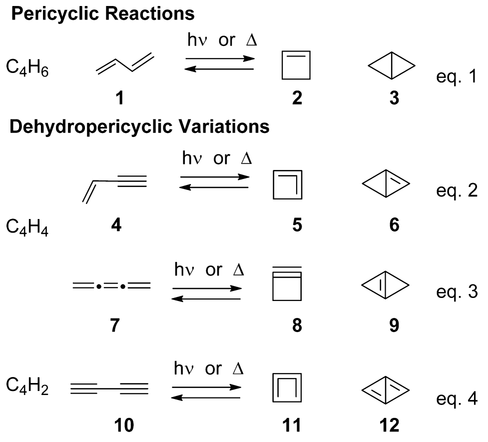
ABSTRACT: The conceptual dehydrogenation of pericyclic reactions yields dehydropericyclic processes, which usually lead to strained or reactive intermediates. This is a simple scheme for inventing new chemical reactions. Computational results on two novel dehydropericyclic reactions are presented here. Conjugated enynes undergo a singlet-state photoisomerization that transposes the methylene carbon. We previously suggested excited-state closure to 1,2-cyclobutadiene followed by thermal ring opening. CCSD(T)//DFT computations show two minima of similar energy corresponding to 1,2-cyclobutadiene, one chiral and closed shell and the second a planar diradical. The chiral structure has a low barrier to ring opening and may best explain results on enyne photoisomerization. The first examples of 1,3-diyne + yne cycloadditions to give *o*-benzynes were reported in 1997. Computations on intramolecular versions of this tridehydro ($-3H_2$) Diels–Alder reaction support a concerted mechanism for the parent triyne (1,3,8-nonatriyne); however, a slight electronic advantage in the concerted path may be outweighed by the difference in entropy of activation for sequential vs simultaneous formation of two new ring bonds.

■ INTRODUCTION

Orbital symmetry control in pericyclic reactions ranks among the great unifying principles in the prediction of chemical reactivity. Many essential concepts of electronic control were presented in early incarnations by Fukui,[1] Zimmerman,[2] Dewar,[3] Longuet-Higgins and Abrahamson,[4] and many others,[5] but the clearest and most durable exposition is found in the elegant series of publications and concise set of rules offered by Woodward and Hoffmann.[6]

Not all symmetry-controlled reactions produce stable products; indeed, some lead to highly strained molecules, diradicals, or even zwitterions.[7] As one well studied example, dehydro-Diels–Alder reactions have been known for many years.[8] These typically lead to strained cyclic cumulenes that often undergo further transformations. We coined the term "dehydropericyclic" to describe the broader class of "dehydrogenated" pericyclic reactions, for which many examples already existed.[9] Dehydro is used in its customary context to describe the conceptual removal of molecular hydrogen. The essential principle of dehydropericyclic reactions is exemplified in Schemes 1 and 2. Interconversions of 1,3-butadiene with cyclobutene and bicyclobutane (eq 1) have been well studied as classic pericyclic reactions.[10] Three dehydropericyclic versions (eqs 2–4) are easily created by systematic removal of hydrogen atom pairs. Each of these reactions is now connected to highly strained cyclic products. Enyne photochemistry (eq 2) is one subject of the present work. Ring opening of cyclobutyne[11] and

Scheme 1. Variations on 1,3-Butadiene Cyclizations



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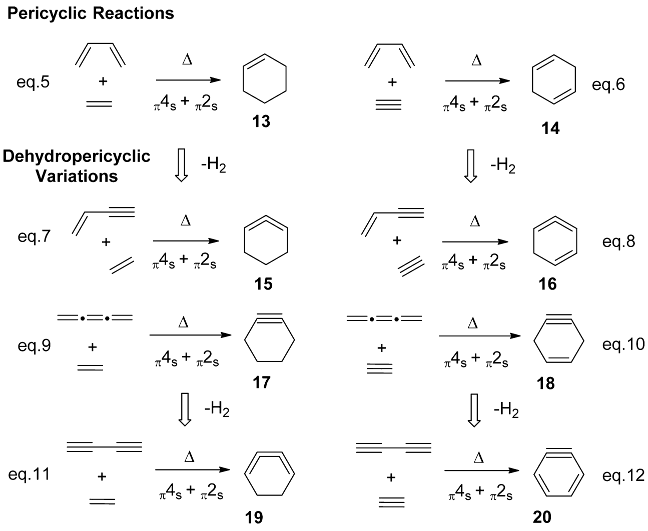
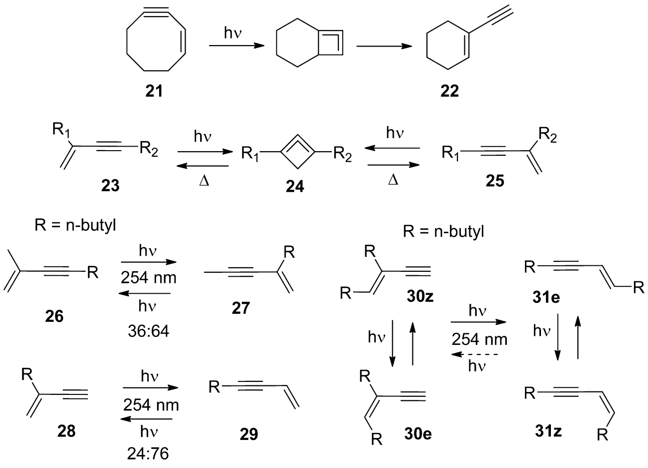
Scheme 2. Variations on the Diels–Alder Cycloaddition



