Synthesis and Thermolysis of Ketal Derivatives of 3-Hydroxy-1,2-dioxolanes

A. L. Baumstark,* P. C. Vasquez, and Y.-X. Chen

LBCS, Department of Chemistry, Georgia State University, Atlanta, Georgia 30303-3083

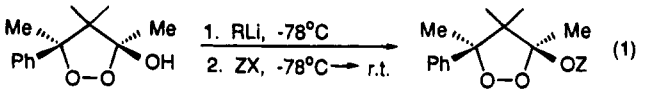
Received April 25, 1994®

3-[(Trimethylsilyl)oxy]-3,4,4,5-tetramethyl-5-phenyl-1,2-dioxolane (**2**), 3-methoxy-3,4,4,5-tetramethyl-5-phenyl-1,2-dioxolane (**3**), and 3-acetoxy-3,4,4,5-tetramethyl-5-phenyl-1,2-dioxolane (**4**) were synthesized from the corresponding 3-hydroxy-1,2-dioxolane (**1a**) under basic conditions. 3-Acetoxy-4,4-dimethyl-3,5,5-triphenyl-1,2-dioxolane (**5**) was also synthesized via this approach. Under acidic conditions, 3-hydroxy-1,2-dioxolane **1a** underwent quantitative decomposition to phenol and 3,3-dimethyl-2,4-pentanedione. This competing degradation was dependent on the nature of the substituents at position-5. Methyl groups at position-5 slowed the degradative rearrangement whereas phenyl groups favored it. 3-Methoxy- and 3-(allyloxy)-4,4,5,5-tetramethyl-3-phenyl-1,2-dioxolanes (**6, 7**) were synthesized under acidic conditions from the appropriate 1,2-dioxolane precursors and the corresponding alcohols. At 60 °C, derivatized 1,2-dioxolanes **2**–**7** were found to be more stable than the corresponding 3-hydroxy-1,2-dioxolanes. The first order rate constants for the thermolysis of 1,2-dioxolanes **2**–**7** were determined. Product studies showed that thermolysis of **2**–**5** yielded pairs of ketones and derivatized carboxylic acids. In addition to R-group migration products, an acetoxy migration product was observed for the thermolysis of **4**. Thermolysis of **6** at 60 °C in benzene yielded methyl benzoate and pinacolone, quantitatively. Thermolysis of **7** yielded products analogous to those for **6**. No evidence for internal trapping of radicals by the carbon–carbon double bond of the allyloxy group in **7** was found. The thermolyis appeared to proceed with peroxy bond homolysis as the rate-determining step. Subsequent β-scissions of the intermediate 1,5-oxygen diradical with interesting rearrangements that show a high preference for alkyl vs phenyl migration account for the observed product distributions. The results suggest that the β-scission/rearrangement mechanism may not be concerted but rather stepwise to yield 1,3-diradical and carbonyl fragments.

The 1,2-dioxolanes, five-membered cyclic peroxides, and related ring systems are of mechanistic as well as of synthetic interest[1] and have been found as natural products.[1b,2] We have developed[3] a versatile route for the synthesis of highly-substituted 3-hydroxy-1,2-dioxolanes (**1**) via O_2-trapping of β-keto radical intermediates generated during α-azo hydroperoxide decomposition. 3-Hydroxy-1,2-dioxolanes have been shown[4] to undergo thermal decomposition to produce pairs of ketones and carboxylic acids. The thermolysis of 3-hydroxy-1,2-dioxolanes was found[4] to proceed via the generation of 1,5-oxygen diradicals as the rate-determining step. Subsequent β-scissions of the 1,5-diradical intermediate proceeded[4] with interesting rearrangements[1] that showed a high preference for alkyl vs phenyl migration.[1] In several cases, only one of two possible β-scission routes was observed.[4] In other cases, approximately a one to one ratio of the two possible β-scissions/rearrangement routes was found. No evidence of hydroxy group migration was noted in the thermolysis of the 3-hydroxy-1,2-dioxolane series. Derivatization of the 3-hydroxy group should provide new insights into the mechanism of β-scission and rearrangement of 1,5-oxygen diradicals. We report here the synthesis and thermolysis of ketal derivatives of 3-hydroxy-1,2-dioxolanes.

Results

Synthesis. Under basic conditions, 3-hydroxy-3,4,4,5-tetramethyl-5-phenyl-1,2-dioxolane (**1a**) underwent reaction with trimethylsilyl chloride, methyl triflate, and acetic anhydride to produce 3-[(trimethylsilyl)oxy]-, 3-methoxy- and 3-acetoxy-3,4,4,5-tetramethyl-5-phenyl-1,2-dioxolanes **2**–**4** in good yield (reaction 1). Perketals



(1)

1a

2 Z = $SiMe_3$
3 Z = Me
4 Z = Ac

2–**4** were isolated as a mixture of cis/trans epimers with the 3-OZ and 5-Ph cis isomer predominant (92–95%, assignment based on NMR interpretation) in a ratio identical to that found in the starting material. 3-Acetoxy-4,4-dimethyl-3,5,5-triphenyl-1,2-dioxolane (**5**) was also synthesized via the above method employing the appropriate precursor (3-hydroxy-3,5,5-triphenyl-4,4-dimethyl-1,2-dioxolane), **1b**. Purification of the perketals was accomplished by chromatography and/or crystallization to yield the major epimer (for **2**–**4**). The compounds were characterized by spectral and physical methods.

