constants refer to the above steps, respectively, B = benzophenone and PhH = benzene.

$$1/\Phi_{\mathrm{biphenyl}} = 1 + \frac{k_2}{k_4} + \frac{k_5[\mathrm{B}]}{k_4[\mathrm{PhH}]} \qquad \text{(I)}$$

$$1/\Phi_{\mathrm{pinacol}} = \frac{1 + \dfrac{k_2}{k_4} + \dfrac{k_5[\mathrm{B}]}{k_4[\mathrm{PhH}]}}{1 + \dfrac{k_5}{2k_4}\dfrac{k_7}{(k_6 + k_7)}\dfrac{[\mathrm{B}]}{[\mathrm{PhH}]}} \qquad \text{(II)}$$

$$\frac{\Phi_{\mathrm{pinacol}}}{\Phi_{\mathrm{biphenyl}}} = 1 + \frac{k_5}{2k_4}\frac{k_7}{(k_6 + k_7)}\frac{[\mathrm{B}]}{[\mathrm{PhH}]} \qquad \text{(III)}$$

Equation II predicts little dependence of Φ_{pin} on [B], as observed. Plots of $1/\Phi_{\mathrm{biphenyl}}$ and $\Phi_{\mathrm{pinacol}}/\Phi_{\mathrm{biphenyl}}$ *vs.* [B]/[PhH] indeed give excellent liner correlations as predicted by eq I and III.[8] From the least-squares slopes and intercepts of the linear plots and the absolute value for k_2 determined by flash methods ($k_2 = 9.0 \times 10^3\ M^{-1}\ \mathrm{sec}^{-1}$),[2,14] absolute values of the rate constants k_4 and k_5 and the ratio k_7/k_6 can be determined. The results are $k_4 = 16.4\ M^{-1}\ \mathrm{sec}^{-1}$, $k_5 = 1.26 \times 10^5\ M^{-1}\ \mathrm{sec}^{-1}$, and $k_7/k_6 = 10^{-2}$. The value for H abstraction from benzene by $^3\mathrm{Ph_2CO}^*$, k_4, agrees very well with the value of 19 $M^{-1}\ \mathrm{sec}^{-1}$ deduced by Saltiel, *et al.*,[4] from lifetime data and trapping of Ph· by $\mathrm{CCl_4}$.

We have also directly measured the lifetime of benzophenone triplets in benzene at room temperature as a function of benzophenone concentration [B^0]. The single photon counting technique was utilized,[2b] in which the phosphorescence lifetime was directly determined in purified benzene[10] using highly purified benzophenone.[15] The results fit the equation

$$1/\tau_{\mathrm{obsd}} = 1/\tau^0 + k_{\mathrm{sq}}[\mathrm{B}^0] \qquad \text{(IV)}$$

where $1/\tau^0$ is the limiting decay rate in the absence of quenchers including ground-state benzophenone, and k_{sq} is the rate constant for self-quenching. The data provide values of $1/\tau^0 = (1.0 \pm 0.1) \times 10^5\ \mathrm{sec}^{-1}$ and $k_{\mathrm{sq}} = 1.6 \times 10^5\ M^{-1}\ \mathrm{sec}^{-1}$ in benzene.[8,16] We have observed self-quenching of $^3\mathrm{Ph_2CO}^*$ in many other solvents; *e.g.*, in purified carbon tetrachloride[14] self-quenching occurs with $1/\tau^0 = 1.14 \times 10^4\ \mathrm{sec}^{-1}$ and $k_{\mathrm{sq}} = 3.25 \times 10^5\ M^{-1}\ \mathrm{sec}^{-1}$. Ledger and Porter[17] recently reported for benzophenone in water that $k_{\mathrm{sq}} = (1.20 \pm 0.2) \times 10^8\ M^{-1}\ \mathrm{sec}^{-1}$.[18]

The value of k_{sq} in benzene from the lifetime studies is in gratifying agreement with the value for k_5 (above) for reaction of $^3\mathrm{B}^*$ with B^0 in benzene from quantum yield determinations. We envisage interaction of triplet- and ground-state benzophenone to give a triplet excimer E, which then partitions between deactivation (step 6) and transfer of an H atom (step 7). By analogy to other H abstraction and decay rate constants, the experimental value of k_7/k_6 is reasonable. It should be noted that no direct spectroscopic evidence for triplet excimers was obtained in this study, and that the results do not *require* the intermediacy of an excimer.[19]

The proposed reaction of $\mathrm{Ph_2CO}$ with itself is confirmed by the following. Benzpinacol is formed on irradiation of high concentrations of $\mathrm{Ph_2CO}$ in $\mathrm{CCl_4}$, wherein Φ_{pin}^{-1} is a linear function of $[\mathrm{B}^0]^{-1}$, and self-quenching of the triplet is also observed. Furthermore, irradiation of degassed molten neat $\mathrm{Ph_2CO}$ gives benzpinacol and other as yet unidentified products.

