Pergamon

Tetrahedron Letters 40 (1999) 4141–4144

TETRAHEDRON
LETTERS

Intramolecular Thermal Cyclotrimerization of an Acyclic Triyne: An Uncatalyzed Process

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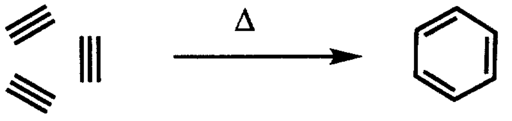
Received 28 January 1999; accepted 30 March 1999

Abstract: Flash vapor pyrolysis of 1,6,11-dodecatriyne at 500 to 600 °C and 0.01 torr affords 1,2,3,6,7,8-Hexahydro-*[as]*-indacene and dehydro derivatives. An uncatalyzed and highly exothermic two-step cycloaromatization mechanism is suggested. This proceeds through initial formation of a 1,4-diradical.

An immense literature describes the metal catalyzed cyclotrimerization of alkynes.[1] By contrast, examples of alkyne thermal trimerization are rare and poorly understood[2], in spite of their potential importance in diverse high temperature processes. In 1866, Berthelot reported that acetylene thermally cyclotrimerizes (eq. 1) to benzene.[2a] Concerted [2+2+2] reaction is unlikely because of the large enthalpic and entropic barriers[3] thus a stepwise process through 1,3-butadiyne has been suggested.[4] High temperature acetylene dimerization has been well characterized in the literature of combustion chemistry.[5] As part of a comprehensive study on novel Diels-Alder routes to strained molecules, we recently reported evidence for a diyne + alkyne cycloaddition to give a benzyne intermediate.[6] In the present work, we describe evidence for a very different cycloaromatization mechanism.



eq. 1

1,6,11-Dodecatriyne (**1**)[7] was chosen as a simple scaffold for studying intramolecular thermal cyclotrimerization. In principle, this might aromatize either by one of several stepwise mechanisms, or by initial alkyne coupling to 1,3,7-cyclododecatriyne, followed by intramolecular cycloaddition. Triyne **1** was subjected to flash vapor pyrolysis at 450 - 600 °C and 0.01 torr to afford a mixture (Scheme 1) consisting primarily of hexahydroindacene (**2**), several products of further dehydrogenation characterized as **3** and **4** (total 35% of C_{12} products; ratio **2** : **3** + **4** *ca.* 1:5)

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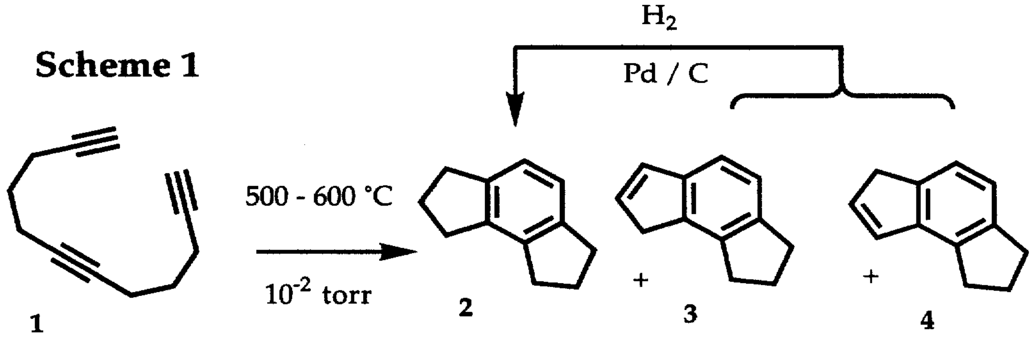
PII: S0040-4039(99)00727-3

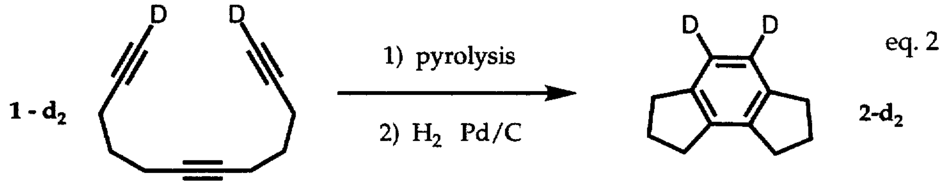
and a variety of lower molecular weight fragmentation products. Hydrogenation of this C_{12} mixture afforded only **2**, which was identical with a sample prepared by independent synthesis.[7,8] Similar results were obtained both in seasoned and new quartz pyrolysis apparatus.

Scheme 1



The percent conversion of **1** increased with temperature, however, the C_{12} product ratio did not change significantly over the range 450 - 600 °C. Pyrolysis of indan is known to give indene.[9] However, when pure **2** was pyrolyzed under identical conditions (600 °C) this afforded only minimal conversion to **3** and **4**. Raising the pressure to ca. 1 torr by bleeding in nitrogen did not significantly change the product ratio; it did not prove feasible to go to higher pressures because of the low volatility of **1**.