® Abstract published in *Advance ACS Abstracts,* October 1, 1994.

(1) (a) Blooworth, A. J.; Eggelte, H. J. In *Singlet O_2*; Frimer, A., Ed.; CRC Press: Boca Raton, FL, 1985; Vol. II, pp 93–203. (b) Saito, I.; Nittala, S. S. In *The Chemistry of Functional Groups, Peroxides*; Patai, S., Ed.; Wiley-Interscience, New York, 1983; pp 311–374. (c) Adam, W. *Acc. Chem. Res.* **1979**, *12*, 390. (d) Nojima, M.; Kusabayashi, S. *Yuki Gosei Kagaku Kyokaishu* **1989**, *47*, 1096.

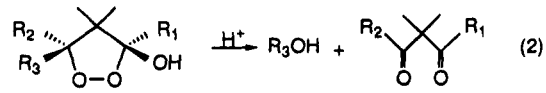
(2) Recent examples include: (a) Rustaiyan, A.; Sigari, H.; Jakupovic, J.; Grenz, M. *Phytochemistry* **1989**, *28*, 2723. (b) Gau, J.; Xie, J.; Iitaka, Y.; Inazama, S. *Chem. Pharm. Bull.* **1989**, *37*, 233. (c) Ruecker, G.; Breitmaier, E.; Mayer, R.; Manns, D. *Arch. Pharm.* **1987**, *320*, 437.

(3) Baumstark, A. L.; Vasquez, P. C. *J. Org. Chem.* **1992**, *57*, 393.

(4) Baumstark, A. L.; Vasquez, P. C. *J. Heterocycl. Chem.* **1992**, *29*, 1781.

0022-3263/94/1959-6692$04.50/0

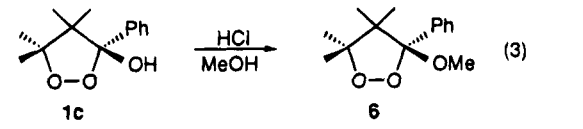
3-Hydroxy-1,2-dioxolane **1a** was found to be inert to the action of methylating agents (MeI, Me_2SO_4, MeOTs) less reactive than methyl triflate under the basic conditions. Under a variety of acidic conditions (e.g. H^+/methanol), 3-hydroxy-1,2-dioxolane **1a** could not be derivatized but rather underwent a rapid quantitative degradation to yield phenol and 3,3-dimethyl-2,4-pentanedione as the sole products (reaction 2). This degradation process was found to be general for this type of dioxolane. For example, 3-hydroxy-1,2-dioxolanes **1b,c** also underwent this degradation (reaction 2) under standard acidic conditions. Moreover, the decomposition of **1b** was found (qualitatively) to be the fastest while that of **1c** was the slowest.



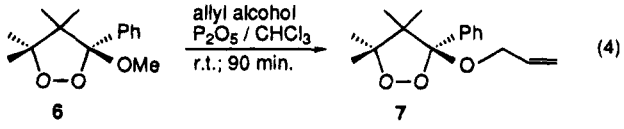
(2)

1a R_1=R_2=Me; R_3=Ph
1b R_1=R_2=R_3=Ph
1c R_1=Ph; R_2=R_3=Me

Two sets of conditions were developed to prepare 3-alkoxy derivatives with 5,5-dimethyl groups under acidic conditions since methyl groups at position-5 were found to slow the acid-catalyzed degradation process (reaction 2). Addition of methanolic HCl to 3-hydroxy-3-phenyl-4,5,5-trimethyl-1,2-dioxolane (**1c**) in anhydrous methanol was found to afford the 3-methoxy derivative **6** in good yield (reaction 3). This is a convenient alternative to the route shown in reaction 1 for this compound and should be useful with other alcohols as well. However, substitution of allyl alcohol for methanol did not yield acceptable results. 3-(Allyloxy)-4,4,5,5-tetramethyl-1,2-dioxolane **7** was synthesized by a catalytic transketalization of compound **6** (reaction 4). As for reaction 3, this method failed if a phenyl group was present on position-5, yielding only degradation products characteristic of reaction 2, quantitatively.

