Transannular Ozonide of 9-*tert*-Butyl-10-methylanthracene

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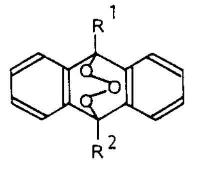
In the reaction of ozone with alkenes and aromatic compounds, primary ozonides are important intermediates and of interest in view of their reactivity and structure.[1] The transannular ozonides obtained from anthracene derivatives, i.e., **1a–f**, were investigated by Bailey and Rigaudy.[1c,2] Due to their instability, however, clear-cut knowledge on structures and chemical and physical properties of these ozonides is still lacking. In this communication we wish to describe a stable (at room temperature) crystalline transannular ozonide, **1g**, and its configuration determined by X-ray crystallography. X-ray study for trioxides has not so far been realized.



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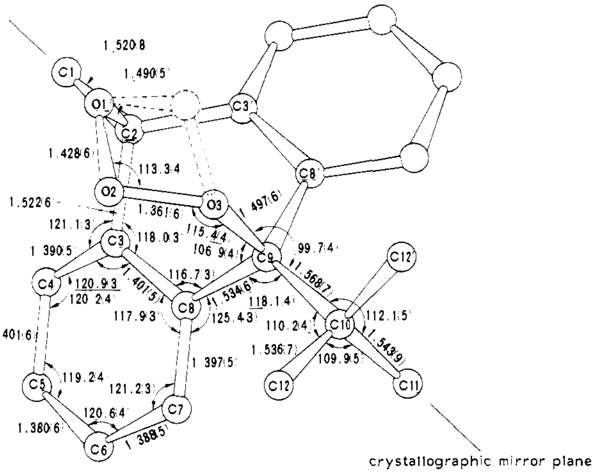
a, $R^1=R^2=H$
b, $R^1=R^2=Me$
c, $R^1=Me$, $R^2=OMe$
d, $R^1=R^2=OMe$
e, $R^1=Me$, $R^2=H$
f, $R^1=Ph$, $R^2=Me$
g, $R^1=t\text{-}Bu$, $R^2=Me$

9-*tert*-Butyl-10-methylanthracene (**2**) was prepared according to Parish's procedure.[3] Ozonation of **2** in acetone at −78 °C, followed by separation of the reaction mixture by column chromatography on silica gel, gave the trioxide **1g** as a major product (64%) along with small amounts of the peroxide **3** (3%) and anthraquinone (**4**) (9%). Recrystallization from $CHCl_3$ yielded pure **1g** as colorless needles, mp 133–134 °C. The spectral and microanalytical data for **1g** and **3** were fully consistent with the assigned structures.[4]

Thermolysis of **1g** in methanol, dioxane, and $CDCl_3$ at elevated temperatures gave 10-methyl-10-(*tert*-butyldioxy)-9-anthrone (**3**) as a major product (e.g., 73% in $CDCl_3$ at 72 °C). An analogous thermal transformation for the transannular peroxides **1b** and **1e** is known to occur.[2a–c] Disappearance of **1g** in a $CDCl_3$ solution in a sealed NMR tube was monitored by NMR at temperatures ranging from 54.4 to 78.0 °C. The decomposition proceeded unimolecularly, yielding the following Arrhenius equation (eq 1).

$$\log k = (14.6 \pm 0.3) - [(28600 \pm 500)/(2.30RT)] \quad (1)$$

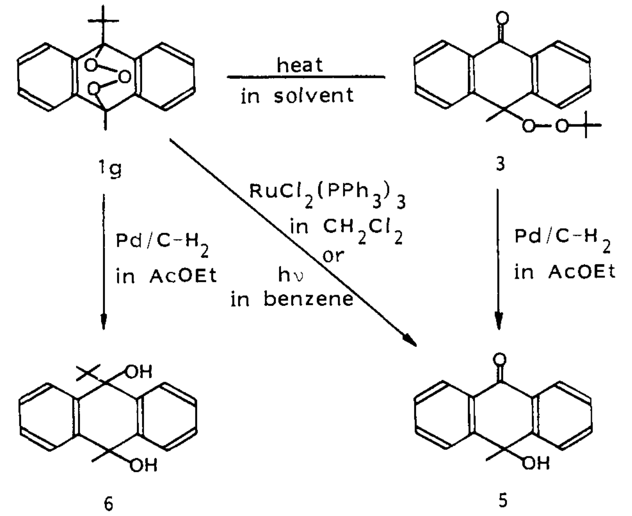
The activation enthalpy $\Delta H^{\ddagger}_{72\,°C} = 27.9 \pm 0.5$ kcal/mol is larger than the value for the transannular ozonide of 9,10-dimethylanthracene **1b** ($\Delta H^{\ddagger}_{30\,°C} = 24.5$ kcal/mol[2d]). This indicates that the bulky *tert*-butyl substituent can stabilize the transannular ozonide structure as compared to the methyl substituent. In contrast, it is known that *cis*-1,2,3-trioxolane structure is destabilized by bulky substituents.[1b]



