

dissolved in 4 mL of trifluoroacetic acid containing 0.50 mmol of  $\text{LiO}_2\text{CCF}_3$ . The mixture was equilibrated at 25 °C, and 1 mL of 0.1 M TTFA in trifluoroacetic acid was added. After standing for 5–15 min shielded from light, the mixture was treated with 2 mL of 1.0 M aqueous KI whereupon the solution immediately turned dark, followed by the formation of a large amount of yellow precipitate. After 15 min, the mixture was extracted with 2.0 mL of methylene chloride. Analysis of the unreacted arene and aryl iodide by gas chromatography yielded the relative reactivities as  $k(\text{mesitylene})/k(\text{pseudocumene}) = [\text{mesityl iodide}]/[\text{pseudocumene}]/[\text{pseudocumyl iodide}]/[\text{mesitylene}] = 2.7$ . The ratio was confirmed by carrying out an indirect competition of mesitylene and pseudocumene against *m*-xylene. Thus these relative reactivities of 11.0 and 3.7, respectively, correspond to an indirect competition of 3.0 which is in agreement with the value obtained from the direct competition. These relative reactivities also agree with those obtained from the kinetic measurements in Table VI.

**Electron Spin Resonance Spectral Measurements.** The samples for ESR spectroscopy were prepared in 2-mm (i.d.) Pyrex tubes sealed in vacuo. In a typical procedure a stock solution consisting of 0.050 M TTFA and 0.25 M  $\text{LiO}_2\text{CCF}_3$  and one consisting of 0.050 M hexamethylbenzene were prepared separately. Each was degassed by three freeze-pump-thaw cycles and protected from moisture and air under an argon atmosphere. The sample tube was connected to a Schlenk adaptor, flame dried in vacuo, and filled with argon. A 0.2-mL aliquot of the TTFA was transferred to the tube under argon with the aid of a hypodermic syringe and platinum needle. The contents were frozen and an 0.2-mL aliquot of the hexamethylbenzene solution added under the same conditions and frozen on top of the TTFA layer. The two separate layers were allowed to melt quickly in a bath at -20 °C, mixed, and inserted

into the ESR cavity maintained at -10 °C by a flow of cold nitrogen. The spectra were recorded on a Varian E112 spectrometer equipped with a Harvey-Wells G502 gaussmeter and Hewlett-Packard Model 5248L electronic counter and model 5255A frequency converter.

**Acknowledgment.** We thank Dr. C. Amatore for help with the kinetics treatment and the National Science Foundation for financial support.

**Registry No.** TTFA, 23586-53-0;  $[(\text{CH}_3)_6\text{C}_6\text{Ti}(\text{O}_2\text{CCF}_3)_3]$ , 92397-33-6;  $[(\text{C}_2\text{H}_5)_6\text{C}_6\text{Ti}(\text{O}_2\text{CCF}_3)_3]$ , 92397-34-7;  $[(\text{CH}_3)_5\text{C}_6\text{HTl}(\text{O}_2\text{CCF}_3)_3]$ , 92397-35-8;  $[1,2,3,4-(\text{CH}_3)_4\text{C}_6\text{H}_2\text{Ti}(\text{O}_2\text{CCF}_3)_3]$ , 92397-36-9;  $[1,2,3,5-(\text{CH}_3)_4\text{C}_6\text{H}_2\text{Ti}(\text{O}_2\text{CCF}_3)_3]$ , 92397-37-0;  $[1,2,4,5-(\text{CH}_3)_4\text{C}_6\text{H}_2\text{Ti}(\text{O}_2\text{CCF}_3)_3]$ , 92397-38-1;  $[1,2,3-(\text{CH}_3)_3\text{C}_6\text{H}_3\text{Ti}(\text{O}_2\text{CCF}_3)_3]$ , 92397-39-2;  $[1,2,4-(\text{CH}_3)_3\text{C}_6\text{H}_3\text{Ti}(\text{O}_2\text{CCF}_3)_3]$ , 92397-40-5;  $[1,3,5-(\text{CH}_3)_3\text{C}_6\text{H}_3\text{Ti}(\text{O}_2\text{CCF}_3)_3]$ , 92397-41-6;  $[1,2-(\text{CH}_3)_2\text{C}_6\text{H}_4\text{Ti}(\text{O}_2\text{CCF}_3)_3]$ , 92397-42-7;  $[1,3-(\text{CH}_3)_2\text{C}_6\text{H}_4\text{Ti}(\text{O}_2\text{CCF}_3)_3]$ , 92397-43-8;  $[1,4-(\text{CH}_3)_2\text{C}_6\text{H}_4\text{Ti}(\text{O}_2\text{CCF}_3)_3]$ , 92420-19-4;  $[t\text{-C}_4\text{H}_9\text{C}_6\text{H}_5\text{Ti}(\text{O}_2\text{CCF}_3)_3]$ , 92397-44-9;  $[i\text{-C}_3\text{H}_7\text{C}_6\text{H}_5\text{Ti}(\text{O}_2\text{CCF}_3)_3]$ , 92397-45-0;  $[\text{C}_2\text{H}_5\text{C}_6\text{H}_5\text{Ti}(\text{O}_2\text{CCF}_3)_3]$ , 92397-46-1;  $[\text{CH}_3\text{C}_6\text{H}_5\text{Ti}(\text{O}_2\text{CCF}_3)_3]$ , 92397-47-2;  $[\text{C}_6\text{H}_6\text{Ti}(\text{O}_2\text{CCF}_3)_3]$ , 92397-48-3;  $(\text{CH}_3)_3\text{C}_6\text{CH}_2\text{C}_6(\text{CH}_3)_4\text{H}$ , 92397-51-8;  $(\text{CH}_3)_4\text{C}_6\text{HCH}_2\text{C}_6(\text{CH}_3)_3\text{H}_2$ , 23946-68-1;  $\text{LiO}_2\text{CCF}_3$ , 2923-17-3; hexamethylbenzene cation radical, 34473-51-3; prehnitene dimer cation radical, 92397-49-4; pentamethylbenzene dimer cation radical, 92397-50-7; pentamethylbenzene-*d*, 16032-49-8; durene-2,5-*d*, 1859-01-4; mesitylene-2,4,6-*d*, 38574-14-0; pentamethylbenzyl trifluoroacetate, 35843-80-2; pentamethylphenyl trifluoroacetate, 1683-07-4; mesitylene, 108-67-8; durene, 95-93-2; pentamethylbenzene, 700-12-9; hexamethylbenzene, 87-85-4; deuterium, 7782-39-0.

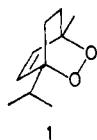
## Mechanism of Endoperoxide Formation. 3. Utilization of the Young and Carlsson Kinetic Techniques<sup>1</sup>

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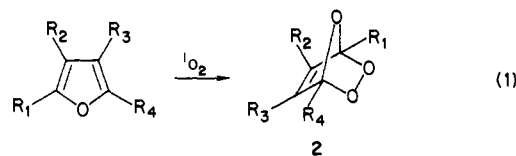
**Abstract:** The rate constants for the additions of singlet oxygen to 39 furans and cyclopentadienes have been determined. The effect of substituents on the observed rate constants was interpreted to suggest that the geometry of singlet oxygen addition is influenced by electron density distributions. The formation of endoperoxides was also compared to the Diels-Alder reaction. The different character of these reactions is compelling evidence for the presence of exciplexes on the reaction surfaces for the formation of endoperoxides.

