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# Kinetics of the Thermolysis of 3,3-Bis(*p*-anisyl)-1,2-dioxetane

William H. Richardson,* James H. Anderegg, Mary E. Price, and Richard Crawford

*Department of Chemistry, San Diego State University, San Diego, California 92182*

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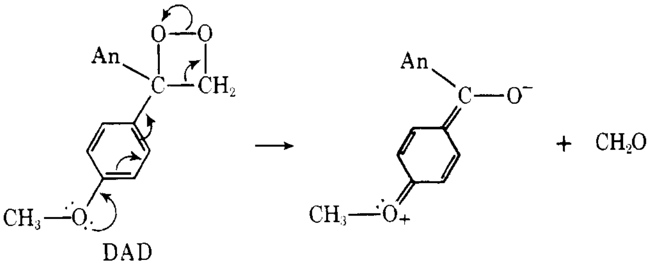
3,3-Bis(*p*-anisyl)-1,2-dioxetane (DAD) was prepared and the kinetics of thermolysis were studied in benzene and methanol solvents in order to probe the possibility of a concerted reaction. Activation parameters for DAD in benzene are $E_a = 20.9 \pm 0.3$ kcal/mol, $\log A = 11.77 \pm 0.18$, $\Delta H^{\ddagger} = 20.2 \pm 0.3$ kcal/mol, $\Delta S^{\ddagger} = -6.8 \pm 0.8$ eu, $\Delta G^{\ddagger} = 22.5 \pm 0.3$ kcal/mol; and in methanol they are $E_a = 21.0 \pm 0.2$ kcal/mol, $\log A = 11.99 \pm 0.16$, $\Delta H^{\ddagger} = 20.3 \pm 0.2$ kcal/mol, $\Delta S^{\ddagger} = -5.8 \pm 0.7$ eu, $\Delta G^{\ddagger} = 22.2 \pm 0.2$ kcal/mol. The unsubstituted model compound, 3,3-diphenyl-1,2-dioxetane (DPD), was previously found to have $E_a$ values in both benzene (22.7 kcal/mol) and methanol (22.2 kcal/mol) which are somewhat larger than those for DAD. In terms of rate enhancement by the *p*-methoxy substituents $k_{\mathrm{DAD}}/k_{\mathrm{DPD}}$ is 3.90 and 4.55 at 60 °C in benzene and methanol, respectively. These data are considered in terms of a concerted process and a stepwise biradical mechanism. The results appear to be most reasonably interpreted in terms of the biradical mechanism where the substituent effect is associated with homolysis of the O–O bond.

Thermolysis of several simply substituted 1,2-dioxetanes appears to be most readily accommodated by a biradical mechanism.[1] Several lines of evidence have led us to this conclusion. First, calculated activation parameters based on a biradical process are in good agreement with the experimental parameters. Second, substituents have little effect on the rates of dioxetane thermolyses. Third, the activation parameters for thermolysis show little sensitivity upon changing from an aprotic nonpolar solvent such as benzene to a protic polar solvent such as methanol. Finally, the biradical mechanism can accommodate the high efficiency of triplet carbonyl production[2] within the context of spin conservation.

Currently we have been searching for dioxetanes that would show the characteristics of a concerted thermolysis reaction.[1d] We have used two approaches in the design of the structure of dioxetanes in an attempt to realize this goal. First, the dioxetane ring has been progressively substituted with phenyl groups.[1d] Thermochemical kinetic calculations indicate that such substitution should progressively weaken the C–C bond of the dioxetane ring. At some point in the successive phenyl substitution, one might anticipate that the C–C and O–O bonds would become sufficiently comparable in energy so that a concerted decomposition would occur. With up to three phenyl substituents, it still appears that a stepwise decomposition occurs.[1d]

A second approach is to design dioxetanes with aryl groups bearing substituents that would facilitate a concerted process. This approach is reported here with 3,3-bis(*p*-anisyl)-1,2-dioxetane (DAD). One may envisage an unzipping of the dioxetane ring in a concerted manner, which is facilitated by the *p*-methoxy substituents in DAD as indicated below, where An = $p\text{-CH}_3\text{OC}_6\text{H}_4$.



It may also be possible to encourage a concerted process by an appropriate choice of solvent. Previously, we have presented arguments to suggest that methanol solvent should facilitate a concerted reaction.[1c] A comparison of activation parameters obtained in benzene and in methanol is used here to assess the possibility of a concerted process for DAD.

