

authentic sample of **1** kindly provided by Professor Glotter.

**Acknowledgment.** Generous support for this work from the National Cancer Institute, National Institutes of Health (Grant CA 28865), is gratefully acknowledged. We thank G. D. Searle and Co. for a generous gift of steroid diacetate **2** and Professor Erwin Glotter of the Hebrew University of Jerusalem for an authentic sample of withanolide E. We are grateful to Dr. John C. Huffman for carrying out the X-ray crystallographic analysis, Dr. R. J. Cooke for experimental assistance during the early stages of the synthesis, and Dr. Günther Neef (Schering AG, Berlin) for unpublished experimental details.

### Fluorine Substituent Effects on Thermal Isomerizations: A New Thermal Reaction of 1,3,5-Hexatrienes

William R. Dolbier, Jr.,\* Keith Palmer, Henryk Koroniak, and Hua-Qi Zhang

Department of Chemistry, University of Florida  
Gainesville, Florida 32611

Virgil L. Goedkin

Department of Chemistry, Florida State University  
Tallahassee, Florida 32306

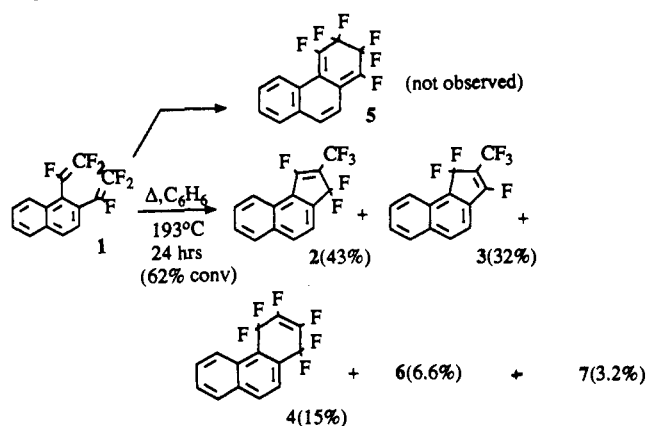
Received September 20, 1990

Fluorine substituents have been observed to have a remarkable effect upon the rate and stereochemical outcome of the butadiene-cyclobutene thermal conrotatory  $4\pi$ -electron electrocyclic interconversion.<sup>1</sup> The substituent effects observed in this system<sup>2</sup> and in other pericyclic systems<sup>3,4</sup> have enhanced one's understanding of the mechanisms of such reactions,<sup>2,5</sup> such that only a small probable effect of fluorine substituents was predicted<sup>6</sup> for the related  $6\pi$ -electron system, i.e., the disrotatory 1,3,5-hexatriene-1,3-cyclohexadiene conversion.

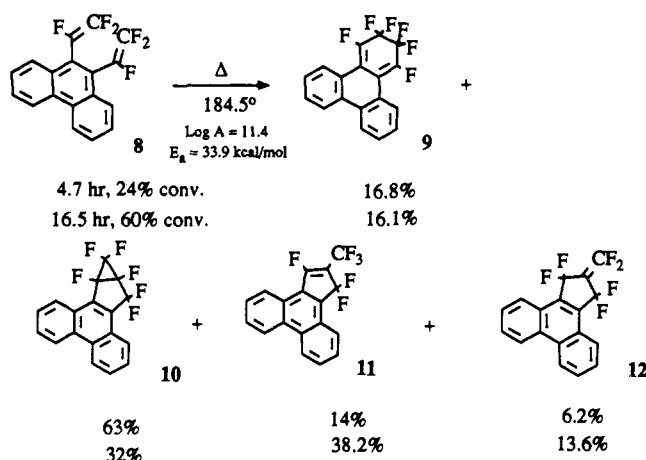
In an attempt to probe this system, a strategy was devised which would utilize the thermolysis of 1,2-bis(trifluorovinyl)naphthalene (**1**).<sup>7,8</sup> In thermal isomerizations, divinyl aromatics had been observed to undergo electrocyclic reactions in a manner similar to their acyclic analogues,<sup>9</sup> and the probable effect of the fluorine substituents upon the thermodynamics of this reaction provided us with the prospect of a fruitful system for kinetic and thermodynamic analysis. In this paper initial results from these studies are reported, wherein the expected normal electrocyclic process is seen to play but a minor role, with a new and virtually unprecedented thermal isomerization being seen to dominate the thermal chemistry of this and a related system.

When **1** was heated in benzene at 193 °C for 24 h, three major products could be isolated and characterized.<sup>10</sup> None of the

expected electrocyclic product **5** could be detected.