In 1908 Gutig<sup>2</sup> isolated a compound which was identified in 1912 by Wallach<sup>3</sup> as ascaridole (1). At the time this was the



only structurally established transannular peroxide. The rational synthesis of endoperoxides by 4 + 2 cycloadditions of singlet oxygen and dienes, however, was not accomplished until 1926,

when Dufraisse published his first<sup>4</sup> of many papers in this area.<sup>5</sup> In 1952 Schenck reported that the heterocyclic compound furan<sup>6</sup> and its derivatives (eq 1) also reacted with oxygen in the presence of a sensitizer and light to produce unstable endoperoxides 2.



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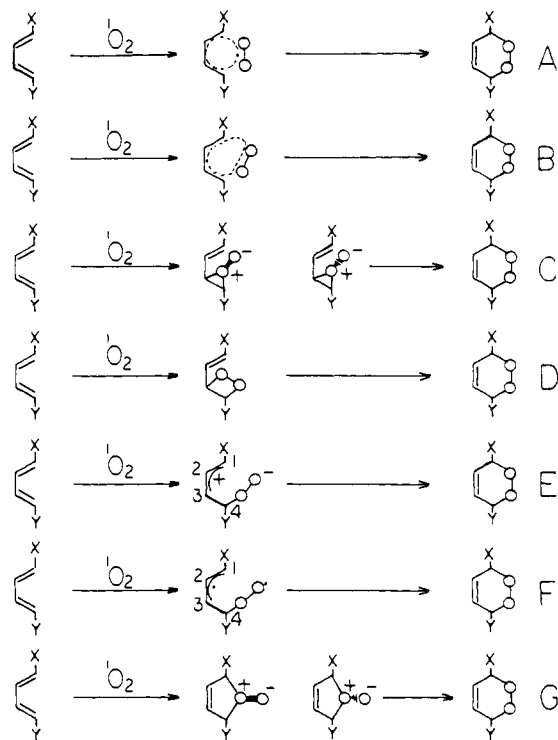


Figure 1. Mechanistic possibilities for the addition of singlet oxygen to 1,3-dienes.

Endoperoxide synthesis has subsequently provided a convenient and important route for the 1,4-functionalization of organic substrates.<sup>7</sup> These reactive compounds can be induced to rearrange,<sup>8</sup> fragment,<sup>9</sup> epoxidize olefins,<sup>10</sup> hydroxylate aromatics,<sup>11</sup> and most recently<sup>12</sup> react with carbonyl compounds to produce 1,2,4-trioxanes.

The formal 4 + 2 cycloaddition reaction of singlet oxygen to 1,3-dienes is the most versatile method for the synthesis of these endoperoxides and is compatible with a large variety of functionality in the diene substrate including latent functionality<sup>13</sup> which can be utilized for subsequent synthetic manipulations. In contrast to the ene, and 2 + 2 cycloaddition, however, the 4 + 2 cycloaddition reaction of singlet oxygen has not received extensive scrutiny.

Despite the lack of experimental evidence, several mechanistic possibilities have been suggested for endoperoxide formation as shown in Figure 1. Mechanisms A and B are concerted 4 + 2 cycloadditions. Mechanism A is a synchronous cycloaddition where both carbon-oxygen bonds are formed to the same extent in the transition state. Mechanism B, on the other hand, is a nonsynchronous cycloaddition where the formation of one carbon-oxygen bond precedes the other. Theoretical,<sup>14</sup> kinetic isotope effect,<sup>15</sup> and substituent effect studies<sup>16</sup> all seem to indicate that

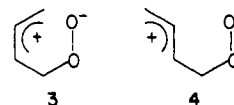
the Diels-Alder reaction proceeds via a nonsynchronous mechanism analogous to mechanism B and suggest that if the singlet oxygen diene reaction is concerted it is also nonsynchronous.

Mechanism C is a nonconcerted reaction proceeding through a distinct intermediate, the *syn*- or *anti*-peroxide. Dewar and Thiel<sup>17</sup> in a MINDO/3 study of the addition of singlet oxygen to 1,3-butadiene have rejected the concerted mechanism and have suggested that a two-step mechanism through a peroxide is actually 9.2 kcal/mol energetically more feasible. Monroe,<sup>18</sup> on the other hand, has rejected the peroxide intermediate on the basis of the insensitivity of the reaction rates to the diene ionization potentials.

The *syn*-peroxide in mechanism C has both the pendant oxygen and the vinyl group on the same face of the epoxide ring, while in its isomer, the *anti*-peroxide, the pendant oxygen and vinyl group are further apart and on opposite faces of the epoxide ring. The calculations of Goddard and Harding<sup>19</sup> showing that the enthalpy of formation of ethylene peroxide is higher than the reported activation barrier for the reaction of propene and singlet oxygen suggest that the *anti*-peroxide may be energetically unobtainable. The transition state leading to the *syn*-peroxide, however, may be lower in energy due to the favorable interaction<sup>20</sup> between the pendant oxygen and the *syn*-vinyl group.

Mechanism D invokes a vinyl-substituted dioxetane as an intermediate. Vinylcyclobutane-cyclohexene rearrangements have been reported,<sup>21</sup> but we are not aware of any vinyl-substituted dioxetane-endoperoxide rearrangement. Rearrangements of endoperoxides to dioxetanes, however, are well documented.<sup>22</sup> Kearns<sup>23</sup> isolated a vinyl-substituted dioxetane, and its isomerization to the endoperoxide was not observed.

Mechanism E involves a zwitterionic intermediate. Rapid rotation in comparison to carbon-oxygen bond formation about bond 3-4 would result in attack from both faces of the allyl cation and nonstereospecific addition of singlet oxygen, contrary to what is experimentally observed. It should be noted that the difficult rotation about the allyl moiety is not necessary to observe nonstereospecific addition if the initial adduct is formed in the closed conformation 3 rather than extended conformation 4.



Mechanism F proceeds through an allylic peroxy biradical. Radicals and zwitterions as intermediates in the ene reactions of singlet oxygen have been suggested to be unlikely because of the ineffectiveness of radical scavengers and the absence of *cis*-*trans* isomerizations and Markovnikov directing effects in these reactions.<sup>24</sup> Biradicals have, however, been seriously considered in Diels-Alder reactions and have been detected on the Diels-Alder energy surfaces for the reactions of halogenated olefins.<sup>25</sup>

Mechanism G is a concerted thermal 4 + 2 cheletropic addition and can be either synchronous or nonsynchronous in character. The [4 + 2] cheletropic reaction has recently been observed in the addition of phosphonium ions to 1,3-dienes<sup>26</sup> but has not been

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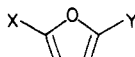
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previously considered as a reaction pathway for endoperoxide formation.<sup>27</sup>

In order to gain additional insight into the mechanism of endoperoxide formation we have kinetically examined the addition of singlet oxygen to 39 substituted furans and cyclopentadienes. The results of these studies are reported here and discussed in light of the mechanisms presented in Figure 1.

