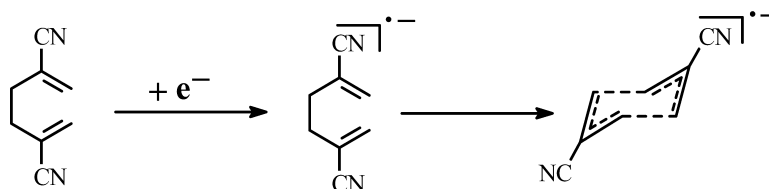Communication

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An Electron-Catalyzed Cope Cyclization. The Structure of the 2,5-Dicyano-1,5-hexadiene Radical Anion in the Gas Phase

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In this Communication, we report the electron-facilitated Cope cyclization of 2,5-dicyano-1,5-hexadiene, **1** (eq 1). Although charge-promoted reactions such as the cationic Diels−Alder reaction[1] and the oxy-accelerated Cope rearrangement[2] are well known, few examples of electron-induced pericyclic reactions have been reported, and those that have been are typically electrocyclic[3−14] and cycloaddition[15−18] reactions. Previous examples of sigmatropic rearrangements of radical anions have been proposed,[19] but it has been suggested that they may arise from dianionic states, and not the radical anions.[20]
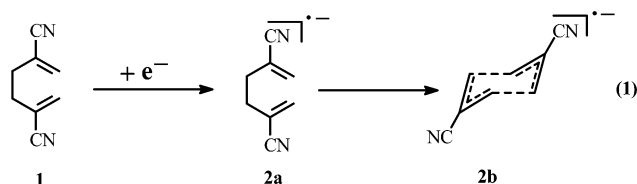

The Cope rearrangement is an example of a reaction that can be promoted by oxidation.[21−24] Simple ionization energy estimates predict that the radical cation Cope rearrangement should have an "inverted" potential energy surface,[21] wherein the cyclic geometry that corresponds to the transition state for reaction of the neutral diene is an intermediate (Figure 1). Thus, matrix isolated 1,5-hexadiene radical cation generated by pulse radiolysis spontaneously cyclizes to the cyclohexane-1,4-diyl radical cation.[25,26] Consequently, Ikeda et al.[27] have used photoinduced electron transfer to afford the cyclization of a phenyl-substituted hexadiene derivative.

Recently reported electronic structure calculations predict that, in select cases, single electron reduction can also catalyze the Cope rearrangement because the electron affinity of the open-shell transition state is much greater than that of the closed-shell hexadiene (Figure 1).[28] For example, cyclization of the radical anion of 2,5-dicyano-1,5-hexadiene (**2a**, eq 1) to form the corresponding cyclohexane-1,4-diyl radical anion **2b** is calculated to be exothermic by 16.2 kcal/mol (B3LYP/6-31+G*).[28] In this work, we provide experimental evidence that **1** does indeed cyclize upon reduction in the gas phase, confirming the theoretical predictions.

Addition of neutral 2,5-dicyano-1,5-hexadiene 10 cm downstream of the electron emission filament in a flowing afterglow−triple quadrupole apparatus[29,30] (operating at room temperature with 0.4 Torr of helium buffer gas flowing at a rate of 200 STP cm^3/s) results in the formation of molecular anion **2** (m/z 132) by thermal electron capture.

The structure of **2** was established by using chemical reactivity. Ion **2** is found to undergo reactions common to organic anions,
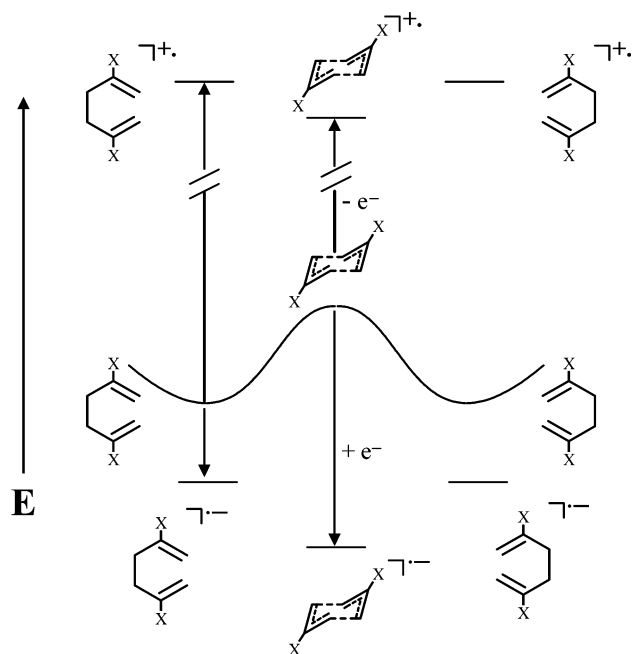

