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Reaction of Atomic and Molecular Carbon with Cyclooctatetraene

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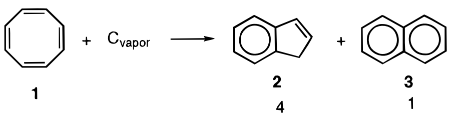
Speculation on the mechanism of fullerene formation has generated considerable interest in the manner in which small carbon fragments interact with cyclic unsaturated systems to generate the polycyclic rings which eventually become fullerenes.[1] In this study, we report a simple example of this reaction in which we demonstrate that C_1 and C_2 react with the monocyclic cyclooctatetraene, **1**, to generate bicyclic systems.[2]

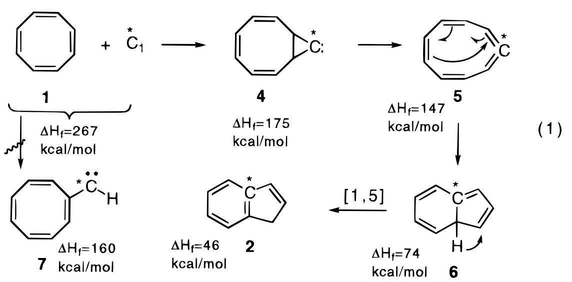
Cocondensation of arc generated carbon vapor with **1** at 77 K generates indene, **2**, and naphthalene, **3**, in a 4:1 ratio as the major volatile products detectable by GC/MS and ^{13}C NMR.[3]



Since these products contain one and two more carbons than **1**, it is logical to assume that they arise from the respective addition of C_1 and C_2 to **1**.

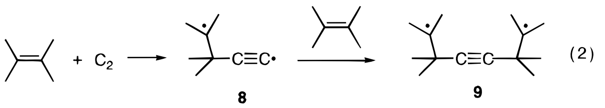
The use of carbon vapor enriched in ^{13}C confirms this assumption.[4] Thus, GC/MS analysis of the products of this reaction reveals that the ratio of ^{13}C enrichment in **3** to that in **2** is 2.2 ± 0.2. An examination of the ^{13}C NMR spectra of the products demonstrates that the label is introduced exclusively at the 9-position in **2** while **3** bears 74 ± 10% of the introduced ^{13}C at the 9 and 10 positions with the remainder distributed equally at the 1 and 2 carbons. The possibility that **3** arises by a subsequent addition of C_1 to **2** is ruled out by a control experiment in which the reaction of ^{13}C enriched carbon vapor with **2** generates **3** as a minor product with the label at the 2-position.

In view of the known propensity of atomic carbon to add to double bonds to generate cyclopropylidenes which ring open to cumulenes,[2,4b] it seems reasonable to propose that initial addition of C_1 to **1** will yield bicyclo[6.1.0]nona-2,4,6-trien-9-ylidene, **4**, which ring expands to 1,2,4,6,8-cyclononapentaene, **5**. Subsequent electrocyclic ring closure generates bicyclo[4.3.0]-nona-2,4,6,8-tetraene, **6**, which rearranges to **2** by a [1,5] sigmatropic hydrogen shift (eq 1). In fact, when Waali and Allison[5] generated **4** from the corresponding dibromide with butyl- or methyllithium, **2** was the sole product with evidence strongly favoring the intermediacy of **5**. The fact that **2** is labeled in the 9-position is in agreement with our proposed mechanism. Although there is considerable precedence for the formation of **2** from **5**, the labeling experiment demonstrates that **5** results from an initial C═C addition by carbon rather than initial C−H insertion to give cyclooctatetraenylmethylene, **7**, which could also produce **5** by ring expansion. Equation 1 shows AM-1[6,7] calculated heats of formation of relevant intermediates confirming the expected exothermicity of each step.



The formation of **3** in the reaction of C_2 with **1** is perhaps more interesting in that little is known concerning the reactions of C_2. Although the label in **3** is found on all of the carbons, it is distributed in a nonstatistical manner, implying that **3** may arise by more than one mechanism. The labeling pattern is consistent with one mechanism which places the label in the 9,10 positions and another which either places it on the 1,2 positions or distributes it statistically on all carbons.

Much of the chemistry that has been observed for C_2 is that of a biradical. Thus, C_2 abstracts hydrogen to give acetylene[8] and adds consecutively to 2 molecules of an acyclic alkene to give biradicals **8** and **9** which abstract hydrogen and/or disproportionate (eq 2).[9] It is the intramolecular version of this latter reaction that we propose leads to the formation of **3** as outlined in Scheme 1. Initial addition of C_2 to **1** generates biradical **10** which can close to cyclopropylidenecarbenes, **11a** and **11b**. Intramolecular addition of conformer **11a** across the ring generates the interesting tetracyclo[4.4.0.$0^{2,10}$.$0^{5,7}$]deca-1(6),3,8-triene, **12**, which can ring open to **3** labeled in the 9, 10 positions.



Although **12** is simply a valence bond tautomer of naphthalene, it does not appear to have received much attention perhaps due to its obvious excess of strain energy. In fact, we have used molecular mechanics calculations[10] to estimate that **12** has 155 kcal of strain energy as compared to **3**. Although one may question whether **12** is actually an energy minimum, AM-1 and ab initio[11] calculations at the 6-31G* level indicate that it has zero negative eigen vectors. An analysis of the rearrangement of **12** to **3** reveals that it is symmetry forbidden and it may be

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(1) Goroff, N. S. *Acc. Chem. Res.* **1996**, *29*, 77 and references cited therein.