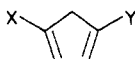
## Results

**Isolation and Identification of Endoperoxides.** The additions of singlet oxygen to furans **5a**, **5d**, **5f**, **5k**, **5l**, **5n**, and **5z** to produce the Schenck endoperoxides<sup>28</sup> **2** were accomplished by irradiating 15–90 mg of the furans in 3:1 CDCl<sub>3</sub>–CH<sub>2</sub>Cl<sub>2</sub> at –78 °C through a sodium nitrite filter<sup>29</sup> utilizing *meso*-tetraphenylporphine as the sensitizer. The spectral data for these endoperoxides (ozonides)



5

- 5a**, X=Y=CH<sub>3</sub>  
**b**, X=Y=*γ*-Bu  
**c**, X=Y=*p*-C<sub>6</sub>H<sub>5</sub>  
**d**, X=Y=H  
**e**, X=Y=Br  
**f**, X=Y=*p*-CO<sub>2</sub>CH<sub>3</sub>  
**g**, X=Y=*p*-CO<sub>2</sub>Et  
**h**, X=Y=*p*-CHO  
**i**, X=H; Y=OCH<sub>3</sub>  
**j**, X=H; Y=*γ*-Bu  
**k**, X=H; Y=CH<sub>3</sub>  
**l**, X=H; Y=Br  
**m**, X=H; Y=CO<sub>2</sub>CH<sub>3</sub>  
**n**, X=H; Y=CO<sub>2</sub>Et  
**o**, X=H; Y=CN  
**p**, X=H; Y=CHO
- 5q**, X=Br; Y=CO<sub>2</sub>Et  
**r**, X=CH<sub>3</sub>; Y=CN  
**s**, X=CH<sub>3</sub>; Y=CHO  
**t**, X=H; Y=*p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>  
**u**, X=H; Y=*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>  
**v**, X=H; Y=C<sub>6</sub>H<sub>5</sub>  
**w**, X=H; Y=*p*-BrC<sub>6</sub>H<sub>4</sub>  
**x**, X=H; Y=*p*-ClC<sub>6</sub>H<sub>4</sub>  
**y**, X=H; Y=*p*-CO<sub>2</sub>EtC<sub>6</sub>H<sub>4</sub>  
**z**, X=H; Y=*p*-CNC<sub>6</sub>H<sub>4</sub>  
**aa**, X=H; Y=*p*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>  
**bb**, X=Y=*p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>  
**cc**, X=Y=*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>  
**dd**, X=Y=*p*-ClC<sub>6</sub>H<sub>4</sub>  
**ee**, X=Y=*p*-BrC<sub>6</sub>H<sub>4</sub>



6

- 6a**, X=Y=*p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>  
**b**, X=Y=*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>  
**c**, X=Y=C<sub>6</sub>H<sub>5</sub>  
**d**, X=Y=*p*-FC<sub>6</sub>H<sub>4</sub>  
**e**, X=Y=*p*-ClC<sub>6</sub>H<sub>4</sub>  
**f**, X=C<sub>6</sub>H<sub>5</sub>; Y=*p*-ClC<sub>6</sub>H<sub>4</sub>  
**g**, X=*p*-ClC<sub>6</sub>H<sub>4</sub>; Y=*p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>  
**h**, X=C<sub>6</sub>H<sub>5</sub>; Y=*p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>

are reported in Table I.<sup>30</sup> Included in Table I are the spectral data for the endoperoxides of **5c** and **5r**, which were taken in pure CH<sub>2</sub>Cl<sub>2</sub>, and the endoperoxide of **5j**, which was produced in 3:1 CDCl<sub>3</sub>–CH<sub>2</sub>Cl<sub>2</sub> using methylene blue as a sensitizer. The spectral data were collected at –70 °C, well below the temperature reported for the dimerization of the endoperoxide of **5a**,<sup>31</sup> and undoubtedly represent the spectral data for the monomeric furan endoperoxides. Consistent with this suggestion is the successful trapping of several of these endoperoxides at low temperatures with diimide.<sup>32</sup> In all cases the ozonides were the only detected products of the photooxygenations.

**Kinetics Studies.** The rate constants for additions of singlet oxygen to furans **5a**–**ee** were measured by utilizing the Carlsson kinetic technique<sup>33</sup> and are reported in Table II. The rate con-

**Table I.** <sup>1</sup>H and <sup>13</sup>C NMR Data at –78 °C for Cyclobutadiene Ozonides<sup>a</sup>

compd	spectral data
<b>2a</b>	<sup>13</sup> C 13.67 (q, <i>J</i> = 129 Hz), 112.59 (b s, with long-range coupling), 134.23 (d, <i>J</i> = 181 Hz); <sup>1</sup> H 1.83 (s, 6 H), 6.38 (s, 2 H)
<b>2d</b>	<sup>13</sup> C 103.88 (ddd, <i>J</i> = 186, 18, 9 Hz), 131.68 (b d, <i>J</i> = 184 Hz); <sup>1</sup> H 6.57 (b, 2 H), 6.61 (b s, 2 H)
<b>2f</b>	<sup>13</sup> C 160.55, 133.12, 108.46, 52.79; <sup>1</sup> H 4.1 (s, 6 H), 6.9 (s, 2 H)
<b>2k</b>	<sup>13</sup> C 13.32 (q, <i>J</i> = 130 Hz), 104.11 (ddd, <i>J</i> = 186, 9, 9 Hz), 112.26 (b s), 131.87 (d, <i>J</i> = 184 Hz), 134.04 (d, <i>J</i> = 181 Hz); <sup>1</sup> H 1.85 (s, 3 H), 6.34 (s, 1 H), 6.38 (d, <i>J</i> = 5.1 Hz, 1 H), 6.48 (d, <i>J</i> = 5.1 Hz, 1 H)
<b>2l</b>	<sup>13</sup> C 103.77, 107.89, 132.38, 136.32; <sup>1</sup> H 6.56 (s, 1 H), 6.66 (d, <i>J</i> = 5.1 Hz, 1 H), 6.70 (d, <i>J</i> = 5.1 Hz, 1 H)
<b>2n</b>	<sup>13</sup> C 13.94 (q, <i>J</i> = 127 Hz), 64.26 (t, <i>J</i> = 147 Hz), 105.12 (ddd, <i>J</i> = 192, 11, 11 Hz), 107.38 (dd, <i>J</i> = 9, 11 Hz), 132.22 (d, <i>J</i> = 188 Hz), 132.93 (d, <i>J</i> = 184 Hz), 161.23 (s); <sup>1</sup> H 1.44 (t, <i>J</i> = 6.6 Hz, 3 H), 4.46 (q, <i>J</i> = 6.6 Hz, 2 H), 6.77 (s, 1 H), 6.79 (d, <i>J</i> = 5.9 Hz, 1 H), 6.86 (d, <i>J</i> = 5.9 Hz, 1 H)
<b>2z</b>	<sup>13</sup> C 105.17, 112.35, 114.49, 118.52, 128.39, 131.87, 132.19, 132.87, 133.14; <sup>1</sup> H 6.78 (s, 1 H), 6.86 (d, <i>J</i> = 5.1 Hz, 1 H), 6.95 (d, <i>J</i> = 5.1 Hz, 1 H), 7.88 (b s, 4 H)
<b>2r</b>	<sup>13</sup> C 13.52 (q, <i>J</i> = 130 Hz), 99.85 (s), 110.18 (s), 115.18 (b s), 132.36 (d, <i>J</i> = 192 Hz), 135.49 (d, <i>J</i> = 192 Hz); <sup>1</sup> H 1.75 (s, 3 H), 5.84 (d, <i>J</i> = 2.2 Hz, 1 H), 5.89 (d, <i>J</i> = 2.2 Hz, 1 H)
<b>2c</b>	<sup>13</sup> C 114.50 (s), 127.32 (s), 127.68 (d, <i>J</i> = 163 Hz), 128.99 (d, <i>J</i> = 164 Hz), 131.46 (d, <i>J</i> = 171 Hz), 133.20 (d, <i>J</i> = 182 Hz); <sup>1</sup> H 5.95 (s, 2 H), 7.52–7.65 (m, 10 H)
<b>2j</b>	<sup>13</sup> C 24.98, 31.51, 104.11, 118.55, 131.51, 132.11; <sup>1</sup> H 1.16 (s, 9 H), 6.42 (s, 1 H), 6.53 (d, <i>J</i> = 5.1 Hz, 1 H), 6.62 (d, <i>J</i> = 5.1 Hz, 1 H)

