

An Intermediate in the Aryl Halide Photocyclization Process detected by Flash Photolysis

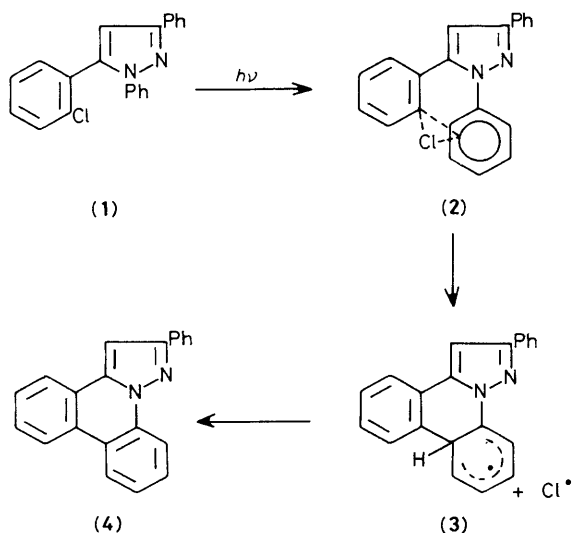
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A transient intermediate which decays in a first-order process with $k = 12.6 \text{ s}^{-1}$ in the photochemical cyclization of 5-(2-chlorophenyl)-1,3-diphenylpyrazole has been observed; because of the relatively long lifetime this is probably a cyclohexadienyl radical.

We have proposed that photocyclization of some aryl halides requires assistance in carbon-halogen bond fragmentation by π -complexation of the forming radical centres.^{1,2} On the basis of steady-state quantum yield measurements the conversion of (1) into (4) was interpreted as passing through stages (2) and (3).¹ Flash photolysis offers a possibility for detection of these reaction intermediates which we have explored.

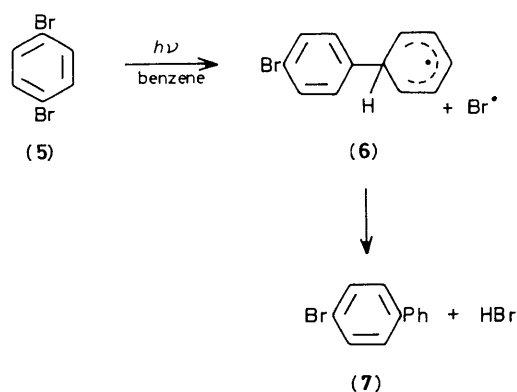
Flash photolysis of (1) was carried out in quartz apparatus using 10^{-4} M solutions in cyclohexane or ethanol. Light from the quartz-iodine lamp monitoring source fell onto a monochromator to which a photomultiplier detector was attached. The photomultiplier output was fed across a load resistor and then into a transient recorder (Datalab DL 1080) which was operated in the pre-trigger mode. Transients were transferred in digital form to a microprocessor (Hewlett Packard HP85).



A transient intermediate with λ_{max} 360 nm and ϵ ca. 2×10^5 was detected. Each flash converted ca. 80% of (1). A typical transient absorption vs. time curve is shown in Figure 1. The decay is a first-order process; a plot of $\log (A - A_\infty)$ vs. time is linear over at least three half-lives. The data are not consistent with a second-order decay process having equal concentrations of the two reactants [a plot of $(A_0 - A)/A_0 A$ vs. time is a curve; A = absorbance].

Table 1. First-order rate constants for decay of the intermediate formed by flash photolysis of (1).

Solvent	Atmosphere	Monitoring λ/nm	k/s^{-1}	Correlation coefficient
Cyclohexane	Ar	380	12.5	0.999
"	Ar	360	12.6	0.999
"	O_2	360	12.5	0.993
"	Air	350	12.7	0.994
Ethanol	Air	380	16.1	0.978



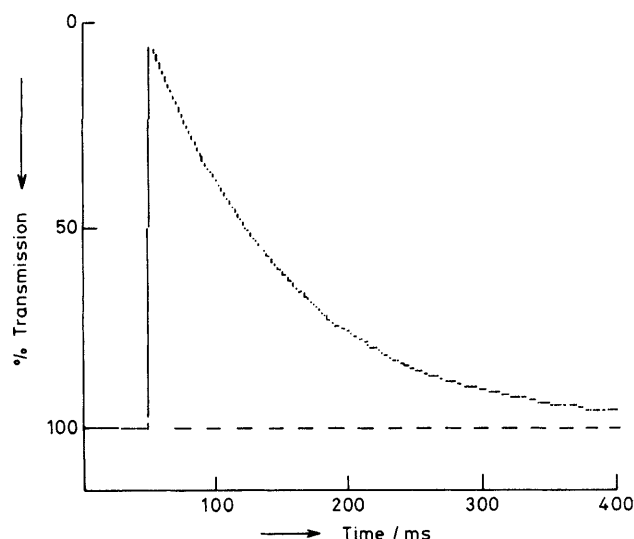


Figure 1. A typical transient absorption-time curve from the flash photolysis of (1) in cyclohexane under Ar; the transient was monitored at 360 nm where (1) does not absorb and (4) shows weak absorption.

Rate constant data for the first-order process are collected in Table 1. Within experimental error, the rate constant in cyclohexane is unchanged by the presence of oxygen, and the yield of the absorbing transient is not sensitive to the presence of oxygen. The decay rate is increased by 20% on changing the solvent from cyclohexane to ethanol in air. We believe this small increase in rate excludes the possibility of photochemical electrocyclicization followed by loss of H^+ and Cl^- from some intermediate by an ionic route because such a solvolysis would be greatly accelerated by the change of solvent from cyclohexane to ethanol.

π -Complexes between benzene and halogen atoms^{3,4} have λ_{max} in the region of 500–600 nm. The bromobenzene–bromine atom complex decays by a first-order process⁴ with $k = 5 \times 10^4 s^{-1}$. Radicals analogous to (3) have been obtained by the addition of hydrogen atoms⁵ or hydroxyl radicals⁶ to dimethylaniline and show λ_{max} 370 and 380 nm respectively.

The intermolecular process (5) \rightarrow (7) has been examined⁷ by flash photolysis and shows a transient which decays during 6 ms in a second-order process involving the simultaneously formed bromine atom. The yield of this transient, attributed to (6), was drastically reduced in the presence of oxygen or perylene, indicating that its generation occurs mainly through a triplet state.

The transient observed is extraordinarily long lived compared to those cited above, and decays by a first-order process. Because of the long lifetime we believe that the transient is attributable to (3) and not to a π -complexed radical. Therefore in order to explain the kinetics of decay it must be assumed that the chlorine atom also formed reacts faster with the solvent to give products which do not react with (3). The fate of the hydrogen atom from the decay of (3) has still to be determined.

The insensitivity of this reaction to the presence of oxygen confirms the reacting state of (1) to be S_1 . We are currently exploring this and related photochemical cyclizations in order to obtain evidence for the existence of π -complexed radical intermediates on a shorter time scale. Data collected at longer monitoring wavelengths indicate an increase in the absorption of the transient on a timescale of ms, followed by its slow first-order decay.

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