(2) For reviews of the chemistry of atomic carbon see: (a) Skell, P. S.; Havel, J.; McGlinchey, M. J. *Acc. Chem. Res.* **1973**, *6*, 97. (b) MacKay, C. In *Carbenes*; Moss, R. A., Jones, M., Jr., Eds.; Wiley-Interscience: New York, 1975; Vol. II, pp 1−42. (c) Shevlin, P. B. In *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum Press: New York, 1980; Vol. I, pp 1−36.

(3) The C atom reactor is modeled after that described by: Skell, P. S.; Wescott, L. D., Jr.; Golstein, J. P.; Engel, R. R. *J. Am. Chem. Soc.* **1965**, *87*, 2829. Products were identified by ^{13}C NMR spectroscopy, mass spectrometry, and CG/MS.

(4) (a) Carbon vapor enriched in ^{13}C was generated as described earlier.[4b] (b) Emanuel, C. J.; Shevlin, P. B. *J. Am. Chem. Soc.* **1994**, *116*, 5991−2.

(5) Waali, E. E.; Allison, N. T. *J. Org. Chem.* **1979**, *44*, 3266.

(6) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

(7) For an extensive MNDO treatment of **4** and **5** and related species see: Kassaee, M. Z.; Nimlos, M. R.; Downie, K. E.; Waali, E. E. *Tetrahedron* **1985**, *41*, 1579.

(8) (a) Skell, P. S.; Harris, R. F. *J. Am. Chem. Soc.* **1966**, *88*, 5933. (b) Skell, P. S.; Plonka, J. H. *J. Am. Chem. Soc.* **1970**, *92*, 5620. (c) Skell, P. S.; Harris, R. F. *Chem. Commun.* **1970**, 689.

(9) Skell, P. S.; Jackman, L. M.; Ahmed, S.; McKee, M. L.; Shevlin, P. B. *J. Am. Chem. Soc.* **1989**, *111*, 4422.

(10) (a) Allinger, N. L.; Hindman, D.; Helmut, H. *J. Am. Chem. Soc.* **1977**, *99*, 3282. (b) The PCMODEL V 5.0 program from Serena Software, Bloomington, IN, was used.

(11) (a) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1968. (b) The SPARTAN V 4.0 program from Wavefunction, Inc., Irvine, CA, was used.

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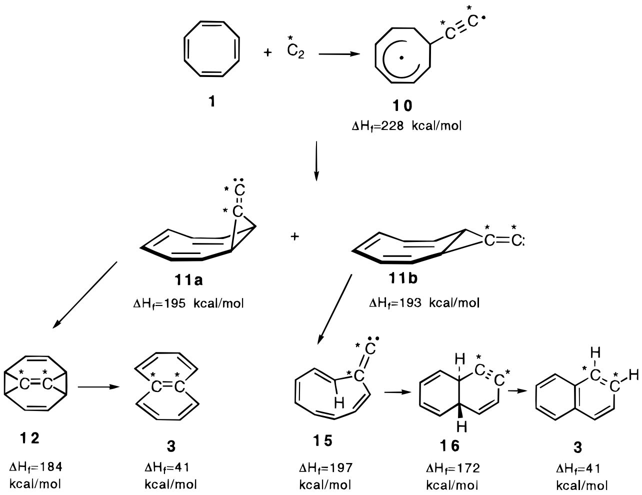
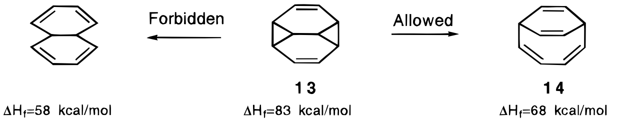
Scheme 1



that **12**, like Dewar benzene,[12] is trapped by symmetry into an energy minimum. These considerations indicate that it may be possible to observe and/or trap **12** on a low-temperature matrix. It is interesting that **13**, a dihydro analog of **12** lacking the ability to aromatize, rearranges by a reverse Diels−Alder reaction yielding **14**.[13] In the case of **12**, this pathway would lead to a cyclohexyne and provide little thermodynamaic driving force.



In order to rationalize the label at the 1,2 positions in **3**, we propose (Scheme 1) that **11b** ring expands to carbene **15** which subsequently undergoes electrocyclic closure and ring expansion to generate *trans*-bicyclo[4.4.0]deca-2,4,7-trien-9-yne, **16**, which can rearrange to appropriately labeled **3** by two [1,5] hydrogen shifts.

The proposed electrocyclic closure and ring expansion of **15** finds analogies in the rapid rearrangement of nonafulvenes to methylene indenes[14] and in the familiar cycloalkylidenecarbene−cycloalkyne rearrangement.[15] The mechanisms in Scheme 1 thus rationalize the labeling results and have analogy in the reactions of related hydrocarbons.

These experiments, which demonstrate that carbon is capable of inserting itself into cyclic unsaturated carbon rings, provide possible mechanisms for carbon cluster formation en route to fullerenes.

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[12] van Tamelen, E. E.; Pappas, S. P.; Kirk, K. L. *J. Am. Chem. Soc.* **1971**, *93*, 6092.

[13] Masamune, S.; Seidner, R. T.; Zenda, H.; Wiesel, M.; Nakatsuka, N.; Bigam, G. *J. Am. Chem. Soc.* **1968**, *90*, 5286.

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