Reactivity of Arylolefin Excited States. Substituent Effects on the Photochemical Hydrogen Migration in 1,1-Diarylpropenes

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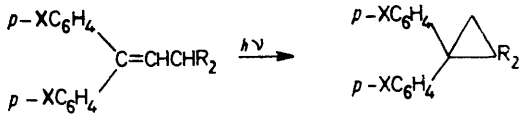
Summary Electron-withdrawing substituents increase the rate of photochemical cyclopropane formation from 1,1-diarylpropenes while electron-donating substituents have a retarding effect.

A systematic study of the effect of polar substituents on the course and/or rate of a photochemical reaction is one of the major means by which one can contribute experimentally to developing photochemical theory. We present here the results of a broad study of substituent effects on the rate of formation of 1,1-diarylcyclopropanes from 1,1-diarylpropenes *via* hydrogen migration (equation 1), a reaction first reported for the parent compound (**1d**) several years ago.[1]

The photolyses of (**1a**—**c**) to (**2a**—**c**) proceeded readily, and the arylcyclopropane photoproducts were easily isolated and identified.† The formation of (**2e**) from (**1e**) was less efficient. Even after prolonged irradiation an amount of (**2e**) sufficient for isolation was not produced, and it was identified as a photoproduct of (**1e**) by comparison of g.l.c. retention times with authentic (**2e**) synthesized independently. No (**2f**) could be detected from (**1f**) (g.l.c.) after prolonged photolysis. Sensitization studies of (**1a**—**e**) using benzophenone and/or xanthone as triplet sensitizers showed that the observed transformations to cyclopropanes are singlet state processes.



(1)

(**1**) (**2**)

a; X = H, R = Me
b; X = CF_3, R = H
c; X = CN, R = H
d; X = R = H
e; X = Me, R = H
f; X = OMe, R = H

Quantum yield studies of cyclopropane formation were carried out on nitrogen-purged cyclohexane solutions of the olefins (**1**) using 254 nm light (see column 2 of Table). For this mechanistic study, however, relative rate constants for reaction, k_r(rel), are a more useful measure of photochemical reactivity than relative reaction efficiencies. Moreover, since all the observed reactions proceed from the singlet state these k_r(rel) values may be obtained from the ϕ_r values, the relative fluorescence quantum yields, ϕ_f, and the relative fluorescence rate constants, k_f, *via* equation (2).‡

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† Preparative scale photolyses were carried out on solutions of the olefins in cyclohexane and/or Bu^{t}OH using Vycor- or Corex-filtered light from a Hanovia 450 medium-pressure mercury arc. All reactions were monitored by g.l.c.

‡ The singlet lifetimes of (**1a**—**f**) proved too short to measure in the singlet counting apparatus available.

Table. Reaction quantum yields and relative fluorescence quantum yields of olefins (**1a—f**)

Compd.	ϕ_r	ϕ_r(rel)[a]	ϕ_f(rel)[a,b]	k_f(rel)[a,c] (approx.)	k_r(rel)[a,c] (approx.)
(**1a**)	0·012	32	0·75	0·87	37
(**1b**)	0·0066	17	0·72	0·91	22
(**1c**)	0·0022	5·8	0·77	$\geqslant$1·0	$\geqslant$7·5
(**1d**)	0·00038	1·0	1·0	1·0	1·0
(**1e**)	$<$0·00012[d]	$<$0·32[d]	2·1	1·1	$<$0·17
(**1f**)	$<$0·00005[e]	$<$0·13[e]	13	—	$<<$1·0

[a] Relative to (**1d**). [b] λ(excitation) = 245 nm, non-degassed cyclohexane solutions (purging with nitrogen had no observable effect), computed from integrated areas under emission curves. [c] Approx. values; see text. [d] The upper limit of detectability in quantum yield experiment; product observed only after prolonged irradiation with more intense light. [e] No cyclopropane observed even after prolonged irradiation with more intense light.

$$k_r(\text{rel}) = \frac{k_r}{k_{r0}} = \frac{\phi_r}{\phi_{r0}} \times \frac{\phi_{f0}}{\phi_f} \times \frac{k_f}{k_{f0}} \qquad (2)$$

In the present case the subscript 0 refers to the values of the constants for (**1d**).

