Photocyclization of Aryl Halides. Part 2.[1] The Upper Excited State Reactivity of 3-(2-Halogenoanilino)-1,3-diphenylprop-2-enones; Hydrogen-bonded Configurational Lock in Photosynthesis

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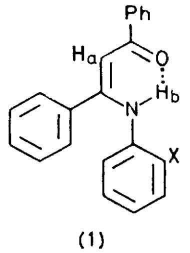
Photocyclization of the internally hydrogen-bonded dibenzoylmethane 2-bromo- and 2-iodo-anils proceeds cleanly, though with low quantum yield, to afford a phenanthridine derivative directly and with very little competition from hydrogen abstraction reactions involving solvent molecules. In contrast, the photoexcited copper complexes of the above anils undergo demetallation as the principal reaction. The cyclization quantum yield from the anils is strongly dependent on the halogen group and is also influenced by the viscosity, but not the polarity, of the solvent. The effects of added air and change of the irradiation wavelength indicate that cyclization proceeds by carbon–halogen bond fission from an upper excited state.

THE photocyclization of benzylideneanilines to phenanthridines [2,3] and other stilbenoid systems [4] to phenanthrenes is hampered by energy-wasting *cis–trans*-photoisomerization. Geometrical isomerization can be blocked by locking the cyclizable *cis*-diphenyl configuration with a link of several covalent bonds and many efficient photocyclizations in the stilbene series illustrate the successful application of this idea.[5] However, the extension to benzylideneanilines is not straightforward. The building of a heterocycle onto the azomethine link in benzylideneaniline of necessity creates a quaternary nitrogen centre. Such charged heterocycles readily undergo the oxidative stilbene-type cyclization.[6] The building of a neutral heterocycle onto benzylideneaniline of necessity removes the double-bond azomethine link and this drastically lowers the efficiency for oxidative photocyclization. In general, a formal stilbenoid system must be present to allow oxidative photocyclization of *i,j*-diphenyl heterocycles.[7]

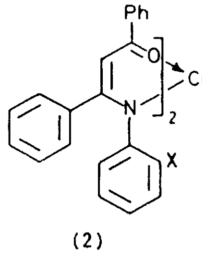
One is forced to look towards dehydrohalogenative photocyclization as a route to both simple and fused ring phenanthridine derivatives. Simple *o*-halogenobenzylideneanilines have not been photocyclized successfully due to the ease with which they undergo photoisomerization and reactions from the *trans*-isomer.[8] The preparation of fused ring phenanthridines by this route is successful,[1,9] though the products cannot easily be degraded to simple phenanthridines. Selective degradation of the polyheterocyclic product would be possible if the configuration holding heterocycle contained a bond with distinguishing properties such as (a) a hydrogen or (b) a co-ordinate bond, *i.e.* virtual heterocycles or metallocenes may serve as configuration-holding rings. A suitable example is provided by (1; X = Cl, Br, or I) which could be metallated to give (2). During the course of these investigations [10] a report appeared on the photocyclization of the co-ordinate compounds (3; X = H, Cl, or Br) to give a product readily converted into phenanthridine by the action of lithium aluminium hydride.[11]

Spectroscopic Properties.—The substrates (1) and (2) (X = H Cl, Br, or I) were prepared by modifications of standard methods. The n.m.r. spectra of the anils (1) are in accordance with the structure given rather than the enol-imine tautomers. Change of the halogen has negligible effect on either the n.m.r. or the u.v. spectral properties but acidification of (1) causes a considerable change in the long wavelength u.v. absorption band indicating the importance of the nitrogen lone pair in the chromophore. Unfortunately none of the compounds (1) could be excited to fluorescence or phosphorescence in ethanol at 80 K at any wavelength, efficient intramolecular processes such as phototautomerism [12] apparently being responsible for the lack of emission.

Preparative Photochemistry.—Irradiation of (1; X = H or halogen) in the presence of and in the absence of oxidants at the longest wavelength absorption band gave negligible reaction. Shorter wavelength radiation also failed to effect a reaction from (1; X = H) and this lack of cyclization reflects the absence of a stilbenoid system in (1). On the other hand, short wavelength (254 nm) irradiation of (1; X = halogen) allowed cyclization depending on the halogen substituent.



