A Comparison of External and Internal Photochemical Heavy-atom Effects in the Acenaphthylene System

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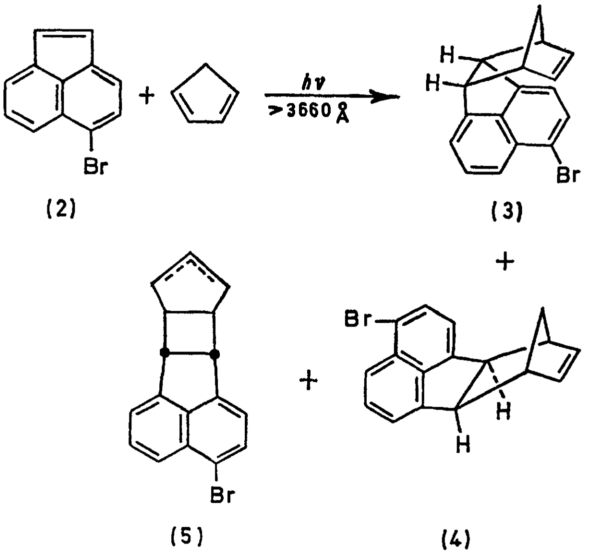
Summary The photocycloaddition of 5-bromoacenaphthylene to cyclopentadiene gives varying proportions of [4 + 2] and [2 + 2]cycloadducts with quantum yields that are less sensitive to external heavy-atoms than the reported reaction of acenaphthylene with cyclopentadiene

THE photocycloaddition of acenaphthylene (**1**) to cyclopentadiene shows a marked sensitivity to external heavy-atom solvents.[1] We report here that the similar reaction of 5-bromoacenaphthylene (**2**) is remarkably insensitive to external heavy-atom solvents (Table).



The cycloadducts (**3**), (**4**), and (**5**) were isolated from thermal or photochemical runs by chromatography of the reaction mixtures over $AgNO_3$-treated silica. The structures are assigned by comparison of their n.m.r. spectra with those of the corresponding cycloadducts of (**1**).[1,2] We find that (**5**) thermally isomerizes to (**3**) on g.l.c. at temperatures above 160°. The interconversion is a symmetry-allowed $[_{\sigma}2_s + _{\pi}2_a]$ 1,3 sigmatropic shift.[3]

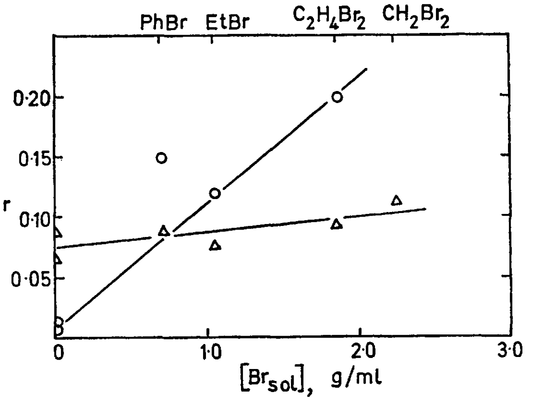


FIGURE. *Quantum yields of cycloaddition to cyclopentadiene of* (**1**) (○) *and* (**2**) (△) *as a function of concentration of bound bromine in the solvent,* $[Br_{sol}]$, *which is calculated by multiplying solvent density times its weight fraction of bromine.*

Except in acetonitrile, the nearly constant ratios of products formed in each solvent suggest that the products arise from the excited triplet state of (**2**). The Figure compares the quantum yields for cycloaddition of (**1**) and (**2**) to cyclopentadiene as a function of the bound bromine in the solvent. Although the cycloaddition of (**2**) is more efficient than that of (**1**) in cyclohexane, the difference in sensitivities to external bromine atoms is such that in the brominated solvents the quantum yield of (**2**) falls behind that of (**1**). Clearly, external and internal atoms are affecting the reaction differently, for otherwise the quantum yield of (**2**) should be at least that of (**1**) in any solvent.

A possible mechanism incorporating a minimum of steps is:

$$\mathrm{A} + h\nu \longrightarrow {}^1\mathrm{A}$$

$$^1\mathrm{A} \xrightarrow{k_{\mathrm{ic}}} \mathrm{A}$$

$$^1\mathrm{A} \xrightarrow{k_{\mathrm{isc}}} {}^3\mathrm{A}$$

$$^3\mathrm{A} \xrightarrow{k_{\mathrm{d}}} \mathrm{A}$$

$$^3\mathrm{A} + \mathrm{C} \xrightarrow{k_{\mathrm{r}}} \text{Products}$$

where A = (**1**) or (**2**), and C = cyclopentadiene. Application of steady-state approximations yields relationship (1) for the quantum yield of reaction, ϕ_r.

$$\phi_r = \left\{ \frac{k_{\mathrm{isc}}}{k_{\mathrm{ic}} + k_{\mathrm{isc}}} \right\} \left\{ \frac{k_{\mathrm{r}}(\mathrm{C})}{k_{\mathrm{d}} + k_{\mathrm{r}}\,(\mathrm{C})} \right\} \qquad (1)$$

The available evidence suggests that external heavy atoms affect k_{isc} much more than other rates, although k_{d} may also be affected.[4] Indeed, the k_{isc} of (**1**) appears to be very sensitive to heavy-atom effects.[5] However, an

TABLE

Quantum yields and product ratios for photoaddition of (**2**) *to cyclopentadiene*[a]

Solvent	Quantum yield, ϕ_r	Product ratio[b] (3) *endo*	(4) *exo*	(5) 2 + 2
Cyclohexane	0·067	0·53	1·93	1·00
Acetonitrile	0·086	0·66	3·00	1·00
Bromobenzene	0·087	0·55	1·68	1·00
Ethyl bromide	0·077	0·60	2·00	1·00
1,2-Dibromoethane	0·093	0·64	1·74	1·00
Methylene bromide	0·112	0·54	1·66	1·00

[a] All samples were degassed with slow nitrogen purge for 30 min prior to each run and then sealed. Concentrations of (**2**) and cyclopentadiene were 0·010 and 3·76 M, respectively. Product mixtures were analysed on a Varian Hy-Fl 1200 with a 4 ft. × 0·125 in. column packed with 3% OV-1 on Chromosorb W at 160°, injector 190°, and detector 250°. [b] Normalized to (**5**).

explanation of our data primarily in terms of variations in k_{isc} appears inadequate, since this requires that enhancement of k_{isc} by external heavy-atoms is by much smaller factors in (**2**) than in (**1**).[6,7]

The results are better explained in terms of the above mechanism if k_d is relatively much larger, compared to $k_r(C)$, in (**2**) than in (**1**). k_{isc} must then also be much larger in (**2**) than in (**1**), enough to compensate for the larger k_d and account for its greater ϕ_r than that of (**1**) in cyclohexane. Examination of equation (**1**) shows that if both k_d and k_{isc} are relatively large, ϕ_r is less sensitive to increases in k_{isc} and more sensitive to opposing increases in k_d. We thus conclude that our data are best accounted for if internal heavy-atoms incerase k_d by much larger factors than do external heavy-atoms, in accord with spectroscopic evidence.[4] Some of the increase in ϕ_r may be arising from a heavy-atom effect on k_r.[5] Preliminary experiments with ferrocene as a quencher and with varying concentrations of cyclopentadiene suggest that this possibility is unlikely.

We acknowledge the support of the Robert A. Welch Foundation and a matching fund grant from the National Science Foundation for purchase of the T-60 n.m.r. spectrometer.

(*Received*, 29*th November* 1971; *Com.* 2042.)

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