Figure 1. Potential energy surfaces of a neutral, cationic (X = H), and anionic (X = CN) Cope rearrangement of 1,5-hexadienes.

such as condensation with CO_2 and CS_2.[31−35] However, unlike what is found with carboxylates formed from closed-shell ions, such as deprotonated cyclohexanecarbonitrile **3**, the CO_2 adduct of **2** reacts with open-shell reagents NO and NO_2 by addition. Sequential
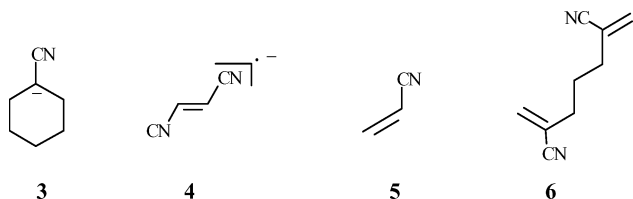

addition of CO_2 and NO or NO_2 has been observed previously for distonic ions such as o-, m-, p-benzyne,[36,37] and m-xylylene ions.[36,37] Radical anions of closed-shell molecules such as fumaronitrile **4** and more highly substituted cyanoethylenes are not found to form adducts with CO_2 or CS_2, suggesting that **2** is not the acrylonitrile-like radical anion **2a**. Attempts to generate the radical anions of acrylonitrile **5** and 2,6-dicyano-1,6-heptadiene, **6**, were unsuccessful, providing additional evidence against **2a** as a stable structure. Moreover, the fact that **6** does not form a stable negative ion is evidence that the formation of **2** is not accompanied by rearrangement involving hydrogen or cyano-group shifts, which should be equally likely to occur for six- or seven-carbon systems. The lack of rearrangement is not surprising because the calculated energy
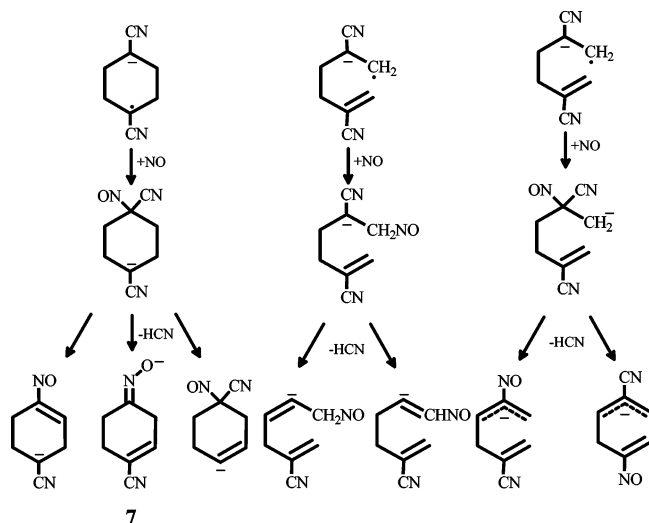
Figure 2. Likely products with *m/z* 135 resulting from the reaction of 2,5-dicyano-1,5-hexadiene radical anion with NO. Products from both the cyclic **2b** and the acyclic **2a** structures are considered. A complete list of possible products resulting from NO addition and direct HCN loss from **2a** and **2b** is provided in the Supporting Information.

