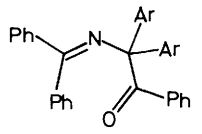
Photochemical Reactivity of Imines from Benzil Mono-oxime Esters

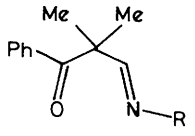
Diego Armesto,[a,*] William M. Horspool,[b] Miguel Apoita,[a] Mar G. Gallego,[b] and Ana Ramos[b]
[a] *Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Complutense, 28040-Madrid, Spain*
[b] *Department of Chemistry, The University, Dundee, DD1 4HN, Scotland*

The synthesis and photochemical reactions of some 1,4-diaza-1,3-dienes have been studied. The photochemical reactivity of these compounds falls into two distinct types. Thus the diazadienes (**7a**—**d**) undergo hydrogen abstraction and cyclisation to 2*H*-imidazoles while diazadiene (**7e**) cyclises by either of two six-electron paths to yield either phenanthridine or quinoxaline derivatives.

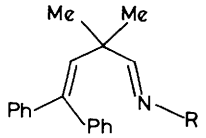
In recent years we have been interested in the influence of an imine group on the photochemical reactivity of organic molecules. Previous studies in this area have been reviewed.[1,2] Our studies have resulted in the discovery of several new photoreactions occurring in molecules such as (**1**),[3] (**2**),[4] (**3**),[5] and (**4**).[6] In the above molecules it is clear that electron transfer from nitrogen plays an important role in determining the outcome of the process. We have also studied the effect of varying the position of the nitrogen within the molecule as in the azadienes (**5**). Here the outcome of the reaction is a six-electron



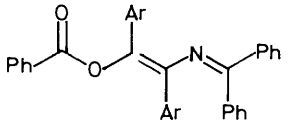
(**1**)



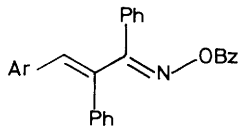
(**2**)



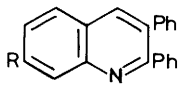
(**3**)



(**4**)



(**5**)

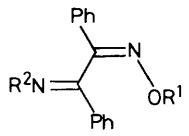


(**6**)

cyclisation resulting in the formation of quinoline derivatives (**6**).[7] The present paper reports our results from a study of the photochemical behaviour of the diazadienes (**7**) and (**8**).

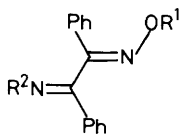
The synthesis of the imino-oximes (**8**) from which the diazadienes (**7**) were prepared has been described previously.[8] The diazadienes (**7**) are readily prepared by benzoylation or acetylation using conventional techniques. The identity of the compounds (**7**) was readily established by spectroscopic and microanalytical data as reported in the experimental.

The photochemical reactivity of the diazadienes (**7**) and (**8**) is dependent on the type of substituent on N-4 and falls into two categories: (*a*) those with an abstractable hydrogen on the substituent at N-4 and (*b*) those where this substituent is a phenyl group. The majority of the irradiations of these compounds were carried out under conventional conditions using an immersion well apparatus.



(**7**)

a; R^1 = Bz, R^2 = Pr^i
b; R^1 = Ac, R^2 = Pr^i
c; R^1 = Bz, R^2 = PhMeCH
d; R^1 = Bz, R^2 = $PhCH_2$
e; R^1 = Bz, R^2 = Ph
f; R^1 = Ac, R^2 = Ph



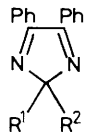
(**9**)

a; R^1 = H, R^2 = Pr^i
b; R^1 = Bz, R_2 = Pr^i
c; R^1 = Ac, R^2 = Pr^i
d; R^1 = Bz, R^2 = PhMeCH
e; R^1 = Bz, R^2 = $PhCH_2$

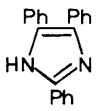
(**8**)

a; R^1 = H, R^2 = Pr^i
b; R^1 = H, R^2 = PhMeCH
c; R^1 = H, R^2 = $PhCH_2$
d; R^1 = H, R^2 = Ph

