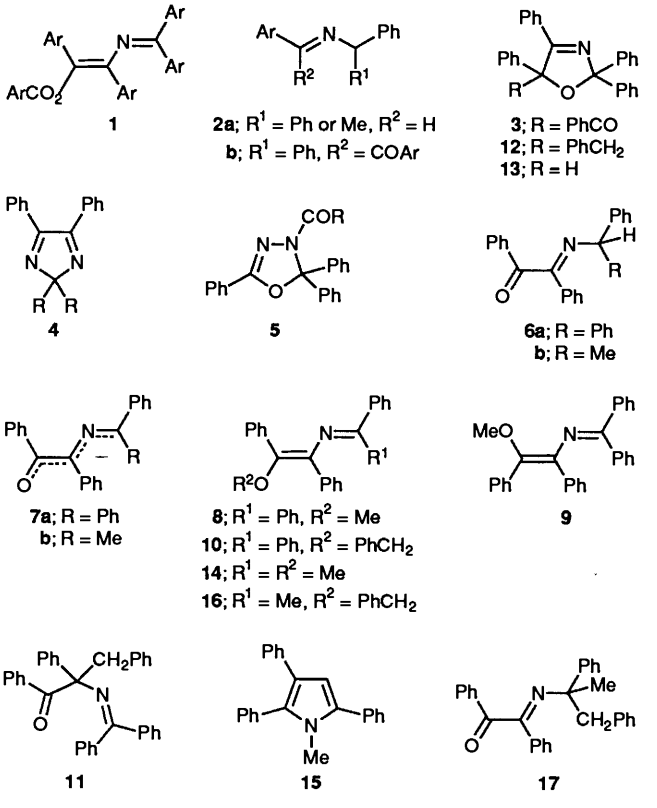
Reaction of Anions from Monoimines of Benzil with Alkylating Agents. Photochemical Reactivity of Some 4-Alkoxy-2-aza-1,3-dienes

Diego Armesto,*,[a] William M. Horspool,[b] Maria J. Ortiz[a] and Santiago Romano[a]
[a] *Departamento de Quimica Organica, Facultad de Ciencias Quimicas, Universidad Complutense, 28040-Madrid, Spain*
[b] *Department of Chemistry, The University, Dundee, DD1 4HN, Scotland*

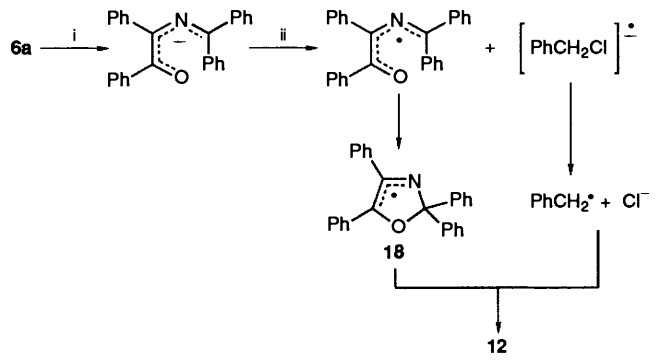
The reaction of benzil benzhydrylmonoimine **6a** with methyl iodide or dimethyl sulphate as the electrophile affords 4-alkoxy-2-aza-1,3-dienes resulting from an *O*-alkylation. When benzyl chloride is employed, products of *O*-alkylation, *C*-alkylation and cyclization are produced, while with toluene-*p*-sulphonyl chloride only cyclization to a dihydro-oxazole takes place. Benzil α-phenylethylmonoimine **6b** yields only products of *C*- and/or *O*-alkylation. In one case, when a large excess of dimethyl sulphate is used, cyclization affords *N*-methyl-2,3,5-triphenylpyrrole. Irradiation of the *O*-alkylated compounds (*E*)- and (*Z*)-4-methoxy-1,1,3,4-tetraphenyl-2-azabuta-1,3-diene and (*E*)-4-benzyloxy-1,1,3,4-tetraphenyl-2-azabuta-1,3-diene in the presence of perchloric acid yields isoquinoline derivatives by a photo-Mannich reaction.