C1–C2–C3 = 115.3(4), C1–C2–O1 = 101.5(4), C3–C2–C3′ = 107.0(5)
C3–C2–O1 = 108.6(4), C8–C9–C8′ = 106.0(5), C2–O1–O2 = 110.0(4)

Figure 1. Molecular structure of the primary ozonide **1g**. Hydrogen atoms are omitted for clarity. Figures denote bond distance (Å) and angles (deg).

Scheme I



The transannular ozonide **1g** was catalytically reduced with Pd/C to a 9,10-dihydroanthracene derivative **6** in 72% yield. Similarly, the peroxide **3** was transformed by catalytic reduction to 10-methyloxanthrone (**5**) in 97% yield. Photolysis through Pyrex of **1g** in benzene gave **5** in 44% yield. Treatment of **1g** at room temperature with $RuCl_2(PPh_3)_3$ that possesses the capacity of one-electron transfer[5] resulted in **5** and anthraquinone (**4**) in 48% and 6% yield, respectively. These reactions (Scheme I) unequivocally established the structure for **1g**.

The NMR (^1H and ^{13}C) spectra for **1g**[4] demonstrate (1) that three methyls of the *tert*-butyl group are nonequivalent, magnetic nonequivalency in the *tert*-butyl methyl groups is sometimes observable even at ordinary temperature,[6] and (2) that, as was observed for **1a**, **1b**, and **1d**,[2d] two aromatic rings in the molecule are nonequivalent due to the slow (on the NMR time scale) conformational interconversion between A and B (eq 2). Coa-

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(1) (a) Murphy, J. S.; Orr, J. R. "Ozone Chemistry and Technology"; Franklin Institute Press: Philadelphia, 1975. (b) Bailey, P. S. "Ozonation in Organic Chemistry"; Academic press: New York, 1978; Vol. 1. (c) Bailey, P. S. *Ibid.* 1982; Vol 2.

(2) (a) Erickson, R. E.; Bailey, P. S.; Davis, J. C., Jr. *Tetrahedron* **1962**, *18*, 388. (b) Rigaudy, J.; Cuong, N. K.; Albouy. J.; Rothschild, J. F. *Tetrahedron Lett.* **1973**, 4439. (c) Rigaudy, J.; Cuong, N. K.; Albouy, J.; Chetrit, A. *Ibid.* **1976**, 1089. (d) Gobert, F.; Altenburger-Combrisson, S.; Albouy, *J. Org. Magn. Reson.* **1979**, *12*, 202.

(3) Parish, R. C.; Stock, L. M. *J. Org. Chem.* **1966**, *31*, 4265.

(4) Transannular ozonide **1g**: ^1H NMR ($CDCl_3$) δ 1.53 (3 H, s), 1.56 (3 H, s), 1.80 (3 H, s), 2.05 (3 H, s), 6.80–7.90 (8 H, m, attributable to two sets of a four spin system); ^{13}C ($CDCl_3$) δ 145.4, 145.2, 141.5, 139.4, 128.9, 128.4, 128.0, 127.5, 127.3, 127.1, 125.8, 124.7, 96.3, 85.7, 37.5, 31.4, 30.7, 29.0, 19.7; IR (Nujol) 1396, 1294, 1246, 1221, 1166, 1067, 768, 744, 676 cm^{-1}; high-resolution; high-resolution mass spectrum, calcd for $C_{19}H_{20}O_3$, 296,1412; obsd. 296.1400.

(5) (a) Matsumoto, H.; Nakano, T.; Takasu, K.; Nagai, Y. *J. Org. Chem.* **1978**, *43*, 1734. (b) Suzuki, M.; Noyori, R.; Hamanaka, N. *J. Am. Chem. Soc.* **1982**, *104*, 2024.

(6) (a) Oki, M.; Suda, M. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 1876. (b) Casy, A. F.; Ison, R. R. *Tetrahedron* **1969**, *25*, 641.

