ther cyclization of **22** leads to **14a** and then to **14** (vide supra). However, even in retrospect it is surprising that the boat-like contour implied in **22** with its severe 1,4-interaction would be of lower energy than the chair conformation shown in the hypothetical **21**. Clearly, the level of predictability of the stereochemical outcome of the 2 + 2 + 2 annulation is not yet satisfactory.

Additional explorations of such multiple annulations both from a general methodological sense and for purposes of a total synthesis of aflavinine are in progress.

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Registry No. **2**, 59357-02-7; (*E*)-**7**, 89105-98-6; (*Z*)-**7**, 89163-40-6; **8**, 75420-43-8; **9**, 75337-05-2; **10**, 89162-97-0; **10** TMS enol ether, 89088-84-6; **11**, 89088-85-7; **12**, 89088-86-8; **13**, 89088-87-9; **14**, 89088-88-0; **15**, 89088-89-1; **16**, 89088-90-4; **17**, 89088-91-5; lithium dimethylcuprate, 15681-48-8; dimethyl(methylene)ammonium chloride, 30354-18-8; $ClSiMe_3$, 75-77-4; $ClCO_2Me$, 79-22-1.

Supplementary Material Available: Atomic coordinates, bond angles, and bond lengths for compound 14 (5 pages). Ordering information is given on any current masthead page.

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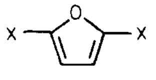
Mechanism of Endoperoxide Formation. 2. Possibility of Exciplexes on the Reaction Coordinates

Summary: The additions of singlet oxygen to phenyl-substituted furans are reported. Different selectivities for the symmetrical and unsymmetrical furans were observed. An exciplex intermediate on the reaction surface is also considered.

Sir: The chemistry of peroxides and the mechanism of their formation have been under investigation for more than 100 years. The rediscovery in the mid 1960s by Foote and Wexler[1] and Corey and Taylor[2] that singlet oxygen was the culprit in many molecular oxidations led to a resurgence in the study of peroxidation. A large number of these studies have focused on the mechanism of the "ene" reaction[3] while the mechanism of endoperoxide formation has been ignored.

We recently[4] reported the rates of additions of singlet oxygen to a series of directly substituted symmetrical (**1**) and unsymmetrical furans (**2**). The selectivity difference of singlet oxygen for these furans and an examination of that data in terms of the Hammett linear free energy relationship led us to suggest that the electronic properties of the furans influenced the geometry of singlet oxygen approach. In this report we (1) present the rates of additions of singlet oxygen to 20 phenyl- and diphenyl-substituted furans and cyclopentadienes, (2) present additional kinetic data collected for furans **1** and **2** with the Young[5] kinetic technique, and (3) discuss these results and the possibility of an exciplex intermediate.



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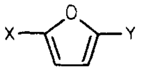

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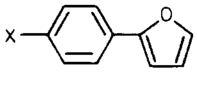
The rates of singlet oxygen additions to furans (series **3** and **4**) and cyclopentadienes (series **5**) were measured by the method of Carlsson[6] and are reported in Table I. The rates for the furans (both series **3** and **4**) are also displayed in Figure 1 by utilizing the Hammett LFER formalism.



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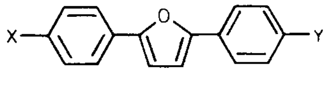

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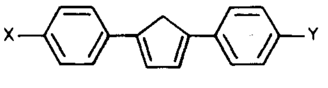

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Examination of these data reveals that the insertion of the phenyl ring between the furan ring and the substituent produces a dramatic attenuation of the effect of substituents on the rates of endoperoxide formations. The rate constant variations for symmetrical furans **1** (a factor of 2800)[4] and unsymmetrical furans **2** (a factor of 10 000)[4] are much larger than those that observed for series **3**, **4**, or **5**. The Hammett reaction constant measured for the unsymmetrical series **3** ($\rho = -1.00$), however, is more negative than that obtained for the symmetrical series **4** ($\rho = -0.55$), consistent with the results obtained earlier[4] for the directly substituted furans.