Scheme 3. Enyne Photoisomerization Reactions



bicyclobutene[12] (eq 3) have been described. We demonstrated thermal automerization of carbon atoms in a 1,3-butadiyne (**10**).[13] Computational models support a stepwise mechanism equivalent to eq 4, passing through the highly unusual structure trialene (**12**) which had been suggested by Schleyer to be "experimentally viable".[14] In a similar fashion, the conventional Diels–Alder cycloadditions (Scheme 2) of ethylene (eq 5) or acetylene (eq 6) are easily shown to have six dehydropericyclic variations (eqs 7–12). In principle, cycloadditions leading to **13**–**20** can all be described by concerted ${}_{\pi}2_s + {}_{\pi}4_s$ mechanisms. Most of these equations represent known reactions.[8]

Our interest in these novel pericyclic reactions arose from investigations on the structure and synthesis of strained cyclic allenes and cumulenes.[15,16] To establish the lower limit of the cyclic allene structure, we explored whether 1,2-cyclobutadiene might result from photocyclization of vinylacetylene.[17] Recognition of the broader dehydropericyclic concept led to our systematic experimental and computational studies of enyne and diyne cycloadditions[18] and an eventual review on this simple concept.[9] We present here the results of continued studies on two of the most fascinating dehydropericyclic reactions in this series: photochemical cyclization of an enyne (eq 2 above) and cycloaddition of a 1,3-diyne with an alkyne (eq 12).

■ COMPUTATIONAL METHODOLOGY

All calculations were carried out with Gaussian 09,[19] Spartan 10,[20] MOLPRO 2010.1,[21] or QCHEM 4.2.[22] Structures were optimized and characterized by frequency analysis at the (U)B3LYP/6-311+G(d,p) or (U)M05-2X/6-311+G(d,p) level of theory followed by single-point calculations at DFT geometries. A "broken-symmetry" guess was used for open-shell singlet DFT and CCSD(T) calculations. MINDO/3 calculations were carried out with Gaussian 09, using numerical frequency analysis. CYLview was used for structure presentation.[23] Reaction energies in the intramolecular diyne + yne section are given relative to the lowest energy conformer of the 1,3,8-nonatriyne.

■ RESULTS AND DISCUSSION

Enyne Photochemistry. Does 1,2-cyclobutadiene (**5**) exist, and is this structure accessible from the photocyclization of vinylacetylene (**4**)? As we posed this improbable question some years ago, the best lead came from the photoisomerization of **21** to **22** (Scheme 3), which had been reported several years earlier by Meier.[24] The authors suggested a 1,2-cyclobutadiene intermediate.[24] Drawing further inspiration from the Bergman rearrangement of enediynes,[25] we reasoned that enyne cyclization should be thermally reversible because of product strain, and thus, irradiation of simple enynes should result in transposition of the methylene carbon, as shown with structures **23**–**25**. Experimental demonstration of this process proved to be surprisingly simple. Irradiation of dilute solutions of enyne **26** at 254 nm resulted in equilibration with **27**; irradiation of either isomer led to a 36:64 photoequilibrium. Triplet sensitization did not result in similar isomerization, supporting a singlet reaction multiplicity. Investigations with a series of simple enynes (**26**–**31**) established the generality of this rearrangement. Irradiation of **30z** or **30e** led to facile isomerization and a slower unidirectional formation of a **31z**/**31e** mixture. The examples studied showed a preference for moving alkyl groups apart, suggesting that steric effects may play a role in the opening of a cyclic intermediate. In the gas phase, vinylacetylene is known to undergo more complex dissociation reactions.[26]

