Photocyclization of Aryl Halides. Part 3.[1] Phenanthridone Photosynthesis from 2-Halogenobenzanilides

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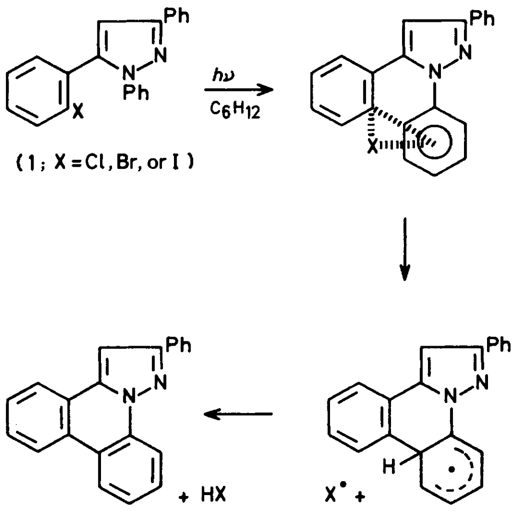
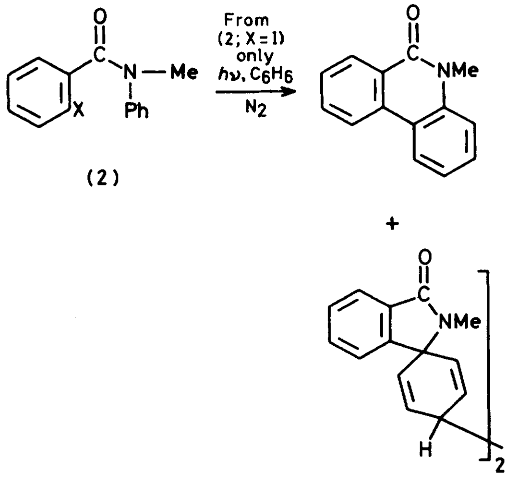
2-Chlorobenzanilides cyclize to phenanthridones in deaerated cyclohexane solution on 254 nm irradiation, whereas 2-bromo- and 2-iodo-benzanilides undergo dehalogenative reduction. These observations are understandable in terms of the assisted homolysis model as applied to configurationally flexible molecules. Cyclization in hydrocarbon media is retarded by triplet quenchers and fails in polar solvents. The cyclization can also be singlet and triplet sensitized. 4'-Substituents influence the cyclization quantum yield by altering the π-donor ability of the aniline ring and the rotational barrier about the amide bond.

EARLIER Parts [1,2] have been concerned with the photocyclization of molecules having adjacent halogenophenyl and phenyl substituents held in a rigid *cis*-configuration. Thus the pyrazoles [2] (1) are efficiently cyclized even when the carbon–halogen bond strength is greater than the energy available from conversion of the excited state to an S_0^v state. Assistance to bond homolysis from complexation of the developing radical centres by the adjacent π-cloud was proposed to account for these reactions.

Conformational mobility of the molecular framework which holds the halogenophenyl and phenyl substituents brings with it the possibility, where an excited state of sufficient energy exists, of carbon–halogen bond fission from an extended configuration leading to reaction with the solvent rather than cyclization. Since the extended conformation is usually preferred on thermodynamic considerations, photocyclization of conformationally mobile systems occurs in poor yield unless aqueous media of low hydrogen atom donor ability are employed.[3]


(1; X = Cl, Br, or I)

Previously [2] we have shown how radical complexation can assist the homolysis of a carbon–halogen bond during cyclization. A corollary which arises from this is that the fissioning bond is effectively weaker in the cyclizable conformation than in the extended form. In a molecule with suitable excited state energy levels, the extended conformer would not allow carbon–halogen bond fission so that cyclization from the folded conformer could be the sole photochemical reaction, assuming a molecular framework which is photostable. In this way solvent reactions can be eliminated leading to high chemical yields of cyclized products. An important qualification is that isomerization paths must be available to the thermodynamically stable conformer enabling it to pass into the cyclizable conformation within the lifetime of the reactive excited state.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2-Iodobenzanilides [4] have been photocyclized to phenanthridones in poor yields. 2-Bromo-derivatives [5] and their benzologues [6] have also been photocyclized though the yields remain poor. Except for one isolated example [6] the chloro-derivatives have not been examined, possibly due to a widely held belief in the photostability of aryl chlorides.[7] These low yields of cyclized products have been attributed to the predominant *trans*-diaryl geometry of benzanilides and higher yields of photocyclized products are found from the 2-halogeno-*N*-methylbenzanilides (2) which predominantly adopt a *cis*-diaryl configuration.[8] Therefore, if the energetics are suitable, the photocyclization of 2-halogenobenzanilides should provide a test of the ideas in the previous paragraph.[9] The photocyclization of 2-halogeno-*N*-alkylbenzanilides has been successful in a number of cases.[5, 10]

The electronic spectral data (Table 1) for benzanilides display no serious alteration upon introduction of the *o*-halogeno-group, though *N*-methylation, which favours the *cis*-diphenyl configuration,[8] gives rise to a markedly weaker and blue-shifted absorption spectrum. Substituents in the 4′-position cause a bathochromic shift in absorption, the largest shift being produced when the group exerts a resonance effect. In contrast, these same substituents cause no change in the position of phosphorescence emission, though alterations in the resolution of vibrational splitting and emission intensity and duration are observed. The phosphorescence lifetime (*ca.* 0.03 s) and the vibrational splitting (1 000—1 450 cm^{-1}) suggest emission from a $^3\pi\pi^*$ state.[11] The internal heavy atom effect exerted by the halogen group is moderate due to the asymmetric nature of the chromophore.