Irradiation of the imino-oxime (**8a**) in acetone led only to isomerization affording an isomer (**9a**) as the sole photochemical product. Compound (**9a**) arises by the *Z*–*E*-isomerisation of the oxime moiety. The basis for this assignment has already been discussed by us in an earlier paper.[8] Indeed the formation of the *E*-oxime was a common occurrence undergone by compounds (**7a**—**d**). These results are reported in the Experimental Section. When the diazadiene (**7a**) was irradiated under identical conditions a high yield (71%) of the imidazole (**10a**) was obtained. The difference in reactivity between these two



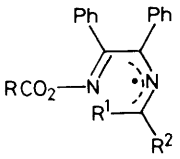
(**10**)



(**10c**)

a; R^1 = Me, R^2 = Me
b; R^1 = Ph, R^2 = Me

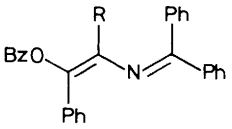
compounds could be due to abstraction of the oxime hydrogen in (**8a**) bringing about *Z*–*E*-isomerisation whereas the diazadiene (**7a**) undergoes hydrogen abstraction to afford the radical (**11a**). Cyclisation of this followed by elimination of a benzoyloxy radical affords the imidazole (**10a**). The cyclisation of such species is not without precedent since we have already reported the cyclisation of radical anions leading to similar products.[9] It is interesting to note that the outcome of the



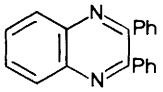
(11)

a; R^1 = Me, R^2 = Me
b; R^1 = Ph, R^2 = Me
c; R^1 = Ph, R^2 = H

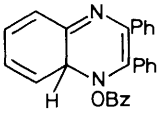
irradiation of the diazadiene (**7a**) is subject to solvent and concentration effects and also to length of irradiation. Thus irradiation of (**7a**) as a 0.035M solution in methylene dichloride also yields the imidazole (**10a**) but only in 30% yield. When a 0.0024M solution is used no imidazole is formed after 1 h. Instead the formation of the *E*-isomer (**9b**) occurs. Prolonged irradiation (5 h) of the 0.0024M solution does afford a low yield of the imidazole (**10a**). The formation of the imidazole in the absence of acetone as the hydrogen abstracting reagent presumably implies that an intermolecular hydrogen abstraction is occurring using the excited benzoate ester as the hydrogen abstracting group. The concentration dependence observed for the reaction is supportive of this proposal as is the failure of the acetyl derivative (**7b**) to afford the imidazole (**10a**) on irradiation in methylene dichloride. It is obvious that the use of a Pyrex filter permits the excitation of the benzoyl group as a potential hydrogen abstracting species. We have previously observed a similar difference in reactivity of acetates and benzoates when irradiation of the dienes (**12**) was carried out through a Pyrex filter.[10] Irradiation of (**7b**) in acetone follows the usual hydrogen abstraction/cyclisation path to afford the imidazole (**10a**) in 32% yield as well as the isomer (**9c**). Both the diazadienes (**7c, d**) afford imidazoles (**10b**) and (**10c**) respectively on irradiation in acetone. These products are accompanied in each case by the isomerization product (**9d**) and (**9e**) respectively.



(12)



(13)

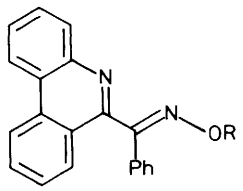


(14)

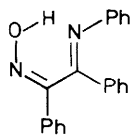
An alternative mode of reaction is seen with the diazadienes (**7e, f**). These compounds are incapable of undergoing the hydrogen abstraction process described above. Thus irradiation of (**7e**) and (**7f**) in methylene dichloride affords the quinoxaline derivative (**13**). The formation of this product arises by a conventional six-electron cyclisation of the type reported recently by us[7] in the formation of quinoline derivatives from the azadienes (**5**). Photocyclisation affords the intermediate (**14**) which subsequently loses benzoic or acetic acid to afford the final product. This reaction can also be carried out in acetone and under these conditions the yield of quinoxaline is increased to 34%. This reaction takes a shorter time and presumably shows that the triplet state is involved.

