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Mechanism of the Cope Rearrangement of Perfluorodienes

Naiyong Jing* and David M. Lemal*

Department of Chemistry, Dartmouth College
Hanover, New Hampshire 03755

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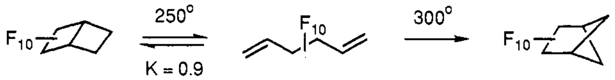
There is much evidence that Cope rearrangement of the prototype hydrocarbon 1,5-hexadiene, variously labeled, proceeds in concerted fashion.[1a,2] We set out to determine whether its fluorocarbon counterpart reacts similarly.

Correa[3] in our laboratory has shown that perfluoro-1,5-hexadiene (**1**) cyclizes reversibly at temperatures around 250 °C, giving perfluorobicyclo[2.2.0]hexane (**2**). At higher temperatures the diene rearranges quantitatively to perfluorobicyclo-[2.1.1]hexane (**3**). On the grounds that these cyclizations are orbital topology-forbidden[4] and that double bonds bearing geminal fluorines readily cycloadd via biradicals,[5] formation of **2** and **3** undoubtedly proceeds via cyclohexanediyl **4** and methylcyclopentanediyl **5**, respectively. That the former forms more readily is consistent with its lower strain energy.[6]



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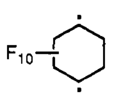

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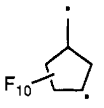

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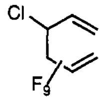
Since Cope rearrangement of diene **1** is degenerate, a label was required to make this process detectable. Therefore, 3-chloroperfluoro-1,5-hexadiene (**6**) was synthesized.[7] Our expectation that the label would not alter the Cope rearrangement mechanism was borne out by the close parallelism found between **1** and **6** in both reactivity and product composition.



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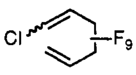

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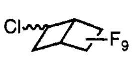

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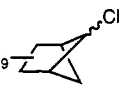

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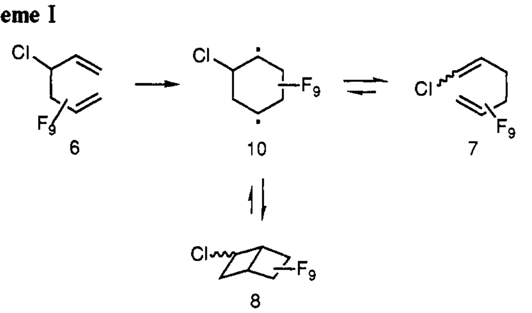
When **6** was heated at 180 °C, no reaction was observed, but at 210 °C rearrangement took place slowly. After 16 h, 10% of the starting material had been transformed into the 2-chloroperfluorobicyclo[2.2.0]hexanes (**8**),[8] but none of the 1-chlorodiene **7**, the Cope product, was detected by ^{19}F NMR. When the reaction was run for 2.5 days at 210 °C, 46% of the starting diene reacted cleanly to give both **7** and **8**, but the **7**:**8** ratio was only 1:10. The *Z*:*E* ratio for **7** was 4:1, a reasonable result on steric grounds. Diene **7** (*Z*:*E* ratio 3:1) was recovered unchanged after being heated for 18 h at 210 °C, but after 3 days at 250 °C, 28% of it had cyclized to **8** (7%, exo/endo ratio 5.5:1) and the 5-chloroperfluorobicyclo[2.1.1]hexanes (**9**) (21%, exo/endo ratio 1.6:1). No diene **6** was detected.[9]

These observations revealed that **7** is stabler than **6** and, more importantly, that cyclization to **8** occurs more readily than Cope rearrangement in either direction. Biradical formation is thus faster than the Cope process. The transition state for a hypothetical concerted Cope rearrangement therefore lies above those leading to the biradical **10** from either **6** or **7**. Hence, *Cope rearrangement must proceed via the biradical.*[10] The course of events is depicted in Scheme I, where the free energy for the transition state leading from **10** to **8** lies below those leading to **6** and **7**.[11]

Scheme I



The transition state connecting chair 1,4-cyclohexanediyl with 1,5-hexadiene has been estimated to lie about 12 kcal/mol (free energy) above the Cope transition state.[1b] This $\Delta\Delta G^{*}$ value continues to be the subject of much controversy,[2] but whatever the true free energy difference may be, *it is overcome with energy to spare in the perfluoro system.*

Probably the underlying reason is the same as that responsible for the thermal formation from perfluorodienes of intramolecular cycloadducts such as **2** and **3**, which in analogous hydrocarbon systems are unstable with respect to the diene.[13,14] It is the driving

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(1) (a) For an excellent summary of the experimental investigations of this problem, see Gajewski, J. J. *Hydrocarbon Thermal Isomerizations*; Academic Press: New York, 1981; pp 166–176. (b) Reference 1a, pp 163–165.

