in the effectively hypervalent molecules, CLi_5 and CLi_6, are not associated with carbon, which remains content with its normal octet. Instead the "extra" electrons contribute to Li–Li bonding and help to start building a metallic "cage" around the central atom. The nature of this central atom is secondary, and hyperlithiation should be a remarkably general phenomenon that can involve all first[1] and second row[7] as well as higher elements. Among metals, lithium is not unique. Experimental examples are known for sodium[8] and for higher alkali metals.[9]

Expressed colloquially, lithium is a "sticky" element and binds to many molecules, especially if another lithium already is present. Thus, CH_4 forms only weak complexes with Li or LiH; these are not considered here. In contrast, CH_3Li binds both Li and LiH much more strongly: CH_3Li_2 (**3**, C_s)[10] and CH_4Li_2 (**4**, C_s) result, both have pentacoordinate carbons. By replacing additional hydrogens by lithiums sequentially CH_2Li_3 (**5**, C_{2v}), $CHLi_4$ (**6**, C_{3v}), CH_3Li_3 (**7**, C_s), CH_2Li_4 (**8**, C_{2v}), and $CHLi_5$ (**9**, C_{4v}) are obtained. These complete the series culminating in **1** and **2**, and most have structures (Chart I) derived from trigonal bipyramidal and octahedral symmetries, respectively. However, **7** is best regarded as a $CH_3Li_2^+Li^-$ ion pair complex (judging from the Mulliken populations)[6] with the negatively charged lithium quite far from carbon. Similar examples have been described, e.g., $OLi_3^+Li^-$ and $NLi_4^+Li^-$,[1,11] but these generally are higher in energy than isomers with higher coordination at the central atom. We stress that many hypermetalated species are expected to be fluxional molecules; some alternative geometries may be only a little higher in energy.

An increasing number of experimental observations point to the existence of such hyperlithiated carbon compounds. Lagow's group[5a,12] obtained a solid product, formulated as "$(CLi_4)_n$", from the reaction of CCl_4 with lithium atoms. This "CLi_4" could also be CLi_5, CLi_6, etc., which would also react with D_2O to give CD_4. Many hyperstoichiometric ions like $CH_3Li_2^+$,[5c] $CH_2Li_3^+$, $CHLi_4^+$, CLi_5^+,[5] $C_2Li_7^+$, $C_2Li_8^+$, $C_3Li_{11}^+$, and $C_3Li_{12}^+$ have been detected by means of flash vaporization mass spectrometry by these workers;[13] at least some of these probably are derived from the corresponding neutral species.

Wu's group at Jülich generated CLi_3 and CLi_4 in the gas phase,[14a] and more recently CLi_5 and very probably CLi_6[14b] by allowing lithium atoms at high temperatures to diffuse through graphite membranes. The ionization potentials and energies of these hyperlithiated molecules, when they can be measured, will provide quantitative data for comparison with computational results.

Although their stoichiometries are startling, hypermetalated molecules are not hypervalent in the strict sense. The extra electrons beyond the usual octet are involved with metal–metal bonding rather than with interactions of the metals with the central atoms.

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Addition of Singlet Oxygen to Conjugated Dienes. The Mechanism of Endoperoxide Formation

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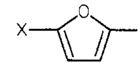
The reactions of singlet oxygen with olefins to produce "ene" type products have undergone extensive scrutiny by a large number of investigators.[1] These studies have led to the development of a significant number of synthetic methods[2] and mechanistic tools.[3] In noticeable contrast to these investigations, the mechanistic details of the reactions of singlet oxygen with 1,3-dienes have received very little attention. Despite the lack of extensive information several mechanisms have been advanced for the formation of endoperoxides. These include a concerted Diels–Alder reaction,[4] a perepoxide intermediate,[5] and the rapid reversible formation of an exciplex followed by collapse to product.[6]

In order to develop a greater insight into the mechanism of this reaction, we have measured the rate constants for the interactions of singlet oxygen with 15 substituted furans[7] **1**. These data are presented in Table I. Careful examination of this table reveals the startling fact that the symmetrically substituted furans react at approximately the same rate as their unsymmetrical analogues.[8] In view of the established electrophilic character of singlet oxygen[1a] this experimental observation cannot be reconciled by a symmetrical mechanism for both sets of compounds.



