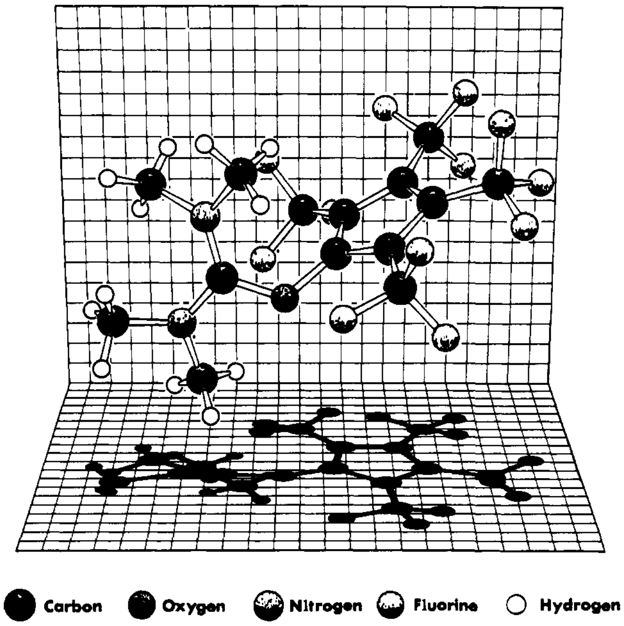


Figure 1. Perspective drawing[7] of the carbonyl ylide **1**.

crystallographic analysis.[6] Figure 1 illustrates the solid-state structure observed for this carbonyl ylide. As would be expected the central COC angle of 121.1 (5)° is close to a trigonal angle of 120° and much larger than the central CSC angle (104°) in thione ylide **2**.

The two carbon–oxygen bonds are quite different in length with a distance of 134.8 (8) pm at the onium terminus and 142.2 (7) pm at the ylide terminus. These distances suggest a partial C–O π bond between the carbonium center and oxygen while the oxygen cyclopentadienylide bond appears to be a single σ bond. This differs from the thione ylide **2** in which both C–S bonds were the same length (intermediate between a CS double and single bond[4a]). This model for bonding in the carbonyl ylide is also supported by the orientation of the two termini as depicted in Figure 2.

The excised ylidic system from **1** is presented in Figure 2 as a view along the bisector of the COC angle with the ylide terminus to the right. The ylide terminus is inclined to the central COC plane with an angle of 55.4° while the urea plane is twisted only 25.4°. The termini are twisted in a conrotated fashion to adopt a sterically least hindered orientation. This orientation is noticeably closer to a planar geometry than the related thione ylide, **2**. Along with the short onium terminus-oxygen bond this geometry suggests a greater participation of an oxygen vs. sulfur lone pair in stabilizing the carbonium center. The stabilization of the anionic center seems to be handled completely within the cyclopentadienyl system.

It is instructive to compare the structure observed for **1** with that calculated by Houk, Griffin, and co-workers for some models of the "push–pull" carbonyl ylides.[3a] For the highly perturbed ylides bearing two amino and two cyano substituents a nonplanar structure in which the ylide terminus is twisted by 90° is preferred. The calculated COC angle is 117° and the C–O bonds are very similar to those observed for **1**. Overall there is good agreement of the calculated structure with that observed for **1**.

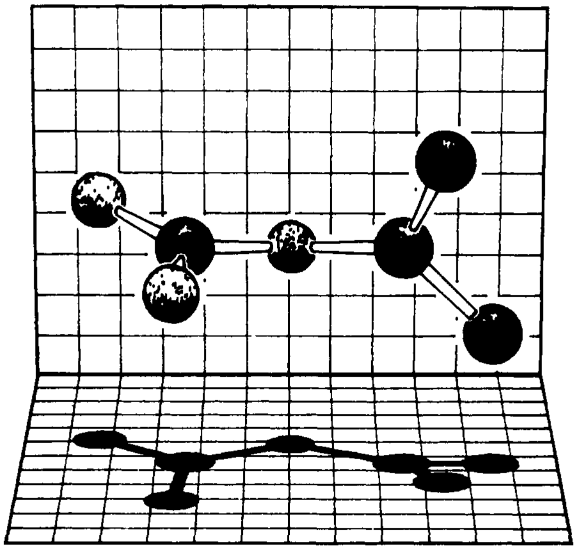


Figure 2. Perspective drawing of the central COC system in **1**.

