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Reaction of Furan-Based *o*-Quinodimethanes with Triplet Oxygen. Formation of Cyclic Peroxides[†,1]

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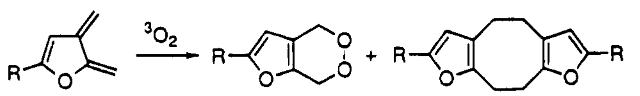
Formation of cyclic peroxides **2a**, **2b**, and **2c** from the reactions of 2,3-dimethylene-2,3-dihydrofuran (**1a**) and the 5-methyl (**1b**) and 5-*tert*-butyl (**1c**) derivatives with triplet oxygen is reported. Thermolysis of cyclic peroxide **2c** gives dialdehyde **5**, hydroxy aldehydes **6** and **7**, and diol **8** as products.

Although the reaction of singlet oxygen ($^1O_2$) with olefins is rapid and very general,[2] the reaction of triplet oxygen ($^3O_2$) with olefins is normally slow.[3] However, certain special types of olefins,[3,4] acetylenes,[3,4] and dienes[3−5] have been observed to react rapidly and directly with triplet oxygen.

During the course of studying the chemistry of 2,3-dimethylene-2,3-dihydrofuran (**1a**)[6] and its 5-alkylated derivatives **1b** and **1c**,[7] we found that each of these furan-based *o*-quinodimethanes when in contact with triplet oxygen gives rise to the corresponding cyclic peroxide **2a**, **2b**, or **2c** in addition to the normal product, the corresponding [4 + 4] dimer **3a**, **3b**, or **3c**. The results of this study are presented and discussed herein.

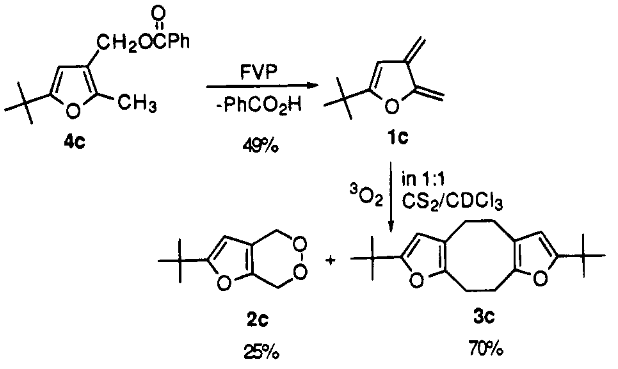


1 **2** **3**

a. R = H
b. R = CH_3
c. R = $C(CH_3)_3$

Results

The flash vacuum pyrolysis (FVP) of (5-*tert*-butyl-2-methyl-3-furyl)methyl benzoate (**4c**) at 550−560 °C and *ca.* 10^{-4} Torr produced a white product band in the cold trap which was cooled to −196 °C.[7] A 1:1 mixture of CS_2 and $CDCl_3$ was added to the trap, and the product mixture was allowed to warm to −78 °C. The ^1H NMR spectrum of the product mixture recorded at −60 °C indicated that 5-*tert*-butyl-2,3-dimethylene-2,3-dihydrofuran (**1c**) was the primary pyrolysis product. When this product mixture was warmed to room temperature without preclusion of oxygen, the major products formed were **2c**, the cyclic peroxide, and **3c**, the [4 + 4] dimer of **1c**. Quantitative ^1H NMR analysis using dibromoethane as the standard indicated that pyrolysis of **4c** gave **1c** in 49% yield[8] and that 95% of **1c** was converted to **2c** (25%) and **3c** (70%) upon **1c** being warmed to room temperature.



We believe that triplet oxygen was responsible for the oxidation of **1c** to peroxide **2c** on the basis of the following facts: (1) only **3c** was formed from **1c** when the solvents (CS_2 and $CDCl_3$) were predeaerated; (2) the yield of **2c** was increased to 80% when oxygen was bubbled through the mixture; (3) the yields of **2c** and **3c**, under the above three different reaction conditions, were essentially unchanged when the reactions were carried out in the dark.

Cyclic peroxide **2c** appears to be stable in a $CS_2/CDCl_3$ solution kept at freezer temperatures for several days. However, it decomposes rapidly after removal of the

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[†] Dedicated to Professor Glen A. Russell on the occasion his 70th birthday.

