CH_2OAc, 2 H), 3.92 (s, ketal, 4 H), 3.15 (t, J = 3.0, C-6, 1 H), 2.10 (s, OAc, 3 H), 1.15–2.00 (m, remaining, 6 H). ^{13}C NMR ($CDCl_3$): 169.9, 106.2, 66.5, 64.1, 63.7, 57.2, 55.0, 34.2, 27.3, 22.7, 20.2. Anal. Calcd for $C_{11}H_{16}O_5$: C, 57.88; H, 7.06. Found: C, 57.79; H, 6.99.

23. Acetoxy Diol: Rearrangement of Epoxy Acetate 22. Method A. Epoxy acetate **22** (230 mg, 1.24 mmol) was dissolved in 2.00 mL of methylene chloride and cooled to −10 °C in an ice/salt bath. To this were added boron trifluoride etherate (10 μL) and glacial acetic acid (74 mg, 1.236 mmol), and the solution was stirred under nitrogen for 1.0 h. The mixture was washed with water (5 mL), dried, and evaporated. The residue was flash chromatographed on silica gel, eluting with 5% methanol in chloroform, and gave 70 mg of tertiary acetoxy diol **23** (22%) as a thick oil. IR ($CHCl_3$): 3500 (br), 2950, 2880, 1720, 1235, 1095 cm^{-1}. ^1H NMR (60 MHz, $CDCl_3$) 4.17 (br s, CH_2O, 1 H), 3.97 (s, ketal, 4 H), 3.60 (br s, CH_2O, 1 H), 3.43 (s, D_2O exchangeable, 2 OH, 2 H), 2.10 (s, OAc), 2.03–1.20 (m, remaining, 7 H). Anal. Calcd for $C_{11}H_{18}O_6$: C, 53.65; H, 7.37. Found: C, 54.02; H, 7.39.

Method B. The procedure of Coxon was employed.[8] Epoxy acetate **22** (21.83 g, 0.09600 mol) was suspended in 300 mL of dry benzene, and to this was added boron trifluoride etherate (11.80 g, 0.105 mol). A white gelatinous precipitate was formed instantaneously. The mixture was shaken for 2 min at room temperature, and to it was added a solution of 10% aqueous sodium acetate (250 mL) all at once. The mixture was shaken briefly and the layers were separated. The aqueous layer was extracted with ethyl acetate (4 × 150 mL) and the combined organic layers were washed with 250 mL of water, dried, and then concentrated to give 20.00 g of acetoxy diol **23** (85%). Spectra of this preparation were identical with those obtained in method A.

24. Oxetane. In an oven-dried, three-necked flask was dissolved acetoxy diol **23** (370 mg, 1.50 mmol) in 5 mL of dry chloroform, under a nitrogen atmosphere. To this was added triphenylphosphine (393 mg, 1.50 mmol). The solution was cooled in an ice bath, and then diisopropyl azodicarboxylate[10] (303 mg, 1.50 mmol) was added via a syringe during a 10-min period. The red color of the azo compound disappeared instantaneously during the addition. Stirring was continued for 4 h at 0 °C. The solution was evaporated to dryness, leaving a thick oil which was flash chromatographed on silica gel, eluting with 3:2 hexane/EtOAc. The acetoxyoxetane **24** was obtained as a thick colorless oil, 202 mg (60%). Only one component was evident on TLC (silica gel, 3:2 hexane/EtOAc) and HPLC. IR ($CHCl_3$): 1727, 1225, 1045, 910 cm^{-1}. ^1H NMR: (60 MHz, $CDCl_3$) 4.85 (dd, J_1 = 6.0, J_2 = 4.0, C-6, 1 H), 4.16 (AB q, J = 3.0, C-8, 2 H), 3.93 (s, ketal, 4 H), 2.13 (s, OAc, 3 H), 2.00–1.15 (m, remaining 6 H). Anal. Calcd for $C_{11}H_{16}O_5$: C, 57.89; H, 7.07. Found: C, 57.89; H, 6.88.

27. 1,3-Dioxane. Acetoxy diol **23** (2.00 g, 8.13 mmol) was dissolved in dry methylene chloride (50 mL). To this was added paraformaldehyde (2.00 g, 66.6 mmol) and 2 drops of concentrated sulfuric acid. The mixture was stirred under nitrogen for 4 h and then diluted with 50 mL of methylene chloride and washed with 50 mL of 10% aqueous $NaHCO_3$. The aqueous layer was back-extracted with methylene chloride (3 × 50 mL) and the combined organic layers were washed with water, dried, and concentrated to give 2.20 g of the crude product. This was flash chromatographed on silica gel, eluting with 1:1 hexane/EtOAc, to give pure **27**, 1.40 g (67.0%). IR (CCl_4): 2970, 2940, 2918, 2880, 1740, 1711, 1453, 1380, 1288, 1253, 1230, 1198, 1189, 1085, 1030 cm^{-1}. ^1H NMR (60 MHz, $CDCl_3$): 5.16 (s, C-4, 2 H), 4.85 (s, C-2, 2 H), 4.23 (s, ketal, 4 H), 2.15 (s, OAc, 3 H), 1.25–2.25 (m, remaining 5 H). ^{13}C NMR ($CDCl_3$): 207.6 (C=O), 169.9 (C-1), 97.4 (C-8), 93.1 (C-4), 77.6 (ketal), 76.2 (C-6), 75.7 (ketal), 66.3 (C-2), 40.7 (C-7), 32.9 (C-9), 27.3 (C-10), 20.2 (acetate CH_3). Anal. Calcd for $C_{12}H_{18}O_6$: C, 55.80; H, 7.02. Found: C, 55.59; H, 6.88.