Finally, we have been able to synthesize other carbonyl ylides through the use of DTTC as a carbene precursor. The chemistry and solution structure of these ylides is currently under study and will be reported in future articles.

Acknowledgment is made to the National Science Foundation (NSF CHE 81-04980) for its support of this work. We also thank Dr. Scott R. Wilson for his work on the X-ray structure of **1** and Dr. Egbert Keller, Kristallographisches Institut der Universität Freiburg, for providing a copy of the SCHAKAL molecular graphics program from which KANVAS was written.

Supplementary Material Available: A complete description of the X-ray crystallographic structure determination of **1** and tables of positional and thermal parameters (5 pages). Ordering information is given on any current masthead page.

---

[6] The crystal data were as follows: $C_{14}H_{12}N_2OF_{12}$, monoclinic, space group $P2_1/c$, a = 995.1 (2) pm, b = 1320.0 (3) pm, c = 1399.3 (3) pm, β = 104.78°, Z = 4, D_c = 1.690 g/cm^{-3}, crystal size 0.10 × 0.15 × 0.18 mm. With 965 reflections of intensity greater than 3 σ, the structure was solved by direct methods (MULTAN 80) and standard difference Fourier techniques. The final R factors were R = 0.0405 and R_w = 0.0409.

[7] The perspective drawings were made with the E. *K*eller–A. J. *A*rduengo *N*eodimensional *V*iews of *A*toms with *S*hadows (KANVAS) program. The back and shadowed planes are at right angles and bear a 50-pm grid. The lighting source is at infinity so that the shadow size is meaningful.

CLi_5, CLi_6, and the Related Effectively Hypervalent First-Row Molecules, $CLi_{5-n}H_n$ and $CLi_{6-n}H_n$[1]

Paul von Ragué Schleyer,* Ernst-Ulrich Würthwein,
Elmar Kaufmann, and Timothy Clark

Institut für Organische Chemie
der Friedrich-Alexander-Universität Erlangen-Nürnberg
D-8520 Erlangen, Federal Republic of Germany

John A. Pople

Department of Chemistry, Carnegie-Mellon University
Pittsburgh, Pennsylvania 15235

Received March 15, 1983

The octet rule predicts the stoichiometries of first-row hydrides remarkably well. Thus, "CH_5" and "CH_6" are only likely to exist as weak complexes between methane and a hydrogen atom or a hydrogen molecule. Surprisingly, when lithium is involved instead of hydrogen, the situation is completely different. Both trigonal-bipyramidal CLi_5 (**1**, D_{3h}) and octahedral CLi_6 (**2**, O_h) are indicated by ab initio calculations using the 3-21G basis set and full geometry optimization[2] to be highly stable toward all possible

---

[1] Part 2 of a series on effectively hypervalent molecules. (a) Part 1: Schleyer, P. v. R.; Würthwein, E.-U.; Pople, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 5839. (b) Schleyer, P. v. R., plenary lecture presented at the Fourth International Congress of Quantum Chemistry, Uppsala, Sweden, June, 1982. Löwdin, P.-O.; Pullman, A., Eds., "New Horizons of Quantum Chemistry"; Reidel: Dordrecht, 1983; pp 95–105.

[2] The GAUSSIAN80 series of programs and the standard basis sets and MP2 routines were used (Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; Schlegel, H. B.; DeFrees, D. J.; Topiol, S.; Kahn, L. R.; Pople, J. A. *QCPE* **1981**, *13*, 406).