Figure 3. CID spectra for *m/z* 135 ion derived from (a) reaction of **2** with NO, and (b) deprotonation of 4-hydroxyimino-1-cyclohexenecarbonitrile.

and 4-hydroxyimino-1-cyclohexenecarbonitrile (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

release, even for the formation of **2b** (28.8 kcal/mol),[28] is much lower than the expected barriers for proton shifts in carbanions.[38,39]

The reaction of **2** with NO leads to formation of a characteristic product at *m/z* 135, resulting from addition and loss of HCN. Surprisingly, the ion at *m/z* 135 is unreactive at thermal energies with common reagents such as CO_2 or CS_2. Moreover, the main fragmentation process upon CID is loss of hydroxyl radical, indicating the presence of a labile oxygen atom. Of the probable addition and loss of HCN products, shown in Figure 2, the most likely to exhibit the properties observed for the ion at *m/z* 135 is the deprotonated oxime **7**, which originates from the cyclic ion. Indeed, the ion with *m/z* 135 has the same CID spectrum as that for authentic **7** (Figure 3) prepared by the deprotonation of the corresponding oxime, 4-hydroxyimino-1-cyclohexenecarbonitrile. Thus, the formation of the oximate by addition of NO and loss of HCN supports the assignment of the cyclic structure. The formation of **7** from **2b** is envisioned as proceeding via equatorial attack of NO to one of the cyano-substituted carbons, followed by stepwise or possibly even concerted elimination of HCN from the axial positions (eq 2). Calculations at the AM1 level of theory predict a distance of 2.7 Å between the cyano-group and axial protons in the adduct ion.

(2)
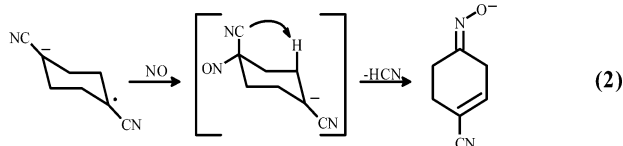
The cyclization of the radical anion of 2,5-dicyano-1,5-hexadiene is the first example of Cope-like reactivity of a radical anion and suggests that reducing agents may be able to catalyze the Cope rearrangement in solution. Experiments designed to explore the scope and applicability of this procedure are in progress.