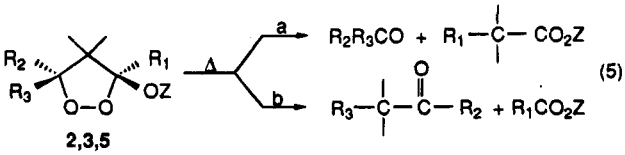


1c 6 (3)



6 7 (4)

Thermal Decomposition. The thermolysis of 3-[(trimethylsilyl)oxy]- (**2**) and 3-methoxy-1,2-dioxolanes **3** were carried out in benzene at 60 °C to yield pairs of ketones and derivatized carboxylic acids (reaction 5). Both sets of products (route a and b) were indicative of fragmentation with R group rearrangement with no phenyl migration observed when in competition with that of a methyl group for route b. For the decomposition of compounds **2–3**, route a was predominant (80–90%). A similar



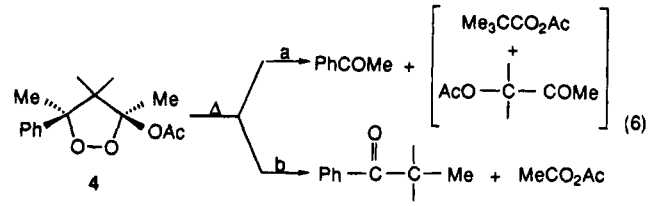
2,3,5 (5)

Table 1. Product Yields[a] and First Order Rate Constants for the Thermolysis of 1,2-Dioxolanes 2–7 in Benzene-d_6 at 60 °C

perketal	R_1	R_2	R_3	Z	R_2R_3CO + R_1CMe_2-CO_2Z, %	R_1CO_2Z + R_3CMe_2-COR_2, %	k_1 s^{-1} (60 °C)
2	Me	Ph	Me	$SiMe_3$	81	18	$5.6 \pm 0.1 \times 10^{-6}$
3	Me	Ph	Me	Me	88	12	$6.9 \pm 0.2 \times 10^{-6}$
4	Me	Ph	Me	Ac	89[b]	11	$4.8 \pm 0.3 \times 10^{-6}$
5	Ph	Ph	Ph	Ac	37	63	$3.7 \pm 0.3 \times 10^{-6}$
6	Ph	Me	Me	Me	–	100	$1.8 \pm 0.2 \times 10^{-6}$ (50 °C)
7	Ph	Me	Me	Allyl	–	100	$4.8 \pm 0.4 \times 10^{-6}$

[a] By ^1H NMR spectroscopy; the ketone and derivatized carboxylic acid product yields for each pair were identical within experimental error (±2%). [b] ZO-CMe_2-COR_1 product 27%, R_1-CMe_2-CO_2Z product 62%.

product distribution was found for the decomposition of **4**. However, the thermolysis of **4** showed an additional product ($ZOCMe_2COR_1$) in which the acetoxy group had undergone migration (reaction 6). The yield of this product corresponded with the lower yield of the corresponding R_1 migration product in route a while that of the other product (ketone) remained unchanged. Thermolysis of **5** yielded route a (37%) and b (63%) products with no acetoxy migration product detected (reaction 5). On the other hand, compounds **6** and **7** only yielded route b products, quantitatively. The route b ketone products were consistent with a high preference of methyl vs phenyl migration. GC-MS data for **2–4** showed only traces of 3-phenyl-3-methylbutanone (phenyl migration product) for route b. The product yields for the thermolysis of **2–7** are summarized in Table 1.



4 (6)

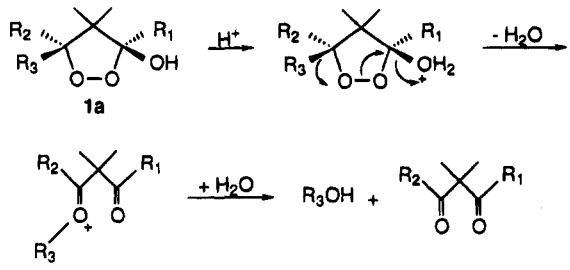
The decomposition of the derivatized 1,2-dioxolanes was found to be of the first order. The first order rate constants (k_1) for thermolysis of compounds **2–7** were determined in benzene-d_6 at 60 °C. For all the cases, the derivatized compounds underwent thermal decomposition slower than the corresponding 3-hydroxy-1,2-dioxolanes.[4] The rate constants for **2–7** showed little variation with substitution pattern as expected for a process with O–O bond scission as the rate-determining step. Complete decomposition of the compounds in benzene at 60 °C required approximately 5 days. The k_1 values are listed in Table 1.

Discussion

Routes for the synthesis of functionalized 1,2-dioxolanes are limited.[1,3] 4-Bromo-1,2-dioxolanes can be prepared by the 5-endo ring closure of allylic hydroperoxides.[5] 3-Alkoxyl- and 3-acetoxy-1,2-dioxolanes have been synthesized[6] by trapping carbonyl oxide intermediates

(5) Courtneidge, J. L.; Bush, M.; Loy, L. S. *Tetrahedron* **1992**, *48*, 3835.
(6) (a) Wojciechowska, B. J.; Chiang, C.-Y.; Kuczkowski, R. L. *J. Org. Chem.* **1990**, *55*, 1120. (b) Wojciechowski, B. J.; Pearson, W. H.; Kuczkowski, R. L. *Ibid.* **1989**, *54*, 115. (c) Keul, H.; Choi, H.-S.; Kuczkowski, R. L. *Ibid.* **1985**, *50*, 3365.