0002-7863/83/1505-5930$01.50/0 © 1983 American Chemical Society

Table I. Dissociation Energies (3-21G//3-21G (MP2/6-31G*//3-21G)) (kcal/mol) of $CLi_{5-n}H_n$ and $CLi_{6-n}H_n$ Species

	species lost			
species	Li	Li_2	HLi	H_2
CH_4Li (C_{3v})	0.1 (0.1)		54.0	64.1 (67.2)
CH_3Li_2 (**3**, C_s)	21.4 (21.5)	33.3 (46.2)	65.9 (62.3)	76.0 (97.9)
CH_2Li_3 (**5**, C_{2v})	32.8	34.1	65.6 (74.7)	65.0
$CHLi_4$ (**6**, C_{3v})	45.0	48.8	68.6	
CLi_5 (**1**, D_{3h})	54.1	61.6		
CH_5Li (C_{3v})			4.6 (5.6)	24.2 (19.5)
CH_4Li_2 (**4**, C_s)	9.8[a] (22.7)	5.9 (8.5)	46.0 (46.1)	67.7 (56.0)
CH_3Li_3 (**7**, C_s)	14.4[a]	31.9	74.0	82.7
CH_2Li_4 (**8**, C_{2v})	11.8[a]	40.6	69.7	65.5
$CHLi_5$ (**9**, C_{4v})	15.3[a]	56.4	72.6	
CLi_6 (**2**, O_h)	14.2[a]	65.2		

[a] These values are underestimated at noncorrelated levels due to differences in spin multiplicity of reactants and products.

Table II. Absolute Energies of Hyperlithiated and Reference Molecules[a]

species	3-21G	6-31G*// 3-21G	MP2/6-31G*// 3-21G
CH_4Li (C_{3v})	−47.358 48	−47.626 53	−47.763 92
CH_3Li_2 (**3**)	−54.168 17	−54.476 76	−54.627 66
CH_2Li_3 (**5**)	−60.958 51	−61.309 27	
$CHLi_4$ (**6**)	−67.771 15		
CLi_5 (**1**)	−74.599 34		
CH_5Li (C_{3v})	−47.914 00	−48.181 73	−48.337 25
CH_4Li_2 (**4**)	−54.755 61	−55.067 04	−55.231 41
CH_3Li_3 (**7**)	−61.572 64	−61.929 03	
CH_2Li_4 (**8**)	−68.358 81	−68.754 69	
$CHLi_5$ (**9**)	−75.177 05		
CLi_6 (**2**)	−82.003 44		
CH_4	−39.976 88	−40.195 17	−40.332 42
H	−0.496 20	−0.499 28	−0.499 28
H_2	−1.122 96	−1.126 81	−1.144 14
Li	−7.381 51	−7.431 37	−7.431 37
HLi	−7.929 84	−7.980 87	−7.995 96
Li_2	−14.769 25	−14.866 92	−14.885 45

[a] For the energies of other reference molecules, see ref 3–5.

dissociation reactions (Table I). For example, loss of a lithium atom from **1** (eq 1) or loss of Li_2 from **2** (eq 2) are both highly endothermic.

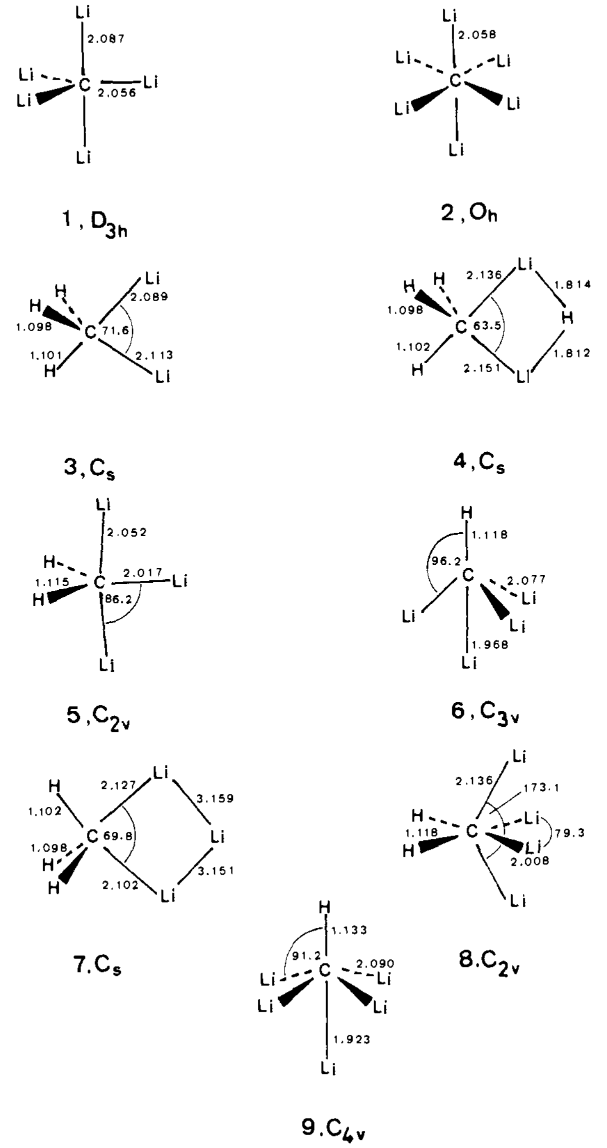
$$CLi_5\ (\mathbf{1}) \rightarrow CLi_4\ (T_d) + Li \quad +54.1\ \text{kcal/mol (3-21G//3-21G)} \quad (1)$$