Previously we have reported the efficient synthesis of 4-aroyloxy-2-azabuta-1,3-dienes **1** by routes involving the double aroylation of anions of imines **2a**[1] or by the more flexible pathway of *O*-acylation of the anions of monoimines **2b** of 1,2-dicarbonyl compounds.[2] Our interest in compounds **1** arose from the observation that the photochemistry of some heavily arylated derivatives is dominated, apparently, by an electron transfer from the electron-rich C=C bond to the acyl group, leading to a novel 1,2-acyl migration followed by cyclization to afford derivatives of dihydro-oxazole, *e.g.* **3** from the azadiene **1**; Ar = Ph.[3] In another study we have shown, in a thermal reaction, that electron transfer between anions of bisimines and nucleophiles resulted in cyclization with the formation of 2*H*-imidazoles **4**.[4] Furthermore, we have reported similar cyclizations, with the anion of benzophenone benzoylhydrazone yielding the dihydro-oxadiazole **5**.[5] Reactivity of this type was unexpected and the present work describes a related study of the reaction of nucleophiles with anions from monomines of benzil.



Results and Discussion

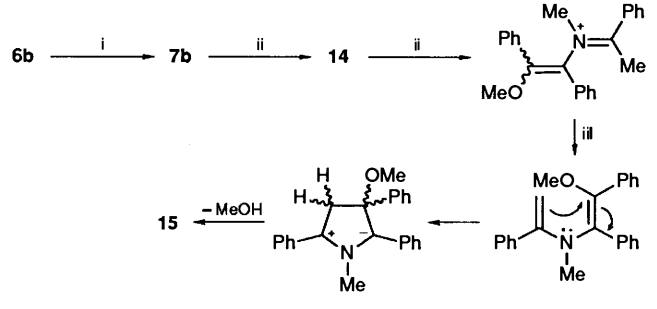
The monoimines **6** were readily prepared by standard methods.[6] Treatment of compound **6a** with sodium hydride in hexamethylphosphoric triamide (HMPA) as the base generated a solution of the anion **7a**. Treatment of this anion with dimethyl sulphate or methyl iodide brought about *O*-alkylation only and the formation of a 2-azadiene as a mixture of *Z*–*E*-isomers. These isomers were readily separated by column chromatography on silica gel and were identified as the (*E*)-isomer **8** (56%) and the (*Z*)-isomer **9** (34%) by standard procedures. The imine **6a** was then treated as its anion with benzyl chloride. Here again the predominant reaction is *O*-alkylation to afford the (*E*)-azadiene **10** (73%). *C*-Alkylation also takes place, yielding the ketoimine **11** (2.4%). A third product was isolated in 15.4% yield and was identified as the dihydro-oxazole **12**. The formation of this compound is reminiscent of the reactions described earlier by us[4,5] involving anions of bisimines and the anion of benzophenone benzoylhydrazone where the anions are converted into radicals by single-electron transfer. In the present example the formation of compound **12** can be explained in a like manner (Scheme 1) where single-electron transfer occurs from the anion **7a** to the alkylating agent. The resultant open-chain radical cyclizes to yield the cyclic radical **18**, which is trapped by a benzyl radical to afford compound **12**. The reaction could be interpreted as an example of an SET-S_N2 process.[7] The failure to observe cyclization with methyl iodide and dimethyl sulphate is presumably due to the absence of the electron-transfer process from the anion to the electrophile and could be associated with the reduction potential of the electrophile.[7] Cyclization also occurred when imine **6a** was treated with sodium hydride and toluene-*p*-sulphonyl chloride. However, in this case the cyclic radical **18** did not combine with a sulphonyl radical and instead abstracted hydrogen to yield the dihydro-oxazole **13** (20%). From these reactions and our earlier observations[4,5] we conclude that in cases where the nucleophile can give rise to a stabilized radical, such as benzyl or toluene-*p*-sulphonyl, the reaction follows an



Scheme 1 *Reagents:* i, NaH, HMPA, THF; ii, $PhCH_2Cl$

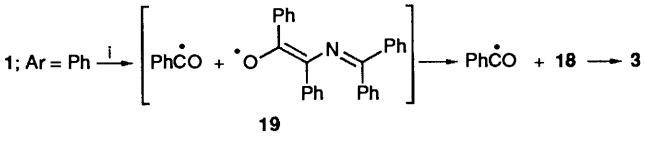
electron-transfer path bringing about the formation of cyclic products in addition to the normal nucleophilic reactions. In the other cases, with methyl iodide and dimethyl sulphate, where a methyl radical would be involved no radical path and, therefore, no cyclization products are obtained.