The Carlsson singlet oxygen kinetic method is a dangerous one-point nondifferential technique which responds to total inhibition of the reaction with no internal check to determine if sensitizer quenching is occurring. To rule out the possibility that rubrene quenching is responsible for the different selectivities of single oxygen toward **1** and **2**, we have measured the rates of single oxygen addition to several furans using a different kinetic technique, the Young[5] method, and a different sensitizer, mesoporphyrin IX dimethyl ester. Examination of these data[7] presented in Table II reveals that the symmetrical furans demonstrate a different selectivity ($\rho^+ = -2.02$, $r = 0.999$) than the asymmetrically substituted furans ($\rho = -4.03$, $r = 0.994$) toward singlet oxygen. The experimentally indistinguishable LFER plots generated by the Young and Carlsson techniques and the similar selectivities exhibited by the phenyl and directly substituted furans mitigates against sensitizer quenching as being responsible for the observed selectivity differences.

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[1] (a) Foote, C. S.; Wexler, S. *J. Am. Chem. Soc.* **1964**, *86*, 3879. (b) Foote, C. S.; Wexler, S. *Ibid.* **1964**, *86*, 3880.

[2] Corey, E. J.; Taylor, W. C.; *J. Am. Chem. Soc.* **1964**, *86*, 3881.

[3] (a) Foote, C. S. *Acc. Chem. Res.* **1968**, *1*, 104. (b) Gollnick, K. *Adv. Photochem.* **1968**, *6*, 1. (c) Kearns, D. R. *Chem. Rev.* **1971**, *71*, 395. (d) Orfanopoulous, M.; Stephenson, L. M. *J. Am. Chem. Soc.* **1980**, *102*, 1417.

[4] Clennan, E. L.; Mehrsheikh-Mohammadi, M. E. *J. Am. Chem. Soc.* **1983**, *105*, 5932.

[5] Young, R. H.; Wehry, R. H.; Martin, R. I. *J. Am. Chem. Soc.* **1971**, *93*, 5774.

[6] Carlsson, D. J.; Suprunchuk, T.; Wiles, D. M. *Can. J. Chem.* **1974**, *52*, 3728.

[7] Furfural, 2-carbomethoxyfuran, and 2,5-dibromofuran all quench diphenylisobenzofuran (DPBF) fluorescence, making their rates unobtainable by using this fluorescence probe. Foote[8] reported similar problems using Young's method with phenols in which the cross-conjugated ketone product quenched diphenylfuran (DPF) fluorescence.

[8] Foote, C. S.; Thomas, M. J. *Photochem. Photobiol.* **1978**, *27*, 683.

Table I. Rate Constants for the Additions of Singlet Oxygen to Furans and Cyclopentadienes

series	compound	$10^{-8}k$,[a,b] L mol^{-1} s^{-1}	series	compound	$10^{-8}k$,[a,b] L mol^{-1} s^{-1}
3	X = OCH_3	0.37	4	X = Y = Cl	0.29
3	X = CH_3	0.24	4	X = Y = Br	0.25
3	X = H	0.18	5	X = Y = OCH_3	1.29
3	X = Br	0.10	5	X = Y = CH_3	1.01
3	X = Cl	0.10	5	X = Y = H	0.87
3	X = CO_2Et	0.07	5	X = Y = F	0.76
3	X = CN	0.04	5	X = Y = Cl	0.65
4	X = Y = OCH_3	0.99	5	X = Cl, Y = H	0.68
4	X = Y = CH_3	0.70	5	X = Cl, Y = OCH_3	0.88
4	X = Y = H	0.52	5	X = H, Y = OCH_3	1.10

[a] Measured in methylene chloride. [b] Rate constants are good to ±10%.

Table II. Rate Constants for the Additions of Singlet Oxygen to Directly Substituted Furans 1 and 2[a]

series	compound	$10^{-8}k$,[b,c] L mol^{-1} s^{-1}
1	X = CH_3	2.6
1	X = *t*-Bu	1.5
1	X = Ph	0.70
1	X = H	0.14
2	X = H, Y = OCH_3	1.6
2	X = H, Y = CH_3	0.84
2	X = H, Y = *t*-Bu	0.64

[a] Measured by utilizing the Young method.[5] [b] Measured in CH_2Cl_2 by using mesoporphyrin IX dimethyl ester as sensitizer. [c] Diphenylisobenzofuran (DPBF) was used as the fluorescer.