Scheme 1



(ozonolysis) with enol ethers and enol esters, respectively. The functionalization of 3-hydroxy-1,2-dioxolanes under basic conditions is a highly effective method for the synthesis of ketal derivatives. The 3-hydroxy-1,2-dioxolane anions are stable under basic conditions. However, the anions are relatively unreactive, presumably due to steric hindrance which limits the utility of the method to reactive "alkylating" agents. Under acidic conditions, 3-hydroxy-1,2-dioxolanes undergo a Criegee-like rearrangement[7] (reaction 2). The effect of substituents on position-5 observed for reaction 2 is consistent with that found for a similar rearrangement of peroxybenzoates[7] in which methyl-substituted compounds were much less reactive than the corresponding phenyl-substituted compounds. A reasonable mechanism for the acid-catalyzed rearrangement of **1a–c** is shown in Scheme 1. Protonation on oxygen-2 of the peroxy function would also produce the same overall reaction via a similar process. This restricts the approach to preparation of compounds with 5,5-dialkyl groups. Nevertheless, a variety of ketal derivatives are accessable via this methodology.

The free-radical mechanism for the thermal decomposition of 1,2-dioxolanes is well established.[1] The product distribution for the thermoloysis of 1,2-dioxolanes **2–7** is consistent[4] with the formation of 1,5-oxygen diradicals in the rate-determining step. The results for **7** show clearly that an allyloxy group is not an effective trap for any of the diradical intermediates. A mechanism consistent with the results is shown in Scheme 2. The major fragmentation routes (a and b) from the intermediate 1,5-oxygen diradical involve β-scission with rearrangement. The relative product distribution (routes a and b) showed a higher percentage of route a products for **2–5** than found for the corresponding 3-hydroxy-1,2-dioxolanes.[4] As observed for the 3-hydroxy-1,2-dioxolanes[4] and related 1,2-dioxolane systems,[1] the route b type rearranged products show a large preference of alkyl over phenyl migration. These and similar findings as well as stereolabeling results[1] have been regarded, in part, as evidence for the concerted nature of the fragmentation of the 1,5-oxygen diradical intermediates.

For route a type fragmentation of 3-hydroxy-1,2-dioxolanes,[4] no hydroxy group migration was observed when in competition with methyl or phenyl migration. The data for route a for **2** and **3** show that this conclusion is also valid for methoxy, trimethylsilyloxy, and allyloxy groups. No migration of these groups was found when in competition with R_1 group migration. However, the results for compound **4** showed that an acetoxy group migration could compete with that of a methyl group (route a). 1,2-Shifts of acetoxy groups are well documented for radical reactions.[8] Two possible interpretations of this result are shown in Scheme 3. β-Scission could lead to a 1,3-diradical intermediate which could either rearrange or close to a 1,4-diradical by attack of the carbonyl of the acetoxy group. A similar acetoxy migration via 1,4-diradical formation has been demonstrated in a diradical process.[8b] Alternatively, formation of this 1,4-diradical could occur directly from the 1,5-oxygen diradical. The direct attack of the acetoxy carbonyl group on the central carbon of the 1,5-oxygen diradical seems less likely since fragmentation of **5** did not show acetoxy migration. This would seem to favor the stepwise mechanism. The result for **5** can be rationalized if phenyl migration is faster than acetoxy migration. This implies that phenyl migration is faster than methyl migration for route a type diradicals.

Interestingly, if the β-scission and rearrangement process from the 1,5-oxygen diradical is stepwise rather than concerted, then route b products must arise from a 1,3-diradical (for compounds **2–4**) by rearrangement as shown in Scheme 4. This requires that the 1,3-diradical does not close to an epoxide under the reaction (thermolysis) conditions and preferably undergoes rearrangement by methyl rather than phenyl migration.

Experimental Section

All solvents (Aldrich) were of reagent grade. Tetrahydrofuran was distilled from over sodium before use (benzophenone as indicator). Benzene was distilled from over calcium hydride before use. The synthesis of pentasubstituted 3-hydroxy-1,2-dioxolanes (hemiperketals) has been reported.[3] ^{1}H, ^{13}C NMR, mp, IR, and kinetic data were recorded as previously reported.[4] Combustion analyses were performed by Atlantic Microlab, Atlanta, GA. The GC-MS analysis of thermolysis products was obtained from a Hewlett Packard 5890 Series II Gas Chromatograph-5971 Series Mass Selective Detector.

Perketals 2–7. Compounds **2–4** were synthesized by the following general procedure: to 0.300 g of 3-hydroxy-3,4,4,5-tetramethyl-5-phenyl-1,2-dioxolane (**1a**) (hemiperketal, 1.35 mmol) in 10 mL of dry THF in a 25 mL three-neck flask at −78 °C under inert atmosphere was added 1.1 equiv of BuLi (2.0 M in cyclohexane, Aldrich) via a syringe. This was followed by addition of 1.1 equiv of the appropriate, dry reagent (trimethylsilyl chloride, methyl triflate, or acetic anhydride). The reaction mixture was allowed to warm to ambient temperature and stirred for at least an additional hour. Upon addition of 15 mL of diethyl ether, the solution became cloudy. The salts were removed by filtration and the filtrate was concentrated under reduced pressure.