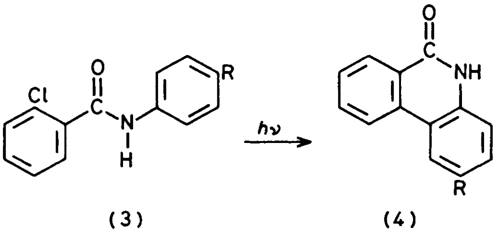
TABLE 1

Spectra data on substituted benzanilides

Benzanilide substituent		U.v. absorption, cyclohexane	Phosphorescence spectrum [a] EtOH glass 77 K		
4′-	2-	$\lambda_{max.}$/nm ($\epsilon_{max.}$/10^4 mol^{-1} cm^{-1})	λ_p/nm	I_p [b]	τ_p/s [c]
H	H	266 (1.12)	409, 435, 455 [d]	1	0.04
H	OMe	268 (1.27), 279 (1.79), 298 (0.97)			
H	Cl	265 (0.95), 280 (0.82)	406, 433, 462	2	
H	Br	262 (0.88), 280 (0.69)	407, 432, 358	4	0.03
H	I	255 (0.94), 280 (0.59)	408, 435, 461 [e]	3	
CF_3	Cl	263 (1.30)	406, 435	8	
CO_2Et	Cl	280 (2.20)	428, 455	7	0.10
Cl	Cl	269 (1.28), 290 (0.87)	410, 431	3	
Me	Cl	273 (0.92), 284 (0.84)	407, 432, 459 [e]	3	0.04
OMe	Cl	284 (1.02), 298 (0.81)	408, 433, 462 [e]	1	0.03

[a] A faint fluorescence occurs at 306—318 nm as an unresolved shoulder on the band due to scattered exciting radiation. [b] Corrected to equal absorption at the exciting wavelength and normalized to the case of (3; R = H). [c] Approximate values corrected for the instrument response time of 0.05 s. [d] R. Schwetlick, J. Stumpe, and R. Noack, *Tetrahedron*, 1979, **35**, 63, give phosphorescence $\lambda_{max.}$ 410 nm, fluorescence $\lambda_{max.}$ 318 nm corresponding to E_T 293 and E_S 414 kJ mol^{-1}. [e] A weak shoulder is present at 370—380 nm.

Preparative Photochemistry.—A dilute solution of (3; R = H) in deaerated cyclohexane upon irradiation at 254 nm gave clean conversion into phenanthridone as evidenced by isosbestic points observed in the u.v. spectra of the photolyte after varying doses of radiation (see Figure 1). In contrast 2-bromo- and 2-iodobenzanilide gave no detectable amounts of phenanthridone as a photoproduct. Irradiation of a variety of 4′-substituted 2-chlorobenzanilides (3; R = CF_3, CO_2Et, CO_2Pr, Cl, H, and Me) gave the corresponding phenanthridone (4) in 67—74% yields as the sole product.



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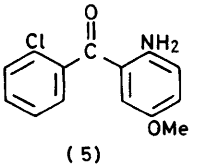

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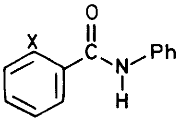

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The reaction of (3; R = OMe) however was significantly slower giving (4; R = OMe) in 23% yield together with a second product whose spectral parameters are consistent with an aminobenzophenone structure (5).

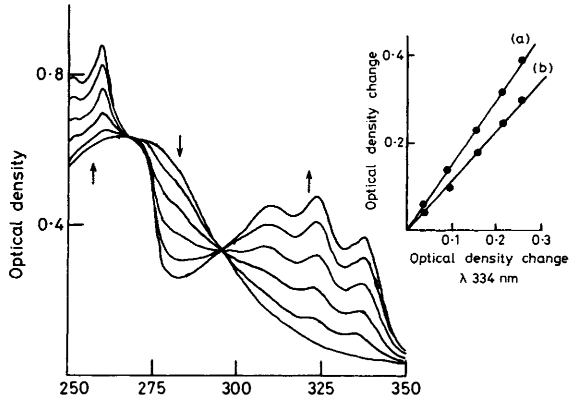


FIGURE 1 Irradiation at 254 nm of 5.77 × 10^{-5}M (3; R = H) in cyclohexane under nitrogen. U.v. spectra run at 9.5, 25.3, 50.1, 65.5, and 78.2% conversion into (4; R = H). Absorbance change at 334 nm plotted as abscissa with the modulus of absorbance changes at (a) 323 and (b) 284 nm as ordinates

Photo-Fries reactions of anilides are well known [12] and can be expected to compete with photocyclization. The products from such a photo-Fries reaction would be the corresponding *o*- and *p*-aminobenzophenones, the former being the more photostable. The present results show that such a reaction of the molecular framework is significant only when the photocyclization has been retarded by substituent effects.

This photocyclization of 2-chlorobenzanilides is a simple and practical phenanthridone synthesis of some generality, the only previous example of which is described in a Japanese patent.[6] The accessibility of the starting material is a distinct advantage over the classical syntheses which begin with biphenyl derivatives.[13] The photocyclization of benzanilide itself,[4] 2-methoxy-,[14] 2-bromo-,[5] and 2-iodo-benzanilides[4] are known to be inefficient and to give product mixtures. Repetition of the photolysis of 2-methoxy- and 2′-methoxy-benzanilide according to the literature conditions showed only small amounts of the phenanthridone to be formed among several products and a large amount of unchanged starting material even after prolonged irradiation.

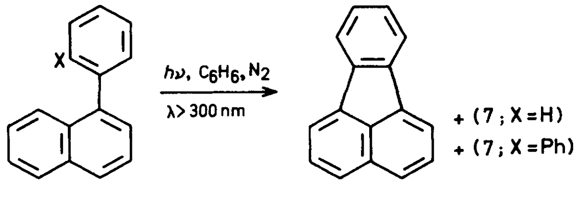
A possible limitation in the present synthesis is the relative insolubility of 2-chlorobenzanilides in cyclohexane, restricting concentrations to the millimolar level. However there is an advantage in that precipitation of the more insoluble phenanthridone occurs during the reaction thus protecting it from photodegradation. For very insoluble substrates, *e.g.* (3; R = CN), changing the solvent to benzene gave success. A comparison using 2-chlorobenzanilide showed that photolyses require a five-fold longer irradiation time per mole in benzene than in cyclohexane since the benzene solvent absorbs most of the incident 254 nm radiation and because the subsequent sensitization process is of limited efficiency.

The absorption spectrum of (3; R = H) extends to wavelengths beyond 300 nm, though the extinction coefficient falls sharply. Therefore deaerated benzene solutions of (3; R = H) were also irradiated through Pyrex ($\lambda > 300$ nm) with a medium pressure mercury arc to give phenanthridone in 68% yield. Such variation of irradiation source and solvent considerably extends the utility of the present phenanthridone synthesis. No cyclization was detectable from 2-bromobenzanilide under identical conditions.

Although hydrocarbon solvents allow high-yield photocyclization of (3; R = H), the use of a variety of more polar solvents and dilute solutions gave no formation of phenanthridone detectable by u.v. spectrometry. The solvents included dioxan, diethyl ether, t-butyl alcohol, acetonitrile, and methanol, and the spectra of the photolysis suggests photo-Fries-type decomposition. A preparative experiment in nitrogen-purged methanol yielded starting material as the only isolable crystalline compound, longer irradiation giving intractable mixtures.

