Tetrahedron Letters, Vol. 34, No. 39, pp. 6201-6204, 1993
Printed in Great Britain

0040-4039/93 $6.00 + .00
Pergamon Press Ltd

Photochemical Electrocyclization of Perfluoro-*E,Z,E*-4,5-dimethyl-2,4,6-octatriene

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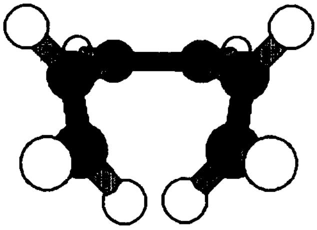
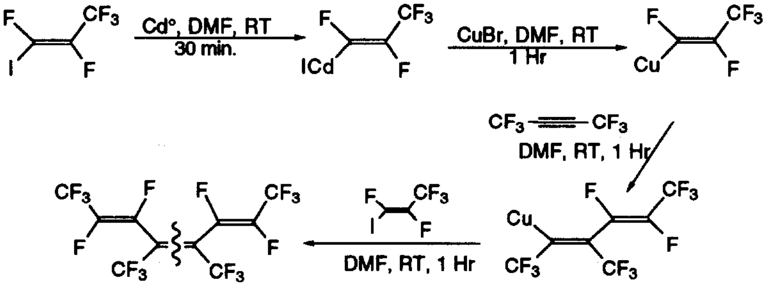
Abstract: Photolysis of the title compound leads to a clean 6-π conrotatory electrocyclic reaction followed by a less-efficient 4-π disrotatory electrocyclic process.

Recent results seem to indicate that the normal boat-like transition state (**1**) for thermal 6-π electrocyclic reaction of 1,3,5-hexatrienes has such stringent steric requirements that virtually any *cis*-substituent at the 1 and/or 6 position will exert a significant inhibitory steric influence upon the cyclization reaction. In Marvell's and Vogel's classic kinetic and stereochemical studies of cyclizations of 1,3,5-hexatrienes, it was found that a single *cis*-methyl group at C_1 was sufficient to increase the activation energy for electrocyclization by ~3-4 kcal/mol, while *cis*-methyl substituents at both C_1 and C_6 totally inhibited the thermal cyclization.[1]



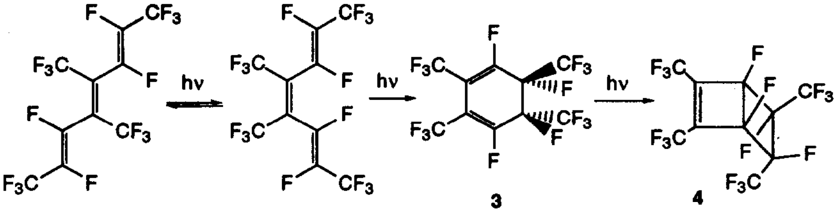
In a recent study of the thermolyses of 1,2-bis(trifluorovinyl)naphthalene and 9,10-bis(trifluorovinyl)phenanthrene, the absence of facile 6-π electrocyclic closure was unexpected in view of the substantial thermodynamic incentive for the reaction.[2] In an attempt to better understand this result we have now examined the thermal and photochemical reactivity of an acyclic perfluorinated triene **3**, which was synthesized as a 1.17:1 mixture of *E,Z,E*- and *E,E,E*-isomers by the sequence of addition and coupling reactions shown below.[3,4]



2 (60%)
E,Z,E/*E,E,E* = 1.17

In a cursory thermal study, it was found that, in contrast to the facile conversion of the parent *cis*-1,3,5-hexatriene to 1,3-cyclohexadiene at temperatures as low as 132 °C,[5] **2** resisted 6-π electrocyclic reaction at temperatures up to 202 °C,[6] this in spite of the ~19-20 kcal/mole greater exothermicity which would be expected for its cyclization.[7] This lack of 6-π electrocyclic reactivity of **2** lends further credibility to the notion of very restrictive steric demands in the transition state for such processes, such that even terminal *cis*-substituents as small as fluorine are strongly inhibiting to the electrocyclic process.

In contrast to its uncooperative thermal behavior, **2** was found to undergo a smooth and quantitative room-temperature photochemical conrotatory 6-π electrocyclic reaction to form, stereospecifically, the perfluoro-1,3-cyclohexadiene species **3**.[9,10]

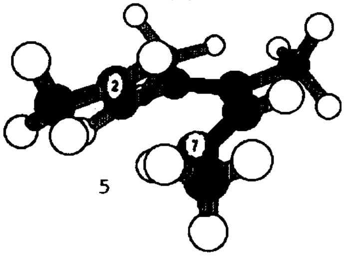


2-*E,E,E* **2-*E,Z,E*** **3** **4**

A second product gradually was formed from **3** upon longer photolysis times. It comprised 13% of the product mixture after 70% conversion (15 hr photolysis) and 18% at 98% conversion (36 hrs). Direct photolysis of pure **3**, either through pyrex (slow) or through quartz (fast) led to quantitative conversion to **4**. (No evidence for reversibility of the formation of **3** was able to be detected during such photolyses.)