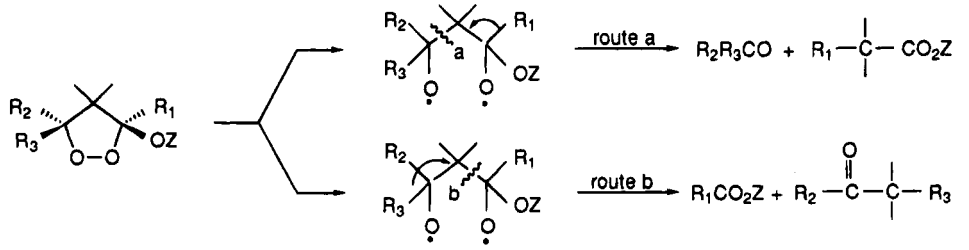
3-[(Trimethylsilyl)oxy]-3,4,4,5-tetramethyl-5-phenyl-1,2-dioxolane (2). 3-[(Trimethylsilyl)oxy]-3,4,4,5-tetramethyl-5-phenyl-1,2-dioxolane (**2**) was purified by chromatography (chromatatron) using 2% ether in petroleum ether as eluent. Compound **2** was obtained as a colorless oil (397 mg, 1.35 mmol) in essentially quantitative yield: ^{1}H NMR ($CDCl_3$) δ 0.24 (s, 9H), 0.51 (s, 3H), 1.21 (s, 3H), 1.31 (s, 3H), 1.66 (s, 3H), 7.43 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 1.7, 20.2, 20.3, 25.0, 25.8, 59.1, 90.2, 109.1, 125.2, 126.5, 127.9, 145.2; IR (neat) cm^{-1} 1254, 1155, 1127, 999, 857; MS base peak 73.0 (EI), 193.2 (CI, isobutane). Anal. Calcd: C, 65.26; H, 8.90. Found: C, 65.33; H, 8.87.

3-Methoxy-3,4,4,5-tetramethyl-5-phenyl-1,2-dioxolane (3). 3-Methoxy-3,4,4,5-tetramethyl-5-phenyl-1,2-dioxolane (**3**) was purified in the same manner as compound **2**. Compound **3** was obtained as a white solid (255 mg, 1.08 mmol) from petroleum ether at −20 °C in 80% yield: mp 56.5–57.5 °C; ^{1}H NMR ($CDCl_3$) δ 0.53 (s, 3H), 1.22 (s, 3H), 1.23 (s, 3H), 1.68 (s, 3H), 3.36 (s, 3H), 7.32 (m, 5H); ^{13}C NMR ($CDCl_3$) δ

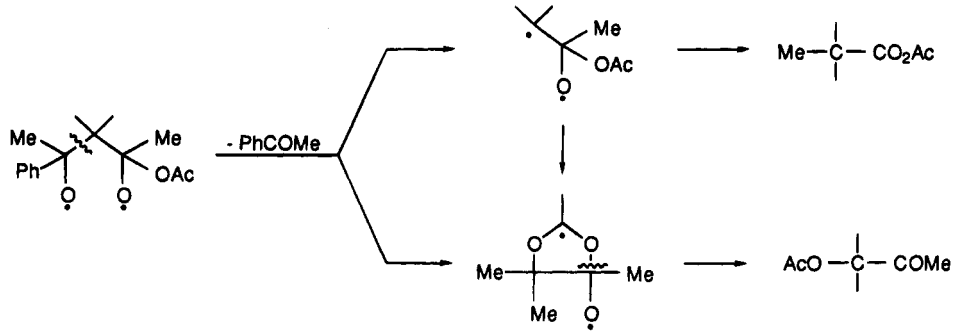
(7) (a) Sawaki, Y. In *Organic Peroxides*; Ando, W., Ed.; John Wiley & Sons Ltd.; Chichester, England, 1992; Chapt. 9, pp 454–5. (b) Sawaki, Y.; Ogata, Y. *J. Am. Chem. Soc.* **1978**, *100*, 856.

(8) (a) Wilt, J. W. In *Free Radicals*; Vol. I Kochi, J. K., Ed.; Wiley Interscience: New York, 1973; Chapt. 8, pp 360–2. (b) DePuy, C. H.; Zabel, D. E.; Wiedemar, W., *J. Org. Chem.* **1968**, *33*, 2198.

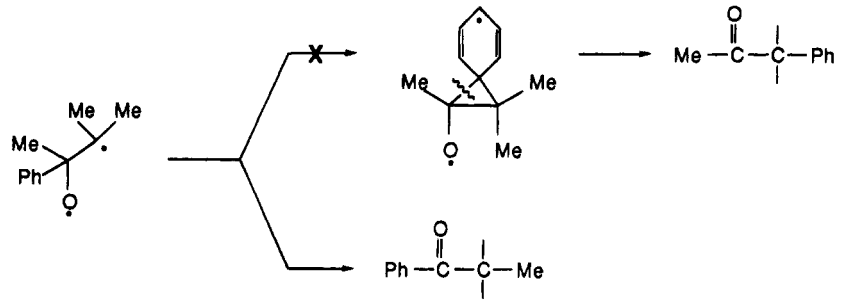
Scheme 2



Scheme 3



Scheme 4



13.5, 19.5, 25.0, 25.9, 48.4, 58.6, 90.4, 109.7, 125.6, 126.6, 127.9, 145.0; IR (neat) cm^{-1} 1155, 1117, 1040, 802; MS base peak 105.0 (EI), 121.1 (CI, isobutane), 117.1 (CI, ammonia). Anal. Calcd: C, 71.16; H, 8.53. Found: C, 71.20; H, 8.54.