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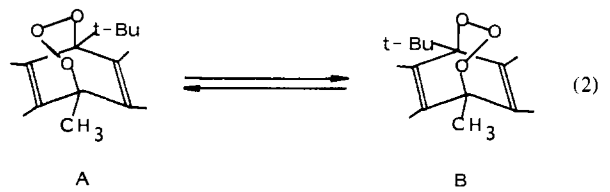
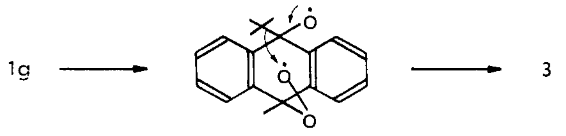


(2)

lescence or broadening of the corresponding ^{1}H NMR (80 MHz) signals was not observed even at 78.0 °C, indicating that energy barriers to rotation of the *tert*-butyl group and to the process A ⇄ B are pretty high.[7]

The stereochemistry of **1g** (Figure 1) was determined by X-ray crystallography.[11] The molecule situates on a crystallographic mirror plane. The O(2) atom is located in either of two positions that deviate by 0.68 Å from the mirror plane. The lengths of two O–O bonds are 1.361 and 1.428 Å, respectively, and two C–O bonds are 1.490 and 1.497 Å, respectively. The O–O–O angle of 113.3° is smaller than the value for ozone (116°).[1b] The calculated value for the unsubstituted 1,2,3-trioxolane is 104.4 ± 1.6°.[12] The fact that the C(9)–C(8)–C(7) angle is larger than the C(2)–C(3)–C(4) angle is ascribable to peri interaction between the *tert*-butyl group and two hydrogen atoms at C(7) and C(7′).

Thus the salient features of the stereochemistry of **1g** are (1) that the two O–O bond distances (1.361 and 1.428 Å) are very different from each other and are unusually short as compared to O–O bonds of typical organic peroxides (1.48 Å)[13,14] and (2) that both of the C–O bonds (1.490 and 1.497 Å) are definitely longer than C–O bond for other alkyl peroxides (1.22–1.48 Å).[13b–e,14] It is interesting to note that the thermal decomposition of **1g** was formally initiated by selective cleavage of the shorter (stronger) peroxide bond, i.e., cleavage of O(2)–O(3) rather than O(1)–O(2) (eq 3). Further study to elucidate this point is in progress.



(3)

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Supplementary Material Available: Listings of atomic coordinates and thermal parameters in crystalline **1g** (3 pages). Ordering information is given on any current masthead page.

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(7) Minimum barriers to the *tert*-butyl rotation and to the oxygen flipping A ⇄ B were estimated as 20 and 19 kcal/mol, respectively, by using eq 4 (T

$$\Delta G_c^{*} = -RT \ln (\pi h \Delta\nu / (2^{1/2} kT)) \qquad (4)$$

= 351 K; $\Delta\nu$ = 2.4 Hz for the *tert*-butyl rotation and 14 Hz[8] for the oxygen flipping). These data suggest that optical resolution of **1g** at room temperature may be possible. Rotational barriers for the *tert*-butyl group are typically less than 13 kcal/mol.[9] Boat–chair interconversion barrier of a cyclic trisulfide has recently been estimated to be ΔG_c^{*} = 17.9 kcal/mol.[10]

(8) A similar $\Delta\nu$ value was obtained for **1b**.[2d]

(9) Sternhell, S. In "Dynamic Nuclear Magnetic Resonance Spectroscopy"; Jackman, L. M., Cotton, F. A., Eds.; Academic Press: New York, 1975; p 163.

(10) Guttenberger, H. G.; Bestmann, H. J.; Dickert, F. L.; Jorgensen, F. S.; Snyder, J. P. *J. Am. Chem. Soc.* **1981**, *103*, 159.

(11) The crystal data of **1g** were as follows: $C_{19}H_{20}O_3$, tetragonal, space group $P4_2cm$, $a = b = 15.516$ (3), $c = 6.384$ (2) Å, $Z = 4$, $D_c = 1.28$ g/cm^3. The intensities in one octant were measured up to $2\theta = 120°$ on a four-circle diffractometer with Ni-filtered Cu Kα radiation. The structure factors of 632 independent reflections with $F > 2\sigma(F)$ were obtained after Lorentz and polarization correlctions and averaging the intensities of equivalent reflections. The structure was solved by the direct method (MULTAN), and refined by the block-diagonal least-squares method to $R = 0.039$. The atomic scattering factors were taken from the "International Tables for X-ray Crystallography", Vol. IV.

(12) (a) Cremer, d. *J. Chem. Phys.* **1979**, *70*, 1898, 1911, 1928. (b) Cremer, D. *J. Am. Chem. Soc.* **1981**, *103*, 3619.