## Results

DAD was prepared by the closure of the corresponding bromohydroperoxide, 1-bromo-2-hydroperoxy-2,2-bis(*p*-anisyl)ethane (BHA). The latter hydroperoxide could be obtained as a white crystalline solid by recrystallization from carbon tetrachloride at low temperature. Recrystallization of DAD proved unsuccessful, so column chromatography on silica gel with and without impregnation with EDTA was attempted. After several attempts, we were unable to obtain any peroxidic fractions from either type of chromatography. For these reasons, DAD was used without further purification. The presence of DAD was detected by the characteristic dioxetane ring $^1$H NMR absorption at $\delta$ 5.68, which disappeared upon heating the solution. A crude rate coefficient of $0.96 \times 10^{-3}$ s$^{-1}$ at 37.5 °C was obtained in carbon tetrachloride solution by following the disappearance of dioxetane ring protons by NMR. This value compares favorably with a rate coefficient of $1.15 \times 10^{-3}$ s$^{-1}$, calculated from the activation parameters for DAD in benzene, as obtained by light emission data. Concentrations of DAD were determined by iodometric biamperometric analyses, which were corrected for contamination by BHA.

Kinetic measurements were obtained from light emission of DAD in the presence of 9,10-dibromoanthracene (DBA) by previously reported methods.[1c] Under these conditions, no light emission was observed from BHA. To avoid spurious transition metal ion catalysis, the methanol solvent was treated with EDTA and EDTA was added to the kinetic cells with either methanol or benzene solvent.[1c,3] In addition, anhydrous sodium sulfate was added to the kinetic cells to avoid contamination by water.

The rate coefficients as a function of temperature and concentration of the dioxetane in benzene solvent are given in Table I. Rate data for the thermolysis of DAD in methanol solvent are shown in Table II. Activation parameters calculated from these data are given in Table III along with the previously reported experimental and calculated activation parameters for 3,3-diphenyl-1,2-dioxetane (DPD).[1b,c] It is seen from Table I that a 50- to 100-fold variation in the initial DAD concentration causes only a small change in the rate coefficient. Thus, the thermolysis of DAD adheres to first-order behavior at low concentrations, as was previously observed with other dioxetanes.[1]

## Discussion

In comparison to 3,3-diphenyl-1,2-dioxetane (DPD), activation energies ($E_a$) are lowered by the di-*p*-methoxy substitution in DAD by 1.8 and 1.2 kcal/mol respectively in benzene and methanol solvents. This does not appear to be

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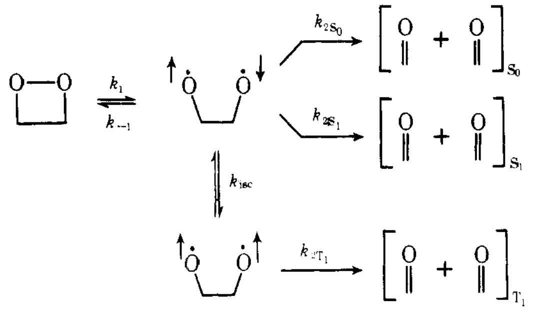
**Table I. Rate Coefficients for the Thermolysis of 3,3-Bis(*p*-anisyl)-1,2-dioxetane (DAD) in Benzene Solvent[a,b]**

| $10^4$[DAD], M | $t$, °C | $10^3k$,[c] $s^{-1}$ |
|---|---|---|
| 1.17 | 25.05 | 0.277 ± 0.002 |
| 1.60 | 25.05 | 0.298 ± 0.006 |
| 117 | 25.10 | 0.238 ± 0.002 |
| 2.03 | 35.15 | 0.767 ± 0.007 |
| 117 | 35.12 | 0.805 ± 0.007 |
| 1.17 | 45.10 | 2.52 ± 0.01 |
| 1.17 | 45.10 | 2.47 ± 0.03 |
| 1.60 | 55.10 | 6.57 ± 0.08 |
| 1.60 | 55.10 | 6.52 ± 0.07 |
| 1.17 | 70.05 | 27.2 ± 0.3 |
| 1.17 | 70.10 | 27.8 ± 0.3 |

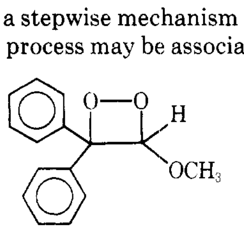
[a] With [DBA] = $2.44 \times 10^{-4}$ M. [b] Solutions were saturated with $Na_2EDTA$ and protected from moisture with anhydrous $Na_2SO_4$. [c] By least squares with standard error.