The imine **6b** reacted with sodium hydride in HMPA and dimethyl sulphate in the same manner as imine **6a** and yielded the azadiene **14** (2%) *via* anion **7b**. When there was only a slight excess of alkylating agent this was the sole product of the reaction as shown by NMR spectroscopy. However, owing to instability, the diene could not be isolated and was prone to hydrolysis to yield benzoin methyl ether (39%) during work-up. In the presence of a large excess of dimethyl sulphate the principal product of the reaction was the pyrrole **15** (80%). This is proposed to be formed from the azadiene **14** by a second alkylation and cyclization by the path shown in Scheme 2. When benzyl chloride was used as the alkylating agent no cyclized compounds were obtained from the reaction and the azadiene **16** (25%), formed by *O*-alkylation, was the principal product. This was accompanied by the *C*-alkylated product **17** (12%). In this example alkylation takes place at the γ-C from the carbonyl group. The difference between this case and that of the alkylation of the anion **7a** with benzyl chloride, where compound **11** was formed, is due to steric effects. It is not clear why the free radical cyclization path does not operate with this imine **6b**. The difference in reactivity may be due to the change in substitution from phenyl to methyl on the terminal carbon that might affect the stability or the oxidation potential of the anion and/or radical.[7]

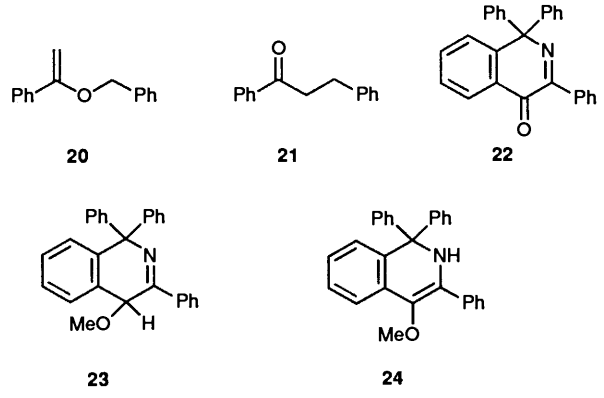


Scheme 2 *Reagents:* i, NaH, HMPA, THF; ii, Me_2SO_4; iii, NaH

Previously we have reported[8] photochemical reactions of 2-azadienes, the outcome of which was dependent upon the degree of twist around the C–N bond. In the cases, *e.g.* diene **1** (Ar = Ph), where the imine and the alkene moieties were shown to be at 40° to each other in the crystal[9] an intramolecular single-electron transfer dominated the reaction and brought about a 1,2-benzoyl migration and cyclization to afford dihydro-oxazoles, *e.g.* **3**. An alternative interpretation for the formation of the dihydro-oxazoles could involve photochemical C–O fission to yield the radical pair **19**, followed by cyclization and recombination (Scheme 3). C–O Bond fission has been reported for benzyl α-styryl ether **20**.[10] In this case a 1,3-benzyl migration yields the ketone **21**. Hence it was important to establish if the 4-alkoxyazadienes **8**, **9** and **10** could undergo photochemical conversion involving the radical-pair reaction path. Failure to follow this reaction mode would provide indirect support for our original postulate of a single-electron transfer involvement in the conversion into dihydro-oxazoles.

