$C_{18}H_{19}NO_2$ 281.1416, found 281.1420. **8d**: R_f 0.28 (3:1 hexane/ether); 90-MHz ^{1}H NMR δ 6.63 (dd, J = 8, 8.5 Hz), 6.20 (dd, J = 10, 7 Hz), 5.90 (t, J = 8.5 Hz), 5.55 (br), 5.15 (s, $PhCH_2$), 4.45 (m), 3.80 (m), 3.15 (d, J = 11 Hz), 2.9–1.60 (br, 5 H); IR 2990, 1710 cm^{-1}; high-resolution mass spectrum m/z calcd for $C_{18}H_{19}NO_2$ 281.1416, found 281.1421.

***N*-Benzoyl-3-azatricyclo[5.3.1.0^{4,10}]undeca-5,8-diene (8e) and *N*-Benzoyl-*N*-allyl-3-aminocyclohepta-1,3,5-triene (9e).** A solution of triene **7e** (825 mg, 3.3 mmol) in dry xylene (218 mL) was refluxed under argon for 5 h to provide after workup and preparative TLC (1:1 hexane/ether) three fractions. The first was 45 mg (5%) of [1,5]-shift product **9e**: R_f 0.40; 360-MHz ^{1}H NMR δ 6.30 (d, H-4, collapses to a singlet upon irradiation at δ 5.9), 5.9 (m, H-2,5,10), 5.3–5.1 (br, H-1, H-6,11's), 4.42 (d, J = 7 Hz, H-9's), 2.05 (t, J = 7 Hz, H-7, collapses to a singlet upon irradiation at δ 5.15); IR 2890, 1665 cm^{-1}; high-resolution mass spectrum m/z calcd for $C_{17}H_{17}NO$ 251.1311, found 251.1306. A second fraction, R_f 0.30, was 279 mg (52%) of benzoylallylamine (**6e**) resulting from cleavage of the C-7–N bond of **7e**. The third fraction was 125 mg (15%) of cycloadduct **8e**: R_f 0.19; 90-MHz ^{1}H NMR δ 7.35 (br, Ph), 6.65 (br, H-8), 6.23 (br, H-6), 6.05–5.55 (br, H-5,9), 4.25 (br, H-4), 3.72 (br, H-2x), 3.25 (br, H-2n), 3.1–2.4 (br, H-1,7,10), 2.05–1.60 (br, H-11's); IR 2940, 1705, 1390 cm^{-1}; UV λ_{max} 219 nm (ϵ 12 000); high-resolution mass spectrum m/z calcd for $C_{17}H_{17}NO$ 251.1311, found 251.1312.

Kinetic Experiments. The starting cycloheptatriene **7d** or **7e** (0.975 mmol in 80 mL of octane, 12 mM solution) was added to refluxing octane (124 °C), aliquots were drawn at hourly intervals and injected into a Waters HPLC Model 440 fitted with a silica gel (Resolvex-Sil from Fischer Scientific) column using either the solvent system 2% 2-propanol in heptane for **7d** or 4% 2-propanol in heptane for **7e**, and the effluent was monitored by ultraviolet absorption at 254 nm with an integrating recorder for detection of the peaks. Peak integrals were adjusted for differences in absorption of **7–9** at 254 nm. Since cycloadduct **8b** was unchanged after 16 h in refluxing xylene, and [1,5]-shift product **9d** was stable for 16 h in refluxing octane, competitive parallel first-order rate constants were determined for effectively irreversible reactions.

Acknowledgment. We thank Dr. Robert Salomon for aid in the determination of kinetic parameters.

Oxymetalation. 21.[1] Regioselectivity, Rearrangement, and Direct 1,2-Dioxolane Formation in the Peroxymercuriation of *cis*- and *trans*-1,2-Diphenylcyclopropane

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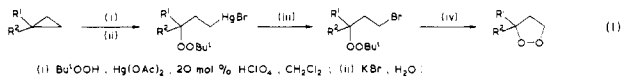
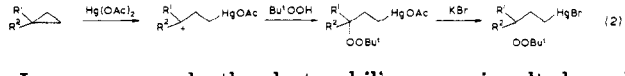
The regiochemistry and stereochemistry of the peroxymercuriation of *trans*- and *cis*-1,2-diphenylcyclopropane (**1a,b**) have been determined. The trans isomer reacted exclusively by 1,3-bond scission to give the threo and erythro γ-peroxymercurials (**3a,b**) along with an unexpected rearrangement product, β-peroxymercurial (**2**). The proportion of **2** varied from 29% for reaction 2 in neat *tert*-butyl hydroperoxide to 68% for reaction with 2 equiv of hydroperoxide in CH_2Cl_2. Methoxymercuriation of **1a** gave only threo and erythro γ-methoxymercurials (**11a,b**) in neat methanol but 60% of rearranged β-methoxymercurial (**10**) with 2 equiv of methanol in CH_2Cl_2. It is suggested that the reactions proceed via the benzylic cation (**12**), which undergoes unimolecular rearrangement by 1,2-phenyl migration competitively with bimolecular trapping by oxy reagent. Rearrangements have not been reported previously in the oxymercuriations of simple cyclopropanes. The cis isomer (**1b**), in contrast, reacted mainly by 1,2-bond scission and yielded the *trans*- and *cis*-1,2-dioxolanes (**15a,b**) and the meso and *d,l* diperoxides (**16a,b**) derived directly from the intermediate γ-peroxymercurials (**18a,b**) by oxidative demercuriation. Trialkylperoxonium intermediates (**19a,b**) are likely to be involved in the production of the dioxolanes. 1,2-Dioxolanes have not been prepared previously by oxidative demercuriation.

In a previous paper,[1] the results of the *tert*-butyl peroxymercuriation of cyclopropane and several mono- and 1,1-disubstituted cyclopropanes were described. A general method was given for the conversion of the resulting γ-peroxymercurials to 1,2-dioxolanes (eq 1).



(1)

(i) Bu^{t}OOH, Hg(OAc)$_2$, 20 mol % HClO$_4$, CH$_2$Cl$_2$; (ii) KBr, H$_2$O; (iii) Br$_2$, NaBr, MeOH; (iv) AgO$_2$CCF$_3$, CH$_2$Cl$_2$



(2)

In every example, the electrophilic mercuric salt cleaved the cyclopropane ring regiospecifically, becoming attached to the least substituted position to give the more stable carbocation. The nucleophile, *tert*-butyl hydroperoxide, added to this more substituted position to give the peroxymercurial (eq 2). This regiochemistry is consistent with the general behavior of mono- and 1,1-disubstituted cyclopropanes toward oxymercuriation.[2]

Oxymercuriations of stereoisomeric cyclopropanes tend to show the same regiochemistry as described above, while the stereochemical outcome may vary considerably.[2] The methoxymercuriation of various stereoisomers of cyclopropanes has been carefully studied by De Puy and McGirk.[3] They found that either retention or inversion can occur at the site of electrophilic substitution but that substantial or complete inversion is found at the site of nucleophilic attack.

(1) Part 20: Bloodworth, A. J.; Chan, K. H.; Cooksey, C. J. *J. Org. Chem.* **1986**, *51*, 2110.

(2) (a) Bloodworth, A. J. In *The Chemistry of Mercury*; McAuliffe, C. A., Ed.; Macmillan: London, 1977; p 182. (b) Larock, R. C. *Organomercury Compounds in Organic Synthesis*; Springer-Verlag: Berlin, 1985; p 32.

(3) De Puy, C. H.; McGirk, R. H. *J. Am. Chem. Soc.* **1974**, *96*, 1121.

