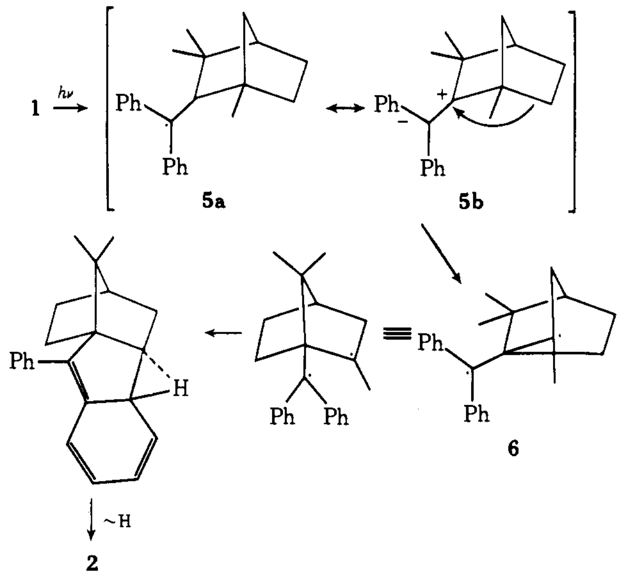
Scheme I



With the data at hand one cannot tell for certain whether **1** rearranges in competition with or subsequent to twisting. The nature of the rearrangement is compatible with the latter. Theory indicates that twisted olefin excited singlet states are highly polarizable and that under appropriate circumstances such as asymmetric substitution substantial net polarization can occur.[2] It has been suggested that orthogonal zwitterionic states are involved in certain diene and triene photochemical reactions and also play a major role in the photochemistry of vision.[2b,c,22,23] In the present reaction, the fact that alkyl migration to C-2 of **1** occurs strongly suggests that this carbon has become electron deficient on excitation and that ionic resonance structure **5b** is a major contributor to the reactive excited state.[24] Thus our observations point toward the intermediacy of a twisted, polar excited state in the rearrangement of **1**. It has previously been suggested that twisted singlet states mediate the photochemical olefin → carbene transformations of certain β-substituted 1,1-diphenylethylenes.[26]

Acknowledgment is made to the National Science Foundation for financial support.