(1)



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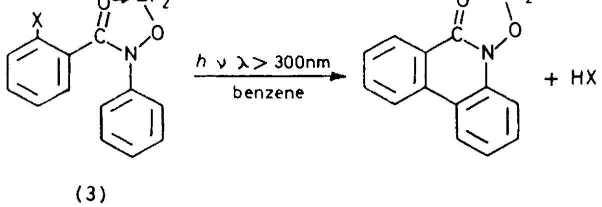
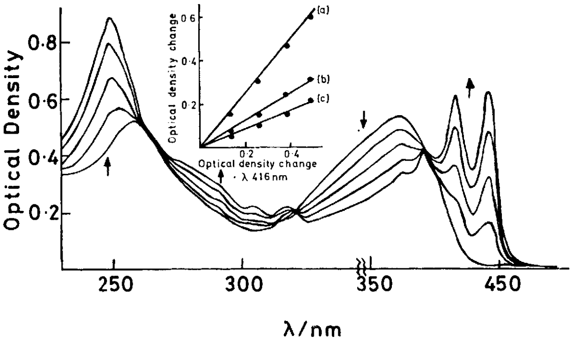


(3)

Irradiation of (1; X = Br and I) in dilute solution in deaerated cyclohexane and following the reaction by u.v. spectroscopy revealed a system with isosbestic points (see Figure) and indicating cyclization with the near absence of side reactions. The chloro-compound reacted more slowly under the same conditions allowing the intervention of secondary processes which caused a deterioration in the isosbestic points.

Under preparative conditions in more concentrated solution, the cyclized product precipitated out as a yellow solid in yields up to 70%. It gave a positive test for halide ion and showed i.r. bands at 2 500—3 000 and 1 680 cm^{-1}, indicative of protonated nitrogen and hydrogen-bonded aryl ketone functions which fit structure (4). However the u.v. spectra of methanol or cyclohexane solutions of (4) correspond to the extended chromophore of (5), suggesting hydrolysis by moisture and (4) can be regenerated by acidification (0.12M-hydrochloric acid in methanol) when the structured long wavelength absorption all but disappears. The pure neutral compound (5), obtained by basification of its salts and then chromatography, showed no i.r. absorption in the carbonyl region.



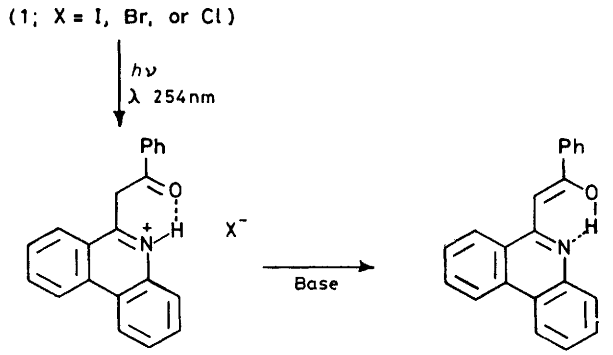
Irradiation at 254 nm of 2.43×10^{-5} mol l^{-1} (1; X = Br) in cyclohexane. U.v. spectra run at 17.5, 34.0, 52.0, and 67.0% conversion into (5). Absorbance change at 416 nm plotted as absicissa with the modulus of absorbance changes at (a) 442, (b) 428, and (c) 350 nm as ordinates

The conversion of (1; X = I) to (5) could also be conducted satisfactorily in methanol and under these conditions the solution remained homogeneous. However, the one-phase conditions are detrimental to the process from the slower reacting bromo-compound due to light absorption by and subsequent photochemistry of the products.

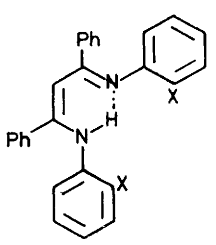
In these experiments no significant quantities of (1; X = H) could be isolated. H.p.l.c. studies showed the existence of small quantities (<4%) of (1; X = H), as the only product besides (5) in the photoreactions of (1; X = Br or I) on 254 nm irradiation in a variety of solvents with or without aeration. The chloro-compound gave several side products besides (1; X = H).