Interestingly a different reaction path is followed when the irradiation of diazadiene (**7e**) is carried out in the presence of $BF_3 \cdot OEt_2$. Under these conditions the nitrogen lone pair presumably becomes co-ordinated to the boron and this complex is photochemically reactive and yields the phenanthridine derivative (**15a**). The change in reaction mode is expected from earlier results[11] that demonstrated the reluctance of Schiff's bases to undergo a *cis*-stilbene type cyclisation unless the nitrogen lone pair was protonated. More recent studies[12] have shown that irradiation of boron trifluoride complexes of Schiff's bases also undergo rapid ring closure to the corresponding phenanthridine derivatives in good yield.

The diazadiene (**8d**) is also photochemically reactive and irradiation in methylene dichloride gives both the quinoxaline (**13**) and a phenanthridine derivative (**15b**). It is surprising to find that a phenanthridine is formed in the absence of acid in view of previous results.[11] However, it is not impossible that the diazadiene (**8d**) undergoes photochemical isomerisation to, for example, (**16**). In this isomer (**16**) the imine nitrogen lone pair can be hydrogen bonded to the oxime proton or, at the extreme,



(15)



(16)

a; R = Bz
b; R = H

the oxime hydrogen can be transferred to the imine nitrogen. Under these circumstances the conditions for the photochemical formation of a phenanthridine can be met and irradiation yields the phenanthridine (**15b**). When the oxime (**8d**) is irradiated in methylene dichloride with BF_3 the imine nitrogen is complexed with the boron and irradiation for a shorter time also yields the phenanthridine (**15b**) in an increased yield. This reaction was equally efficient in the presence or absence of oxygen.

The phenanthridine (**15b**) can be converted into (**15a**) by benzoylation under standard conditions.

The experiments described above show that the diazadienes (**7**) and (**8**) can undergo a variety of different reaction types, hydrogen abstraction and cyclisation, *Z*–*E*-isomerisation, and six-electron cyclisations leading to the quinoxaline and the phenanthridine skeleta. As far as can be judged from the experiments there is no evidence for electron-transfer involvement.

Experimental

M.p.s were determined on a Buchi 510D apparatus in open capillaries and are uncorrected. I.r. spectra were recorded on a Perkin-Elmer 257 spectrophotometer and band positions are reported in wavenumbers. N.m.r. spectra were recorded on a Varian T-60A spectrometer for protons and a Brucker WP 60FT for carbon with chemical shifts (δ) expressed in p.p.m. downfield from internal Me_4Si. U.v./visible spectra were recorded in methylene dichloride solution using a Perkin-Elmer 550 spectrometer. The mass spectra were run by Dr. P. Bladon at the University of Strathclyde using an A.E.I. (Kratos) MS 9 mass spectrometer fitted with a Mass Spectrometry Services Solid State Console and a G.E.C. 905 computer.

Imino-oximes (**8**) were synthesized by the method described by us previously.[8]

Synthesis of 1-*Acyloxy*-1,4-*diaza*-1,3-*dienes* (**7**).—These were synthesized by reaction of the imino-oximes (**8**) with the corresponding acyl chloride in a ratio of 1:1 or 1:1.1.

General method. Benzoyl or acetyl chloride was added to a solution of the imino-oxime in pyridine (2 ml). The mixture was stirred for 2 h at room temperature and then diethyl ether was added. The pyridine was removed by repeated extraction of the ethereal solution with dilute HCl (10% aqueous). The solution was dried ($MgSO_4$), filtered, and the solvent was removed by evaporation under reduced pressure. The resultant product was purified either by crystallization or by column chromatography on silica gel using hexane–ethyl acetate (8:2) as eluant.

1-*Benzoyloxy*-5-*methyl*-2,3-*diphenyl*-1,4-*diazahexa*-1,3-*diene* (**7a**). From (**8a**) (2 g, 7.5 mmol) and benzoyl chloride (0.86 ml, 7.5 mmol). This gave (**7a**) (2.73 g, 98%) as colourless crystals, m.p. 155—157 °C (from EtOH); $\nu_{max.}$(KBr) 1 750 and 1 620 cm^{-1}; $\delta_H(CDCl_3)$ 1.0—1.2 (6 H, dd, 2 × Me), 3.6 (1 H, m, CH), 7.2—7.5 (9 H, m, ArH), and 7.7—8.0 (6 H, m, ArH); $\delta_C(CDCl_3)$ 162.92, 162.14, 157.29, 135.56—127.03, 54.97, 23.49, and 23.18; $\lambda_{max.}(CH_2Cl_2)$ 253 nm (ε 38 000 dm^3 mol^{-1} cm^{-1}) (Found: C, 77.6; H, 5.9; N, 7.9. $C_{24}H_{22}N_2O_2$ requires C, 77.81; H, 5.99; N, 7.56%).

