

Photochemical Synthesis of Quinoline Derivatives by Cyclization of 4-Aryl-*N*-benzoyloxy-2,3-diphenyl-1-azabuta-1,3-dienes

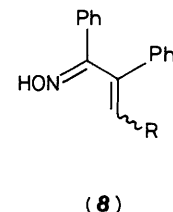
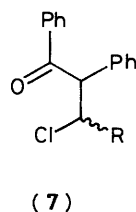
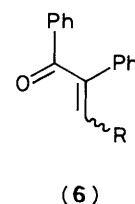
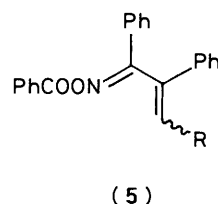
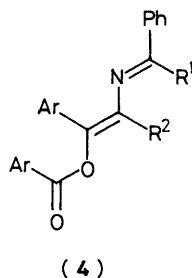
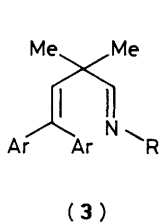
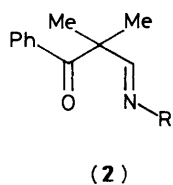
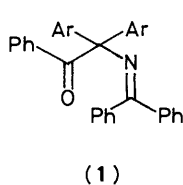
Diego Armesto,^{a,*} Mar G. Gallego,^b and William M. Horspool^b

^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 the photochemical reactions of a series of 4-aryl-*N*-benzoyloxy-2,3-diphenyl-1-azabuta-1,3-dienes are described. The photochemical cyclization affords good yields of 2,3-diphenylquinoline derivatives.

The photochemistry of molecules containing the imine group has been a subject of study for many years the results of which have been reviewed.^{1,2} In recent years we have been interested in the effect of the incorporation of an imine group on the photochemical reactivity of organic molecules. As a result we have observed the novel photoreactions of the imines (1),³ (2),⁴ (3),⁵ and (4).⁶ It is clear from these results that the incorpor-



R
 a: Ph
 b: C₆H₄OMe-*p*
 c: C₆H₄Cl-*p*
 d: C₆H₄Me-*p*

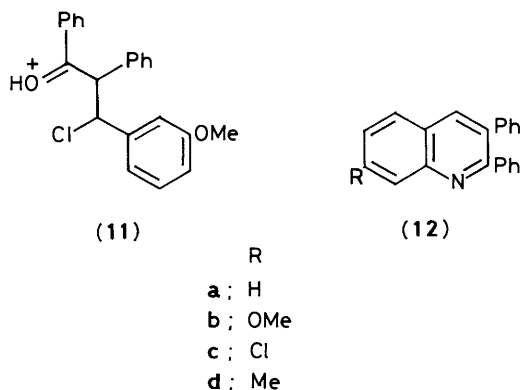
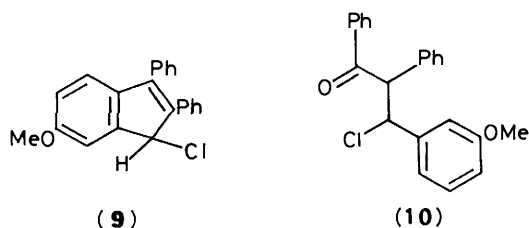
ation of a nitrogen into the system has a profound effect on the course of the reaction and the behaviour of these molecules is substantially different from the reactions of the carbon analogues. Of particular interest to the present study are the reactions of the 2-azadienes (4) an area of study which has suffered from neglect. Within this we have shown that rearrangement by a 1,2-benzoyl migration⁶ can take place but that conformational aspects are also important.⁷ The present study has sought to evaluate the influence of the position of the nitrogen within the diene skeleton and thus a study of the 1-azabuta-1,4-dienes (5), was undertaken.