(2) On the basis of quantum mechanical calculations, Dewar has advocated a stepwise pathway: Dewar, M. J. S.; Jie, C. *J. Am. Chem. Soc.* **1987**, *109*, 5893; *J. Chem. Soc., Chem. Commun.* **1989**, 98. However, the highest level *ab initio* calculations carried out to date support a concerted mechanism: Houk, K. N.; Gustafson, S. M.; Black, K. A. *J. Am. Chem. Soc.* **1992**, *114*, 8565. Dupuis, M.; Murray, C.; Davidson, E. R. *J. Am. Chem. Soc.* **1991**, *113*, 9756. See also: Borden, W. T.; Loncharich, R. J.; Houk, K. N. *Annu. Rev. Phys. Chem.* **1988**, *39*, 213.

(3) Correa, R. A., Ph.D. Dissertation, Dartmouth College, 1990. Correa, R. A.; Jing, N.; Lemal, D. M., *J. Org. Chem.*, in press.

(4) Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781.

(5) Bartlett, P. D.; Hummel, K.; Elliott, S. P.; Minns, R. H. *J. Am. Chem. Soc.* **1972**, *94*, 2898 and references therein.

(6) In principle, the central bond of **2** could be the first new bond formed, leading to a 1,2-dimethylcyclobutanediyl intermediate. This biradical would suffer from the strain in the 4-membered ring. Though the strain energies of highly fluorinated cyclobutane rings remain a matter of controversy, we and others have adduced evidence that the numbers do not differ dramatically from the 26.4 kcal/mol found for the parent hydrocarbon (Rahman, M. M., Secor, B. A.; Morgan, K. M.; Shafer, P. R.; Lemal, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 5986 and references therein). Whether the biradical were secondary or primary might not be energetically significant in these fluorocarbon species, as BDE(CF_3CF_2-H) and BDE($(CF_3)_2CF$-H) are the same within experimental error (ref 15).

(7) Dedek, V.; Chvátal, Z. *J. Fluo. Chem.* **1986**, *31*, 363.

(8) The exo and endo isomers were formed in the ratio 6:1, presumably for steric reasons.

(9) At 300 °C, the ultimate products from either diene **6** or **7** are bicyclo[2.1.1]hexanes.

(10) For a search for other Cope rearrangements which proceed via a 1,4-diyl, see Berson, J. A.; Owens, K. A. *J. Am. Chem. Soc.* **1990**, *112*, 5973. Berson, J. A. *Chemtracts: Org. Chem.* **1989**, *2*, 213.

(11) Studies of the thermal ring opening of labeled bicyclo[2.2.0]hexanes to hexadienes have shown that the 1,4-cyclohexanediyl intermediate that cleaves to diene does so predominantly in a chair conformation (ref 12). Since the same conformational factors favoring a chairlike over a boatlike transition state should be present in the perfluoro system, it is a good surmise that **9** is generated mostly in a chair conformation from **6** or **7** and then undergoes a ring flip to the boat form required for closure to **8**. If so, *both* transition states intervening between the chair biradical and **8** lie below those leading to **6** and **7**.

(12) Goldstein, M. J.; Benzon, M. S. *J. Am. Chem. Soc.* **1972**, *94*, 5119. Paquette, L. A.; Schwartz, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 3215. Roth, W. R.; Martin, M. *Tetrahedron Lett.* **1967**, 3865.

(13) Cremer, S.; Srinivasan, R. *Tetrahedron Lett.* **1960**, 24.

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force for highly fluorinated double bonds to become saturated,[15] as reflected, for example, in the much greater exothermicity of polymerization of tetrafluoroethylene as compared with ethylene ($\Delta\Delta H = -14.5$ kcal/mol).[16] While a concerted Cope transition state requires partial double bond character among all six participating carbons, a biradicaloid transition state has two sp^3 carbons and two where the new σ-bond is forming that, by the Hammond postulate,[17] closely approach sp^3 hybridization.[18]

Acknowledgment. We wish to thank the Air Force Office of Scientific Research and the National Science Foundation for financial support.

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(14) Srinivasan, R.; Levi, A. A. *J. Am. Chem. Soc.* **1963**, *85*, 3363.

(15) The thermodynamics of fluorine substitution at unsaturated and saturated carbons is discussed in detail in: Smart, B. E. *Mol. Struct. Energ.* **1986**, *3*, 141.

(16) Joshi, R. M.; Zwolinski, B. J. In *Vinyl Polymerization;* Ham, G. E., Ed.; Marcel Dekker: New York, 1967; Vol. 1, Part 1, Chapter 8.

(17) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334.

(18) Though multiple fluorines at a radical center cause pyramidalization, a single one generally does not (Krusic, P. J.; Bingham, R. C. *J. Am. Chem. Soc.* **1976**, *98*, 230). Thus, the developing radical centers in the biradicaloid transition state are probably sp^2 hybridized.