The product (4) is a simple phenanthridine derivative and thus the conversion of (1) into (4) constitutes a phenanthridine photosynthesis without the need of a holding ring. Further mild photodegradation of (4) should be possible as demonstrated by the appearance, shown using t.l.c., of simple phenanthridines upon irradiation (λ > 300 nm) of (4) in acidified methanol. A Norrish Type I process is presumed.[13]

Photochemical studies with (2; X = H or halogen) indicated a facile demetallation reaction under the usual photolysis conditions. The free ligand so produced then underwent the reactions reported above. A related demetallation has been reported previously for copper(II) diketonates and arises out of a photochemical charge-transfer process.[14] The use of a copper(II) complex as the configurational lock was therefore abandoned.



(4) (5)



(6)

Photochemical Kinetics.—The influence of change of halogen on the cyclization rates of (1) is as commonly expected with an order of reactivity I > Br > Cl.[15] Quantum yields for product formation (ϕ) are given in Table 1. There is a small increase in ϕ in the presence of air, which is unusual. The most likely explanation is that in absence of air there is photodecomposition of the product, giving rise to an apparent decrease in ϕ, both

TABLE 1

Quantum yields for the appearance of cyclization product (5) from irradiation of (1) in 2×10^{-4}M solution at 254 nm and $I_{\text{abs.}} = 2 \times 10^{-4}$E l^{-1} h^{-1}, taken to <1.5% conversion

	$\eta_{20°}$ [a]/ cP	$10^4\phi$ for (1), X = Cl [b]	Br	I	Atmosphere
Hexane	0.31	1.6	160	920	Air
Methanol	0.55	1.0	86	520	Air
Cyclohexane	0.98	1.2	110	460	Air
Cyclohexane	0.98	0.8	88	430	Nitrogen
Ethane-1,2-diol	21	0.04	11	43	Air

[a] Taken from J. A. Riddick and W. B. Bunger, 'Organic Solvents,' Wiley, New York, 1970, 3rd edn. [b] The chloro-compound gives smaller amounts of other products.

by direct absorption and in a process sensitized by (1) and which increases in importance as ϕ decreases in value. Such a photodecomposition is probably a Norris Type I process and will be quenched by air. Cyclization proceeds *via* unquenchable states.

There is a dependence of ϕ on solvent viscosity which is evident from the data in Table 1. This supports a homolytic pathway for cyclization.[1] The further lowering of ϕ in polar solvents appears to be caused by faster photodecomposition of the cyclized product due to its higher molar absorptivity at 254 nm in methanol. A comparison of the u.v. spectra of (1) in cyclohexane and methanol indicates that the compound still exists as the keto-enamine in methanol. Since the cyclized compound is still the principal product from irradiation in methanol, the intramolecular hydrogen bond must still exist in this solvent.

This photocyclization, (1) $\longrightarrow$ (4), shows an unprecedented wavelength dependence (see Table 2) for an aryl halide photoreaction in solution. The results were obtained from the initial conversion rates of optically dense solutions and are therefore free of the corrections necessary due to partial absorption of broad band radiation by dilute solutions and screening effects discussed by Kreysig *et al.*[16] Complete elimination of internal screening appears impossible in these cyclizations even though conversions were kept below 1.5% and some minor trends in ϕ values given in Table 1 have already been ascribed to light absorption by the product and subsequent photoreaction.

TABLE 2

Wavelength dependence of the quantum yield for the appearance of cyclized product (5) from irradiation of (1) in 2×10^{-4}M solution in cyclohexane under air, taken to <1.5% conversion

Irradiation wavelength (nm)	$I_{abs.}$/ 10^{-4}E l^{-1} h^{-1}	$10^4 \phi$ for (1)		
		Cl	Br	I
254	2.0	1.2	110	460
315	0.5	0.2	4	90
335	0.3	0.4	0.4	9
370	1.3	0.1	1	4

Ichimura and Mori observed the wavelength dependence of chlorobenzene dehalogenative reduction in the vapour phase.[17] Two other possible examples of wavelength dependence in the solution phase are the dehalogenation of 2-chlorobiphenyl [18] and iodobenzene,[19] both of which show lowered quantum yields on irradiation at the foot of the $S_0 \longrightarrow S_1$ absorption band. This region of the spectrum contains $S_0 \longrightarrow T_1$ bands which could show a different reactivity but also, in the case of 2-chlorobiphenyl, the dechlorination product absorbs more strongly in this region leading to considerable internal screening and therefore apparently lower ϕ values.