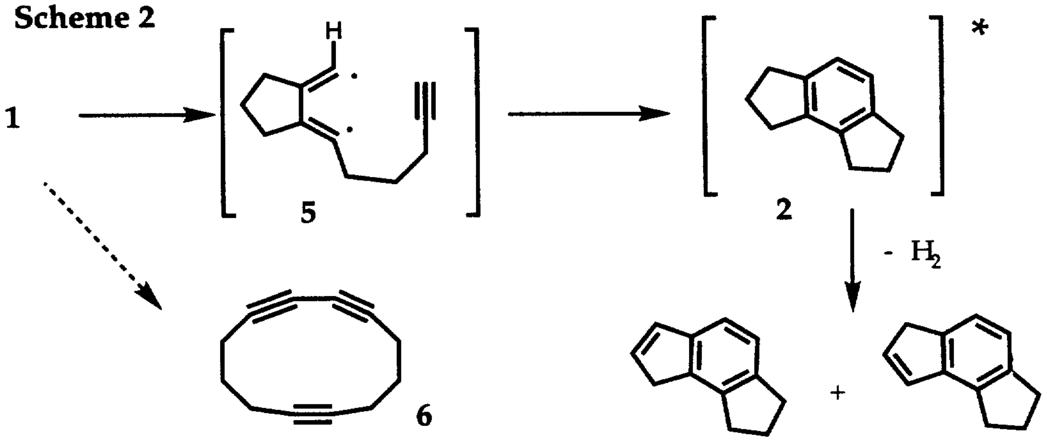
In order to probe the reaction mechanism, we carried out the synthesis[7] and pyrolysis (eq. 2) of **1-d$_2$**. ^{1}H NMR analysis of the C_{12} products showed that essentially all of the label appeared in the aromatic ring.[10] This result shows conclusively that cyclization does not occur by initial alkyne coupling to 1,3,7-cyclododecatriyne; that process would result in loss of deuterium.



eq. 2

These experiments demonstrate that intramolecular alkyne thermal cyclotrimerization can occur at surprisingly low temperature. If we exclude both catalytic processes[1] and concerted [2+2+2] cyclization[3], then several stepwise mechanisms must be considered (Scheme 2). Recent work by Gleiter and co-workers shows that such 1,4-diradical species can be generated by alkyne thermolysis and are readily trapped by hydrogen abstraction.[11] In the present work, initial formation of a single bond would give 1,4-diradical **5**, which should be trapped by the alkyne to directly generate an aromatic ring. Ab initio calculations, in progress, indicate that both dimerization of acetylene to a diradical and trapping of this diradical to give benzene have barriers much smaller than that predicted for concerted cyclotrimerization. We believe this mechanism is supported by the spontaneous formation of **3** and **4**, a result attributed to "hot molecule" chemistry in which the initial product **2** is generated in a highly exothermic final step. Dehydrogenation of thermally activated **2** to **3** + **4** then occurs before excess energy is lost through collisions.[12] DFT calculations at the pBP86/DN* level predict that the conversion **1** –> **2** will be exothermic by 131 kcal/mol.[13]

Scheme 2



Cyclization of triyne **1** is a remarkable process in which three rings are formed in one synthetic step and at modest temperature. It has been suggested that the Berthelot benzene synthesis[2a] proceeds through initial dimerization to a butadiyne.[4] However, the present work suggests a simpler aromatization process; we believe the most likely mechanism involves an initially formed 1,4-diradical[11] which is trapped by an alkyne. This provides a straightforward route leading from alkynes to aromatic rings. The simplicity of these two steps suggests that similar reactions may play a major role in diverse high temperature processes that result in polycyclic aromatics, fullerenes, or soot.

Acknowledgements. This work was supported by grant CHE-9616388 from the National Science Foundation. Helpful discussions with Professors Maitland Jones Jr. and Glen Miller are gratefully acknowledged.

References

(1) Recent reviews: (a) Vollhardt, K. P. C. *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 539; (b) Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081; (c) Grotjahn, D. B. in *Comprehensive Organometallic Chemistry II*, ; Abel, E. W., Stone, F. G., Wilkinson, G. (Eds.), Pergamon, 1995, Volume 12, p 741. (d) A silyl radical catalyzed process has also been described: Yang, J.; Verkade, J. G. *J. Am. Chem. Soc.* **1998**, *120*, 6834.