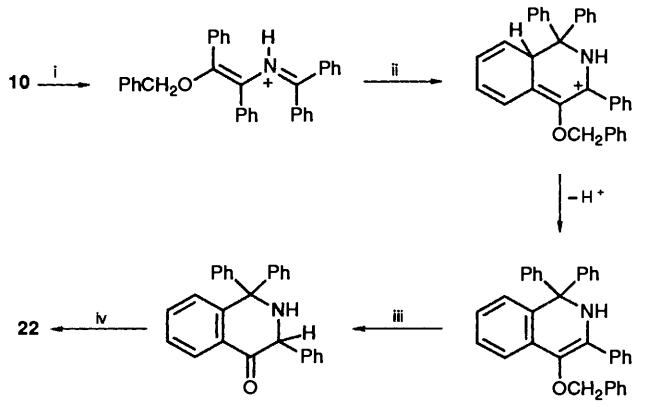


Scheme 3 *Conditions:* i, *hν*



The (*E*)- and (*Z*)-azadienes **8** and **9** and (*E*)-azadiene **10** have the same substitution pattern on the diene skeleton as the azadiene **1** (Ar = Ph). However, the photochemical behaviour of compounds **8**, **9** and **10** could be markedly different since the absence of a benzoyl group means that there is no terminus for the intramolecular electron transfer. Therefore it was predicted that direct irradiation of the azadienes **8**–**10** could not follow the path described previously.[3] This was confirmed on irradiation, and instead of group migration and cyclization only C=C bond isomerization took place. With azadiene **10**, isomerization to the (*Z*)-isomer was detected by NMR spectroscopy. All attempts to isolate this compound failed. Therefore, the absence of product other than those arising by (*E*)–(*Z*) isomerization provides no evidence to substantiate a mechanism which might involve C–O bond fission, cyclization, and recombination.

The other type of photoreaction which the azadienes **1** undergo is cyclization to isoquinolinones in the presence of acid.[11] This behaviour was seen when the electron-transfer step was suppressed by protonation of the nitrogen. This type of reactivity was also found with the azadiene **10**, which on irradiation in the presence of perchloric acid afforded the isoquinolinone **22** (56%) identical with that obtained[11] from the irradiation of azadiene **1** (Ar = Ph). The cyclization, a photo-Mannich reaction (Scheme 4), was followed by hydrolysis during work-up to afford compound **22**. Photocyclization was also observed on irradiation of the azadienes **8** and **9** in acid medium. Thus, irradiation of the (*E*)-isomer **8** in methylene dichloride with added perchloric acid yielded a mixture of the (*E*)- and (*Z*)-isomers (**8** and **9**; 42%) and the dihydroisoquinoline **23** (38%). Analogous behaviour was found for the (*Z*)-isomer **9**. This photocyclization is similar to that observed for compound **10**. Interestingly, the dihydroisoquinoline **23** did not undergo the conversion into the isoquinolinone **22**. Presumably the absence of a good leaving group inhibits the hydrolysis step in



Scheme 4 *Reagents and conditions:* i, $HClO_4$, CH_2Cl_2; ii, *hν*; iii, hydrolysis; iv, oxidation

Scheme 4 and the photo-Mannich reaction stops at the ether **23**. Isoquinoline **23** underwent thermal isomerization in solution to afford isomer **24**. Both of these isoquinolines (**23** and **24**) were unstable and microanalytical data were not obtained. The identity of the compounds was based on the NMR spectroscopic data recorded in the Experimental section.

The results obtained in this study with the anions of the benzil monoimines (**6a** and **b**) show that the type of reaction that they undergo is dependent upon the electrophile used. The interpretation of the reactions suggests that an electron-transfer process might be involved and the cyclization reactions could be examples of SET-S_N2 reactions.

The data obtained from the irradiation of the *O*-alkylated compounds **8**–**10** shows that no C–O bond fission had occurred. The absence of this reaction path provided evidence in conformation of our original single electron-transfer mechanism for the photochemical conversion of the azadienes **1** into the dihydro-oxazoles **3**. Irradiation of the *O*-alkylated compounds **8**–**10** in the presence of perchloric acid afforded another example of the photo-Mannich reaction to isoquinoline derivatives.

Experimental

M.p.s were determined on a Buchi 510D apparatus in open capillaries and are uncorrected. IR spectra were reported in KBr discs (unless otherwise stated), using a Perkin-Elmer 257 spectrophotometer. NMR spectra were recorded for solutions in deuteriochloroform unless otherwise stated, using a Varian T-60A for ^1H and a Varian FT-80A for ^{13}C spectra, with chemical shifts (δ) expressed in ppm downfield from internal Me_4Si, and coupling constants J are given in Hz. UV–visible spectra were recorded in methylene dichloride solution using a Perkin-Elmer 550 spectrometer. Mass spectra were determined on a Varian MAT-711 spectrometer.