<sup>a</sup> <sup>1</sup>H and <sup>13</sup>C values are given in δ.

**Table II.** Carlsson Second-Order Rate Constants for the Reactions of Singlet Oxygen with Furans<sup>a</sup>

compd <sup>b,c</sup>	<i>k</i> × 10 <sup>-8</sup> M <sup>-1</sup> s <sup>-1</sup>	compd	<i>k</i> × 10 <sup>-8</sup> M <sup>-1</sup> s <sup>-1</sup>
<b>5a</b>	1.3	<b>5p</b>	0.00051
<b>5b</b>	0.94	<b>5q</b>	0.00015
<b>5c</b>	0.52	<b>5r</b>	0.0015
<b>5d</b>	0.12	<b>5s</b>	0.0053
<b>5e</b>	0.020	<b>5t</b>	0.37
<b>5f</b>	0.00020	<b>5u</b>	0.24
<b>5g</b>	0.00045	<b>5v</b>	0.18
<b>5h</b>	0.024	<b>5w</b>	0.10
<b>5i</b>	1.2	<b>5x</b>	0.10
<b>5j</b>	0.61	<b>5y</b>	0.07
<b>5k</b>	0.62	<b>5z</b>	0.04
<b>5l</b>	0.0067	<b>5aa</b>	0.24
<b>5m</b>	0.00085	<b>5bb</b>	0.99
<b>5n</b>	0.0013	<b>5cc</b>	0.70
<b>5o</b>	0.00011	<b>5dd</b>	0.29
		<b>5ee</b>	0.25

<sup>a</sup> Rates measured in methylene chloride. <sup>b</sup> *k*<sub>ox</sub>(rubrene) = 3.3 × 10<sup>7</sup> L mol<sup>-1</sup> s<sup>-1</sup>. <sup>c</sup> Rates are accurate to ±10%.

stants are derived by examining the ability of the furans to quench the self-sensitized photooxidation of rubrene. (See the Experimental Section for the details of the kinetic determination.) The rates determined in this manner reflect both physical (*k*<sub>q</sub>) and chemical (*k*<sub>r</sub>) quenching of singlet oxygen. The physical quenching component of the rates of reactions of furans **5a** and **5c**, however, have been shown to be negligible.<sup>34</sup>

The final concentrations of rubrene were determined spectrophotometrically at 440 nm after concomitant photolysis of solutions with and without added furan. The concentrations of rubrene in solutions containing **5b**, **5f**, and **5z** continued to decrease slowly

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**Table III.** Stern-Volmer Data for the Quenching of Singlet Excited Rubrene<sup>a,b</sup>

compd	concn range, M	$k_q\tau$
<b>5aa</b>	0-4.7 × 10 <sup>-3</sup>	1645.7
<b>5h</b>	0-2.74 × 10 <sup>-2</sup>	153.1
<b>5f</b>	0-1.13	no quenching
<b>5z</b>	0-1 × 10 <sup>-2</sup>	no quenching
<b>5p</b>	0-0.51	no quenching

<sup>a</sup>λ (excitation) 461 nm; λ (emission) 577 nm. <sup>b</sup>Measured in CH<sub>2</sub>-Cl<sub>2</sub>.

**Table IV.** Young Second-Order Rate Constants for the Reactions of Singlet Oxygen with Furans<sup>a</sup>

compd	$k \times 10^{-8}$ M <sup>-1</sup> s <sup>-1</sup>	compd	$k \times 10^{-8}$ M <sup>-1</sup> s <sup>-1</sup>
<b>5a</b>	2.6	<b>5i</b>	1.6
<b>5b</b>	1.5	<b>5k</b>	0.84
<b>5c</b>	0.70	<b>5j</b>	0.64
<b>5d</b>	0.14		

<sup>a</sup>Rates were measured in methylene chloride using 1,3-diphenylisobenzofuran.

even after the photolysis was complete. No other furans exhibited this phenomenon. The rate constants reported in Table II were determined by utilizing the concentrations of rubrene determined immediately after photolysis and before the slow thermal decreases in rubrene concentrations could occur.<sup>35</sup> The dark additions of these endoperoxides, derived from polymer bound Rose Bengal sensitized photooxidations, to solutions of rubrene also resulted in dramatic decreases in the optical density at 440 nm, implicating a bimolecular reaction. A cycloreversion to produce singlet oxygen, a process which has been documented for **5c**,<sup>36</sup> cannot be responsible for this observation since cycloreversions of these endoperoxides under the reaction conditions do not occur. Instead, a single oxygen atom donation of the type discovered by Adam<sup>37</sup> and Saito<sup>11</sup> which resulted in the oxidations of olefins and aromatic compounds is the most likely candidate for these bimolecular processes.

The high furan concentrations (3.26 × 10<sup>-4</sup> M for **5a** to 2.26 M for **5q**) necessary to compete with rubrene for singlet oxygen demanded that we examine the possibility that differential quenching of rubrene excited states contributes to the observed furan reactivity differences. Quenching of rubrene excited states would lead to deceptively high rate constants since two channels become available for quenching rubrene photoperoxide formation, direct reaction with and quenching of sensitized singlet oxygen formation.

Fluorescence quenching was examined since recent evidence<sup>38,39</sup> demonstrated that substantial amounts of singlet oxygen is produced by quenching both singlet and triplet excited rubrene. Stern-Volmer examinations of rubrene emission at 577 nm for a select number of furans verify that fluorescence quenching is unimportant except for furans **5h** and **5aa**. These data are reported in Table III. Furan **5aa** with a *p*-nitrophenyl ring and the dialdehyde **5h** react as rapidly as 2-(*p*-methylphenyl)furan (**5u**), and dibromide **5e**, respectively. These observations are inconsistent with anticipated substituent effects but easily rationalized on the basis of the ability of these furans to quench rubrene fluorescence. Electrochemical studies<sup>40</sup> also reveal that **5h** and **5aa** are more easily reduced than any other furan examined in Table II.