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(1) Based on work by C.-H. Chou in partial fulfillment of the requirement for the Ph.D. degree at Iowa State University.

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(8) No other significant product was obtained; the remaining material is accounted for by char in the pyrolysis tube and the polymer of **1c** formed during the transfer of **1c** to solution.[7]

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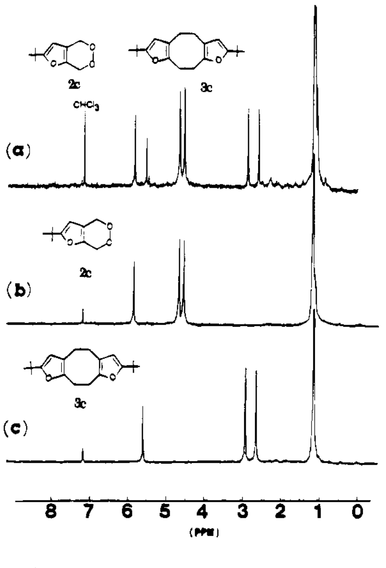
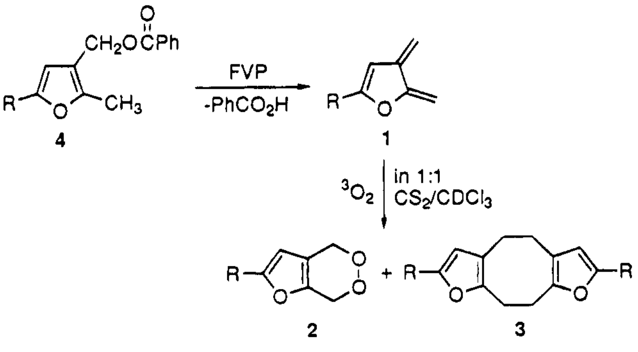


Figure 1. (a) ^{1}H NMR spectrum of a mixture of **2c** and **3c** resulting from reaction of **1c** with $^3O_2$ in 1:1 $CS_2/CDCl_3$. (b) ^{1}H NMR spectrum of the isolated cyclic peroxide **2c** in $CDCl_3$. (c) ^{1}H NMR spectrum of the isolated [4 + 4] dimer **3c** in $CDCl_3$.

solvent and decomposes during the course of conventional column chromatography. Nevertheless, **2c** was isolated from the product mixtures by flash column chromatography, and its ^{1}H and ^{13}C NMR spectra were recorded. In Figure 1, for the purpose of comparison, the ^{1}H NMR spectra of a mixture of **2c** and **3c** resulting from **1c** (a) and isolated **3c** (c) are presented in addition to that of isolated **2c** (b).

FVP of (2-methyl-3-furyl)methyl benzoate[6] (**4a**) and (2,5-dimethyl-3-furyl)methyl benzoate[7] (**4b**) gives 2,3-dimethylene-2,3-dihydrofuran (**1a**) and 5-methyl-2,3-dimethylene-2,3-dihydrofuran (**1b**), respectively, as the primary products. When a 1:1 $CS_2/CDCl_3$ solution of either **1a** or **1b** was allowed to warm to room temperature even without preclusion of oxygen, the corresponding [4 + 4] dimer **3a** or **3b** was formed quantitatively (>96%) and only traces or none of the corresponding cyclic peroxide **2a** or **2b** was produced. However, when oxygen was bubbled through the solutions of **1a** or **1b** at −78 °C for 3 h and then the solutions were allowed to warm to room temperature, 15% of cyclic peroxide **2a** and 35% of cyclic peroxide **2b** were formed.

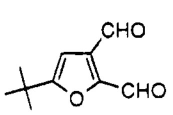


		2	3
a.	R = H	15%	85%
b.	R = CH₃	35%	65%

Attempts to isolate **2a** and **2b** from their respective product mixtures by flash column chromatography were unsuccessful, presumably due to the instability of **2a** and **2b**. Nevertheless, evidence for the formation of **2a** and **2b** was obtained by recording the ^{1}H NMR spectra of the products from **1a** and **1b** in oxygen-saturated 1:1 $CS_2/CDCl_3$ solutions.