These observations also have important consequences in energy transfer experiments, *i.e.*, where benzophenone or other $^3\mathrm{n},\pi^*$ ketones are used as triplet sensitizers in benzene. In the case where $[\mathrm{B}^0] \gg [\mathrm{A}^0]$, the experimental arrangement recommended to minimize light absorption by the substrate and complications due to direct photolysis of A, self-quenching may compete with energy transfer. Even if the efficiency of triplet formation of a reactive triplet of A on direct photolysis is 100%, $\Phi^{\mathrm{A}}_{\mathrm{sens}}$ will often be less than $\Phi^{\mathrm{A}}_{\mathrm{direct}}$. Observed inefficiencies on sensitization need not be due to the relative triplet excitation energies of B and A, nor to the efficiency of intersystem crossing of A, but rather may be due to the competing self-quenching process, as is well documented in the case of $^3\pi,\pi^*$ sensitizers.[1,20] Thus, extending the warning given by Chapman,[20] the results of triplet sensitization experiments using $^3\mathrm{n},\pi^*$ or $^3\pi,\pi^*$ sensitizers, particularly in "inert" solvents such as benzene, must be interpreted with great caution. Furthermore, considerable revision may be required of interpretations of sensitization data already in the literature.

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(15) Benzophenone from Aldrich was purified by recrystallization, sublimation and distillation at reduced pressure, the middle fraction being collected. Analysis by glpc under a variety of conditions invariably gave only a single peak. The maximum possible level of impurities seems too low to account for the self-quenching effects.

(16) A preliminary report of self-quenching of $^3\mathrm{Ph_2CO}^*$ in benzene, as determined using laser flash photolysis, has been given by L. A. Singer, R. E. Brown, and J. Parks, 163rd National Meeting of the American Chemical Society, Boston, Mass., April 1972, Abstract ORGN 23. They find $1/\tau^0 = 1.3 \times 10^5\ \mathrm{sec}^{-1}$ and $k_{\mathrm{sq}} = (4.4 \pm 0.1) \times 10^5\ M^{-1}\ \mathrm{sec}^{-1}$.

(17) M. B. Ledger and G. Porter, *J. Chem. Soc., Faraday Trans. 1*, 3, 539 (1972).

(18) The possible contribution of dioxetane formation to self-quenching, as documented for acetone by Yang, *et al.*, will be examined using suitably labeled compounds; see N. C. Yang, W. Eisenhardt and J. Libman, *J. Amer. Chem. Soc.*, **94**, 4030 (1972).

(19) Analogously, the interaction of $^3\mathrm{Ph_2CO}^*$ with benzene could also be described formally in terms of partitioning of an exciplex between decay and H transfer, equally consistent with the kinetics.

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Generalized Frontier Orbitals of Alkenes and Dienes. Regioselectivity in Diels–Alder Reactions

Sir:

Applications of perturbation molecular orbital theory[1,2] to reactivity in cycloadditions have evolved from

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(1) E. Heilbronner and H. Bock, "Das HMO-Modell und Seine Anwendung," Verlag Chemie, GmbH, Weinheim/Bergstr., Germany, 1968; M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969; R. Hoffmann, *Accounts Chem. Res.*, **4**, 1 (1971).

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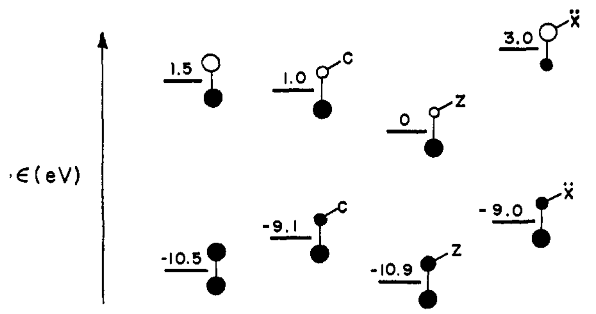

Figure 1. Frontier orbital energies and coefficients for dienophiles (C = CHCH$_2$, Ph, etc.; Z = CHO, CN, etc.; X = R, OR, NR$_2$, etc.)