Isolation and spectroscopic characterization of this ultimate photoproduct clearly indicated that its structure had the bicyclo[2.2.0]hex-2-ene structure, **4**.[11] The trans stereochemistry of the 5,6-bis-trifluoromethyl groups of both **3** and **4**, and hence the conrotatory nature of the cyclization of **2**, was confirmed by the observation of four individual CF_3 absorbtions in the ^{19}F NMR spectrum of **4**.[11]

These results provide a dramatic demonstration of the differences between the sterically-restrictive, boat-like disrotatory thermal transition state and the probable helical conrotatory photochemical process. In the helical conformation (**5**), which should allow synchronous C_1-C_6 bond-formation from the singlet excited state, neither the fluorine substituents nor the CF_3 groups would be in a position to give rise to detrimental steric interactions.



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It has been hypothesized that the choice of pathways in potentially complex photochemical studies of 1,3,5-hexatrienes[12] can be predicted on the basis of ground state conformational preferences.[13] Consistent with this mechanistic scenario, based upon calculations done on perfluoro-1,3-butadiene and perfluoro-1,3,5-hexatriene,[14] it appears likely that the doubly *cis*-skewed, helical conformation **5** would represent a low energy and thus accessible conformation of **2** in which C_2 and C_7 would be perfectly aligned to undergo the allowed 6-π antarafacial (conrotatory) ring closure which is observed.

Considering the potential complexity of products which could have been formed in the photolysis of **2**, based upon analogy to results from hydrocarbon 1,3,5-hexatrienes,[12] the photochemistry of the cis/trans mixture of **2** turned out to be remarkably clean. *E,E,E*-Triene apparently only underwent geometric isomerization to the *E,Z,E*-isomer, with neither isomerization of the other double bonds nor cyclobutene formation being observed. Also, no 1,5-cyclization to products of the commonly seen bicyclo[3.1.0]hex-2-ene type were observed, another indication that the ground state of the *cis*-triene must indeed conform largely to a helical structure such as **5**.

Acknowledgement: Support of this research in part by the National Science Foundation is gratefully acknowledged.

References and Footnotes

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4. **2**: ^{19}F NMR (*n*-pentane) *E,Z,E*: ϕ-60.3 (bs, 6F), -69.2 (dd overlapped with *E,E,E* triene signal, 6F, $^4J_{FF}$ = 19 Hz, $^3J_{FF}$ = 10 Hz), -139.8 (dq, 2F, $^3J_{FF}$ = 141.7 Hz, $^4J_{FF}$ = 19.2 Hz), -158.2 (dm overlapped with *E,E,E* triene signal, 2F, $^3J_{FF}$ = 141 Hz), *E,E,E*: -63.1 (bs, 6F), -69.7 (dd, 6F, $^4J_{FF}$ = 20.2 Hz, $^3J_{FF}$ = 10.0 Hz), -136.3 (dq, 2F, $^3J_{FF}$ = 143.3 Hz, $^4J_{FF}$ = 20.2 Hz), -158.2 (dm, 2F, $^3J_{FF}$ = 143.3 Hz); UV in *n*-pentane, λ^{max} = 257nm, E^{max} = 1882.4 cm^2/mol; Exact Mass, Calcd for $C_{10}F_{16}$ = 423.9744, Found = 423.9741.
5. Lewis, K. E.; Steiner, H. . *J. Chem. Soc.* **1964**, 3080.
6. Disappointingly, geometric isomerization of the central double bond of **2** commenced at 150 ^{o}C, and at higher temperatures interconversion of all possible geometric isomers was observed, along with a reversible 4-π electrocyclic process which formed isomeric perfluoro-1,3,4-trimethyl-4-(1-propenyl)cyclobutenes.
7. Using a thermodynamic comparison of cyclobutene and perfluorocyclobutene as a measure.[8]
8. Smart, B.E. in *Molecular Structure and Energetics,* Editors: Liebman, J.F., Greenburg, A., VCH Publishers, Inc., Deerfield Beach, FL, Vol. 3 (1986), 141.
9. The photolyses were carried out by suspending the sample in a Rayonet Reactor (Model RPR-204) equipped with four low pressure mercury bulbs of type RUL 2537 A.
10. **3**: ^{19}F NMR ϕ -59.5 (m, 6F), -75.5 (m, 6F), -108.0 (m, 2F), -201.4 ppm (m, 2F); UV in *n*-pentane, λ^{max} = 261 nm, E^{max} = 915.6 cm^2/mol; Exact Mass, Calcd for $C_{10}F_{16}$ = 423.9744, Found = 423.9746.
11. **4**: ^{19}F NMR, ϕ -63.7 (bs, 3F), -64.2 (m, 3F), -73.2 (m, 3F), -75.9 (m, 3F), -174.4 (m 1F), -187.5 (m, 1F), -190.0 (m, 1F), -192.0 ppm(dm, 1F, J_{FF} = 15 Hz); Exact Mass, Calcd for $C_{10}F_{16}$ = 423.9744, Found = 423.9749.
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(Received in USA 8 July 1993; accepted 30 July 1993)