Results and Discussion

The synthesis of the azadienes (5) was readily carried out using conventional methods. The route chosen is based on the condensation of arenecarbaldehydes with deoxybenzoin. This path had been used previously by Kohler and Nygaard⁹ for the synthesis of the enone (6a) by the acid induced condensation of deoxybenzoin with benzaldehyde. This affords the chloro ketone (7a) which on treatment with base undergoes elimination of HCl to yield the enone (6a). The conversion of this enone (6a) into the

corresponding oxime (8a) and ultimately to the diene (5a) was carried out by conventional methods. The identity of the final product, the diene (5a), was readily established by standard techniques. The i.r. spectrum shows a benzoate carbonyl at 1740 cm⁻¹ and the ¹³C n.m.r. spectrum clearly shows the resonance positions for the C=N and the C=O at 166.8 and 163.8 p.p.m. respectively in accord with previous results.⁶ The above method was used to synthesize the other dienes (5c—d) all of which are readily characterized by standard techniques.

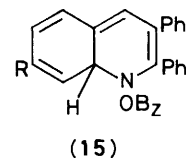
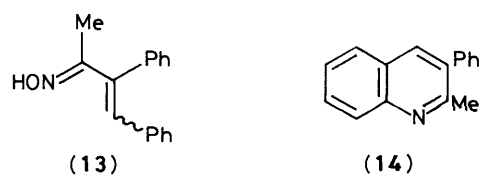
In one case, when the condensation of deoxybenzoin was tried with *m*-methoxybenzaldehyde, the reaction failed to yield the expected chloro ketone. A product was obtained in high yield the spectroscopic properties of which identified it as the cyclized compound (9). The change from the normal reaction path described above is readily explained. Thus condensation of *m*-methoxybenzaldehyde with deoxybenzoin affords the chloro ketone (10). This then undergoes protonation of the carbonyl oxygen affording (11) which can readily cyclize with the methoxy substituted aryl group ultimately to afford the product (9). The electrophilic cyclization can take place either *ortho*- or *para*- to the methoxy group but spectroscopic analysis indicates that only one isomer is present and this is assigned as the 6-MeO compound (9).



The dienes (**5**) all exhibit strong u.v. absorptions 300–350 nm region and the irradiations of the compounds were carried out in conventional apparatus using a Pyrex filter. All of the dienes (**5**) were photoreactive and were converted in less than 1 h into a mixture of products. The time for each reaction was determined by following the reaction by thin layer chromatography and each was stopped prior to complete consumption of the starting material in order to prevent over irradiation which might have been unprofitable. The resultant mixtures were readily separated by column chromatography on silica gel. Typically the diene (**5a**) afforded recovered starting material (30%), benzoic acid (44%), a mixture of highly polar material (20%), and a quinoline compound (**12a**) (43%). The identity of this compound was readily achieved by comparison with authentic data and by the synthesis of the corresponding picrate.⁹ All of the other dienes (**5b–d**) behaved in an analogous manner and yielded the corresponding quinoline derivatives (**12b–d**).

The formation of a quinoline derivative (**12**) by photochemical cyclization of a diene (**5**) does have literature precedent in that Glinka¹⁰ reported with little comment that the oxime (**13**) is transformed photochemically into the quinoline (**14**). The cyclization in this example and those reported by us can be rationalized readily in terms of a six-electron process involving the atoms of the diene skeleton and the 4-aryl group. This cyclization is typical for six electron systems and is similar to the transformation of 1,4-diphenylbuta-1,3-diene into 1-phenyl-naphthalene¹¹ or to cyclizations of the *cis*-stilbene type.¹² In our example cyclization affords the intermediate (**15**) which will readily undergo elimination of benzoic acid, presumably by a thermal process, to afford the final product. The influence of substituents on the cyclization has not been quantitatively evaluated but it would appear that there is little effect exerted by the substituted 4-aryl group.

At the outset of this study we were interested in the effect of changing the position of the nitrogen within the diene skeleton. Our previous results with the 2-azadienes (**4**) showed that electron transfer was important for the outcome of the photo-



reaction. It was important to know if the proximity of the nitrogen atom to the ester group would affect transfer. However, the results obtained in this study show that the nitrogen does not influence the outcome of the reaction. The absence of an electron transfer in this case is probably due to the fact that oxime esters have an ionization potential higher than in other imine systems and as a result electron transfer is minimized. This has already been demonstrated in our study of the oxime acetates (**3**; R = OAc).⁵

