Photocyclisation of 2-Halogenobenzanilides: An Extreme Example of Halogen Atom, Solvent, and Isomer Dependence. A Practical Phenanthridine Synthesis

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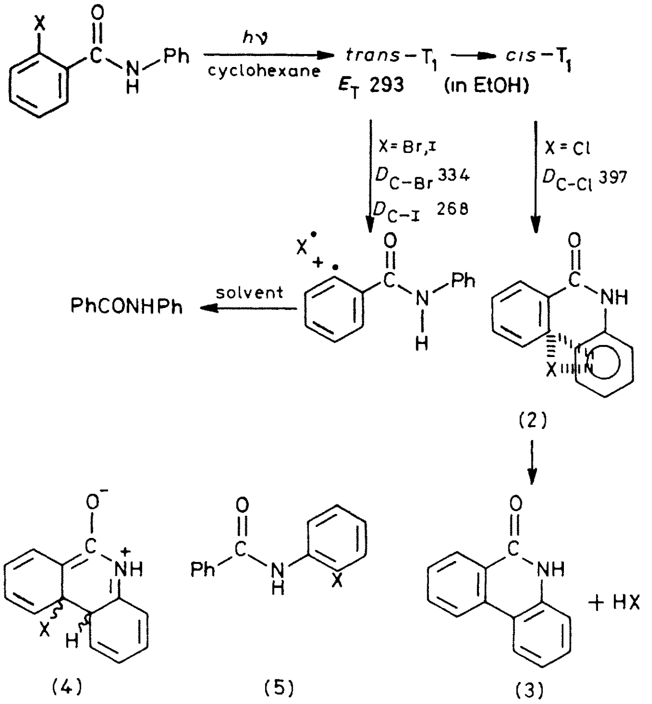
Summary 2-Chlorobenzanilides photocyclise to phenanthridones by assisted homolysis of the carbon–chlorine bond.

Assistance to carbon–halogen bond photohomolysis by radical complexation[1] results in a formal lowering of dissociation energy for the fissioning bond An important corollary of this process is that flexible molecules with suitable excited state and bond energy values will undergo homolysis only in configurations where assistance is available so that exclusive cyclisation would occur and free radical reactions from an extended conformation and involving solvent molecules would be avoided. Assuming that no other photoreaction paths are significant, the yields of cyclised product should be high. The 2-halogenobenzanilides illustrate this point.



SCHEME Energies in kJ mol^{-1}

Irradiation at 254 nm of (**1**, X = Cl) in deaerated cyclohexane gives nearly quantitative cyclisation to (**3**) with isosbestic points observed by u.v. spectroscopy, whereas (**1**, X = Br or I) gives benzanilide as the initial product with no detectable (**3**). Benzanilide gives rise to secondary products *via* the photo-Fries reaction.[2] Irradiation of (**1**, X = OMe) gives no (**3**) under similar conditions implying that the electrocyclic path *via* (**4**, X = OMe) is slow compared to skeletal decomposition.[3] This halogen atom dependent reaction is understandable in terms of the possibility of unassisted fission from the *trans*-configuration of (**1**, X = Br and I) (see energy data in the Scheme) but not from (**1**, X = Cl). No dimers appear to be involved. The *trans*-form of benzanilides is thermodynamically stable[4] and indeed we obtained benzanilide in good yield by decomposition of the exciplex formed between (**1**, X = Cl) and photoexcited diethylaniline according to the procedure of Sakurai, Tosa, and Pac.[5]

TABLE. Conversion of 2-chlorobenzanilides into phenanthridones by 254 nm irradiation of 10^{-3}M solutions in cyclohexane under nitrogen

4′ Substituent on (**1**, X = Cl)	Phenanthridone[a]		
	ϕ	Yield/%	M.p./°C
CF_3	0.15	74	291—293
CO_2Et	0.15	70	271—272
Cl	0.25	67	326—327[b]
H	0.20	71	292—294[c]
Me	0.14	67	250—252
OMe	7.4×10^{-3}	23	228—230

[a] All compounds had satisfactory spectral and analytical data. [b] H. Gilman and J. Eisch, *J. Am. Chem. Soc.*, 1957, **79**, 5479, give m.p. 327 °C. [c] L. Oyster and H. Adkins, *J. Am. Chem. Soc.*, 1921, **43**, 208, give m.p. 293 °C.