Acknowledgment. This work was supported by a PSC grant from the CUNY. We gratefully acknowledge the gracious gift of time and expertise by Dr. John Blount (Hoffmann LaRoche) who performed the X-ray analyses. Dr. S. Choudhry (Hoffmann LaRoche) also was also of great help.

Supplementary Material Available: X-ray structural data for compounds **16**, **19**, and **20** (20 pages). Ordering information is given on any current masthead page.

Stereochemical Evidence for an Alkylated Perepoxide Intermediate

A. J. Bloodworth,*[1a] Kevin J. Bowyer,[1a] and John C. Mitchell*[1b]

Departments of Chemistry, University College London, 20 Gordon Street, London WC1H OAJ, U.K., and Royal Holloway and Bedford New College, University of London, Egham Hill, Surrey TW20 OEX, U.K.

Received November 26, 1986

Peroxymercuration of (*Z*)-pent-2-ene afforded single stereoisomers of 2-(bromomercurio)-3-(*tert*-butylperoxy)pentane (M1) and 3-(bromomercurio)-2-(*tert*-butylperoxy)pentane (M2), which were separated by medium pressure liquid chromatography. Iodinolysis of each of these gave a pair of epimeric β-iodopentyl *tert*-butyl peroxides (I1A and I1B from M1, and I2A and I2B from M2), which were similarly separated. When treated with silver trifluoroacetate, the regioisomers I1A and I2A each yielded the *same* 5:3 mixture of 3-(*tert*-butylperoxy)-2-(trifluoroacetoxy)pentane (T1) and 2-(*tert*-butylperoxy)-3-(trifluoroacetoxy)pentane (T2). Independent experiments showed that the starting iodides and the product trifluoroacetates were stereochemically stable under the reaction conditions. Hence, the results are taken to provide compelling evidence for the intermediacy of a *tert*-butylated perepoxide (P_A) that is sufficiently long-lived to be attacked at each ring carbon atom. However, the epimeric regioisomers I1B and I2B each reacted with silver trifluoroacetate to afford a single, new, trifluoroacetate with retention of both regio- and stereochemistry. This is taken to provide evidence for a new mechanism of substitution involving a six-centered cyclic transition state. Product correlations for similar substitutions with analogous bromo peroxides for which stereochemistries are identified by assuming trans addition for peroxymercuration and retention of configuration during bromodemercuration indicate that the alkylated perepoxide (P_A) has the structure with *cis*-alkyl groups. This was confirmed by identifying the stereochemistry of T1 and T2 by $LiAlH_4$ reduction to *threo*-pentane-2,3-diol.

The formation of perepoxides **1** as intermediates in chemical reactions has been vigorously disputed in the scientific literature for the past 25 years.[2,3] Perepoxides have been postulated to mediate in the singlet oxygenation of alkenes[4] and in the base-induced reactions of β-hydro-

(1) (a) University College London. (b) Present address: City of London Polytechnic, London EC3N 2EY, U.K.

(2) Sharp, D. B.; *Abstracts of Papers*, 138th National Meeting of the American Chemical Society, New York; American Chemical Society: Washington, DC; 1960; p 79.

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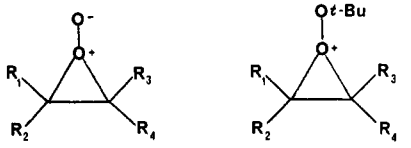
peroxy bromides.[5] More recently we have proposed the intermediacy of related alkylated perepoxides **2** in the reactions of β-*tert*-butylperoxy iodides with silver trifluoroacetate.[6] However, the substitution pattern (R_1 = R_2 = alkyl, and R_3 = R_4 = H) led to regiospecific product formation, and the possibility that species **2** is a transition state rather than a discreet intermediate could not be ruled out.



1 **2**

The existence of three-membered-ring ionic species as intermediates rather than transition geometries has been discussed primarily for phenonium ions involved in Wagner–Meerwein-type rearrangements. The description of these structures as reaction intermediates has been supported by the observation of anchimeric assistance in the departure of leaving groups,[7] by stereochemical selection in reaction products,[7a,8] and by direct NMR observation in a superacid medium.[9]

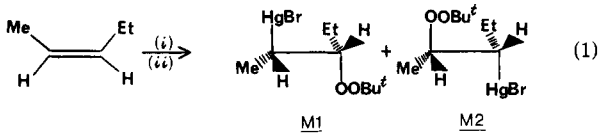
We report herein the use of a stereochemical probe to provide compelling evidence for the existence of an alkylated perepoxide intermediate (**2**, R_1 = Me, R_3 = Et, and R_2 = R_4 = H) that is sufficiently long-lived to be attacked at each ring carbon atom.

Results and Discussion

Our approach was based on the idea that regioisomeric β-iodopentyl *tert*-butyl peroxides with matched stereochemistries should afford a common alkylated perepoxide and hence an identical mixture of two trifluoroacetate substitution products.