This approach to 7-substituted quinolines might have some synthetic value since substitution at this site is normally difficult. This difficulty arises from the fact that electrophilic substitution of quinolines introduces substituents at positions 5 and 8 while nucleophilic attack takes place at C-2.¹³ Alternative approaches to quinolines substituted at C-7 suffer from the problem of using intermediates which, in some cases, are difficult to synthesize.¹³

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 Bruker WP 60FT for carbon with chemical shifts (δ) expressed in p.p.m. downfield from internal Me₄Si. 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. All 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 dienes (300 mg, *ca.* 0.7 mmol) in anhydrous methylene dichloride (400 ml) were purged for 1 h with deoxygenated nitrogen and irradiated under a positive pressure of nitrogen. After completion of the irradiation the solvent was removed under reduced pressure and the products were separated by chromatography on silica gel using mixtures of ethyl acetate–hexane as eluant. Thin layer chromatography was carried out on Merck DC-Plastikfolien Kieselgel 60 F₂₅₄ using hexane–ethyl acetate mixtures as eluant.

Synthesis of Enones (6).—Benzoylstilbene (**6a**) was synthesized by the previously reported method.⁹ The other compounds were prepared by the analogous path as follows.

β -Chloroaryldeoxybenzoins (**7**).—Deoxybenzoins (20 mmol) and the aldehyde (20 mmol) were dissolved in dry ether and the solution cooled to 0 °C. Dry HCl was then passed through the mixture for 8 h. The temperature was maintained at 0 °C during this time. The mixture was allowed to stand at room tem-

perature overnight. The solvent was then removed under reduced pressure and the resulting solid was filtered and washed with ethanol.

Dehydrohalogenation.—The enones were obtained by heating the β -chloroaryldeoxybenzoin with fused potassium acetate and sodium carbonate (ratio 1:3:1) in methanol (150 ml) for periods in the range 3–18 h. After cooling, the mixture was filtered and the solvent was removed by evaporation under reduced pressure. The enones were isolated and purified by chromatography on silica gel using hexane–ethyl acetate mixtures as eluant.

Chloro ketone (7b). Deoxybenzoin (4 g, 20 mmol) and *p*-methoxybenzaldehyde (3.4 g, 25 mmol) yielded the *ketone* (7b) (3.4 g, 48%) as colourless crystals, m.p. 144–146 °C (lit.,¹⁴ m.p. 144 °C); ν_{\max} 1 670 cm^{-1} ; δ_{H} (CDCl_3) 8.0–7.8 (2 H, m, ArH), 7.7–7.2 (10 H, m, ArH), 7.0–6.8 (2 H, m, ArH), 5.7 (1 H, d, *J* 10 Hz, =CH), 5.3 (1 H, d, *J* 10 Hz, =CH), and 3.7 (3 H, s, MeO).

Chloro ketone (7c). Deoxybenzoin (4 g, 20 mmol) and *p*-chlorobenzaldehyde (3.5 g, 25 mmol) yielded the *ketone* (7c) (3.0 g, 42%) as colourless crystals, m.p. 122–124 °C (lit.,¹⁵ m.p. 113–115 °C); ν_{\max} 1 670 cm^{-1} ; δ_{H} (CDCl_3) 8.2 (2 H, m, ArH), 8.0–7.8 (2 H, m, ArH), 7.7–7.2 (10 H, m, ArH), 5.7 (1 H, dd, *J* 10 Hz, =CH), and 5.2 (1 H, dd, *J* 10 Hz, =CH).

Chloro ketone (7d). Deoxybenzoin (4 g, 20 mmol) and *p*-tolualdehyde (3.0 g, 25 mmol) yielded the *ketone* (7d) (5.0 g, 75%) as colourless crystals, m.p. 151–152 °C (lit.,¹⁴ m.p. 151 °C); ν_{\max} 1 680 cm^{-1} ; δ_{H} (CDCl_3) 8.2 (2 H, m, ArH), 7.6–7.0 (12 H, m, ArH), 5.8 (1 H, d, *J* 11 Hz, =CH), 5.3 (1 H, d, *J* 11 Hz, =CH), 2.2 (3 H, s, Me).