Scheme I

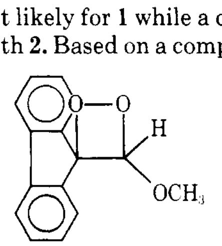


the result of compensating changes in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, since $\Delta G^{\ddagger}$ is about 1.0 kcal/mol lower for DAD compared to DPD in both solvents. In terms of relative rates ($k_{DAD}/k_{DPD}$) at 60 °C, the two *p*-methoxy substituents accelerate the rate by factors of 3.90 and 4.55 respectively in benzene and methanol solvents.

First of all, it should be noted that the substituent effect of the two *p*-methoxy groups in DAD is small compared to the unsubstituted model DPD. Previously, we had found that the biradical scheme shown below readily accommodated our data for other substituted dioxetanes, including DPD.[1a-d] It seems most likely then that DAD is undergoing thermolysis according to Scheme I with little or no progress toward a concerted decomposition. In one report,[4] where a change from a stepwise to a concerted process may be occurring, there is a considerably greater decrease in $E_a$ than is observed between DAD and DPD. For example, the Arrhenius activation energy decreases from 26.1 kcal/mol for **1** to 21.0 kcal/mol for **2**,[4] where a stepwise mechanism is most likely for **1** while a concerted process may be associated with **2**. Based on a comparison of **1** and **2**, one might expect a greater decrease in $E_a$ between DAD and DPD if a concerted process was operative with DAD.



**1**



**2**

One test that we have used previously to probe the possibility of a concerted reaction is a comparison of kinetic data in benzene vs. methanol solvent.[1c] Here it is expected that the activation energy would be decreased and the rate increased upon changing from benzene to methanol solvent if a concerted process is operative. This expectation is based upon the development of the polar carbonyl bond in the activated complex of the concerted process, which should be stabilized by the polar-protic methanol solvent. This prediction finds support in the solvent effect associated with the $\beta$ scission of the *tert*-butoxy radical.[5] As seen from Table III, the activation parameters for DAD in benzene and methanol are the same within experimental error. These data also suggest that a concerted process is not operative or at least little progress has been made in breaking the C–C bond of the dioxetane ring in the activated complex of the rate-determining step.

**Table II. Rate Coefficients for the Thermolysis of 3,3-Bis(*p*-anisyl)-1,2-dioxetane (DAD) in Methanol Solvent[a-c]**

| $t$, °C | $10k$, $s^{-1}$ | $t$, °C | $10\ k$,[d] $s^{-1}$ |
|---|---|---|---|
| 17.89 | 0.180 ± 0.002 | 35.08 | 1.22 ± 0.01 |
| 17.89 | 0.175 ± 0.001 | 35.08 | 1.46 ± 0.01 |
| 25.13 | 0.437 ± 0.003 | 35.08 | 1.32 ± 0.01 |
| 25.13 | 0.432 ± 0.005 | 45.03 | 3.90 ± 0.02 |
| 25.13 | 0.427 ± 0.012 | 45.03 | 3.90 ± 0.01 |
| 35.08 | 1.28 ± 0.01 | 55.22 | 10.9 ± 0.1 |
| | | 55.22 | 11.2 ± 0.1 |

[a] Solutions were saturated with $Ha_2EDTA$ and protected from moisture with anhydrous $Na_2SO_4$. [b] [DAD] = $1.40 \times 10^{-4}$ M. [c] [DBA] = $5.50 \times 10^{-4}$ M. [d] Least-squares analysis with standard error in individual measurements.