Provided that reactants and products are stereochemically stable, this result cannot arise by any other reasonable mechanism, i.e., S_N2, S_N2' (anchimerically assisted substitution with an alkylated perepoxide transition state), or S_Ni (cyclic) (frontside displacement via a six-centered cyclic transition state), each of which afford a single trifluoroacetate.

Preparation of the β-Iodopentyl Peroxides. To prepare the required starting materials, we first carried out the peroxymercuration of (*Z*)-pent-2-ene (eq 1). This



M1 M2 (1)

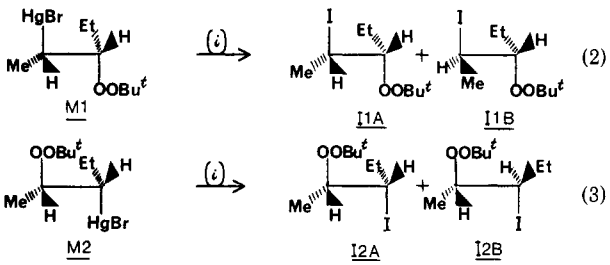
(i) $Hg(OAc)_2$, 2 HOOBu-*t*, 0.2 $HClO_4$, CH_2Cl_2; (ii) KBr, H_2O

afforded a mixture of two regioisomers which, by analogy with model systems,[10,11] are assumed to result from stereospecific trans addition as shown (only one enantiomer of chiral structures is shown throughout this paper, but all compounds were racemic). The products were separated by medium pressure chromatography and were labeled, in order of elution, M1 (ca. 33% of the mixture) and M2.

The structures were established from ^1H and $^1H\{^1H\}$ NMR spectra. The C*H*HgBr and C*H*OOBu-*t* resonances were unambiguously identified from chemical shifts by comparison with model compounds.[12] For M1, the C*H*HgBr resonance appeared as a doublet of quartets, whereas the C*H*OOBu-*t* resonance appeared as an approximate doublet of triplets.

Irradiation of C*H*OOBu-*t* caused the C*H*HgBr resonance to collapse to a quartet, whereas irradiation of C*H*HgBr caused the C*H*OOBu-*t* resonance to collapse to a doublet of doublets (The CH_2 protons of the ethyl group are diastereotopic.). This established that M1 was a 2-mercurio-3-peroxypentane. Similar double-resonance experiments confirmed that M2 was a 2-peroxy-3-mercuriopentane and additional supporting evidence for this assignment came from the observation in the ^{13}C NMR of three-bond ^{13}C–^{199}Hg coupling to *both* C-1 and C-5.

Iododemercuration of each peroxymercurial afforded a pair of diastereoisomeric iodides (eq 2 and 3). These were



(i) I_2, CH_2Cl_2

separated by medium pressure chromatography and were labeled I1 or I2 to indicate the mercurial from which they were derived (M1 or M2, respectively), and A or B in order of elution.

The regiochemistries of these iodides follow straightforwardly from those of the parent mercurials if iododemercuration is assumed to be a free-radical chain process. However, the structures were confirmed independently by ^1H and $^1H\{^1H\}$ NMR in a way analogous to that for the peroxymercurials (above). It is noteworthy that replacement of bromomercurio substituents by iodide led to an upfield shift in the C*H*OOBu-*t* resonance of about 0.15 ppm in the A isomers and 0.8–0.9 ppm in the B isomers. The latter effect was so dramatic that we sought confirmation of the methine proton assignment by selective $^{13}C\{^1H\}$ NMR, making use of the fact that the C*H*OOBu-*t* resonances can be assigned unambiguously by analogy with model compounds and appear some 30 ppm downfield of the C*H*I resonances. Using this technique with I2B, it was confirmed that the methine multiplet at δ 3.43 was due to C*H*OOBu-*t* and that at δ 4.40 arose from C*H*I.

The stereochemical assignments of the A and B isomers rest upon correlations of product trifluoroacetates with

(3) (a) Frimer, A. A. *Chem. Rev.* **1979**, *79*, 359. (b) Adam, W. *Chem.-Ztg.* **1975**, *99*, 143. (c) Mitchell, J. C. *Chem. Soc. Rev.* **1985**, 399.

(4) See, for example: (a) Jefford, C. W.; Rimbault, C. G. *J. Am. Chem. Soc.* **1978**, *100*, 6437. (b) Bellarmine, M.; Orfanopoulos, M.; Stephenson, L. M. *J. Am. Chem. Soc.* **1979**, *101*, 3111. (c) McCapra, F.; Beheshti, I. *J. Chem. Soc., Chem. Commun.* **1977**, 517. (d) Schaap, A. P.; Recher, S. G.; Faler, G. R.; Villasenor, S. R. *J. Am. Chem. Soc.* **1983**, *105*, 1691.

(5) (a) Kopecky, K. R.; Scott, W. A.; Lockwood, P. A.; Mumford, C. *Can. J. Chem.* **1978**, *56*, 1114. (b) Kopecky, K. R.; Filby, J. E.; Mumford, C.; Lockwood, P. A.; Ding, J. *Can. J. Chem.* **1975**, *53*, 1103.

(6) Bloodworth, A. J.; Bowyer, K. J.; Mitchell, J. C. *J. Org. Chem.* **1986**, *51*, 1790.

(7) (a) Brown, H. C.; Kim, C. J.; Lancelot, C. J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1970**, *92*, 5244. (b) Brown, H. C.; Kim, C. J. *J. Am. Chem. Soc.* **1971**, *93*, 5765.