2-Bromo- and 2-iodo-benzanilide show quite different photoreactivity in deaerated cyclohexane. Irradiation of the iodo-compound at 254 nm resulted in an orange precipitate giving a positive test for iodide ion. Basification of this material gave a brown oil showing a carbonyl absorption band at ν 1 620 cm^{-1}. This and other spectral information suggest that the orange precipitate is 2-aminobenzophenone hydriodide. H.p.l.c. monitoring of the photoreaction showed that benzanilide is formed as an intermediate and is further transformed to the final product. Under appropriate conditions benzanilide could be isolated in 15% yield from the reaction. Irradiation of 2-bromobenzanilide afforded a precipitate of 2-aminobenzophenone hydrobromide and we were unable to detect any benzanilide as intermediate. This photolysis proceeded more slowly so that the expected steady-state concentration of benzanilide would be lower than for the iodo-compound.

These reactions demonstrate an extreme example of halogen atom-dependent photoreactivity which has a close parallel in the reactivity of the 1-phenylnaphthalenes (7; X = Cl, Br, or I).[15] The proportion of (8) in the photoproducts is large for the chloro-compound but negligible from the iodo-compound while the bromo-compound is intermediate.

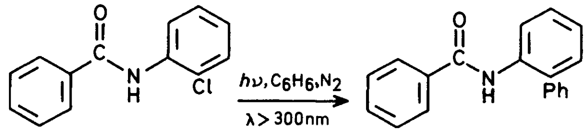


(7; X = Cl, Br, or I) (8)

Benzophenone (E_T 284 kJ mol^{-1})[16] sensitized irradiation of 2-chloro- and 2-bromo-benzanilide in deaerated benzene solution gave no phenanthridone though the starting material was slowly consumed. Xanthone (E_T 309 kJ mol^{-1})[16] sensitized irradiation however gave a 50% yield of phenanthridone from 2-chlorobenzanilide whereas the bromo-analogue failed to cyclize. Therefore the conversion of 2-chlorobenzanilide into phenanthridone appears to proceed *via* the triplet state; more evidence for this will be presented shortly. Unfortunately, quantitative sensitization studies would be of questionable value due to the polarity effect exerted by the ketone sensitizer at the required concentrations. The triplet energies of (6; X = Cl, Br, or I) measured from the structured phosphorescence emission in ethanol at 80 K are all close to 293 kJ mol^{-1}. Anilides however are sensitive to hydrogen-bonding effects of the solvent[17] so this figure would be altered somewhat in non-hydrogen-bonding solvents such as benzene or cyclohexane at room temperature. The successful sensitization by xanthone implies that the relevant triplet energy will not be far from 309 kJ mol^{-1}.

The currently accepted bond dissociation energies, D_{C-X}, for aryl halides are 397, 334, and 268 kJ mol^{-1} for X = Cl, Br, and I respectively,[18] but a lowering of D_{C-X} has been observed by *o*-substituents.[19] Further, we are using gas-phase D_{C-X} values for the interpretation of reactions in solution. Remembering the uncertainties in the relevant D_{C-X} and E_T values, we believe that a simple homolysis of the carbon–halogen bond from the T_1 state of the *trans*-form of (6; X = Br or I) accounts for their dehalogenative reduction. In the case of the chloro-compound (6; X = Cl) a similar fission is energetically disfavoured, instead rotation about the peptide bond in the T_1 state occurs followed by assisted homolysis[2] and ring closure.

An alternative mechanistic possibility is that the bromo- and iodo-compounds react as described but the chloro-compound undergoes a photochemical electrocyclization in preference to the more energy-demanding carbon–halogen bond homolysis with subsequent loss of hydrogen chloride by bond heterolysis. The relative sluggishness towards cyclization of 2-methoxybenzanilides with loss of methanol noted in the literature and confirmed by us does not support such a mechanism.



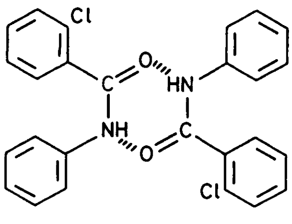
(9) (10)

A further piece of evidence against the electrocyclization mechanism is provided by the photodecomposition of 2′-chlorobenzanilide (9). This compound on irradiation at 254 nm in deaerated cyclohexane gave intractable mixtures which contained no phenanthridone detectable by u.v. spectrometry. Small amounts of phenanthridone were detected in the photolyte upon changing to benzene solvent. Irradiation in benzene at wavelengths above 300 nm resulted in a 55% yield of (10) and a detectable amount of phenanthridone. 4′-Chlorobenzanilide was photostable under similar conditions. Both 2- and 2′-chlorobenzanilide should give phenanthridone by a photochemical electrocyclization step whereas the electron-rich aniline ring is more able to provide assistance towards carbon–chlorine bond homolysis than the electron-poor benzoyl ring.[20]

The photochemical behaviour of 2-chloro-*N*-methylbenzanilide shows interesting points of difference to that of 2-chlorobenzanilide. When exposed to 254 nm radiation under similar conditions in deaerated cyclohexane, the *N*-methyl compound gave *N*-methylphenanthridone in only 11% yield after chromatography of the reaction mixture. This low yield was caused by competing photo-Fries reaction of the benzanilide and by photodecomposition of the formed *N*-methylphenanthridone. *N*-Methylation is known to increase the probability for heterolysis of the amide bond[21] and this can be demonstrated by comparing the rates of photodecomposition of phenanthridone and *N*-methylphenanthridone in cyclohexane, the latter being the faster. Thus the thermodynamically favoured *cis*-configuration of phenyl rings in the *N*-methylbenzanilide is not in itself a sufficient condition for cyclization in high chemical yield.

Photochemical Kinetics.—The effect of photochemical variables on the cyclization quantum yield of 2-chlorobenzanilide (ϕ°) was examined. The symbol ϕ is retained for quantum yields determined in the presence of a quencher or a sensitizer.

(a) *Concentration of 2-chlorobenzanilide*. Nitrogen-purged cyclohexane solutions, 2, 10, and 40 × 10^{-4} molar in (3; R = H), gave ϕ° values of 0.20, 0.21, and 0.21, respectively, upon irradiation at 254 nm. The intramolecular nature of the reaction (3) ⟶ (4) is thereby demonstrated with no involvement of hydrogen-bonded dimers (11) analogous to those found with the benzoic acids.[22] If species such as (11) were present



(11)

the *cis*-configuration would have allowed photocyclization to phenanthridone irrespective of the halogen substituent, which is contrary to experimental observation.