0022-3263/88/1953-2668$01.50/0

Table I. Molar Percentages of Peroxymercurials, Dioxolanes, and Diperoxides

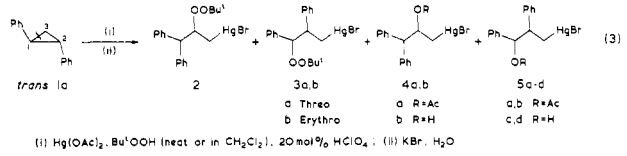
expt	compd	conditions	2/10	3a/11a	3b/11b	15a	15b	16a	16b
1	1a	dilute *t*-BuOOH[a]	68	22	10	trace			
2	1a	neat *t*-BuOOH[b]	29	43	28	trace			
3	1a	neat MeOH[c]	0	40	60				
4	1a	dilute MeOH[d]	60	26	14				
5	1b	neat *t*-BuOOH[b]	8	10	5	33	trace	27	17
6	1b	dilute *t*-BuOOH[e]	16	3	2	49	21	6	3

[a] 1.29 mmol of cyclopropane, CH_2Cl_2, 2.45 mmol of *t*-BuOOH, 1.29 mmol of $Hg(OAc)_2$, and $HClO_4$. [b] 1.29 mmol of cyclopropane, neat *t*-BuOOH, 1.29 mmol of $Hg(OAc)_2$, and $HClO_4$. [c] Same as *b*, except neat MeOH was used. [d] Same as *a*, except 2.45 mmol of MeOH was used. [e] Same as *a*, except 2.57 mmol of $Hg(OAc)_2$ was used.

In this paper, we describe the regio- and stereochemistry of the peroxymercuriation of *cis*- and *trans*-1,2-diphenylcyclopropane. The results presented here show that the isomers behave quite differently: the trans isomer exhibited the usual regiochemistry (1,3-bond cleavage) and gave the expected erythro and threo γ-peroxymercurials but also an unexpected β-peroxymercurial from rearrangement, whereas the cis isomer gave the opposite regiochemistry (1,2-bond cleavage) and yielded 1,2-dioxolanes derived directly from the intermediate γ-peroxymercurials.

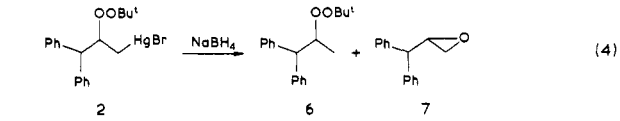
Results and Discussion

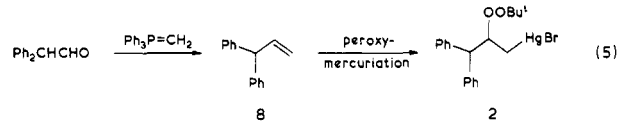
***trans*-1,2-Diphenylcyclopropane.** Compound **1a** was allowed to react with mercuric acetate and *tert*-butyl hydroperoxide in dichloromethane (expt 1, Table I). Perchloric acid was added as a catalyst. After anion exchange with aqueous potassium bromide, the products were separated by chromatography to give the rearranged peroxymercurial (**2**) and the threo (**3a**) and erythro (**3b**) peroxymercurials in 53% isolated yield (eq 3). The rearranged acetoxy- and hydroxymercurials (**4a,b**) and threo and erythro acetoxy- and hydroxymercurials (**5a–d**) were obtained in 29% yield. All of these products are derived from an expected C_1–C_3 bond scission process where mercury is attached to the least substituted carbon atom. The rearranged peroxymercurial **2** was produced in the largest amount (68 mol %, Table I). It is assumed that the trace of dioxolane (**15a**) found in the mixture was derived from the small amount of *cis*-**1a** impurity (3.8%) present in the starting material (a C_1–C_2 scission; see later).



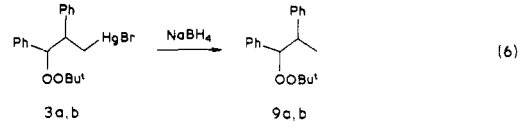
(i) $Hg(OAc)_2$, Bu^tOOH (neat or in CH_2Cl_2), 20 mol% $HClO_4$; (ii) KBr, H_2O

As far as we know, the rearrangement shown in eq 3 is the first reported example found in the oxymercuriation of a simple cyclopropane. Two bicyclic examples, 2,2,4,4-tetramethylbicyclo[1.1.0]butane and bicyclo[3.1.0]hexane, have been shown to give rearrangement.[4,5] The structure of compound **2** was assigned by comparing its ^1H NMR spectrum with those of **3a,b**. In addition, the products (**6** and **7**) obtained upon reduction with sodium borohydride are typical of those obtained from β-peroxymercurials (eq 4).[6] Finally, compound **2** was independently synthesized by the sequence shown in eq 5. The alkene, 3,3-diphenylpropene (**8**), reacted without rearrangement to give **2**, and **3a,b** were not detected.





The structures of the threo and erythro diastereomers (**3a,b**) could not be assigned by measuring the vicinal coupling constants of the mercurials as both yielded the same value of 7.3 Hz. In fact, this method of assigning configuration has proven to be unreliable because intramolecular attraction between the *tert*-butylperoxy group and mercury alters the population of the various conformers.[7] However, when diastereomers **3a** and **3b** were reduced with sodium borohydride to *threo*- and *erythro*-**9a,b** (eq 6), the vicinal coupling constants obtained were



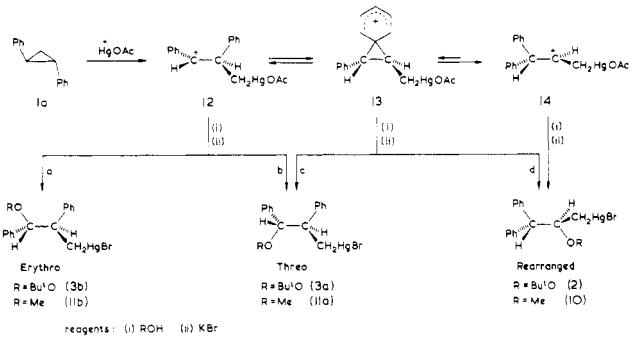
7.0 and 8.3 Hz, respectively. Vicinal coupling constants and the chemical shifts of the methyl groups have been used reliably to assign structure in the 1,2-diphenyl-1-propyl system.[8]

When *trans*-**1a** was peroxymercuriated in neat *tert*-butyl hydroperoxide (expt 2), the isolated yield of peroxymercurials was increased to 71% while the yield of threo and erythro acetoxy- and hydroxymercurials (**5a–d**) was reduced to 10%. Likewise, the higher concentration of nucleophile led to a decrease in the amount of rearranged mercurial (**2**) to 29 mol % so that the threo and erythro diastereomers were now the major products (Table I).