References and Notes

(1) 2-(Diphenylmethylene)-1,3,3-trimethylbicyclo[2.2.1]heptane.
(2) (a) C. E. Wulfman and S. Kumei, *Science*, **172**, 1061 (1971); (b) L. Salem, *ibid.*, **191**, 822 (1976); (c) L. Salem, *Acc. Chem. Res.*, **12**, 87 (1979); (d) B. R. Brooks and H. F. Schaefer III, *J. Am. Chem. Soc.*, **101**, 307 (1979).
(3) D. H. R. Barton, F. S. Guziec, Jr., and I. Shahak, *J. Chem. Soc., Perkin Trans. 1*, 1794 (1974).
(4) Preparative-scale photolyses were carried out with unfiltered (quartz) light from a Hanovia 450-W medium-pressure mercury arc. Progress of the reactions was monitored by gas chromatography.
(5) While the absolute configuration of the product **2** is not provided by the X-ray data, the enantiomer of **2** shown is that derived from **1** (obtained from D-fenchone[3]) via the mechanism in Scheme I.
(6) "International Tables for X-ray Crystallography", Vol. I, The Kynoch Press, Birmingham, England, 1969, p 105.
(7) $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$.
(8) Irradiation of a methanol solution of **4** to 94% conversion afforded three products in yields of ~11, 11, and 6%. The NMR spectra of the two major products showed inter alia singlets at δ 4.00 and 4.45, suggesting structures analogous to **2** and **3**. We have been unable to obtain the minor product in a quantity sufficient for characterization.
(9) Quantum yield studies utilized the 2537-Å light from a low-pressure mercury lamp, a merry-go-round apparatus, and potassium ferrioxalate actinometry.
(10) H. Kristinsson and G. W. Griffin, *J. Am. Chem. Soc.*, **88**, 378 (1966).
(11) (a) S. S. Hixson, *J. Am. Chem. Soc.*, **98**, 1271 (1976); (b) S. S. Hixson and T. P. Cutler, *ibid.*, **95**, 3032 (1973).
(12) S. S. Hixson, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, **73**, 531 (1973).
(13) (a) H. E. Zimmerman and R. D. Little, *J. Am. Chem. Soc.*, **96**, 5143 (1974); (b) H. E. Zimmerman and C. J. Samuel, *ibid.*, **97**, 4025 (1975).
(14) J. Saltiel, J. D'Agostino, E. D. Megarity, L. Metts, K. R. Neuberger, M. Wrighton, and O. C. Zafirion, "Organic Photochemistry", Vol. 3, O. L. Chapman, Ed., Marcel Dekker, New York, 1973, p 1.
(15) H. E. Zimmerman, K. S. Kamm, and D. P. Werthemann, *J. Am. Chem. Soc.*, **97**, 3718 (1975).
(16) M. H. Hui and S. A. Rice, *J. Chem. Phys.*, **61**, 833 (1974).
(17) M. C. Bruni, F. Momicchioli, I. Baraldi, and J. Langlet, *Chem. Phys. Lett.*, **36**, 484 (1975).
(18) P. M. Crosby and K. Salisbury, *J. Chem. Soc., Chem. Commun.*, 477 (1975).
(19) K. G. Ghiggino, K. Hara, G. R. Mant, D. Phillips, K. Salisbury, R. P. Steer, and M. D. Swords, *J. Chem. Soc., Perkin Trans. 2*, 88 (1978).
(20) An X-ray crystal structure determination of 1,1-diphenyl-2,2-di-*tert*-butylethylene revealed that the double bond in this olefin is twisted by 24°; see A. Mugnoli and M. Simonetta, *J. Chem. Soc., Perkin Trans. 2*, 1831 (1976).
(21) I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules", Academic Press, New York, 1965, p 89.
(22) W. G. Dauben and J. S. Ritscher, *J. Am. Chem. Soc.*, **92**, 2925 (1970).
(23) W. G. Dauben, M. S. Kellog, J. I. Seeman, N. D. Wietmeyer, and P. H. Wendschuh, *Pure Appl. Chem.*, **33**, 197 (1973).
(24) It is assumed that the migration step **5** → **6** affords directly the ground state of **6** which has predominantly diradical character.[25]
(25) L. Salem and C. Rowland, *Angew. Chem., Int. Ed. Engl.*, **11**, 92 (1972).
(26) (a) S. S. Hixson, *J. Am. Chem. Soc.*, **97**, 1981 (1975); (b) S. S. Hixson, J. C. Tausta, and J. Borovsky, *ibid.*, 3230 (1975).

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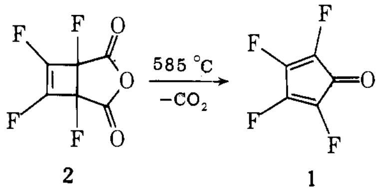
Perfluorocyclopentadienone

Sir:

We report here the synthesis and some chemistry of the title compound. Unlike cyclopentadienone itself, which has been observed only at low temperatures in matrix isolation,[1] the perfluoro derivative can be conveniently manipulated at room temperature as an orange vapor.[2,4]

Sublimation in vacuo through a Vycor tube heated to 585 °C transforms tetrafluorocyclobutenedicarboxylic anhydride[5] (**2**) into dienone **1** in a remarkably clean fragmentation process.



Trapped at −196 °C, the dienone can be preserved neat or in solution at low temperatures or sublimed on warming into a gas storage bulb to be kept for many hours at low pressure. At room temperature it dimerizes very rapidly in the liquid phase.