Cyclization *via* carbon–halogen bond homolysis from the lowest excited state of (2) is inefficient because of the low energy of this state. The onset of the longest wavelength absorption band of (2) is *ca.* 440 nm which gives $E_{T_1} < E_{S_1} < 272$ kJ mol^{-1}. This figure can be compared with bond energy data for the phenyl to halogen bond where $D_{C-X} = 397, 334$, and 268 kJ mol^{-1} for X = Cl, Br, and I, respectively.[20] Population of higher energy excited states will surmount this obstacle when cyclization can occur in competition with $S_n \longrightarrow S_1$ internal conversion. The latter processes are known to be rapid,[21] but the rate of crossing into the dissociating state and subsequent bond homolysis would be of a similar magnitude.[22] S_2 (and T_2) can be populated by irradiating the absorption band centred at *ca.* 260 nm. The onset of this band is buried under the longer wavelength absorption band but can be estimated as at longer wavelengths than 300 nm, *i.e.* $E_{T_2} < E_{S_2} < 397$ kJ mol^{-1}. When this value is considered along with the bond strength data, the expected quantum yield order for bond cleavage is $\phi_I > \phi_{Br} \gg \phi_{Cl}$ as observed. Irradiation at 315 or 335 nm excites both bands, the contribution to the reactive S_2 state increasing at shorter wavelengths.

This upper excited state reactivity in an aryl halide may well be a common occurrence in other systems where the energy of the first excited state is too low to permit carbon–halogen bond fission. It should be noted that this observed wavelength effect on photocyclization could have arisen if the competing phototautomerism decreased in efficiency as the existing wavelength was decreased. However, we believe that such an explanation is an unlikely possibility.

In Part 1,[1] we presented evidence for a carbon–halogen bond fragmentation with simultaneous complexation of the forming radical centres by the π-cloud of the adjacent benzene ring. Briefly, the evidence presented was (*a*) quantitative formation of cyclized product and no replacement of halogen by hydrogen, and (*b*) insensitivity of quantum yield to the halogen used even when the excited state energy was less than the carbon–halogen bond strength. The reaction described here shows a high mass yield for cyclization but also the formation of a significant yield (<4%) for replacement of halogen by hydrogen. This, together with dependence of the quantum yield on the halogen group can be accommodated if we assume only weak complexation of the radical centres which form during bond homolysis of (1) so that energy close to D_{C-X} is required to achieve reaction. Such a situation is expected in view of the weak π-donor ability of the electron-deficient phenyl ring in (1) where this ring is conjugated to the carbonyl group.

From the present study we can draw the following conclusions. The use of hydrogen-bonded or coordinatively bonded configurational locks holds considerable promise for future photosynthetic endeavours. Upper excited state reactivity of aryl halides may be a common occurrence in systems where the energy of the lowest excited state is too low to permit carbon–halogen bond fission.

EXPERIMENTAL

Quantum Yield Determinations.—The radiation source was a medium pressure mercury arc lamp (Thorn; 250 W;

ME/D) and a high radiance grating monochromator combination mounted on an optical bench, focusing being aided by a quartz lens. Since this source emitted poorly in the 250 nm region, it was replaced for such work by a low pressure mercury arc lamp (Hanovia; 15 W; PCR-1L) filtered through 2 cm of an aqueous solution of $CoSO_4 \cdot 7H_2O$ (117 g l^{-1}) and $NiSO_4 \cdot 6H_2O$ (333 g l^{-1}). Radiation intensities were monitored (*a*) using a photodiode and nanoammeter to check the total output of the lamp, reflected from the entrance slit of the monochromator, and (*b*) by ferrioxalate actinometry[23] carried out concurrently with sample irradiation in a merry-go-round cell holder with 1 × 1 × 4 cm septum sealed quartz cells. The temperature of the photolytes remained at 20 ± 2 °C. The intensities at different wavelengths were brought to the same order of magnitude by using appropriate slits.

Quantum yields of cyclization were calculated by dilution of an aliquot portion, then measurement of the appearance rate of the long wavelength vibronic bands in the u.v. spectrum due to (5), together with actinometry. Conversions were kept below 1.5% to minimise screening and quenching of photocyclization by the more conjugated product. No complications arose due to formation of the hydrohalide (4) which is apparently hydrolysed by atmospheric moisture, and indeed the u.v. spectrum of the photolyte was unchanged by the addition of triethylamine. The photoreduction product (1; X = H) was determined by h.p.l.c analysis of the photolyte after removing mineral acid by washing with aqueous sodium hydrogencarbonate. Samples in polar solvents were evaporated and redissolved in benzene before injection: column Spherisorb silica S5W (25 cm × 0.36 cm diam.), elution with dichloromethane, flow rate 1.2 ml min^{-1}, eluate monitoring wavelength 390 nm.

