is a strong band at 1536 cm^{-1} which is consistent with the ring breathing mode found in other fluorinated epoxides.[5,16] The ^{1}H NMR spectrum consists of eight peaks located centrosymmetrically at 35.3, 38.0, 40.4, and 43.1 Hz from the center. The chemical shift in CDCl$_3$ is 5.85 ppm (Me$_4$Si internal reference). Analysis of the spectrum gives the following coupling constants: J_{HF}(gem) = 78.6 Hz, J_{HF}(cis or trans) = 5.1 Hz, and J_{HF}(cis or trans) = 2.7 Hz. The chemical shift and coupling constants correlate well with those reported for *cis*-1,2-difluoroethylene oxide.[5,21] The mass spectral fragmentation patterns are similar to those found in other fluorinated epoxides.[5,22] Trifluoroethylene ozonide was characterized by IR, NMR, and mass spectrometry. The gas-phase infrared spectrum consists of strong absorptions in the 1350–1050-cm^{-1} region which is very reasonable as compared to other similar ozonides.[1,3,5,10] The ^{1}H NMR spectrum consists of four peaks located centrosymmetrically at 39.1 and 36.7 Hz from the center. The chemical shift in (CD$_3$)$_2$CO is 7.63 ppm (Me$_4$Si internal reference). This compares well with the chemical shift of 7.60 ppm found in *trans*-1,2-difluoroethylene ozonide in the same solvent.[23] Analysis of the spectrum gives the following coupling constants: J_{HF}(gem) = 75.8 Hz, J_{HF}(trans) = 2.4 Hz, and J_{HF}(cis) = 0 Hz. These values compare well with those found in vinyl fluoride ozonide and *trans*-1,2-difluoroethylene ozonide.[5,10] The mass spectral fragmentation patterns are similar to other fluorinated ozonides.[1,3,5,10] *trans*-1,2-Difluoroethylene ozonide was identified by its known gas-phase infrared spectrum.[5]

Acknowledgment is made to Philip Ralli for help in obtaining NMR spectra and Karl Moschner for help with the mass spectrometer. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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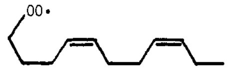
Received June 30, 1980

Serial Cyclization of Peroxy Free Radicals: Models for Polyolefin Oxidation

Sir:

The fate of peroxy radicals formed in autoxidation is dependent on several factors involving both the conditions of oxidation and molecular structure. In polyunsaturated materials, intramolecular addition of peroxy radicals to double bonds to form cyclic peroxides has been demonstrated,[1-4] and cyclic peroxides may well be primary products in the oxidative degradation of polyolefins such as diene polymers as well as in the autoxidation of isoprenoid and lipid natural products.[5] We chose peroxy radical **1** as a model for polybutadiene autoxidation, and we report here the isolation and characterization of novel polycyclic polyperoxides resulting from the serial cyclization of radical **1**. This study establishes the validity of the concept of serial cyclization in polymer and natural-product oxidation and provides information about factors important in the stereochemical control of free-radical cyclization.



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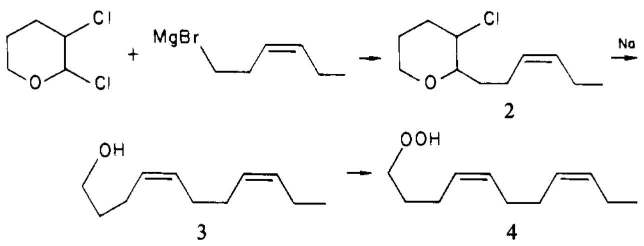
Scheme I



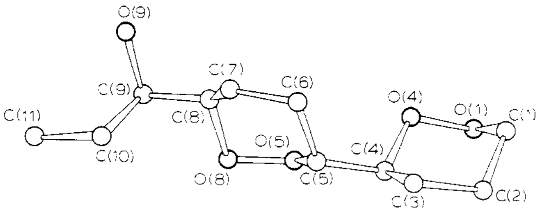
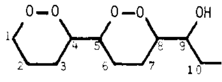


Figure 1. Structure and solid-state conformation of **5a**.