The mass spectrum of **1** shows a parent peak at *m/e* 152 and a very prominent peak at *m/e* 124 ($M^+ - 28$), probably the tetrafluorocyclobutadiene radical cation. Its IR spectrum has been measured in the vapor phase at room temperature, but resolution is much better in an argon matrix at 12 K. The double-bond stretching region is reproduced in Figure 1. Since fluorinated double bonds have stretching frequencies in the ketone region, all three bands probably represent strongly coupled vibrations.[6] Comprising multiplets of equal area at 136.86 and 173.41 ppm,[7] the ^{19}F NMR spectrum (CH_2Cl_2, −90 °C) is of the AA′XX′ type, with intraset $|J|$ values of 11.2 and 27.4 Hz and interset J values of ±11.8 and ∓17.9 Hz (Figure 2). The electronic spectrum of the vapor at room temperature reveals an intense maximum at 198.5 and a broad, weak maximum at 390 nm [cf. 3-*tert*-butylcyclopentadienone, $\lambda_{max}^{isooctane}$ 200 nm (log ε 4.71) and 380 (>1.9)].[8]

Dimerization of tetrafluorocyclopentadienone yields a single isomer whether the reaction occurs in the vapor phase, neat liquid or solvents ranging widely in polarity. Remarkably, this

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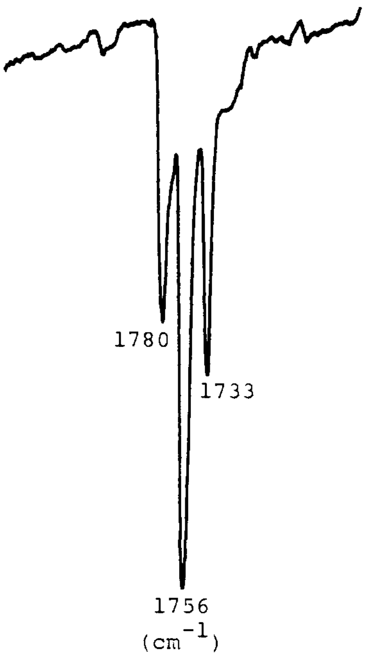


Figure 1. Double-bond stretching region of the IR spectrum of **1** (Ar matrix, 12 K).

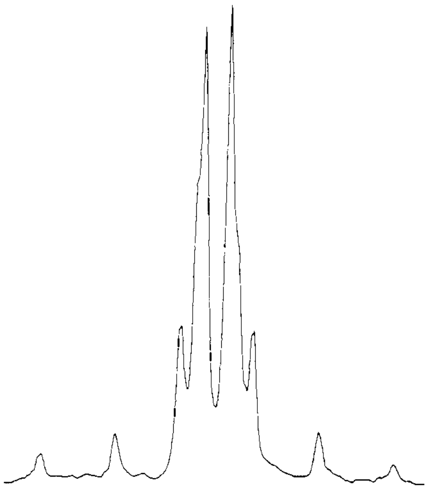
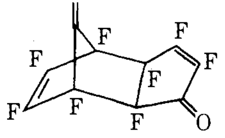
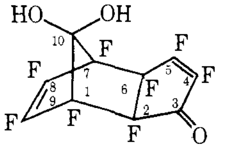


Figure 2. High-field half of the ^{19}F NMR spectrum of **1** (CH_2Cl_2, −90 °C).

dimer appears to have the exo configuration **3**[9], as explained below; IR (vapor) 1901 (w) and 1858 (bridge CO[10]), 1773,



3

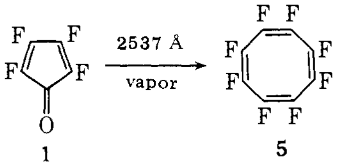


4

1739, 1706 cm^{-1}; UV (vapor) λ_{max} 207, λ_{sh} 220 nm; MS 276 (M^+ − CO); ^{19}F NMR (CD_3CN) 119.0 (F_5), 129.5 (F_4), 141.8 and 142.2 (F_8 and F_9), 184.0 and 184.7 (F_2 and F_6), 216.2 ppm (F_1 and F_7).

