JOC The Journal of Organic Chemistry
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Concerted vs Stepwise Mechanisms in Dehydro-Diels−Alder Reactions

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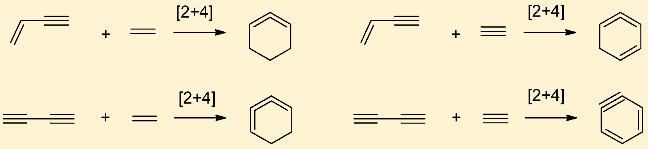
S *Supporting Information*



ABSTRACT: The Diels−Alder reaction is not limited to 1,3-dienes. Many cycloadditions of enynes and a smaller number of examples with 1,3-diynes have been reported. These "dehydro"-Diels−Alder cycloadditions are one class of dehydropericyclic reactions which have long been used to generate strained cyclic allenes and other novel structures. CCSD(T)//M05-2X computational results are reported for the cycloadditions of vinylacetylene and butadiyne with ethylene and acetylene. Both concerted and stepwise diradical routes have been explored for each reaction, with location of relevant stationary points. Relative to 1,3-dienes, replacement of one double bond by a triple bond adds 6−6.5 kcal/mol to the activation barrier; a second triple bond adds 4.3−4.5 kcal/mol to the barrier. Product strain decreases the predicted exothermicity. In every case, a concerted reaction is favored energetically. The difference between concerted and stepwise reactions is 5.2−6.6 kcal/mol for enynes but diminishes to 0.5−2 kcal/mol for diynes. Experimental studies on intramolecular diyne + ene cycloadditions show two distinct reaction pathways, providing evidence for competing concerted and stepwise mechanisms. Diyne + yne cycloadditions connect with arynes and ethynyl-1,3-cyclobutadiene. This potential energy surface appears to be flat, with only a minute advantage for a concerted process; many diyne cycloadditions or aryne cycloreversions will proceed by a stepwise mechanism.

■ INTRODUCTION

The Diels−Alder cycloaddition is not limited to 1,3-dienes. Cycloadditions of enynes have been known for over 100 years[1−3] with many recent reports of new examples.[4−16] Similar [2 + 4] reactions of diynes have been described but still are rare.[17−21] "Dehydro"-Diels−Alder cycloadditions[22] are one class of dehydropericyclic reactions[23] which are derived conceptually by systematic removal of hydrogen atom pairs. These novel processes have long been used to generate strained cyclic allenes[24−28] and other reactive molecules.

Scheme 1 illustrates the dehydropericyclic principle and summarizes the six most fundamental Diels−Alder cycloadditions. Dehydropericyclic variations with an enyne or diyne (eqs 3−6) lead to a reactive intermediate, either a strained cyclic cumulene or, in the final example, *o*-benzyne. In earlier work, we reported intramolecular examples of each Diels−Alder variation and used MP4//MP2 theory to predict energetics for concerted reactions.[17,29] In the present study, we have endeavored to provide more accurate energetics and mechanisms for these dehydropericyclic variations on the Diels−Alder cycloaddition.

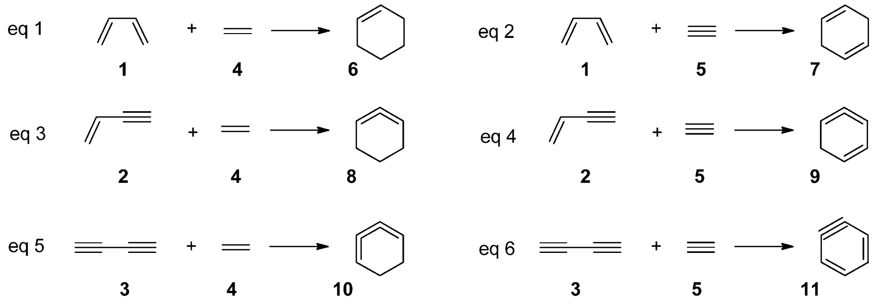
The question of concerted vs stepwise mechanisms for the parent Diels−Alder reaction has been the subject of much debate,[30−44] now convincingly resolved in favor of a concerted mechanism for the simplest versions. Many cycloaddition transition states are, however, significantly asynchronous, depending on polarity and structure.[45] The preferred mechanism is a subtle question of structure and reaction dynamics.[33,46] In general, concerted reactions are believed to be favored by only a few kcal/mol relative to their stepwise counterparts, which proceed through diradical intermediates. Transition states for enyne cycloadditions (eqs 3 and 4) must be asynchronous, even if concerted. For 1,3-diynes (eqs 5 and 6), a symmetrical transition state structure is possible, but this requires substantial deformation of the linear diyne. We recently reported that no concerted transition state exists for the similar [2 + 4] cycloaddition of *o*-benzyne to 1,3-butadiyne.[47] This highly exothermic reaction is predicted to favor a stepwise [2 + 2] route. These considerations have led us to model both concerted and stepwise pathways for dehydro variations on the Diels−Alder reactions.

Portions of these reaction surfaces have been described in earlier computational investigations. We reported MP4SDTQ/6-31G(d)//MP2/6-31G(d) computations on concerted mechanisms, predicting barriers of 30.8, 31.6, 35.8, and 35.5 kcal/mol for eqs 3−6, respectively.[17,29] Ananikov[48] and Lu[49] later used MP2 and DFT methods to study intramolecular enyne cycloadditions. Bachrach has reported MP4//MP2 transition states and energetics for addition of a phosphaenyne and vinylacetylene to ethylene.[50] All of these calculations supported concerted mechanisms and, for hydrocarbons, yielded activation barriers within a few kcal/mol of those cited above. Addition of 1,3-diynes to the $Si{=}Si$ bond appears to favor [2 + 2] products;

Received: July 27, 2011
Published: October 6, 2011

dx.doi.org/10.1021/jo201567d | *J. Org. Chem.* 2011, 76, 9320−9328

Scheme 1. Diels–Alder and Dehydro-Diels–Alder Reactions



DFT computations support a stepwise mechanism.[51,52] In addition to our earlier study,[17,29] several groups have viewed eq 6 in reverse, describing computations to model the endothermic concerted cycloreversion of *o*-benzyne (**11**), a reaction of likely importance in combustion chemistry as a mechanism for benzene decomposition.[53−55] Lower levels of theory (UHF or B3LYP/6-31G*) predict a stepwise mechanism for benzyne cycloreversion,[55] but as in our initial study, the most recent calculations favor a concerted process.[53]

