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Perfluorotropilidene Valence Isomers and the Perfluorotropylium Ion

William P. Dailey and David M. Lemal*

Department of Chemistry, Dartmouth College
Hanover, New Hampshire 03755

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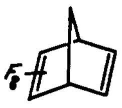
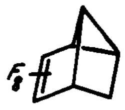
We wish to report a novel series of valence isomerizations of strained fluorocarbons, a series that has led to the first observation of the perfluorotropylium ion.

Irradiation of an acetonitrile solution of perfluoronorbornadiene (*1*)[1,2] with the full medium-pressure mercury arc rearranged the carbon skeleton in an unexpected fashion, yielding perfluorotricyclo[3.2.0.0^{2,7}]hept-3-ene (**2**). This fluorocarbon gave rise to a complex but first-order ^{19}F NMR spectrum (CH_3CN) with multiplets at δ 113.5 and 143.2 (gem F's, J_{gem} = 173 Hz), 144.7 and 156.9 (vinyl F's), 202.9, 210.9, 219.5, and 226.6 (bridgehead F's)[3] and IR (vapor) $\nu_{C=C}$ 1741 cm^{-1}. Upon continued irradiation the NMR signals of **2** diminished in intensity with concomitant growth of a new set of resonances attributable to bicyclo[3.2.0]hepta-2,5-diene **3**: ^{19}F NMR (CH_3CN) δ 112.75 and 116.75 (gem F's, AB quartet, J_{gem} = 264 Hz), 111.5, 122.5, 139.6, and 154.0 (vinyl F's), 177.2, 187.9 (bridgehead F's); IR (vapor) $\nu_{C=C}$ 1787 (4-ring), 1760 cm^{-1} (5-ring); bp 71 °C (740 mm).[4]



1



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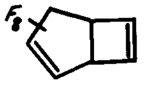
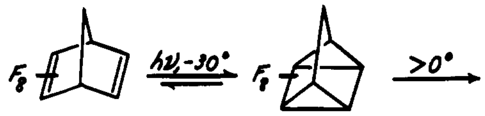


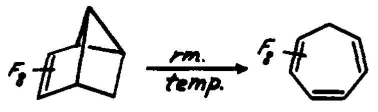
3

On the possibility that thermal chemistry had played a role in these surprising transformations, irradiation of **1** was repeated under similar circumstances, but at −30 °C. The ^{19}F spectrum of fluorocarbon **2** failed to appear, but in its stead there arose three new multiplets in the ratio 1:2:1 corresponding to perfluoroquadricyclane (**4**):[5] ^{19}F NMR δ 131.8 (F_7's, triplet, J_{app} = 4.8 Hz), 215.3 (F_2, F_3, F_5, F_6, triplet, J_{app} = 14.4), 234.1 (F_1, F_4, quintet of triplets, J_{app} = 14.4, 4.8) (Figure 1). Photoisomerization of **1** was apparently a reversible process, yielding about 60% of the quadricyclane in the photostationary state.[6]

When the reaction mixture was allowed to warm above 0 °C in the dark, the quadricyclane spectrum disappeared with simultaneous growth of signals for the tricyclic fluorocarbon **2** ($t_{1/2}$ $\simeq$ 50 min at 8 °C). Standing at room temperature or gentle warming brought about yet another rearrangement, as **2** cleanly isomerized to perfluorotropilidene (**5**) ($t_{1/2}$ $\approx$ 1 h at 45 °C).