The immediate question posed by these experimental results is whether 1,2-cyclobutadiene can be a plausible intermediate. There remains some ambiguity about what represents an allene at geometric extremes. In the cyclic allene series, decreasing ring size leads to a rapid increase in strain, with the allene unit increasingly bent and twisted toward planarity.[15a,b] The five-membered ring homologue, 1,2-cyclopentadiene, with an estimated strain energy of 51 kcal/mol, has already acquired a modest degree of diradical character but is predicted to remain chiral (C_2 symmetry).[15a,c] Eschewing an "allene" label, Tuononen[27] describes 1,2-cyclopentadiene as "carbene-like" even though this structure behaves chemically like a cyclic allene[28] and is chiral. Following this trend toward increasing planarity and diradical character, the logical terminus of this series is a planar singlet diradical corresponding to **32** (Figure 1). As we showed earlier, structure **32** corresponds to an energy minimum and the triplet **33** is at slightly higher energy.[17] Zwitterionic states (**34**) are also possible but represent electronic excited states for simple allenes.[29] Our later studies showed a second minimum on this surface which corresponds to **35** at similar energy to **32**.[15a] Bertrand has described four- and five-membered ring structures like **36** as allenes.[30] However, as pointed out by Christl,[31] these are better considered to be zwitterions which are stabilized by proximate

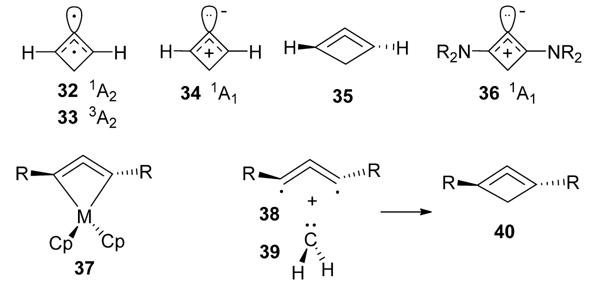


Figure 1. Potential structures for 1,2-cyclobutadienes.

lone pair electrons. Bridged structure **35** has precedent. There are a number of reports on 3-metalla-1,2-cyclobutadienes of general structure **37** which are chiral and thus have the structural characteristics of a cyclic allene.[32] An earlier MINDO/3 study by Dewar and co-workers reported a structure similar to **35** but with a planar allene;[33] however, our application of current optimization and frequency analysis methods with MINDO/3 located only saddle points with C_{2v} or C_2 symmetry. As suggested by Dewar, the simplest description of bonding in **35** (Figure 1) is through union of diradical **38** and carbene **39**. A more recent comprehensive study on the C_4H_4 surface by Zwier and co-workers does not appear to have located structure **35**.[34]

In the present study, we have explored the potential surface around **32** and **35** to help define their role in enyne photochemistry. Our computed energetics of the CCSD(T)//DFT surface connecting **35** with vinylacetylene (**4**) and the singlet diradical structure **32** are shown in Figure 2. Table 1 summarizes the energetics at different levels of theory while important stationary points are reproduced in Figure 3.

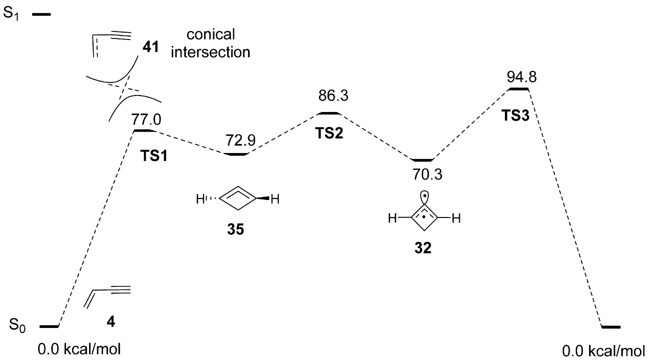


Figure 2. CCSD(T)//B3LYP relative energies for enyne rearrangements on the singlet potential energy surface.

Table 1. DFT and CCSD(T) Relative Energies (kcal/mol)

structure	ΔE_{rel} DFT[a]	ΔE_{rel}(CCSD(T))[b]
4	0.0	0.0
32	67.2	70.3
34	78.7	78.8
35	70.6	72.9
TS1	72.2	77.0
TS2	81.3	86.3
TS3	89.3	94.8
42 (triplet)	52.2	59.6
TS4 (triplet)	93.9	98.7
33 (triplet)	68.0	70.9

[a] (U)B3LYP/6-311+G(d,p) + ZPVE. [b] CCSD(T)/6-311+G(d,p)//B3LYP + ZPVE.