■ COMPUTATIONAL METHODOLOGY

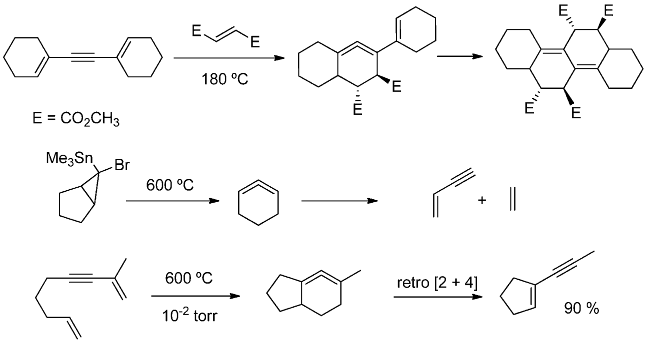
All calculations were carried out with Gaussian 03 Revision E.01,[56] Gaussian 09, Revision B.01,[57] Spartan 06, or Spartan 08.[58] Structures were optimized and characterized by frequency analysis at the M05-2X/6-311+G(d,p) level of theory,[59−63] followed by single point (U)CCSD(T)/6-311+G(d,p) calculation. A "broken-symmetry" guess was used for open shell singlet wave functions. For each transition state, we calculated the intrinsic reaction coordinate (IRC) to verify connection to reactants or product. Unscaled DFT zero point vibrational energy (ZPVE) corrections have been applied to both DFT and CCSD(T) energies. The M05-2X functional[60] was chosen because it has been shown to provide improved descriptions of alkyne and cumulene relative energies.[64] Benchmark computations at this same level of theory for the cycloaddition of butadiene with ethylene and acetylene (eqs 1 and 2) gave activation barriers of 24.8 and 25.7 kcal/mol, respectively. These values agree very well with earlier predictions.[65,66]

■ RESULTS AND DISCUSSION

We began by optimizing reactants, products, and concerted transition states with a closed shell M05-2X/6-311+G(d,p) wave function, followed by single point CCSD(T)/6-311+G-(d,p) calculation and correction with the DFT ZPVE. At the levels of theory investigated, all concerted transition states were found to be stable, relative to becoming open shell. Stepwise mechanisms were next examined using open shell DFT calculations. For eqs 3 and 4, addition to both ends of the enyne was considered. We did not explore the full conformational space available for stepwise reactions but only modeled geometries judged likely to lie along the reaction path and connected by IRC calculations to the transition state structures. In every case, the IRC showed a smooth connection between products and reactants. A summary of results for each cycloaddition in eqs 3–6 follows.

Enyne–Ene Cycloaddition. Enyne–ene cycloadditions present an expedient route to 1,2-cyclohexadienes, which have a chiral structure[67] and an estimated strain energy of ca. 32 kcal/mol.[24,50] Several examples of cycloreversion have also been reported. Scheme 2 presents selected examples of this reaction as a cycloaddition or a cycloreversion.[29,68,69] Additional examples are cited in the recent review by Wessig and Müller.[22]

Scheme 2. Selected Examples of Enyne–Ene Reactions

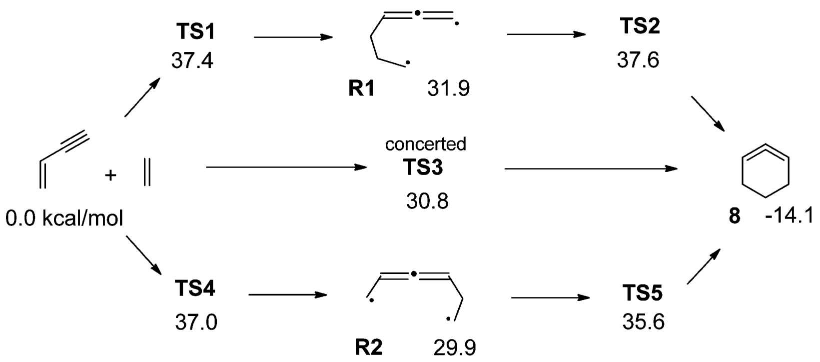


The results of our calculations on enyne–ene cycloadditions are presented in Scheme 3, where energetics are summarized relative to reactants. Figure 1 shows structures for stationary points. The reaction leading to cyclic allene **8** is predicted to be moderately exothermic, with a concerted barrier 6 kcal/mol above diene + alkene cycloaddition at the same level of theory. Two stepwise pathways are predicted to lie 6–7 kcal/mol above concerted **TS3**. Potential diradical intermediates **R1** and **R2** represent shallow energy minima. Energetics of the two stepwise routes are surprisingly similar. These results clearly favor a concerted mechanism for the cycloaddition of vinylacetylene and ethylene. The 26 kcal/mol diminished exothermicity, relative to reaction of 1,3-butadiene, is attributed to the 32 kcal/mol of strain in cyclic allene **8**. Structures for stationary points agree well with expectation, with bond lengths for **TS3** similar to other Diels–Alder reactions.[70] **TS2** and **TS3** are "early" transition states, consistent with their high exothermicity.