(b) *Quenchers*. The cyclization quantum yield from 2 × 10^{-4} molar solutions of (3; R = H) (E_T 293 kJ mol^{-1}) in deaerated cyclohexane was reduced by factors of 1.9 and over 20 by the admission of atmospheric oxygen (E_T 96 kJ mol^{-1})[16] in saturated solution (2.1 × 10^{-3}M)[23] and 0.2 molar piperylene (E_T 246 kJ mol^{-1}),[16] respectively.

TABLE 2

Naphthalene quenching of the cyclization (3) ⟶ (4) (R = H) on irradiation at 254 nm of 2 × 10^{-4}M-cyclohexane solutions

10^4 [Naphthalene]/M	$f_{\text{abs.}}$ [a]	ϕ^0/ϕ [b]
0	1.00	1.00
6	0.80	1.02
15	0.65	1.21
23	0.46	1.52
47	0.26	1.49
103	0.15	1.45
130	0.11	1.40

[a] Fraction of radiation absorbed by (3; R = H), determined from the optical densities of diluted solutions. [b] Cyclization quantum yields with (ϕ) and without (ϕ^0) additive. The ϕ values have been corrected for the fraction of incident radiation directly absorbed by the quencher.

In spite of possible complications with singlet quenching, naphthalene (E_T 259 kJ mol^{-1})[16] was selected for further quantitative experiments because of its relatively low extinction coefficient at the irradiating wavelength and its involatility during deaeration by nitrogen purging. The data in Table 2 give an initial linear segment in a Stern–Volmer plot (Figure 2), though serious deviations occur at higher quencher concentrations. Assuming similar Stern–Volmer kinetics, the initial slope of 2 × 10^2 l mol^{-1} in Figure 2 agrees reasonably well with a value of 4 × 10^2 l mol^{-1} calculated from the single data point available for oxygen.

All these facts point to the intermediacy of a lowest triplet excited state of (3; R = H) in the photocyclization. The apparent lifetime (τ) of this triplet state is deduced to be 20 ns from the Stern–Volmer

TABLE 3

Quantum yields (ϕ) for the cyclization of 2-chlorobenzanilide and 2-chloro-*N*-methylbenzanilide to the phenanthridone by irradiation of 2 × 10^{-4}M solutions in undeoxygenated cyclohexane containing added 1,4-dioxan at 254 nm

	ϕ^0/ϕ	
[1,4-Dioxan]/M	2-Chlorobenzanilide [a]	2-Chloro-*N*-methylbenzanilide
0.00	1.00	1.00
0.30	1.56	1.41
0.60	1.96	1.92
1.20	3.45	2.22

[a] U.v. monitoring corrected for the observed variation of the extinction coefficient of phenanthridone with solvent composition.

expression $\phi^0/\phi = 1 + k_q\tau[Q]$ where the rate constant of diffusion-controlled quenching, k_q, is taken to be 10^{10} l mol^{-1} s^{-1} in cyclohexane at 20 °C.[16]

(c) *Solvent.* Kinetic measurements confirmed the lack of cyclization of (3; R = H) in polar media observed during preparative-scale experiments, both with and without deaeration. Polar solvents also retard the photo-Fries reactions of anilides [24] so such a process is not significantly responsible for reducing cyclization rates by competition. Both acetonitrile and 1,4-dioxan gave rate-reduction factors of at least 50 compared to cyclohexane and similar experiments on 2-chloro-*N*-methylbenzanilide indicated a rate reduction here of at least 25-fold.

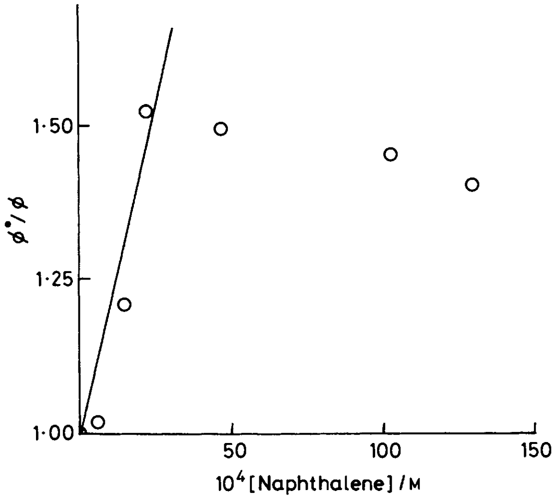


FIGURE 2 Naphthalene quenching of the photoconversion of 2-chlorobenzanilide (2 × 10^{-4}M) into phenanthridone (quantum yield ϕ) in deaerated cyclohexane, irradiation at 254 nm

The effect of added 1,4-dioxan on the cyclization of 2-chlorobenzanilide and 2-chloro-*N*-methylbenzanilide was examined in some detail (see Table 3). Hydrogen bonding and solvation effects between polar additives and the anilides are known [24] and these could lead to static quenching of photoreactivity by interacting with either the ground or the excited state. In the case of benzanilides, the T_1 state is of the $\pi\pi^*$ type which could be a strongly polar species. Therefore stabilization of the T_1 state by solvation would lead to a reduction in the energy available which could prevent it from reaching the transition state of the carbon–chloride bond fission process. Since the *N*-methyl compound shows only a marginally reduced solvent effect even though it has a complete changeover in the thermodynamically stable geometrical configuration, we can infer that solvent-induced inhibition of the *cis–trans*-isomerization process is of only secondary importance in determining the present solvent effect. Inhibition of *cis–trans*-isomerization is however known for some polar stilbenes.[25]

TABLE 4

Quantum yields (ϕ) for the cyclization of 2-chlorobenzanilide to phenanthridone in deaerated benzene at 20 °C on irradiation at 254 nm

[Substrate]/M	$10^2\ \phi$	[Substrate]/M	$10^2\ \phi$
2.4	1.93	7.6	4.84
2.4	1.65	8.1	5.17
2.9	2.53	11.0	5.61
5.1	4.07	12.1	5.61
5.7	3.63		

(d) *Sensitizers.* The benzene-sensitized conversion of 2-chlorobenzanilide into phenanthridone has preparative significance so this reaction was examined further. Quantum yield varies with substrate concentration (Table 4) and a linear relationship (Figure 3) was found between ϕ^{-1} and $[ArCl]^{-1}$, where ArCl refers to 2-chlorobenzanilide. This linear relationship can be understood