To exclude the possibility that rubrene triplet quenching is occurring we have measured the rates of singlet oxygen addition to several furans using a different kinetic technique, the Young<sup>41</sup>

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**Table V.** Carlsson Second-Order Rate Constants for the Reactions of Singlet Oxygen with Cyclopentadienes<sup>a</sup>

compd <sup>b,c</sup>	$k \times 10^{-8}$ M <sup>-1</sup> s <sup>-1</sup>	compd	$k \times 10^{-8}$ M <sup>-1</sup> s <sup>-1</sup>
<b>6a</b>	1.29	<b>6e</b>	0.65
<b>6b</b>	1.01	<b>6f</b>	0.68
<b>6c</b>	0.87	<b>6g</b>	0.88
<b>6d</b>	0.76	<b>6h</b>	1.10

<sup>a</sup>Rates were measured in methylene chloride. <sup>b</sup> $k_{ox}$  (rubrene) = 3.3 × 10<sup>7</sup> L mol<sup>-1</sup> s<sup>-1</sup>. <sup>c</sup>Rates are accurate to ±10%.

**Table VI.** Comparison of the Experimental Rate of Endoperoxide Formation to the Calculated Mechanistic Extreme Values

compd series ( $k_1, k_2, k_3$ )	$(k_1 k_3)^{1/2} \times 10^{-5}$	$(k_1 + k_3)^{1/2} \times 10^{-5}$	$k_2 \times 10^{-5}$ <sup>a</sup>
<b>5d, 5k, 5a</b>	390	710	620
<b>5d, 5j, 5b</b>	340	530	610
<b>5d, 5v, 5c</b>	250	320	180
<b>5d, 5i, 5e</b>	49	70	6.7
<b>5d, 5m, 5f</b>	4.9	60	0.85
<b>5d, 5n, 5g</b>	7.3	60	1.3

<sup>a</sup>Experimental values for unsymmetrical furans, M<sup>-1</sup> s<sup>-1</sup>.

method, and a different sensitizer, mesoporphyrin IX dimethyl ester. The Young kinetic technique utilizes 1,3-diphenylisobenzofuran (DPBF) as the singlet oxygen acceptor and follows its substrate-induced inhibition by monitoring its fluorescence as a function of time. (See the Experimental Section for the details of the kinetic determination.) The results from the use of this kinetic method are reported in Table IV.

Acceptable rates for the reaction of furan **5j** were obtained by keeping its concentration and conversion low. These measures were necessary since the endoperoxide derived from **5j** or a product of its decomposition quenched the DPBF fluorescence. Thomas and Foote<sup>42</sup> observed a similar phenomenon in a study of the singlet oxygenation of phenols in which a cross-conjugated ketone product quenched their fluorescent probe. The other furans that were examined did not exhibit this behavior. The rates for furans **5e**, **5h**, **5m**, and **5p**, however, were not obtainable by this technique due to their rapid quenching of the DPBF fluorescence. Similar results were obtained in an attempt to use 2,5-diphenylfuran as the singlet oxygen acceptor.

The experimentally indistinguishable rates generated by the Young and Carlsson techniques for the limited number of furans reported in Table IV mitigates against triplet sensitizer quenching as being responsible for the observed selectivity differences.

We have also measured the rate constants for additions of singlet oxygen to 1,4-substituted cyclopentadienes **6a-h**. These data, which were collected by the Carlsson method, are reported in Table V.

## Discussion

The mechanistic possibilities for endoperoxide formation as presented in Figure 1 can be classified either as synchronous, those reactions in which the two new carbon-oxygen bonds are formed to the same extent, or nonsynchronous, in which the timing of formation of these bonds in the rate-determining transition state are different.

The question of synchronization in the Diels-Alder reaction has been extensively examined.<sup>43</sup> Dewar<sup>44</sup> has convincingly argued for an asynchronous Diels-Alder transition state based on a kinetic argument. Application of this kinetic argument to furan endoperoxide formations provides valuable insight into the mechanisms of these reactions. This kinetic technique can be conveniently illustrated for the reactions of furan (**5d**) (rate constant =  $k_1$ ),

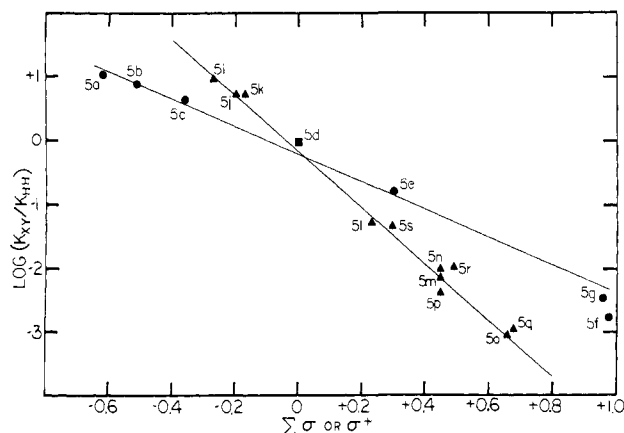
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**Figure 2.** Hammett linear free-energy relationships for the addition of singlet oxygen to symmetrical ( $\sigma^+$ ) and unsymmetrical ( $\sigma$ ) furans.<sup>75,76</sup>

2-carbethoxyfuran (**5n**) (rate constant =  $k_2$ ), and 2,5-dicarbethoxyfuran (**5g**) (rate constant =  $k_3$ ). Three distinct situations can exist: (1) The reactions of all three furans are synchronous. The ratios of rate constants  $k_1/k_2$  and  $k_2/k_3$  should consequently be identical, and the rate constant for furan **5n** should be equal to the geometric mean of the two other rate constants (eq 2).

$$k_2 = (k_1 k_3)^{1/2} \quad (2)$$

(2) One or more of the furans can react to form an intermediate in which only one of the carbon-oxygen bonds is intact. In this event  $k_2$  will be equal to the arithmetic mean of  $k_1$  and  $k_3$  (eq 3).

$$k_2 = (k_1 + k_3)/2 \quad (3)$$

(3) One or more of the furans can react to form the endoperoxide via a concerted but asynchronous mechanism. In this final situation  $k_2$  will have a value between the extremes given by eq 2 and 3.

The experimentally determined rate constants for unsymmetrical endoperoxide formations ( $k_2$  in Table VI) do not conform to situation 1, 2, or 3, and these values actually fall outside the range defined by eq 2 and 3. These results are in dramatic contrast to those observed for Diels-Alder reactions<sup>43-45</sup> and strongly underscore the different character of these ostensibly topologically similar reactions.

These different reaction characters are also evident in an examination of the activation enthalpies for the two reactions. Endoperoxide formations, like many reactions of singlet oxygen,<sup>46</sup> have enthalpies of activation near zero.<sup>34a,47</sup> Diels-Alder reactions on the other hand have very large activation enthalpies.<sup>48</sup> Gorman<sup>46</sup> has suggested that the near zero activation enthalpies observed for singlet oxygen ene reactions are indicative of the reversible formation of an exciplex on the reaction coordinate. The similar activation parameters observed for the ene and the 4 + 2 cycloaddition reactions of singlet oxygen, and the unique character of the 4 + 2 cycloaddition in comparison to Diels-Alder reactions which do not generally involve charge-transfer intermediates,<sup>49</sup> are strongly suggestive that exciplexes are on the reaction coordinates for furan endoperoxide formations.