(2) (a) Bertholet, M. C. R. *Held. Seances. Acad. Sci.* **1866**, 905. (b) Berthelot, M. *Liebigs Ann. Chem.* **1867**, *141*, 173. (c) Barkovich, A. J.; Strauss, E. S.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1977**, *99*, 832. (d) Breitkopf, V.; Hopf, H.; Klarner, F. G.; Witulski, B.; Zimny, B. *Liebigs Ann.* **1995**, 613. (e) Viehe, H. G. *Angew. Chem. Int. Ed. Engl.* **1965**, *4*, 746; (f) Viehe, H. G.; Merenyi, R.;

Oth, J. F. M.; Senders, J. R.; Valange, P. *Angew. Chem. Int. Ed. Engl.* **1964**, *3*, 755.

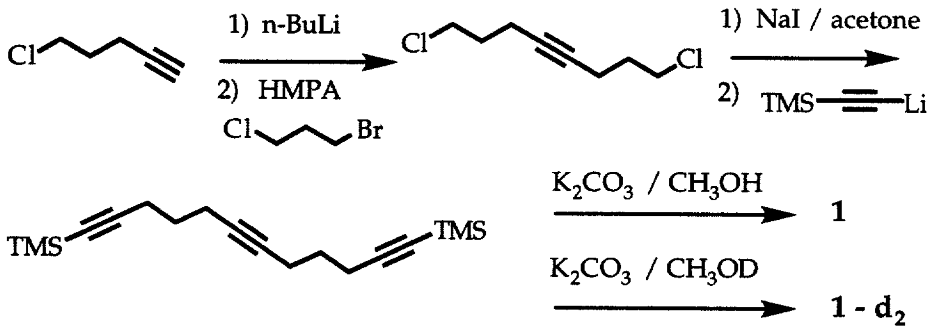
(3) (a) Bach, R. D.; Wolber, G. J.; Schlegel, H. B. *J. Am. Chem. Soc.* **1985**, *107*, 2837. (b) Houk, K. N.; Gandour, R. W.; Strozier, R. W.; Rondan, N. G.; Paquette, L. A. *J. Am. Chem. Soc.* **1979**, *101*, 6779. (c) Wagenseller, P. E.; Birney, D. M.; Roy, D. *J. Org. Chem.* **1995**, *60*, 2853. (d) Jiao, H.; Schleyer, P. v. R. *J. Phys. Org. Chem.* **1998**, *11*, 655. The best predicted enthalpic barrier for concerted cyclotrimerization is 49 - 50 kcal/mol. The entropy of activation at 200 °C would add at least 15 kcal/mol to this figure.

(4) (a) Fields, E. K.; Meyerson, S. *Tetrahedron Lett.* **1967**, *6*, 571. (b) Fields, E. K.; Meyerson, S. In *Advances in Physical Organic Chemistry*; Gold, V., Ed.; Academic: New York, **1968**; Vol. 6, p. 1.

(5) See for example: (a) Miller, J. A.; Melius, C. F. *Combust. Flame* **1992** *91*, 21. (b) Miller, J. A.; Volponi, J. V.; Pauwels, J.-F. *Combust. Flame* **1996** *105*, 451. (c) Melius, C. F.; Miller, J. A.; Evleth, E. M. *Symp. (Int.) Combust.*, **1992**, 24th, 621-8.

(6) Bradley, A. Z.; Johnson, R. P. , *J. Am. Chem. Soc.* , **1997**, *119*, 9917.

(7) Triynes **1** and **1-d$_2$** were synthesized as below. Metal catalyzed cyclization of **1** has been reported previously: Hubert, A. J. *J. Chem. Soc., Chem. Commun.* **1984**, 1967.



(8) Erden, I.; Xu, F. P.; Sadoun, A.; Smith, W.; Sheff, G.; Ossun, M. *J. Org. Chem.* **1995**, *60*, 813.

(9) Penninger, J. M. L. *Int. J. Chem. Kinet.* **1982**, *14*, 761.

(10) By ^{1}H NMR integration, **1-d$_2$** was 90% deuterated. In the pyrolysis product, **2-d$_2$**, integration showed > 76 % loss of the aromatic resonance.

(11) (a) Gleiter, R.; Ritter, J. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2470. (b) Roth, W. R.; Wasser, T.; Gleiter, R. Weigl, H. *Leibigs Ann.* **1997**, 1329. (c) Gleiter, R.; Weigl, H, Hagerhauer, G. *Eur. J. Org. Chem.* **1998**, 1447.

(12) For other examples of reactions attributed to "hot - molecule" processes, see: (a) Martin, H. D.; Urbanek, T.; Pfoehler, P.; Walsh, R. *J. Chem. Soc., Chem. Commun.* **1985**, , 964. (b) Flowers, M. C.; Frey, H. M.; Hopf, H. *J. Chem. Soc., Chem. Commun.* **1972**, 1284. (c) Flowers, M. C.; Frey, H. M. *J. Amer. Chem. Soc.* **1972**, *94*, 8636.

(13) Calculated using Spartan, Version 5.0, Wavefunction, Inc. Total energies from pBP86/DN*//pBP86/DN* calculations are: triyne **1** -465.62749 hartrees; indacene **2** -465.83646.