Enone (6b). The *ketone* (7b) (2.2 g, 6.3 mmol), potassium acetate (1.8 g, 18.8 mmol), and sodium carbonate (0.7 g, 6.3 mmol) were heated at reflux in methanol for 8 h. Chromatography using hexane–ethyl acetate (1:1) gave the desired *enone* (6b) (1.4 g, 73%) as colourless crystals, m.p. 80–82 °C (from methanol) (lit.,¹⁴ m.p. 85 °C); ν_{\max} (CHCl_3) 1 640 cm^{-1} ; δ_{H} (CDCl_3) 8.0–7.8 (2 H, m, ArH), 7.6–7.3 (9 H, m, ArH and =CH), 7.1–6.8 (4 H, dd, ArH), and 3.7 (3 H, s, MeO).

Enone (6c). The *ketone* (6c) (1.3 g, 3.6 mmol), potassium acetate (1.1 g, 10.8 mmol), and sodium carbonate (0.38 g, 3.6 mmol) were heated at reflux in methanol for 10 h. Chromatography using hexane–toluene (4:6) gave the desired *enone* (6c) (1.0 g, 70%) as colourless crystals, m.p. 91–93 °C (from ethanol); ν_{\max} (CHCl_3) 1 650 cm^{-1} ; δ_{H} (CDCl_3) 8.0–7.8 (2 H, m, ArH) and 7.5–7.0 (13 H, m, ArH and =CH).

Enone (6d). The *ketone* (6d) (5.0 g, 15 mmol), potassium acetate (4.4 g, 45 mmol), and sodium carbonate (1.6 g, 15 mmol) were heated at reflux in methanol for 18 h. Chromatography using hexane–ethyl acetate (9:1) gave the desired *enone* (6d) as a mixture of isomers (4.0 g, 89%) as colourless crystals, m.p. 89–90 °C (from ethanol) (lit.,¹⁴ m.p. 95 °C); ν_{\max} (CHCl_3) 1 670 cm^{-1} ; δ_{H} (CDCl_3) 8.2–7.9 (2 H, m, ArH), 7.6–7.0 (13 H, m, ArH and =CH), and 2.3 (3 H, s, Me).

Synthesis of Oximes (8).—**Oxime (8a).** Benzoylstilbene (6a) (5.6 g, 19.6 mmol), hydroxylamine hydrochloride (2.0 g, 29.4 mmol), and pyridine (2.3 g, 29.4 mmol) were heated at reflux in ethanol (100 ml) for 14 h. Work-up gave the *oxime* (8a) (2.12 g, 36%) as colourless crystals, m.p. 208–209 °C (from ethanol) (lit.,¹⁶ m.p. 208 °C); ν_{\max} (KBr) 3 260 cm^{-1} ; δ_{H} ($[\text{}^2\text{H}_6\text{O}]\text{DMSO}$) 11.4 (1 H, s, OH), 7.6–6.8 (15 H, m, ArH), and 6.46 (1 H, s, =CH).

Oxime (8b). The *enone* (6b) (1.05 g, 3.3 mmol), hydroxylamine hydrochloride (0.35 g, 5 mmol), and pyridine (0.39 g, 5 mmol) were heated at reflux in ethanol (100 ml) for 42 h. Work-up and chromatography (using hexane–ethyl acetate, 19:1) gave the *oxime* (8b) (1.0 g, 92%) as colourless crystals, m.p. 193–195 °C (from ethanol); ν_{\max} (CHCl_3) 3 300 cm^{-1} ; δ_{H} ($[\text{}^2\text{H}_6\text{O}]\text{DMSO}$) 11.4 (1 H, s, OH), 7.7–6.2 (15 H, m, ArH), and 3.6 (3 H, s, MeO).

Oxime (8c). The *enone* (6c) (0.90 g, 2.8 mmol), hydroxylamine hydrochloride (0.29 g, 4.2 mmol), and pyridine (0.33 g, 4.2 mmol) were heated at reflux in ethanol (100 ml) for 52 h. Work-up and chromatography (using hexane–ethyl acetate, 1:1) gave the *oxime* (8c) (0.90 g, 95%) as colourless crystals, m.p. 185–187 °C (from ethanol); ν_{\max} (CHCl_3) 3 300 cm^{-1} ; δ_{H} ($[\text{}^2\text{H}_6\text{O}]\text{DMSO}$) 11.5 (1 H, s, OH), 7.3–6.8 (14 H, m, ArH), and 6.4 (1 H, s, =CH).