(8) Cram, D. J. *J. Am. Chem. Soc.* **1952**, *74*, 2129.

(9) (a) Olah, G. A.; Porter, R. D. *J. Am. Chem. Soc.* **1971**, *93*, 6877. (b) Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 173.

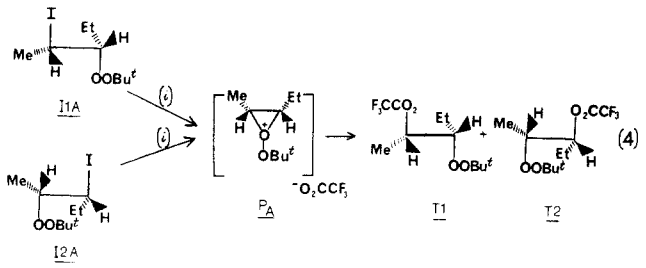
(10) Bloodworth, A. J.; Courtneidge, J. L. *J. Chem. Soc., Perkin Trans. 1* **1981**, 3258.

(11) Bloodworth, A. J.; Griffin, I. M. *J. Chem. Soc., Perkin Trans. 2* **1975**, 531.

(12) Bloodworth, A. J.; Griffin, I. M. *J. Chem. Soc., Perkin Trans. 1* **1975**, 195.

those similarly obtained from β-bromopentyl *tert*-butyl peroxides prepared by configuration-preserving bromodemercuration[10] of M1 and M2 and of the corresponding peroxymercurials derived from (*E*)-pent-2-ene (see later).[13]

Reaction with Silver Trifluoroacetate. When treated with silver trifluoroacetate, I1A and I2A each gave the *same* pair of trifluoroacetates (T1 and T2) in the *same* ratio of 5:3 (eq 4). T1 was eluted more quickly than T2



(i) AgO_2CCF_3, CH_2Cl_2

on medium pressure chromatography, and the regiochemistries shown in eq 4 were established by ^1H and $^1H\{^1H\}$ NMR as for the peroxymercurials (above), assuming that the methine multiplets at higher field were due to C*H*OOBu-*t*.

Independent experiments showed that the reactants and products are stereochemically stable under the reaction conditions. Thus, examination of residual I1A or I2A when each was treated with 0.5 molar equiv of silver trifluoroacetate revealed no isomerization. Again, a 5:1 mixture of T1 and T2, obtained by medium pressure chromatography, was unchanged after exposure to silver trifluoroacetate under conditions comparable to those of the substitutions in eq 4.

These results therefore provide compelling evidence for the formation of an alkylated perepoxide intermediate (P_A) that is sufficiently long-lived for attack by trifluoroacetate anion to take place at both C-2 and C-3.[14] The substitutions involve retention–retention of stereochemistry in the nonmigrated products (T1 from I1A and T2 from I2A) and inversion–inversion in the migrated products (T1 from I2A and T2 from I1A). The slight predominance of T1 over T2 is consistent with preferred attack at the less sterically hindered site of P_A i.e., at the carbon bearing a methyl rather than an ethyl group.

We expected, therefore, that I1B and I2B would similarly afford a common alkylated perepoxide (P_B) and hence an identical mixture of two new trifluoroacetates (T3 and T4), but this was not the case. Thus, I1B gave a *single* new product (T3), and I2B similarly gave a *single* new product (T4). That T1, T2, T3, and T4 were all different isomers was shown most clearly by ^{13}C NMR (see Table I). ^1H and $^1H\{^1H\}$ NMR experiments (cf. those for M1 and M2 above) revealed that the substitution had proceeded

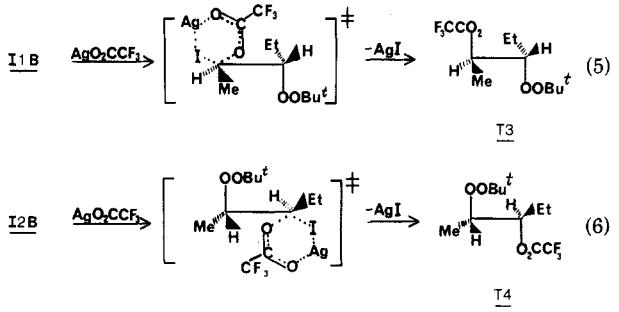
Table I. ^{13}C NMR Data for Iodides and Trifluoroacetates[a-c]

isomer	chemical shifts (ppm)
I1A	11.20, 21.47, 21.87, (26.49), 28.48, (80.36), 88.41
I1B	10.46, 24.16, 24.66, (26.69), 31.78, (80.19), 87.82
I2A	14.40, 14.72, (26.41), 26.76, 41.06, (80.25), 82.74
I2B	14.61, 17.05, (26.65), 29.72, 44.74, (80.21), 80.89
T1[d]	10.06, 14.56, 21.12, (26.33), 74.96, (80.11), 84.57
T1[e]	10.12, 14.60, 20.91, (26.36), 74.77, (80.11), 84.46
T2[d]	9.27, 14.19, 22.65, (26.33), 79.22, (80.11), 80.46
T2[e]	9.39, 14.20, 22.56, (26.36), 79.11, (80.11), 80.40
T3	10.92, 14.74, 20.96, (26.46), 75.51, (80.00), 85.18
T4	9.83, 12.59, 23.28, (26.32), 79.06, 79.95, (80.22)

[a] Iodides in $CDCl_3$ and trifluoroacetates in C_6H_6/C_6D_6, with internal Me_4Si reference. [b] Resonances in parentheses are due to the *tert*-butyl group. [c] Trifluoroacetate resonances were not observed. [d] For a mixture of T1 and T2 from I1A. [e] For a mixture of T1 and T2 from I2A.

with unchanged regiochemistry. In establishing this, it was again assumed that the methine multiplets at higher field were due to C*H*OOBu-*t* (cf. T1 and T2 assignments).