The photocyclisation of (**1**, X = Cl) is quenched by air, piperylene, and naphthalene and can be singlet (benzene) or triplet (xanthone) sensitised to give (**3**) in yields of 66% and 50% respectively, implicating T_1 as the reactive excited state. Polar solvents, either neat or as minor additives in cyclohexane almost completely retard the reaction and very similar behaviour is seen in the case of the *N*-methylated derivative of (**1**, X = Cl). Solvation[6] of the polar T_1 state lowers the available energy thus making the transition state (**2**) inaccessible.

Irradiation of (**5**, X = Cl) at 254 nm leads to photodecomposition instead of formation of (**3**) and under milder conditions ($\lambda > 300$ nm, benzene solvent) yields 54% of (**5**, X = Ph). In contrast, 4′-chlorobenzanilide is relatively photostable. Weak assistance from the carbonyl group in the *trans*-form of (**5**, X = Cl) to the fissioning carbon–chlorine bond appears to be responsible for this reaction. Of considerable relevance is the recent report of benzothiazole photosynthesis from 2-chlorothioacetanilides.[7]

A series of phenanthridones have been synthesised by irradiation of 4′-substituted 2-chlorobenzanilides, and the reaction work-up procedure is very simple. The simplicity of the method is in marked contrast to older syntheses.[8] Earlier photochemical methods from (**1**, X = H),[9] (**1**, X = I),[9,3] or (**1**, X = OMe)[3] are slow or give substantial amounts of side products. To our knowledge there is only one other isolated example of a 2-chlorobenzanilide photocyclisation and none of the above features of this reaction was recognised.[10]

The principal effects of 4^1-substitution on the quantum yield (ϕ) for cyclisation and on the yield of cyclised product (see Table) appear to be due to changes in the rotational barrier about the peptide bond and to changes in the π-donor strength of the aniline ring.

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[1] J. Grimshaw and A. P. de Silva, *J. Chem. Soc., Chem. Commun.*, 1979, 193.
[2] D. Bellus, *Adv. Photochem.*, 1971, **8**, 109.
[3] Compare G. R. Lenz, *J. Org. Chem.*, 1974, **39**, 2839; Y. Kanaoka and K. Itoh, *J. Chem. Soc. Chem. Commun.*, 1973, 647.
[4] For closely related examples see J. Grimshaw and J. Trocha Grimshaw, *J. Chem. Soc., Perkin Trans. 2*, 1975, 215.
[5] C. Pac, T. Tosa, and H. Sakurai, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 1169.
[6] D. Schulte-Frohlinde, H. Blume, and H. Gusten, *J. Phys. Chem.*, 1962, **66**, 2485; D. Gegiou, K. A. Muszkat, and E. Fischer, *J. Am. Chem. Soc.*, 1966, **90**, 3907.
[7] R. Paramasivam, R. Palaniappan, and V. T. Ramakrishran, *J. Chem. Soc., Chem. Commun.*, 1979, 260.
[8] B. R. T. Keene and P. Tissington, *Adv. Heterocycl. Chem.*, 1971, **13**, 315.
[9] B. S. Thyagarajan, N. Kharasch, H. B. Lewis, and W. Wolf, *Chem. Commun.*, 1967, 614.
[10] K. Ito, T. Naruchi, and K. Komoriya, *Japan Kokai*, 78 77067 (*Chem. Abs.*, 1978, **89**, 163,430).