If endoperoxide formation occurs by collapse of an exciplex and if exciplex formation is fast relative to endoperoxide formation, the rate of disappearance of singlet oxygen is given by eq 4 where

$$-d[{}^1\text{O}_2]/dt = k_2 K [{}^1\text{O}_2][\text{furan}] \quad (4)$$

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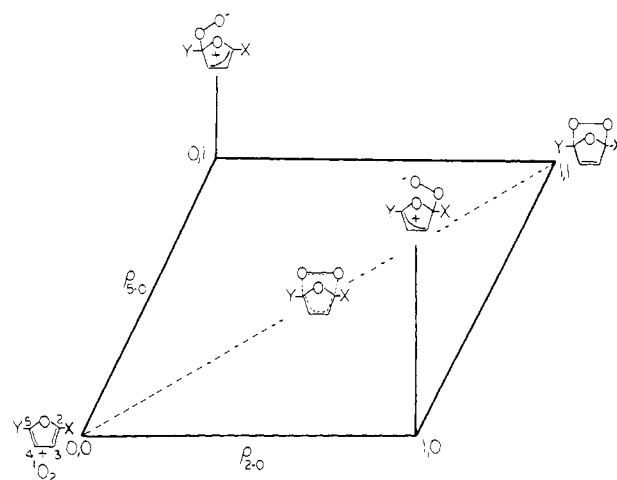
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**Figure 3.** More O'Ferrall-Jencks diagram for the addition of singlet oxygen to furans.

$K$  is the equilibrium constant for exciplex formation. A reaction which obeys such a rate expression should follow a linear free-energy relationship. The reaction constant will be a composite value which is a measure of the susceptibility of the equilibrium constant and  $k_2$  to substituent effects (eq 5).

$$\log \frac{k_{\text{obsd}}(\text{X})}{k_{\text{obsd}}(\text{H})} = \log \frac{k_{2\text{X}}}{k_{2\text{H}}} + \log \frac{K_{\text{X}}}{K_{\text{H}}} = \sigma_{\text{X}}(\rho_{\text{K}} + \rho_{\text{K}}) \quad (5)$$

Examination of the kinetic data in Table II in terms of the Hammett LFER (Figure 2) surprisingly demonstrates that two distinct linear correlations are observed. Singlet oxygen exhibits an enhanced selectivity for unsymmetrically substituted ( $\rho = -4.5$ ,  $r = -0.996$ ) in comparison to symmetrically substituted furans. The symmetrical furans are also better correlated to  $\Sigma\sigma^+$  ( $\rho^+ = -2.2$ ,  $r = -0.996$ ) than  $\Sigma\sigma$  ( $\rho = -2.6$ ,  $r = -0.975$ ), reminiscent of several Diels-Alder reactions.<sup>49</sup> The aryl-substituted furans **5t-ee** exhibit a similar phenomenon. In this case the selectivity differences of singlet oxygen for these furans are suppressed in comparison to the directly substituted furans but two distinct linear correlations are again observed.

The dual correlation result can be understood within the framework of an exciplex mechanism if one makes the reasonable assumption that the geometry of the exciplex and its transition state for collapse to the endoperoxide are different for the symmetrical and unsymmetrical furans. Different electronic demands by the geometrically different exciplexes and/or the transition states for their collapse would result in the observation of two distinct linear free-energy relationships. Irie<sup>50</sup> has demonstrated that the rates of quenching of (*R*)-(-)-1,1'-binaphthyl fluorescence by (*S*)-(-)- and (*R*)-(+)-*N,N*-dimethyl-1-phenylethylamines are different. This observation is a manifestation of the subtle dependence of geometry on the kinetics and presumably thermodynamics of exciplex formations.

The dual correlation result could also be a manifestation of partitioning differences of the exciplex along the reaction and quenching coordinates in the two series of compounds. The absence of a detectable quenching component in the reactions of **5a** and **5c** does not mean that quenching in **5n** and **5g** does not dominate their reactivity.<sup>51</sup>

In addition to these two possibilities, different solvation requirements for the structurally different transition states and exciplexes can also contribute to the observed singlet oxygen selectivity difference. This suggestion seems to conflict with the often observed lack of solvent effects on singlet oxygen reactions.<sup>52</sup> This is not, however, necessarily the case. Two transition states may have different solvation requirements but yet be insensitive to changes in solvent. This is especially the case for reactions which

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have very small activation barriers such as singlet oxygen reactions. The dramatic dependence of furan substitution pattern on the geometry and kinetics of exciplex formation is undoubtedly a result of the extreme polarizability and electrophilicity of singlet oxygen.

Our mechanistic suggestion for this reaction can be most conveniently visualized by examination of a More O'Ferrall-Jencks<sup>53</sup> diagram (Figure 3). The two structural axes in this diagram are the C<sub>2</sub>-oxygen and C<sub>5</sub>-oxygen bond orders. The two asynchronous extrema are represented as zwitterions (mechanism E), although our data cannot rule out the possibility that these extrema can be best represented as diradicals (mechanism F) or perepoxides (mechanism C).

The transition states and exciplexes for reactions of the symmetrical furans lie on the diagonal between the starting materials and endoperoxide (ozonide) products. The geometries of the transition states in these reactions are symmetrical ( $\rho_{5-0} = \rho_{2-0}$ ), and consequently these reactions are concerted 1,4-cycloadditions (mechanism A). We see no need at this time to suggest a synchronous cheletropic transition state (mechanism G) for these reactions but cannot rigorously exclude it. The positions of the exciplexes and transition states on the diagonal are a function of the total exergonicity of product formations as suggested by the Hammond postulate.

The transition states for the reactions of the unsymmetrical furans are found on a trajectory<sup>53</sup> connecting the two nonconcerted extrema and containing the topological point which represent the transition state for the parent furan **5d**.

## Conclusion

The kinetic work reported in this paper has demonstrated that symmetrical and unsymmetrical furans exhibit different selectivities toward singlet oxygen. We have suggested that this selectivity difference could be due to (1) different electronic demands, (2) different solvation requirements, and (3) partitioning differences of the structurally different exciplexes along reaction and quenching coordinates.

Despite our lack of information on the relative contributions of these factors to the magnitude of the selectivity difference, we have also suggested that different approach geometries of singlet oxygen to the symmetrical and unsymmetrical furans are the underlying reason for the startling observation.

Dewar<sup>54</sup> has pointed out that synchronous two-bond processes are in general prohibited since their activation energies are expected to be approximately twice that of two-step reactions. Reactions such as synchronous endoperoxide formations which have very small activation barriers, however, are anticipated exceptions to this generalization.