Because of the more favorable thermodynamics of the system, the thermolysis of 9,10-bis(trifluorovinyl)phenanthrene (**8**)<sup>12</sup> was examined, and it provided greater insight into this chemistry. While a small amount of electrocyclic product **9** was detected in this system,<sup>13</sup> again the *major* observed reaction was that which had been observed for **1**. After one half-life, the major product was **11**, but by examination of the early stages of the reaction it became clear that **11** was being formed from an intermediate (**10**) which apparently was itself the major direct product of the thermolysis of **8**. Indeed, at 24% conversion of **8**, 63% of the product mixture was **10**.



Bicyclo[3.1.0]hex-2-enes such as **10** have, of course, been observed as major products in the *photochemistry* of acyclic 1,3,5-hexatrienes<sup>14</sup> as well as of divinyl aromatics,<sup>15</sup> but are virtually unprecedented products in thermal reactions of such substrates.<sup>16</sup> The structure of **10** was confirmed spectroscopically,<sup>10</sup> and it was indeed found also to be the major product from photolysis of **8**. Thermolysis of **10** also proceeded smoothly ( $k_{10}/k_8 = 1.94$  at 180 °C), and it was thus demonstrated that **10** was the precursor of both **11** (38%) and **12** (62%), but not of **9**. Therefore, it would appear that in the thermolysis of **8** a competition between the expected, normal electrocyclic process to form orthoquinoid species **9** and a new thermal process which leads to the major bicyclo[3.1.0]hexene product **10** is being observed.

(1) Dolbier, W. R., Jr.; Koroniak, H.; Burton, D. J.; Heinze, P. L.; Bailey, A. R.; Shaw, G. S.; Hansen, S. W. *J. Am. Chem. Soc.* **1987**, *109*, 219 and references therein.

(2) Kirmse, W.; Rondan, N. G.; Houk, K. N. *J. Am. Chem. Soc.* **1984**, *106*, 7989.

(3) Rondan, N. G.; Houk, K. N. *J. Am. Chem. Soc.* **1985**, *107*, 2099.

(4) Dolbier, W. R., Jr.; Phanstiel, O., IV. *Tetrahedron Lett.* **1988**, 29, 53.

(5) Dolbier, W. R., Jr.; Alty, A. C.; Phanstiel, O., IV. *J. Am. Chem. Soc.* **1987**, *109*, 3046.

(6) Evanseck, J. F.; Spellmeyer, D. C.; Houk, K. N., personal communication.

(7) Synthesized by the bis Pd(0)-catalyzed coupling of (trifluorovinyl)zinc with 1,2-diiodonaphthalene.<sup>8</sup>

(8) Heinze, P. L.; Burton, D. J. *J. Org. Chem.* **1988**, *53*, 2714.

(9) Heimgartner, H.-J.; Hansen, H.-J.; Schmid, H. *Helv. Chim. Acta* **1972**, *55*, 1385.

(10) All new compounds reported in this paper were purified by glpc and were characterized by <sup>1</sup>H, <sup>13</sup>C, and especially <sup>19</sup>F NMR spectroscopy. High-resolution mass spectrometry confirmed their molecular formulas. An X-ray crystal structure verified the structure of **3**.<sup>11</sup>

(11) Crystallographic data are available as supplementary material.

(12) Synthesized by an unusual bis Pd(0)-catalyzed coupling of (trifluorovinyl)zinc with 9-iodo-10-nitrophenanthrene.

(13) <sup>19</sup>F NMR data of the orthoquinoid products: **9**,  $\delta$  135.9 (t,  $J = 12.1$  Hz, 2 F), 132.6 ppm (d,  $J = 12.1$  Hz, 4 F); **5**,  $\delta$  131.96 (m, 1 F), 132.52 (m, 2 F), 132.77 (m, 2 F), 142.48 ppm (m, 1 F).

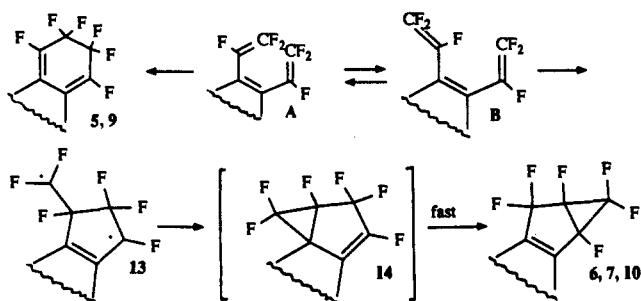
(14) Meinwald, J.; Mazzocchi, P. H. *J. Am. Chem. Soc.* **1966**, *88*, 2850.