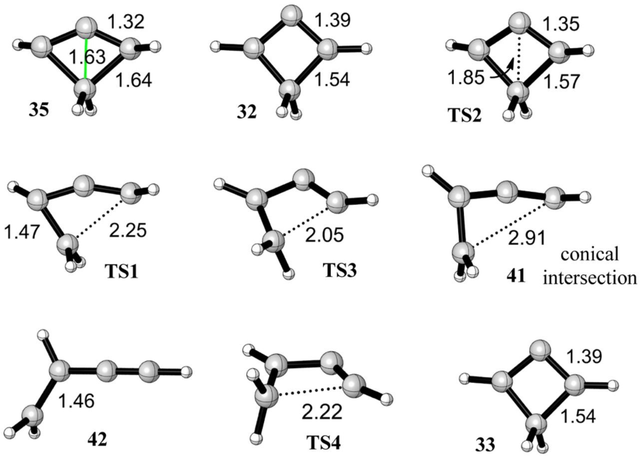


Figure 3. Optimized structures for singlet and triplet stationary points (distances in Å) and the conical intersection geometry.

The most novel structure on this surface is **35**, which represents an energy minimum with MP2, DFT, or CASSCF-(8,8) methods. Both CASSCF occupation numbers and the T_1 diagnostic value[35] (0.016) from CCSD(T)//B3LYP calculation support representation of **35** as a single closed-shell electronic configuration. Electron density contour maps (Figure S1) do not support a formal C2−C4 bond, even though this distance is nearly identical to C1−C4 and C3−C4. This structure demonstrates that carbon can participate in bridged bonding as in **37** (Figure 1). We find a low barrier for ring opening of **35** to vinylacetylene (**4**) via **TS1**. The IRC for ring opening of **35** to **4** traces a process that is best described as conrotatory, exactly as might be expected based on orbital symmetry control. The much larger predicted barrier of 24.5 kcal/mol for ring opening of planar diradical **32** reflects cleavage of a stronger σ bond. There is a low barrier connecting cyclic allene **35** and diradical **32**, which means that if **32** were formed by photorearrangement, it would likely isomerize via **TS2** to **35**, followed by ring opening through **TS1**.

One further key to understanding this process was location of the conical intersection, which is the point of excited-state−ground-state approach. Using a CASSCF(4,4)/6-311+G(d,p) wave function and the state-average method, we located **41** as a geometry for this conical intersection. The structure at this point has a nearly orthogonal double bond and a shortened C1−C4 distance. This is similar to the well-studied 1,3-butadiene−cyclobutene excited-state surface.[36] A more thorough analysis of this excited state surface is desirable, but results in hand led us to conclude that enyne photocyclization to **35**, followed by thermal ring opening, is the most likely mechanism for enyne photoautomerization. What is striking about **35** is just how high in energy this lies (72.9 kcal/mol) relative to vinylacetylene. Thermal reactions of vinylacetylenes are unlikely to access this structure because of competitive lower energy rearrangements.[37]

The absence of a triplet rearrangement is easily explained by data in Figure 4 and Table 1, which shows CCSD(T)//DFT energetics for triplet species. As expected, triplet vinylacetylene optimizes to a structure (**42**) with a fully twisted alkene π bond and the energetics for closure to triplet **33** via **TS4** are unfavorable.