Monoimines **6** were synthesized using the method described previously.[6]

General Procedure for the Alkylation of Monoimines **6**.—A dispersion of sodium hydride (13.0–16.0 mmol) in anhydrous HMPA (60 cm^3) was placed under nitrogen in a dried, 250 cm^3, three-necked, round-bottomed flask containing a magnetic stirring bar. Subsequently, a solution of the corresponding monoimine (2.7–3.2 mmol) in anhydrous tetrahydrofuran (THF) (5 cm^3) was added to the mixture at room temperature and the resultant highly coloured reaction mixture was stirred for 15 min after which it was cooled to 0 °C using an ice-bath. Then the corresponding electrophilic reagent was added dropwise. After the addition of approximately an equimolar amount of the electrophilic reagent (2.7–3.2 mmol) the colour of the carbanion disappeared. The solution was warmed to 50 °C and stirred for 20–30 min, after which the colour reappeared. The reaction mixture was then cooled to 0 °C and the addition of electrophilic reagent was resumed until the intense colour had been discharged. The process was repeated until the colour did not redevelop after stirring of the mixture for 1 h at 50 °C. A total amount of 8.0–13.0 mmol of the electrophilic reagent had been added. The reaction mixture was poured into diethyl ether (200 cm^3)–ice to avoid partial hydrolysis of the resultant products by local concentration of base. The ethereal layer was separated and the aq. layer was extracted with diethyl ether (5 × 50 cm^3). The ethereal layers were combined and dried ($MgSO_4$). Diethyl ether was removed by rotatory evaporation. The product mixtures were separated by column chromatography on silica gel with different mixtures of hexane–ethyl acetate as eluent.

Synthesis of 4-*Methoxy*-1,1,3,4-*tetraphenyl*-2-*azabuta*-1,3-*diene* **8** *and* **9** *by using Dimethyl Sulphate*.—Monoimine **6a** (1.0 g, 2.7 mmol), sodium hydride (0.4 g, 13.3 mmol) and dimethyl sulphate (1.0 g, 8.0 mmol). Conventional work-up, followed by chromatography with hexane–ethyl acetate (49:1) as eluent, gave the following in order of elution: *azadiene* **8** (0.47 g, 45%) as yellow crystals, m.p. 84 C (from EtOH); ν_{max}/cm^{-1} 1620 and 1590; δ_H 7.7–6.8 (18 H, m, ArH), 6.5–6.4 (2 H, m, ArH) and 3.2 (3 H, s, MeO); δ_C 168.6 (C=N), 140.5–126.4 (aryl C) and 57.9 (MeO); λ_{max} (EtOH)/nm 246 (ε 20 500 dm^3 mol^{-1} cm^{-1}) and 308 (12 200); *m/z* 389 (M^+, 18%), 374 (33), 269 (26), 182 (22), 165 (36), 105 (100) and 77 (55) (Found: C, 86.4; H, 5.8; N, 3.5. $C_{28}H_{23}NO$ requires C, 86.37; H, 5.91; N, 3.60%); *azadiene* **9** (0.46 g, 44%) as yellow crystals, m.p. 119 °C (from EtOH); ν_{max}/cm^{-1} 1630 and 1595; δ_H 7.5–7.4 (2 H, m, ArH), 7.4–7.0 (18 H, m, ArH) and 3.0 (3 H, s, MeO); δ_C 169.4 (C=N), 139.3–126.0 (aryl C) and 56.2 (MeO); λ_{max} (EtOH)/nm 244 (22 700); *m/z* 389 (M^+, 5%), 374 (8), 269 (6), 182 (32), 165 (10), 121 (18), 105 (100) and 77 (52) (Found: C, 86.1; H, 5.9; N, 3.4%).

Using Methyl Iodide.—Monoimine **6a** (1.0 g, 2.7 mmol), sodium hydride (0.4 g, 13.3 mmol) and methyl iodide (1.2 g, 8.0 mmol). Conventional work-up, followed by chromatography with hexane–acetate (49:1) as eluent, gave the following in order of elution: azadiene **8** (0.58 g, 56%) and azadiene **9** (0.35 g, 34%).

