

Strained 6-Membered Cyclic Cumulenes as Intermediates in Dehydro Diels-Alder Cycloadditions

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Condensation of the Research

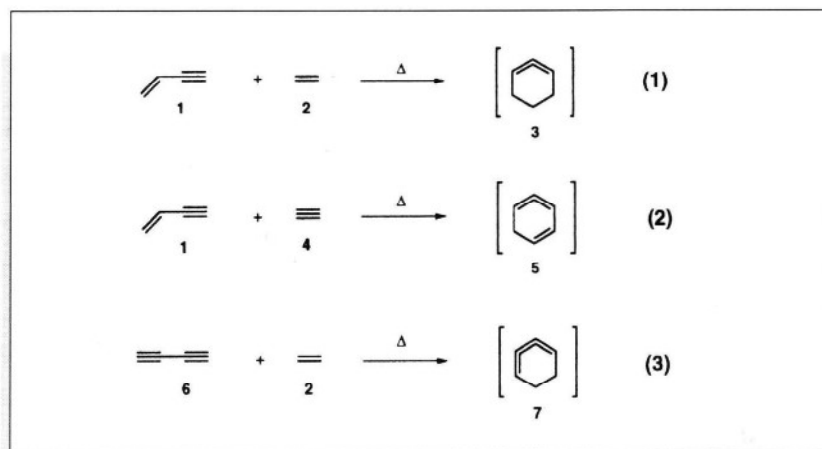
Purpose of the Study *To clarify whether strained cyclic cumulenes are intermediates in dehydro Diels-Alder [4+2] cycloadditions*

Background [4+2] Cycloadditions of conjugated dienes are well studied and fully documented.¹ Although there are some scattered literature reports concerning uncatalyzed,^{2,3} protic or Lewis acid^{3,4} and Pd-catalyzed⁵ dehydro Diels-Alder cycloadditions the intermediacy of 6-membered cyclic allenes in these reactions is still uncertain due to their high strain energies.⁶

What Researchers Accomplished Predicted thermodynamic parameters for thermally initiated dehydro Diels-Alder cycloadditions (Eqs. 1–3, Scheme 1) were estimated by ab initio calculations (Table 1). Synchronous bond formation was assumed in the location of transition states.⁷

The activation parameters (ΔG^\ddagger and ΔH^\ddagger) are ca. 5 kcal/mol higher for Equations 1 and 2 and ca. 10 kcal/mol higher for Equation 3 than those for the corresponding addition reactions of butadiene with ethylene⁷ and acetylene.⁸ These increased activation parameters and endothermicity of Equation 1 explain why it is so difficult to involve unactivated enynes in the uncatalyzed cycloaddition reactions.^{2–5} Equation 3, which did not have precedents in literature, is predicted to be substantially endothermic.

Although the authors' prediction for the exothermicity of Equation 2 is slightly lower than that reported by Danheiser (–29.7 kcal/mol),³ their semi-



Scheme 1 Strained cyclic intermediates in dehydro [4+2] Diels-Alder cycloadditions.

empirical calculations for intramolecular reactions would diminish ΔG^\ddagger for each case by 4–5 kcal/mol due to lowered activation entropy.

Enynes **8,11** and diyne **16** were prepared by known procedures and checked in intramolecular cycloaddition reactions under flash vacuum pyrolysis conditions.

Pyrolysis of **8** afforded enyne **10**, which might arise, according with authors assumption, from cyclic allene **9** via cycloreversional loss of ethylene. Thermolysis of **11** gave the mixture of methylindanes **13** and **15**, together with ynediene **14**. Methylindan **13** is a major product, which is an agreement with Danheiser's results on liquid-phase thermolysis.³ 1,2,4-Cyclohexatriene (**5**) was previously confirmed by calculations,⁹ as well as trapping type experiments¹⁰ thus involvement of its analog **12** as an intermediate looks quite reasonable. Thermolysis of **16** gave a mixture of trace amount of indanes **19** and **20** along with ynediene **18** as a major product. Last, according with the authors' belief, this might result from electrocyclic ring opening of cyclohexatriene **17**.