Hydroperoxide **4**, prepared according to Scheme I, served as a precursor to **1**.[6] Thus, 0.2 M **4** in benzene under oxygen was treated with 0.1 to 1.0 radical equiv of di-*tert*-butyl hyponitrite (DTBN)[7] initiator at 30 °C. After approximately 50% consumption of **4** (48–72 h), the reaction was terminated by cooling to 0 °C, followed by addition of an amount of triphenylphosphine equal to the initial number of moles of **4**. Thin-layer chromatography showed two peroxide-positive products (R_f 0.39 and 0.29)[8] in addition to alcohol **3** and Ph$_3$PO. High-performance LC[9] provided four major crystalline peroxide products (**5a–d**) with retention volumes and percentage of peroxide mixture as follows: **5a**, 69 mL, 30%; **5b**, 78 mL, 33%; **5c**, 120 mL, 15%; **5d**, 132 mL, 22%. Product accountability approached 70%, and **5a–d** were far and away the dominant products of the reaction as judged by high-performance LC and TLC. Although compound **5** has four chiral centers and thus eight diastereomers are possible, it is highly significant that only four major racemic products having this polycyclic structure were found.

The four peroxide products **5a–d** gave similar ^{1}H and ^{13}C NMR spectra which notably lacked any vinylic proton or carbon signals. ^{1}H NMR spectra generally displayed a triplet [δ 1.0 (3 H, CH$_3$)], a broad multiplet [δ 1.2–2.2 (10 H)], a multiplet [δ 3.5 (1 H α to OH)], and another broad multiplet [δ 4.2, 5 H α to -O-O-]. In addition to having a single signal between 9.5 and 10.1 ppm, the ^{13}C NMR spectra contained a group of five signals from 22 to 26 ppm, two signals in the 73-ppm region, and three more



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(6) (a) Hydroperoxide **4** is a mixture of *E* and *Z* isomers at Δ_4 while the stereochemistry about Δ_8 is only *Z*. The Δ_4 *E* and *Z* isomers may be separated by high-performance LC. The synthesis of **4** follows literature procedures directly. See ref 1 and also: Ansell, L.; Selleck, K. *J. Chem. Soc.* **1956**, 1238. (b) Wawzorek, S.; Klimstra, P. D.; Kallio, R. E. *J. Org. Chem.* **1960**, *25*, 621. This procedure was used for synthesis of the hydroperoxide from the mesylate.

(7) (a) Mendenhall, G. D. *J. Am. Chem. Soc.* **1974**, *96*, 5000. (b) Kiefer, H.; Traylor, T. G. *Tetrahedron Lett.* **1966**, 6163.

(8) TLC was carried out on silica plates (Merck Co.) with ether solvent.

(9) High-performance LC was carried out on a Whatman Magnum 9 10-μm silica column with refractive index detection. Solvent used in the chromatography was 5% isopropyl alcohol/hexane.

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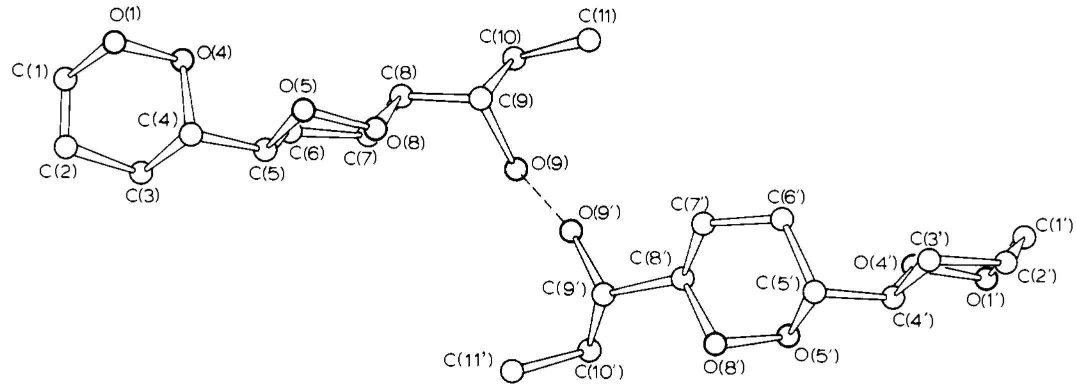


Figure 2. Structure and solid-state conformation of the two molecules defining the asymmetric crystal unit of **5b**.