The small substituent effect observed with DAD as compared to DPD seems most reasonably assigned to the breaking of the O–O bond (i.e., $k_1$ in Scheme I). In support of this proposal, a comparison of the thermolysis kinetics of benzoyl peroxide (**3**) and its *p,p*′-dimethoxy derivative (**4**) may be considered.[6] At 80 °C the relative rates ($k_4/k_3$) in acetophenone and dioxane are 3.61[6a] and 2.81,[6b] respectively. These values are similar to those found for $k_{DAD}/k_{DPD}$ (3.90 and 4.55 at 60 °C in benzene and methanol solvent, respectively). Furthermore, the activation energy is decreased in proceeding from **3** to **4** by 1.5 kcal/mol in acetophenone and by 1.0 kcal/mol in dioxane solvent. The decrease in activation energy with the di-*p*-methoxy substitution in the benzoyl peroxide series is then similar as well to that observed with the dioxetanes (1.8 and 1.2 kcal/mol in benzene and methanol solvent, respectively).

Enhanced light emission from DAD in the presence of DBA is indicative of triplet carbonyl formation.[7] This observation is also most readily explained in terms of Scheme I rather than a concerted process, since in the latter process a violation of spin conservation results. Since this rule has found such wide applicability,[8] considerable doubt is cast upon a concerted mode which involves triplet carbonyl production. One could argue that they are two competing reactions: a concerted decomposition of DAD to give singlet carbonyl products and a second reaction to give triplet carbonyl products. Although the first process avoids the problem of spin conservation violation, the second reaction introduces this problem once again. At least, at this point in our understanding of the thermolyses of simply substituted dioxetanes, the generalized Scheme I would appear to accommodate all of the observations with the greatest economy.

Recently, the volume of activation was determined for tetramethyl-1,2-dioxetane (TMD) to be 11 ± 3 $cm^3$/mol.[9] This value is considerably larger than the expected value of about 5 $cm^3$/mol for either homolysis of one bond in Scheme I with $k_{-1} \ll (k_{2S_0} + k_{2S_1} + k_{2T_1})$ or a concerted rupture of two bonds.[10] It appears that the only way to rationalize the $\Delta V^*$ value for TMD is to propose that $k_{-1}$ and $(k_{2S_0} + k_{2S_1} + k_{2T_1})$ are more nearly comparable. This proposal has certain restrictions, considering our substituent studies, including the present results with DAD. Very small substituent changes

**Table III. Activation Parameters for 3,3-Bis(*p*-anisyl)-1,2-dioxetane[e] (DAD) and 3,3-Diphenyl-1,2-dioxetane[f] (DPD).**

| dioxetane | solvent | $E_a$[a] | log $A$ | $\Delta H^{\ddagger}$ [a,b] | $\Delta S^{\ddagger}$ [c] | $\Delta G^{\ddagger}$ [a,b] |
|---|---|---|---|---|---|---|
| DAD | benzene | 20.9 ± 0.3 | 11.77 ± 0.18 | 20.2 ± 0.3 | −6.8 ± 0.8 | 22.5 ± 0.3 |
| DAD | methanol | 21.0 ± 0.2 | 11.99 ± 0.16 | 20.3 ± 0.2 | −5.8 ± 0.7 | 22.2 ± 0.2 |
| DPD | benzene | 22.7 ± 0.1 | 12.36 ± 0.06 | 22.0 ± 0.1 | −4.1 ± 0.3 | 23.4 ± 0.1 |
| DPD | methanol | 22.2 ± 0.2 | 12.12 ± 0.08 | 21.6 ± 0.2 | −5.1 ± 0.5 | 23.3 ± 0.2 |
| DPD (calcd) | | 22.6 | 12.71 | 21.9 | −2.5 | 22.7 |

[a] Kcal/mol. [b] Calculated at 60 °C. [c] eu. [d] Calculated on the basis of the stepwise biradical process. [e] Registry no. 67087-29-0. [f] Registry no. 53399-67-0.