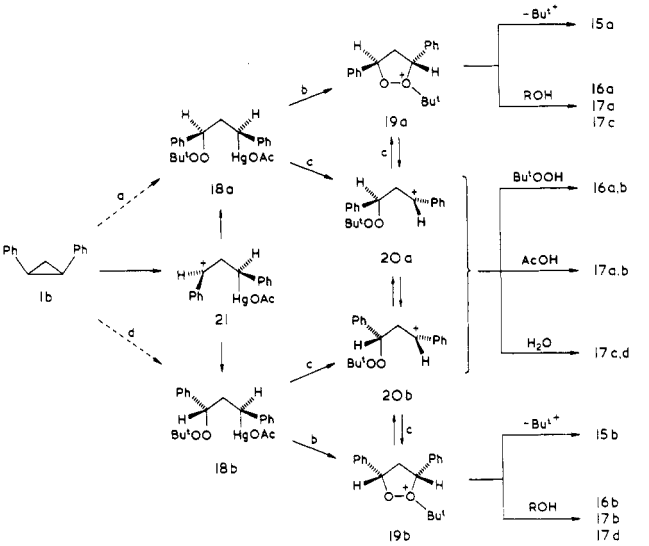
The methoxymercuriation of *trans*-1,2-diphenylcyclopropane in neat methanol has been reported[9,10] to give exclusively the threo and erythro γ-methoxymercurials (**11a,b**). We repeated this experiment (expt 3) and also found no evidence of any rearranged methoxymercurial (**10**). However, when compound **1a** was allowed to react with mercuric acetate and 2 equiv of methanol in dichloromethane (expt 4), we obtained 60 mol % of the rearranged mercurial (**10**) as shown in eq 7 and in Table

(4) Müller, E. *Chem. Ber.* **1975**, *108*, 1394.
(5) Bloodworth, A. J.; Chan, K. H.; Cooksey, C. J.; Hargreaves, N., unpublished work.
(6) Bloodworth, A. J.; Courtneidge, J. L. *J. Chem. Soc., Perkin Trans. 1* **1982**, 1797.
(7) Bloodworth, A. J.; Griffin, I. M. *J. Chem. Soc., Perkin Trans. 2* **1975**, 531.
(8) Kingsbury, C. A.; Best, D. C. *J. Org. Chem.* **1967**, *32*, 6. Methyl doublets in the threo series have larger chemical shifts than the same group in the erythro series.
(9) Bandaev, S. G.; Shabarov, Yu. S.; Hantschmann, A.; Weissenfels, M. *J. Prakt. Chem.* **1980**, *322*, 643.
(10) Shabarov, Yu. S.; Sychkova, L. D.; Bandaev, S. G.; Subbotin, O. A. *J. Gen. Chem. USSR (Engl. Transl.)* **1975**, *45*, 2258.

Scheme I

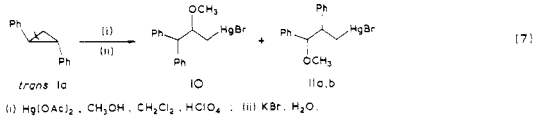


Scheme II[a]



[a] Bond rotation in **20a** actually provides the enantiomer of **20b** and vice versa, but racemic materials were used throughout and single structures are drawn for the sake of simplicity.

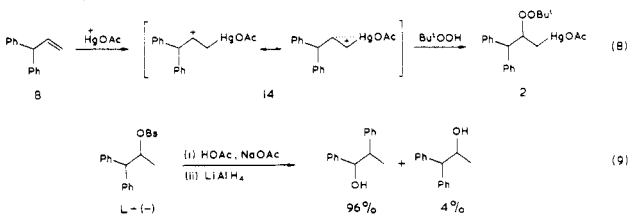
I. The structures were established by ^1H and ^{13}C NMR, elemental analysis, and reduction of the methoxymercurials with sodium borohydride. An independent experiment showed that perchloric acid did not catalyze the isomerization of **1a** into **8** over a period of time similar to that of the oxymercuriations.



(7)

The results can be explained by employing the cations **12**, **13**, and **14** (Scheme I). Under dilute conditions in dichloromethane, cation **12** has time to form the more stable of the two possible bridged phenonium cations **13**. Attack by the nucleophile, *tert*-butyl hydroperoxide or methanol, by pathways c and d leads to the threo isomer **3a** or **11a** and the rearranged isomer **2** or **10**. Of the two diastereomers, it may be expected that the threo isomer would predominate because the erythro isomer may only be produced from cation **12** or from the less stable of the two possible bridged phenonium ions. Cation **14** would also yield the rearranged mercurial **2** or **10**.

Presumably cation **14** is stabilized by the neighboring mercury atom (mercurinium ion formation), and the greater strength of this interaction compared with any related stabilization of cation **12** (homomercurinium ion) may provide some of the driving force for the observed rearrangement. Certainly, in the peroxymercuriation of 3,3-diphenylpropene, the reverse rearrangement to afford **3a,b** was not observed (eq 5 and 8), yet in the solvolysis of 1,1-diphenylprop-2-yl brosylate (eq 9), where mercurinium ion stabilization is not available, nearly complete rearrangement was found.[11]



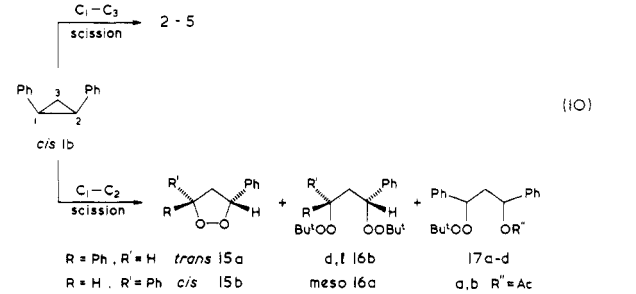
(8)

(9)

When a high concentration of nucleophile was present (neat reactions), a substantial reduction in rearrangement was observed in both methanol and *tert*-butyl hydroperoxide. This is as expected since the rate of bimolecular trapping of the first-formed cation **12** will be appreciably increased while the rate of unimolecular rearrangement presumably will be little affected. Nevertheless, we were surprised to see that cation **12** would still rearrange in neat *tert*-butyl hydroperoxide to the extent of 29 mol % even though the rearrangement was completely suppressed in methanol (expt 2 and 3, Table I). Consequently, we investigated the possibility that *tert*-butyl hydroperoxide was involved in a radical mechanism. However, no change was observed when the reaction was conducted in the presence of 2,6-di-*tert*-butyl-4-methylphenol as radical inhibitor. It seems likely that the main reason for the differing extents of rearrangement in the neat solvents is merely the relative concentrations of the two nucleophiles, 25 mol/L for methanol versus 10 mol/L for *tert*-butyl hydroperoxide.

Our results provide little information concerning the nature of any "edge-mercuriated" cyclopropane intermediate (homomercurinium ion) formed early in the reaction profile. A slight preference for the formation of the erythro methoxymercurial **11b** over that of the threo methoxymercurial **11a** may indicate net inversion by solvent. Systems studied previously,[3] however, show a much higher amount of inversion, often approaching 90–100%. Our stereochemical results are better explained by the rapid conversion of any edge-mercuriated intermediate into cations such as those shown in Scheme I.

***cis*-1,2-Diphenylcyclopropane.** Compound **1b** was allowed to react with mercuric acetate in neat *tert*-butyl hydroperoxide (expt 5). After the usual workup procedure, the products were separated by chromatography to give the compounds shown in eq 10.



(10)

We had expected to see mercurials derived from C_1–C_2 bond scission because this had been previously reported[10,12] in the acetoxymercuriation of compound **1b**. However, we could find no sign of any mercurial with the structure **18a,b** (Scheme II). Instead, products derived from the oxidative demercuriation (eq 11) of **18a,b** were found. Oxidative

(11) Cram, D. J.; Abd Elhafez, F. A. *J. Am. Chem. Soc.* **1954**, *76*, 28.

(12) Shabarov, Yu. S.; Sychkova, L. D.; Bandaev, S. G. *J. Organomet. Chem.* **1975**, *99*, 213.

$$R\text{-}HgOAc + Hg(OAc)_2 \longrightarrow R^+ + Hg_2(OAc)_2 + \bar{O}Ac \qquad (11)$$

demercuriation has been observed before in systems where benzylic carbocations are formed.[3,12-14] Thus, *trans*-3,5-diphenyl-1,2-dioxolane (**15a**, 33 mol %, 10% isolated yield) and a mixture of *meso*- and *d,l*-1,3-bis(*tert*-butylperoxy)-1,3-diphenylpropane (**16a,b**, 44 mol %) were isolated. In addition, 24% of the starting cyclopropane was recovered.