3-Acetoxy-3,4,4,5-tetramethyl-5-phenyl-1,2-dioxolane (4). 3-Acetoxy-3,4,4,5-tetramethyl-5-phenyl-1,2-dioxolane (**4**) was purified by recrystallization from petroleum ether at −20 °C to yield 275 mg (1.04 mmol) of white crystals of **4** (77% yield): mp 81.5−84 °C dec; ^1H NMR ($CDCl_3$) δ 0.59 (s, 3H), 1.31 (s, 3H), 1.68 (s, 3H), 2.10 (s, 3H), 7.40 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 16.4, 19.6, 22.4, 24.8, 25.2, 60.0, 89.8, 112.7, 125.5, 126.9, 128.1, 143.9, 168.6; IR (neat) cm^{-1} 1749, 1227, 1016, 961; MS base peak 105.0 (EI), 121.1 (CI, isobutane), 138.1 (CI, ammonia). Anal. Calcd: C, 68.16; H, 7.63. Found: C, 68.26; H, 7.65.

3-Acetoxy-4,4-dimethyl-3,5,5-triphenyl-1,2-dioxolane (5). 1,2-Dioxolane **5** was prepared by the procedure employed for the synthesis of compounds **2**−**4** using 51 mg (0.147 mmol) of 3-hydroxy-4,4-dimethyl-3,5,5-triphenyl-1,2-dioxolane.[3] Purification was achieved by recrystallization from petroleum ether at −20 °C to yield 55.2 mg (0.142 mml, 96.5%) of white crystals of pure **5**: mp 124−126 °C; ^1H NMR ($CDCl_3$) δ 0.71 (s, 3H), 1.34 (s, 3H), 1.72 (s, 3H), 7.15−7.33 (m, 11H), 7.52 (d, 2H), 7.80 (d, 2H); ^{13}C ($CDCl_3$) δ 19.6, 21.0, 23.6, 62.9, 91.2, 112.1, 125.3, 126.4, 126.5, 127.1, 127.7, 128.2, 128.3, 136.2, 141.1, 143.5, 167.0; IR (neat) cm^{-1} 1742, 1265, 1018; MS base peak 105 (EI), 183.1 (CI, isobutane). Anal. Calcd 1/3 H_2O: C, 76.12; H, 6.30; found: C, 76.14; H, 6.25; C, 76.23; H, 6.25. To determine the active oxygen content, 0.0311 g of peroxide **5** was dissolved in 25 mL of acetic anhydride containing 1 g of KI. The solution was kept oxygen free by addition of dry ice. The heterogeneous mixture was heated to 60 °C for 2 h and then was titrated with $Na_2S_2O_3$ to yield 97.2% active oxygen.

3-Methoxy-4,4,5,5-tetramethyl-3-phenyl-1,2-dioxolane (6). 1,2-Dioxolane **6** was prepared by a procedure similar to that used by Snider et al.[9] for a six-ring system. To a solution of 33.34 mg (0.15 mmol) of 3-hydroxy-3-phenyl-4,4,5,5-tetramethyl-1,2-dioxolane in 160 μL of anhydrous methanol solution at 0−5 °C (ice bath) was added, via syringe, 80 mL of a saturated hydrogen chloride−methanol solution. The mixture was stirred for 3 h at room temperature. The solvent was removed under reduced pressure. After chromatography (5% ether−petroleum ether was used for eluent), 30.0 mg (0.127 mmol, 84.6%) of 3-methoxy-4,4,5,5-tetramethyl-3-phenyl-1,2-dioxolane was obtained as a colorless solid: mp 54.0−55.5 °C; ^1H NMR ($CDCl_3$) δ 0.59 (s, 3H), 1.14 (s, 3H), 1.25 (s, 3H), 1.48 (s, 3H), 3.09 (s, 3H), 7.35 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 18.9, 23.5, 24.1, 24.4, 49.8 (OCH_3), 58.3, 87.6, 111.6, 126.5, 128.1, 128.3, 136.2; IR (KBr) cm^{-1} 1094, 850; MS (70 eV) 205 $(M - OCH_3)^+$ (EI). Anal. Calcd: C, 71.16; H, 8.53. Found: C, 70.85; H, 8.51.