When **2c** was subjected to GC analysis using injection temperatures higher than 150 °C, it rearranged to four products in nearly equal amounts. Attempts to separate these products, **5**−**8**, failed, but GC/MS analysis indicated that their molecular weights are 180, 182, 182, and 184, respectively. Furthermore, GC/IR analysis showed that three of the products, **5**−**7**, contain aldehyde groups (characterized by their strong C═O-stretching bands in the 1705−1690 cm^{-1} region and the medium intense aldehydic C−H-stretching absorptions in the 2830−2700 cm^{-1} region) and that two of these products, **6** and **7**, and the fourth product, **8**, contain hydroxy groups (characterized by their medium to strong C−O-stretching bands in the 1020−1010 cm^{-1} region and the broad O−H-stretching absorptions in the 3500−3000 cm^{-1} region).

On the basis of the above results and reports in the literature that thermolysis of cyclic peroxides gives rise to diones, hydroxy ketones, and diols,[5b,g,9−12] the structures of **5**−**8** are assigned as follows:



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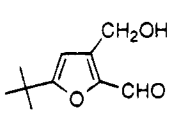
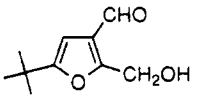
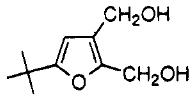


6 (or 7)



7 (or 6)



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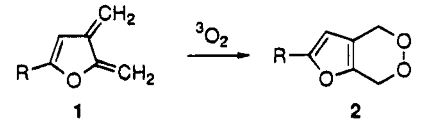
Discussion

Although the reaction of olefins with $^3O_2$ is normally slow, several *o*-quinodimethanes and related compounds have been shown to react rapidly with $^3O_2$ to give cyclic peroxides.[5b,d,g−i] The rapid reaction of the furan-based *o*-quinodimethanes (**1**) with $^3O_2$ to give cyclic peroxides **2** fits into this pattern. Possible mechanisms for the spin-forbidden addition of triplet oxygen to olefins have been presented.[3−5]



a. R = H
b. R = CH₃
c. R = C(CH₃)₃

The rapid thermolysis of cyclic peroxide **2c** in the GC injection port to give dialdehyde **5**, hydroxy aldehydes **6** and **7**, and diol **8** as products has literature precedent. Salomon and co-workers[10] reported that 2,3-dioxabicyclo[2.2.1]heptane (**9**) in D_2O solution rearranges thermally to give a diketone and a hydroxy ketone as major products. Adam and Arce[11] reported that gas-phase pyrolysis at 315 °C of 4-ethylidene-3,3,5,5-tetramethyl-1,2-dioxolane (**10**) forms by cleavage of the peroxide bond an intermediate diradical which then undergoes rearrangement and fragmentation to give several hydroxy- and carbonyl-containing products. Baumstark and Vasqu-

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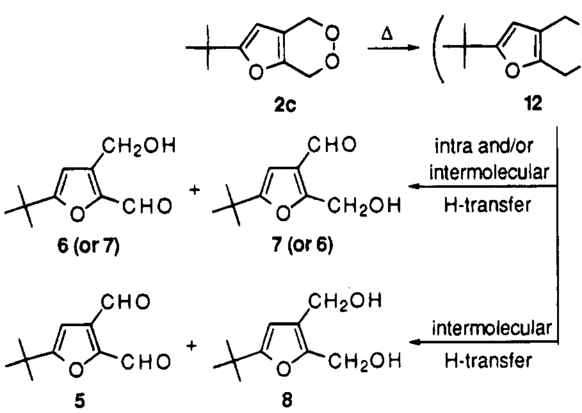
Scheme 1



ez[12] reported that the thermolysis of pentasubstituted 3-hydroxy-1,2-dioxolanes (**11**) in benzene yields pairs of ketones and carboxylic acids by initial peroxide bond homolysis to form the 1,5-oxygen diradical which fragments by β-scission with rearrangement.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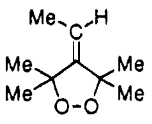
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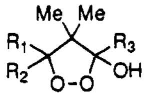
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Thermolysis of **2c** to give products **5** to **8** can thus be rationalized by homolysis of the peroxide bond of **2c** to generate 1,6-diradical **12**, followed by intra- and/or intermolecular hydrogen transfer to give **6** and **7** and intermolecular hydrogen transfer to give **5** and **8** (Scheme 1). The fact that the amounts of **5** and **8** are comparable to those of **6** and **7** suggest that intermolecular hydrogen transfers are more important since one would expect a greater total yield of **6** and **7** if intramolecular hydrogen transfers dominated. Also, since the reaction takes place rapidly in the GC injection port, induced decomposition could be important as well.

