Differing Substituent Effects on Rates and Regioselectivities in the Di-π-methane Rearrangement. New Photochemical Theory: Excitation Distribution (the ΔP Matrix), Reaction Inhibition by Vertical Excited State Stabilisation, Ground *Vs.* Excited State Control[1]

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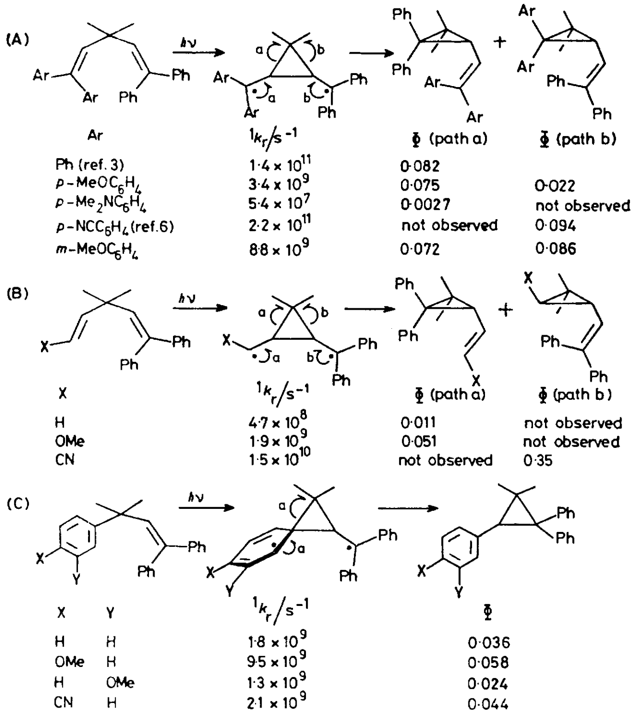
Summary A consistent pattern of control of regioselectivity by substituents was observed in three di-π-methane systems while the effect on rates varied with the system; from this three new concepts were derived: (i) a method allowing one to discern how excitation energy is partitioned throughout a molecule initially and during transformation to product, (ii) evidence that excessive vertical excited state stabilization can inhibit reactions, (iii) exercise of excited or ground state substituent effects on a reaction depending on whether the unit bearing the substituent is appreciably excited at the critical point on the reaction hypersurface.

The di-π-methane rearrangement[2] has developed into one of the most encountered photochemical reactions. Therefore, it is important to establish its many facets. Substituent effects on excited state rates[3] and on regioselectivity[4] were of primary concern in the present study.

The three types of systems in the Scheme were investigated, and efficiencies and S_1 rates are depicted.†

† Reactant and product syntheses will be reported in a subsequent full paper. Product structures were established by independent synthesis or degradation. All compounds analysed satisfactorily.

The first striking observation was the regioselectivity effected by cyano- and methoxy-substitution (Scheme). Throughout, cyclopropyldicarbinyl diradical ring opening (path b) retaining cyano- or cyanophenyl-stabilization of a diradical centre is observed rather than opening retaining a diphenyl-stabilized diradical centre (path a). Similarly, retention of a diphenyl-stabilized diradical centre (path a) is favoured over methoxy- or *p*-methoxyphenyl-stabilization (path b). Dimethylaminophenyl effected complete regioselectivity similar to that enforced by *p*-methoxyphenyl, while *m*-methoxyphenyl exhibited weak selectivity paralleling that of *p*-cyanophenyl.



Ar	$^1k_r/s^{-1}$	Φ (path a)	Φ (path b)
Ph (ref. 3)	$1·4 \times 10^{11}$	0·082	
p-MeOC$_6$H$_4$	$3·4 \times 10^{9}$	0·075	0·022
p-Me$_2$NC$_6$H$_4$	$5·4 \times 10^{7}$	0·0027	not observed
p-NCC$_6$H$_4$ (ref. 6)	$2·2 \times 10^{11}$	not observed	0·094
m-MeOC$_6$H$_4$	$8·8 \times 10^{9}$	0·072	0·086

X	$^1k_r/s^{-1}$	Φ (path a)	Φ (path b)
H	$4·7 \times 10^{8}$	0·011	not observed
OMe	$1·9 \times 10^{9}$	0·051	not observed
CN	$1·5 \times 10^{10}$	not observed	0·35

X	Y	$^1k_r/s^{-1}$	Φ
H	H	$1·8 \times 10^{9}$	0·036
OMe	H	$9·5 \times 10^{9}$	0·058
H	OMe	$1·3 \times 10^{9}$	0·024
CN	H	$2·1 \times 10^{9}$	0·044

SCHEME. Three types of di-π-methane rearrangement.