the primordial frontier orbital treatments of reactivity,[3,4] through increasingly sophisticated calculational procedures,[5–7] and back to simple qualitative frontier orbital methods.[8–10] Experimental verifications of the essential correctness of the latter approach have been obtained from correlations of Diels–Alder or 1,3-dipolar reaction rates with ionization potentials of the donor addend or the electron affinity of the acceptor addend.[11]

The problem of regioselectivity in cycloadditions has been treated by both numerical methods[6,7b,12–15] and frontier orbital methods,[8,16,17] but the failure of some of the former calculations to properly account for regioselectivity phenomena has been occasionally cited as evidence for the nonoccurrence of the concerted mechanism of the Diels–Alder reaction.[18] Even for the successful calculations and frontier orbital approaches, the origin of the phenomenon of regioselectivity in Diels–Alder reactions has remained largely ensnared in a labyrinth of numbers.

We wish to report generalizations about the frontier orbital energies and coefficients of the major classes of dienes and dienophiles based, where possible, on experimental rather than calculated quantities. These generalizations clearly reveal the origin of regioselectivity and reactivity not only in concerted Diels–Alder reactions, but in a variety of cycloadditions which occur by both concerted and nonconcerted mechanisms. Insight into possible sources of failure of some of the calculational methods is obtained also by this approach.

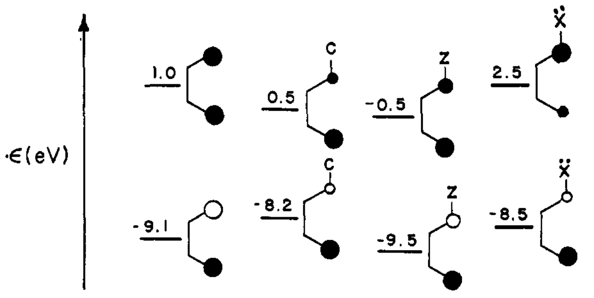

Figure 2. Frontier orbital energies and coefficients for 1-substituted dienes.

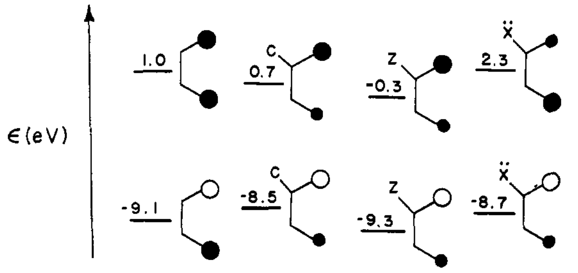

Figure 3. Frontier orbital energies and coefficients for 2-substituted dienes.

Approximate energies and coefficients for substituted alkenes and 1- and 2-substituted butadienes are shown in Figures 1–3. The energies of the HO orbitals are typical values for the particular class of compounds obtained from photoelectron spectroscopy. More typical ranges for the various subclasses of compounds are: ethylene, 10.5;[19] electron-rich alkenes (X): alkylethylenes, 8.6–9.6;[19–21] haloethylenes, 10.1–10.3;[19] vinyl ethers, 9.1;[11b] enamines, 7.3–8.8;[11b] conjugated alkenes (C): 8.2–9.2;[11c,19,22] electron-deficient alkenes: (one Z) 10.7–11.1;[11c,19,23] (two Z) 11.0–11.3.[23,24] For many of the substituted dienes, estimates based on the effect of substituents on alkene ionization potentials had to be made.

The LU orbital energies are estimated from electron affinities available for some electron-deficient alkenes,[11a,25,26] but are for the most part estimated from considerations of substituent effects on charge-transfer specta,[25] polarographic reduction potentials,[27] and electronic (π–π^*) absorption spectra.

The figures are in accord with qualitative notions of substituent effects on orbital energies;[8,9] that is, conjugating substituents (C) compress the frontier orbital separation, electron-releasing substituents (X) raise

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(3) Additional applications of PMO theory to cycloadditions are reviewed by W. C. Herndon, *Chem. Rev.*, 72, 157 (1972).

(4) K. Fukui in "Molecular Orbitals in Chemistry, Physics, and Biology," P.-O. Löwdin and B. Pullman, Ed., Academic Press, New York, N. Y., 1964, p 513ff; *Bull. Chem. Soc. Jap.*, **39**, 498 (1966); R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, **87**, 4388 (1965).