Synthesis of (E)-4-*Benzyloxy*-1,1,3,4-*tetraphenyl*-2-*azabuta*-1,3-*diene* **10**.—Monoimine **6a** (1.0 g, 2.7 mmol), sodium hydride (0.4 g, 13.3 mmol) and benzyl chloride (1.2 g, 9.3 mmol). Conventional work-up, followed by chromatography with hexane-ethyl acetate (99:1) as eluent, gave the following in order of elution: the *dihydro-oxazole* **12** (0.19 g, 15%) as crystals, m.p. 121 °C (from EtOH); ν_{max}/cm^{-1} 1630; δ_H 8.0–6.8 (25 H, m, ArH) and 4.2 (2 H, J_1 11, J_2 16, CH_2); δ_C 165.0 (C=N), 144.6–125.9 (aryl C), 113.3 and 110.1 (quaternary C-2 and C-5) and 66.0 (CH_2); *m/z* 374 (M^+ − 91, 7%), 358 (3), 269 (100), 194 (4), 165 (77), 105 (67), 91 (52) and 77 (43) (Found: C, 87.9; H, 5.7; N, 3.2. $C_{34}H_{27}NO$ requires C, 87.74; H, 5.81; N, 3.01%); *azadiene* **10** (0.9 g, 73%) as yellow crystals, m.p. 77 °C (from EtOH); ν_{max}/cm^{-1} 1620 and 1590; δ_H 7.7–6.8 (23 H, m, ArH), 6.6–6.4 (2 H, m, ArH) and 4.4 (2 H, s, CH_2); δ_C 168.5 (C=N), 139.2–126.7 (aryl C) and 72.5 (CH_2); λ_{max}(EtOH)/nm 243 (28 000); *m/z* 465 (M^+, 5%), 374 (100), 334 (10), 269 (54), 165 (82), 105 (79), 91 (18) and 77 (21) (Found: C, 87.8; H, 5.7; N, 2.9. $C_{34}H_{27}NO$ requires C, 87.74; H, 5.81; N, 3.01%); *keto imine* **11** (0.03 g, 3%) as crystals, m.p. 143 °C (from EtOH); ν_{max}-($CHCl_3$)/cm^{-1} 1675 (C=O) and 1625 (C=N); δ_H 7.8–6.5 (25 H, m, ArH) and 3.5 (2 H, s, CH_2); δ_C 198.2 (C=O), 166.7 (C=N), 143.4–125.7 (aryl C), 75.8 (quaternary C) and 48.0 (CH_2); *m/z*

374 ($M^+ - 91$, 25%), 360 (100), 269 (48), 179 (24), 165 (72), 105 (37), 91 (17) and 77 (23) (Found: C, 87.6; H, 5.9; N, 2.8. $C_{34}H_{27}NO$ requires C, 87.74; H, 5.81; N, 3.01%).

Reaction of Compound **6a** *with Toluene-*p*-sulphonyl chloride.*—Monoimine **6a** (1.0 g, 2.7 mmol), sodium hydride (0.4 g, 13.3 mmol) and toluene-*p*-sulphonyl chloride (1.5 g, 7.8 mmol). Conventional work-up, followed by chromatography with hexane–ethyl acetate (49:1) as eluent gave the following in order of elution: starting material **6a** (0.45 g, 45% recovery); the dihydro-oxazole **13** (0.2 g, 20%) as crystals, m.p. 128 °C (lit.,[12] 127–128 °C); ν_{max}/cm^{-1} 1655; δ_H 7.8–7.1 (m, ArH); δ_C 166.3 (C=N), 163.7, 144.9–125.8 (aryl C), and 116.6, 110.3, 109.9 and 108.9; *m/z* 375 (M^+, 10%), 270 (19), 167 (100), 105, (69) and 77 (17) (Found: C, 86.5; H, 5.5; N, 3.6. $C_{27}H_{21}NO$ requires C, 86.40; H, 5.60; N, 3.73%).