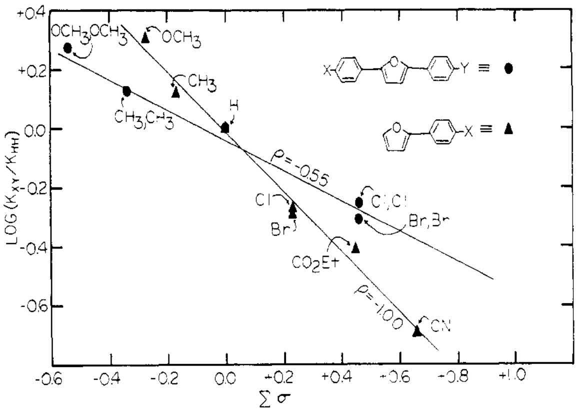

Figure 1. The Hammett LFER plots for the 2-phenyl- and 2,5-diphenyl-substituted furans.

Several authors[9] have suggested that exciplexes are commonly encountered intermediates on singlet oxygen reaction surfaces (see eq 1). The ostensibly depressed rate

$$\text{furan} + {}^1O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} F\cdots O_2 \xrightarrow{k_2} FO_2 \qquad (1)$$

constants observed for the unsymmetrical furans bearing electron-withdrawing groups can be readily understood within the framework of the exciplex mechanism. If such exciplexes are intermediates on the reaction surface, the rate constants we have measured are given by eq 2, where

$$k_{\text{obsd}} = Kk_2 \qquad (2)$$

K is the equilibrium constant for exciplex formation and k_2 is the rate of collapse of the exciplex to form the product. A deceptively small k_{obsd} (See eq 2) and larger negative Hammett reaction constant would be expected[10] if one assumes that the equilibrium constants (K) for the unsymmetrical furans bearing the electron-withdrawing groups are smaller than expected on the basis of electronic considerations alone (perhaps due to the unsymmetrical geometry of the exciplex).[11] Experimental evidence that the thermodynamics of exciplex formations are indeed a function of exciplex geometry is obtained from the work of Irie.[12] Significant differences in the rates of quenching of (*R*)-(−)-1,1′-binaphthyl fluorescence by (*S*)-(−)- and (*R*)-(+)-*N*,*N*-dimethyl-1-phenylethylamines were suggested to demonstrate the subtle geometric dependence on exciplex formation, and presumably thermodynamics.

In summary, we have demonstrated that (1) selectivity differences for symmetrical and unsymmetrical furans are not restricted to compounds in which the substituent is directly attached to the furan nucleus, (2) differential quenching of the sensitizer cannot be utilized to explain the selectivity differences, and (3) compatible with but not demanded by our experimental results are the involvement of symmetrical and unsymmetrical exciplexes. Different electronic demand and solvation requirements can also be invoked as contributing factors which produce the observed selectivity variance.

Excited state complexes were first observed by Forster in 1954;[13] however, their involvement in singlet oxygen chemistry has only been suggested recently.[9] We agree with the earlier suggestion[9] of the ubiquitous nature of these exciplexes in singlet oxygen reactions and we hope to provide additional evidence for the population of these intermediates in the near future.

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(9) (a) Hurst, J. R.; Schuster, G. B. *J. Am. Chem. Soc.* **1982**, *104*, 6854. (b) Gorman, A. A.; Gould, I. R.; Hamblett, I. *Ibid* **1982**, *104*, 7098. (c) Gollnick, K.; Griesbeck, A. *Tetrahedron Lett.* **1983**, *24*, 3303.

(10) Decomposition of the endoperoxides to reform the furans and singlet oxygen has been ruled out as a contributor to the deceptively small k_{obsd}. Solutions of several of the endoperoxides at −78 °C in an NMR probe did not produce the furan on warming to room temperature.

(11) Such an argument can also be invoked to rationalize the increased rates of asymmetrically substituted furans bearing electron-donating groups.

(12) Yorozu, T.; Hayashi, K.; Irie, M. *J. Am. Chem. Soc.* **1981**, *103*, 5480.

(13) Forster, Th.; Kasper, K. *Z. Physik. Chem.* (*Wiesbaden*) **1954**, *1*, 275.