Experimental Section

Methods and Materials. Some general methods and materials have been described previously.[6] ^{1}H NMR spectra were recorded on Varian A-60 or JEOL FX-90Q spectrometers. ^{13}C NMR spectra were recorded on JEOL FX-90Q or NICOLET-300 spectrometers. Gas chromatography/infrared spectra analyses (GC/IR) were performed using a Hewlett-Packard 5880A instrument and an IBM IR/90 spectrometer. GC analyses were performed using a Hewlett-Packard HP 5840 A instrument equipped with a 25 m, SP 2100 thin film (methylsilicone-coated) capillary column.

Reaction of 5-*tert*-Butyl-2,3-dimethylene-2,3-dihydrofuran (1c) with ^{3}O$_2$. A quantity of *ca.* 0.4 g (*ca.* 1.5 mmol) of (5-*tert*-butyl-2-methyl-3-furyl)methyl benzoate (**2c**), prepared as described previously,[7] was pyrolyzed at 550 °C using the general pyrolysis procedure[6,7] to give 49% yield of **1c**: ^{1}H NMR (1:1 CS$_2$/CDCl$_3$, −60 °C) δ 5.40 (s, 1 H), 5.08 (m, 1 H), 4.78 (s, 1 H), 4.74 (m, 1 H), 4.57 (m, 1 H), 1.16 (s, 9 H). Oxygen was bubbled into the product solution at −78 °C for 3 h, and the solution was then allowed to warm slowly to room temperature. Quantitative ^{1}H NMR analysis indicated that 95% of **1c** was converted to the cyclic peroxide **2c** (80%) and the [4 + 4] dimer **3c** (15%) upon **1c** being warmed to room temperature. After separation of **2c** and **3c** by flash column chromatography on silica gel (an eluent of 5% ether in hexanes was used first to elute **3c** and then changed to 40% ether in hexanes for the elution of **2c**), their spectral data were recorded. **2c**: IR (CS$_2$) 2960, 2920, 2860, 1355, 1330, 1290, 1220, 1200, 1180, 1090, 975, 935, 800 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 5.90 (s, 1 H), 4.73 (s, 2 H), 4.61 (s, 3 H), 1.24 (s, 9 H); ^{13}C NMR (CDCl$_3$) δ 164.50, 146.24, 120.40, 104.53, 67.85, 66.55, 32.64, 28.95. **3c**: the mp, ^{1}H NMR spectrum (CDCl$_3$), and ^{13}C NMR spectrum (CDCl$_3$) agree with those reported.[7]

Thermolysis of Cyclic Peroxide 2c (2-*tert*-Butyl-5,6-dioxa-4,5,6,7-tetrahydrobenzofuran). Thermolysis of **2c** was carried out by injecting a sample of **2c** into the gas chromatograph at injection temperatures higher than 150 °C. Four products, **5**–**8**, were obtained from **2c** in almost equal amounts, and their GC/MS and GC/IR spectral data are listed as follows. Compound **5**: GC/MS (70 eV) *m/e* (% base peak) 181.96 (0.10), 180.98 (6.17), 180.00 (66.42), 164.96 (57.39), 152.02 (41.69), 136.98 (61.81), 123.02 (10.88), 109.00 (57.92), 108.02 (12.85), 94.98 (100.00), 91.04 (21.50), 81.06 (24.93), 79.04 (43.27), 77.02 (31.37), 68.92 (14.10), 68.12 (11.82), 67.02 (22.03), 66.04 (10.62), 65.02 (26.09), 63.02 (12.63), 57.06 (47.82), 55.04 (33.90), 53.04 (58.05), 51.02 (29.16), 50.00 (12.12); GC/IR 2950, 2830–2700, 1705, 1530 cm^{-1}. Compound **6**: GC/MS (70 eV) m/e (% base peak) 184.00 (0.22), 183.02 (5.36), 182.00 (50.06), 166.98 (100.00), 153.02 (6.05), 139.02 (6.76), 121.02 (8.16), 93.04 (17.01), 91.04 (18.29), 79.04 (15.61), 77.02 (28.68), 69.04 (17.80), 67.04 (12.39), 65.04 (11.97), 57.04 (17.62), 55.04 (28.83), 53.02 (21.35), 51.02 (17.98); GC/IR 3500, 2950, 2830–2740, 1705, 1560, 1180, 1010, 780 cm^{-1}. Compound **7**: GC/MS (70 eV) *m/e* (% base peak) 184.06 (0.06), 183.00 (4.64), 182.00 (45.69), 166.98 (100.00), 153.00 (2.46), 139.00 (9.17), 125.02 (5.35), 93.04 (15.19), 91.04 (22.34), 79.04 (13.24), 77.02 (29.74), 69.06 (10.62), 67.04 (13.20), 65.04 (15.71), 57.04 (11.23), 55.04 (30.03), 53.02 (23.52), 51.02 (14.42); GC/IR 3500–3000, 2950, 2830–2750, 1690, 1520, 1280, 1020, 790 cm^{-1}. Compound **8**: GC/MS (70 eV) *m/e* (% base peak) 185.12 (0.47), 184.04 (19.53), 169.00 (95.60), 166.98 (11.77), 165.98 (10.83), 150.98 (100.00), 123.02 (89.48), 95.04 (10.99), 91.02 (16.09), 79.06 (19.00), 77.02 (31.63), 67.06 (21.43), 65.04 (13.58), 57.04 (18.52), 55.02 (32.73), 53.04 (30.85), 51.02 (22.06); GC/IR 3500–3000, 2950, 1400, 1370, 1010 cm^{-1}.