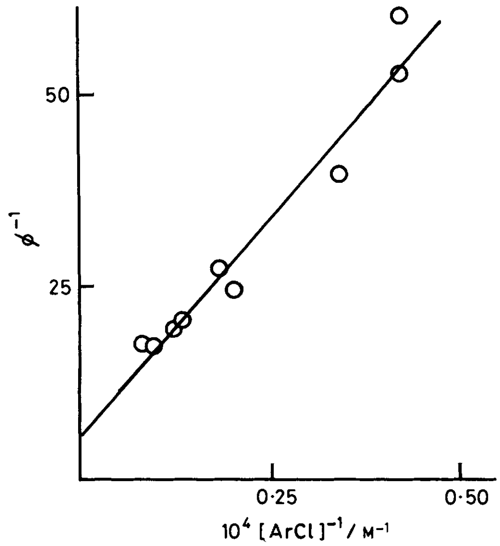
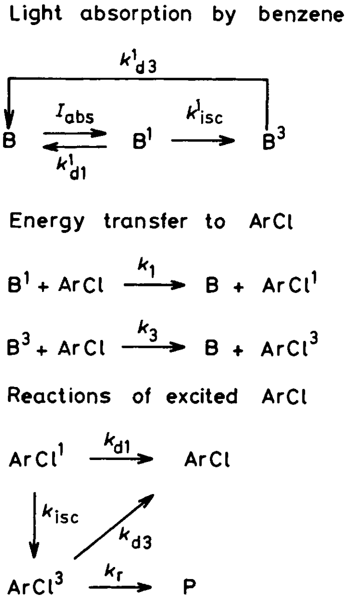


FIGURE 3 Variation of quantum yield (ϕ) for the photoconversion of 2-chlorobenzanilide (ArCl) into phenanthridone sensitized by benzene solvent with irradiation at 254 nm under nitrogen

in terms of Scheme 1, where B and P refer to benzene and phenanthridone respectively. For the purposes here it is sufficient to describe the reaction to give a product by one step with a rate constant k_r. This step is expanded in Scheme 2.



SCHEME 1 Benzene (B)-sensitized reaction of 2-chlorobenzanilide (ArCl) to give phenanthridone (P)

The previously recorded studies with energy-transfer agents indicated that cyclization of ArCl proceeds mainly *via* the T_1 state even when this substrate was excited directly into its S_1 state. An S_1 state produced by benzene sensitization would also be expected to undergo rapid intersystem crossing to the T_1 state which would then be transformed into P. The weakness of the fluorescence of ArCl at 80 K is also consistent with a high triplet yield. Thus in hydrocarbon solvents at room temperature $k_{isc} > k_{d1}$. Assuming that steady-state kinetics apply to the processes in Scheme 1, we can derive relationship (1).

$$\phi = \frac{k_r}{k_r + k_{d3}} \cdot [\text{ArCl}] \cdot \frac{\left\{\dfrac{k_3 k^1{}_{isc}}{k^1{}_{d3} + k_3[\text{ArCl}]} + \dfrac{k_{isc} \cdot k_1}{k_{isc} + k_{d1}}\right\}}{k^1{}_{d1} + k^1{}_{isc} + k_1[\text{ArCl}]} \qquad (1)$$

Since k_1 and k_3 are rate constants for energy transfer in exothermic reactions (benzene [16] has E_S 452 and E_T 351 kJ mol^{-1}, the corresponding values for ArCl being 384 and 293 kJ mol^{-1}, respectively) their magnitude would be close to that of the rate constant for diffusive processes in benzene [16] at room temperature, which is *ca.* 10^{10} s^{-1}. Hentz *et al.*[26,27] have evaluated the various photoprocesses in benzene and report $k^1{}_{isc}$ and $k^1{}_{d3}$ to be 2×10^7 and 2×10^8 s^{-1}, respectively, for neat benzene. Remembering that $k_{isc} > k_{d1}$ and that [ArCl] = 2—10 × 10^{-4}M, inequality (2) can be deduced (in orders of magnitude, $10^{10} > 10^9$).

$$\frac{k_{isc} k_1}{k_{isc} + k_{d1}} > \frac{k_3 \cdot k^1{}_{isc}}{k^1{}_{d3} + k_3[\text{ArCl}]} \qquad (2)$$

Equation (1) can now be simplified and rearranged to derive the linear relationship (3) between ϕ^{-1} and [ArCl]$^{-1}$ observed experimentally.

$$\phi^{-1} = \frac{(k_r + k_{d3})}{k_r} \cdot \frac{(k_{isc} + k_{d1})}{k_{isc}} \cdot \frac{(k^1{}_{d1} + k^1{}_{isc})}{k_1} [\text{ArCl}]^{-1} + \frac{(k_r + k_{d3})}{k_r} \cdot \frac{(k_{isc} + k_{d1})}{k_{isc}} \qquad (3)$$

A least-squares analysis of the experimental data gives

$$\frac{k_{isc}}{(k_{isc} + k_{d1})} \cdot \frac{k_r}{(k_r + k_{d3})} = 0.17 \qquad (4)$$

relationship (4) which can be independently tested from data obtained in another solvent. This relationship concerns only rate constants for the various conversions of ArCl. The quantum yield of cyclization by direct irradiation of ArCl in a transparent solvent, with other properties similar to those of benzene, would be according to the transformations of ArCl in Scheme 1. Application of the steady-state hypothesis to this situation gives relationship (5). A comparison of relationships (4) and

$$\phi^0 = \frac{k_{isc}}{(k_{isc} + k_{d1})} \cdot \frac{k_r}{(k_r + k_{d3})} \qquad (5)$$

(5) shows that the benzene-sensitized experiments predict ϕ^0 0.17 and in cyclohexane we obtained ϕ^0 0.20 which is in good agreement.

A further test of relationship (3) is obtained by noting that for this linear relationship expressed in Figure 3,

$$\frac{\text{intercept}}{\text{slope}} = 530 \text{ l mol}^{-1} = \frac{k_1}{(k^1{}_{d1} + k^1{}_{isc})} \qquad (6)$$

equation (6) holds. Now, $(k^1{}_{d1} + k^1{}_{isc})^{-1} = \tau = 27 \times 10^{-9}$ s where τ_1 is the singlet lifetime of neat benzene.[27] Combining this data gives $k_1 = 2 \times 10^{10}$ l mol^{-1} s^{-1}, which is close to the value expected for a diffusion-controlled exothermic energy transfer.[16]

(e) *Substituents*. Data illustrating the effect of substituents on the quantum yields of cyclization of 2-chlorobenzanilides (3) are collected in Table 5. No precipitation of phenanthridone product occurred during these experiments and analysis for product was carried out by u.v. absorption at the longest wavelength band listed. Due to the difficulty of quantitative dissolution of the phenanthridones the extinction coefficient was determined in benzene–cyclohexane (40 : 60). The co-solvent benzene does not significantly affect the value of $\varepsilon_{max.}$, tested by diluting cyclohexane solutions of phenanthridone with benzene.