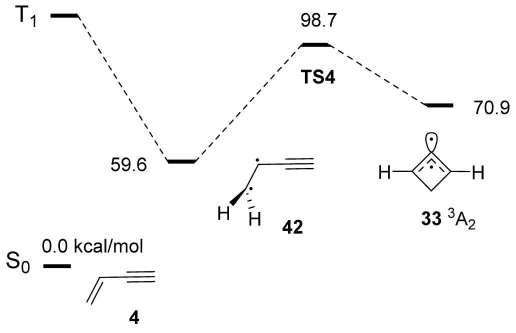


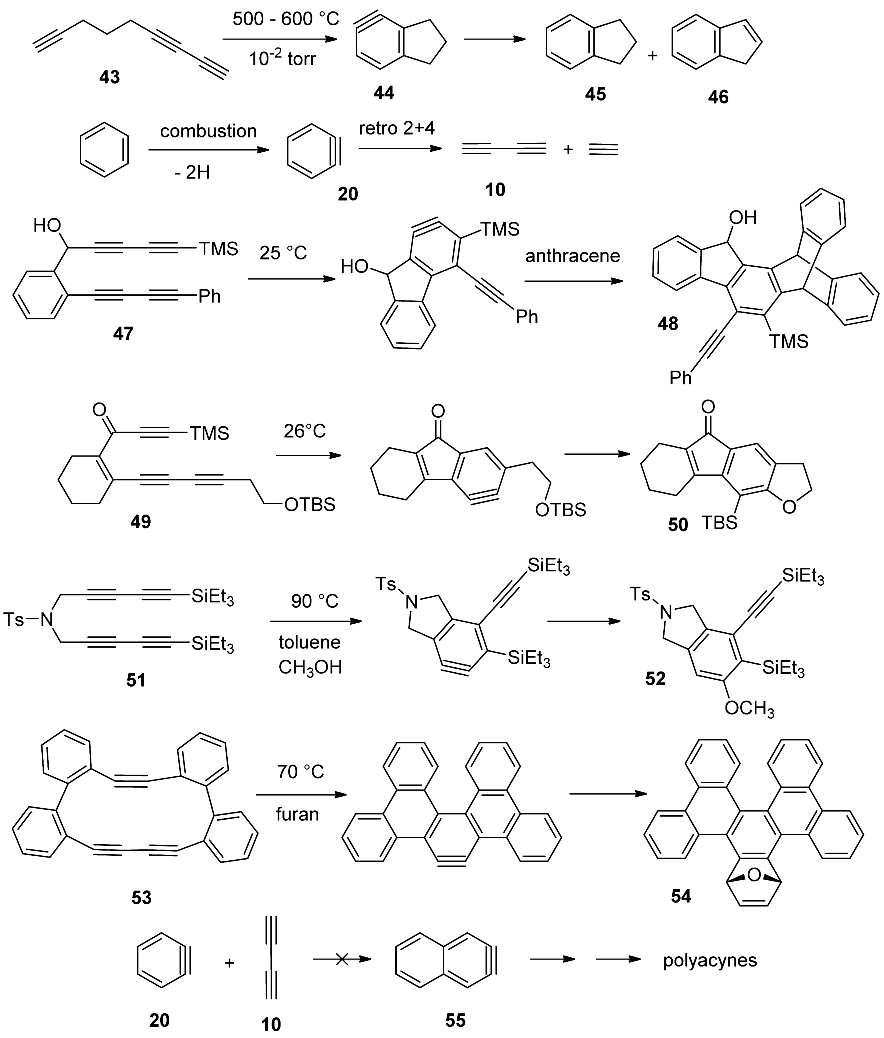
Figure 4. CCSD(T)//DFT energetics for triplet cyclization.

In answer to the question posed above, theory tells us that 1,2-cyclobutadiene should exist as a high energy reactive intermediate and supports its intermediacy in the photoisomerization of enynes. Indeed, two candidate structures exist for 1,2-cyclobutadiene, one a planar diradical (**32**) and one closed shell (**35**).

Diyne + Yne Cycloaddition. Can the [2 + 4] cycloaddition of ethyne with a 1,3-diyne lead directly to *o*-benzyne? This reaction seems to have first been suggested by Fields and Meyerson[38] to explain the Berthelot synthesis of benzene, which was observed in low yield through thermal trimerization of acetylene.[39] At the outset, a tridehydro Diels–Alder reaction ($-3H_2$) seemed improbable because of the required bending for three triple bonds in the transition state; however, we had already demonstrated the first intramolecular diyne + ene cycloaddition to give a 1,2,3-cyclohexatriene (Scheme 2, eq 11).[18c] Choosing the simplest possible substrate for an intramolecular reaction, we showed in 1997 that flash vacuum pyrolysis of triyne **43** yielded indan (**45**) and indene (**46**) (Scheme 4).[18b] Indene is almost certainly a secondary product of hydrogen abstraction by another benzyne intermediate or thermal dehydrogenation of **45**. Pyrolysis of indan or indene results in dimerization to chrysene,[40] but that was not observed under these low pressure conditions. Deuterium substitution of the alkyne hydrogens in **43** supported a straightforward [2 + 4] mechanism which would pass through **44**. As our paper went to press in 1997, we noted that Ueda's group in Japan had just reported solution-phase cyclization of polyynes, and they also suggested a benzyne mechanism, as illustrated by conversion of **47** to **48**.[41] Many examples have now been reported by the same group.[41,42] These reactions are reported to proceed at much lower temperatures than our flash vacuum pyrolysis conditions.

Our earlier computational studies supported concerted mechanisms for all of the parent enyne and diyne cycloaddition