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Additional insight into the mechanisms can be obtained by examining the kinetic data utilizing the Hammett LFER approach (Figure 1). Two distinct linear correlations are observed. The asymmetrically substituted furans fall on a line characterized by a large negative reaction constant ($\rho = -4.5$, $r = -0.996$). The symmetrical furans, on the other hand, are better correlated to $\sum\sigma^+$ ($\rho^+ = -2.2$, $r = -0.996$) than $\sum\sigma$ ($\rho = -2.6$, $r = -0.975$)[9] and exhibit a much smaller reaction constant.[10] These data support the postulate that the furans have two transition states available for reaction. The linear free energy relationship that describes this situation is given by eq 1. This equation relates

$$\log (k_{XY}/k_{HH}) = \log [(k_{sym} + k_{unsym})/k_{HH}] = \log (10^{\rho_{sym}\Sigma\sigma} + 10^{\rho_{unsym}\Sigma\sigma}) \quad (1)$$

the nonlinear relative reactivities to the different electronic de-

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(8) An exception to this observation is the enhanced reactivity of the 2,5-dialdehyde **9**. Studies are underway to unravel this apparent discrepancy. In particular quenching of the excited state of rubrene with **9** may provide an explanation.

(9) Several Diels–Alder reactions have been shown to correlate better to σ^+ than σ. Sauer, J.; Sustmann, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 779.

(10) Dimethylfuran **4** and diphenylfuran **6** have been shown to quench singlet oxygen by chemical reaction rather than by energy transfer. The observation of a linear correlation that includes both these compounds implies that all the rate constants in Table I are measures of chemical reactivity. (a) Gorman, A. A.; Lovering, G.; Rodgers, M. A. J. *J. Am. Chem. Soc.* **1979**, *101* 3050. (b) Usui, Y.; Kamogawa, K. *Photochem. Photobiol.* **1974**, *19*, 245.

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Table I. Second-Order Rate Constants[a] for the Reactions of Singlet Oxygen with 2-Substituted and Symmetrical 2,5-Disubstituted Furans

compd	$k \times 10^{-8}$,[b,c] s^{-1}	compd	$k \times 10^{-8}$,[b,c] s^{-1}
X = Y = CH_3 (**4**)	1.3	X = H; Y = OCH_3 (**11**)	1.2
X = Y = *t*-Bu (**5**)	0.94	X = H; Y = CH_3 (**12**)	0.62
X = Y = Ph (**6**)	0.52	X = H; Y = Br (**13**)	0.0067
X = Y = H (**7**)	0.12	X = H; Y = CHO (**14**)	0.00051
X = Y = Br (**8**)	0.020	X = H; Y = CO_2Et (**15**)	0.0013
X = Y = CHO (**9**)	0.024	X = H; Y = CN (**16**)	0.00011
X = Y = CO_2Et (**10**)	0.00045	X = CH_3; Y = CHO (**17**)	0.0053
		X = Br; Y = CO_2Et (**18**)	0.00015

[a] Rates measured in methylene chloride by the method of Carlsson.[7] [b] k_{ox}(rubrene) = 3.3×10^7 L mol^{-1} s^{-1}. [c] Rates are accurate to ±10%.

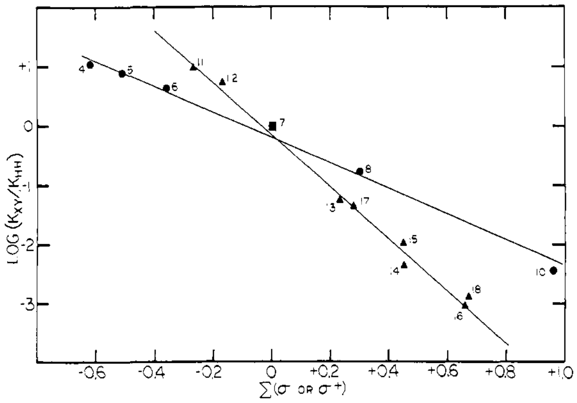


Figure 1. Hammett LFER plots for the additions of singlet oxygen to symmetric (σ^+) and unsymmetrical furans (σ).

mands (ρ_{sym} and ρ_{unsym}) in the two different transition states. When $k_{sym} \gg k_{unsym}$, as is the case for the symmetrical furans, one of the exponential terms can be neglected and the relative rates are successfully correlated to the sum of the substituent constants. We suggest that the asymmetric electron density distribution in furans **11**–**18** induces the formation of an asymmetric transition state while the symmetrical furans react via a synchronous Diels–Alder transition state.[11]