That *new* trifluoroacetates were obtained reveals that the substitutions must have proceeded with retention of configuration, since inversion would lead to formation of T1 from I1B and T2 from I2B. Retention of both regio- and stereochemistry points to the hitherto unestablished S_N2 (cyclic) mechanism for these substitutions (eq 5 and 6).



Addition of methanol to the reaction mixtures afforded further evidence for the proposed mechanisms. Thus, inclusion of 4 equiv of methanol in the I2A reaction mixture afforded a product with two methoxy singlets in the ^1H NMR in addition to the signals for T1 and T2. In contrast, no methoxy resonances were observed in an analogous reaction with I2B. Furthermore, it was shown that no appreciable methanolysis of T1 and T2 occurred under the reaction conditions. These results are consistent with the formation of the intermediate P_A as a cation capable of separation from the trifluoroacetoxy anion and thus of being trapped by methanol at both C-2 and C-3. Again, the nonincorporation of methanol with I2B is consistent with the proposed transition state (eq 6), since the S_N2 (cyclic) mechanism precludes incorporation of external nucleophiles.[14]

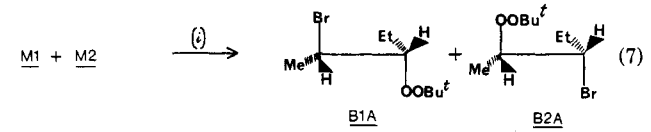
Stereochemical Assignments. At this stage we knew that the A isomers underwent substitution via an alkylated perepoxide intermediate whereas the epimeric B isomers underwent substitution by an S_N2 (cyclic) mechanism, but we did not know which stereochemistry corresponded to which mechanism. In an attempt to answer this question, we initially tried to identify the stereochemistries of the iodo peroxides by carrying out stereospecific iododemercuration, but this was unsuccessful. Consequently, we sought to correlate the products with those obtained from analogous reactions of bromoperoxides produced by configuration-preserving bromodemercuration.[10] The small amounts of impurities that contaminate the bromo peroxides[13] were no longer a serious drawback, since all that

(13) Although β-bromopentyl *tert*-butyl peroxides could be obtained stereoselectively, the requisite conditions provided products containing small amounts of impurities that could not be removed by medium pressure chromatography and which interfered with the ^1H NMR analysis. Hence, most of the work was carried out with the iodo peroxides since these could be isolated cleanly.

(14) A referee has suggested that the present data for the A series do not discount equilibrating species in which the *tert*-butylperoxy group shuttles between the two methinyl carbons, assuming that bond rotation about the methinyl carbons is slower (partial bonding by peroxy oxygen to the cationic center) than nucleophilic attack and equilibration rate. Although we cannot discount this, the proposed peroxonium ion P_A accounts for our experimental observations without recourse to this more elaborate interpretation. However, nonequilibrating unsymmetrical peroxonium ions could account for the result in the B series, except for the lack of methanol incorporation.

was required was to identify the product trifluoroacetates by ^{13}C NMR.

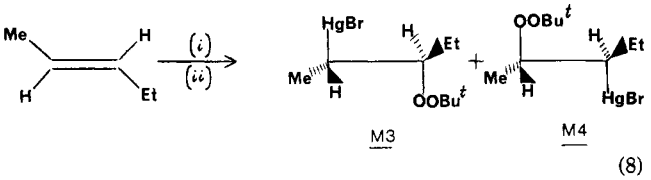
Bromodemercuration of a mixture of M1 and M2 under conditions favoring retention[10] afforded a mixture of bromo peroxides B1A and B2A (eq 7). Treatment of this mixture



(7)

(i) Br_2, NaBr, MeOH

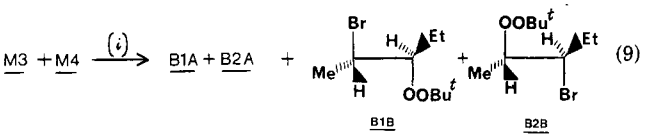
with silver trifluoroacetate yielded the same mixture of T1 and T2 as that obtained from the *individual* iodides I1A and I2A, and thus the iodides are assigned the analogous stereochemistries as shown in eq 2 and 3. By way of confirmation, (*E*)-pent-2-ene was peroxymercurated to give two new compounds M3 and M4, which were again assigned stereochemistries on the assumption of trans addition (eq 8). Brominolysis of this mixture under the same



(8)

(i) $Hg(OAc)_2$, 2 HOOBu-*t*, 0.2 $HClO_4$, CH_2Cl_2; (ii) KBr, H_2O

conditions gave four bromo peroxides, with the new bromides B1B and B2B predominating over B1A and B2A by a ratio of about 2:1 (eq 9). This is consistent with the

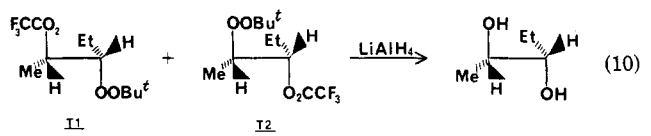


(9)

(i) Br_2, NaBr, MeOH

lower selectivity for retention found for brominolysis, under these conditions, of peroxymercurials derived from (*E*)-but-2-ene and (*E*)-hex-3-ene compared with those derived from the corresponding (*Z*)-alkenes.[10] Treatment with silver trifluoroacetate then afforded all four trifluoroacetates with T3 and T4 together accounting for about 67% of the mixture, thereby indicating that T3 and T4 were derived from B1B and B2B. This, in turn, confirms the stereochemistries assigned to the analogous iodides I1B and I2B as shown in eq 2 and 3.