Reference to the Scheme reveals a dramatic spread of S_1 rates, as determined by single-photon counting,[3] ranging from *ca.* 10^7 to 10^{11} s^{-1}. These excited singlet rates were drastically inhibited (Scheme) by *p*-dimethylamino and *p*-methoxy in system A while *p*-methoxy in system C and methoxy in system B enhanced the rates. In general, however, cyano-substitution led to rate increases throughout. In the case of system C our single-photon counting rates parallel the relative rates obtained by Hixson.[5]

To assist understanding of the sources of these effects we utilized PPP–SCF–CI calculations (up to 100 singly and 5050 doubly excited configurations) of the S_1 vertical excited states of reactants and of the S_1 cyclopropyldicarbinyl diradicals. In each series the trend showed the more exothermic bridging energy calculated tended to correspond to the more rapid S_1 rearrangement rate. Particularly nice correlations were found in series A and B where linear plots (Figure 1) of $\log(^1k_r)$ *vs.* ΔE(bridging) resulted (correlation coeff. for A = 0·96, for B = 0·91). The calculations also revealed that the carbinyl carbons of the diradical are electron rich and that both *p*-cyano- and *p*-methoxy-groups stabilize S_1 of the diradical, independent of their effect on ΔE(bridging). Stabilization of the diradical is thus a conjugative effect not necessarily paralleling the electron-donating ability of the substituents.

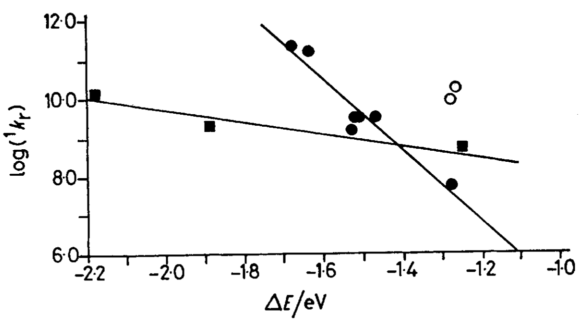


FIGURE 1. Correlation between log (^1k_r) and bridging energies for systems A and B. Correlation coefficient (excluding *meta*-compounds) = 0·96 for series A and 0·91 for series B. ● Series A (*para*), ○ Series A (*meta*). ■ Series B.

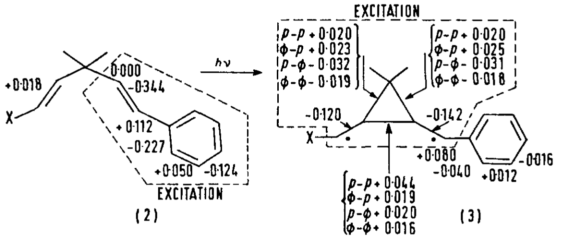
There are several remarkable features of these results. One is the striking experimental rate inhibition in series A by *p*-dimethylamino and *p*-methoxy; this inhibition is in accord with the calculations of S_1 bridging energies but not relatable to stabilization of the diradical alone since these groups cause stabilization and yet rate inhibition in these series. Another remarkable feature is the greater rate enhancement in series C by *p*-methoxy compared to *m*-methoxy although *meta*-transmission is more characteristic of excited state reactions.[7,8] These effects are understood in terms of the new theory developed below.

In series A, R_X = [product with $(p\text{-X-C}_6\text{H}_4)_2\text{C=CH-}$)]/[product with $\text{Ph}_2\text{C=CH-}$] is equivalent to k_X/k_H where these are the rates for the two modes of cyclopropyldicarbinyl diradical opening (a and b, respectively in the Scheme). A plot of $\log(R_X)$ *vs.* the Hammett σ constants gives a linear plot (correlation coeff. 0·96) with a slope of $\rho = -2·07$. This shows that in the ring-opening process the carbinyl carbon generating the vinyl group becomes very electron-deficient compared to the carbinyl carbon becoming part of the three-membered ring. The same effect is seen qualitatively as controlling the regioselectivity of series B while in series C rearomatization dominates. An unusual feature is that ground-state σ constants gave this correlation. Here for the second time, ground-state behaviour was observed.