TABLE 3

U.v. absorption and n.m.r. spectral data for compounds (1)

	U.v. spectrum in solvent[a]						N.m.r. spectrum[b] CDCl$_3$	
	Cyclohexane		Methanol		Methanol–0.12M HCl			
Compound	$\lambda_{max.}$/nm	$10^{-4}\epsilon_{max.}$/ l mol^{-1} cm^{-1}	$\lambda_{max.}$/nm	$10^{-4}\epsilon_{max.}$/ l mol^{-1} cm^{-1}	$\lambda_{max.}$/nm	$10^{-4}\epsilon_{max.}$/ l mol^{-1} cm^{-1}	δ_a	δ_b
(1; X = H)	254	1.62	250	1.31	250	1.17	6.15	12.97
	376	2.33	376	2.60	364	1.82		
(1; X = Cl)	257	1.44	253	1.43	256	1.20	6.21	12.88
	373	1.80	374	2.49	364	1.83		
(1; X = Br)	257	1.66	255	1.47	257	1.14	6.23	12.80
	373	2.12	374	2.47	358	1.88		
(1; X = I)	259	1.68	257	1.42	257	1.14	6.26	12.70
	373	2.04	374	2.30	358	1.86		

[a] The two absorption bands appear symmetrical about $\lambda_{max.}$. [b] The aromatic protons appear as a cluster of lines at δ 6.5—8.0; H_b resonance disappears on shaking with deuterium oxide.

3-(2-*Halogenoanilino*)-1,3-*diphenylprop*-2-*enones*.—*Method A*.[24] Equimolar amounts of dibenzoylmethane and freshly distilled aniline or 2-chloroaniline were refluxed in absence of a solvent until violent bumping ensued. The mixture was then cooled and diluted with a small volume of benzene. The crystals which separated upon cooling were removed (benzanilide from the experiment with aniline and 2-chloroaniline hydrochloride from the experiment with 2-chloroaniline) and the filtrate evaporated to an orange oil which solidified on standing. The product was obtained by crystallization of this orange solid from ethanol. 3-Anilino-1,3-diphenylprop-2-en-1-one formed yellow needles (30%), m.p. 95—98° (lit.,[24] 98—100°) (Found: C, 84.0; H, 5.8; N, 4.5. Calc. for $C_{21}H_{17}NO$: C, 84.3; H, 5.7; N, 4.7%). 3-(2-*Chloroanilino*)-1,3-*diphenylprop*-2-*enone* formed yellow needles (44%), m.p. 91—93° (Found: C, 75.6; H, 4.9; N, 4.3. $C_{21}H_{26}ClNO$ requires C, 75.7; H, 4.8; N, 4.2%).

Method B.[25] Equimolar amounts of dibenzoylmethane and freshly distilled aniline, 2-bromoaniline, or 2-iodoaniline were refluxed in xylene in a Dean–Stark water separator in the presence of toluene-4-sulphonic acid (5 mole %). Refluxing was ceased when t.l.c. (silica; benzene eluant) showed the absence of starting material and the mixture was evaporated to yield an orange oil. Column chromatography on silica and elution with benzene gave (1) and (6) which were purified by crystallization from ethanol and chloroform–ethanol, respectively, (1; X = H) (22%); 3-(2-*Bromoanilino*)-1,3-*diphenylprop*-2-*enone* (45%), m.p. 108—110° (Found: C, 66.9; H, 4.4; N, 3.6. $C_{21}H_{16}BrNO$ requires C, 66.7; H, 4.2; N, 3.7%), and its 2-*bromophenyl imine* (1%), m.p. 169—172° (Found: C, 60.7; H, 4.0; N, 5.3. $C_{27}H_{20}Br_2N_2$ requires C, 60.9; H, 3.8; N, 5.3%), *m/e* 534, 532 and 530; and 3-(2-*iodoanilino*)-1,3-*diphenylprop*-2-*enone* (47%), m.p. 127—128° (Found: C, 59.2; H, 3.8; N, 3.1. $C_{21}H_{16}INO$ requires C, 59.3; H, 3.8; N, 3.3%).