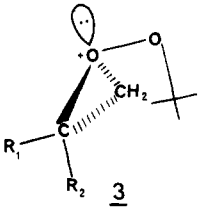
It is concluded, therefore, that the alkylated perepoxide (P_A) has the structure with cis vicinal alkyl groups (eq 4). This was confirmed by identifying the stereochemistries of the product trifluoroacetates T1 and T2 by reducing a mixture of them with lithium aluminum hydride (eq 10).



(10)

This afforded *threo*-pentane-2,3-diol, which was identified by comparison with an authentic sample prepared independently by epoxidation of (*Z*)-pent-2-ene followed by acid hydrolysis.

It is noteworthy that no cross-over of reaction pathways was observed in the product distributions of the A vs. B isomers. It is difficult to estimate the degree to which the configuration at the peroxide-bearing carbon atom will affect the energies of the S_N2 (cyclic) transition states (cf. eq 5 and 6), but it seems reasonable to expect that this will be small compared with the difference in energy of the isomeric alkylated perepoxides. The major factor in determining the mechanism selected is therefore likely to be the relative stabilities of the isomeric alkylated perepoxides, and the results then indicate that the species with the *cis*-alkyl groups is the more stable. This in turn suggests that steric interactions between the methyl and ethyl groups must be less important than those involving the *tert*-butoxy group. Support for this type of interaction, where the *tert*-butoxy group significantly interacts with the ring substituents comes from MINDO/3 calculations on similar systems.[15] Thus, for a variety of ring substituents (R_1, R_2) on peroxonium ion **3**, MINDO/3-optimized



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geometries indicate a preferred orientation in which the *tert*-butyl group lies trans-periplanar to the lone pair of electrons on the cationic oxygen. The geometry assumed by these systems may be an example of extended σ-conjugation through the *tert*-butyl–oxygen bond to the oxonium lone pair of electrons, stabilizing this particular conformation.[16] Hence in the cis species (P_A), a configuration can be adopted in which there is no steric interaction between the *tert*-butoxy group and the alkyl groups, whereas one such interaction must necessarily occur in the trans isomer.

Experimental Section

General methods have been described previously.[6] All products were colorless oils. The compositions of the mixtures that were analyzed were confirmed by ^{13}C NMR.

Preparation of *tert*-Butyl Peroxymercurials, M1 and M2. A mixture of 2-(bromomercurio)-3-(*tert*-butylperoxy)pentane (M1) and 3-(bromomercurio)-2-(*tert*-butylperoxy)pentane (M2) was prepared from (*Z*)-pent-2-ene by peroxymercuration and anion exchange using the procedure previously described.[10] M1 and M2 were separated and purified by medium pressure chromatography (50 cm × 2.25 cm, silica gel, 2% EtOAc in light petroleum ether (bp 60–80 °C).

For M1 (26% yield): ^1H NMR (200 MHz) ppm 0.98 (t, 3 H, $^5CH_3$), 1.29 (s, 9 H, *t*-Bu), 1.48 (d, 3 H, $^1CH_3$), 1.60 (m, 1 H) and 1.72 (m, 1 H, $^4CH_2$), 2.58 (m, 1 H, ^2CHHg), and 4.00 (m, 1 H, ^3CHO); ^{13}C NMR ppm 10.42 (q, $^5CH_3$), 18.72 (q, $^1CH_3$), 26.71 (q, $C(CH_3)_3$), 26.94 (t, $^4CH_2$), 52.05 (d, ^2CHHg), 80.77 (s, $C(CH_3)_3$), and 90.01 (d, ^3CHO).

For M2 (53% yield): ^1H NMR (200 MHz) ppm 1.10 (t, 3 H, $^5CH_3$), 1.27 (s, 9 H, *t*-Bu), 1.31 (d, 3 H, $^1CH_3$), 1.90 (m, 2 H, $^4CH_2$), 2.55 (m, 1 H, ^3CHHg), and 4.35 (m, 1 H, ^2CHO); ^{13}C NMR ppm 16.89 (q, $^3J_{Hg-C}$ = 110 Hz, $^5CH_3$), 20.49 (q, $^3J_{Hg-C}$ = 110 Hz, $^1CH_3$), 26.10 (t, $^4CH_2$), 26.56 (q, $C(CH_3)_3$), 65.36 (d, $^1J_{Hg-C}$ = 1560 Hz, ^3CHHg), 80.46 (s, $C(CH_3)_3$), and 82.55 (d, $^2J_{Hg-C}$ = 120 Hz, ^2CHO).

For a mixture of M1 and M2: Anal. Calcd for $C_9H_{19}BrHgO_2$: C, 24.58; H, 4.35. Found: C, 24.81; H, 4.30.