Reaction of 2,3-Dimethylene-2,3-dihydrofuran (1a) with ^{3}O$_2$. A quantity of *ca.* 0.4 g (*ca.* 1.85 mmol) of (2-methyl-3-furyl)methyl benzoate (**4a**), prepared as described previously,[13] was pyrolyzed at 700 °C using the general pyrolysis procedure[6,13] to give a 55% yield of **1a**: ^{1}H NMR (1:1 CS$_2$/CDCl$_3$, −60 °C) δ 6.68 (m, 1 H), 5.73 (m, 1 H), 5.17 (m, 1 H), 4.90 (s, 1 H), 4.75 (m, 1 H), 4.58 (m, 1 H). Oxygen was bubbled into the product solution at −78 °C for 3 h, and the solution was then allowed to warm slowly to room temperature. Quantitative ^{1}H NMR analysis indicated that **1a** was converted quantitatively to the corresponding cyclic peroxide **2a** (15%) and the [4 + 4] dimer **3a** (85%). Compounds **2a** and **3a** were identified by their ^{1}H NMR spectral data. **2a**: ^{1}H NMR (1:1 CS$_2$/CDCl$_3$, 35 °C) δ 7.25 (d, J = 1.6 Hz, 1 H), 6.30 (d, J = 1.6 Hz, 1 H), 4.76 (s, 2 H), 4.65 (s, 2 H). **3a**: ^{1}H NMR spectrum (CS/CDCl$_3$, 35 °C) agrees with that reported.[13]

Reaction of 5-Methyl-2,3-dimethylene-2,3-dihydrofuran (1b) with ^{3}O$_2$. A quantity of *ca.* 0.4 g (*ca.* 1.75 mmol) of (2,5-dimethyl-3-furyl)methyl benzoate (**4b**), prepared as described previously,[7] was pyrolyzed at 600 °C using the general pyrolysis procedure[6,7] to give a 92% yield of **1b**: ^{1}H NMR (1:1 CS$_2$/CDCl$_3$, −60 °C) δ 5.44 (m, 1 H), 5.07 (m, 1 H), 4.76 (m, 2 H), 4.58 (m, 1 H), 2.00 (s, 3 H). After oxygen was bubbled into the product solution at −78 °C for 3 h and the solution was allowed to warm slowly to room temperature, **1b** was converted quantitatively to the cyclic peroxide **2b** (35%) and the [4 + 4] dimer **3b** (65%). Compounds **2b** and **3b** were identified by their ^{1}H NMR spectral data. **2b**: ^{1}H NMR (1:1 CS$_2$/CDCl$_3$, 35 °C) δ 5.91 (d, J = 0.7 Hz, 1 H), 4.74 (s, 2 H), 4.63 (s, 2 H), 2.23 (d, J = 0.7 Hz, 3 H. **3b**: ^{1}H NMR spectrum (1:1 CS$_2$/CDCl$_3$, 35 °C) agrees with that reported.[7]

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