Products derived from C_1–C_3 scission were also present in the mixture. Thus, a total of 23 mol % of rearranged **2**, *threo*-**3a**, and *erythro*-**3b** peroxymercurials was obtained (expt 5, Table I).

When the reaction was conducted in dichloromethane with 2 equiv each of *tert*-butyl hydroperoxide and mercuric acetate (expt 6), all of the cyclopropane was consumed and larger amounts of dioxolanes **15a,b** (70 mol %, 39% isolated yield) were obtained. There was a corresponding decrease in the amounts of diperoxides **16a,b** (9 mol %) obtained from this reaction, but diastereomers **17a,b** and **17c,d**, also derived from the C_1–C_2 scission and oxidative demercuriation, were additionally isolated. The fraction of mercurials (**2** and **3a,b**) obtained from C_1–C_3 bond cleavage was virtually unchanged at 21 mol %.

An attempt was made to isolate the intermediate mercurials **18a,b** by carrying out an inverse addition of 0.5 equiv of mercuric acetate over a period of 4.5 h. The reaction mixture was identical with that obtained from the 2-equiv reaction (expt 6) except that 74% of unreacted cyclopropane was present. Mercurials **18a,b** could not be detected. The percentage of unreacted cyclopropane expected was calculated from the product distribution by assuming that mercurials **2** and **3a,b** consume 1 equiv of $Hg(OAc)_2$ whereas production of compounds **15**, **16**, and **17** requires 2 equiv of $Hg(OAc)_2$. This gave a value of 72% unreacted cyclopropane, which agrees well with that observed. Thus, the overall process of conversion of cyclopropane **1b** to dioxolanes requires 2 equiv of mercuric acetate (eq 10 and 11).

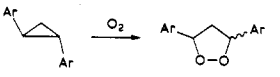
Several observations may be made in comparing the results of reactions conducted in neat versus dilute *tert*-butyl hydroperoxide: (a) the combined mole percentages of C_1–C_2- and C_1–C_3-derived scission products are similar, (b) the amount of 1,2-dioxolanes is increased under dilute conditions, (c) the amount of diperoxides is decreased under dilute conditions, but both sets of conditions give mixtures of meso and *d,l* isomers, and (d) both *trans*- and *cis*-1,2-dioxolanes are produced under dilute conditions, whereas only trans-1,2-dioxolane is found in the neat reaction.

The proportions of C_1–C_2 versus C_1–C_3 bond cleavage may depend upon the nature of the electrophile, but they are not expected to vary with the concentration of the nucleophile. A mechanism is proposed in Scheme II that accounts for the other facts listed above. Pathways a and d may be described as retention–retention (or inversion–inversion) and retention–inversion processes, respectively. It is likely, however, that the peroxymercuriation of compound **1b** proceeds by way of an open carbocation (**21**) to give a mixture of diastereomers **18a,b**. Pathway b involves concerted intramolecular nucleophilic attack and demercuriation to give trialkylperoxonium ions **19a,b**, which upon loss of *tert*-butyl cation give dioxolanes **15a,b**. This process is similar to the silver salt induced cyclizations reported earlier.[1,15] The dioxolanes may also be produced by a stepwise mechanism (path c) whereby the demercuriation step occurs to give benzylic cations **20a,b** (eq 11) followed by formation of peroxonium ions **19a,b**. The acyclic products **16a,b**, **17a,b**, and **17c,d** could be formed by attack of the appropriate nucleophile either on peroxonium ions **19a** and **19b** or on benzylic cations **20a** and **20b**.

That diperoxides **16a,b** are formed at the expense of dioxolanes **15a,b** when the concentration of *tert*-butyl hydroperoxide is high (neat) is consistent with the intermediacy of either **19a,b** or **20a,b**. The more demanding observation is that whereas only *trans*-dioxolane **15a** is formed under these conditions, a mixture of diperoxides **16a,b** is obtained. This can be accommodated within Scheme II if the loss of *tert*-butyl cation from **19a** is fast enough to compete with the alternative processes, whereas the corresponding loss from **19b** (or the formation of **19b** by pathway c) is not. Under dilute conditions the rate of bimolecular trapping is reduced and formation of *cis*-dioxolane **15b** competes successfully.

Small amounts of pure *trans*-dioxolane **15a** could be obtained by analytical HPLC, but to isolate larger amounts required column chromatography of the crude mixture of organomercuric acetates, dioxolanes, and diperoxides. The dioxolanes and diperoxides separated cleanly from the mercurials, and pure *trans*-dioxolane was easily isolated from this mixture by crystallization from petroleum ether. As far as we know, 1,2-dioxolanes have not been prepared previously by oxidative demercuriation.

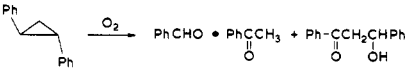
It has been reported[16] that photooxygenation of diarylcyclopropanes bearing strongly electron-donating groups gave excellent yields of *cis*- and *trans*-dioxolanes (eq 12). When less electron-rich cyclopropanes, including



(12)

e.g. Ar = 4-$Me_2NC_6H_4$, 4-$MeOC_6H_4$

compounds **1a,b**, were photooxygenated, however, no dioxolanes were found and various oxidation products such as benzaldehyde and acetophenone were isolated (eq 13).



(13)

We found that benzaldehyde and acetophenone are produced by thermal decomposition of the diphenyldioxolanes, in keeping with previous observations for the corresponding bis(4-methoxyphenyl)dioxolanes.[16]

Since our method can be applied to diarylcyclopropanes that do not bear electron-donating substituents, it should prove to be complementary to the photooxygenation procedure. Thus, in addition to the previously unknown dioxolanes reported in this paper, the 3,5-bis(4-chlorophenyl)-1,2-dioxolanes have now been prepared.[17]

Experimental Section

^1H and ^{13}C NMR spectra were obtained on Varian XL 200 or XL 400 spectrometers in $CDCl_3$ solutions. Infrared spectra were measured with a Perkin-Elmer 983 instrument. Mass spectra were obtained on a VG 7070 F/H mass spectrometer and a Finnigan INCOS data system. *tert*-Butyl hydroperoxide was purified as described previously.[18] Other reagents were commercial samples

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that were used as received.

***trans*- and *cis*-1,2-Diphenylcyclopropane (1a,b).** A mixture of cis and trans isomers was obtained from benzal acetophenone by the base-catalyzed decomposition of the pyrazoline derivative.[19] The isomers were separated by careful distillation through a 25-cm silvered and evacuated column packed with glass spirals and using a partial-take-off head. Seven fractions were collected. The cis isomer was obtained in the lower boiling fractions (bp 132 °C (1.5 mmHg)) and it readily solidified. The higher boiling fractions contained the trans isomer (bp 144 °C (1.8 mmHg)).

The fractions containing mixtures of isomers were combined and redistilled. It was relatively easy to remove the cis isomer (bp 122 °C (0.5 mmHg)) in 90.9% purity with the packed column. This material was recrystallized twice from 95% ethanol to give the pure cis isomer, mp 35–36 °C (lit.[20] mp 38–39 °C). Gas chromatographic analysis on a 2-m column containing OV 17 at 200 °C showed no sign of the trans isomer; δ_H (200 MHz) 1.41 m (2 H), 2.48 dd (2 H, J = 6.4, 8.6 Hz), 7.02 m (10 H); δ_C (50 MHz) 11.36, 24.30, 125.55, 127.62, 128.94, 138.33.