Alkylation of Monoimine **6b** *with Dimethyl Sulphate.—Method A.* Monoimine **6b** (1.0 g, 3.2 mmol), sodium hydride (0.5 g, 15.9 mmol) and dimethyl sulphate (1.6 g, 12.8 mmol). Conventional work-up, followed by chromatography with hexane–ethyl acetate (4:1) as eluent, gave the following in order of elution: the pyrrole **15** (0.86 g, 87%) as crystals, m.p. 182 °C (from Et_2O) (lit.,[13] 180–182 °C); ν_{max}/cm^{-1} 1600; δ_H 7.2–6.6 (15 H, m, ArH), 6.1 (1 H, s, ArH) and 3.1 (3 H, s, Me); δ_C 136.6–122.7 (aryl C), 108.7 (C-4) and 33.6 (Me); λ_{max}/nm 256 (20 000) and 300 (22 300); *m/z* 309 (M^+, 100%), 308 (12), 293 (12), 232 (2), 191 (10), 91 (4) and 77 (9) (Found: C, 89.5; H, 6.0; N, 4.4. $C_{23}H_{19}N$ requires C, 89.32; H, 6.15; N, 4.53%); azadiene **14** (0.02 g, 2%) as an unstable yellow oil; ν_{max}/cm^{-1} 1600; δ_H *inter alia* 3.8 (s, MeO).

Method B. Monoimine **6b** (1.0 g, 3.2 mmol), sodium hydride (0.5 g, 15.9 mmol) and dimethyl sulphate (1.0 g, 8.0 mmol). Conventional work-up, followed by chromatography with hexane–ethyl acetate (9:1) as eluent, gave the following in order of elution: azadiene **14** (0.03 g, 3%); recovered monoimine **6b** (0.42 g, 42%); benzoin methyl ether (0.28 g, 39%) as crystals, m.p. 50 °C (lit.,[14] 46–48 °C); δ_H 8.1–7.8 (2 H, m, ArH), 7.6–7.2 (8 H, m, ArH), 5.5 (1 H, s, CH) and 3.4 (3 H, s, MeO).

Alkylation of Monoimine **6b** *with Methyl Iodide.*—Monoimine **6b** (1.0 g, 3.2 mmol), sodium hydride (0.5 g, 15.9 mmol) and methyl iodide (1.4 g, 9.6 mmol). Conventional work-up, followed by chromatography with hexane–ethyl acetate (9:1) as eluent, gave the following in order of elution: azadiene **14** (0.02 g, 2%); recovered starting material **6b** (0.39 g, 39%); benzoin methyl ether (0.35 g, 48%).

Alkylation of Monoimine **6b** *with Benzyl Chloride.*—Monoimine **6b** (1.0 g, 3.2 mmol), sodium hydride (0.5 g, 15.9 mmol) and benzyl chloride (1.2 g, 9.6 mmol). Conventional work-up, followed by chromatography with hexane–ethyl acetate (49:1) as eluent, gave the following in order of elution: acetophenone (0.1 g, 24%); azadiene **16** (0.32 g, 25%) as an unstable yellow oil; ν_{max}(liq. film)/cm^{-1} 1630; δ_H 8.1–6.7 (20 H, m, ArH), 4.6 (2 H, s, CH_2) and 2.0 (3 H, s, Me); δ_C 166.2 (C=N), 144.3–125.6 (aryl C), 72.4 (CH_2) and 25.7 (Me); *keto imine* **17** (0.15 g, 12%) as crystals, m.p. 103 °C; ν_{max}/cm^{-1} 1660 and 1625 δ_H 7.7–7.5 (2 H, m, ArH), 7.4–7.0 (18 H, m, ArH), 4.5 (2 H, s, CH_2) and 1.4 (3 H, s, Me); δ_C 198.7 (C=O), 164.2 (CN), 144.4–125.2 (aryl C), 62.0 (quaternary C), 24.6 (CH_2) and 21.3 (Me); *m/z* 403 (M^+, 3%), 388 (1), 312 (5), 298 (100), 207 (17), 105 (48), 91 (32) and 77 (24) (Found: C, 86.2; H, 6.1; N, 3.6. $C_{29}H_{25}NO$ requires C, 86.35; H, 6.20; N, 3.47%).