A smooth correlation (Figure 4) is found between ϕ^0 and the Hammett σ constant for the *para*-substituent. A similar substituent effect has been encountered in the photo-oxidation of 4-substituted stilbenes to the corres-

TABLE 5

Quantum yields for the photocyclization of substituted 2-chlorobenzanilides to phenanthridones at 254 nm in cyclohexane; ϕ^0 in deaerated solution, ϕ in aerated solution

Substrate (3), R =	*para*-substituent constant σ [a]	Substituted phenanthridine $\lambda_{max.}$ [b]/nm	Substituted phenanthridine $10^{-4}\,\epsilon_{max.}$ [b]/ l mol^{-1} cm^{-1}	ϕ^0	ϕ^0/ϕ
CF_3	+0.54	332	0.90	0.15	2.1
CO_2Et	+0.45	335	1.02	0.15	3.4
Cl	+0.23	346	0.86	0.21	4.0
H [c]	0.00	336	0.82	0.20 [c]	1.9
Me	−0.17	344	0.80	0.14	3.0
OMe	−0.27	356	0.77	0.0074	3.8
2-Chloro-*N*-methylbenzanilide		341	0.86	0.050	1.7

[a] Taken from G. R. Barlin and D. D. Perrin, *Q. Rev.*, 1966, **20**, 75. [b] Determined in benzene–cyclohexane (40 : 60) because of solubility problems. [c] Reaction quenched by piperylene (0.2M) when $\phi^0/\phi > 20$.

ponding phenanthrenes.[28] Phenanthrene formation however involves an electrocyclic mechanism which appears to be inapplicable to our case so that the underlying causes of these two similar substituent effects are expected to be different.

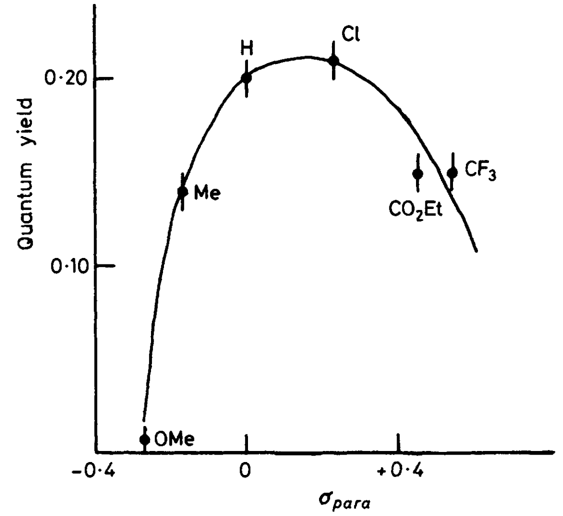
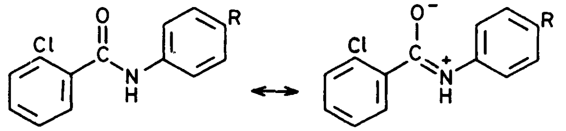


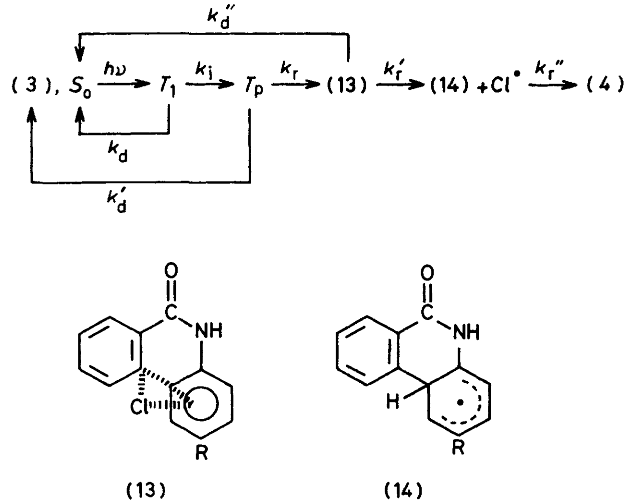
FIGURE 4 Influence of *p*-substitution on the quantum yield for the photoconversion of (3) into (4) in deaerated cyclohexane, irradiation at 254 nm

The electronic effect of a 4′-substituent may influence the reactivity of 2-chlorobenzanilide in at least three ways. First, the ability of the aniline ring to act as a π-donor towards the developing radical centres during carbon–chlorine bond fission will increase with the electron-releasing nature of the 4′-substituent. Secondly, the energy barrier to rotation about the amide bond, which rotation is crucial for cyclization, increases with the electron-releasing nature of the 4′-substituent.[29] In the valence bond representation electron-releasing substituents increase the contribution of canonical form (12) and thus increase the carbon–nitrogen bond order.



(12)

Thirdly, excited-state energies are also subject to substituent effects and the u.v. absorption maxima (Table 1) of the benzanilides indicate such an effect on the $S_0 \longrightarrow S_1$ transition. However according to the phosphorescence emission maxima (Table 1), the $T_1 \longrightarrow S_0$ transition is not altered in energy. Thus the substituent effect shown in Figure 4 has to be rationalised on the basis of the first two points above, though the irregular trend in the triplet lifetimes of substituted 2-chlorobenzanilides, as measured by ϕ^0/ϕ in Table 5, is a complicating factor.



SCHEME 2 Reaction scheme for the photocyclization of 2-chlorobenzanilides

Summarizing the first two points, electron-withdrawing substituents are expected to decrease the overall rate of cyclization because of the first effect, while electron-donating substituents decrease this rate because of the second effect and we therefore have a qualitative explanation of the experimental observation. The course of cyclization is illustrated in Scheme 2. Irradiation leads to the *trans*-triplet T_1 which affords the twisted triplet T_P produced by a 90° rotation about the amide bond. The idea of such twisted excited states was originally proposed to account for the photoisomerization of alkenes. The fission of the carbon–chlorine bond of strength 397 kJ mol^{-1} with an initially available energy of E_T 293 kJ mol^{-1} suggests assistance to bond homolysis by analogy with the reactions of pyrazoles discussed in Part 1.[2] This assistance can be depicted in structure (13) as π-complexation of developing radicals which result from crossing of T_P into an S_0^v state. In Scheme 2 intermediate (13) is given the status of a reaction intermediate but it could also be considered as only a transition state. Where the carbon–halogen bond is weaker than carbon–chlorine, direct bond fission from T_1 becomes possible and this leads to a radical with the incorrect conformation for cyclization.