The distillation residues were combined and distilled through a 15-cm silvered and evacuated Vigreux column. Three fractions were collected, with the highest boiling fraction (bp 113 °C (0.17 mmHg)) yielding nearly pure trans isomer. Gas chromatographic analysis showed this fraction to be 96.2% trans and 3.8% cis; δ_H (200 MHz) 1.44 dd (2 H, J = 5.9, 7.5 Hz), 2.16 dd (2 H), 7.20 m (10 H); δ_C (100 MHz) 18.40, 28.19, 125.67, 125.68, 128.31, 142.37.

Oxymercuriation of 1,2-Diphenylcyclopropane (General Procedure). Mercuric acetate (0.41 g, 1.29 mmol or as indicated in Table I) was placed in a small flask. One of the following was then added: 3 mL of *tert*-butyl hydroperoxide or methanol for neat reactions; a solution of 0.22 g (2.45 mmol) of *tert*-butyl hydroperoxide or 0.078 g (2.45 mmol) of methanol in 3 mL of dichloromethane for dilute reactions. Either *cis*- or *trans*-1,2-diphenylcyclopropane (0.25 g, 1.29 mmol) was added to the mixture. Following the addition of 3 drops of 60% aqueous perchloric acid with a Pasteur pipet, the mixture was stirred magnetically for 20–22 h at room temperature. In the case of neat reactions, the excess *tert*-butyl hydroperoxide or methanol was removed on a vacuum line prior to workup. Water (10 mL) was added, and the mixture was extracted with dichloromethane (10 mL). The aqueous layer was extracted with more dichloromethane (10 mL), and the combined organic phases were dried ($MgSO_4$) and rotoevaporated to give the crude organomercuric acetates in the case of *trans*-1,2-diphenylcyclopropane or organomercuric acetates plus dioxolanes and diperoxides in the case of the cis isomer.

Dichloromethane (3 mL) and a solution of potassium bromide (2.4 mmol) in water (2.2 mL) were added and the mixture was stirred vigorously with a magnetic stirrer for 1 h. Dichloromethane and water (10 mL each) were added, and the organic phase was removed. Following extraction with more dichloromethane (5 mL), the combined organic phases were dried ($MgSO_4$), rotoevaporated, and placed under vacuum at 0.05 mmHg to give the crude organomercuric bromides. The mixtures were separated by chromatography on a 25 cm × 2 cm diameter column of silica (Merck Kieselgel 60, 70–230 mesh, 0.063–0.20 mm), eluting with a 1:1 mixture of petroleum ether (60–80 °C) and dichloromethane. In some cases, the mixtures were separated by flash chromatography using fine silica (Woelm 32–63 μm) with similar results. The fractions were checked for composition by TLC on silica (Kieselgel 60 F_{254}). Products were visualized under UV light, by spraying with dithiazone solution (mercury compounds) and by spraying with acidic ferrous thiocyanate (dioxolanes). The peroxymercurials were eluted in the following order (some overlap): 3-(bromomercurio)-1,1-diphenylprop-2-yl *tert*-butyl peroxide (**2**), *threo*-3-(bromomercurio)-1,2-diphenylpropyl *tert*-butyl peroxide (**3a**), and erythro isomer **3b**. Cyclopropane starting material elutes before the mercurials. The acetoxy- and hydroxymercurials (**4a,b** and **5a–d**) were eluted with dichloromethane or in some cases with ethyl acetate. Expt 1: 0.050 g of **1a**, 0.310 g (53% based upon consumed **1a**) of **2** and **3a,b** 0.100 g (18%) of **4a,b**, 0.070 g (11%) of **5a–d**; expt 2: 0.036 g of **1a**, 0.439 g (71%) of **2** and **3a,b**, 0.060 g (10%) of **5a–d**.

Methoxymercurials separated cleanly in the following order: *threo*-3-(bromomercurio)-1-methoxy-1,2-diphenylpropane (**11a**), erythro isomer **11b**, and 3-(bromomercurio)-2-methoxy-1,1-diphenylpropane (**10**). The last compound was eluted with dichloromethane. No attempt was made to isolate compounds corresponding to **4a,b** or **5a–d**. Expt 3: 0.047 g of **1a**, 0.323 g (62%) of **11a,b**; expt 4: 0.022 g of **1a**, 0.343 g (55%) of **10** and **11a,b**.

When *cis*-1,2-diphenylcyclopropane was peroxymercuriated, dioxolanes (**15a,b**) and diperoxides (**16a,b**) were formed along with the mercurials. They cochromatographed with the mercurials. If the potassium bromide step is omitted, however, the dioxolanes and diperoxides elute well ahead of the organomercuric acetates. Compounds **17a–d**, when isolated, were eluted with dichloromethane. Some of the dioxolane decomposed on the column to give acetophenone and benzaldehyde. Expt 5: 0.060 g of **1b**, 0.041 g (7%) of **2** and **3a,b**, 0.023 g (10%) of **15a**, 0.050 g (14%) of **16a,b** (no attempt was made to isolate **4**, **5**, or **17**); expt 6: 0.088 g (12%) of **2** and **3a,b**, 0.012 g (3%) of **4a,b**, 0.032 g (6%) of **5a–d**, 0.113 g (39%) of **15a,b**, 0.023 g (5%) of **16a,b**, 0.063 g (13%) of **17a–d**. A colorless solid residue, insoluble in water and dichloromethane, was found in the reaction flask prior to workup. This solid turned black when aqueous sodium hydroxide was added, indicating the presence of a mercurous salt. The mole percentages of peroxymercurials, dioxolanes, and diperoxides, adjusted to 100%, are given in Table I.

Peroxymercuriation of *trans*-1,2-Diphenylcyclopropane. 3-(Bromomercurio)-1,1-diphenylprop-2-yl *tert*-butyl peroxide (**2**): δ_H (200 MHz) 1.09 s (9 H), 1.90 dd (1 H, J = 12.1, 6.5 Hz), 2.19 dd (1 H, J = 12.1, 4.8 Hz), 4.02 d (1 H, J = 7.7 Hz), 5.07 m (1 H), 7.29 m (10 H); δ_C (100 MHz) 26.45, 36.26, 57.31, 81.10, 83.87, 126.61, 126.92, 128.29, 128.59, 128.77, 128.77, 140.91, 141.45; MS, no molecular ion, m/z 471–477 (7 peaks, M^+ – *t*-BuCO), 292–298 $(CH_2HgBr)^+$, 277–283 $(HgBr)^+$, 210 (M^+ – HgBr – *t*-BuO), 167 $(Ph_2CH)^+$. Anal. Found: C, 40.50; H, 4.17. Required for $C_{19}H_{23}BrHgO_2$: C, 40.47; H, 4.11. Mp 131–132 °C.

threo-3-(Bromomercurio)-1,2-diphenylpropyl *tert*-butyl peroxide (**3a**): δ_H (200 MHz) 1.11 s (9 H), 2.21 dd (1 H, J = 11.8, 6.3 Hz), 2.30 dd (1 H, J = 11.8, 8.4 Hz), 3.52 ca. quartet (1 H), 5.06 d (1 H, J = 7.3 Hz), 7.23 m (10 H); δ_C (50 MHz) 26.57, 36.38, 50.14, 81.00, 89.51, 126.87, 127.18, 127.67, 128.10, 128.55, 128.86, 139.88, 144.23. Anal. Found: C, 41.04; H, 4.23. Calcd: C, 40.47; H, 4.11. Mp 83–86 °C.

erythro-3-(Bromomercurio)-1,2-diphenylpropyl *tert*-butyl peroxide (**3b**): δ_H (200 MHz) 1.05 s (9 H), 1.91 dd (1 H, J = 11.9, 9.9 Hz), 2.05 dd (1 H, J = 11.9, 6.0 Hz), 3.58 m (1 H), 4.99 d (1 H, J = 7.3 Hz), 7.25 m (10 H); δ_C (50 MHz) 26.33, 35.86, 48.04, 80.93, 90.03, 126.96, 127.31, 127.64, 127.75, 128.44, 128.44, 138.65, 144.02. Anal. Found: C, 40.67; H, 4.22. Calcd: C, 40.47; H, 4.11. Mp 126–127 °C.