1 *4*



2 *5*

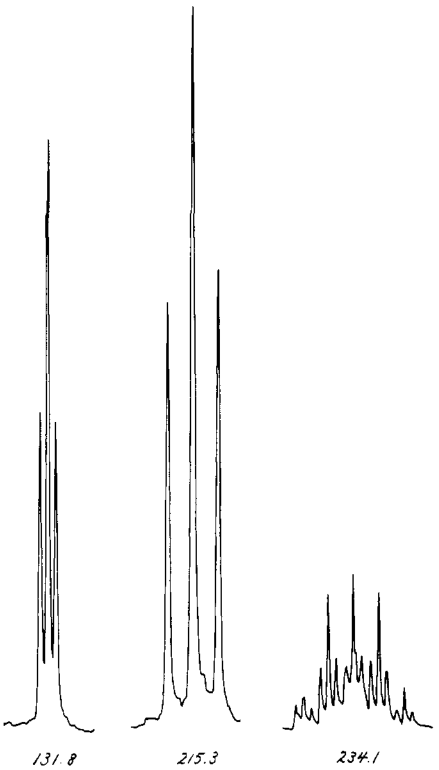
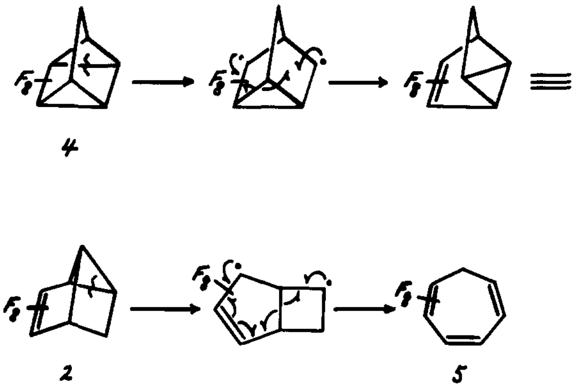


Figure 1. ^{19}F NMR spectrum of perfluoroquadricyclane (**4**) in acetonitrile.[3]

Scheme I



Though this triene is known,[7] it has been quite inaccessible, and no spectrocopic data for the compound have been reported: ^{19}F NMR (CH_3CN) δ 87.5 (F_7's, t of t, J_{app} = 15, 10 Hz), 145.9 (F_1, F_6, m), 148.4 (F_2, F_5, m), 150.4 (F_3, F_4, m);[8] IR (vapor) 1708 cm^{-1}. Ultraviolet irradiation of **5** rapidly isomerized it to the bicyclic diene **3**.[9]

Both the **4** → **2** and **2** → **5** transformations were approximately first order kinetically, and neither was accelerated by the presence of massive amounts of hydrogen fluoride or potassium fluoride. Thus, these extremely facile rearrangements appear to be unimolecular in nature. A reasonable mechanism for the two valence isomerizations is presented in Scheme I. The proposed pathway for the **4** → **2** reaction will be recognized as the thermal part of a di-π-methane rearrangement.[10] This transformation is the more

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(1) Banks, R. E.; Haszeldine, R. N.; Prodgers, A. *J. Chem. Soc., Perkin Trans. 1* **1973**, 596–598.

(2) We have developed a new synthetic route to **1**, which will be reported elsewhere.

(3) Chemical shifts are reported in ppm upfield from trichlorofluoromethane.

(4) A satisfactory elemental analysis was obtained.

(5) Norbornadiene itself gives quadricyclane upon irradiation with short-wavelength ultraviolet light. Dauben, W. G.; Cargill, R. L. *Tetrahedron* **1961**, 197–201.

(6) Because of the extreme lability of the quadricyclane this composition was not approached from the other direction. After depletion of the quadricyclane by warming in the dark above 0 °C, however, irradiation at −30 °C rapidly replenished it.

(7) Dodsworth, D. J.; Jenkins, C. M.; Stephens, R.; Tatlow, J. C. *J. Chem. Soc., Chem. Commun.* **1972**, 803–804.

(8) These assignments, which are tentative for the δ 145.9 and 148.4 resonances, are based on spin-decoupling experiments.

(9) The parent tropilidene photocyclizes analogously to bicyclo[3.2.0]hepta--2,5-diene. Dauben, W. G.; Cargill, R. L. *Tetrahedron* **1961**, *12*, 186–189.

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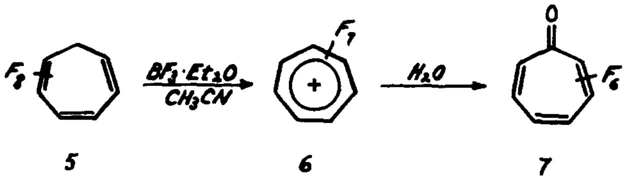
remarkable by contrast with the thermal behavior of the parent quadricyclane, which proceeds quantitatively to a different product, norbornadiene, and requires far more vigorous conditions ($t_{1/2}$ = 3.9 h at 154 °C).[5,11] Thermolysis of the hydrocarbon counterpart[12] of **2** has not yet been studied. Substitution of fluorine for hydrogen on a cyclopropane ring increases ring strain in increments of roughly 5 kcal/mol per fluorine according to O'Neal and Benson.[13] On this basis perfluoroquadricyclane should suffer ≈30 kcal/mol and tricycloheptene **2** ≈15 kcal/mol more strain than the parent hydrocarbons. This extra energy incorporated into skeletons that are already highly strained is probably the key to their extraordinary lability.[14] Perfluorinated carbon skeletons comprising cyclopropane rings fused to other small rings are virtually unknown; our results suggest that such molecules as a class will be highly reactive.