1-*Acetoxy*-5-*methyl*-2,3-*diphenyl*-1,4-*diazahexa*-1,3-*diene* (**7b**). From (**8a**) (1 g, 3.8 mmol) and acetyl chloride (0.3 ml, 4.2 mmol). This gave (**7b**) (0.8 g, 70%) as colourless crystals, m.p. 82—83 °C (from hexane); $\nu_{max.}$(KBr) 1 775 and 1 630 cm^{-1}; $\delta_H(CDCl_3)$ 0.9—1.1 (6 H, dd, 2 × Me), 1.9 (3 H, s, Me), 3.3 (1 H, m, CH), 6.9—7.2 (6 H, m, ArH), and 7.4—7.6 (4 H, m, ArH); $\delta_C(CDCl_3)$ 167.39, 161.17, 156.81, 135.29—126.92, 54.96, 23.39, 23.02, and 19.18; $\lambda_{max.}(CH_2Cl_2)$ 249 nm (22 000) (Found: C, 74.2; H, 6.8; N, 9.0. $C_{19}H_{20}N_2O_2$ requires C, 74.02; H, 6.49; N, 9.09%).

1-*Benzoyloxy*-2,3,5-*triphenyl*-1,4-*diazahexa*-1,3-*diene* (**7c**). From (**8b**) (1.3 g, 4.0 mmol) and benzoyl chloride (0.5 ml, 4.3 mmol). This gave (**7c**) (1.5 g, 88%) as colourless crystals, m.p. 108—110 °C (from EtOH); $\nu_{max.}$(KBr) 1 750 and 1 630 cm^{-1}; $\delta_H(CDCl_3)$ 1.4 (3 H, dd, Me), 4.6 (1 H, m, CH), 6.7—7.4 (16 H, m, ArH), and 7.5—7.8 (4 H, m, ArH); $\lambda_{max.}(CH_2Cl_2)$ 253 nm (28 000) (Found: C, 80.3; H, 5.5; N, 6.3. $C_{29}H_{24}N_2O_2$ requires C, 80.53; H, 5.59; N, 6.48%).

1-*Benzoyloxy*-2,3,5-*triphenyl*-1,4-*diazapenta*-1,3-*diene* (**7d**). From (**8c**) (0.8 g, 2.5 mmol) and benzoyl chloride (0.3 ml, 2.6 mmol). This gave (**7d**) (0.8 g, 75%) as colourless crystals, m.p. 111—113 °C (from EtOH); $\nu_{max.}$(KBr) 1 750 and 1 620 cm^{-1}; $\delta_H(CDCl_3)$ 4.5 (2 H, s, Me) and 6.8—7.8 (20 H, m, ArH); $\delta_C(CDCl_3)$ 163.05, 161.76, 160.82, 138.86—126.71, 58.30; $\lambda_{max.}(CH_2Cl_2)$ 252 nm (32 000) (Found: C, 80.2; H, 5.4; N, 6.8. $C_{25}H_{22}N_2O_2$ requires C, 80.36; H, 5.30; N, 6.69%).

1-*Benzoyloxy*-2,3,4-*triphenyl*-1,4-*diazabuta*-1,3-*diene* (**7e**). From (**8d**) (1.0 g, 3.3 mmol) and benzoyl chloride (0.4 ml, 3.3 mmol). This gave (**7e**) (1.1 g, 78%) as pale yellow crystals, m.p. 138—140 °C (from EtOH); $\nu_{max.}$(KBr) 1 760 and 1 625 cm^{-1}; $\delta_H(CDCl_3)$ 6.5—7.8 (m, ArH); $\delta_C(CDCl_3)$ 162.9, 162.0, 161.0, 149.5, and 135.3—119.1; $\lambda_{max.}(CH_2Cl_2)$ 260 nm (33 000) (Found: C, 80.1; H, 5.1; N, 7.0. $C_{27}H_{20}N_2O_2$ requires C, 80.18; H, 4.98; N, 6.93%).