The relative ϕ_f values are given in the Table. It was not possible to calculate the k_f values for (**1a—f**) from their absorption spectra since in every case much of the $S_0 \rightarrow S_1$ absorption band is buried under the much more intense $S_0 \rightarrow S_2$ band. However, an estimate of the relative k_f values is sufficient to allow significant conclusions about the effects of substituents on k_r to be drawn, and a comparison of extinction coefficients of the first vibrational bands within the $S_0 \rightarrow S_1$ transitions for the olefins provides such an estimate.[3] This was done for (**1a**), (**1b**), (**1d**), and (**1e**) which have very similar spectra and where a distinct band is present. Such an estimate is not possible with (**1c**) and (**1f**) where the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ overlap is particularly severe. In the case of (**1c**) analogy with the effects of *p*-cyano substituents on the k_f value (calculated from the u.v. spectra) of other diphenylethylene[4] systems allows us to say that k_f(rel) for (**1c**) is almost certainly $\geqslant$1·0. We have no such close diphenylethylene models to use for estimating k_f(rel) for (**1f**), but it seems certain from the very low ϕ_r (no reaction observed) and the high ϕ_f(rel) that k_r(rel) for (**1f**) is $<<$1·0.§

We emphasize the approximate nature of the relative k_f values shown in the Table and of the relative k_r values thus derived. However, two significant points clearly emerge from our data: (i) electron-withdrawing substituents on the aromatic ring substantially enhance the rate of reaction while electron-donating groups slow it down; (ii) *gem*-dimethyl substitution at the migration origin greatly increases the rate.

This effect of polar substituents on migration reactivity has been noted in previous studies (though with a more limited number of substituents) on the 1,2-migrations of phenyl and methyl groups in styryl systems.[2] The effect on the present diphenylpropene reaction is more dramatic and revealing since (a) the rate differences are substantial, and (b) it is shown by substituents covering a fairly wide range of inductive and mesomeric effects. The similar effects on reaction rate of the *p*-CF_3 (which exerts predominantly an inductive effect) and the *p*-CN (which has a large mesomeric effect) groups is particularly impressive, especially when it is noted that the CF_3 groups exert very little effect on the basic u.v. spectrum of (**1d**) whereas the CN groups produce a large change. One rationale of these substituent effect data regards the photochemical reactivity of the olefin π,π^* states as arising from their electron-deficient nature owing to promotion of one of the bonding electrons; electron-donating substituents which decrease the electron deficiency at the migration terminus decrease migratory reactivity, while electron-withdrawing groups have the opposite effect. Alternatively, the substituents could be exerting their effect primarily by raising (Me, OMe) or lowering (CF_3, CN) the energy of the bonding π orbital which is left half-vacant upon excitation. Lowering the π orbital energy would enhance its interaction with the reactive γ C–H bond and increase reactivity.¶ Regardless, it is clear that in the present case considering the reaction rate as reflecting the stability of a diradical species such as (**3**) is not a useful approach.

$$Ar_2\dot{C}\text{–}CH_2\text{–}\dot{C}H_2$$

(**3**)

The *gem*-dimethyl effect is substantial and accommodates various views of the substituent effects. A similar rate enhancement by a *gem*-dimethyl group has been noted indirectly in the di-π-methane rearrangement.[6]

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§ The effect of a *p*-methoxy substituent on the k_f of (**1d**) is most unlikely to be as great as it is on the k_f of benzene [k_f(anisole)/k_f(benzene) = 13·5].[5] For substituted styryl systems[2] where the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ bands are better separated we calculate k_f(*p*-OMe)/k_f(*p*-H) = *ca.* 2·4.

¶ A referee has suggested a substituent may affect the reaction by virtue of its effect on the S_1–S_2 energy gap.

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[3] This approach has been used by others when band overlap has been a problem; see, for example, M. G. Rockley and K. Salisbury, *J.C.S. Perkin II*, 1973, 1582; J. R. Platt, *J. Chem. Phys.*, 1951, **19**, 263.
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