3-(Allylloxy)-4,4,5,5-tetramethyl-3-phenyl-1,2-dioxolane (7). Compound **7** was synthesized by a procedure based on an improved method for methoxymethylation under mild conditions developed by Fuji.[10] To a stirred solution of 48.0 mg (0.20 mmol) of 3-methoxy-4,4,5,5-tetramethyl-3-phenyl-1,2-dioxolane and 597.8 mg (700 μL, 10.3 mmol) of allyl alcohol in 3 mL of $CHCl_3$ (dried over phosphorus pentoxide) was added 56.8 mg (0.40 mmol) of phosphorus pentoxide at 0 °C (ice bath). The mixture was stirred at room temperature for 1.5 h. After evaporation of the solvent, the residue was extracted with 15 mL of pentane. Removal of pentane left an oil which was dissolved in 15 mL of ether. The ethereal solution was washed

(9) Snider, B. B.; Shi, Z. *J. Org. Chem.* **1990**, *55*, 5669.
(10) Fuji, K.; Nakano, S.; Fujita, E. *Synthesis* **1975**, 276.

with chilled saturated sodium bicarbonate and dried over magnesium sulfate. The solvent was removed under reduced pressure. The crude material was purified by chromatography (6% ether–petroleum ether was used for eluent) to yield 41.3 mg (0.157 mmol) of 3-(allyloxy)-4,4,5,5-tetramethyl-3-phenyl-1,2-dioxolane as a colorless oil (78.5%): ^{1}H NMR ($CDCl_3$) δ 0.60 (s, 3H), 1.18 (s, 3H), 1.25 (s, 3H), 1.50 (s, 3H), 3.51–3.58 (m, 1H), 4.04–4.10 (m, 1H), 5.07–5.11 (m, 1H), 5.23–5.30 (m, 1H), 5.86–5.96 (m, 1H), 7.33 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 18.8, 23.5, 24.0, 24.6, 58.5, 63.5, 87.6, 111.5, 115.2, 128.1, 128.4, 135.1, 136.5, 141.1; IR (neat) cm^{-1} 1647, 1083; MS 205 ($M - OCH_2CH{=}CH_2)^+$ (El). Anal. Calcd: C, 73.25; H, 8.45. Found: C, 73.03; H, 8.51.

Kinetic Studies. The kinetic experiments were carried out by the following general procedure. A 0.04–0.07 mmol sample of pure 1,2-dioxolane derivative was weighed into a 5 mm NMR sample tube, and 50 mg of anisole (internal standard) and 0.500 mL of perdeuterobenzene (Norrell, Inc. 1% TMS) were added. The sealed NMR tube was heated in a constant temperature bath ($T \pm 0.2$ °C) in the dark. Reaction progress was followed by monitoring the disappearance (^{1}H NMR electronic integration) of the most upfield methyl group signal of the dioxolane vs that of the internal standard. The NMR sample was placed in an ice bath after removal from the constant temperature bath before and after NMR analysis. Reaction time was taken as the composite of time spent in the constant temperature bath. The thermolyses were extremely slow. No discoloration was noted. First order plots were linear for at least two half lives ($r = 0.99$). Variation between duplicate runs was less than 10% of the value of k_1.

Product Studies. The following general procedure was employed for the thermolysis of 3,4,4,5,5-pentasubstituted-3-hydroxy-1,2-dioxolanes O-derivatives **2**–**7**. A ~0.1 M solution of the peroxide in benzene-d_6 was heated at ~60 °C in a sealed NMR tube until complete disappearance of the starting material (~5 days). Thermolysis of 1,2-dioxolane **5** was carried out in deuterochloroform (~2 days). The final ^{1}H NMR spectrum was recorded and the relative peak intensities were determined. The crude reaction mixture was analyzed by GC-MS. The products were isolated by chromatographic methods (chromatatron) and low temperature distillation and identified by comparison of physical and spectral (IR, NMR, MS) data with those of authentic samples.

From **2**: Acetophenone and 2,2-dimethyl-1-phenylpropanone were identified by comparison with commercial samples (Aldrich). Trimethylsilyl acetate was prepared by reaction of acetic acid and trimethylsilyl chloride by standard methods: ^{1}H NMR (C_6D_6) 0.22 (s, 9H), 1.71 (s, 3H). Trimethylsilyl (2,2-dimethylpropionate was prepared from 2,2-dimethylpropionic acid and trimethylsilyl chloride by standard methods: ^{1}H NMR (C_6D_6) δ 0.24 (s, 9H), 1.15 (s, 9H); MS (GC) 174 (0.3%), 159 (51%), 73 (100%).

From **3**: Acetophenone, methyl 2,2-dimethylpropionate, 2,2-dimethyl-1-phenylpropanone, and methyl acetate were identified by comparison with authentic samples (Aldrich).

From **4**: Acetophenone (88%), acetic anhydride, and 2,2-dimethyl-1-phenylpropanone were identified by comparison with commercial samples (Aldrich). 3-Acetoxy-3-methyl-2-butanone (27%) was prepared by reaction of 3-hydroxy-3-methyl-2-butanone and acetyl chloride by standard methods: ^{1}H NMR ($CDCl_3$) δ 1.48 (s, 6H), 2.10 (s, 3H), 2.14 (s, 3H); MS (GC) 144 (4.5%), 101 (77.5%), 59 (100%). Acetic 2,2-dimethylpropionic anhydride was prepared by reaction of 2,2-dimethylpropionic acid and acetic anhydride: ^{1}H NMR ($CDCl_3$) δ 1.23 (s, 9H), 2.22 (s, 3H); MS (GC) 144 (0.7%), 57 (100%).