(13) (a) Silbert, L. S. In "Organic Peroxides"; Swern, D., Ed.; Wiley: New York, 1971; Vol. 2, p 649. (b) Numan, H.; Wieringa, J. H.; Wynberg, H.; Hess, J.; Vos, A. *J. Chem. Soc., Chem. Commun.* **1977**, 591. (c) Groth, P. *Acta Chem. Scand.* **1970**, *24*, 2137. (d) Wilson, R. M.; Gardner, E. J.; Elder, R. C.; Squire, R. H.; Florian, L. R. *J. Am. Chem. Soc.* **1974**, *96*, 2955. (e) Jeffery, J.; Mawby, R. J.; Hursthouse, M. B.; Walker, N. P. C. *J. Chem. Soc., Chem. Commun.* **1982**, 1411.

(14) One of the referees pointed out that these structural features are peculiar and appear inexplicable. At this stage we can only say that the trioxide **1g** is a peculiar species due to some interactions and constraints, which are not entirely obvious.

Bilayer-Induced Diastereomeric Kinetic Differentiation

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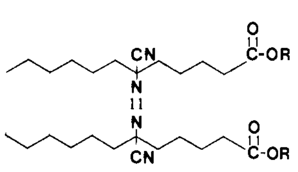
While the physical aspects of lipid bilayers and monolayers have been the focus of considerable investigation,[2] use of bilayers as oriented hosts for chemical reactants has received far less attention.[3] In this communication, we report the synthesis of a new amphipathic diazene, **1**, and the thermal decomposition of **1** in



1, meso, (±); R = H

2, meso, (±); R = CH_3

phosphatidylcholine multilamellar vesicles (MLV's).[2,4] Our results support the notion that reactivity and the stereochemical course of reaction may be affected by utilizing lipid bilayers as the solvent medium.

The free radical initiator, **1**, was prepared by standard procedures[5] from methyl 6-oxododecanoate. The meso and (±) diastereomers of **1**[6] were readily separated by chromatography. The isomer that eluted last on reverse-phase high-pressure liquid chromatography (HPLC, C18: methanol/water/acetic acid;

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(1) (a) Department of Chemistry. (b) Department of Anatomy.

(2) Tanford, C. "The Hydrophobic Effect: Formation of Micelles and Biological Membranes", 2nd ed.; Wiley: New York, 1980.

(3) Several researchers have utilized bilayers or micelles as solvents for chemical reactions. Bilayer work has focused primarily on regioselectivity while applications in micelles have had a broader focus. See, for example: (a) Ross, A. H.; Radhakrishnan, R.; Robson, R. J.; Khorana, H. G. *J. Biol. Chem.* **1982**, *257*, 4152–4161. (b) Bayley, H.; Knowles, J. R. *Biochemistry* **1980**, *19*, 3883–3892. (c) Brunner, J.; Richards, F. M. *J. Biol. Chem.* **1980**, *255*, 3319–3329. (d) Whitten, D. G.; Russell, J. C.; Schmehl, R. H. *Tetrahedron* **1982**, *38*, 2455–2474. (e) Breslow, R.; Kitabatake, S.; Rothbard, J. *J. Am. Chem. Soc.* **1978**, *100*, 8156–8160. (f) Lee, H.; deMayo, P. *Chem. Commun.* **1979**, 493–494. (g) Okahata, Y.; Ihara, H.; Kunitake, T. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 2072–2076.

(4) Jain, M. K.; Wagner, R. C. "Introduction to Biological Membranes"; Wiley: New York, 1980.

(5) The synthesis is a modification of procedures used for AIBN preparation. Methyl 6-oxododecanoate was reacted with hydrazine hydrate to give the azine, which was then reacted with HCN(l) to afford the cyanohydrazine. Bromine oxidation gave a mixture of **2** meso and **2** (±). Overall yield was 30% for the three-step sequence.

(6) 1 meso: mp 108.5–110 °C; anal. ($C_{26}H_{44}N_4O_4$) C, H. 1 (±): mp 114.5–116 °C. anal. ($C_{26}H_{44}N_4O_4$) C, H. Both diastereomers exhibited similar ^{1}H and ^{13}C NMR. ^{13}C (15 MHz, CD_2Cl_2) δ 14.1 (CH_3), 22.9, 24.2, 24.6, 29.3, 31.8, 33.9, 37.2, 37.5, 77.5 (quaternary C), 117.9 (C≡N), and 179.5 (COOH); ^{1}H (250 MHz, CD_2Cl_2) δ 0.88 (t, 6 H, CH_3's), 1.3 (m, 2 H), 1.7 (m, 4 H), 2.0–2.3 (m, 8 H), 2.4 (m, 4 H); UV (CH_3OH) λ_{max} = 345 (ϵ = 21).

(7) We carried out low-angle X-ray studies to convince ourselves that **1** does incorporate into the lipid bilayer. A discussion of the low-angle X-ray work is presented in supplementary material to the manuscript.

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