Table I. ^{13}C NMR Spectral Data for 5a-d

isomer	stereochemistry^a	C_1	C_4/C_5	C_9	C_{11}
5a	4*S*,5*R*,8*R*,9*R*	73.05	81.17, 81.58	73.50	9.58
5b	4*S*,5*R*,8*R*,9*S*	73.05	81.46, 81.62	73.13	10.07
5c	4*R*,5*R*,8*R*,9*R*	72.69	81.91, 81.99	73.62	9.58
5d	4*R*,5*R*,8*R*,9*S*	72.69	82.07, 82.07	73.10	10.07

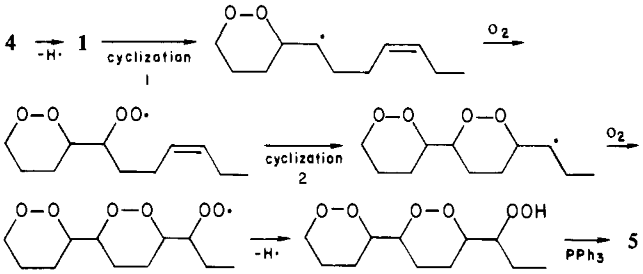
^{a} The products are all racemic mixtures; the stereochemistry for only one enantiomer is specified.

between 81 and 83 ppm. These spectra were taken to be consistent with structure **5**, and combustion analysis supported this assignment.

Single-crystal X-ray analysis of **5a** and **5b**, the two major products formed, not only confirmed their gross structure assignment but also established the relative stereochemistry as 4*S*,5*R*,8*R*,9*R* in **5a** and 4*S*,5*R*,8*R*,9*S* in **5b**. Crystals of both **5a** and **5b** belong to the orthorhombic system,[10] with one molecule in the asymmetric crystal unit of the former and two in that of the latter. The crystal structures were solved by direct methods by use of MULTAN.[11] Full-matrix least-squares refinement of atomic positional and thermal parameters[12] converged at R^{13} = 0.064 over 687 statistically significant reflections[14] for **5a** and R = 0.045 over 1571 reflections for **5b**. Views of the solid-state conformations (Figures 1 and 2) clearly show that all of the dioxane rings adopt chair conformations with equatorial substituents.[15,16] Preference for a gauche O-C-C-O arrangement is indicated by the fact that, despite their different solid-state environments, all three molecules (one of **5a** and two of **5b**) possess this common feature around the C_4-C_5 bond, and two out of these three also have a similar arrangement around the C_8-C_9 bond. The exception to this conformational preference is encountered around the C_8-C_9 bond in one of the **5b** molecules where the departure from a gauche conformation may be ascribed to the influence of crystal packing forces associated with the O-H···O-(hydroxy) hydrogen bonds which link molecules in the solid state.

Stereochemistries for **5c** and **5d** may be deduced by consideration of the structures defined for **5a** and **5b** in conjunction with the ^{13}C NMR spectral data presented in Table I. Assignments may be made on the basis of the observation that signals for given carbon atoms in these four molecules break into pairs possessing equal, or nearly equal, chemical shifts. This pairing of chemical shifts reflects the local stereochemical environment. For example, the signals assigned to C_1, C_4, and C_5 in compounds **5a** and **5b** have similar chemical shifts, and the stereochemistry of these two isomers at C_4 and C_5 is identical. It follows, therefore, that similarity of chemical shifts implies similarity of configuration at carbon atoms. That isomers **5c** and **5d** also have ^{13}C spectra paired at C_1, C_4, and C_5 suggests identical stereochemistry at C_4 and C_5 in these compounds, viz., *R*,*R*.[17] Application of similar arguments for signals due to C_9 and C_{11} leads to the conclusion that **5a** and **5c** have the same stereochemistry at C_8 and C_9 (*R*,*R*), while **5b** and **5d** have *R*,*S* stereochemistry at C_8 and C_9. This line of reasoning implies that, like **5a** and **5b**, **5c** and **5d** have diequatorial substituents on the second 1,2-dioxane ring. In fact, we would expect no correlation of ^{13}C chemical shifts such as noted in Table I if substituents on the dioxane ring were to be anything other than diequatorial in **5c** and **5d**.