1-*Acetoxy*-2,3,4-*triphenyl*-1,4-*diazabuta*-1,3-*diene* (**7f**). From (**8d**) (1.0 g, 3.3 mmol) and acetyl chloride (0.2 ml, 3.3 mmol). This gave (**7f**) (1.0 g, 88%) as colourless crystals, m.p. 135—136 °C (from EtOH); $\nu_{max.}$(KBr) 1 780 and 1 615 cm^{-1}; $\delta_H(CDCl_3)$ 2.06 (3 H, s, Me), 6.6—7.6 (13 H, m, ArH), and 7.7—8.0 (2 H, m, ArH); $\delta_C(CDCl_3)$ 167.48, 161.12, 160.63, 149—118.9, and 19.3; $\lambda_{max.}(CH_2Cl_2)$ 259 nm (23 500) (Found: C, 76.7; H, 5.6; N, 8.2. $C_{22}H_{18}N_2O_2$ requires C, 76.34; H, 5.49; N, 8.48%).

Preparative Photolyses.—The majority of the photolyses were carried out in an immersion well apparatus with a Pyrex filter and a 400 W medium-pressure Hg arc lamp. Solutions of the diazadienes were purged for 1 h with de-oxygenated nitrogen and irradiated under a positive pressure of nitrogen except where stated. Other conditions for the irradiations are detailed at the appropriate place. After completion of the irradiation the solvent was removed under reduced pressure and the products were separated by flash chromatography on silica gel.

Irradiation of (**8a**). A solution of the diazadiene (**8a**) (371 mg, 1.4 mmol) in acetone (330 ml) was irradiated for 1 h. Chromatography using hexane–ethyl acetate (9:1) gave the following: starting material (**8a**) (70 mg, 19%); mixture of (**8a**) and isomer (**9a**) (134 mg, 36%); isomer (**9a**) (149 mg, 40%) $\nu_{max.}$(Nujol) 3 300—2 400 and 1 620 cm^{-1}; δ_H(DMSO) 1.2 (6 H, d, 2 × Me), 3.8 (1 H, m, CH), 7.1—8.0 (10 H, m, ArH), and 11.8 (1 H, s, OH).

Irradiation of (**7a**). (*a*) A solution of the diazadiene (**7a**) (332 mg, 0.9 mmol) in acetone (330 ml) was irradiated for 1 h. Chromatography using hexane–ethyl acetate (9:1) gave the following: 2,2-dimethyl-4,5-diphenyl-2*H*-imidazole (**10a**) (157 mg, 71%), m.p. 78—80 °C (lit.,[13] m.p. 78—80 °C) identical with an authentic sample prepared by the method of Katritzky *et al.*[13] Further elution with hexane–ethyl acetate (1:1) gave benzoic acid (50 mg, 45%).

(*b*) A solution of the diazadiene (**7a**) (250 mg, 0.7 mmol) in methylene dichloride (18 ml) was irradiated for 2.75 h in a serum capped Pyrex test-tube strapped to the immersion well of the standard photochemical apparatus. Chromatography using hexane–ethyl acetate (9:1) gave the following: starting material (**7a**) (170 mg, 68%); 2,2-dimethyl-4,5-diphenyl-2*H*-imidazole (**10a**) (50 mg, 30%). Further elution with hexane–ethyl acetate (1:1) gave benzoic acid (20 mg, 24%).

(*c*) A solution of the diazadiene (**7a**) (300 mg, 0.8 mmol) in methylene dichloride (330 ml) was irradiated for 1 h. Chromatography using hexane–diethyl ether (9:1) gave the following: starting material (**7a**) (200 mg, 67%); isomer (**9b**) (70 mg, 23%); $\nu_{max.}$(film) 1 750 and 1 620 cm^{-1}; $\delta_H(CDCl_3)$ 1.2 (6 H, d, 2 × Me), 4.1 (1 H, m, CH), and 7.3—8.2 (15 H, m, ArH).