Perfluoronorbornadiene (**1**) fragmented cleanly to perfluorobenzene with loss of difluorocarbene at 240 °C ($t_{1/2} \simeq$ 30 min). The reaction was expected,[15] but the vigor of the conditions required to effect this orbital-topology-allowed, lienar cheletropic elimination[16] is noteworthy. Perfluorocyclopropane extrudes difluorocarbene at temperatures above 160 °C without aromatization as a driving force.[17] The juxtaposition of these two fragmentations highlights once again the large strain energy content of highly fluorinated cyclopropanes.

Tropilidene **5** reacted readily with boron trifluoride etherate in acetonitrile to yield a species whose ^{19}F spectrum was a sharp singlet at δ 99.5. That this species was the perfluorotropylium ion (**6**)[18] was confirmed by its immediate hydrolysis to the known perfluorotropone (**7**)[7,19] by small amounts of water. The ^{19}F NMR spectrum of the tropone (CH_3CN) comprised multiplets of equal area at δ 128.6, 138.2, and 143.8. IR ($CDCl_3$) 1655, 1627, 1535, 1525, 1436, 1385, 1365, 1270, 983 cm^{-1}; MS, m/e 214 (M^+).



Further studies relating to the perfluorotropylium ion are under way, including alternative synthetic approaches, isolation of tropylium salts, and exploration of their reactivity.

Acknowledgment. The National Science Foundation (CHE-7924309) and the Air Force Office of Scientific Research (AFOSR-83-0047) have provided generous financial support for this work.

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(10) For a review of the di-π-methane rearrangement, see: Zimmerman, H. E. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, pp 131-166.

(11) Frey, H. M. *J. Chem. Soc.* **1964**, 365-367.

(12) Story, P. R. *J. Am. Chem. Soc.* **1961**, *83*, 3347-3349. Franzus, B.; Synder, E. I. *Ibid.* **1963**, *85*, 3902-3903. Brown, H. C.; Bell, H. M. *Ibid.* **1963**, *85*, 2324.

(13) O'Neal, H. E.; Benson, S. W. *J. Phys. Chem.* **1968**, *72*, 1866-1887.

(14) Dolbier has studied extensively the labilizing influence of geminal fluorines on cyclopropane derivatives. Dolbier, W. R., Jr. *Acc. Chem. Res.* **1981**, *14*, 195-200.

(15) The much more difficult extrusion of :CH_2 does not occur in the pyrolysis of norbornadiene, which yields tropilidene, cyclopentadiene, acetylene, and toluene. Herndon, W. C.; Lowry, L. L. *J. Am. Chem. Soc.* **1964**, *86*, 1922-1926 and references contained therein.

(16) Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781-932.

(17) The decomposition is very slow at 160 °C, but even an unrealistically conservative extrapolation (assuming $\Delta S^{\ddagger} = 0$) to 240 °C indicates faster reaction for the cyclopropane than for **1**. Birchall, J. M.; Haszeldine, R. N.; Roberts, D. W. *J. Chem. Soc., Perkin Trans. 1* **1973**, 1071-1078.

(18) The chemical shift is at quite low field for vinyl fluorine but is consistent with the strong deshielding observed in other fluorocarbenium ions. Perfluorocyclopropenium ion, for example, gives rise to a singlet at δ 63.1 (in sulfur dioxide, referenced to external trichlorofluoromethane). Sargeant, P. B.; Krespan, C. G. *J. Am. Chem. Soc.* **1969**, *91*, 415-419.

(19) Guy, J. J.; Hamor, T. A.; Jenkins, C. M. *J. Fluorine Chem.* **1975**, *5*, 89-91. Hamor, M. J.; Hamor, T. A. *Acta Crystallogr.*, **1976**, *B32*, 2475-2480.