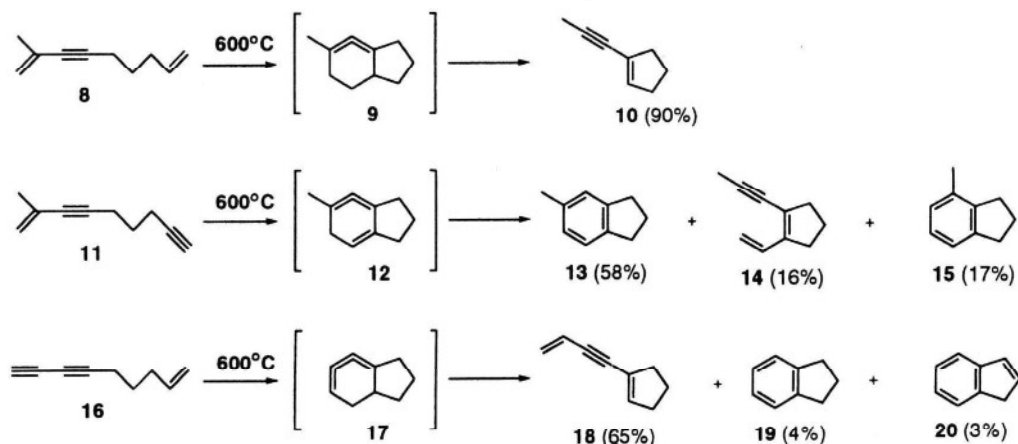
Table 1. Predicted reaction energetics (kcal/mol) from ab initio calculations^{a,b}

	Equation 1	Equation 2	Equation 3
ΔH_R^c	-12.7	-25.4	0.63
$\Delta H^\ddagger c$	30.8	31.5	35.8
ΔG_R	0.9	-13.4	13.4
ΔG^\ddagger	42.0	42.0	47.4
$T\Delta S_R$	-13.6	-12.0	-12.8
$T\Delta S^\ddagger$	-11.2	-10.5	-11.6

^aMP4SDTQ/6-31G**//MP2/6-31G* level of calculation.

^bTemperature 25°C.

^c ΔH values calculated from total electronic energies with ZPVE corrections.



Commentary on the Research

The calculations on energetics for the [4+2] dehydro Diels-Alder reaction, based on assumption of synchronous bond formation are quite informative. While the concerted, synchronous nature of prototype Diels-Alder reaction is now agreed upon, there is still discussion about the mechanisms of substituted cases.¹¹ Although the authors' predictions for Equation 2 enthalpy are slightly higher than Danheiser's estimations, their experimental results on pyrolysis of **11** are in agreement with his work. The thermolysis of **16** deserves a special note. To the best of our knowledge, this is the first successful example of uncatalyzed diyne-ene [4+2] cycloaddition. We believe that the experimental and theoretical investigations done by authors not only expand the scope of the Diels-Alder reaction, but also provide substantial supports for intermediacy of strained cyclic cumulenes for the dehydro version of this intriguing reaction.

References

1. See for example: Roush, W.R. *Adv. Cycloaddit* **1990**, *2*, 91 and references therein.
2. Butz, L.W., Gaddis, A.M., Butz, E.W.J., Davies, R.E. *J. Org. Chem.* **1940**, *5*, 379.
3. Danheiser, R.L., Gould, A.E., Fernandez de la Predilla, R., Helgason, A.L. *J. Org. Chem.* **1994**, *59*, 5514.
4. See for example: Miller, B., Ionescu, D. *Tetrahedron Lett* **1994**, *35*, 6615.
5. Saito, S., Salter, M.M., Gevorgyan, V., Tsuboya, N., Tando, K., Yamamoto, Y. *J. Am. Chem. Soc.* **1996**, *118*, 3970.
6. For review see: Johnson, R.P. *Chem. Rev.* **1989**, *89*, 1111 and references therein.
7. Houk, K.N., Li, N., Evanseck, J.D. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 682.
8. Coxon, J.M., Grice, S.T., Maclagan, R., McDonald, D.Q. *J. Org. Chem.* **1990**, *55*, 3804.
9. Janoschek, R. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 476.
10. Christl, M., Braun, M., Muller, G. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 473.
11. Dewar, M.J.S., Pierini, A.B. *J. Am. Chem. Soc.* **1984**, *106*, 203.