Preparation of β-Iodopentyl *tert*-Butyl Peroxides: I1A, I1B, I2A, and I2B. A mixture of 3-(*tert*-butylperoxy)-2-iodopentanes I1A and I1B was prepared by iododemercuration of peroxymercurial M1 using the procedure previously described.[6] The components were separated by medium pressure chromatography (50 cm × 2.25 cm, silica gel, 1% EtOAc in light petroleum

(15) Mitchell, J. C.; Braybrook, J. H.; Barrett, J.; Courtneidge, J. L. *J. Chem. Soc., Perkin Trans. 2*, submitted for publication.
(16) Dewar, M. J. S. *J. Am. Chem. Soc.* **1984**, *106*, 669.

(bp 60–80 °C)) and were further purified by trap-to-trap distillation under reduced pressure. 2-(*tert*-Butylperoxy)-3-iodopentanes I2A and I2B were similarly obtained from M2.

For I1A (23% yield): ^{1}H NMR (60 MHz) ppm 1.00 (t, 3 H, $^5CH_3$), 1.2–2.0 (m, 2 H, $^4CH_2$), 1.20 (s, 9 H, *t*-Bu), 1.76 (d, J = 7 Hz, 3 H, $^1CH_3$), 3.86 (dt, J = 7 and 4 Hz, 1 H, ^{3}CHO), and 4.57 (dq, J = 7 and 4 Hz, 1 H, ^{2}CHI).

For I1B (33% yield): ^{1}H NMR (60 MHz) ppm 1.00 (t, 3 H, $^5CH_3$), 1.25 (s, 9 H, *t*-Bu), 1.3–1.9 (m, 2 H, $^4CH_2$), 1.88 (d, J = 7 Hz, 3 H, $^1CH_3$), 3.17 (dt, J = 7 and 4 Hz, 1 H, ^{3}CHO), and 4.61 (dq, J = 7 and 4 Hz, 1 H, ^{2}CHI).

For I2A (20% yield): ^{1}H NMR (60 MHz) ppm 1.04 (t, 3 H, $^5CH_3$), 1.20 (s, 9 H, *t*-Bu), 1.23 (d, J = 7 Hz, 3 H, $^1CH_3$), 1.4–2.0 (m, 2 H, $^4CH_2$), and 3.97–4.47 (m, 2 H, ^{2}CHO and ^{3}CHI).

For I2B (25% yield): ^{1}H NMR (200 MHz) ppm 1.07 (t, J = 3 Hz, 3 H, $^5CH_3$), 1.21 (d, J = 6 Hz, 3 H, $^1CH_3$), 1.5–2.0 (m, 2 H, $^4CH_2$), 1.27 (s, 9 H, *t*-Bu), 3.43 (dq, J = 6 and 4 Hz, 1 H, ^{2}CHO), and 4.40 (dt, J = 6 and 4 Hz, 1 H, ^{3}CHI); all ^{13}C NMR data are given in Table I.

For a mixture of I1A, I1B, I2A, and I2B: Anal. Calcd for $C_9H_{19}IO_2$: C, 37.77; H, 6.69. Found: C, 37.52; H, 6.73.

Reaction of β-Iodopentyl *tert*-Butyl Peroxides with Silver Trifluoroacetate. Silver trifluoroacetate (86 mg, 0.30 mmol) was added to a solution of the β-iodopentyl *tert*-butyl peroxide (100 mg, 0.35 mmol) in methylene chloride (50 mL) at reflux, and the mixture was stirred for 1 h. The mixture was then filtered through a sintered glass funnel (5-cm diameter) containing silica gel (0.5 cm) covered with Celite (0.2 cm). The methylene chloride was removed under vacuum to afford the β-(trifluoroacetoxy)-pentyl *tert*-butyl peroxide(s) (T).

For T1 + T2 (yield from I1A, 59 mg, 0.22 mmol, 62%; yield from I2A, 51 mg, 0.19 mmol, 54%); ^{1}H NMR (60 MHz) ppm 0.8–1.9 (m, 8 H, $^5CH_3$, $^4CH_2$, and $^1CH_3$), 1.22 (s, 9 H, *t*-Bu), 3.8–4.3 (m, 1 H, ^{3}CHOO of T1 and ^{2}CHOO of T2), and 5.0–5.6 (m, 1 H, $^2CHO_2CCF_3$ of T1 and $^3CHO_2CCF_3$ of T2); IR (C=O) 1779 cm^{-1}.

For T3 (yield from I1B, 60 mg, 0.22 mmol, 63%): 0.8–1.9 (m, 5 H, $^5CH_3$ and $^4CH_2$), 1.22 (s, 9 H, *t*-Bu), 1.33 (d, J = 7 Hz, 3 H, $^1CH_3$), 3.87 (dt, J = 7 and 3 Hz, 1 H, ^{3}CHOO), and 5.40 (dq, J = 7 and 3 Hz, 1 H, $^2CHO_2CCF_3$); IR (C=O) 1779 cm^{-1}.

For T4 (yield from I2B, 55 mg, 0.20 mmol, 58%): 0.8–1.9 (m, 8 H, $^5CH_3$, $^4CH_2$, and $^1CH_3$), 1.22 (s, 9 H, *t*-Bu), 4.16 (dq, J = 7 and 3 Hz, 1 H, ^{2}CHOO), and 5.30 (dt, J = 7 and 3 Hz, 1 H, $^3CHO_2CCF_3$); IR (C=O) 1782 cm^{-1}; all ^{13}C NMR data are given in Table I.