Scheme II



Scheme II accounts for formation of the polycyclic peroxides from hydroperoxide **4**. The fact that only four diastereomers of **5** are formed in significant amounts is noteworthy, for it is indicative of stereochemical control in the second cyclization step (Scheme II, cyclization 2). The stereocontrol in the cyclization process may be understood if one assumes a chairlike six-membered transition state with diequatorial substituents as shown.

Cyclization to form six-membered ring peroxides consequently favors α,α′ trans diequatorial substitution in contrast to the situation with five-membered-ring cyclization where α,α′ cis substitution is preferred.[18,19] This stereochemical control demands

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(10) Crystal data: **5b**, a = 9.198 (4), b = 10.122 (4), c = 26.343 (10) Å, space group $Pn2_1a$ ($Pna2_1$ with b and c axes interchanged), U = 2453 Å^3, Z = 8, d_{calcd} = 1.263 g cm^{-3}; **5a**, a = 8.880 (4), b = 26.296 (10), c = 5.193 (2) Å, space group $P2_12_12_1$, U = 1213 Å^3, Z = 4, d_{calcd} = 1.277 g cm^{-3}.

(11) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1971**, *A27*, 368.

(12) See paragraph at end of paper regarding supplementary material.

(13) $R = \sum||F_o| - |F_c||/\sum|F_o|$.

(14) Intensity data were recorded on an Enraf-Nonius CAD-3 automated diffractometer (Ni-filtered Cu Kα radiation, λ = 1.5418 Å; θ-2θ scans) by use of procedures detailed elsewhere; see: Miller, R. W.; McPhail, A. T. *J. Chem. Soc., Perkin Trans. 2*, **1979**, 1527.

(15) Mean endocyclic lengths and angles follow: C-C 1.520, C-O 1.444, O-O 1.463 Å; C-C-C 110.1°, C-C-O 109.5°, C-O-O, 106.9°.

(16) Mean dihedral angles in the dioxane rings follow: C-O-O-C 72.4°, O-O-C-C 66.3°, O-C-C-C 55.0°, C-C-C-C 48.4°.

(17) The products are all racemic mixtures; the stereochemistry for only one enantiomer is specified. The structural assignments were further confirmed by comparison of the partially decoupled 250-MHz ^{1}H NMR spectra.

(18) Beckwith, A. L. J.; Wagner, R. D. *J. Am. Chem. Soc.* **1979**, *101*, 7099.

identical configurations at C_5 and C_8 and accounts for the fact that four of the eight possible diastereomers are observed as major products.[20] We also note a stereochemical preference in the addition of oxygen to free-radical centers at C_5 and C_9; viz., products with vicinal chiral centers having opposite configuration are favored. Thus, **5b** (having opposite configuration at both pairs of vicinal centers, C_4/C_5 and C_8/C_9) is the major isomer formed while **5c**, which has identical configuration at these centers, is the minor product.

Although the formation of peroxide compounds by a mechanism like the one outlined in Scheme II has been proposed in the autoxidation of natural and synthetic polymers,[21,22] no serial cyclization products have been previously characterized.[23] From the present study, we suggest that serial cyclization is an important mechanistic pathway in polyolefin autoxidation, and we anticipate that peroxides containing many consecutive rings could form. While serial cyclization was demonstrated here for 1,5-diene systems, homoconjugated dienes like those present in unsaturated fatty acids and esters would also be capable of serial cyclization.[5] Such cyclization products may thus be important derivatives of lipid natural products, and we are currently investigating this possibility.

Acknowledgment. Crystallographic calculations, performed at the Triangle Universities Computation Center, Research Triangle Park, NC, were supported by a grant of computer time from Duke University. The research was supported by grants from the National Science Foundation and the Army Research Office.

Supplementary Material Available: Tables of atomic positional and thermal parameters, interatomic distances and angles, and lists of observed and calculated structure amplitudes for **5a** and **5b** (31 pages). Ordering information is given on any current masthead page.

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(22) Mayo, F. R. *Ind. Eng. Chem.* **1960**, *52*, 614.

(23) The evidence presented here does not necessarily contradict that of Gemmer and Golub who indicate that the major products of thermal oxidation of polybutadiene are epoxides and alcohols: Gemmer, R. V.; Golub, M. A. *Polym. Preprints Am. Chem. Soc., Div. Polym. Chem.* **1976**, *17(2)*, 676. Their work was generally carried out at temperatures between 90 and 180 °C where the peroxide products we find at 30 °C would not be expected to survive.