Enyne–Yne Cycloadditions. Cycloaddition of vinylacetylene with acetylene (eq 4) should give 1,2,4-cyclohexatriene (**9**). This benzene isomer is a well-known reactive intermediate, most commonly accessed by Hopf cyclization of dienynes[71−73] and estimated to possess an allene strain energy of 34 kcal/mol.[24] Scheme 4 shows selected examples of this synthetically important cycloaddition.[29,74−76] Additional examples are described in a recent review.[22]

Scheme 5 and Figure 2 summarize CCSD(T)//DFT results for the cycloaddition of vinylacetylene and acetylene. Stationary point structures agree well with expectations. The reaction is predictably more exothermic because of the higher energy alkyne component and has a barrier to concerted reaction that is slightly above vinylacetylene + ethylene. Two stepwise routes through diradical intermediates **R3** and **R4** are 4–5 kcal/mol higher in energy. We conclude that for the parent hydrocarbons

Scheme 3. CCSD(T)//M05-2X Energetics (kcal/mol) of Enyne−Ene Cycloadditions



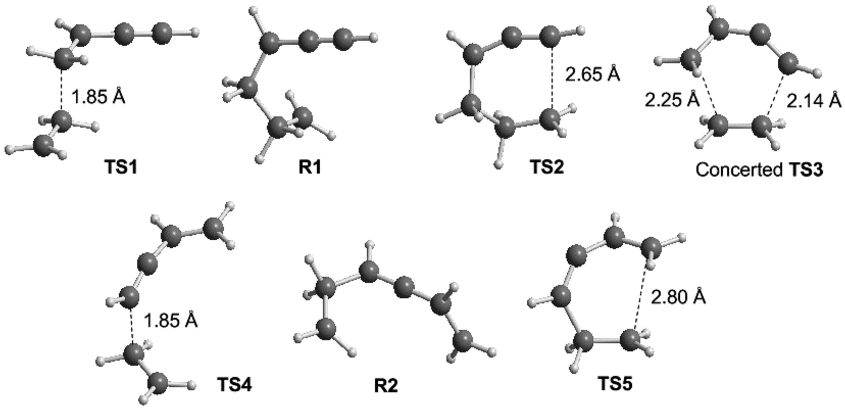
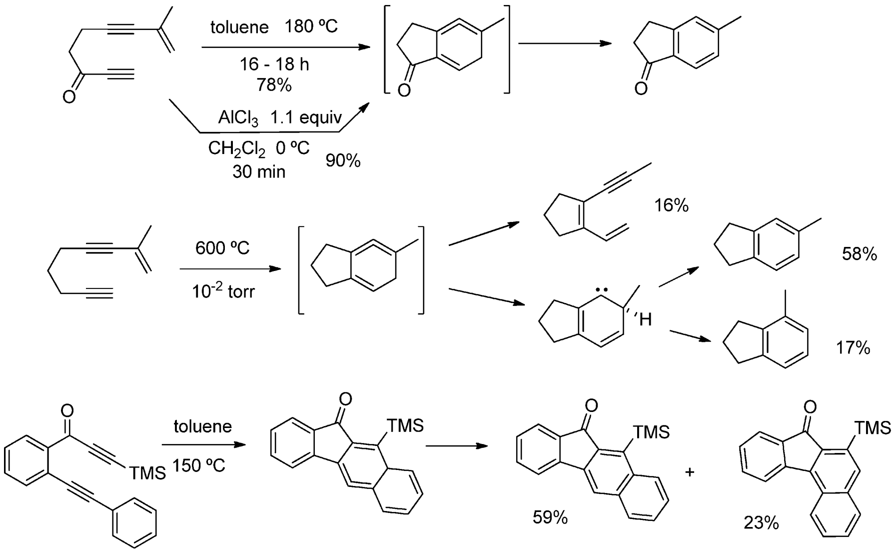


Figure 1. Stationary points in enyne−ene cycloadditions.

Scheme 4. Selected Examples of Enyne−Yne Cycloadditions



vinylacetylene and acetylene cycloaddition favors a concerted reaction pathway.

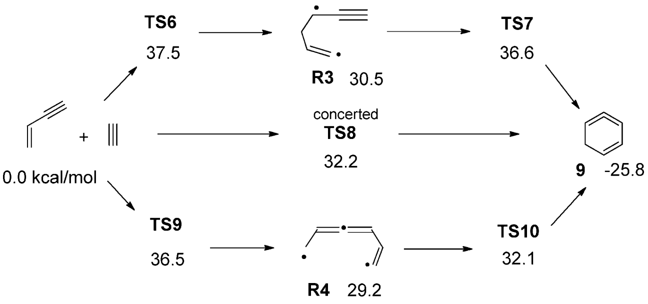
Kinetic data for the gas-phase pyrolysis of a mixture of vinylacetylene + acetylene to give benzene have been reported by two groups.[77,78] The activation energy for formation of benzene is reported to be 30.1 ± 1.3 kcal/mol.[78] If we assume cycloaddition to be the rate-determining step en route to benzene, this agrees well with our predicted value. We have previously noted that cyclic allene **9** should have a very low C−H dissociation energy to give phenyl radical, which can then give benzene by hydrogen abstraction.[79] Other studies have shown that **9** can proceed to benzene by sequential hydrogen shifts, passing through a carbene intermediate.[71−73]

Diyne−Ene Cycloaddition. Diyne−ene cycloadditions, which should generate an intermediate 1,2,3-cyclohexatriene (**10**), are the rarest in this ensemble. The sole example we are aware of was reported by our group in 1996.[29] We have shown that cyclic cumulene **10** is easily generated in solution[80] and has a predicted strain energy of 50 kcal/mol.[24] We reported earlier that flash vacuum pyrolysis of **12** (Scheme 6) gives predominantly **15**, which is presumed to arise from ring-opening of **13**, as well as one unidentified isomer and smaller amounts of indene and indan.

Further studies in our group have now shown that the unidentified product is **17**, whose structure was proven by independent synthesis. The formation of **17** supports a competitive stepwise route passing through diradical **14** and then cyclobutene **16**, which undergoes electrocyclic ring-opening. Similar pyrolysis of homologue **18** at slightly lower temperature resulted in **20** and **21**, whose structures were proven by independent synthesis. In this case, the stepwise reaction product **21** dominates.