(15) Pomerantz, M.; Gruber, G. W. *J. Am. Chem. Soc.* **1971**, *93*, 6615.

(16) There is one other example in the literature of a thermal cyclization of an acyclic triene (an alkylamino triene) to a bicyclo[3.1.0]hex-2-ene product: Bellas, M.; Bryce-Smith, D.; Clarke, M. T.; Gilbert, A.; Klunkin, G.; Krestanovich, L.; Manning, C.; Wilson, S. *J. Chem. Soc., Perkin Trans. I* **1977**, 2571.

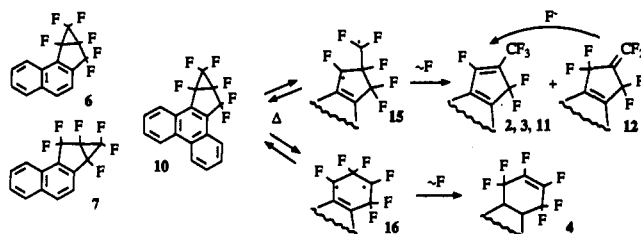
A reexamination of the early stages of the thermal rearrangement of the naphthalene system **1** ( $k_8/k_1 = 4.0$  at 193 °C) led to the observation, isolation, and demonstration of the intermediacy of analogous bicyclo[3.1.0]hexene precursors to **2** (namely, **6** and **7**), while verifying that **5** was not observable at any stage of the reaction.<sup>17</sup>

The probable mechanism for formation of the bicyclohexene products from **1** and **8** is given below. Thermal electrocyclic ring



closure to orthoquinoid products **5** and **9** would have to occur from a conformation of the type A, which would maximize the steric and/or electrostatic repulsions of the fluorine substituents of the trifluorovinyl groups of **1** and **8**. It is likely because of such destabilizing interactions that a conformation of the type B ends up being the reactive one in these reactions.<sup>18</sup> Five-membered-ring formation from B will lead to diradical **13**, which, in a manner similar to that proposed for the photochemical process, can cyclize to a bicyclo[3.1.0]hexene species **14**, which will have lost considerable aromatic stabilization and thus should convert rapidly to the observed bicyclo[3.1.0]hexene products via a vinylcyclopropane rearrangement.

The actual observed thermolysis products can derive readily from such bicyclohexene intermediates via the diradical pathways shown below.<sup>19</sup> Note that a product analogous to **12** is not observed from **6** or **7**, while one like **4** is not formed from **10**.



Examples of unambiguous radical rearrangements involving shift of F are themselves rare enough in the literature to be worthy of comment. While there is little doubt that F<sup>•</sup>-catalyzed rearrangements converting **12** to **11**,<sup>21</sup> as well as interconverting **2** and **3**, are intervening after long reaction times, it has been shown that the reactions leading to **6**, **7**, and **10** as well as to **2**, **3**, **4**, **11**, and **12** are not catalyzed by F<sup>•</sup>, and thus the intervention of diradical intermediates would appear to be unambiguously indicated in these reactions.

In conclusion, it has been observed that bis(trifluorovinyl) aromatics **1** and **8** undergo a novel thermal rearrangement in preference to the normal electrocyclic cyclization process. Further studies which will examine whether this new reaction extends to

(17) Photolysis of **1** resulted in the formation of **5** as the major product.<sup>13</sup> **5** could also be characterized via its Diels-Alder reaction with diethyl acetylenedicarboxylate.

(18) The relative thermodynamics of the two systems **1** and **8** probably dictates why **5** is not formed thermally from **1** while formation of **9** from **8** at least competes with the new cyclization process.

(19) There is precedent for the observed rearrangement of the perfluorinated bicyclo[3.1.0]hexene system in the reported high-temperature reaction of CF<sub>2</sub> with perfluoroindene.<sup>20</sup>

(20) Karpov, V. M.; Platonov, V. E.; Stolyarova, T. A.; Yakobson, G. G. *Izv. Akad. Nauk SSSR, Ser. Khim.* 1981, 1586.

(21) Conversion of **12** to **11** is very rapid upon addition of traces of F<sup>•</sup> to the product mixture.

fluorine-substituted acyclic 1,3,5-hexatriene systems are underway, and details regarding the interesting photochemistry of these systems will be reported soon.

**Acknowledgment.** Support of this research in part by the National Science Foundation is gratefully acknowledged.

**Supplementary Material Available:** Abbreviated experimental description of crystal data, data collection and reduction, and structure determination and refinement, table of experimental details, labeled ORTEP diagram, and tables of positional and thermal parameters, interatomic distances with esd's, interatomic angles with esd's, selected torsion angles, and least-squares planes with distances of selected atoms from planes for compound **3** (10 pages). Ordering information is given on any current masthead page.