Copper Complexes (2).—The ligand (1) (2 mmol) in refluxing methanol (50 ml) was treated with boiling methanol (75 ml) previously saturated with copper(II) acetate and sodium acetate. The solution turned dark brown and soon deposited a crystalline precipitate. After 30 min the solution was cooled and the crystalline precipitate (75—100% yield) was collected and washed with methanol: *complex* (2; X = H), m.p. 256—258° (Found: C, 76.6; H, 4.9; N, 4.1. $C_{42}H_{32}CuN_2O_2$ requires C, 76.5; H, 4.9; N, 4.2%); *complex* (2; X = Cl), m.p. 255—257° (Found: C, 69.0; H, 4.2; N, 3.7. $C_{42}H_{30}Cl_2CuN_2O_2$ requires C, 69.3; H, 4.1; N, 3.9%); *complex* (2; X = Br), m.p. 265—267° (Found: C, 62.0; H, 3.7; N, 3.4. $C_{42}H_{30}Br_2CuN_2O_2$ requires C, 61.7; H, 3.7; N, 3.4%); *complex* (2; X = I), m.p. 258—260° (Found: C, 55.3; H, 3.6; N, 3.1. $C_{42}H_{30}CuI_2N_2O_2$ requires C, 55.3; H, 3.3; N, 3.1%).

Preparative Photochemistry of (1; X = Br *or* I).—A rapidly stirred solution of the substrate (1.0 mmol) in cyclohexane (400 ml) under nitrogen was irradiated with a low pressure mercury arc (72 W; Ultra Violet Products PCQ-XI) through quartz. A yellow precipitate of (4) formed and this was periodically removed by filtration. In the iodo-case, the precipitate underwent some photodecomposition turning brown at moderate conversions, and the irradiation was therefore discontinued after partial reaction. Crude yields of (4; X = Br or I) ranged from 40 to 70%. Both of these gave a positive test for halide ion with aqueous silver nitrate and had $\nu_{max.}$ 2 500—3 000, 1 680, 1 640, 1 610, and 1 600 cm^{-1}. Precipitated (4) was dissolved in methanol, combined with the final photolyte and methanol washings of the apparatus, and evaporated to a red oil which was subjected to preparative t.l.c. using silica with dichloromethane eluant. The cyclized product (5) so obtained was further purified by crystallization from ethanol as bright yellow feathery needles in 32 and 27% yields from (1; X = Br and I), respectively.

9-(2-*Hydroxy*-2-*phenylvinyl*)*phenanthridine* had m.p. 130—132° (Found: C, 84.9; H, 5.2; N, 4.8. $C_{21}H_{15}NO$ requires C, 84.9; H, 5.1; N, 4.7%); $\nu_{max.}$ 1 620, 1 600, and 1 350 cm^{-1}; δ 6.67 (1 H, s), 7.40 (8 H, m), 8.03 (5 H, m), and 15.63br (1 H, s, disappears on D_2O treatment); m/e 297 (M^+); $\lambda_{max.}$ (cyclohexane) (10^{-4} $\varepsilon_{max.}$/l mol^{-1} cm^{-1}) 247 (3.90), 278 (1.33), 289 (1.10), 304 (0.66), 317 (0.62), 335sh, 351sh, 374 (1.14), 394 (1.90), 416 (3.50), and 442 nm (3.70); $\lambda_{max.}$ (methanol) (10^{-4} $\varepsilon_{max.}$/l mol^{-1} cm^{-1}) 246 (3.90), 282 (1.45), 317 (0.60), 345 (0.60), 394 (2.05), 414 (3.80), and 439 nm (4.20); $\lambda_{max.}$ (methanol; 0.12M in HCl) (10^{-4} ε/l mol^{-1} cm^{-1}) 248 (5.25), 315 (0.90), 368 (0.65), 408 (0.35), and 434 nm (0.25).

No precipitate formed during irradiation of the substrate (1.0 mmol) in methanol (400 ml) as above and the progress of the reaction was monitored by t.l.c. The bromo-case showed the appearance of consecutive reactions at rather low conversions when irradiation was terminated. Work-up of the photolytes as above gave (5), identical to the above by m.p. and behaviour on t.l.c., in yields of 7 and 42% from (1; X = Br and I), respectively.

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