(*d*) A solution of the diazadiene (**7a**) (600 mg, 1.6 mmol) in methylene dichloride (380 ml) was irradiated for 5 h. Chromatography using hexane–ethyl acetate (4:1) gave the following: starting material (**7a**) (40 mg, 8%); 2,2-dimethyl-4,5-diphenyl-2*H*-imidazole (**10a**) (70 mg, 17%). Further elution gave a mixture of unidentified polar material.

Irradiation of (**7b**). (*a*) A solution of the diazadiene (**7b**) (311 mg, 1.0 mmol) in acetone (330 ml) was irradiated for 30 min. Chromatography using hexane–diethyl ether (9:1) gave the following: starting material (**7b**) (40 mg, 13%); isomer (**9c**) (74 mg, 24%); $\nu_{max.}$(film) 1 770 and 1 620 cm^{-1}; $\delta_H(CDCl_3)$ 1.2 (6 H, d, 2 × Me), 2.2 (3 H, s, Me), 3.7 (1 H, m, CH), and 6.9—7.8 (10 H, m, ArH); 2,2-dimethyl-4,5-diphenyl-2*H*-imidazole (**10a**) (80 mg, 32%).

(*b*) A solution of the diazadiene (**7b**) (305 mg, 1.0 mmol) in methylene dichloride (330 ml) was irradiated for 1 h. Chromatography using hexane–diethyl ether (9:1) gave the following: starting material (**7b**) (160 mg, 52%); isomer (**9c**) (52 mg, 17%); and products of decomposition.

Irradiation of (**7c**). A solution of the diazadiene (**7c**) (244 mg, 0.6 mmol) in acetone (330 ml) was irradiated for 1.5 h. Chromatography using toluene gave the following: starting material (**7c**) (85 mg, 35%); isomer (**9d**) (36 mg, 15%); $\nu_{max.}$(film) 1 750 and 1 620 cm^{-1}; $\delta_H(CDCl_3)$ 1.5 (3 H, d, Me), 4.9 (1 H, m, CH), and 7.0—8.1 (20 H, m, ArH). Further elution with toluene–ethyl acetate (9:1) gave 2-methyl-2,4,5-triphenyl-2*H*-imidazole (**10b**) (72 mg, 41%), m.p. 107—108 °C (lit.,[13] m.p. 80—82 °C) which was identified by comparison with an authentic sample.[13]

Irradiation of (**7d**). A solution of the diazadiene (**7d**) (318 mg, 0.8 mmol) in acetone (330 ml) was irradiated for 30 min. Chromatography using hexane–ethyl acetate (9:1) gave the following: starting material (**7d**) (31 mg, 10%); isomer (**9e**) (49 mg, 15%); $\nu_{max.}$(film) 1 750 and 1 630 cm^{-1}; $\delta_H(CDCl_3)$ 4.8 (2 H, s, methylene) and 7.0—8.1 (20 H, m, ArH). Further elution

with hexane–ethyl acetate (4:1) gave 2,4,5-triphenyl-2*H*-imidazole (**10c**) (60 mg, 27%); $\nu_{max.}$(Nujol) 3 100, 1 600, and 1 580 cm^{-1}; δ_H(DMSO) 7.0—7.7 (13 H, m, ArH), 7.8—8.0 (2 H, m, ArH), and 12.4 (1 H, br s, NH).[14]

Irradiation of (**7e**). A solution of the diazadiene (**7e**) (300 mg, 0.74 mmol) in methylene dichloride (400 ml) was irradiated for 4 h. Chromatography using hexane–ethyl acetate (19:1) gave the following: 2,3-diphenylquinoxaline (**13**) (40 mg, 20%), m.p. 117—119 °C (lit.,[15] m.p. 119—121 °C) identified by comparison with an authentic sample;* starting material (**7e**) (150 mg, 50%); highly polar material (100 mg).

A solution of the diazadiene (**7e**) (300 mg, 0.74 mmol) in acetone (400 ml) was irradiated for 1.5 h. Chromatography using hexane–diethyl ether (9:1) gave the following: 2,3-diphenylquinoxaline (**13**) (70 mg, 34%); starting material (**7e**) (164 mg, 54%); highly polar material (70 mg).