One additional example of diyne + ene reaction has been reported. In a recent study of surface chemistry, reaction of butadiyne with Si(100), Ge(100), or Si(111) surfaces (Scheme 6) led to spectroscopic evidence for cyclobutenes (**23**) rather than a cyclic cumulene (**22**). Computations supported a stepwise mechanism.[51]

Scheme 5. CCSD(T)//M05-2X Energetics (kcal/mol) of Enyne−Yne Cycloaddition



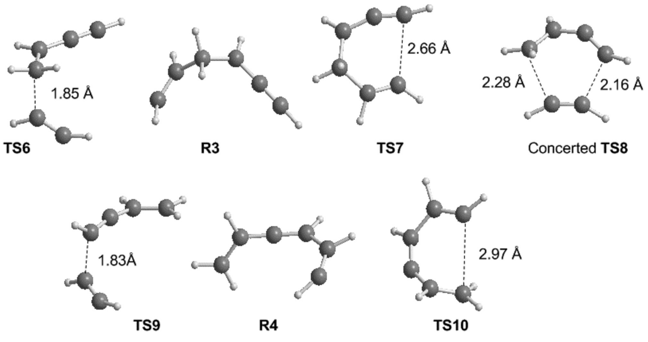
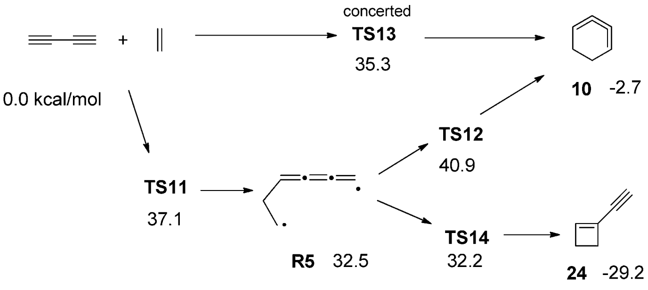


Figure 2. Stationary points in enyne−yne cycloaddition.

Computational results for the cycloaddition of butadiyne with ethylene are summarized in Scheme 7 and Figure 3. We find a symmetrical concerted pathway (**TS13**) that is only slightly lower than the barrier (**TS11**) to formation of diradical **R5**. In this case, the concerted and stepwise routes are predicted to have different outcomes. Concerted reaction can lead directly to cyclic 1,2,3-butatriene **10**. Diradical **R5** might also close to **10**, but the lower energy and more exothermic path leads to cyclobutene **24**.

Scheme 7. CCSD(T)//M05-2X Energetics (kcal/mol) of Diyne−Ene Cycloadditions



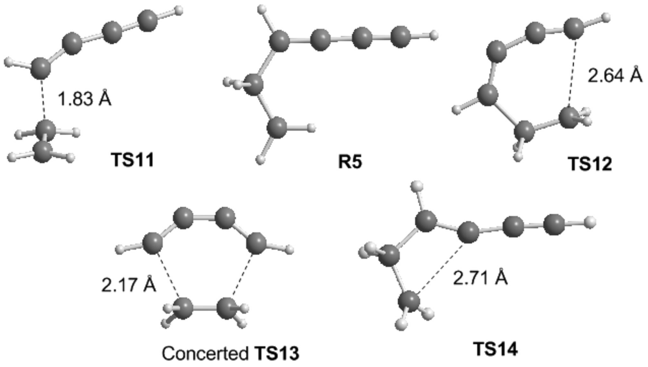
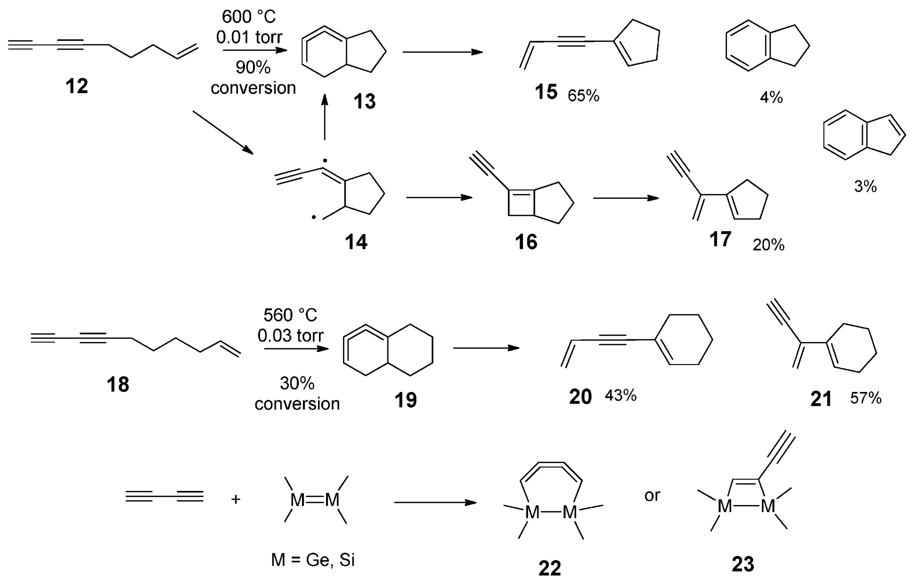


Figure 3. Stationary points in diyne−ene cycloadditions.

Scheme 6. Diyne−Ene Cycloadditions



Cyclic cumulenes such as **10**, **13**, and **19** should have low barriers to electrocyclic ring-opening. For **10**, we predict a CCSD(T)//DFT barrier of 24.9 kcal/mol for ring-opening to 1,5-hexadien-3-yne and a reaction exothermicity of 36.3 kcal/mol. The reverse cyclization would thus have a barrier of 61.2 kcal/mol, which indicates that 1,2,3-cyclohexatrienes are unlikely to be accessible by dienyne thermolysis.

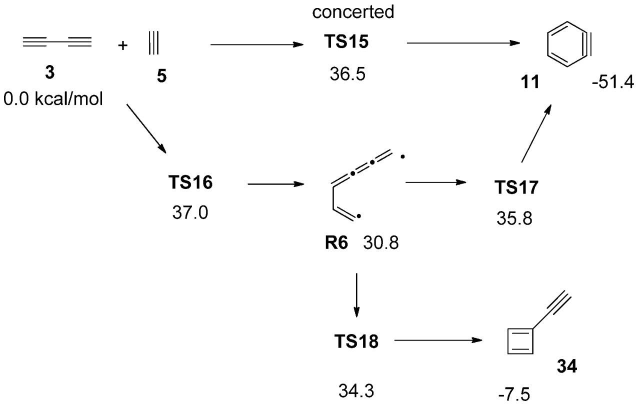
For diyne + ene cycloadditions, the concordance between experiment and theory is striking. Our computations (Scheme 7) show that the stepwise and concerted mechanisms diverge, leading either to cyclic cumulene **10** or cyclobutene **24**, both of which should undergo facile secondary reaction. Experimental results for **12** and **18** show products (Scheme 6) that are similarly consistent with two divergent pathways.

