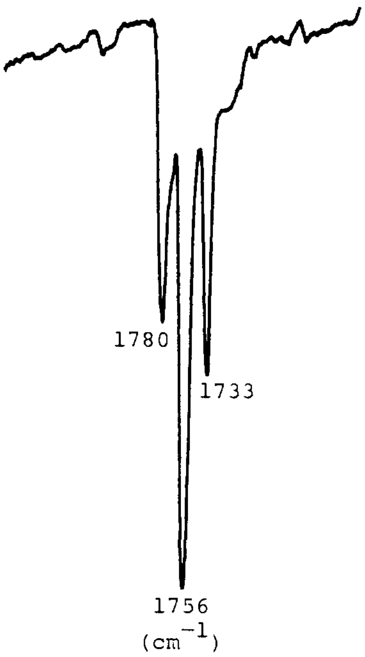


**Figure 1.** Double-bond stretching region of the IR spectrum of **1** (Ar matrix, 12 K).

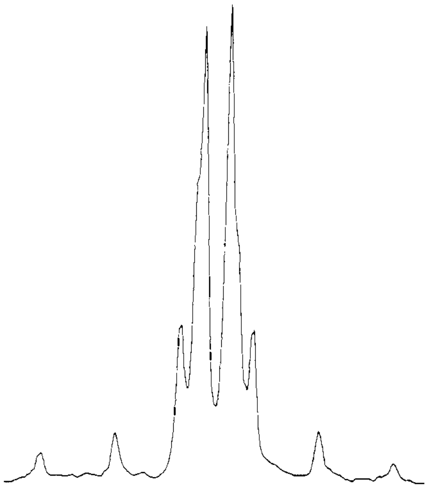
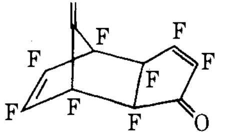
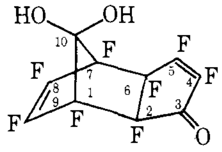


**Figure 2.** High-field half of the $^{19}$F NMR spectrum of **1** ($CH_2Cl_2$, −90 °C).

dimer appears to have the exo configuration **3**[9], as explained below: IR (vapor) 1901 (w) and 1858 (bridge CO[10]), 1773, 1739, 1706 cm$^{-1}$; UV (vapor) $\lambda_{max}$ 207, $\lambda_{sh}$ 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 $F_7$).



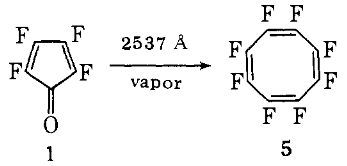
**3**



**4**

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.

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(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).
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(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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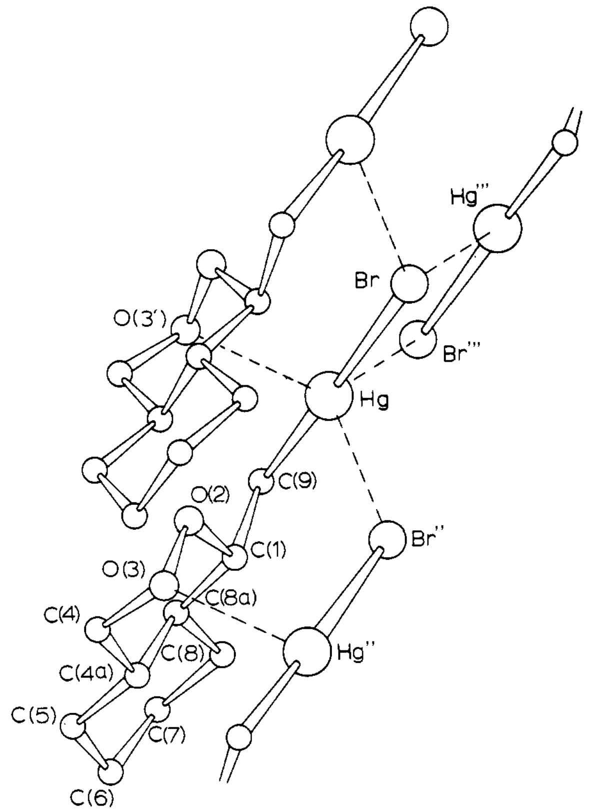
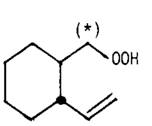
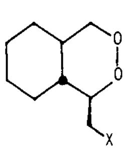


**Figure 1.** Atom numbering scheme and solid-state conformation of **2a**. Some distances follow: Hg-C(9), 2.12 (3); Hg-Br, 2.440 (4), Hg··O(3'), 3.15 (3); Hg··Br'', 3.544 (4); Hg··Br''', 3.629 (4) Å. Some angles follow: O(3')··Hg··Br'', 90.1 (4); O(3')··Hg··Br''', 136.4 (4); Br''··Hg··Br''', 133.3 (1)°.