3-(Bromomercurio)-1,1-diphenylprop-2-yl acetate (**4a**): δ_H (200 MHz) 1.86 s (3 H), 2.04 m (2 H), 4.02 d (1 H, J = 9.5 Hz), 6.06 m (1 H), 7.29 m (10 H); δ_C (100 MHz) 21.18, 36.97, 58.73, 75.48, 126.94, 127.84, 128.02, 128.14, 128.73, 129.71, 140.92, 141.52, 170.59.

3-(Bromomercurio)-1,1-diphenylpropan-2-ol (**4b**): δ_H (200 MHz) 2.04 dd (1 H, J = 11.9, 4.9 Hz), 2.19 dd (1 H, J = 11.9, 6.0 Hz), 2.04 broad s (1 H), 3.74 d (1 H, J = 8.6 Hz), 4.96 m (1 H), 7.34 m (10 H); δ_C (100 MHz) 40.88, 62.25, 73.43, 127.32, 127.42, 127.98, 128.61, 129.24, 129.28, 140.65, 141.98.

threo- and *erythro*-3-(Bromomercurio)-1,2-diphenylpropyl acetate (**5a,b**): δ_H (200 MHz) 2.13 and 1.80 singlets ($OCOCH_3$), 1.90–2.30 and 3.30–3.70 overlapping multiplets for CH_2 and CH, 5.95 (J = 6.8 Hz) and 5.89 (J = 9.4 Hz) doublets (CHO), 7.28 m (phenyls); product ratio 3:1.

threo- and *erythro*-3-Bromomercurio)-1,2-diphenylpropanol (**5c,d**): δ_H (200 MHz) 1.90–2.30 and 3.30–3.70 overlapping multiplets for CH_2 and CH, 4.89 (J = 6.4 Hz) and 4.76 (J = 8.6 Hz) doublets (CHO), 7.28 m (phenyls); product ratio 6:1.

Radical Inhibition Experiment. Two reactions were run in parallel using *tert*-butyl hydroperoxide in dichloromethane under the conditions of expt 1. In one reaction, dichloromethane (3 mL) containing 2,6-di-*tert*-butyl-4-methylphenol (0.015 g, 0.068 mmol) was added to mercuric acetate prior to the addition of the other reagents; the other reaction was run without the inhibitor. The

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reactions were each run for 21 h and worked up in the same manner. The ^1H NMR spectra were identical in all ways, except that the unreacted inhibitor was present in one spectrum. The product compositions were the same as those obtained in expt 1.

Methoxymercuriation of *trans*-1,2-Diphenylcyclopropane. 3-(Bromomercurio)-2-methoxy-1,1-diphenylpropane (**10**): δ_H (200 MHz) 2.00 dd (1 H, J = 12.2, 2.5 Hz), 2.29 dd (1 H, J = 12.2, 6.8 Hz), 3.32 s (3 H), 3.90 d (1 H, J = 6.7 Hz), 4.54 td (1 H), 7.31 m (10 H); δ_C (100 MHz) 37.73, 56.92, 58.94, 82.11, 126.96, 127.11, 128.39, 128.77, 128.95, 129.08, 141.19, 142.51. Anal. Found: C, 37.72; H, 3.32. Required for $C_{16}H_{17}BrHgO$: C, 37.99; H, 3.39. Mp 104–107 °C.

threo-3-(Bromomercurio)-1-methoxy-1,2-diphenylpropane (**11a**): δ_H (200 MHz) 2.12 d (2 H, J = 7.3 Hz), 3.29 s (3 H), 3.31 m (1 H), 4.29 d (1 H, J = 7.3 Hz), 7.15 m (10 H); δ_C (50 MHz) 35.53, 52.07, 57.00, 86.99, 126.71, 126.98, 127.60, 127.68, 128.30, 128.56, 139.84, 144.66. Anal. Found: C, 38.11; H, 3.40. Calcd: C, 37.99; H, 3.39. Mp 99–100 °C.

erythro-3-(Bromomercurio)-1-methoxy-1,2-diphenylpropane (**11b**): δ_H (200 MHz) 1.87 dd (1 H, J = 11.7, 9.2 Hz), 2.00 dd (1 H, J = 11.7, 5.8 Hz), 3.16 s (3 H), 3.51 m (1 H), 4.34 d (1 H, J = 7.2 Hz), 7.24 m (10 H); δ_C (50 MHz) 37.06, 50.83, 57.13, 87.84, 126.81, 127.53, 127.73, 128.42, 128.54, 128.54, 138.77, 144.31; MS, no molecular ion, m/z 381–387 $(PhCHCH_2HgBr)^+$, 277–283 $(HgBr)^+$, 225 $(M^+ - HgBr)$, 121 $(PhCHOCH_3)^+$. Anal. Found: C, 38.36; H, 3.42. Calcd: C, 37.99; H, 3.39. Mp 138–139 °C.

Reduction of Mercurials with Sodium Borohydride. Reduction of *threo*-3-(bromomercurio)-1-methoxy-1,2-diphenylpropane (**11a**): A solution of mercurial (0.098 g, 0.194 mmol) in dichloromethane (3 mL) was added over a 5-min period to a magnetically stirred and ice-cooled mixture of sodium borohydride (0.070 g, 1.85 mmol), 2 M aqueous sodium hydroxide (0.6 mL), and dichloromethane (1 mL). The solutions were deoxygenated, and the reaction was run under a nitrogen atmosphere. After 15 min, the reaction mixture was filtered through phase-separating paper, the aqueous layer was washed with dichloromethane, and the combined organic phases were rotoevaporated to give 0.044 g (92%) of *threo*-1-methoxy-1,2-diphenylpropane;[9] δ_H (200 MHz) 1.37 d (3 H, J = 7.1 Hz), 2.99 ca. quintet (1 H), 3.20 s (3 H), 4.17 d (1 H, J = 6.8 Hz), 7.13 m (10 H); MS, no molecular ion, m/z 195 $(M^+ - CH_3O)$, 194 $(M^+ - CH_3OH)$, 193 $(M^+ - CH_3OH - H)$, 179 $(M^+ - CH_3OH - CH_3)$, and 121 $(PhCHOCH_3)^+$.

Similarly erythro isomer **11b** gave *erythro*-1-methoxy-1,2-diphenylpropane[9] in 89% yield; δ_H (200 MHz) 1.03 d (3 H, J = 7.1 Hz), 3.03 m (1 H), 3.08 s (3 H), 4.19 d (1 H, J = 8.2 Hz), 7.24 m (10 H); MS, no molecular ion, pattern similar to that of the threo isomer. Reduction of the rearranged peroxymercurial **2** followed by separation of the mixture by column chromatography on silica (1:1 petroleum ether and dichloromethane) gave 1,1-diphenylprop-2-yl *tert*-butyl peroxide (**6**) and 1,1-diphenyl-2,3-epoxypropane (**7**): R_f values (Kieselgel 60 F_{254}, 1:1 petroleum ether and CH_2Cl_2) were 0.50 and 0.31, respectively.