## Experimental Section

Gas chromatographic analyses were carried out on a Perkin-Elmer Sigma 3B utilizing a column packed with 5% SE30 on Chromosorb P. All melting points were determined with a Thomas-Hoover capillary melting point apparatus and are uncorrected. Proton, carbon, and oxygen NMR spectra were obtained on a JEOL FX270 at 270, 67.83, and 36.54 MHz, respectively. The proton and carbon chemical shift are referenced to Me<sub>4</sub>Si and the oxygen chemical shifts by substitution to water. Mass spectra were obtained on a VG-ZAB-1F by electron impact. Infrared spectra were taken on a Beckman Microlab 600 spectrometer. Kinetic studies were completed on a Hitachi 100-80 spectrophotometer and a Perkin-Elmer MPF-2A spectrofluorometer.

Furan (**5d**), 2-methylfuran (**5k**), 2-methoxyfuran (**5i**), 2,5-dimethylfuran (**5a**), furfural (**5p**), 5-bromofuroic acid, 2-carbomethoxyfuran (**5m**), and 5-methylfurfural (**5s**) were all obtained commercially (Aldrich) and purified immediately before use. Furans **5b**,<sup>55</sup> **5c**,<sup>56</sup> **5e**,<sup>57</sup> **5f**,<sup>58</sup> **5g**,<sup>58</sup> **5j**,<sup>59</sup> **5n**,<sup>60</sup> **5o**,<sup>61</sup> **5q**,<sup>60</sup> **5r**,<sup>62</sup> **5t**,<sup>63</sup> **5u**,<sup>63</sup> **5v**,<sup>63</sup> **5w**,<sup>63</sup> **5x**,<sup>63</sup> **5y**,<sup>64</sup> **5aa**,<sup>65</sup> **5bb**,<sup>66</sup> **5cc**,<sup>56</sup>

**5dd**,<sup>56</sup> and **5ee**<sup>67</sup> were all produced by literature procedures. Cyclopentadienes **6a**,<sup>68</sup> **6c**,<sup>69</sup> **6e**,<sup>70</sup> **6f**,<sup>71</sup> and **6h**<sup>71</sup> were also produced by their literature procedures. All compounds gave satisfactory spectral and physical data.

**2,5-Furandicarboxaldehyde (5b)**. Chromium trioxide, 7.11 g (0.071 mol), was added to a magnetically stirred solution of 11.7 mL (0.145 mol) of pyridine in 100 mL of methylene chloride. The flask was stoppered with a drying tube, and the deep burgundy solution was stirred for 15 min at room temperature. At the end of this period, a solution of 1.5 g (0.012 mol) of (hydroxymethyl)furfural in 10 mL of CH<sub>2</sub>Cl<sub>2</sub> was added in one portion. A black tarlike deposit separated immediately. After being stirred an additional 15 min at room temperature the solution was decanted from the residue, and the methylene chloride was removed. A black residue was obtained. The residue was taken up in ether, filtered to remove insoluble chromium salts, and then washed with 5% NaOH and saturated sodium chloride. Evaporation of the solvent gave 1 g of crude dialdehyde which was recrystallized from carbon tetrachloride. Sublimation gave 0.9 g of pure furan dicarboxaldehyde: <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 179.22, 154.16, 119.34; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 9.87 (s, 2 H), 7.47 (s, 2 H); <sup>17</sup>O NMR (CH<sub>2</sub>Cl<sub>2</sub>) δ 231, 502; mp 108–110 °C (lit.<sup>72</sup> mp 109–110 °C); yield 68%.

**2-Bromofuran (5l)**. A mixture of 12 g (0.0628 mol) of 5-bromofuroic acid, 45 mL of quinoline, and 3.0 g of copper powder was placed in a 100-mL round-bottom flask attached to a 40-cm Vigreux column. The mixture was heated with a woods metal bath, and the condensate at the top of the column was collected at 87–93 °C. The condensate was purified by fractional distillation to give 7.5 g (81% yield) of 2-bromofuran: bp 92–93 °C (580 mmHg) [lit.<sup>57</sup> bp 52–54 °C (180 mmHg)]; <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 144.29, 121.95, 112.46, 111.18; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.39 (b s, 1 H), 6.34 (b s, 1 H), 6.27 (b s, 1 H).

**2-(p-Cyanophenyl)furan (5z)**. A mixture of 6.65 g (0.0298 mol) of 2-(p-bromophenyl)furan and 3 g (0.33 mol) of copper cyanide in 30 mL of quinoline was refluxed in a woods metal bath for 2 h. The solution was then cooled and treated with 100 mL of dilute HCl. The solid was filtered and washed with water, dilute NaOH, and finally water. The crude product was passed through a 2.5-cm diameter, 38-cm-long silica gel column with ether/*n*-hexane (20/80) as elutant. Three grams (59% yield) of pure product was obtained: <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 151.96, 143.66, 134.61, 132.55, 123.93, 118.93, 112.24, 110.28, 108.16; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.72 (d, *J* = 8.8 Hz, 2 H), 7.63 (d, *J* = 8.8 Hz, 2 H), 7.53 (d, *J* = 1.5 Hz, 1 H), 6.8 (d, *J* = 3.6 Hz, 1 H), 6.52 (dd, *J* = 1.5, 3.6 Hz, 1 H); mp 64–65 °C (lit.<sup>73</sup> 65–66 °C).

**1,4-Bis(p-fluorophenyl)-1,3-cyclopentadiene (6d)** was synthesized by the method of Drake and Adams.<sup>69</sup> <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 163.64, 160.00, 144.40, 132.25, 132.19, 127.79, 126.38, 126.27, 115.72, 115.42, 41.10; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.47–7.52 (m, 4 H), 6.99–7.06 (m, 4 H), 6.83 (s, 2 H), 3.71 (s, 2 H); high-resolution mass spectrum, calcd for C<sub>17</sub>H<sub>12</sub>F<sub>2</sub>, *m/e* (M<sup>+</sup>) 254.0908, found *m/e* (M<sup>+</sup>) 254.0915; mp 157–158 °C.

**1,4-Bis(p-methylphenyl)-1,3-cyclopentadiene (6b)** was synthesized by the method of Drake and Adams.<sup>69</sup> <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 145.16 (s), 136.34 (s), 133.36 (s), 129.31 (d, *J* = 133 Hz), 127.33 (d, *J* = 134 Hz), 124.72 (d, *J* = 153 Hz), 40.83 (t, *J* = 125 Hz), 14.82 (q, *J* = 122 Hz); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.55 (d, *J* = 8.1 Hz, 4 H), 7.14 (d, *J* = 8.1 Hz, 4 H), 6.87 (s, 2 H), 3.73 (s, 2 H), 2.34 (s, 6 H); IR (cm<sup>-1</sup>) 3010, 2900, 2940, 1500, 1490; high-resolution mass spectrum, calcd for C<sub>29</sub>H<sub>18</sub>, *m/e* (M<sup>+</sup>) 246.1409, found *m/e* (M<sup>+</sup>) 246.1406; mp 190.5–192 °C; Yield 15.4%.

**1-(p-Methoxyphenyl)-4-(p-chlorophenyl)-1,3-cyclopentadiene (6g)** was synthesized by the method of Drake and Adams.<sup>69</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.25–7.5 (m, 6 H), 6.85–6.9 (m, 2 H), 6.8 (m, 2 H), 3.85 (s, 3 H), 3.70 (s, 2 H); high-resolution mass spectrum, calcd for C<sub>18</sub>H<sub>15</sub>ClO, *m/e* (M<sup>+</sup>) 282.0813, found *m/e* (M<sup>+</sup>) 282.0815; mp 206–207.5 °C.