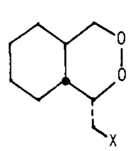
substitution on second-row elements such as sulfur and phosphorus as well as at cyclopropane carbon. Carbon radical substitution on the peroxide bond[9] occurs readily, and recently we have suggested[10] that studies of suitably substituted cyclic peroxides may provide pertinent information regarding the stereochemical preference of the $S_H2$ reaction. In particular, the geometric disposition of the attacking radical and the peroxide bond may be constrained in appropriate compounds thereby providing "test cases" for the substitution reaction. We report here a study of intramolecular carbon radical substitution on the peroxide bond in **2c** and **3c** where the geometry of the isomeric radicals is fixed by the rigid *trans*-decalin frame of the cyclic peroxide.



1, (*) = $^{13}C$



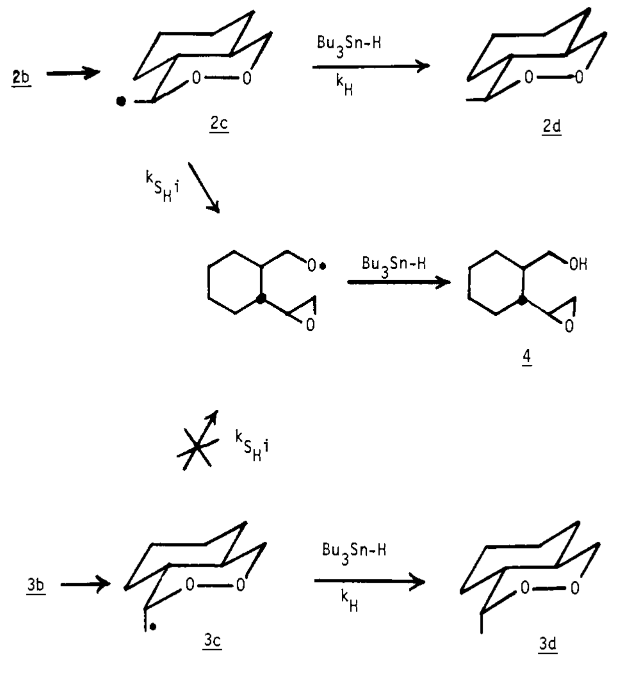
2a X = HgBr
2b X = Br
2c X = •
2d X = H



3a X = HgBr
3b X = Br
3c X = •
3d X = H

The β-mercuri bromo peroxides **2a** and **3a** were formed as a 3:1 mixture by peroxymercuration[11] of the unsaturated hydroperoxide **1**[12] which was prepared from *trans*-2-vinylcyclohexanemethanol[13] by standard procedures.[14] Separation of the equatorial isomer **2a** from the axial isomer **3a** was effected by high performance liquid chromatography,[15] and its identity was established unequivocally by a single-crystal X-ray analysis. Monoclinic crystals of **2a** belong to space group $P2_1/c(C_{2h}^5)$, with $a$ = 11.79 (1), $b$ = 11.44 (1), $c$ = 8.31 (1) Å; $\beta$ = 95.36 (10)°; $U$ = 1116 Å$^3$; $d_{\mathrm{calcd}}$ = 2.808 g cm$^{-3}$; $Z$ = 4. The crystal structure was solved by the heavy-atom method. Full-matrix least-squares refinement of nonhydrogen atom positional and thermal parameters has resulted in an $R$[16] value of 0.13 over 1469 statistically significant reflections.[17] The chair forms[18] of both six-membered rings and the equatorial nature of the C(1) substituent are apparent from the view of the solid-state conformation of **2a** shown in Figure 1. The mercury atom coordination is distorted trigonal-bipyramidal with its covalently bonded carbon and bromine atoms occupying axial sites while two weakly coordinated bromine atoms and an oxygen atom from adjacent molecules define the basal plane.[19] Interestingly, in the latter association the mercury atom is axially oriented with regard to the 2,3-dioxadecalin system.[20]