were observed with a progressive replacement of methyl with phenyl groups on the dioxetane ring.[1a–d] With DAD compared to DPD, it appears that the small substituent effect can be attributed to step $k_1$ in Scheme I, by analogy to benzoyl peroxides. These substituent effects then require that $k_{-1}$ must be less than $(k_{2S_0} + k_{2S_1} + k_{2T_1})$. It is possible that $k_{-1}$ is only somewhat less than $(k_{2S_0} + k_{2S_1} + k_{2T_1})$. For cyclobutane pyrolysis, which appears to be best explained in terms of a biradical mechanism, the activation energies associated with the back reaction ($k_{-1}$) and the forward reaction ($k_2$) from the biradical are estimated to be 6.6 and 8.3 kcal/mol, respectively.[11] Since the $\pi$ bond in carbonyls is of lower energy than the $\pi$ bond in olefins,[12] it was initially thought that the comparable activation energies in the dioxy biradical process would be skewed so that $E_{-1} \gg E_2$. This reasoning is, of course, based on the ground state energies of the product carbonyls vs. olefins and the activation energies may not be proportional to the ground state energies. In fact, reactions of 1,4-biradicals (or zwitterions) have been suggested to be subject to orbital symmetry rules.[14] In effect, the orbital memory may not be lost in proceeding from the reactant to the intermediate biradical and on to the product. Since the $[2_S + 2_S]$ reaction of the dioxetane to carbonyl products is forbidden, this would mean that the biradical to carbonyl process is also forbidden. This could result in a more substantial activation energy for the biradical to carbonyl process than was previously anticipated. With this reasoning, one can rationalize the substituent effect data and the value of $\Delta V^*$ for TMD, where $k_{-1}$ is less but more nearly comparable to $(k_{2S_0} + k_{2S_1} + k_{2T_1})$.[15]

## Experimental Section[16]

**1,1-Bis(*p*-anisyl)ethanol.** This carbonyl was prepared in 94% yield, by a method which was similar to a previously reported procedure,[17] from *p,p'*-dimethoxybenzophenone (Aldrich) and methylmagnesium iodode. The resulting crude semisolid was not further purified, since the carbinol was found to undergo dehydration upon recrystallization from 95% ethanol which contained a few drops of 6 N sodium hydroxide. Spectral data were in accord with the expected product: IR 3610, 3500 (OH), 3050, 3010 (Ar-H), 2960, 2845 cm$^{-1}$ (aliph C-H); NMR 3.70, (s, 6.0, $CH_3O$), 1.79 (s, 3.1, $CH_3$), 4.46 (s, 0.80, OH), 6.90 (AB, $J$ = 9.0 Hz, 8.8, Ar-H).

**1,1-Bis(*p*-anisyl)ethene.** A 10.8 g (41.9 mmol) sample of the above carbinol was treated with 50 mL of 20% sulfuric acid in acetic acid for 10 min.[18] Water (50 mL) was added and the mixture was extracted with methylene chloride. After washing the methylene chloride extract with water and drying it over magnesium sulfate, rotoevaporation gave 10.75 g of a light tan solid. Recrystallization from 30 mL of benzene/16 mL of 95% ethanol gave 7.75 g (77% yield) of white plates, mp 140–141.5 °C (lit.[19] mp 142–144 °C). A second crop was obtained upon partial concentration of the filtrate, which upon recrystallization from cyclohexane gave 1.32 g (13% yield) of white plates, mp 126–128 °C. Spectral data of the first crop showed: IR 3100, 890 ($=CH_2$), 3050, 3010 (ArH), 2960, 1845 (aliph CH), 1620 cm$^{-1}$ (C=C); NMR 3.70 (s, 5.9, $CH_3O$), 5.09 (s, 2.0, $=CH_2$), 6.83, (AB, $J$ = 11.4 Hz, 8.0, ArH).

**1-Bromo-2-hydroperoxy-2,2-bis(*p*-anisyl)ethane (BHA).** The above olefin (3.0 g, 12.5 mmol) was dissolved in 40 mL of dry tetrahydrofuran (THF) and the solution was cooled to −10 °C under a nitrogen atmosphere. Hydrogen peroxide (45 mL of 1.37 M) in THF was added. The hydrogen peroxide solution was prepared from 98% hydrogen peroxide (FMC) and anhydrous THF and then dried for 24 h at 25 °C over anhydrous magnesium sulfate. To affect solution of the olefin, it was necessary to raise the temperature to 0 °C and then 1.72 g (6.00 mmol) of 1,3-dibromohydantoin (Matheson Coleman and Bell) was added in portions over a 30-min period with stirring.[20] The reaction flask was wrapped with aluminum foil during the reaction. After the addition of the brominating agent was completed, the mixture was allowed to stir at 0 °C for 45 min, gradually warmed to room temperature over about 30 min, and then stirred for an additional 1.5 h. The mixture was then transferred to a separatory funnel containing 50 mL of ether and 50 mL of 5% sodium bicarbonate solution. After shaking, the organic phase was separated and further washed with 5% sodium bicarbonate solution and then with water. The ether phase was dried over anhydrous sodium sulfate and then rotevaporated to give a light yellow semisolid, which gave a positive peroxide test to potassium iodide starch paper. A biamperometric titration of the product indicated that BHA was obtained in 65% yield. The crude product was recrystallized from carbon tetrachloride at about −20 °C to give a white solid, mp 91–92.5 °C dec, 97.7% pure by iodometric analysis: NMR 3.71 (s, 6.1, $CH_3O$), 4.10 (s, 2.0, $CH_2$), 7.33 (s, 0.77, OOH), 6.86, (AB, J = 10 Hz, 8.1, ArH).