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both frontier orbital energies, and electron-withdrawing substituents (Z) lower both frontier orbital energies. Most of the last type of substituents (–COS, –COR, –CN) are both electron withdrawing and conjugating, so that the overall lowering of the HO is much less than that of the LU. For the diene orbital energies, the same effects operate, except that the magnitude of energy changes, which are roughly proportional to the square of the coefficient at the point of attachment, falls in the order ethylene > 1-diene > 2-diene.[8,22]

The relative magnitudes of the coefficients in Figures 1–3 are derived, for the most part, from calculations,[17,28] but are in agreement with qualitative considerations. Conjugating substituents increase the relative magnitude of the coefficient of the unsubstituted terminus of ethylene at the expense of the coefficient of the substituted terminus in both the HO and LU. Electron-releasing groups increase the remote coefficient in the HO and the nearby coefficient in the LU, as expected on inductive grounds.[8] For alkyl groups, the two coefficients are nearly identical in the LU.[17,28] Electron-withdrawing groups have exactly the opposite effect from that of donor groups if they interact only inductively (*e.g.*, $-CF_3$), but since most of the groups of this type are also conjugating, the LU's have the greater magnitude of the remote coefficient strengthened, while the difference in the HO coefficient magnitudes is diminished or reversed. CNDO/2,[28] INDO,[29] and *ab initio* SCF[30] calculations indicate that the HO coefficient at the unsubstituted terminus is largest, while Hückel,[8] extended Hückel,[28] and MINDO/2[31] calculations give the opposite result for the HO coefficients. Photoelectron spectra support the former calculations, because β-methylation of acrolein or methyl acrylate raises the highest π orbital energy by 1.39 and 1.64 times more, respectivity, than does α-methylation.[23]

The substituted butadiene orbitals in Figures 2 and 3 can be derived from similar considerations. The only equivocal cases involve 1-electron-withdrawing substituted dienes, where terminal coefficients are very similar for both the HO and LU orbitals.[28,32]

Once the relative coefficient magnitudes and orbital energies are known, the preferred Diels–Alder regioisomer can be predicted using the following generalizations. (1) The principal stabilization of the transition state will arise from interaction of the HO–LU pair of addend frontier orbitals which are closest in energy. (2) The larger terminal coefficient on each addend will become bonded preferentially in the transition state.[33]

The most frequently observed Diels–Alder reactions of unsymmetrical addends involve "conjugated" or "electron-rich" dienes and "conjugated" or "electron-deficient" dienophiles. For these reactions, the diene HO–dienophile LU interaction is largest (energy separation smallest), and the "ortho" regioisomer is favored with 1-substituted butadienes, the "para" regioisomer with 2-substituted butadienes. The other frontier orbital interaction also favors the same regioisomer. These regioisomers are preferred experimentally.[34] Similar considerations correctly rationalize the regioselectivity of Diels–Alder reactions of heterodienophiles.[35]

The coefficients at C-1 and -4 in the HO and LU of 1-substituted electron-deficient dienes are nearly the same, so that regioselectivity should be less pronounced in reactions of such compounds. This seems contrary to the few examples known,[34] and may indicate the influence of secondary orbital interactions between substituents.[15]

The only reversal of the "ortho–para" Alder regioselectivity rule should occur in reactions where the LU orbital of electron-rich dienes or dienophiles plays a controlling role. However, such a situation will not normally occur, since the LU of electron-rich alkenes is of high energy. Only when both diene and dienophile are electron rich will the "meta" orientation be favored.

Consideration of orbital energies and coefficients in this way reveals some of the difficulties that may arise from use of calculated frontier orbital energies and coefficients. First, calculated orbital energies often deviate from experimental energies, not only in an absolute sense, but in a relative sense as substituents are varied. Thus, orbital interactions which are in reality insignificant may be considered to be of great importance if calculated orbital energies are used. This may be the origin of the greater success of frontier orbital treatments than full calculations in some cases.[15] Second, with electron-deficient dienophiles, the use of some calculational methods gives incorrect relative magnitudes of HO coefficients and, therefore, incorrect regioselectivity predictions. Examples of this problem are the reversal of predictions for acrolein dimerization using Hückel or SCF calculations[6] as well as difficulties in predictions for regioselectivity with other electron-deficient addends.[6,13–15]

With the availability of generalized frontier orbital energies and coefficients summarized in Figures 1–3, qualitative applications to the rationalization and prediction of reactivity and regioselectivity in a multitude of concerted and nonconcerted reactions of alkenes are made possible.

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On Lewis Acid Catalysis of Diels–Alder Reactions

Sir:

The Diels–Alder reaction is the archetype of a concerted, intermolecular cycloaddition,[1] and yet Diels–

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