$$CLi_6\ (\mathbf{2}) \rightarrow CLi_4\ (T_d) + Li_2 \quad +65.2\ \text{kcal/mol (3-21G//3-21G)} \quad (2)$$

The related series of molecules $CLi_{5-n}H_n$ (n = 0–4) and $CLi_{6-n}H_n$ (n = 0–5) behave similarly (Table I). A number of geometries were explored for each species; the lowest energy structures (with bond lengths and angles) are illustrated in Chart I. Single point calculations with the larger 6-31G* basis set including correlation corrections at the MP2 level were performed on the smaller species. Total energies are listed in Table II.

How is it possible for CLi_5, CLi_6, and the other hyperlithiated molecules to violate the maximum stoichiometry expected on the basis of the octet rule? The high symmetries and the C–Li distances in **1** and **2**, only slightly longer than those found for CH_3Li (2.001 Å) or CLi_4 (1.929 Å) at 3-21G,[3] show that all the lithiums are bound to carbon. Indeed, all these molecules exhibit the bonding that we find to be general for such *hypermetalated* species, e.g., OLi_3 and OLi_4.[1] CLi_6 (**1**) is an illustrative example. In octahedral symmetry, the occupancy of the 10 valence electrons is $(3a_{1g})^2(2t_{1u})^6(4a_{1g})^2$. The $3a_{1g}$ and $2t_{1u}$ orbitals are analogous to the valence orbitals found in T_d or O_h symmetry. If only four valence orbitals are occupied, C–Li bonding results, but the Li–Li contacts are antibonding. This is shown, e.g., by the overlap populations, for the octet molecules CLi_4 (T_d),[4] CLi_5^+ (D_{3h}),[5] and CLi_6^{2+} (O_h).[5] However, the HOMO in the 10 valence electron species, CLi_6, is totally symmetric ($4a_{1g}$) and possesses an additional spherical node. The Li–Li bonding character of this $4a_{1g}$ orbital is revealed by the positive overlap populations and the large coefficients on the lithium atoms. The 12 pair-wise bonding contacts between adjacent lithium atoms in CLi_6 contribute significant stabilization to the whole system.

Chart I



The indicated charges (3-21G) on carbon[6] do not increase appreciably as more lithium atoms are added: CLi_4 (C, −0.81), CLi_5 (C, −0.81), and CLi_6 (C, −0.93). Thus, the extra electrons

---

(3) Whiteside, R. A.; Frisch, M. J.; Binkley, J. S.; DeFrees, D. J.; Schlegel, H. B.; Raghavachari, K.; Pople, J. A. "Carnegie-Mellon Quantum Chemistry Archive", 2nd ed.; Carnegie-Mellon Press: Pittsburgh, PA, 1981.

(4) Würthwein, E.-U.; Sen, K. D.; Pople, J. A.; Schleyer, P. v. R. *Inorg. Chem.* **1983**, *22*, 0000.

