

Tetrahedron Letters 40 (1999) 4141-4144

TETRAHEDRON LETTERS

## Intramolecular Thermal Cyclotrimerization of an Acyclic Triyne: An Uncatalyzed Process

Martin G. Kociolek and Richard P. Johnson\*

Department of Chemistry University of New Hampshire Durham, New Hampshire 03824

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. © 1999 Elsevier Science Ltd. All rights reserved.

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



1,6,11-Dodecatriyne (1)<sup>7</sup> 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<sub>12</sub> products; ratio 2 : 3 + 4 *ca.* 1:5)

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.<sup>7,8</sup> Similar results were obtained both in seasoned and new quartz pyrolysis apparatus.



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.<sup>9</sup> 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<sup>7</sup> and pyrolysis (eq. 2) of **1-d**<sub>2</sub>. <sup>1</sup>H NMR analysis of the C<sub>12</sub> products showed that essentially all of the label appeared in the aromatic ring.<sup>10</sup> 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.



These experiments demonstrate that intramolecular alkyne thermal cyclotrimerization can occur at surprisingly low temperature. If we exclude both catalytic processes<sup>1</sup> and concerted [2+2+2] cyclization<sup>3</sup>, 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.<sup>11</sup> 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.<sup>12</sup> DFT calculations at the pBP86/DN\* level predict that the conversion 1 --> 2 will be exothermic by 131 kcal/mol.<sup>13</sup>



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<sup>2a</sup> proceeds through initial dimerization to a butadiyne.<sup>4</sup> However, the present work suggests a simpler aromatization process; we believe the most likely mechanism involves an initially formed 1,4-diradical<sup>11</sup> 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

 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<sub>2</sub> 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 <sup>1</sup>H NMR integration, **1-d**<sub>2</sub> was 90% deuterated. In the pyrolysis product, **2-d**<sub>2</sub>, 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.