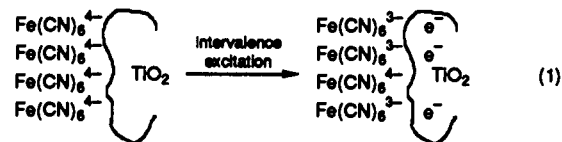
### Surface Intervalence Enhanced Raman Scattering from Fe(CN)<sub>6</sub><sup>4-</sup> on Colloidal Titanium Dioxide. A Mode-by-Mode Description of the Franck-Condon Barrier to Interfacial Charge Transfer

Robert L. Blackburn, Christopher S. Johnson, and Joseph T. Hupp\*

Department of Chemistry, Northwestern University  
Evanston, Illinois 60208-3113  
Received September 12, 1990

One of the key requirements in any quantitative description of electron-transfer kinetics, in any environment, is an accurate estimate of internal or vibrational reorganization energetics.<sup>1</sup> We have recently shown that complete mode-by-mode descriptions of vibrational reorganization for selected metal-to-ligand<sup>2</sup> and metal-to-metal (or intervalence)<sup>3</sup> charge-transfer events in solution can be obtained by applying time-dependent scattering theory<sup>4,5</sup> to pre- or postresonance Raman spectra.<sup>6</sup> The quantities obtained are redox-induced normal coordinate displacements ( $\Delta$ ), force constants ( $f$ ), and individual components ( $\chi_i'$ ) of the total vibrational reorganization energy ( $\chi_i$ ). We now report an extension of this methodology to an interfacial charge transfer reaction.

The reaction chosen was optical electron transfer from Fe(CN)<sub>6</sub><sup>4-</sup> to colloidal titanium dioxide:<sup>7,8</sup>



(1) For general reviews, see: (a) Sutin, N. *Prog. Inorg. Chem.* 1983, 30, 441. (b) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* 1985, 811, 265. (c) Newton, M. D.; Sutin, N. *Annu. Rev. Phys. Chem.* 1984, 35, 437.

(2) Doorn, S. K.; Hupp, J. T. *J. Am. Chem. Soc.* 1989, 111, 4704.

(3) (a) Doorn, S. K.; Hupp, J. T. *J. Am. Chem. Soc.* 1989, 111, 1142. (b) Doorn, S. K. Ph.D. Dissertation, Northwestern University, 1990.

(4) (a) Heller, E. J.; Sundberg, R. L.; Tannor, D. *J. Phys. Chem.* 1982, 86, 1822. (b) Tannor, D. J.; Heller, E. J. *J. Chem. Phys.* 1982, 77, 202. (c) Lee, S. Y.; Heller, E. J. *J. Chem. Phys.* 1977, 71, 4777. (d) Heller, E. J. *Acc. Chem. Res.* 1981, 14, 368. (e) Morris, D. E.; Woodruff, W. H. *J. Phys. Chem.* 1985, 89, 5795.

(5) See also: (a) Warshel, A.; Dauber, P. *J. Chem. Phys.* 1977, 66, 5477. (b) Myers, A. B.; Mathies, R. A. In *Biological Applications of Raman Spectroscopy*; Spiro, T. G., Ed.; John Wiley and Sons: New York, 1987; Vol. 2. (c) Schomacher, K. T.; Bangcharoenpaupong, O.; Champion, P. M. *J. Chem. Phys.* 1984, 80, 4701. (d) Hizhnyakov, V.; Tehver, I. *J. Raman Spectrosc.* 1988, 19, 383.

(6) Related experimental applications of time-dependent Raman scattering theory: (a) Tutt, L.; Zink, J. I. *J. Am. Chem. Soc.* 1986, 108, 5830. (b) Zink, J. I.; Tutt, L.; Yang, Y. Y. *ACS Symp. Ser.* 1986, 307, 39. (c) Yang, Y. Y.; Zink, J. I. *J. Am. Chem. Soc.* 1985, 107, 4799. (d) Tutt, L.; Tannor, D.; Heller, E. J.; Zink, J. I. *Inorg. Chem.* 1982, 21, 3858. (e) Zink, J. I. *Coord. Chem. Rev.* 1985, 64, 93. (f) Truhlsen, M. O.; Dollinger, G. D.; Mathies, R. A. *J. Am. Chem. Soc.* 1987, 109, 586.

(7) Vrachnou, E.; Grätzel, M.; McEvoy, A. J. *J. Electroanal. Chem.* 1989, 258, 193.