Irradiation of (**7f**). A solution of the diazadiene (**7f**) (300 mg, 0.87 mmol) in methylene dichloride (400 ml) was irradiated for 4 h. Chromatography using hexane–ethyl acetate (19:1) gave the following: 2,3-diphenylquinoxaline (**13**) (51 mg, 25%); starting material (**7f**) (150 mg, 50%); highly polar material (98 mg).

Irradiation of (**7e**). A solution of the diazadiene (**7e**) (300 mg, 0.77 mmol) and BF_3·OEt_2 (0.15 ml, 1.15 mmol) in methylene dichloride (400 ml) was irradiated for 20 min. The reaction mixture was poured into water and the layers separated. The methylene dichloride layer was dried ($MgSO_4$), filtered, and evaporated to dryness. Chromatography of the residue using hexane–ethyl acetate (19:1) gave the following: benzil (70 mg, 43%); starting material (**7e**) (50 mg, 17%); phenanthridine (**15a**) (38 mg, 13%) as colourless crystals, m.p. 149—152 °C (from EtOH); $\nu_{max.}$(KBr) 1 740 and 1 610 cm^{-1}; δ_H($CDCl_3$) 7.0—8.8 (m, ArH); δ_C($CDCl_3$) 171.7, 163.8, 163.3, 154.8, 143.5, and 136.6—122.4; $\lambda_{max.}$(CH_2Cl_2) 250 nm (81 300); *m/z* 402 (M^+, 16%), 281 (36), 253 (17), 179 (43), 151 (12), 122 (19), 105 (100), and 77 (65) (Found: C, 80.3; H, 4.4; N, 6.8. $C_{27}H_{15}N_2O_2$ requires N, 80.59; H, 4.47; N, 6.96%); highly polar material (110 mg).

Irradiation of (**8d**). (*a*) A solution of the oxime (**8d**) (0.3 g, 1 mmol) in methylene dichloride (400 ml) was irradiated for 2.5 h. Chromatography of the residue using hexane–ethyl acetate (97:3) gave the following: diphenylquinoxaline (**13**) (22 mg, 8%); recovered starting material (**8d**) (180 mg, 60%); phenanthridine oxime (**15b**) (53 mg, 18%) as colourless crystals m.p. 215—217 °C (from EtOH); $\nu_{max.}$(KBr) 3 000, 1 610, 1 590, 970, 680 cm^{-1}; δ_H[$(CD_3)_2SO$] 7.4—8.5 (11 H, m, ArH), 8.9—9.1 (2 H, m, ArH), and 11.8 (1 H, s, OH); $\lambda_{max.}$(CH_2Cl_2) 254 nm (47 400); *m/z* 298 (M^+, 100), 281 (55), 279 (12), 267 (67), 195 (12), 179 (47), 151 (18), and 77 (11). (Found): M^+, 298.1110. $C_{20}H_{15}N_2O$ requires M^+, 298.1181); highly polar material (30 mg).

(*b*) A solution of the oxime (**8d**) (0.3 g, 1 mmol) and BF_3·OEt_2 (0.25 ml, 2 mmol) in methylene dichloride (400 ml) was irradiated for 15 min. Chromatography of the residue using hexane–ethyl acetate (97:3) gave the following: diphenylquinoxaline (**13**) (30 mg, 12%); recovered starting material (**8d**) (22 mg, 7%); phenanthridine oxime (**15b**) (130 mg, 44%); highly polar material (100 mg).

The above was repeated without purging with nitrogen on the following scale. The oxime (**8d**) (0.18 g, 0.6 mmol) and BF_3·OEt_2 (0.07 ml, 0.6 mmol) in methylene dichloride (400 ml) was irradiated for 10 min. Chromatography of the residue using hexane–ethyl acetate (97:3) gave the following: diphenylquinoxaline (**13**) (13 mg, 6%); recovered starting material (**8d**) (72 mg, 41%); phenanthridine oxime (**15b**) (61 mg, 35%); highly polar material (30 mg).