Oxime (8d). The *enone* (6d) (4.6 g, 15.4 mmol), hydroxylamine hydrochloride (1.6 g, 23.1 mmol), and pyridine (1.82 g, 23.1 mmol) were heated at reflux in ethanol (100 ml) for 13 h. The reaction mixture was cooled and the crystalline solid was filtered off to afford the *oxime* (8d) (2.3 g, 48%) as colourless crystals, m.p. 198–200 °C (from ethanol); ν_{\max} (KBr) 3 140 cm^{-1} ; δ_{H} ($[\text{}^2\text{H}_6\text{O}]\text{DMSO}$) 11.4 (1 H, s, OH), 7.7–7.3 (10 H, m, ArH), 7.0–6.8 (4 H, dd, ArH), 6.4 (1 H, s, =CH), and 2.1 (3 H, s, Me).

Synthesis of the Azadienes (5).—**N-Benzoyloxy-2,3,4-triphenyl-1-azabuta-1,3-diene (5a).** The *oxime* (8a) (0.59 g, 1.97 mmol) and benzoyl chloride (0.23 ml, 1.97 mmol) gave the desired *azadiene* (5a) (0.76 g, 100%) as colourless crystals, m.p. 145–148 °C (from ethanol); ν_{\max} (KBr) 1 740 cm^{-1} ; δ_{H} (CDCl_3) 7.0–7.9 (ArH); δ_{C} (CDCl_3) 168.9 (C=N), 163.6 (C=O), and 148.6–127.8 (ArC); λ_{\max} (CH_2Cl_2) 235 (ϵ 17 800 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) and 330 nm (19 700); m/z 403 (M^+ , 1%), 297 (64), 180 (33), 165 (24), 105 (100), 89 (18), and 77 (60) (Found: C, 83.4; H, 5.1; N, 3.8. $\text{C}_{28}\text{H}_{21}\text{NO}_2$ requires C, 83.37; H, 5.21; N, 3.47%).

N-Benzoyloxy-4-*p*-methoxyphenyl-2,3-diphenyl-1-azabuta-1,3-diene (5b). The *oxime* (8b) (0.50 g, 1.52 mmol) and benzoyl chloride (0.18 ml, 1.52 mmol) gave the desired *azadiene* (5b) (0.40 g, 91%) as colourless crystals, m.p. 165–166 °C (from ethanol–water); ν_{\max} (KBr) 1 740 cm^{-1} ; δ_{H} (CDCl_3) 7.8 (2 H, m, ArH), 7.5–7.3 (13 H, m, ArH), 7.0–6.7 (5 H, m, ArH and =CH), and 3.7 (3 H, s, MeO); δ_{C} (CDCl_3) 166.8 (C=N), 163.8 (C=O), 159.4–113.7 (ArC), and 55.0 (MeO); λ_{\max} (CH_2Cl_2) 235 (34 000) and 336 nm (26 000); m/z 433 (M^+ , 36%), 329 (26), 328 (100), 312 (20), 197 (29), 105 (39), and 77 (20) (Found: M^+ , 433.1672. $\text{C}_{29}\text{H}_{23}\text{NO}_3$ requires M^+ , 433.1672).

N-Benzoyloxy-4-*p*-chlorophenyl-2,3-diphenyl-1-azabuta-1,3-diene (5c). The *oxime* (8c) (0.45 g, 1.35 mmol) and benzoyl chloride (0.15 ml, 1.35 mmol) gave the desired *azadiene* (5c) (0.50 g, 84%) as colourless crystals, m.p. 169–170 °C (from ethanol–water); ν_{\max} (CHCl_3) 1 740 cm^{-1} ; δ_{H} (CDCl_3) 7.8–6.9 (m, ArH and =CH); δ_{C} (CDCl_3) 168.6 (C=N), 163.6 (C=O), and 138.2–128.5 (ArC and C=C); λ_{\max} (CH_2Cl_2) 238 (38 000) and 313 nm (19 000); m/z 437 (M^+ , 12%), 332 (26), 316 (23), 201 (13), 105 (100), and 77 (22) (Found: M^+ , 437.1188. $\text{C}_{28}\text{H}_{20}\text{ClNO}_2$ requires M^+ , 437.1178).