Supporting Information Available: Structures of possible products formed by addition of NO and direct loss of HCN, table of reactivity for **2**, a list of CID products for the *m/z* 135 ion and **7**, and synthesis procedures for 2,5-dicyano-1,5-hexadiene, 2,6-dicyano-1,6-heptadiene,
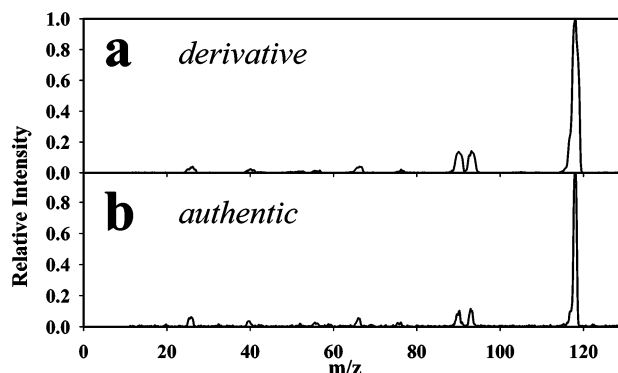
References
(1) Bauld, N. L. In *Advances in Electron-Transfer Chemistry*; Mariano, P. S., Ed.; JAI: Greenwich, 1992; Vol. 2, pp 1–66.
(2) Paquette, L. A. *Tetrahedron* **1997**, *53*, 13971–14020.
(3) Fox, M. A.; Hurst, J. R. *J. Am. Chem. Soc.* **1984**, *106*, 7626–7627.
(4) Dodd, J. R.; Pagni, R. M.; Watson, C. R., Jr. *J. Org. Chem.* **1981**, *46*, 1688–1692.
(5) Gerson, F.; Huber, W.; Müllen, K. *Helv. Chim. Acta* **1979**, *62*, 2109–2128.
(6) Bauld, N. L.; Cessac, J. *J. Am. Chem. Soc.* **1975**, *97*, 2284–2285.
(7) Elschenbroich, C.; Gerson, F.; Boekelheide, V. *Helv. Chim. Acta* **1975**, *58*, 1245–1253.
(8) Bauld, N. L.; Young, J. D. *Tetrahedron Lett.* **1974**, *36*, 3143–3146.
(9) Bauld, N. L.; Hudson, C. E. *Tetrahedron Lett.* **1974**, *36*, 3147–3150.
(10) Nelsen, S. F.; Gillespie, J. P. *J. Org. Chem.* **1973**, *38*, 3592–3596.
(11) Bauld, N. L.; Chang, C.-S.; Farr, F. R. *J. Am. Chem. Soc.* **1972**, *94*, 7164–7165.
(12) Russell, G. A.; Ku, T.; Lokensgard, J. *J. Am. Chem. Soc.* **1970**, *92*, 3833–3834.
(13) Katz, T. J.; Talcott, C. *J. Am. Chem. Soc.* **1966**, *88*, 4732–4733.
(14) Rieke, R.; Ogliaruso, M.; McClung, R.; Winstein, S. *J. Am. Chem. Soc.* **1966**, *88*, 4729–4730.
(15) Roh, Y.; Jang, H.-Y.; Lynch, V.; Bauld, N. L.; Krische, M. J. *Org. Lett.* **2002**, *4*, 611–613.
(16) Janssen, R. G.; Motevalli, M.; Utley, J. H. P. *Chem. Commun.* **1998**, 539–540.
(17) Delauney, J.; Mabon, G.; Orliac, A.; Simonet, J. *Tetrahedron Lett.* **1990**, *31*, 667–668.
(18) Müllen, K.; Huber, W. *Helv. Chim. Acta* **1978**, *61*, 1310–1326.
(19) Miller, L. L.; Boyer, R. F. *J. Am. Chem. Soc.* **1971**, *93*, 646–650.
(20) Kiesele, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 254.
(21) Bauld, N. L.; Bellville, D. J.; Pabon, R.; Chelsky, R.; Green, G. *J. Am. Chem. Soc.* **1983**, *105*, 2378–2382.
(22) Lorenz, K.; Bauld, N. L. *J. Catal.* **1985**, *95*, 613–616.
(23) Miyashi, T.; Konno, A.; Takahashi, Y. *J. Am. Chem. Soc.* **1988**, *110*, 3676–3677.
(24) Dai, S.; Pappas, R. S.; Chen, G.-F.; Guo, Q.-X.; Wang, J. T.; Williams, F. *J. Am. Chem. Soc.* **1989**, *111*, 8759–8761.
(25) Guo, Q.-X.; Qin, X.-Z.; Wang, J. T.; Williams, F. *J. Am. Chem. Soc.* **1988**, *110*, 1974–1976.
(26) Williams, F.; Guo, Q.-X. *J. Am. Chem. Soc.* **1989**, *111*, 4133–4134.
(27) Ikeda, H.; Minegishi, T.; Abe, H.; Konno, A.; Goodman, J. L.; Miyashi, T. *J. Am. Chem. Soc.* **1998**, *120*, 87–95.
(28) Wenthold, P. G. *J. Chem. Soc., Perkin Trans. 2* **1999**, 2357–2363.
(29) Graul, S. T.; Squires, R. R. *Mass Spectrom. Rev.* **1988**, *7*, 263–358.
(30) Marinelli, P. J.; Paulino, J. A.; Sunderlin, L. S.; Wenthold, P. G.; Poutsma, J. C.; Squires, R. R. *Int. J. Mass Spectrom. Ion Processes* **1994**, *130*, 89–105.
(31) Bierbaum, V. M.; DePuy, C. H.; Shapiro, R. H. *J. Am. Chem. Soc.* **1977**, *99*, 5800–5802.
(32) DePuy, C. H.; Bierbaum, V. M. *Tetrahedron Lett.* **1981**, *22*, 5129–5130.
(33) DePuy, C. H.; Bierbaum, V. M.; Damrauer, R.; Soderquist, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 3385–3386.
(34) DePuy, C. H.; Bierbaum, V. M.; Robinson, M. S.; Davico, G. E.; Gareyev, R. *Tetrahedron* **1997**, *53*, 9847–9856.
(35) Hare, M.; Emrick, T.; Eaton, P. E.; Kass, S. R. *J. Am. Chem. Soc.* **1997**, *119*, 237–238.
(36) Hammad, L. A.; Wenthold, P. G. *J. Am. Chem. Soc.* **2000**, *122*, 11203–11211.
(37) Wenthold, P. G.; Hu, J.; Squires, R. R. *J. Am. Chem. Soc.* **1996**, *118*, 11865–11871.
(38) Wilt, J. W. In *Free Radicals*; Kochi, J. K., Ed.; Wiley and Sons: New York, 1973; pp 333–501.
(39) Valko, L.; Simon, P. *Chem. Phys.* **1985**, *99*, 447.

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