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Photocyclisation of 1,3-Diphenyl-5-(2′-halogenophenyl)pyrazoles: a Mechanism of Homolytic Carbon–Halogen Bond Fission Assisted by Radical Complexation

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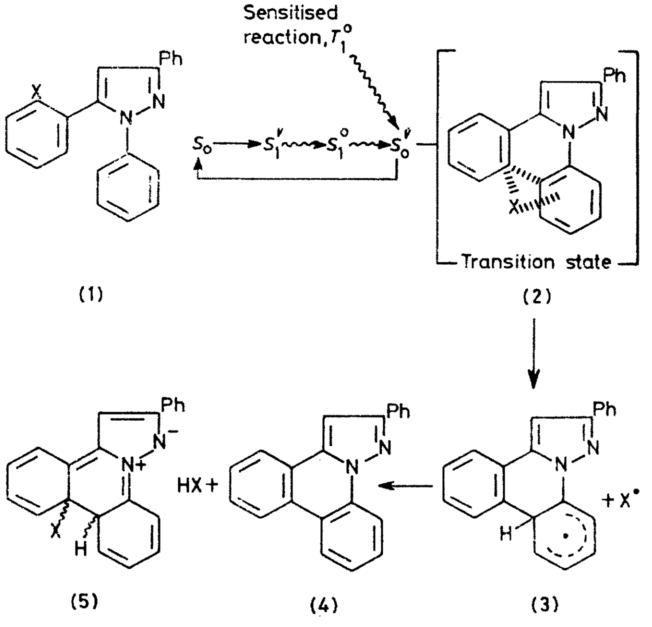
Summary Photocyclisation of 1,3-diphenyl-5-(2′-halogenophenyl)pyrazoles proceeds in high quantum yield from the S_0^v state followed by homolytic cleavage of the carbon–halogen bond assisted by intramolecular radical complexation whereas that of 1,3-diphenyl-5-(2′-methoxyphenyl)pyrazole proceeds by a different and low quantum yield pathway.

THE photocyclisation of the halogenophenylpyrazoles[1] (1) to give (4) (Scheme) proceeds in *ca.* 80% isolated yield in deoxygenated methanol. H.p.l.c. monitoring shows close to quantitative cyclisation and the replacement of halogen by hydrogen (due to hydrogen abstraction from the solvent) cannot be detected (detection limit 0·2%) at any stage of the reaction. On a simple homolysis model one would expect some competition for the phenyl σ-radicals by the solvent against the intramolecular cyclisation. Such competition has been observed previously.[2,3]

The quantum yields of cyclisation (ϕ) in a given solvent (see Table) show no correlation with the corresponding bond dissociation energies and this appears to be a rare, or even unique case where $\phi_{Br} > \phi_{Cl} > \phi_I$. The solvent effects on ϕ are similar for all the halogeno-compounds showing a smooth dependence on viscosity even though the solvents differ in polarity and availability of hydrogen towards radical abstraction. This is evidence for a non-polar intermediate in the rate controlling step and the viscosity dependence implies a step involving the separation of species.[4] The sum of evidence indicates that these separating species are the delocalised radical (3) and the halogen atom and that phenyl σ-radicals are not involved. As one moves from halogen to other substituents with higher bond strengths, the ϕ values fall rapidly but remain viscosity dependent when X = OAc. At even higher bond strengths when X = OMe, there is a sudden change to a mechanism dependent on solvent polarity. Thus the radical mechanism cannot operate at very high bond strengths when other available high energy pathways must be utilized. Such could be an electrocyclic reaction[5] *via* the intermediate (5; X = OMe) which is in accord with the observed polarity dependence. Cyclisation *via* such intermediates has been speculated in related cases.[6]



SCHEME

TABLE. 254 nm Irradiation of aerated 4×10^{-3} M solution of (**1**) to give (**4**) at 35 °C (*I ca.* 4·5 Einstein min^{-1})[a]

Solvent	η (35 °C)[b]/cP	Z[c]	ϕ[d] Group X				
			Cl	Br	I	OAc	OMe
Hexane	0·28	<54·0	0·38	0·45	0·35		
Methanol	0·49	83·6	0·33	0·42	0·27	0·015	0·0032
Cyclohexane	0·80	<54·0	0·34	0·40	0·21	0·011[e]	<0·0001
1,4-Dioxan	1·00				0·20		
t-Butyl alcohol	3·00	71·3	0·21	0·20	0·12	0·009[e]	<0·0001
Ethane-1,2-diol	12	85·1	0·09	0·09	0·021	0·0042	0·0041

[a] −193 °C Luminescence data for the halogenopyrazoles in EtOH: $E_s = 351$, $E_T = 272$ kJ mol^{-1}; $D_{\text{Ph-X}}$: I, 238; Br, 297; Cl, 360; OH, 439 kJ mol^{-1} (M. Szwarc and D. Williams, *J. Chem. Phys.*, 1952, **20**, 1171). [b] Interpolated from J. A. Riddick and W. B. Bunger, 'Organic Solvents,' 3rd edn., Wiley, New York, 1970. [c] Solvent polarity parameter (E. M. Kosower, *J. Amer. Chem. Soc.*, 1958, **80**, 3253). [d] Maximum error ±10%, measurement by u.v. spectroscopy and uranyl oxelate actinometry. [e] Concurrent formation of another product in very minor amount.

For the halogen cases, the observed insensitivity of ϕ (in cyclohexane) towards air and piperylene rules out phenyl σ-radicals and halogenophenylpyrazole triplet states (which can be shown to be quenchable) from being intermediates in the unsensitized reaction. The reaction (**1**) → (**4**), where X = Cl, Br, or I, can be sensitized in cyclohexane by benzophenone at 80% of the unsensitized rate (triphenylene gives 65% of this rate) so it must be concluded that inter-system crossing is inefficient in the unsensitized reaction. Of the other possible paths for depletion of the S_1^0 state, a non-predissociative reaction from S_1^0 is unlikely because of the near identity in rates and products for the sensitized and direct reactions. A predissociation from S_1^v into a repulsive state (*i.e.*, $^3\sigma\sigma^*$) is made unlikely by the observed wavelength independence[7] of ϕ over the whole absorption band. Thus we are brought to the conclusion that internal conversion of S_1^0 into S_0^v leads to reaction. S_0^v States can also be reached, at a somewhat lower energy, from T_1 which is populated in the sensitized reactions.

The low energy requirements for cyclisation are demonstrated by (a) the occurrence of the sensitized reaction and (b) the similar ϕ values for the chloro-, bromo-, and iodo-compounds in the direct photoreaction. This seems to result from anchimeric assistance[8] from the 1-phenyl ring by π-complexing with the developing radical centres of the carbon–halogen bond, with a transition state best represented by (**2**).

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[8] For related thermal cases, see: 'Free Radicals,' ed. J. Kochi, Wiley, New York, 1973, vol. 1, p. 137.