Peroxide **6**: δ_H (200 MHz) 1.04 s (9 H), 1.24 d (3 H, J = 6.0), 3.96 d (1 H, J = 8.4 Hz), 4.74 m (1 H), 7.27 m (10 H); MS, no molecular ion, m/z 195 $(M^+ - t\text{-BuOO})$, 194 $(M^+ - t\text{-BuOOH})$, 193 $(M^+ - t\text{-BuOOH} - H)$, 179 $(M^+ - t\text{-BuOOH} - CH_3)$, 167 $(Ph_2CH)^+$.

Epoxide **7**: δ_H (200 MHz) 2.54 dd (1 H, J = 4.8, 2.6 Hz (gem and trans vic, respectively), 2.87 dd (1 H, J = 4.8, 3.8 Hz (gem and cis vic, respectively), 3.53 m (1 H), 3.85 d (1 H, J = 6.9 Hz), 7.25 m (10 H); MS, accurate mass found 210.1028, $C_{15}H_{14}O$ requires 210.1044.

Threo peroxymercurial **3a** gave *threo*-1,2-diphenylpropyl *tert*-butyl peroxide (**9a**); δ_H (200 MHz) 1.16 s (9 H), 1.38 d (3 H, J = 7.1 Hz), 3.12 ca. quintet (1 H), 4.94 d (1 H, J = 7.0), 7.27 m (10 H).

Erythro peroxymercurial **3b** gave *erythro*-1,2-diphenylpropyl *tert*-butyl peroxide (**9b**); δ_H (200 MHz) 0.98 s (9 H), 1.09 d (3 H, J = 7.1 Hz), 3.07 ca. quintet (1 H), 4.85 d (1 H, J = 8.3 Hz), 7.27 m (10 H); δ_C (100 MHz) 17.62, 26.29, 44.46, 80.27, 90.44, 126.31, 127.38, 127.45, 127.84, 127.92, 128.11, 140.48, 143.66. When the reduction was conducted in air with vigorous magnetic stirring, **9b** was obtained along with an equal amount of 3-(*tert*-butylperoxy)-2,3-diphenylpropanol; δ_H (200 MHz) 1.07 s (9 H), 3.20 m (1 H), 3.81 m (2 H), 5.19 d (1 H, J = 7.0 Hz), 7.25 m (10 H); δ_C (100 MHz) 26.37, 53.63, 63.91, 80.52, 86.44, 127.00, 127.62, 127.92, 128.00, 128.23, 129.14, 138.56, and 139.73; IR (CCl_4) 3584 (free OH), 3437 (broad, H-bonded OH), 1000 cm^{-1} (CH_2O).

Preparation of 3,3-Diphenylpropene (8). Methyltriphenylphosphonium bromide (8.93 g, 0.025 mmol) was added over a 10-min period to a mixture of butyllithium (18 mL of 1.55 M in hexanes, 0.028 mmol) and dry tetrahydrofuran (42 mL) with stirring and under a nitrogen atmosphere. After 1 h, a solution of diphenylacetaldehyde (4.90 g, 0.025 mmol) in dry THF (10 mL) was added to the mixture over a 6-min period. After the mixture was stirred for 20.5 h at room temperature, ether (250 mL) was added and the mixture was filtered. The ether extracts were washed with water (3 × 100 mL), treated with a saturated sodium chloride solution, and dried ($MgSO_4$). The crude material contained 3,3-diphenylpropene, diphenylacetaldehyde, and triphenylphosphine oxide with R_f values (Kieselgel 60 F_{254}, 1:1 petroleum ether and CH_2Cl_2) of 0.67, 0.32, and 0, respectively. The product was chromatographed on silica (290 g of silica, 1:1 petroleum ether and dichloromethane) to give 1.62 g (33%) of 3,3-diphenylpropene (**8**). Some contaminating material, with NMR peaks of 0.8–1.5 ppm, chromatographed with the product. It was easily removed under vacuum distillation using a Büchi GKR-50 (Kugelrohr) apparatus; δ_H (60 MHz) 4.6–5.4 m (3 H, Ph_2CH and $=CH_2$), 6.0–6.7 m (1 H, $-CH=$), 7.2 s (10 H);[21] δ_C (100 MHz) 55.00, 116.26, 126.22, 128.27, 128.47, 140.46, 143.12; MS, accurate mass found 194.1094, $C_{15}H_{14}$ requires 194.1095; IR, terminal double bond appears at 917 cm^{-1}, with no evidence for 1,1-diphenylpropene at 967 and 892 cm^{-1}.[22]

Peroxymercuriation of 3,3-Diphenylpropene. A solution of 3,3-diphenylpropene (**8**) (0.25 g, 1.29 mmol) in dichloromethane (2 mL) was added dropwise (2 min) to a magnetically stirred mixture of mercuric acetate (0.41 g, 1.29 mmol), *tert*-butyl hydroperoxide (0.23 g, 2.55 mmol), 60% aqueous perchloric acid (3 drops), and dichloromethane (3 mL). After 15 min, the reaction mixture was worked up, treated with potassium bromide, and flash chromatographed using dichloromethane to separate the first two components and ethyl acetate to remove the last component: 0.40 g (55%) of peroxymercurial **2**, 0.13 g (18%) of acetoxymercurial **4a**, and 0.067 g (10%) of hydroxymercurial **4b**. The R_f values (Kieselgel 60 F_{254}, CH_2Cl_2) were 0.66, 0.33, and 0.10, respectively.

Peroxymercuriation of *cis*-1,2-Diphenylcyclopropane. The mixture was separated on an analytical HPLC unit using 20% CH_2Cl_2/petroleum ether with two columns of silica (5 μm) placed in series (10 cm × 4.5 mm diameter + 25 cm × 7 mm diameter); flow rate 3.0 mL/min and 5-mg sample size. Fraction 1, *trans*-dioxolane (**15a**); fraction 2, *cis*-dioxolane (**15b**) and meso diperoxide (**16a**); fraction 3, *d,l* diperoxide (**16b**) and rearranged peroxymercurial (**2**); fraction 4, threo peroxymercurial (**3a**) and a compound thought to be 3,3-bis(*tert*-butylperoxy)-1,3-diphenylpropanol. This product may be derived from a dioxolane decomposition product, 1-hydroxy-1,3-diphenylpropan-3-one, by acid-catalyzed perketal formation.

trans-3,5-Diphenyl-1,2-dioxolane (**15a**): δ_H (200 MHz) 3.06 t (2 H, J = 7.1 Hz), 5.47 t (2 H), 7.44 m (10 H); δ_C (100 MHz) 51.07, 82.77, 126.62, 128.38, 128.68, 138.42. MS, accurate mass found 226.0984, $C_{15}H_{14}O_2$ requires 226.0993; m/z 208 $(M^+ - H_2O)$, 120 $(PhCOCH_3)^+$, 106 $(PhCHO)^+$, 105 $(PhCO)^+$. Anal. Found: C, 79.39; H, 6.19. Required for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24.

cis-3,5-Diphenyl-1,2-dioxolane (**15b**): δ_H (200 MHz) 2.73 dt (1 H, J = 12.3, 7.6 Hz), 3.49 dt (1 H, J = 12.3, 7.4 Hz), 5.46 t (2 H), 7.40 m (10 H); δ_C (100 MHz) 51.66, 83.35, 126.56, 128.25, 128.67 138.80.