In order to understand the dramatic rate inhibition by *p*-dimethylamino and methoxy in series A and the ground state *para*-transmission effects, a new theory was derived using the SCF–CI calculations.

We required a simple way of determining the distribution of electronic excitation in a photochemical reactant and also in the molecule as it transforms itself. This is helpful in understanding photochemical processes. A useful approach compares ground- and excited-state wave functions by use of bond orders. For each pair of orbitals, r and t, the change in bond order on excitation is defined as $\Delta P_{rt} = P^*_{rt} - P^0_{rt}$. If there is no excitation at this point in the molecule, the excited-state (*i.e.* P^*_{rt}) and ground-state bond orders (*i.e.* P^0_{rt}) will be the same and ΔP_{rt} will be zero. Excitation is concentrated in portions of the molecule where the ΔP_{rt} values are non-zero. Where these are negative, the excited state is more antibonding than the ground state while positive ΔP_{rt} values indicate the excited state to be more bonding at these sites. Since bond orders are available from virtually any type of calculation, simple or sophisticated, the method is quite general. It can be applied to vertical excited states or to species which have partially reacted.

We have applied the method to a variety of examples using SCF–CI calculations. The method also can be employed qualitatively.[9] As an example of a quantitative application consider the di-π-methane rearrangement[2,3] of 1,1-diphenyl-3,3-dimethylpenta-1,4-diene (note case 1 of system B, Scheme). Our SCF–CI calculations were applied to the truncated system (**2**) with only one phenyl group for simplicity. Our computations led to a ΔP matrix containing all the ΔP_{rt} values as elements.‡ However, we focus attention on only a few of special interest; see Figure 2.



(**2**) (**3**)

a, X = H; *b*, X = OMe; *c*, X = CN

FIGURE 2. ΔP_{rt} values for the bridging process. The numbers given apply only to (**2a**) and (**3a**), but these are similar to those for the remaining two cases. *p-p*, *p-ϕ*, *ϕ-p*, *ϕ-ϕ* refer to overlap between *p*-orbitals and/or hybrids. In the *p-ϕ* and *ϕ-p* cases, the symbol refers to the orbital at the methane carbon. Conformation with carbinyl *p*- and Walsh three ring *p* orbitals coplanar. Excitation heaviest in dotted areas.

First, excitation is concentrated in the styryl units of the dienes (**2a**—**c**), in agreement with intuition. Next, as the reaction moves towards product, excitation diffuses from the phenyl group into the cyclopropyldicarbinyl diradical unit of (**3a**—**c**). This behaviour has proven characteristic of all the di-π-methane systems.

We use this reasoning to explain the anomalous excited singlet rate inhibition by *p*-dimethylamino- and *p*-methoxy-substitution in the tetra-aryl version of the divinylmethane rearrangement (system A, Scheme). Analysis of the energies of bridging in this system reveals that the *p*-dimethylamino- and *p*-methoxy-examples are the least favourable and that this effect derives from excessive stabilization of the *para*-substituted styryl unit of the vertical singlet excited state reactant, a stabilization which is much greater than that of the diradical. This system (*i.e.* A) differs from those of systems B and C in that in the latter two there is no stabilization of S_1 reactant by substitution, since the substituent is on an unexcited portion of the molecule.

Our last point is that the substituted phenyl ring in system C is unexcited both in vertical S_1 and also, interestingly, in the diradical. Thus we are dealing with an unexcited aryl ring throughout, and ground-state substituent effects are expected. Such is not always the case in photochemistry; we have noted[7] *meta*-transmission in excited aromatic rings.[8] Our calculations led to a parallel result for systems A and B after bridging where the aryl groups substituted on the cyclopropyldicarbinyl diradical centres have acquired a ground-state electron distribution during bridging.

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‡ In related studies we have utilized excitation energy terms in place of bond order changes; these are defined as $\Delta E = P^*_{rt}[F^*_{rt} + H^*_{rt}] - P^0_{rt}[F^0_{rt} + H^0_{rt}]$ where H_{rt} and F_{rt}, for excited and ground states, have the usual significance (H. E. Zimmerman, 'Quantum Mechanics for Organic Chemists,' Academic Press, New York, 1975, note especially Ch. V). This correction is useful where overlapping orbitals have varying *s*-character, since an *s*-weighted bond is energetically significant.

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