

## Perturbational Molecular Orbital Method applied to [2 + 4] Cycloadditions: Olefins plus *o*-Quinones

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WE have investigated several photochemical cycloadditions by a perturbational molecular orbital (PMO) method, and now report results for the thermal and photochemical cycloadditions of stilbene and but-2-ene with *o*-benzoquinone, tetrachloro-*o*-benzoquinone, and 9,10-phenanthraquinone.

In the PMO method, initially proposed by Dewar,<sup>1</sup> separate wave functions are obtained for the two reactants, and their possible interactions are treated by the perturbation theory. The stabilizing perturbation energy is calculated by well known formulae.<sup>1,2</sup> The major part of the perturbation energy arises from symmetry-allowed interactions of high-lying occupied orbitals of each reacting molecular species with low-lying vacant, or partially vacant, orbitals of the other reactant. The magnitudes of the perturbation energies for stereoselective, concerted, allowed<sup>3</sup> Diels-Alder reactions are of the order of 1.6 to 1.8 units.<sup>2</sup> (The units are in terms of  $\gamma^2/\beta$  where  $\gamma$  is a perturbation exchange integral and  $\beta$  is the usual Hückel exchange integral.) We postulate that other reaction pathways may intervene if PMO energies are small.

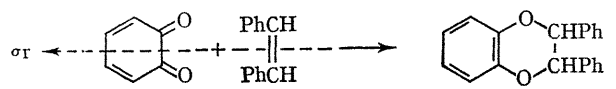
The model which we choose for the ground state of *o*-quinone is  $Q8^2 Q7^2 Q6^2 Q5^2$ . The  $\pi-\pi^*$  triplet is  $Q8^2 Q7^2 Q6^2 Q5^1 Q4^1$ , and the  $n-\pi^*$  triplet is taken to be  $Q8^2 Q7^2 Q6^2 Q5^2 Q4^2$ . Concerted [4 + 2] cycloaddition is assumed. The largest interaction for thermal reaction to yield dihydro-1,4-dioxin is occupied stilbene level 6 with vacant *o*-quinone level 4,  $S6 \rightarrow Q4$ . Other important interactions are  $S8 \rightarrow Q4$ ,  $Q5 \rightarrow S5$ , and  $Q7 \rightarrow S7$ . The total perturbation energy is 2.62 units.

A concerted photochemical ( $n-\pi^*$  triplet) reaction to yield the same product is still stabilized by one-half of the interactions  $S6 \rightarrow Q4$  and  $S8 \rightarrow Q4$ , and by all of the interactions  $Q5 \rightarrow S5$  and  $Q7 \rightarrow S5$ . Additional stabilizing interactions of half-occupied level  $Q4$  with the symmetric vacant levels of the stilbene moiety arise for the photochemical reaction. The total stabilization energy is 1.79 units. The concerted reaction is therefore allowed for either the thermal or the photochemical reactions, in disagreement with a recent conjecture of Bryce-Smith and Gilbert<sup>5</sup> and in disagreement with their interpretation of the Woodward-Hoffmann rules.

Calculated perturbation energies for several systems are given in the Table. For the benzoquinones, two pathways are calculated, cycloaddition to yield either a bicyclo-octadiene or the 1,4-dioxin, the reaction to give the observed dioxin being favoured in every case. Several other experiments are in good agreement with the PMO calculations. The thermal reaction of *trans*-stilbene with tetrachloro-*o*-benzoquinone is highly selective,<sup>5</sup> the photochemical reaction less so.<sup>5</sup> The photochemical reaction of stilbene with 9,10-phenanthraquinone is even less stereoselective.<sup>6</sup> An absence of selectivity is reported for the photochemical reaction of either *cis*- or *trans*-but-2-ene with 9,10-phenanthraquinone.<sup>6,7</sup> Our prediction that the photochemical reaction of but-2-ene with *o*-quinones will be highly selective has not been tested.

The absence of competing two-step reactions leading to cycloaddition products is certainly not proved by these calculations. In fact, competing two-step pathways are necessary in order to account for the fact that the cycloadditions still proceed (albeit with little or no stereoselectivity) when calculated perturbation energies for the concerted reactions are small. However the calculations do indicate that concerted photochemical cycloaddition reactions are still possible even if the thermal reaction is highly stereoselective, and the results therefore show that a concerted cycloaddition mechanism for the photochemical

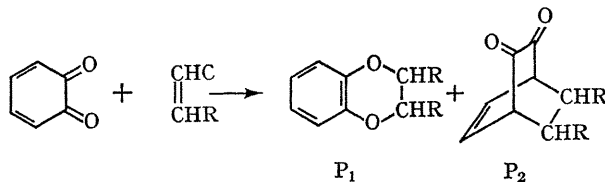
FIGURE. Molecular orbitals of *o*-benzoquinone and stilbene.



<i>o</i> -Benzoquinone		Stilbene	
Coeff. of oxygen atoms	Energy levels ( $\beta$ )	Energy levels ( $\beta$ )	Coeff. of carbon atoms
<i>A</i> 0.150	$Q1 - 2.13$	$-2.21 S1$	0.315 <i>A</i>
		$-2.06 S2$	0.109 <i>S</i>
		$-1.50 S3$	0.405 <i>A</i>
<i>A</i> 0.186	$Q2 - 1.20$	$-1.16 S4$	0.182 <i>S</i>
<i>S</i> 0.160	$Q3 - 1.10$	$-0.50 S5$	0.438 <i>A</i>
<i>S</i> 0.484	$Q4 0.26$	$0.50 S6$	0.438 <i>S</i>
<i>A</i> 0.362	$Q5 0.76$	$1.16 S7$	0.182 <i>A</i>
<i>S</i> 0.336	$Q6 1.50$	$1.50 S8$	0.405 <i>S</i>
<i>A</i> 0.558	$Q7 1.58$	$2.06 S9$	0.109 <i>A</i>
<i>S</i> 0.357	$Q8 2.36$	$2.21 S10$	0.315 <i>S</i>

The Figure illustrates the method as applied to cycloaddition reactions of *o*-benzoquinone and stilbene. The depicted eigenvalues and vectors are the results of Hückel MO calculations with parameters suggested by Streitwieser.<sup>4</sup> *S* or *A* indicates symmetry or asymmetry of the eigenvector to the vertical plane  $\sigma_v$  of the reactant molecules.

## Calculated PMO energies for concerted reactions



Reactants		Thermal reactions		Photochemical reactions ( $n-\pi^*$ )		Photochemical reactions ( $\pi-\pi^*$ )	
		P <sub>1</sub>	P <sub>2</sub>	P <sub>1</sub>	P <sub>2</sub>	P <sub>1</sub>	P <sub>2</sub>
<i>o</i> -Quinone	+ stilbene	2.62	1.59	1.73	1.40	1.64	1.21
Tetrachloro- <i>o</i> -quinone	+ stilbene	2.47	0.69	1.79	0.68	1.67	0.66
9,10-Phenanthraquinone	+ stilbene	1.74	—	1.28	—	1.26	—
<i>o</i> -Quinone	+ but-2-ene	4.60	2.13	2.65	1.72	2.54	1.48
Tetrachloro- <i>o</i> -quinone	+ but-2-ene	4.23	0.62	2.46	0.60	2.36	0.58
9,10-Phenanthraquinone	+ but-2-ene	2.02	—	1.35	—	1.33	—

reaction of stilbene with tetrachloro-*o*-quinone cannot be dismissed.

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