Scheme 4. Diyne + Yne Cycloadditions and Cycloreversion



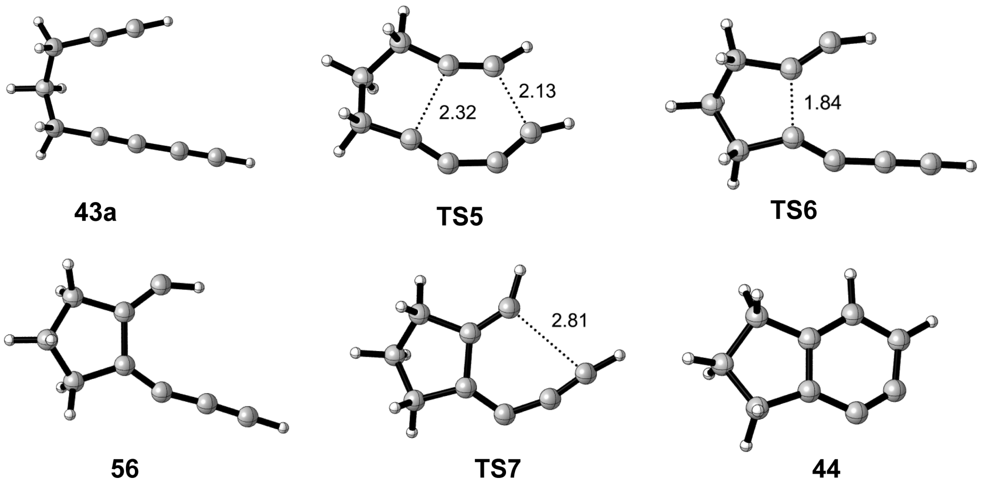


Figure 5. Optimized structures for stationary points (distances in Å) from computations at the (U)M05-2X/6-311+G(d,p) level of theory.

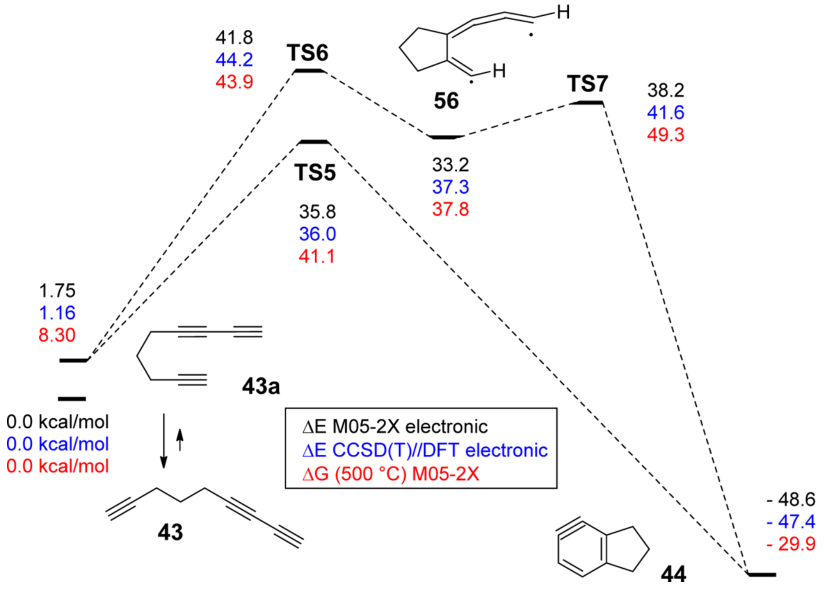


Figure 6. Relative energies for intramolecular diyne + yne cycloaddition.

reactions (Scheme 2, eqs 7, 8, 11, and 12). For the intermolecular diyne + yne reaction, we find only a small advantage for the concerted mechanism relative to a two-step process passing through a diradical intermediate.[18a]

The diyne + yne cycloaddition has had an interesting history since its initial discovery in 1997. Unaware that this cycloaddition was already known, several groups investigating the mechanism for combustion of benzene have reported experimental and computational studies on cycloreversion of *o*-benzyne (**20**, Scheme 4).[43] This is believed to be an important process in the combustion of simple arenes. Sterenberg has reported a metal-templated version.[44] More recently, Hoye rediscovered the solution-phase reaction of tethered polyynes[45] which was first shown by Ueda; his group has greatly expanded its synthetic utility with a number of creative elaborations of the benzyne intermediate.[45,46] One example is the multistep cyclization of **49** to **50**. Parallel studies by Lee have focused on nucleophilic trapping, as in cyclization of **51** to **52**.[47] Lee's group has also shown that intramolecular Alder−ene reactions,[47d] similar to those reported by Danheiser,[48] can provide an alternative cyclization mechanism. In one spectacular example, Tobe has recently reported thermal cyclization of the cyclic polyyne **53** with the benzyne intermediate trapped as product **54**.[49] During its 18-year history, the diyne + yne cycloaddition has been discovered both by intention and by accident and has recently been described as a "new chapter in aryne chemistry".[50] This is now both a powerful synthetic reaction and one likely to be important in combustion. Early discoveries of this reaction have already been relegated to footnotes.[45] One remaining challenge is the possibility of linear acene synthesis (**20** → **55** and beyond) by repetitive addition of butadiynes to benzynes. Computations predict a stepwise mechanism that is derailed to the [2 + 2] cycloaddition product, and our attempts to observe this chemistry in the solution phase were unsuccessful.[51] It is possible that metal catalysis or some other strategy will favor the [2 + 4] reaction channel and provide a new route to polyacenes.