For a mixture of T1, T2, T3, and T4, purified by medium pressure chromatography (50 cm × 2.25 cm, silica gel, 1% EtOAc in light petroleum ether (bp 60–80 °C)) followed by trap-to-trap distillation under reduced pressure: Anal. Calcd for $C_{11}H_{19}F_3O_4$: C, 48.52; H, 7.03. Found: C, 48.32; H, 6.95.

Preparation of β-Bromopentyl *tert*-Butyl Peroxides B1A and B2A. A mixture of M1 and M2 was treated with bromine and sodium bromide in methanol[10] to afford a mixture of bromo peroxides B1A and B2A: ^{1}H NMR (60 MHz) ppm 0.7–2.1 (m, 8 H), 1.22 (s, 9 H), and 3.8–4.6 (m, 2 H).

Preparation of β-Bromopentyl *tert*-Butyl Peroxides B1B and B2B. Peroxymercuration of (*E*)-pent-2-ene using the procedure previously described[10] afforded a mixture of M3 and M4: ^{1}H NMR (60 MHz) ppm 0.9–2.1 (m, 8 H), 1.30 (s, 9 H), 2.8–3.2 (m, 1 H), and 4.0–4.6 (m, 1 H). Brominolysis as described above gave a 2:1 mixture of B1B + B2B and B1A + B2A: ^{1}H NMR (60 MHz) ppm 0.7–2.2 (m, 8 H), 1.25 (s, 9 H), and 3.5–4.6 (m, 2 H).

Reduction of T1 and T2. A solution of T1 + T2 (0.93 g, 3.4 mmol) in diethyl ether (50 mL) was added during 1 h to a vigorously stirred suspension of $LiAlH_4$ (0.30 g, 7.9 mmol) in diethyl ether (25 mL) at reflux, and the mixture was kept at reflux for a further 1 h. Ethyl acetate (2.0 g) was then added dropwise to destroy unreacted $LiAlH_4$. After 15 min, the mixture was allowed to cool, and water (0.30 mL), then 15% aqueous NaOH (0.30 mL), and then water (0.90 mL) were added dropwise. The mixture was filtered through Celite and shaken with brine (50 mL), and the organic layer was isolated. The aqueous layer was extracted with diethyl ether (2 × 50 mL). The organic phases were combined and dried ($MgSO_4$), and the solvent was removed under reduced pressure to afford an oil (0.19 g, 1.8 mmol, 54%) with spectroscopic characteristics identical with those of authentic *threo*-pentane-2,3-diol: ^{1}H NMR (60 MHz) ppm 0.7–1.8 (m, 8 H), and 3.0–4.2 (m, 4 H); ^{13}C NMR ppm 9.93, 19.50, 26.20, 70.57, and 77.56.

Acknowledgment. We thank the S.E.R.C. for the award of an Earmarked Studentship.

Cation Binding Properties and Molecular Structure of the Crystalline Complex (Aza-12-crown-4)$_2$•NaI

Banita D. White,[†] Kristin A. Arnold,[†] Robin L. Garrell,[‡] Frank R. Fronczek,[§] Richard D. Gandour,[§] and George W. Gokel*[†]

Departments of Chemistry, University of Miami, Coral Gables, Florida 33124, University of Pittsburgh, Pittsburgh, Pennsylvania 15260, and Louisiana State University, Baton Rouge, Louisiana 70803-1804

Received August 18, 1986

Aza-12-crown-4 forms a 2:1 sandwich complex similar to that known for 12-crown-4 sodium iodide, except that the presence of >NH in each ring makes Na–donor bonds unequal in strength and leads to hydrogen bonding with the counterion. The heteroatoms of each macroring are coplanar, and both nitrogens are on the same side of the complex (twist angle 43° from eclipsed). This may be due to a long (and weak) hydrogen bond to iodide, an interaction confirmed by analysis using Raman spectroscopy. The previously unreported 1:1 and 2:1 cation affinity constants (anhydrous MeOH, 25 °C) for this macrocycle are log $K_{S(1:1)}$ = 1.3 ± 0.1 and log $K_{S(2:1)}$ = 2.0 ± 0.1, respectively.

The recognition that naturally occurring macrocyclic ionophores such as valinomycin,[1] enniatin,[2] and beauvericin[3] all form three-dimensional complexes with cations has renewed interest in small-ring systems. When two small macrorings are present in the same molecular array, they can cooperate to form intramolecular sandwich complexes

[†] University of Miami.
[‡] University of Pittsburgh.
[§] Louisiana State University.

(1) (a) Brockmann, H.; Schmidt-Kastner, G. *Chem. Ber.* **1955**, *88*, 57. (b) Grell, E.; Funck, T.; Eggers, F. *Membranes* **1975**, *5*, 1. (c) Pinkerton, M.; Steinrauf, L. K.; Dawkins, P. *Biochem. Biophys. Res. Commun.* **1969**, *35*, 512. (d) Duax, W. L.; Hauptmann, H.; Weeks, C. M.; Norton, D. A. *Science (Washington, D.C.)* **1972**, *176*, 911.
(2) Hilgenfeld, R.; Saenger, W. *Top. Curr. Chem.* **1982**, *101*, 1–82.

0022-3263/87/1952-1128$01.50/0