N-Benzoyloxy-4-*p*-methylphenyl-2,3-diphenyl-1-azabuta-1,3-diene (5d). The *oxime* (8d) (2.2 g, 7.0 mmol) and benzoyl chloride (0.8 ml, 7.0 mmol) gave the desired *azadiene* (5d) (2.05 g, 70%) as colourless crystals, m.p. 167–168 °C (from ethanol); ν_{\max} (CHCl_3) 1 740 cm^{-1} ; δ_{H} (CDCl_3) 7.8 (m, 2 H, ArH), 7.5–6.9 (18 H, m, ArH and =CH), and 2.2 (3 H, s, Me); δ_{C} (CDCl_3) 169.1 (C=N), 163.6 (C=O), 138.4–128.5 (ArC and C=C), and 21.1 (Me); λ_{\max} (CH_2Cl_2) 256 (27 500) and 234 nm (27 000); m/z 417 (M^+ , 10%), 312 (10), 296 (70), 206 (10), 193 (10), 178 (20), 165 (10), 122 (15), 119 (25), 105 (100), and 77 (40) (Found: M^+ , 417.17258. $\text{C}_{29}\text{H}_{23}\text{NO}_2$ requires M^+ , 417.1723).

Irradiation of 4-Aryl-N-benzoyloxy-2,3-diphenyl-1-azabuta-1,3-dienes (5a–d).—**Diene (5a).** The diene (5a) (300 mg, 0.75 mmol) was irradiated for time: 30 min. Chromatography using hexane–ethyl acetate (98:2) gave the following: recovered diene (5a) (90 mg, 30%), benzoic acid (40 mg, 44%), 2,3-diphenylquinoline (12a) (90 mg, 43%) as colourless crystals, m.p. 68–69 °C (from ethanol); ν_{\max} (CHCl_3) 3 040, 3 020, 2 980,

2 960, 1 590, 1 480, 960, 900, and 700 cm^{-1} ; $\delta_{\text{H}}(\text{CDCl}_3)$ 8.0—7.7 (m, ArH); $\delta_{\text{C}}(\text{CDCl}_3)$ 158.2, 147.1, 140.2, 139.9, 137.4, 134.4, and 129.9—126.6 (ArC); $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)$ 238 (31 000) and 260 nm (34 000); m/z 281 (M^+ , 6%), 280 (100), 252 (6), and 139 (18). [This quinoline was identified by the synthesis of its picrate, m.p. 224—226 °C (lit.⁹ m.p. 223—224 °C)]. Unidentified polar products were eluted in the last fractions (60 mg).

Diene (5b). The diene (5b) (300 mg, 0.69 mmol) was irradiated for 45 min. Chromatography using hexane–ethyl acetate (96:4) gave the following: recovered diene (5b) (40 mg, 13%), benzoic acid (15 mg, 18%), 7-methoxy-2,3-diphenylquinoline (12b) (70 mg, 33%) as colourless crystals, m.p. 143—144 °C (from ethanol); $\nu_{\text{max}}(\text{CHCl}_3)$ 2 960, 2 940, 2 840, 1 620, 1 600, 1 580, 1 490, 1 480, 850, 700, and 650 cm^{-1} ; $\delta_{\text{H}}(\text{CDCl}_3)$ 8.15—7.22 (14 H, m, ArH) and 4.0 (3 H, s, MeO); $\delta_{\text{C}}(\text{CDCl}_3)$ 161.1, 158.7, 149.1, 140.8, 137.7, 137.2, 132.6, 131.2, 129.9—107.79, and 55.7 (Me); $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)$ 256 (46 000) and 342 nm (8 800); m/z 311 (M^+ , 75%), 310 (100), 267 (65), and 134 (8) (Found: M^+ , 311.131 01. $\text{C}_{22}\text{H}_{17}\text{NO}$ requires M^+ , 311.1306). Unidentified polar products were eluted in the last fractions (100 mg).