Diyne–Yne Cycloaddition. This type of cycloaddition or cycloreversion is of growing mechanistic importance. We showed in 1997 that flash vacuum pyrolysis of triyne **25** yields products consistent with intramolecular cycloaddition to produce benzyne **26**.[17] Beginning in the same year, Ueda and co-workers have reported many related examples of intramolecular diyne + yne cycloaddition.[18–20,81–89] As one example, cyclization of **27** is reported to occur under surprisingly mild conditions to yield **29**, believed to come from trapping benzyne intermediate **28**. Another recent example was provided by Tsui and Sterenberg, who showed that metal templated polyyne **30** undergoes very facile cyclization, in which the presumed benzyne intermediate **31** is trapped to afford **32**. Several groups have studied the cycloreversion of benzyne, a species known to arise from sequential loss of hydrogen atoms from benzene and phenyl radical (**33**). This process is believed to play a role in combustion chemistry of aromatic compounds.[53–55]

In principle, repetitive aryne + diyne cycloaddition might provide an efficient route to acynes or acenes. There appear to be no clear examples of this reaction, however, and we recently reported computation showing that cycloaddition of *o*-benzyne with 1,3-butadiyne should favor a stepwise [2 + 2] route.[47]

Computational results for the cycloaddition of butadiyne with acetylene are summarized in Scheme 9 and Figure 4. Both B3LYP and M05-2X functionals, in combination with the 6-311+G(d,p) basis set, support the existence of a closed-shell

Scheme 9. CCSD(T)//M05-2X Energetics (kcal/mol) of Diyne–Yne Cycloadditions



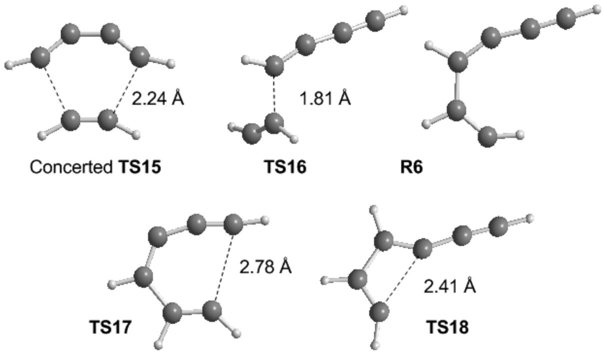
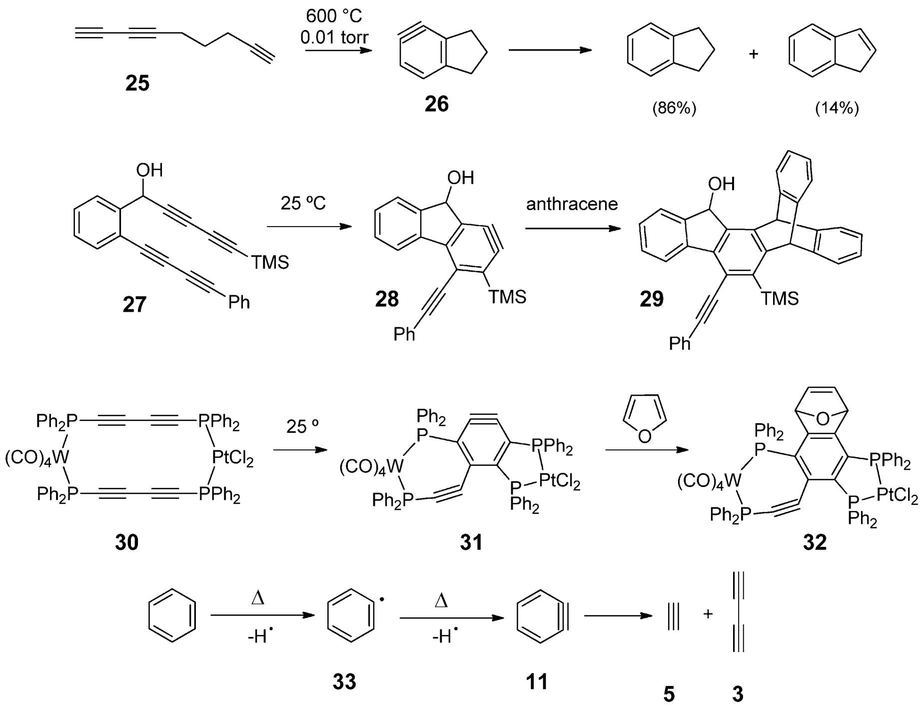


Figure 4. Stationary points in diyne–yne cycloadditions.

Scheme 8. Diyne–Yne Reactions



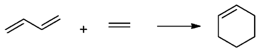
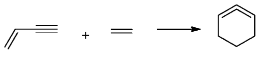
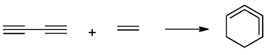
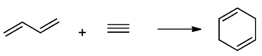
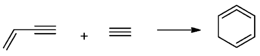
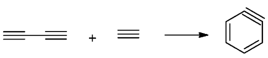
concerted transition state (**TS15**). Our CCSD(T)//DFT computations show that the concerted and stepwise routes to **11** have very similar energetics, with only a 0.5 kcal/mol advantage for concerted reaction.