The bridging carbonyl of **3** hydrates with extraordinary ease to form **4**:[11,12] IR (KBr) 3400 (br), 1775, 1758, 1707 cm^{-1}; ^{19}F NMR (CD_3CN) 118.2 (F_5), 139.6 (F_4), 149.0 and 149.7 (F_8 and F_9), 186.3 and 187.8 (F_2 and F_6), 218.0 ppm (F_1 and F_7). While the chemical shifts of the fluorines at C-2 and C-6 in **3** are affected only modestly by the hydration reaction, that of the C-4 fluorine is displaced 10.1 ppm, the largest shift of all. These comparisons argue strongly for the exo configuration for the dimer and its hydrate. Treatment of the latter with trifluoroacetic anhydride brings about slow reversion to the former.

Photolysis of perfluorocyclopentadienone at 2537 Å in the vapor phase smoothly yields perfluorocyclooctatetraene (**5**),



probably via perfluorocyclobutadiene.[5,13,14] The reaction is strongly inhibited by inert gas. In an argon matrix at 12 K the dienone is stable to irradiation with the full high pressure mercury arc.

Further transformations of perfluorocyclopentadienone, especially its cycloadditions, are under investigation in our laboratory.

Acknowledgment. The authors thank E. D. Laganis for measuring the NMR spectrum of **1** and the National Science Foundation for generous financial support.

References and Notes

(1) O. L. Chapman and C. L. McIntosh, *Chem. Commun.*, 770 (1971).
(2) This result was not anticipated, for (1) multiple fluorine substitution generally destabilizes a π-electron system,[3] (2) frontier orbital theory (based on Hückel MO's) predicts slightly greater dimerization reactivity for the fluorinated than for the parent dienone, and (3) fluorine's small size belies steric inhibition of dimerization.
(3) R. D. Chambers, "Fluorine in Organic Chemistry", Wiley, New York, 1973, pp 142–144.
(4) Though its dimer and numerous trapping products are well characterized, perchlorocyclopentadienone remains unknown: W. H. Dietsche, *Tetrahedron Lett.*, 201 (1966), and references contained therein; M. Akhtar, D. M. Bratby, J. C. Chadwick, and G. I. Fray, *Tetrahedron*, **32**, 2265 (1976).
(5) M. J. Gerace, D. M. Lemal, and H. Ertl, *J. Am. Chem. Soc.*, **97**, 5584 (1975).
(6) Symmetric and antisymmetric stretching of all three double bonds (both A_1) and antisymmetric stretching of the C–C double bonds (B_1).
(7) All ^{19}F NMR chemical shifts are reported in parts per million upfield from internal $CFCl_3$.
(8) E. W. Garbisch, Jr., and R. F. Sprecher, *J. Am. Chem. Soc.*, **91**, 6785 (1969).
(9) The marked preference generally observed for endo stereochemistry in the dimerization of cyclopentadienones is discussed in ref 8.
(10) Apparently the bridge carbonyl stretching absorption is split into two bands, but the reason for this is not clear.
(11) Dimer **3** decarbonylates slowly but spontaneously at *room temperature*, another notable consequence of fluorine substitution.
(12) Owing to their lability, neither **3** nor **4** has been obtained analytically pure.
(13) Perfluorocyclobutadiene has also been postulated as an intermediate in the similar vapor phase photochemistry of anhydride **2**.[5] This earlier surmise is very likely correct, but part of the original case for it has been undermined by further study. The matter will be discussed in a future publication.
(14) For other examples of photoextrusion of carbon monoxide from cyclopentadienones, see G. Maier, S. Pfriem, U. Schäfer, and R. Matusch, *Angew. Chem., Int. Ed. Engl.*, **17**, 520 (1978); G. Maier, *ibid.*, **13**, 425 (1974).

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A Fixed-Geometry Study of the S_H2 Reaction on the Peroxide Bond

Sir:

Although the stereochemical preferences of radical substitution reactions have been of theoretical interest for over 40 years,[1,2] little experimental evidence relating to this question has been reported. Observations[3-8] suggest that back-side approach by a radical on the rupturing bond is preferred for

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