Scheme I



The β-bromo peroxides **2b** and **3b** were prepared from the mercuri bromides by reaction with molecular bromide.[21] Further, all of the peroxide derivatives were prepared enriched at C(4) with 24.1% $^{13}C$ so that $^{13}C$ NMR analysis was simplified and made more sensitive. The bromo peroxides **2b** and **3b** were reacted with 0.114 M tributyltin hydride[10] and the products were analyzed by $^{13}C$ NMR. **2b**, the equatorial isomer, reacted to form peroxide **2d** (86%) and the radical substitution product ($S_Hi$), **4** (14%).[22] Based on Scheme I, we calculated[10] $k_{S_Hi}$, the rate of carbon radical attack on the peroxide bond for **2c**, to be 1.2 × 10$^4$ s$^{-1}$. This rate is analogous to rates of intramolecular carbon radical attack on the peroxide bond found earlier.[10] The axial isomer, **3b**, reacted with 0.114 M tributyltin hydride to form the peroxide **3d**.[23] In contrast to the equatorial isomer, *no epoxy alcohol product,* ***4****, could be detected by* $^{13}C$ *NMR analysis* in the hydride reaction of the axial compound. Although the peroxides **2d** and **3d** were unstable to gas chromatography, **4** could be analyzed by this technique. Analysis of the reactions (0.114 M) of **3b** with tributyltin hydride showed trace amounts (<10$^{-4}$ M, lower than our $^{13}C$ detection limit) of **4** to be present. **2c** and **3c** thus follow dramatically different reaction pathways. The equatorial isomer **2c** leads to significant amounts of the $S_Hi$ product, **4**, but the axial isomer **3c** leads primarily to **3d** with only traces of the $S_Hi$ product observed. In fact, from these data, we calculate that $k_{S_Hi}$ for the equatorial isomer is, at a minimum, two-three orders of magnitude greater than $k_{S_Hi}$ for the axial isomer.[24]

β-Mercuri bromo peroxides **2a** and **3a** were independently subjected to demercuration with basic $NaBH_4$,[25] a reaction also known to involve alkyl radical intermediates.[26] **2a,** the equatorial isomer, leads to a 50:50 mixture of peroxide **2d** and epoxy alcohol **4**, the $S_Hi$ product. In contrast, the axial isomer **3a** leads cleanly to peroxide **3d** with no epoxy alcohol, **4,** being observed. The presumed radical intermediates **2c** and **3c** thus show the same reaction pathway preferences in these reactions as were observed in the tin hydride reaction of the β-bromoperoxides **2b** and **3b.**

Inspection of molecular models, as well as the X-ray crystal data, for equatorial **2a** suggest that a colinear radical–peroxide bond arrangement is easily achieved for this radical isomer, **2c.** In fact, the $\cdot CH_2$-C-O-O torsion angle for the equatorial isomer is 176 (2)°, not significantly different from the ideal value of 180°. Thus, the geometry of this isomer is fixed in an array that favors back-side radical substitution on the peroxide bond. The axial radical **3c** is constrained to attack the peroxide bond by a side-on pathway. The crucial $\cdot CH_2$-C-O-O torsion angle for this isomer is 60°, a geometry which apparently does not offer the possibility of substitution.

We conclude that carbon radical substitution on the peroxide bond does, indeed, follow a colinear approach pathway. The $S_H2$ and $S_N2$ pathways for reaction on first-row elements are thus apparently similar, with back-side displacement being the rule.

**Acknowledgments.** Support for this research by NSF Grant No. CHE 77-26088 is gratefully acknowledged. Crystallographic calculations, performed on an IBM 370/165 computer located at the Triangle Universities Computation Center, Research Triangle Park, N.C., were supported by a grant of computer time from Duke University.

**Supplementary Material Available:** Tables of atomic positional and thermal parameters, interatomic distances and angles, and a list of observed and calculated structure amplitudes (16 pages). Ordering information is given on any current masthead page.