In the present work, we explored the effect of a three-carbon tether and polar or conjugating substituents on the energetics and mechanism of intramolecular diyne + yne cycloadditions. We note that a parallel computational study on diyne + yne cycloadditions by Kuwata[52] and co-workers is reported in this same issue. As in our previous work,[18a] we have studied both concerted and stepwise mechanisms using (U)M05-2X/6-311+G(d,p) optimization for stationary points, followed by higher levels of theory at these geometries. For each concerted transition state, the wave function exhibited no orbital instability. This supports the existence of both concerted and stepwise reaction pathways.

We focus first on the chemistry of **43**, a reaction (Scheme 4) we reported in 1997. Structures for optimized stationary points are reproduced in Figure 5. The concerted transition state **TS5** shows synchronous bond formation, with typical distances for nascent bonds, while the sequence **TS6** → diradical **57** → **TS7** leads to the same product **44** by sequential bond formation. Attempts to locate a stepwise transition state for stepwise nine-membered ring formation led only to **TS5**. Figure 6 summarizes DFT and CCSD(T)//DFT energies relative to the lowest energy conformer of **43**. Estimated relative DFT free energies at 500 °C are provided to model the entropic effects of reaction at high temperature. DFT and CCSD(T)//DFT results favor a concerted mechanism, with the stepwise diradical pathway slightly higher and diradical intermediate **56** lying in a shallow minimum relative to closure to product. The transition state for concerted diyne + yne cycloaddition (**TS5**, Figure 6) is unusual because of nascent aromatic character in two dimensions. At a bond distance of 2.1−2.3 Å, in-plane bonding dominates, and the π aromaticity, which will contribute to product stability, makes only a small contribution because of the modest out of plane $\pi - \pi$ overlap. Birney has made similar observations for the trimerization of acetylene.[53]

CCSD(T) calculations can provide accurate results for species with singlet diradical character, overcoming large spin contamination in the reference wave function.[54] In the present case, the T_1 diagnostic[35] values for **TS6**, **56**, and **TS7** were all ca. 0.048, which suggests caution in the reliability of these energies. In order to more clearly resolve the concerted vs stepwise question, more recent methodological advances were applied for the open-shell singlets. The relative energies for **43a**, **TS5**, and the triplet state of **TS6** were first obtained at the complete basis set (CBS) limit of coupled-cluster theory with single, double, and perturbative triple excitations [CCSD(T)/CBS] using the focal point approach of Allen and co-workers.[55,56] A restricted HF reference (RHF) was utilized for these computations. The T_1 diagnostic[35] did not exceed 0.02, indicating that a single reference determinant suffices to describe these species. To reliably position the open-shell singlet state of **TS6**, the relative energy difference between the triplet and open-shell singlet states was obtained using equation-of-motion spin-flip CCSD (EOM-SF-CCSD) theory.[57] A triple-ζ cc-pVTZ basis was employed for this computation (382 basis functions), along with a restricted open-shell HF (ROHF) reference. This computationally intensive methodology has been shown to yield highly accurate results.[58] Figure 7 summarizes energies from this method. Our predicted barrier relative to **43** via **TS5** should now be 35.1 kcal/mol (33.9 + 1.16), with the stepwise mechanism through **TS6** 2.7 kcal/mol higher. Thus, on the basis of purely electronic energies, a concerted cycloaddition mechanism should be favored for triyne **43**.

Simple thermodynamics further complicates this prediction. The relative free energies in Figure 6 show that thermal corrections estimated at 500 °C (primarily due to entropy changes) should add approximately 10.3, 2.1, and 11.1 kcal/mol to the electronic barriers for **TS5**, **TS6**, and **TS7**, respectively. These numbers are approximate because they are based on a simple rigid-rotor harmonic oscillator method. This yields an advantage for the stepwise mechanism in a **TS5**/**TS6** comparison which will be lost in the second cyclization step at **TS7**. The safest conclusion is that both concerted and stepwise reaction channels exist for cyclization of **43** to **44**, and these are likely to be quite competitive in energy.

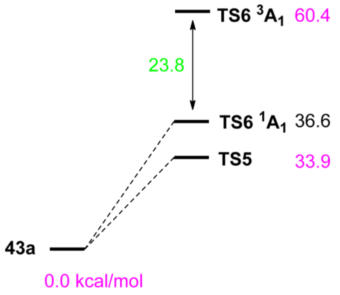


Figure 7. Truncated potential energy surface for the intramolecular diyne + yne cycloaddition. Relative energies for **43a**, **TS5**, **TS6** ($^3A_1$) were obtained at CCSD(T)/CBS (magenta). The relative energy between **TS6** ($^3A_1$) and **TS6** ($^1A_1$) was determined with EOM-SF-CCSD/cc-pVTZ (green).