General Procedure for the Irradiation of Azadienes **8**, **9** *and* **10**.—The photolyses were carried out in an immersion-well apparatus in which the solutions of azadienes in methylene dichloride (380 cm^3) were purged with nitrogen prior to and during irradiation. The solutions were irradiated, through a Pyrex filter, by using a 400 W medium-pressure Hg arc lamp. The solvent was then removed under reduced pressure and the crude photolysates were chromatographed on a column of silica gel with mixtures of hexane–ethyl acetate as eluent. When perchloric acid was used, after completion of the irradiation, solid Na_2CO_3 was added to neutralize the solution. The photolysate was then filtered and the solvent was removed under reduced pressure. The residue was treated with water and extracted into chloroform. The extract was washed with water, dried ($MgSO_4$), filtered, and evaporated to dryness under reduced pressure. The resultant oil was separated by chromatography on a column of silica gel with mixtures of hexane–ethyl acetate as eluent.

Irradiation of Azadiene **8**.—Azadiene **8** (0.5 g, 1.3 mmol) was irradiated for 30 min. Work-up yielded an orange oil, which was chromatographed on silica gel (50 g) with hexane–ethyl acetate (49:1) as eluent. This yielded the following in order of elution: starting azadiene **8** (0.35 g, 70% recovery) and azadiene **9** (0.12 g, 24%).

Irradiation of Azadiene **8** *in the Presence of Perchloric Acid.*—Azadiene **8** (0.5 g, 1.3 mmol) and perchloric acid (0.64 g, 6.4 mmol) were irradiated for 40 min. Work-up, after the addition of sodium carbonate (0.68 g, 6.4 mmol), yielded an orange oil, which was chromatographed on silica gel (60 g) with hexane–ethyl acetate (9:1) as eluent. This yielded the following in order of elution: starting azadiene **8** (0.16 g, 32% recovery), azadiene **9** (0.05 g, 10%) and the dihydroisoquinoline **23** (0.19 g, 38%) as an oil; ν_{max}(liq. film)/cm^{-1} 1635; δ_H 7.5–7.0 (20 H, m, ArH and CH) and 3.0 (3 H, s, MeO); δ_C 162.2 (C=N), 146.8–126.3 (aryl C), 98.3 (tertiary C), 71.6 (quaternary C) and 52.7 (MeO). During the irradiation samples were examined by TLC (after 10, 20, 30 and 40 min) and the presence of the dihydroisoquinoline **23** was observed after only 10 min. Dihydroisoquinoline **23** isomerized in $CDCl_3$ to the isomeric dihydroisoquinoline **24**, δ_H 8.0–6.9 (20 H, m, ArH and NH) and 3.3 (3 H, s, Me); δ_C 146.7–126.3 (aryl C), 69.7 (quaternary C) and 52.0 (MeO).

Irradiation of Azadiene **9**.—Azadiene **9** (0.05 g, 0.2 mmol) was irradiated for 30 min. After irradiation a sample was examined by TLC and the azadienes **8** and **9** were observed. The ^1H NMR spectrum of the crude photolysate showed the presence of azadienes **8** and **9** in the ratio of 1:2.

Irradiation of Azadiene **9** *in the Presence of Perchloric Acid.*—The azadiene **9** (0.03 g, 0.1 mmol) and perchloric acid (0.04 g, 0.4 mmol) were irradiated for 30 min. During the irradiation samples were examined by TLC (after 10, 20 and 30 min). After 10 min irradiation only *Z*–*E*-isomerization was observed. After 30 min the dihydroisoquinoline **23** was detected.

Irradiation of Azadiene **10**.—Azadiene **10** (0.22 g, 0.49 mmol) was irradiated for 50 min. Work-up yielded only recovered azadiene **10**. ^1H and ^{13}C NMR spectra of a deoxygenated sample (after 50 min) showed the presence of the (*Z*)-azadiene **10**: δ_H 4.55 (s, CH_2); δ_C 70.5 (CH_2).

Irradiation of Azadiene **10** *in the Presence of Perchloric Acid.*—Azadiene **10** (0.4 g, 0.86 mmol) and perchloric acid (0.43 g, 4.3 mmol) were irradiated for 30 min. Work-up, after the addition of sodium carbonate (0.46 g, 4.3 mmol), yielded an orange oil, which was chromatographed with hexane–ethyl acetate (19:1) as eluent. This yielded the following in order of elution: the

isoquinolinone **22** (0.18 g, 56%), as orange crystals m.p. 188–190 °C (from EtOH), (lit.,[11] 188–190 °C); recovered azadiene **10** (0.1 g, 25%).

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