From **5**: Benzophenone was identified by comparison with a commercial sample (Aldrich). 2-Methyl-1,2-diphenyl-1-propanone;[11] ^{1}H NMR ($CDCl_3$) δ 1.60 (s, 6H), 7.17–7.40 (m, 8H), 7.46 (d, 2H); MS (GC) 224 (7.2%), 119 (69.5%), 105 (100%). Acetic 2-methyl-2-phenylpropionic anhydride [^{1}H NMR (C_6D_6) of reaction mixtures shows 1.62 (s, 6H), 2.22 (s, 3H)] was found to be sensitive to hydrolysis; the anhydride was completely hydrolyzed during purification by chromatatron to produce 2-methyl-2-phenylpropanoic acid:[12] ^{1}H NMR ($CDCl_3$) δ 1.61 (s, 6H), 7.26 (s, 5H), 12.8 (bs, 1H). Acetic benzoic anhydride (^{1}H NMR of the reaction mixture shows singlet at 2.11 ppm) was completely hydrolyzed to produce benzoic acid which was compared to commercial sample (Aldrich).

From **6**: 3,3-Dimethyl-2-butanone (100%) and methyl benzoate (100%) were identified by comparison with commercial samples (Aldrich).

From **7**: 3,3-Dimethyl-2-butanone (100%) was identified by comparison with a commercial sample (Aldrich). Allyl benzoate (100%):[13] ^{1}H NMR ($CDCl_3$) δ 4.81–4.84 (m, 2H), 5.26–5.45 (m, 2H), 5.97–6.12 (m, 1H), 7.41–7.59 (m, 3H), 8.05–8.09 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 65.5, 118.2, 128.3, 129.6, 130.1, 132.2, 133.0, 166.3; MS (GC) 162 (4.3%), 105 (100%), 77 (35.6%).

Degradation of 3-Hydroxy-3,4,4,5,5-pentasubstituted-1,2-dioxolanes, 1a–c, in Acidic Media. To 10.0 mg (0.045 mmol) of dioxolane **1a–c** was added 2 mL of a cold solution (0 °C) of the reagent (1 mg of *p*-toluenesulfonic acid in methanol, 1 M hydrogen chloride in acetic acid, or 1 M hydrogen chloride in anhydrous ether). The resulting solution was stirred at 0 °C for 1 h and then was kept at room temperature for 18 h. The solvent was removed under reduced pressure. NMR analysis of the residue after evaporation showed complete loss of starting material. Chromatography (chromatatron) of the reaction residue for 3-hydroxy-3,4,4,5-tetramethyl-5-phenyl-1,2-dioxolane (**1a**) yielded quantitatively 3,3-dimethyl-2,4-pentanedione and phenol. Similarly, 3-hydroxy-4,4-dimethyl-3,5,5-triphenyl-1,2-dioxolane (**1b**) and 3-hydroxy-4,4,5-trimethyl-3,5-diphenyl-1,2-dioxolane (**1c**) produced in quantitative yields 2,2-dimethyl-1,3-diphenyl-1,3-propanedione and 2,2-dimethyl-1-phenyl-1,3-butanedione, respectively (identified by comparison with authentic samples).[14]

Degradation of 3-Hydroxy-4,4,5,5-tetramethyl-3-phenyl-1,2-dioxolane (1c) in Trifluoroacetic Acid at 0 °C. To 10.0 mg (0.045 mmol) of 3-hydroxy-4,4,5,5-tetramethyl-3-phenyl-1,2-dioxolane (**1c**) in 0.5 mL of $CDCl_3$ (Aldrich) was injected 34.7 μL (0.45 mmol) of trifluoroacetic acid at 0 °C (ice bath). No 1,2-dioxolane was detected after 46 min (standing) at 0 °C. The reaction mixture was poured into 2 mL of dichloromethane. The organic layer was washed with 5% sodium bicarbonate solution and dried over $MgSO_4$. Solvent removal yielded 7.9 mg (0.042 mmol, 92.4%) of 2,2-dimethyl-1-phenyl-1,3-butanedione as a colorless oil.[14]

Acknowledgment is made to the National Science Foundation (CHE-9017230) for support of this research. NMR instrumentation was obtained, in part, by an NSF Equipment grant (CHE-8409599).

(11) Wolfe, S.; Berry, T. E.; Peterson, M. R. *Can. J. Chem.* **1976**, *54*, 210.
(12) Kawai, N.; Shioiri, T. *Chem. Pharm. Bull.* **1983**, *31*, 2564.
(13) Shono, T.; Ishige, O., Uyama, H.; Kashimura, S. *J. Org. Chem.* **1986**, *51*, 546.
(14) Choudhary, A.; Baumstark, A. L. *Synthesis* **1989**, 688.