The results in Scheme 9 also suggest an interesting connection between *o*-benzyne and ethynyl-1,3-cyclobutadiene (**34**). Diradical **R6** has a slightly lower barrier for closure to **34**, but this may be reversible at high temperature. This is a complex and remarkably flat potential energy surface, with four transition states separated by less than 3 kcal/mol, but spanning a wide range of molecular geometries. Doering has described this type of potential surface as a caldera.[90,91]

SUMMARY AND CONCLUSIONS

The energetics of concerted Diels−Alder reactions are summarized in Table 1. We compare here the cycloadditions of butadiene, vinylacetylene, and butadiyne with ethylene and acetylene. Our results show that replacement of one double bond with a triple bond adds 6 or 6.5 kcal/mol to the activation barrier; a second triple bond adds 4.5 or 4.3 kcal/mol to the cycloaddition barrier. Reaction exothermicity is decreased in proportion to product strain.[24] A notable exception is eq 6, which generates the aromatic product *o*-benzyne. Predicted barriers to concerted reaction agree surprisingly well with earlier MP4//MP2 results.[17,29,50]

Table 1. CCSD(T)/6-311+G(d,p)//M052X/6-311+G(d,p) + ZPVE Energetics (kcal/mol) of Concerted Diels−Alder Reactions

	Cycloaddition	ΔE_a	ΔE_r	Product Strain
eq 1		24.8	-40.1	~0
eq 3		30.8	-14.1	32
eq 5		35.3	-2.7	50
eq 2		25.7	-52.7	~0
eq 4		32.2	-25.8	34
eq 6		36.5	-51.4	48.8

Dehydropericyclic reactions provide common routes to reactive intermediates.[23] For the Diels−Alder cycloaddition, dehydro versions have been known for over a century, with many new examples reported in recent years.[4−22] Our calculations support concerted mechanisms for cycloadditions of vinylacetylene with ethylene and ethyne to produce highly strained cyclic allenes as products. In these cases, stepwise reaction is 5.2−6.6 kcal/mol higher in energy, based on the first step. Potential diradical intermediates lie in shallow energy minima. For cycloadditions of 1,3-butadiyne, we are still able to locate concerted transition states; however, the advantage of synchrony is small. With diyne + ene cycloaddition, our experimental studies and computational models for the parent structures both support well-defined stepwise and concerted reaction pathways. Diyne + yne cycloadditions connect with arynes and ethynyl-1,3-cyclobutadiene as products. This potential energy surface appears to be flat with only a minute advantage for a concerted process; many diyne cycloadditions or aryne cycloreversions will likely proceed by a stepwise mechanism.

EXPERIMENTAL SECTION

Warning. Although we experienced no difficulties with these compounds, unsubstituted diynes such as **12** and **18** are potentially explosive and should be handled with care.

1-Nonen-6,8-diyne (12). To a solution of 1,4-bis(trimethylsilyl)-1,3-butadiyne (2.00 g, 10.3 mmol) in THF (20 mL) at −78 °C was added methyllithium/lithium bromide (6.90 mL, 10.3 mmol). The mixture was warmed to ambient temperature, stirred for 3.5 h, and then cooled to −78 °C, and 5-bromo-1-pentene (1.84 g, 12.3 mmol) in HMPA (20 mL) was added dropwise. After 20 h at ambient temperature, the reaction was quenched with water and extracted with pentane (4 × 25 mL). Extracts were washed with water, dried over $MgSO_4$, and concentrated to give 2.92 g of colorless oil. This was dissolved in methanol (10 mL), and anhydrous K_2CO_3 (779 mg, 5.63 mmol) was added. After 17 h at ambient temperature, the mixture was quenched with water (25 mL) and extracted with pentane (3 × 25 mL). Extracts were dried over $MgSO_4$ and concentrated. Column chromatography (silica gel, pentane) yielded 1-nonen-6,8-diyne (**12**) as a clear oil (595 mg, 48.9% overall). Further purification of **12** was carried out by preparative gas chromatography (5% SE-30, 130 °C). ^1H NMR ($CDCl_3$): δ 5.71−5.83 (ddt, 1 H, J = 17.0, 10.2, 6.6 Hz), 5.03−5.10 (ddt, 1 H, J = 17.0, 2.0, 1.6 Hz), 4.99−5.03 (ddt, 1 H, J = 10.2, 2.0, 1.3 Hz), 2.26−2.32 (td, 2 H, J = 7.1, 1.3 Hz), 2.13−2.21 (m, 2 H), 1.98 (t, 1 H, J = 1.3 Hz), 1.65 (quintet, 2 H, J = 7.1 Hz). ^{13}C NMR: δ 137.6, 115.8, 78.3, 68.7, 65.2, 64.8, 32.9, 27.3, 18.6. HRMS *m*/*z* calcd for C_9H_9 (M−H) 117.0704, found 117.0698.

1-Decene-7,9-diyne (18). The procedure above was carried out with 1,4-bis(trimethylsilyl)-l,3-butadiyne (1.00 g, 5.15 mmol), MeLi/LiBr (3.5 mL of a 1.5 M solution in ether, 5.20 mmol), and 6-bromo-l-hexene (857 mg, 5.26 mmol) to give 1.26 g of oil. Reaction as above with anhydrous K_2CO_3 (883 mg, 6.39 mmol), and purification afforded 1-decene-7,9-diyne (**18**, 239 mg, 52% overall) as a clear liquid. Further purification of **18** was carried out by preparative GC (5% SE-30, 110 °C). ^1H NMR ($CDCl_3$): δ 5.80 (ddt, lH, J = 17.1, 10.2, 6.7 Hz), 5.02 (dq, 1H, J = 17.1, 1.7 Hz), 4.97 (dp, 1H, J = 10.2, 1.1 Hz), 2.28 (td, 2H, J = 6.8, 0.9 Hz), 2.07 (q, 2H, J = 6.9. Hz), 1.96 (t, 1H, J = 1.1 Hz), 1.53 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 138.5, 115.0, 78.5, 68.6, 64.9, 64.7, 33.3, 28.1, 27.6, 19.1. HRMS *m*/*z* calcd for $C_{10}H_{l1}$ (M−H) 131.0860, found 131.0865.

Pyrolysis of l-Nonen-6,8-diyne. 1-Nonen-6,8-diyne (**12**, 188 mg) was passed during 30 min through a horizontal quartz tube packed with quartz chips, maintained at 600 °C and 0.07 Torr. The product was collected in a cold trap (−78 °C), then dissolved in 5 mL of pentane, filtered through a plug of silica, and concentrated to give 162 mg of oil. Capillary GC indicated conversion to four major products. Components were isolated by preparative scale gas chromatography (120 °C) and identified by comparison of spectral data with those of authentic samples: 1-nonen-6,8-diyne (**12**, 2.9%, retention time 7.8 min), 1-(1-methylene-prop-2-ynyl)-cyclopentene (**17**, 20.2%, 8.3 min), indan (3.8%, 10.3 min), 1-(3-buten-1-yn-1-yl)-cyclopentene (**15**, 64.5%, 10.6 min), indene (2.4%, 11.6 min), three unidentified minor products (total 6.2%).