Diene (5c). The diene (5c) (300 mg, 0.69 mmol) was irradiated for 40 min. Chromatography using hexane–ethyl acetate (94:6) gave the following: recovered diene (5c) (52 mg, 36%), benzoic acid (23 mg, 27%), 7-chloro-2,3-diphenylquinoline (12c) (151 mg, 70%) as colourless crystals, m.p. 146—148 °C (from ethanol); $\nu_{\text{max}}(\text{CHCl}_3)$ 1 610, 1 585, 1 575, 1 550, 1 490, 1 480, 1 470, 1 440, 1 410, 810, 700, and 650 cm^{-1} ; $\delta_{\text{H}}(\text{CDCl}_3)$ 8.28—8.15 (2 H, m, ArH) and 7.88—7.2 (12 H, m, ArH); $\delta_{\text{C}}(\text{CDCl}_3)$ 159.5, 147.7, 140.1, 139.7, 137.6, 137.1, 135.4, 134.8, and 129.8—125.6; $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)$ 237 (137 000) and 257 nm (114 000); m/z 315 (M^+ , 100), 279 (25), 157 (31), 139 (45), 126 (19), and 101 (22) (Found: C, 79.6; H, 4.2; Cl, 11.5; N, 4.2. $\text{C}_{21}\text{H}_{14}\text{ClN}$ requires C, 79.87; H, 4.43; Cl, 11.25; N, 4.44%). Unidentified polar products were eluted in the last fractions (82 mg).

Diene (5d). The diene (5d) (300 mg, 0.72 mmol) was irradiated for 40 min. Chromatography using hexane–ethyl acetate (95:5) gave the following: recovered diene (5d) (50 mg, 17%), benzoic acid (27 mg, 31%), 7-methyl-2,3-diphenylquinoline (12d) (110 mg, 52%) as colourless crystals, m.p. 115—117 °C (from ethanol); $\nu_{\text{max}}(\text{CHCl}_3)$ 1 620, 1 600, 1 590, 1 550, 1 490, 1 440, 1 410, 1 370, 1 260, 1 020, 810, 800, and 700 cm^{-1} ; $\delta_{\text{H}}(\text{CDCl}_3)$ 8.22, 8.0, 7.9, 7.8, 7.6—7.2 (14 H, m, ArH), and 2.6 (3 H, s, Me); $\delta_{\text{C}}(\text{CDCl}_3)$ 158.0, 147.3, 140.3—127.8, and 21.6 (Me); $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)$ 240 (37 300), 258 (41 800), and 335 nm (4 500); m/z 295 (M^+ , 50), 294 (100), 180 (14), 147 (23), 139 (12), 103 (13), and 77 (12) (Found: C, 88.9; H, 5.9; N, 4.6. $\text{C}_{22}\text{H}_{17}\text{N}$ requires C, 89.50; H, 5.76; N, 4.74%). Unidentified polar products were eluted in the last fractions (90 mg).

Reaction of Deoxybenzoin with m-Methoxybenzaldehyde.—Deoxybenzoin (4 g, 20 mmol) was treated with *m*-methoxy-

benzaldehyde (3.4 g, 25 mmol) under the same conditions as described previously. Conventional work-up gave the *indene* (9) (4.7 g, 70%), m.p. 135—137 °C; $\nu_{\text{max}}(\text{CHCl}_3)$ 3 000, 1 610, 1 590, 700, and 670 cm^{-1} ; $\delta_{\text{H}}(\text{CDCl}_3)$ 7.6—6.9 (13 H, m, ArH), 5.8 (1 H, s, CH), and 3.9 (3 H, s, MeO); $\delta_{\text{C}}(\text{CDCl}_3)$ 159.4, 145.2, 140.9—121.7, 114.3, 111.2 (ArC), 60.1 (CH), and 55.8 (MeO); m/z 332 (M^+ , 50%), 297 (100), 252 (40), 148 (30), and 107 (10) (Found: M^+ , 332.0967. $\text{C}_{22}\text{H}_{17}\text{ClO}$ requires M^+ , 232.0964).

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