3,3-Bis(*tert*-butylperoxy)-1,3-diphenylpropanol: δ_H (200 MHz) 1.28 s (18 H), 2.24 dd (1 H, J = 11.8, 7.9 Hz), 2.40 dd (1 H, J = 11.8, 5.1 Hz), 5.28 dd (1 H, J = 7.9, 5.1 Hz), 7.36 m (10 H); δ_C (100 MHz) 26.58, 39.50, 81.38, 84.33, and phenyl peaks (126.02–140.00). No signal appeared for the quaternary carbon.

3-(*tert*-Butylperoxy)-1,3-diphenylpropyl acetate (1:1 mixture of **17a,b**): δ_H (200 MHz) 1.18 s (OO-*t*-Bu), 2.00 and 1.98 singlets ($OCOCH_3$), 1.80–2.40 overlapping multiplets for CH_2, 4.94 and 4.80 ca. triplets (CHOO), 5.88 and 5.72 ca. triplets (CHO), and 7.32 m (phenyls).

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Thermal Decomposition of *trans*-Dioxolane 15a and Isolation of Diperoxides 16a,b. This reaction was conducted in neat *tert*-butyl hydroperoxide with 0.82 g (2.57 mmol) of mercuric acetate. The potassium bromide step was omitted. An attempt was made to remove the *trans*-dioxolane by trap-to-trap distillation at 100 °C (0.1 mmHg). NMR analysis of the distillate showed the presence of a nearly 1:1 mixture of benzaldehyde acetophenone, but no dioxolane was found. The distillate was separated by flash chromatography on silica using CH_2Cl_2 as the eluent: benzaldehyde eluted first (R_f 0.42, CH_2Cl_2) followed by acetophenone (R_f 0.30, CH_2Cl_2). Each compound was identified by comparison of its ^1H NMR spectrum with that of an authentic sample. The residue from the distillation was column chromatographed (silica) using CH_2Cl_2 to give fractions containing varying amounts of diperoxides (**16a,b**) and *trans*-dioxolane (**15a**). The mixture was separated on an analytical HPLC unit under the conditions listed above. Fraction 1, *trans*-dioxolane (**15a**); fraction 2, meso diperoxide (**16a**); fraction 3, *d,l* diperoxide (**16b**).

meso-1,3-Bis(*tert*-butylperoxy)-1,3-diphenylpropane (**16a**): δ_H (200 MHz) 1.17 s (18 H), 2.02 dt (1 H, J = 14.1, 6.8 Hz), 2.63 dt (1 H, J = 14.1, 7.3 Hz), 4.87 t (2 H), 7.32 s (10 H); δ_C (100 MHz) 26.51, 40.02, 80.03, 82.56, 127.33, 127.79, 128.19, 140.84; MS, no molecular ion at 372, stable fragments found at m/z 226 (M^+ - *t*-BuOO - *t*-Bu) and 146 (*t*-BuOO-*t*-Bu$^+$), other fragments found at 315 (M^+ - *t*-Bu), 283 (M^+ - *t*-BuOO), 193 (PhCH=CHCHPh$^+$), 73 (*t*-BuO$^+$), and 57 (*t*-Bu$^+$).

d,l-1,3-Bis(*tert*-butylperoxy)-1,3-diphenylpropane (**16b**): δ_H (200 MHz) 1.17 s (18 H), 2.25 t (2 H, J = 6.9 Hz), 4.98 t (2 H), 7.32 s (10 H); δ_C (100 MHz) 26.51, 40.47, 80.07, 82.30, 127.12, 127.72, 128.17, 141.19; MS, no molecular ion, pattern similar to that of the meso isomer.

Inverse Addition of 0.5 equiv of Mercuric Acetate. *tert*-Butyl hydroperoxide (0.22 g, 2.45 mmol) was dissolved in dichloromethane (3 mL), and *cis*-cyclopropane **1b** (0.25 g, 1.29 mmol) and aqueous perchloric acid (3 drops) were added. Mercuric acetate (0.21 g, 0.66 mmol) was added in 13 portions to the magnetically stirred solution over a period of 4.5 h. Stirring was continued for a further 17.5 h. The reaction was worked up in the usual way. The NMR spectrum was identical with that obtained in expt 6, except for the presence of 74% unreacted cyclopropane **1b**. As a comparison, the percentage of unreacted cyclopropane was calculated by assuming that mercurials **2** and **3a,b** (C_1-C_3 scission, 19%) were derived from 1 equiv (0.070 mmol) of mercuric acetate/1 equiv (0.070 mmol) of cyclopropane, while compounds **15**, **16**, and **17** (C_1-C_2 scission, 81%) used 2 equiv (0.590 mmol) of mercuric acetate/1 equiv (0.295 mmol) of cyclopropane; calculated 0.925 mmol of unreacted cyclopropane and 0.365 mmol of products or 72% unreacted cyclopropane.

Preparation of *trans*-Dioxolane 15a. To an ice-cooled and magnetically stirred mixture of mercuric acetate (6.37 g, 20 mmol), dichloromethane (23 mL), *tert*-butyl hydroperoxide (1.71 g, 19 mmol), and aqueous perchloric acid (23 drops) was added dropwise a solution of *cis*-1,2-diphenylcyclopropane (1.94 g, 10 mmol, 90.9% pure) in dichloromethane (2 mL). The ice bath was removed, and the reaction was allowed to proceed for 22 h. Water and dichloromethane (25 mL of each) were added to the mixture. Following separation, the aqueous layer was extracted with CH_2Cl_2 (2 × 25 mL). The dried extracts were rotoevaporated. The mixture (3.26 g) was column chromatographed on a 45 cm × 4 cm diameter column of silica (70-230 mesh) and eluted with 1:1 petroleum ether (60-80 °C) and CH_2Cl_2. The dioxolane/diperoxide fraction began to appear after about 475 mL of eluent and was nearly all removed after another 400 mL of solvent; 0.30 g (15%) of *cis*- and *trans*-dioxolane (**15a,b**) mixed with some diperoxides (**16a,b**). Some benzaldehyde and acetophenone were observed, indicating decomposition of the dioxolanes on the column. No attempt was made to elute the organomercuric acetates. Pure *trans*-dioxolane (0.050 g) was obtained by adding petroleum ether (60-80 °C, 4 × 2 mL) to the crude dioxolane at room temperature and collecting it on a sintered funnel. The ^1H NMR spectrum was identical with that obtained on the HPLC sample (see earlier).

Kinetics of Thermal and Hydrolytic Decomposition of 1,3,4-Dioxazol-2-one Derivatives

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The synthesis of model compounds **5** and **6** for the homopolymers of vinyl- and isopropenydioxazol-2-ones is described. These compounds are hydrolyzed to hydroxamic acids which can be estimated colorimetrically by complexation with Fe^{3+}. The hydrolylitic rates have been determined and the thermolysis rates were followed by measuring undecomposed dioxazolones by the colorimetric method. The isopropyldioxazolone was 100 times faster in thermal decomposition in the bulk than the *tert*-butyl-substituted one and this difference is reduced in presence of polar solvents. The results explain the previously observed differences in the thermal stability of the two polymers.

Introduction

The synthesis of isocyanate functional polymers is of considerable interest due to the high chemical reactivity of this functional group. Poly(vinyl isocyanate) has been prepared by polymerization of vinyl isocyanate[2] and by the generation of acyl azide groups on the polymer followed by Curtius rearrangement.[3] A much more recent approach to the synthesis of isocyanates has been through the thermolytic cleavage of 1,3,4-dioxazol-2-ones.[4] Endo et al.[5] observed the generation of isocyanates on polymer backbones by the thermolysis of polymers prepared from 5-isopropenyl-1,3,4-dioxazol-2-one (**2**). The synthesis and

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