In conclusion, we believe that the assisted-homolysis model for bond fission offers hope for the efficient photocyclization of conformationally flexible molecules and should provide a general mechanistic approach which is alternative to that which employs exciplex interactions.[30]

EXPERIMENTAL

Available spectrometers were Pye–Unicam SP 8000 (u.v.) and Baird Atomic SFR-100 (luminescence) instruments. Quantum yields were determined on a merry-go-round apparatus with excitation at 254 nm of optically dense samples as described in Part 2. The rate of formation of phenanthridone was determined by measuring the rate of appearance of the long wavelength absorption bands along with concurrent ferrioxalate actinometry.[31]

Preparative photochemical reactions were carried out using either a cylindrical low-pressure mercury lamp (PCQ-X1; 72 W; Ultra-Violet Products) which surrounded the reaction vessel or a high-pressure mercury lamp (TQ-150; 150 W; Hanau) fitting into an immersion well within the reaction vessel.

Benzanilides.—These were prepared by the Schotten–Bauman reaction from the appropriate substituted benzoyl chloride and aniline and crystallized from ethanol. Most are known compounds, the new compounds are listed here: *2-chloro-4′-trifluoromethylbenzanilide*, m.p. 151—152° (Found: C, 56.0; H, 3.1; N. 4.8. $C_{14}H_9ClF_3NO$ requires C, 56.2; H, 3.0; N, 4.7%); *2-chloro-4′-cyanobenzanilide*, m.p. 178—179° (Found: C, 65.4; H, 3.3; N, 10.8. $C_{14}H_9ClN_2O$ requires C, 65.6; H, 3.5; N, 10.9%); *2-chloro-4′-ethoxycarbonylbenzanilide*, m.p. 122—123° (Found: C, 63.2; H, 4.7; N, 4.8. $C_{16}H_{14}ClNO_3$ requires C, 63.4; H, 4.6; N, 4.6%); *2-chloro-4′-propoxycarbonylbenzanilide*, m.p. 75—78° (Found: C, 64.2; H, 5.0; N, 4.4. $C_{17}H_{16}ClNO_3$ requires C, 64.2; H, 5.1; N, 4.4%); *2,4′-dichlorobenzanilide*, m.p. 123—125° (Found: C, 58.5; H, 3.6; N, 5.4. $C_{13}H_9Cl_2NO$ requires C, 58.6; H, 3.4; N, 5.3%); *2-chloro-4′-methoxybenzanilide*, m.p. 130—131° (Found: C, 64.5; H, 4.8; N, 5.4. $C_{14}H_{12}ClNO_2$ requires C, 64.4; H, 4.6; N, 5.4%). All benzanilides showed $\nu_{max.}$ 3 300 (N–H stretch) and 1 670—1 690 cm^{-1} (conjugated amide carbonyl stretch).

Phenanthridones from 2-Chlorobenzanilides.—A rapidly stirred solution of the 2-chlorobenzanilide (0.3—1.0M) in cyclohexane (400 ml) was irradiated in a quartz vessel under nitrogen with a low-pressure mercury lamp (254 nm). When the starting material had been consumed as judged by t.l.c., usually after 1—7 h, the photolyte, usually a suspension, was combined with material washed from the photolysis vessel with methanol and evaporated to dryness. The residual solid was crystallized, usually from ethanol, to give the phenanthridone in yields of 67—74%. Prepared in this way were: *8-trifluoromethylphenanthridone* * (4; R = CF_3), m.p. 291—293° (Found: C, 63.7; H, 2.9; N, 5.3. $C_{14}H_8F_3NO$ requires C, 63.9; H, 3.0; N, 5.3%), crystallized from chloroform–ethanol; *8-ethoxycarbonylphenanthridone*, m.p. 271—272° (Found: C, 71.9; H, 5.0; N, 5.1. $C_{16}H_{13}NO_3$ requires C, 71.9; H, 4.9; N, 5.2%); *8-propoxycarbonylphenanthridone*, m.p. 246—247° (Found: C, 72.4; H, 5.4; N, 4.7. $C_{17}H_{15}NO_3$ requires C, 72.6; H, 5.3; N, 5.0%), crystallized from acetic acid; 8-chlorophenanthridone, m.p. 326—327° (lit.,[32] 327—328°); phenanthridone, m.p. 292—294° (lit.,[33] 291—292°); *8-methylphenanthridone*, m.p. 250—252° (Found: C, 80.2; H, 5.4; N, 6.8. $C_{14}H_{11}NO$ requires C, 80.3; H, 5.3; N, 6.7%). Phenanthridones showed $\nu_{max.}$ 3 160 (N–H stretch), 3 030 (aromatic C–H stretch), and 1 670 cm^{-1} (conjugated amide carbonyl stretch).

Photoreaction of 2-chloro-4′-methoxybenzanilide gave two products which were separated by preparative t.l.c. on silica, elution with chloroform to give *8-methoxyphenanthridone*, m.p. 228—230° (Found: C, 74.8; H, 4.8; N, 6.4. $C_{14}H_{11}NO_2$ requires C, 74.7; H, 4.9; N, 6.2%) crystallized from ethanol (yield 25%) and a small amount of an amorphous orange solid assigned structure (5) on the basis of its spectral properties, $\nu_{max.}$ 1 630 and 1 590 cm^{-1}; $\lambda_{max.}$ (methanol) 235, 340, and 400 nm; *m/e* 263 (20%, M^+), 262 (13), 261 (61, M^+), 260 (6), 246 (13), 226 (16, $M^+ - Cl$), 141 (39, C_6H_4ClCO), 139 (100, C_6H_4ClCO), 113 (10, C_6H_4Cl), and 111 (26, C_6H_4Cl).

Photoreaction of 2-Methoxy- and 2′-Methoxy-benzanilide.—2-Methoxybenzanalide (150 mg, 0.66 mol) in nitrogen-purged benzene (90 ml) and ethanol (10 ml) was irradiated through quartz at 254 nm for 16 h. Only a trace of phenanthridone was detectable by t.l.c. Irradiation of 2′-methoxybenzanilide under similar conditions or on changing the solvent to cyclohexane, methanol, or benzene gave no isolable quantity of phenanthridone though much photodecomposition was apparent in every case.

Benzene-sensitized Preparative Reactions.—2-Chloro-4′-cyanobenzanilide (130 mg, 0.5 mmol) dissolved in nitrogen-purged benzene (400 ml) was irradiated in a quartz vessel with a low-pressure mercury lamp. When t.l.c. monitoring indicated complete reaction (after 5 h), the pale yellow suspension was evaporated to yield a cream solid which was crystallized from acetic acid and sublimed *in vacuo* to yield 64% of *8-cyanophenanthridone*, m.p. 300° (Found: C, 76.6; H, 3.7; N, 12.8. $C_{14}H_8N_2O$ requires C, 76.4; H, 3.6; N, 12.7%); $\nu_{max.}$ 3 160, 3 020, 2 230 (C=N stretch), 1 690, and 1 620 cm^{-1}; *m/e* 220 (M^+). 2-Chlorobenzanilide under the same conditions afforded phenanthridone in 66% yield.