(5) (a) Jemmis, E. D.; Chandrasekhar, J.; Würthwein, E.-U.; Schleyer, P. v. R.; Chinn, J. W., J.; Landro, F. J.; Lagow, R. J.; Luke, B.; Pople, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 4275. (b) Schleyer, P. v. R.; Tidor, B.; Jemmis, E. D.; Chandrasekhar, J.; Würthwein, E.-U.; Kos, A. J.; Luke, B. T.; Pople, J. A. *Ibid.* **1983**, *105*, 484. Also: (c) Chandrasekhar, J.; Pople, J. A.; Seeger, R.; Seeger, U.; Schleyer, P. v. R. *Ibid.* **1982**, *104*, 3651.

(6) Mulliken population analysis was used despite its known shortcomings. See: Grier, D. L.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1982**, *104*, 3556.

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.

Acknowledgment. This work benefitted from stimulating discussions with C. H. Wu and with R. J. Lagow; both are thanked for information prior to publication. The Fonds der Chemischen Industrie and the National Science Foundation (CHE-79-01061) provided support. The project was facilitated by an award of the Alexander von Humboldt Foundation.

---

(7) Würthwein, E.-U.; Kos, A. J., unpublished calculations.

(8) Peterson, K. I.; Dao, P. D.; Castleman, A. W., Jr. "Abstracts of Papers", National Meeting of the American Chemical Society, Las Vegas, NV, Apr 1982; American Chemical Society: Washington, D.C., 1982, PHYS 173.

(9) Simon, A. *Struct. Bonding* (*Berlin*) **1979**, *36*, 81.

(10) Also calculated by: MacLean, W.; Schultz, J. A.; Pedersen, L. G.; Jarnagin, R. C. *J. Organomet. Chem.* **1979**, *175*, 1.

(11) Klimenko, N. M.; Zakzhevskii, V. G.; Charkin, O. P. *Koord. Khim.* **1982**, *8*, 903.

(12) See: Shimp, L. A.; Morrison, J. A.; Gurak, J. A.; Chinn, J. A., Jr.; Lagow, R. J. *J. Am. Chem. Soc.* **1981**, *103*, 5951 and earlier papers. Also: Landro, F. J.; Gurak, J. A.; Chinn, J. W., Jr.; Newman, R. M.; Lagow, R. J. *Ibid.* **1982**, *104*, 7345.

(13) Gurak, J. A.; Chinn, J. W., Jr.; Lagow, R. J. *J. Am. Chem. Soc.* **1982**, *104*, 2637. Lagow, R. J., private communication.

(14) (a) Wu, C. H.; Ihle, H. R. *Chem. Phys. Lett.* **1979**, *61*, 54. (b) Wu, C. H., private communication.

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

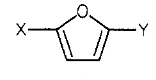
Edward L. Clennan* and M. E. Mehrsheikh-Mohammadi

Department of Chemistry, University of Wyoming
Laramie, Wyoming 82071

Received March 9, 1983

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.



1

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-

---

(1) (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.

(2) Gollnick, K.; Kunh, J. J. In "Singlet Oxygen"; Wasserman, H. H., Murray, R. W., Ed.; Academic Press: New York, 1979.

(3) (a) Grdina, S. B.; Orfanopoulos, M.; Stephenson, L. M. *J. Am. Chem. Soc.* **1979**, *101*, 3111. (b) Adams, D. R.; Wilkinson, F. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 586. (c) Young, R. H.; Brewer, D.; Keller, R. A. *J. Am. Chem. Soc.* **1973**, *95*, 375.

(4) Monroe, B. M. *J. Am. Chem. Soc.* **1981**, *103*, 7253.

(5) Dewar, M. J. S.; Theil, W. *J. Am. Chem. Soc.* **1977**, *99*, 2338.

(6) Gorman, A. A.; Gould, I. R.; Hamblett, I. *J. Am. Chem. Soc.* **1982**, *104*, 7098.

(7) The rates were measured by examining the inhibition of the self-sensitized photooxidation of rubrene. Carlsson, D. J.; Suprunchuk, T.; Wiles, D. M. *Can. J. Chem.* **1974**, *52*, 3728.

(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.

0002-7863/83/1505-5932$01.50/0 © 1983 American Chemical Society