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(11) A. J. Bloodworth and G. S. Bylina, *J. Chem. Soc., Perkin Trans. 1*, 2434 (1972).
(12) $^1H$ and $^{13}C$ NMR spectra, as well as C and H analyses, were consistent with the structures of all new compounds reported.
(13) *trans*-2-Vinylcyclohexanol was prepared by $LiAlH_4$ reduction of *trans*-2-vinylcyclohexanecarboxaldehyde. The aldehyde was prepared by addition of lithium divinylcuprate to 1-cyclohexenecarboxaldehyde.
(14) N. A. Porter, M. O. Funk, Dennis Gilmore, Ramdas Isaac, and John Nixon, *J. Am. Chem. Soc.*, **98,** 6000 (1976).
(15) LC was carried out on a Whatman "Magnum 9" μ silica column with 5% $CH_2Cl_2$, 25% $CHCl_3$, 70% $C_6H_{14}$ solvent.
(16) $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
(17) Intensity data were recorded on an Enraf-Nonius CAD-3 automated diffractometer (Ni-filtered Cu $K\alpha$ radiation, $\lambda = 1.5418$ Å; $\theta - 2\theta$ scans) by use of procedures detailed elsewhere; see, e.g., C. D. Garner, N. C. Howlader, F. E. Mabbs, A. T. McPhail, R. W. Miller, and K. D. Onan, *J. Chem. Soc., Dalton Trans.*, 1582 (1978). Although the colorless lathlike crystals are stable over long periods when exposed to ordinary light, they darken and deteriorate fairly rapidly in the X-ray beam. Consequently, it proved necessary to use three different crystals to obtain a complete data set; measurements from different crystals were put on a common scale by comparison of intensities from a number of common reflections. Data from the individual crystals were corrected for crystal deterioration by remeasuring the intensity of a strong reflection after each batch of 99 measurements and scaling the data appropriately. Absorption corrections were also applied to the intensity data.
(18) The C(1)–O(2)–O(3)–C(4) torsion angle is −75 (3)°. With a mean endocyclic torsion angle of 64° the 2,3-dioxacyclohexane ring is overall more puckered than the cyclohexane ring in **2a** where the corresponding value of 58° is close to normal.
(19) Displacements of atoms from the O(3′), Br″, Br‴ plane follow: Hg, −0.083; C(11), −2.176; Br, 2.343; O(2), −2.511; O(3), −3.060.
(20) Angles subtended at O(3′) follow: O(2′)–O(3′)–Hg, 115 (2); C(4′)–O(3′)–Hg, 131 (2)°.
(21) J. R. Nixon, M. A. Cudd, and N. A. Porter, *J. Org. Chem.*, **43**, 4048 (1978).
(22) **4** was independently prepared by epoxidation of *trans*-2-vinylcyclohexanemethanol.
(23) Greater than 90% product accountability was attained in all the tin hydride reactions reported here.
(24) The trace amounts of **4** found in the axial isomer reaction may possibly be formed from traces of **2b** present in **3b.** The LC separation of **2a** and **3**a had an α value of 1.15 and it seems likely that trace **2b** (undetectable by $^{13}C$ NMR and LC) was present in **3b.**
(25) B. Giese, *Angew. Chem., Int. Ed. Engl.*, **15**, 173 (1976).
(26) See, for example, C. C. Hill and G. M. Whitesides, *J. Am. Chem. Soc.*, **96,** 870 (1974).

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*Received August 13, 1979*

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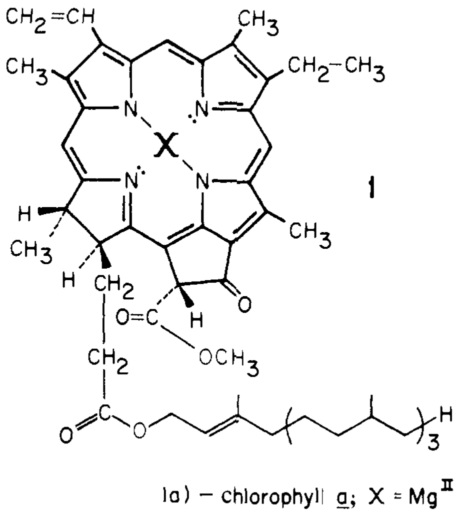
## Hydration Behavior of Chlorophyll *a*: A Field Desorption Mass Spectral Study

*Sir:*

In vivo and in vitro studies of chlorophylls have indicated that chlorophyll–chlorophyll[1,2] and chlorophyll–water[3,4] interactions are central to an understanding of chlorophyll function in photosynthesis.[5,6] This study examines in more detail the nature of chlorophyll–chlorophyll and chlorophyll–water interactions by use of field desorption mass spectrometry.[7]

The literature contains conflicting reports concerning the possibility of obtaining anhydrous chlorophyll *a*[1a] in vitro and the stoichiometry of in vitro chlorophyll hydrates. One group has reported a structure and spectrum for anhydrous chlorophyll *a* dimers,[8a] a photoelectron spectrum for anhydrous chlorophyll *a*,[8b] and has subsequently stated "We have been unable to observe anhydrous chlorophyll." [8c] The data presented below indicate that (1) it is possible to obtain anhydrous chlorophyll *a* under mild conditions; (2) it is possible for chlorophyll *a* to exist with only tetracoordinate magnesium; and (3) field desorption data appear to favor a 1:1 stoichiometry for hydrated chlorophyll *a*.

Chlorophyll *a* (**1a**) and pheophytin *a* (**1b**) were prepared by standard procedures;[9] anhydrous chlorophyll *a* was obtained by dissolution in carbon tetrachloride followed by evaporation



1

1a) – chlorophyll a; X = $Mg^{II}$
1b) – pheophytin a; X = H,H

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