Long-wavelength Irradiation of 2-Chlorobenzanilide.—2-Chlorobenzanilide (230 mg) in benzene (100 ml) was irradiated in a Pyrex vessel under nitrogen with a high-pressure mercury lamp (λ > 300 nm) for 14 h to complete loss of starting material. Evaporation of the solvent and crystallization of the residue from ethanol afforded phenanthridone (68%). An identical experiment with a 14 h irradiation of 2-bromobenzanilide gave no phenanthridone detectable by t.l.c.

Photodecomposition of 2-Bromo- and 2-Iodo-benzanilide.—2-Iodobenzanilide (160 mg) was dissolved in nitrogen-

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* Non-systematic numbering.

purged cyclohexane (400 ml) and irradiated in a quartz vessel with a low-pressure mercury lamp and with rapid stirring. The solution became yellow and an orange precipitate formed. The precipitate was collected and showed $\nu_{max.}$ 2 500—3 100 cm^{-1} ($R_3\overset{+}{N}$–H stretch); $\lambda_{max.}$ (MeOH) 285, 335, and 410 nm, and gave a positive test for halide ions. It was dissolved in a small volume of methanol and partitioned between ether and aqueous sodium hydrogencarbonate. The ether layer was extracted with dilute hydrochloric acid, the resulting aqueous layer basified with sodium hydrogencarbonate, and the product extracted with ether. After drying (Na_2SO_4), evaporation of the solvent left a brown oil, $\nu_{max.}$ 3 340, 1 620, and 1 590 cm^{-1}; $\lambda_{max.}$ (cyclohexane) 235, 305, and 364 nm; m/e 197 (56%, M^+), 196 (63), 107 (100), 105 (100, $Ph\overset{+}{C}O$), 77 (64, Ph^+), and 74 (100). The evidence suggests an aminobenzophenone structure for this product. 2-Bromobenzanilide under similar conditions gave a brown precipitate with $\nu_{max.}$ 2 500—3 100 cm^{-1} and from which an aminobenzophenone, m/e 197 (M^+), could be obtained.

These experiments were repeated with h.p.l.c. analysis of portions [silica column, dichloromethane–cyclohexane (9 : 1), flow rate 1.2 ml min^{-1}, monitoring at 260 nm]. Prior to analysis the samples were washed with aqueous hydrochloric acid to remove basic material. Gradual disappearance of starting material and the appearance and subsequent disappearance of benzanilide was indicated with a maximum yield of 15% for the iodo-case and 1% for the bromo-compound. Photodecomposition of 2-iodobenzanilide for optimum time, evaporation of the solvent and preparative t.l.c. (silica, dichloromethane) of the residue gave benzanilide (15% yield), identified by m.p. and mixed m.p.

Triplet-sensitized Conversion of 2-Chlorobenzanilide.—(a) *Using benzophenone*. A solution of 2-chlorobenzanilide (115 mg, 0.5 mmol) and benzophenone (600 mg, 3.3 mmol) in nitrogen-purged benzene was irradiated at $\lambda > 350$ nm (high-pressure mercury lamp, filtered with 2.5 10^{-3}M-bismuth trichloride in 8M-hydrochloric acid)[34] in Pyrex apparatus for an extended period. Monitoring by t.l.c. gave no indication of the formation of phenanthridone though the starting material was slowly consumed. 2-Bromobenzanilide behaved in the same manner.

(b) *Using xanthone*. A solution of 2-chlorobenzanilide (230 mg, 1 mmol) and xanthone (500 mg, 2.5 mmol) in nitrogen-purged benzene (100 ml) was irradiated in a Pyrex vessel with a high-pressure mercury lamp ($\lambda > 300$ nm). Under these conditions *ca.* 92% of the incident radiation, calculated for λ 313 nm, was absorbed by the xanthone. After 18 h, t.l.c. showed complete disappearance of starting material, the solvent was removed, and the residue chromatographed on a column of silica eluting with chloroform–ether. Xanthone was retained on the column and evaporation of the eluant afforded phenanthridone (50% yield). Under identical conditions 2-bromobenzanilide gave no phenanthridone detectable by t.l.c.

Photoreaction of 2-Chlorobenzanilide and Diethylaniline.—A solution of 2-chlorobenzanilide (150 mg, 0.66 mmol), diethylaniline (660 mg, 6.6 mmol), and triethylamine in nitrogen-purged methanol (130 ml) was irradiated with a high-pressure mercury lamp in Pyrex apparatus for 30 min when t.l.c. monitoring indicated complete reaction. Evaporation of the solvent left a brown oil which was partitioned between benzene and dilute hydrochloric acid. Evaporation of the dried (Na_2SO_4) benzene layer left a solid which was crystallized from ethanol to give benzanilide (67% yield) identified by m.p. and mixed m.p.

N-*Methylphenanthridone from* 2-*Chloro*-N-*methylbenzanilide.*—2-Chlorobenzanilide (450 mg) in nitrogen-purged cyclohexane (400 ml) was irradiated with a low-pressure mercury lamp in quartz apparatus for 4 h when t.l.c. indicated complete reaction. Evaporation of the photolyte and preparative t.l.c. (silica, benzene) gave, after crystallization from ethanol, *N*-methylphenanthridone (11% yield), m.p. 105—108° (lit.,[35] 107—108°) undepressed on admixture with a sample prepared by methylation[36] of phenanthridone.

Photoreaction of 2′-Chlorobenzanilide in Benzene.—2′-Chlorobenzanilide (230 mg) in nitrogen-purged benzene (100 ml) was irradiated with a high-pressure mercury lamp in Pyrex apparatus ($\lambda > 300$ nm) for 24 h when t.l.c. indicated complete reaction. Evaporation of the photolyte and preparative t.l.c. (silica, dichloromethane) gave a small amount of phenanthridone identified by its t.l.c. and u.v. properties, and 2-benzoylaminobiphenyl, m.p. 87—88° (lit.,[37] 85—86°) (55% yield), identified by comparison with an authentic sample.

4′-Chlorobenzanilide was photostable under these conditions as determined by t.l.c. examination of the photolyte.

Irradiation of 2′-chlorobenzanilide in benzene or in cyclohexane with a low-pressure mercury lamp in quartz apparatus caused loss of starting material and the formation of intractable products with no indication by u.v. spectroscopy of the formation of phenanthridone except in trace amounts.

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