**3,3-Bis(*p*-anisyl)-1,2-dioxetane (DAD).** This dioxetane was prepared by a previously reported method,[1b,20] whereby BHA was cyclized at 0 °C with sodium hydroxide in methanol containing 2 mol % $Na_2EDTA$. After quenching with cold water, the mixture was rapidly extracted with cold carbon tetrachloride. Attempts to crystallize DAD failed. When chromatographed on silica (with or without $Na_2EDTA$ impregnation),[21] the dioxetane decomposed on the column. The NMR spectrum of the unpurified carbon tetrachloride solution showed, in addition to several other absorptions, the following absorptions: 5.68, (s, 2.0, $CH_2$), 3.77 (s, 6.0, $CH_3O$), 7.33 (AB, $J$ = 9 Hz, Ar). The aromatic region contained other absorptions so that it was not possible to obtain a reliable integral.

The net amount of DAD in a carbon tetrachloride solution was determined by the difference between biamperometric iodometric peroxide analyses[22] before and after heating the sample at 42 °C for about 6 h. During the heating period DAD decomposed, while in an independent experiment, BHA was found to be stable. In one such analysis the initial and final peroxide concentrations were $8.04 \times 10^{-3}$ M and $5.09 \times 10^{-4}$ M, respectively. This corresponds to 6.3% BHA and 93.7% DAD in the peroxidic fraction.

**Kinetic Methods.** Rate measurements were made by the emission technique in the presence of DBA according to a previously reported method.[1bc,23] In one instance, the rate of disappearance of DAD was followed by monitoring the dioxetane ring protons in carbon tetrachloride solution at 37.5 °C by NMR.

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**Registry No.**—BHA, 67087-30-3; 1,1-bis(*p*-anisyl)ethanol, 31067-02-4; *p,p'*-dimethoxybenzophenone, 39193-85-6; 1,1-bis(*p*-anisyl)ethene, 4356-69-8; 1,3-dibromohydantoin, 3304-74-3.

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(16) Temperatures of kinetic measurements and melting points are corrected. The NMR spectra were measured in carbon tetrachloride with a Varian EM-390 spectrometer. The NMR data are reported on the $\delta$ scale in parts per million as ($\delta$, coupling, area).
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# Cyclic Peroxides by Intramolecular Peroxymercuration of Unsaturated Hydroperoxides

J. R. Nixon, M. A. Cudd, and N. A. Porter*[19]

*P. M. Gross Chemical Laboratories, Duke University, Durham, North Carolina 27706*