**Kinetics Studies. The Carlsson Technique.** Three-milliliter solutions of rubrene in methylene chloride with and without a furan substrate were

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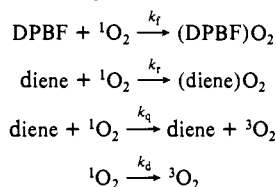
irradiated on a merry-go-round for 4.2-5 min. The 456-nm line of the 450-W medium-pressure mercury vapor Hanovia lamp was isolated by a  $\text{CuCl}_2/\text{CaCl}_2$  filter solution. The samples were open to the air during irradiation to allow oxygen to diffuse in to replace the oxygen consumed during the reaction. The optical densities of the samples at 440 nm before and after irradiation were measured on a Hitachi 100-80 spectrophotometer. All solutions were shielded from the light as much as possible during preparation and after irradiation. The absorbance of rubrene was adjusted to be approximately 1.82-1.86 at the beginning of the experiment. The furan concentrations were adjusted so that about 25% of the rubrene was consumed. While 50% of the rubrene was consumed in cuvettes with no furan. Reaction rate constants were calculated from

$$k_A = \frac{k_{\text{ox}}([R]_f^{\text{D}} - [R]_f^{\text{O}}) + k_d \ln ([R]_f^{\text{D}}/[R]_f^{\text{O}})}{[D] \ln ([R]/[R]_f^{\text{D}})}$$

where  $k_{\text{ox}} = 3.3 \times 10^7 \text{ s}^{-1}$  and is the rate constant for the reaction of singlet oxygen with rubrene in methylene chloride.  $[R]$  is the initial rubrene concentration and  $[R]_f^{\text{D}}$  and  $[R]_f^{\text{O}}$  are the final rubrene concentrations in the presence and absence of diene (furan).  $[D]$  is the furan concentration and  $k_d$  is the rate of decay of singlet oxygen in methylene chloride ( $1 \times 10^4 \text{ s}^{-1}$ ).<sup>74-76</sup>

Two kinetic determinations were made for each compound. Each kinetic run resulted in two rate constants. If there was not good agreement among these four numbers ( $\pm 10\%$ ) an additional kinetic determination was conducted.

**Young's Kinetic Technique.** The rate of disappearance of diphenylisobenzofuran (DPBF) due to reaction with singlet oxygen is monitored at its emission wavelength of 460 nm. The kinetic scheme for the disappearance of DPBF in the presence of diene substrates is given by



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(76) The precipitation of furan **5f** during kinetic runs would be expected to lead to a slower than expected rate constant. Indeed, examination of Figure 2 reveals a negative deviation of the point for **5f** from the Hammett linear regression line.

The steady-state treatment for the disappearance of DPBF gives

$$-\frac{d[\text{DPBF}]}{dt} = K \left[ \frac{k_f[\text{DPBF}]}{k_r[\text{DPBF}] + k_r[\text{diene}] + k_q[\text{diene}] + k_d} \right]$$

The fluorescent acceptor (DPBF) is present in extremely low concentrations so that its disappearance is cleanly first order.

$$-\frac{d[\text{DPBF}]}{dt} = K \left[ \frac{k_f[\text{DPBF}]}{k_r[\text{diene}] + k_q[\text{diene}] + k_d} \right]$$

Under conditions in which the diene does not appreciably react a plot of log fluorescence vs. time is linear with slope  $S$ . A plot of  $S_0/S_D$  where

$$S = K \left[ \frac{k_f}{k_r[\text{diene}] + k_q[\text{diene}] + k_d} \right]$$

$S_0$  is the slope in the absence and  $S_D$  in the presence of diene vs. diene concentration has a slope of  $(k_r + k_q)/k_d$ .

The Young kinetic studies were carried out with a Perkin-Elmer MPF-2A spectrophotometer. The photolyzing light absorbed by the dye was produced by a Sylvania 750 Q/Cl tungsten-halogen lamp operated at 36-45 vs. This irradiation source was placed at right angles to the excitation (418 nm) and emission (460 nm) light paths and focused through a Corning 3-68 filter (cutoff 540 nm). Eight stock solutions with a variety of diene concentrations were utilized for each determination. At least two determinations were made for each compound, and additional measurements were made if good agreement ( $\pm 10\%$ ) was not obtained.

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**Registry No.** **5a**, 625-86-5; **5b**, 4789-40-6; **5c**, 955-83-9; **5d**, 110-00-9; **5e**, 32460-00-7; **5f**, 4282-32-0; **5g**, 53662-83-2; **5h**, 823-82-5; **5i**, 25414-22-6; **5j**, 7040-43-9; **5k**, 534-22-5; **5l**, 584-12-3; **5m**, 611-13-2; **5n**, 614-99-3; **5o**, 617-90-3; **5p**, 98-01-1; **5q**, 6132-37-2; **5r**, 13714-86-8; **5s**, 620-02-0; **5t**, 17113-31-4; **5u**, 17113-32-5; **5v**, 17113-33-6; **5w**, 14297-34-8; **5x**, 17221-37-3; **5y**, 35461-96-2; **5z**, 64468-77-5; **5aa**, 28123-72-0; **5bb**, 1230-48-4; **5cc**, 57196-75-5; **5dd**, 36710-36-8; **5ee**, 36710-35-7; **5fa**, 13693-26-0; **5fb**, 89088-41-5; **5fc**, 4982-34-7; **5fd**, 89088-42-6; **5fe**, 58864-06-5; **5ff**, 80109-14-4; **5fg**, 89088-43-7; **5fh**, 80109-11-1;  $\text{O}_2$ , 7782-44-7.

## Oxetane: The First X-ray Analysis of a Nonsubstituted Four-Membered Ring

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**Abstract:** Oxetane ( $\text{C}_3\text{H}_6\text{O}$ ), melting point 174 K, was crystallized on a four-circle diffractometer equipped with a nitrogen gas stream low temperature device. Its structure has been determined by means of single-crystal X-ray analysis at 90 and 140 K. The crystals are orthorhombic, with space group  $Pnam$  and unit cell dimensions  $a = 8.620$  (4) Å,  $b = 6.384$  (15) Å,  $c = 6.038$  (13) Å,  $V = 332.3$  Å<sup>3</sup> at 90 K and  $a = 8.657$  (1) Å,  $b = 6.401$  (5) Å,  $c = 6.010$  (5) Å,  $V = 333.0$  Å<sup>3</sup> at 140 K,  $Z = 4$ . Three-dimensional diffractometer data were refined by least-squares methods to final  $R$  values of 3.8% (90 K data) and 4.1% (140 K data). In the crystal the oxetane four-membered ring has exact  $C_2$  symmetry and this ring was found to be nonplanar. The angle of pucker is 10.7 (1)° (90 K data) and 8.7 (2)° (140 K data), respectively. The endocyclic C-O bond length, 1.460 (1) Å at 90 K, is unusually large for a C-O single bond.

From the present knowledge of the stereochemistry of cyclobutane and its heterocyclic analogues it is generally accepted that

the cyclobutane ring exists in a puckered form with a puckering angle of approximately 30°, whereas oxetane is planar.<sup>1</sup> The