Houk has reported DFT computations that predict that additional conjugation lowers the barriers and moves the reaction profile toward a stepwise mechanism for the intermolecular diyne + yne cycloaddition.[59] We have studied tethered versions to determine the effect of intramolecular reaction and simultaneous conjugation with additional carbonyl and alkyne functionality. Table 2 summarizes free energy comparisons based on DFT calculations. Transition-state structures (Figure S2) for concerted reactions support moderately asynchronous character, with nascent bond distances ranging from 2.10 to 2.37 Å. All concerted transition states were stable relative to becoming open shell, indicating that two reaction channels should exist. In these calculations, two structures (**58** and **60**) slightly favor the concerted mechanism; two others (**57** and **59**) favor a stepwise route. Given the results presented above, it is reasonable to expect that a higher level theory would lower energies for the diradical species, favoring stepwise mechanisms in all cases. Results reported in parallel studies by Kuwata and co-workers strongly support this conclusion.[52] Ultimately, the existence of low energy stepwise reactions must be related to the well-known propensity of polyynes to oligomerize and even to explode.[60]

In answer to the second question posed above, there is now ample evidence that the intramolecular 1,3-diyne + yne cycloaddition does occur and can lead to *o*-benzyne intermediates by both concerted and stepwise reaction mechanisms.

■ SUMMARY AND CONCLUSIONS

Orbital symmetry control points the way for many remarkable chemical reactions;[6] dehydropericyclic reactions probe the limits of orbital symmetry control and provide routes to many unusual chemical substances.[9] In the present work, we have used theory to support the mechanisms for two new reactions reported previously by our research group. Our experimental studies have shown that simple enynes undergo a photochemically initiated 1,3-transposition of the methylene carbon.[17] The logical intermediate in this rearrangement is a 1,2-cyclobutadiene (**24**, Scheme 3). On the excited-state surface, we

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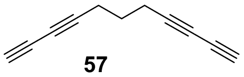
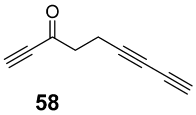
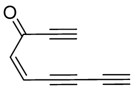
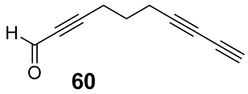
Table 2. (U)M05-2X[a] Relative Free Energies (25 °C) of Concerted and Stepwise Cycloadditions

Reactant ΔG_{rel} = 0.0 kcal/mol	Concerted TS	Stepwise TS1	Diradical Intermediate	Stepwise TS2	Benzyne Product
 **57**	39.0	34.7	22.6	32.7	-38.3
 **58**	36.9	37.8	29.0	34.2	-50.3
 **59**	30.8	30.1	21.8	28.2	-46.2
 **60**	33.1	33.8	25.4	32.3	-45.5

[a] (U)M05-2X/6-311+G(d,p).

have located a conical intersection structure (**41**) in which the alkene π bond is twisted and the structure is moving toward forming a C1−C4 bond. On the ground-state surface, we find a diradical structure (**32**) that is consistent with expectations for the cyclic allene series but with a ring-opening barrier too large to be a plausible intermediate in photorearrangements. A more likely intermediate is a novel chiral structure (**35**) with a low barrier to ring opening that is structurally similar to known metallacyclocumulenes[32] and demonstrates a highly unusual bonding scheme for carbon. This very high energy structure (Figure 2) would only be accessible from the excited-state surface.

In 1997, we sought evidence for the diyne + yne cycloaddition by exploring the simplest intramolecular example of this reaction using flash vacuum pyrolysis. Our experiments[18b] and computations[18a] supported cycloaddition to give a benzyne intermediate. At about the same time, Ueda reported intramolecular diyne + yne reactions in the solution phase.[41] This novel cycloaddition is now becoming an important synthetic methodology,[45,46d,47d,g] and its reversion is believed to be of importance in combustion of aromatic hydrocarbons.[43] We have previously shown that the concerted and stepwise mechanisms for intermolecular diyne + yne cycloadditions are very close in energy. According to our computations, tethering the reactive components in **43** and **57**−**60** does not change that conclusion. For the parent hydrocarbon **43**, the highest level of theory we can apply yields a slight (2.7 kcal/mol) advantage for concerted reaction, but this may be outweighed by the difference in entropy of activation for sequential vs simultaneous formation of two new ring bonds.

The dehydropericyclic concept provides a simple framework for inventing new reactions and generating reactive intermediates.[9] Although dehydropericyclic reactions follow the same set of orbital symmetry directions, the linear geometry and thermodynamic instability of triple bonds has a dramatic effect on transition-state geometries and reaction energetics. The present work underscores the remarkable persistence of symmetry control for reactions that may have seemed quite unlikely to occur at all.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01488.

Cartesian coordinates and total energies for stationary points (PDF)

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Notes

The authors declare no competing financial interest.

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