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Absolute Rate Constants for Additions of Phenylchlorocarbene to Alkenes

Sir:

The reactivity of carbenes toward alkenes has been extensively characterized by competition (relative rate) experiments,[1] but very little is known about the absolute kinetics of these reactions. Tyerman reported an activation energy of ~6 kcal/mol for the addition of CF_2 to $CF_2{=}CF_2$ in the gas phase,[2] whereas Nefedov et al. derived E_a = 11.2 kcal/mol for CF_2 addition to cyclopentadiene (580–720 °C, gas phase).[3] The competition between intramolecular 1,2-hydride shift and intermolecular addition of F_2CHCF to alkenes (gas phase, 167–350 °C) has been kinetically analyzed. Measured relative Arrhenius parameters and the application of several approximations to the intramolecular reaction afforded E_a = 11.7 and 11.9 kcal/mol, respectively, for F_2CHCF additions to propene and *cis*-butene.[4] These activation parameters and requisite rate constants for (singlet) CF_2 and F_2CHCF additions either derive from complicated kinetic analyses or require various approximations in their derivation. The situation is somewhat better for addition reactions of triplet diphenylcarbene and fluorenylidene.

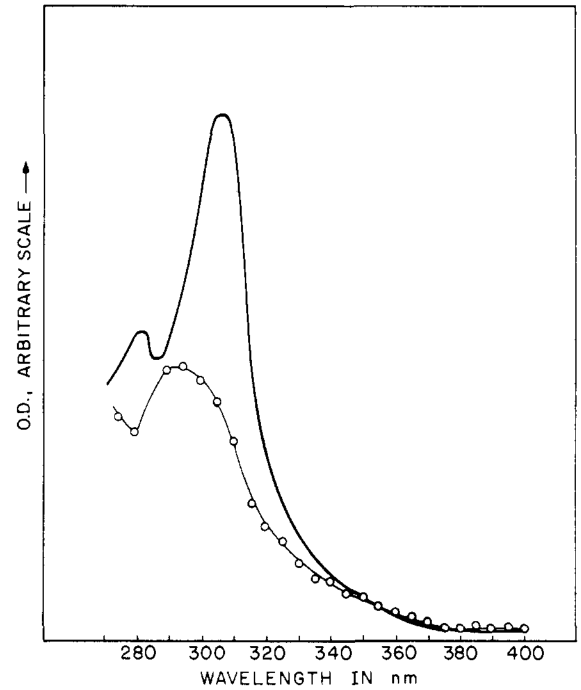

Figure 1. Absorption spectra of phenylchlorocarbene. The solid line is the spectrum recorded at 77 K in 3-methylpentane. The dotted line is the point-by-point (transient) spectrum obtained at 23 °C in isooctane at 5-nm intervals with ~15-nm bandpass.

Analysis of the decay of the Ph_2C triplet ESR signal in solid diphenylethylene (~90–105 K) gave $E_a = 7.8 \pm 0.3$ kcal/mol for the addition reaction.[5,6] Flash photolysis of diphenyldiazomethane (benzene, 25 °C) in the presence of varying concentrations of butadiene gave $k_2 = 6.5 \times 10^5$ M^{-1} s^{-1} for the triplet Ph_2C/butadiene cyclopropanation.[6,7] Spectroscopic monitoring of the olefinic quenching of triplet fluorenylidene, generated by flash photolysis of 9-diazofluorene, gave rate constants for the cyclopropanation of various alkenes; e.g., $CH_2{=}CHCN$, 7.1×10^5; *trans*-$NCCH{=}CHCN$, 4.7×10^7 (M^{-1} s^{-1}).[8] In addition, rate constants for reactions of *singlet* fluorenylidene with alkenes could be obtained, albeit indirectly, by monitoring the yield of triplet fluorene in the presence and absence of quencher and combining these data with the observed rate constant for singlet → triplet crossing. Singlet fluorenylidene is thus reported to be highly reactive and indiscriminate in additions to seven electron-rich or electron-poor alkenes (e.g., $k_2 \sim 3 \times 10^8$ M^{-1} s^{-1} for $Me_2C{=}CHMe$ or $CH_2{=}CHCN$).[8]

We are pleased to report here the first directly measured absolute rate constants for olefin additions of a selective, singlet

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