Pyrolysis of l-Decen-7,9-diyne. l-Decen-7,9-diyne (**18**, 65.5 mg) was passed through a horizontal quartz tube packed with quartz chips, maintained at 560 °C and 0.025 Torr. The product was collected in a cold trap (−78 °C) to give 45 mg of a yellow oil. Capillary GC (110 °C) indicated a 29% conversion. Products were isolated by preparative GC (15% SE-30, 100 °C) and identified by comparison to authentic samples: 1-(1-methylene-prop-2-ynyl)-cyclohexene (**21**, 57%) and 1-(3-buten-1-yn-1-yl)-cyclohexene (**20**, 43%).

1-(3-Buten-1-yn-1-yl)-cyclopentene (15). This substance and the alcohol precursor below have been prepared earlier by a different synthetic route.[92] To a solution of vinyl bromide (2.91 g, 27.2 mmol) in diethylamine (30 mL) at 0 °C was added tetrakis(triphenylphosphine) palladium(0) (l.00 g, 0.87 mmol) and copper(I) iodide (329.9 mg, l.73 mmol). The mixture was warmed to ambient temperature, and 1-ethynylcyclopentanol (2.00 g, 18.0 mmol) was added dropwise. After 6.5 h at ambient temperature, the reaction was quenched with water (25 mL) and extracted with diethyl ether. Extracts were washed with 5% HCl (3 × 15 mL), saturated $NaHCO_3$ (20 mL), water (20 mL), dried over $MgSO_4$, and concentrated under reduced pressure. Column chromatography (silica gel, pentane/diethyl ether 5:1) yielded 1-(3-buten-1-yn-1-yl)-cyclopentanol as a brown oil (1.67 g, 12.3 mmol, 68.3%). ^{1}H NMR ($CDCl_3$): δ 5.77−5.87 (dd,1H, *J* = 17.4, 11.0 Hz), 5.57−5.64 (dd,1H, *J* = 17.4, 2.1 Hz), 5.43−5.47 (dd, 1H, *J* = 11.0 Hz), 2.51 (s,1H), 1.93−1.98 (m, 4H), 1.70−1.89 (m, 2H). ^{13}C NMR: δ 126.7, 116.9, 93.7, 81.7, 74.7, 42.3, 23.4.

A mixture of the above-prepared alcohol (624 mg, 4.58 mmol) and *p*-toluenesulfonic acid (1.74 g, 9.17 mmol) in THF (30 mL) was refluxed for 15 h. Water was added, and the mixture was extracted with pentane (3 × 25 mL). Extracts were washed with saturated Na_2CO_3, dried over $MgSO_4$, and concentrated. Column chromatography (silica gel, pentane) yielded **15** as a clear oil (446 mg, 84.2%). Further purification of **15** was carried out by preparative GC (120 °C). ^{1}H NMR ($CDCl_3$): δ 6.08 (quintet, 1 H, *J* = 2.1 Hz), 5.90−5.98 (dd, 1 H, *J* = 17.4, 11.0 Hz), 5.59−5.65 (dd, 1H, *J* = 17.4 Hz), 5.44−5.49 (dd, 1 H, *J* = 11.0 Hz), 2.41−2.50 (m, 4 H), 1.92 (quintet, 2 H, *J* = 7.3 Hz). ^{13}C NMR: δ 138.3, 126.2, 124.4, 117.3, 89.2, 87.4, 36.3, 33.4, 23.3. HRMS *m*/*z* calcd for C_9H_{10} 118.0783, found 118.0786.

1-(3-Buten-1-yn-1-yl)-cyclohexene (20). This substance and the alcohol precursor below have been prepared earlier by a different route.[93] The procedure above was carried out with vinyl bromide and 1-ethynyl-1-cyclohexanol to give 1-(3-buten-1-yn-1-yl)-cyclohexanol (98% yield). ^{1}H NMR ($CDCl_3$): δ 5.78 (dd, 1H, *J* = 17.5, 11.0 Hz), 5.56 (dd, 1H, *J* = 17.5, 2.2 Hz), 5.40 (dd,1H, *J* = 11.0, 2.2 Hz), 2.71 (s, 1H), 1.87 (m, 2H), 1.46−1.66 (m,7H), 1.21 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 126.8, 116.9, 93.7, 82.9, 68.9, 39.9, 25.2, 23.3.

Phosphorus tribromide (1.9 g, 7.0 mmol) was added dropwise to a cooled (0 °C) solution of the alcohol (528 mg, 3.5 mmol) in pyridine (20 mL). A heavy white precipitate formed immediately. The dark red mixture was warmed to ambient temperature, stirred for 4 h, and then was poured over cracked ice and extracted with pentane (5 × 20 mL). Extracts were washed with 5% HCl, then water, dried over $MgSO_4$, and concentrated. Column chromatography (silica gel, pentane) yielded 1-(3-buten-1-yn-1-yl)-cyclohexene (**20**) as a clear liquid (221 mg, 48%). Further purification by preparative GC (column C, 110 °C) was performed. ^{1}H NMR ($CDCl_3$): δ 6.10 (septet, 1H), 5.89 (dd,1H, *J* = 17.5, 11.1 Hz), 5.56 (dd, 1H, *J* = 17.5, 2.2 Hz), 5.39 (dd, 1H, *J* = 11.1, 2.2 Hz), 2.11 (m, 4H), 1.60 (m,4H). ^{13}C NMR ($CDCl_3$): δ 135.2, 125.7, 120.7, 117.5, 92.0, 85.7, 29.2, 25.8, 22.4, 21.6; HRMS *m*/*z* calcd for $C_{10}H_{12}$ (M+) 132.0939, found 132.0938.