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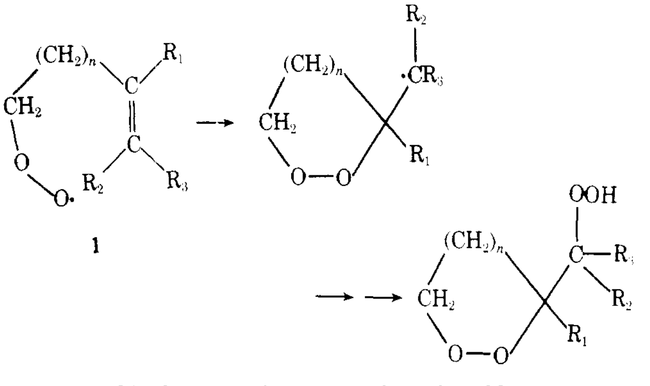
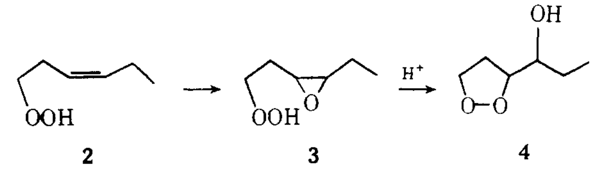
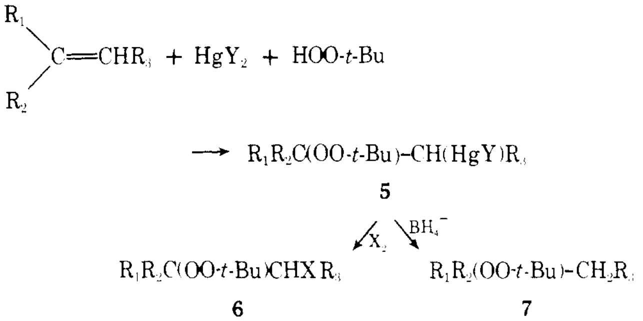
Unsaturated hydroperoxides undergo cyclization when treated with mercuric nitrate or trifluoroacetate. The $\beta$-mercurated cyclic peroxide products are isolated by high-pressure liquid chromatography as the alkyl mercuric bromides. Yields of analytically pure cyclic peroxides range from 60 to 90%. Treatment of the $\beta$-mercurated peroxides with molecular bromine gives the $\beta$-bromo cyclic peroxides in 80–90%, while reaction of the $\beta$-mercurated peroxides with borohydride leads to the parent cyclic peroxides in yields that range from 10 to 100%.

Cyclization reactions of unsaturated hydroperoxides have provided a synthetic approach for the preparation of a variety of cyclic peroxides. Thus, unsaturated hydroperoxides undergo cyclization,[1,2] presumably via a peroxy radical such as **1**, when subjected to autoxidation conditions. Cyclization of unsaturated hydroperoxides can also be induced by generating an electron deficient site from the olefin functionality. For example, the hydroperoxide **2** is converted[2] to a $\beta$-hydroxy cyclic peroxide **4** via the oxirane–hydroperoxide **3**. The discovery that compounds like **4** have interesting pharmacological properties[3] prompted us to explore other methods of generating cyclic peroxides from unsaturated hydroperoxides. In particular, we sought to extend the established method of intermolecular olefin peroxymercuration to our unsaturated hydroperoxides.


**1**


**2** **3** **4**

Peroxymercuration of olefins has been effectively employed as a method for the preparation of $\beta$-substituted peroxides.[4–6] A variety of substituted olefins react with mercuric salts such as the acetate, trifluoroacetate, or nitrate in the presence of hydroperoxides to yield the $\beta$-mercurated peroxide **5**. These compounds can be efficiently converted into the corresponding $\beta$-halogeno or $\beta$-hydrido peroxides by halogenodemercuration[4] or hydridodemercuration.[5] We report here that intramolecular peroxymercuration is affected by reacting hydroperoxides such as **2** with mercuric(II) compounds. The versatile $\beta$-mercurated cyclic peroxides so generated are a source of several new cyclic peroxide compounds.

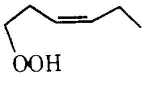


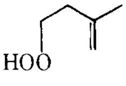
$$\mathrm{R_1R_2C{=}CHR_3 + HgY_2 + HOO\text{-}}t\mathrm{\text{-}Bu \longrightarrow R_1R_2C(OO\text{-}}t\mathrm{\text{-}Bu)\text{–}CH(HgY)R_3}\ (\mathbf{5})$$

$$\mathbf{5} \xrightarrow{X_2} \mathrm{R_1R_2C(OO\text{-}}t\mathrm{\text{-}Bu)CHXR_3}\ (\mathbf{6}) \qquad \mathbf{5} \xrightarrow{BH_4^-} \mathrm{R_1R_2(OO\text{-}}t\mathrm{\text{-}Bu)\text{–}CH_2R_3}\ (\mathbf{7})$$

## Results and Discussion

**The Synthesis of $\beta$-Mercuri Cyclic Peroxides.** The unsaturated hydroperoxides **2**, **8**, **9**, and **10** react with 1 equiv of $Hg(NO_3)_2 \cdot H_2O$ in dichloromethane at 22 °C. The products formed are isolated as the mercuric bromides, and the cyclic peroxides so generated are isolated and purified by high-


**2**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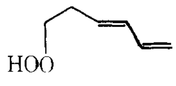
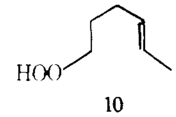

**9**


**10**