It might be argued for the symmetrically substituted compounds that the absence of a substantial kinetic effect upon introduction of the second substituent requires an unsymmetrical mechanism in which the second double bond is not involved. However, we point out that in the "early" transition states of these exothermic reactions a strong resonance interaction with the second double bond would be expected. This expectation is verified with the measurements of the rates of singlet oxygen addition to unsymmetrical furans **17** (X = CH_3, Y = CHO) and **18** (X = Br, Y = CO_2Et). The effects of the second substituents are additive, and both compounds fall on the correlation line determined by the unsymmetrical furans. The absence of a large kinetic effect of the second identical substituent forces us to postulate different geometries of approach with different electronic requirements. The success of this treatment for endoperoxide formations is undoubtedly a result of the extreme electrophilic character of singlet oxygen and its susceptibility to subtle electron density changes in organic substrates.

The structures of the transition states in both the synchronous and asymmetric reactions can be conveniently analyzed with the aid of a More O'Ferrall–Jencks diagram[12] as shown in Figure 2. The two structural axes in this diagram are the C_2–oxygen and C_5–oxygen bond orders. The two nonconcerted extrema are represented as zwitterions although our data cannot rule out the possibility that these extrema can be best represented as diradicals **2** or as perepoxides **3**. The free energy contours for a given reaction cannot be added at this time to the diagram because of the lack of sufficient experimental data; however, some generalizations can be made. The transition states for the synchronous reactions lie on the diagonal between the starting materials and the endoperoxide products. The positions of these transition states on the diagonal are a function of the total exergonicity of product formations as suggested by the Hammond postulate. In contrast, the transition states of the reactions of unsymmetrical furans in which substituent X is varied and Y = H are found on a trajectory[13] connecting the two nonconcerted extrema and containing the topological point that represents the transition state of the parent furan (X = Y = H).

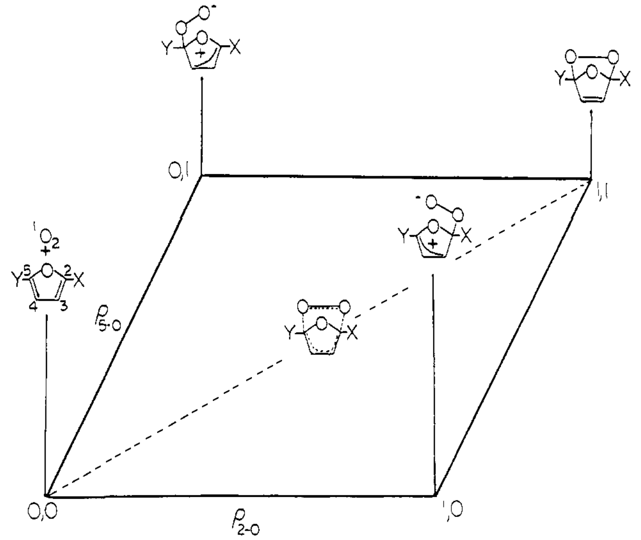
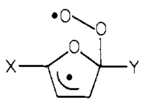


Figure 2. Energy surface for the conversions of furans into ozonides.



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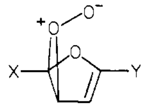

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McIver's rules[14] and MINDO/3[15] calculations predict an unsymmetrical transition state in the Diels–Alder reaction between ethylene and butadiene. Neither the starting material, 1,3-butadiene, nor the product, cyclohexene, have a plane of symmetry,[16] and there seems to be no compelling reason to require this symmetry element in the transition state. The symmetrical furans, however, and the endoperoxide products (ozonides) have planes of symmetry that can be conserved on the reaction surface by requiring a symmetrical transition state.

Pulsed-laser photolysis studies to determine activation barriers and the effect of solvents on the rates of these reactions are currently under investigation and will be reported at a future data.

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Registry No. **4**, 625-86-5; **5**, 4789-40-6; **6**, 955-83-9; **7**, 110-00-9; **8**, 32460-00-7; **9**, 823-82-5; **10**, 53662-83-2; **11**, 25414-22-6; **12**, 534-22-5; **13**, 584-12-3; **14**, 98-01-1; **15**, 614-99-3; **16**, 617-90-3; **17**, 620-02-0; **18**, 6132-37-2; oxygen, 7782-44-7.

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