Epoxidations with Selective Peracids

J. Rebek, Jr.,* L. Marshall, R. Wolak, and J. McManis

Department of Chemistry, University of Pittsburgh
Pittsburgh, Pennsylvania 15260

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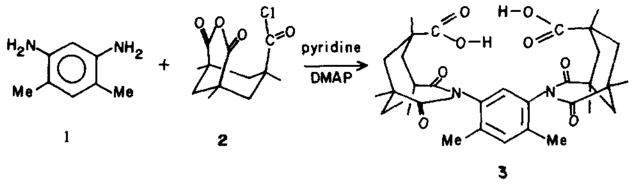
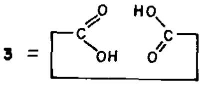
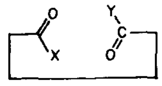
The reaction of peracids with olefins continues to be a general and reliable method of epoxide synthesis. One reason for its consistency lies in the reaction's insensitivity to steric effects, a feature that leads to the familiar sequence[1] of reactivity shown below. An unfortunate corollary is that cis, trans, and 1,1-disubstituted olefins react at nearly the same rate, as do both faces of a given alkene. Consequently, cis/trans and enantioselectivity with conventional peracids is poor. Only with allylic alcohols, where preassociation between olefin and epoxidizing agent is possible, can such selectivity be seen.[2] Here we introduce the first peracids to show general cis/trans selectivity and present evidence that bears on the transition structure.

Relative Reactivities With Peracids

Condensation of the diamine[3] **1** with 2 equiv of the anhydride acid chloride[4] **2** in hot pyridine containing a catalytic amount of 4-(dimethylamino)pyridine (DMAP) gave the diacid **3**, mp >355 °C in 95% yield.[5] With $SOCl_2$ the diacid gave the dihalide **4a**, mp 297-303 °C (95-100%). Treatment of the diacid with 1 equiv of either $Me_3O^+BF_4^-$ or $Et_3O^+BF_4^-$ in the presence of EtN(i-Pr)$_2$ in methylene chloride provided the corresponding monoesters (mp 331-333 and 277-278 °C, respectively). The monoesters were easily converted to their acid chlorides **4b** (mp 266-268 °C) and **4c** (mp 233-237 °C) in equally high yield.







4a X = Y = Cl
4b X = OMe, Y = Cl
4c X = OEt, Y = Cl

The corresponding peracids were generated in situ by treating **4** with excess H_2O_2 in $CDCl_3$ or CH_2Cl_2 containing an equivalent of pyridine. The appropriate olefin pairs were present in 5- to 10-fold excess. The peracid of m-chlorobenzoic acid was likewise generated as the standard reagent; its selectivity was unchanged from that of crystalline peracid under these conditions. Table I summarizes results of the epoxidations.

It can be seen that as the size of the alkyl group of the ester

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(1) Swern, D. "Organic Peroxides"; Wiley: New York, 1971; Vol. 2, p 355. For a study of cis/trans selectivity, see: Stumpf, W.; Rombusch, K. *Justus Liebigs Ann. Chem.* **1965**, *687*, 136-149.

(2) Henbest, H. B.; Wilson, R. A. L. *J. Chem. Soc.* **1957**, 1958-1965. For recent studies, see: Hasan, I.; Kishi, Y. *Tetrahedron Lett.* **1980**, 4229-4232. Johnson, M. R.; Kishi, Y. *Ibid.* **1979**, 4347-4350. Narula, A. S. *Ibid.* **1981**, 2017-2020. Itoh, T.; Jitsukawa, K.; Kameda, K.; Teranishi, S. *J. Am. Chem. Soc.* **1979**, *101*, 159-169. Chautemps, P.; Pierre, J.-L. *Tetrahedron* **1976**, *32*, 549-557. For asymmetric epoxidation of allylic alcohols using other hydroperoxides, see: Katsuki, T.; Sharpless, K. B. *J. Am. Chem. Soc.* **1980**, *102*, 5974-5976.

(3) Noelting, E.; Thesmar, G. *Ber.* **1902**, *35*, 628-650.

(4) Kemp, D. S.; Petrakis, K. S. *J. Org. Chem.* **1981**, *46*, 5140-5143.

(5) All new compounds were characterized by a full complement of spectra, including high-resolution mass spectra.

0002-7863/84/1506-1170$01.50/0