The phenanthridine (**15a**) was also synthesized from the oxime (**15b**) as follows. The oxime (**15b**) (0.13 g, 0.44 mmol) was dissolved in dry pyridine (3 ml) and the solution was cooled in an ice-bath. Benzoyl chloride (0.05 ml, 0.44 mmol) was added dropwise. After the addition was complete the mixture was kept at 0 °C for 15 min. and then poured into HCl (10% aqueous). The mixture was extracted into ether, and the ethereal layer was washed, dried ($MgSO_4$), filtered, and evaporated to dryness. This yielded the phenanthridine (**15a**) (0.15 g, 82%).

* 2,3-Diphenylquinoxaline is prepared easily by heating at reflux a mixture of equimolar amounts of *o*-phenylenediamine and benzil in toluene for 6 h.

Acknowledgements

We thank the British Council and the Ministerio de Educacion y Ciencia of Spain for Fleming Fellowships to two of us (M. G. G. and A. R.), the Comisión Asesora de Investigación Científica y Técnica (Grant No. PB 85/0040), and NATO (Grant 0734/87) for financial assistance.

References

1 A. C. Pratt, *J. Chem. Soc. Rev.*, 1977, **6**, 63.
2 A. Padwa, *Chem. Rev.*, 1977, **77**, 1.
3 D. Armesto, M. G. Gallego, R. Perez-Ossorio, and W. M. Horspool, *Tetrahedron Lett.*, 1983, **24**, 1089; *J. Chem. Soc., Perkin Trans. 1*, 1986, 799.
4 D. Armesto, A. Ramos, R. Perez-Ossorio, and W. M. Horspool, *J. Chem. Soc., Perkin Trans. 1*, 1986, 91.
5 D. Armesto, J. A. F. Martin, R. Perez-Ossorio, and W. M. Horspool, *Tetrahedron Lett.*, 1982, **23**, 2149; D. Armesto, W. M. Horspool, J. A. F. Martin, and R. Perez-Ossorio, *J. Chem. Res.*, 1986, (*S*), 46; (*M*), 631; D. Armesto, W. M. Horspool, F. Langa, and R. Perez-Ossorio, *J. Chem. Soc., Perkin Trans. 2*, 1987, 1039; D. Armesto, W. M. Horspool, and F. Langa, *J. Chem. Soc., Chem. Commun.*, 1987, 1874.
6 D. Armesto, M. J. Ortiz, R. Perez-Ossorio, and W. M. Horspool, *Tetrahedron Lett.*, 1983, **24**, 1197; D. Armesto, W. M. Horspool, M. J. Ortiz, and R. Perez-Ossorio, *J. Chem. Soc., Perkin Trans. 1*, 1986, 623.
7 D. Armesto, M. G. Gallego, and W. M. Horspool, *J. Chem. Soc., Perkin Trans. 1*, 1989, 1623.
8 D. Armesto, M. G. Gallego, W. M. Horspool, A. Ramos, and M. Apoita, *Synthesis*, 1989, 488.
9 D. Armesto, M. G. Gallego, W. M. Horspool, and A. Ramos, *Tetrahedron Lett.*, 1988, **29**, 3581.
10 D. Armesto, M. G. Gallego, and W. M. Horspool, *J. Chem. Soc., Perkin Trans. 1*, 1987, 2663.
11 G. M. Badger, C. P. Joshua, and G. E. Lewis, *Tetrahedron Lett.*, 1964, 3711.
12 S. Prebhakar, A. M. Lobo, and M. A. Tavares, *J. Chem. Soc., Chem. Commun.*, 1978, 884.
13 A. R. Katritzky, S. B. Borja, and J. Marquet, *J. Chem. Soc., Perkin Trans. 1*, 1983, 2065.
14 'The Aldrich Library of Infrared Spectra,' ed. C. J. Pourchet, 3rd edn., 1981, p. 1219 F; 'The Aldrich Library of NMR Spectra,' ed. C. J. Pourchet, 2nd edn., 1983, **2**, 488C.
15 J. Wolff, *J. Prakt. Chem.*, 1898, **57**, 546.

Received 17*th February* 1989; *Paper* 9/00760A