1-(1-Methylene-2-propyn-1-yl)-cyclopentene (17). To a solution of trimethylsilylacetylene (6.1 g, 63 mmol) in THF (100 mL) at −78 °C was added dropwise a 2.5 M solution of *n*-BuLi in THF (25 mL, 63 mmol). After 30 min, cyclopenten-1-carboxaldehyde (3.0 g, 31 mmol) in THF was added, and the mixture was warmed to ambient temperature and stirred 12 h. The product was isolated by quenching with saturated aqueous ammonium chloride and extraction with diethyl ether (3 × 100 mL). Extracts washed with brine, dried over Na_2SO_4, and concentrated to a yellow oil. Vacuum distillation at (0.03 Torr, 63 °C) afforded the intermediate alcohol l-cyclopent-l-enyl-3-trimethylsilanyl-prop-2-yn-l-ol (5.9 g, 88%) as a clear liquid. ^{1}H NMR ($CDCl_3$): δ 5.81 (s, lH), 4.94 (s, 1H), 2.35−2.46 (m, 4H), 1.88−1.98 (m, 2H), 0.18 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 143.2, 128.3, 104.8, 90.0, 62.2, 32.5, 31.6, 23.6, 0.06. IR (neat): 3320 cm^{-1}.

Solid CrO_3 (17 g, 17 mmol) was added in portions into a mechanically stirred mixture of CH_2Cl_2 (100 mL) and pyridine (27 mL). After 90 min, the above-prepared alcohol (5.0 g, 28 mmol) in CH_2Cl_2 was added slowly. After 4 h, the organic layer was decanted, and the remaining solid was washed with CH_2Cl_2 (2 × 50 mL). Organic fractions were combined, washed with 1 M NaOH (3 × 50 mL), water (50 mL), 5% HCl (3 × 50 mL), and $NaHCO_3$ (75 mL), then dried over Na_2SO_4, and concentrated to give a dark oil. Vacuum distillation (0.015 Torr, 62 °C) afforded 3.4 g (59% yield) of l-cyclopent-l-enyl-3-trimethylsilanylpropynone as a clear oil. ^{1}H NMR ($CDCl_3$): δ 7.09−7.11 (m, 1H), 2.53−2.63 (m, 4H), 1.96−2.03 (m, 2H), 0.25 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 175.7, 151.3, 147.3, 101.3, 96.9, 34.2, 29.9, 23.4, −0.4. IR: 2175, 1620 cm^{-1}.

n-BuLi (2.5 mL, 2.5 M in THF, 6.3 mmol) was added in dropwise to an ice-cooled solution of methyltriphenylphosphonium bromide (3.7 g, 6.2 mmol) in THF (20 mL). After 45 min, the above-prepared ketone (1.0 g, 5.2 mmol) in THF was added dropwise. The reaction was stirred overnight, then quenched with water, extracted with diethyl ether (3 × 100 mL), dried over $MgSO_4$, and concentrated. Without further purification, the product was dissolved in methanol (30 mL), and K_2CO_3 (1.1 g) was added. After stirring overnight and quenching with water, the product was isolated by pentane extraction. Purification by chromatography over silica gel gave 1-(1-methylene-2-propyn-1-yl)-cyclopentene (**17**) as a colorless oil (0.40 g, 65%). ^{1}H NMR ($CDCl_3$): δ 6.16 (s, 1H), 5.51 (s, 1H), 5.35 (s, 1H), 2.95 (s, 1H), 2.44−2.49 (m, 4H), 1.95−1.99 (m, 2H). ^{13}C NMR ($CDCl_3$, 90.56 MHz, center peak of $CDCl_3$ set to 77.17 ppm): δ 141.8, 132.6, 126.8, 121.3, 82.5, 76.9, 33.3, 31.7, 23.7. IR (neat): 3310, 2980, 2930, 2840 cm^{-1}. HRMS *m*/*z* calcd for C_9H_{10} (M+) 118.0783, found 118.0777.

1-(1-Methylene-2-propyn-1-yl)-cyclohexene (21). The procedure above was repeated with cyclohexen-1-carboxaldehyde to obtain l-cyclohex-l-enyl-3-trimethylsilanyl-prop-2-yn-l-ol (95% yield) as a clear liquid; bp 73 °C (0.04 Torr). ^{1}H NMR ($CDCl_3$): δ 5.91 (s, 1H), 4.71(d, 4.9 Hz, 1H), 2.16−2.19 (m, 1H), 2.06−2.08 (m, 4H), 1.65−168 (m, 2H), 1.58−1.59 (m, 2H), 0.20 (s, 9H); ^{13}C NMR δ 136.7, 125.1, 104.8, 90.6, 67.2, 25.0, 24.1, 22.5, 22.2, −0.2. IR (neat): 3360, 2940 cm^{-1}. Oxidation as above with CrO_3/pyridine yielded 1-cyclohex-1-enyl-3-trimethylsilanylpropynone (80% yield) as a clear oil; bp 62 °C (0.04 Torr). ^{1}H NMR ($CDCl_3$): δ 7.26−7.38 (m,1H), 2.31−2.34 (m, 2H), 2.21−2.24 (m, 2H), 1.62−1.64 (m, 4H), 0.24 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 179.5, 148.2, 140.6, 100.5, 97.8, 26.8, 22.5, 21.8, 21.4, −0.6. Wittig olefination and deprotection of the ketone, as described above, followed by column chromatography, yielded the desired product **21** as a colorless oil (58% yield for the final step). ^{1}H NMR ($CDCl_3$): δ 6.43 (s, 1H), 5.47 (s, 1H), 5.44 (s, 1H), 3.00 (s, 1H), 2.16−2.19 (m, 4H), 1.68−171 (m, 2H), 1.54−1.60 (m,2H). ^{13}C NMR ($CDCl_3$): δ 134.0, 131.5, 130.0, 118.8, 77.9, 77.2, 26.0, 24.8, 22.8, 22.2. IR (neat): 3400, 2940, 2830 cm^{-1}. HRMS *m*/*z* calcd for $C_{10}H_{12}$ (M+) 132.0939, found 132.0941.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

General experimental procedures, summary table of total energies and Cartesian coordinates for stationary points, NMR spectra for the pyrolytic chemistry of **12** and **18**, complete Gaussian references. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENTS

We are grateful for generous support from the National Science Foundation (CHE-0910826 and CHE-9616388).

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