

## A Synthesis of Isoquinolinones by the Photochemical Cyclization of 2-Azabuta-1,3-dienes in the Presence of Acids

Diego Armesto,\* Mar G. Gallego, Maria J. Ortiz, and Santiago Romano

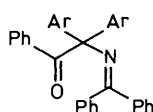
Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Complutense, 28040-Madrid, Spain

William M. Horspool

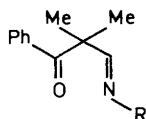
Department of Chemistry, The University, Dundee, DD1 4HN, Scotland

A study of the photochemical reactions of a series of 2-azabuta-1,3-dienes in the presence of perchloric acid or boron trifluoride-diethyl ether is reported. The photochemical reaction affords cyclization of all of the dienes to yield novel isoquinolinone derivatives. The reaction is interpreted as involving protonation, or complexation of the nitrogen lone pair. This prevents an electron transfer reaction which has been reported to yield novel dihydro-oxazole derivatives. Instead a photochemical Mannich reaction results in cyclization with the production of the isoquinolinone skeleton.

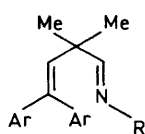
The photochemistry of molecules containing the imine group has been a subject of study for many years the results of which have been reviewed.<sup>1,2</sup> In recent years we have been interested in the effect of the incorporation of an imine group on the photochemical reactivity of organic molecules. As a result we have observed the novel photoreactions of imines (1),<sup>3</sup> (2),<sup>4</sup> (3),<sup>5</sup>



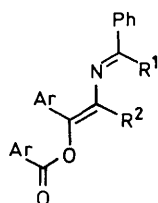
(1)



(2)



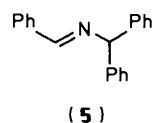
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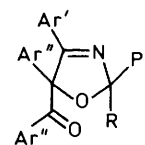
(4)

	R <sup>1</sup>	R <sup>2</sup>	Ar
a	Ph	Ph	Ph
b	Ph	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	Ph
c	Ph	<i>p</i> -CNC <sub>6</sub> H <sub>4</sub>	<i>p</i> -CNC <sub>6</sub> H <sub>4</sub>
d	Ph	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub>	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub>
e	Me	Ph	Ph
f	Ph	Ph	<i>m</i> -MeC <sub>6</sub> H <sub>4</sub>
g	Ph	Ph	<i>m</i> -MeOC <sub>6</sub> H <sub>4</sub>
h	Ph	Ph	<i>m</i> -CNC <sub>6</sub> H <sub>4</sub>

and (4).<sup>6</sup> It is clear from these results that the incorporation 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 all-carbon analogues. The photoreactivity of the 2-azadienes (4) is an area which has suffered from neglect. Within this we have shown that rearrangement by a 1,2-benzoyl migration<sup>6</sup> can take place but that conformational aspects are also important.<sup>7</sup> The present study reports on the photochemical reactivity of these dienes in



(5)



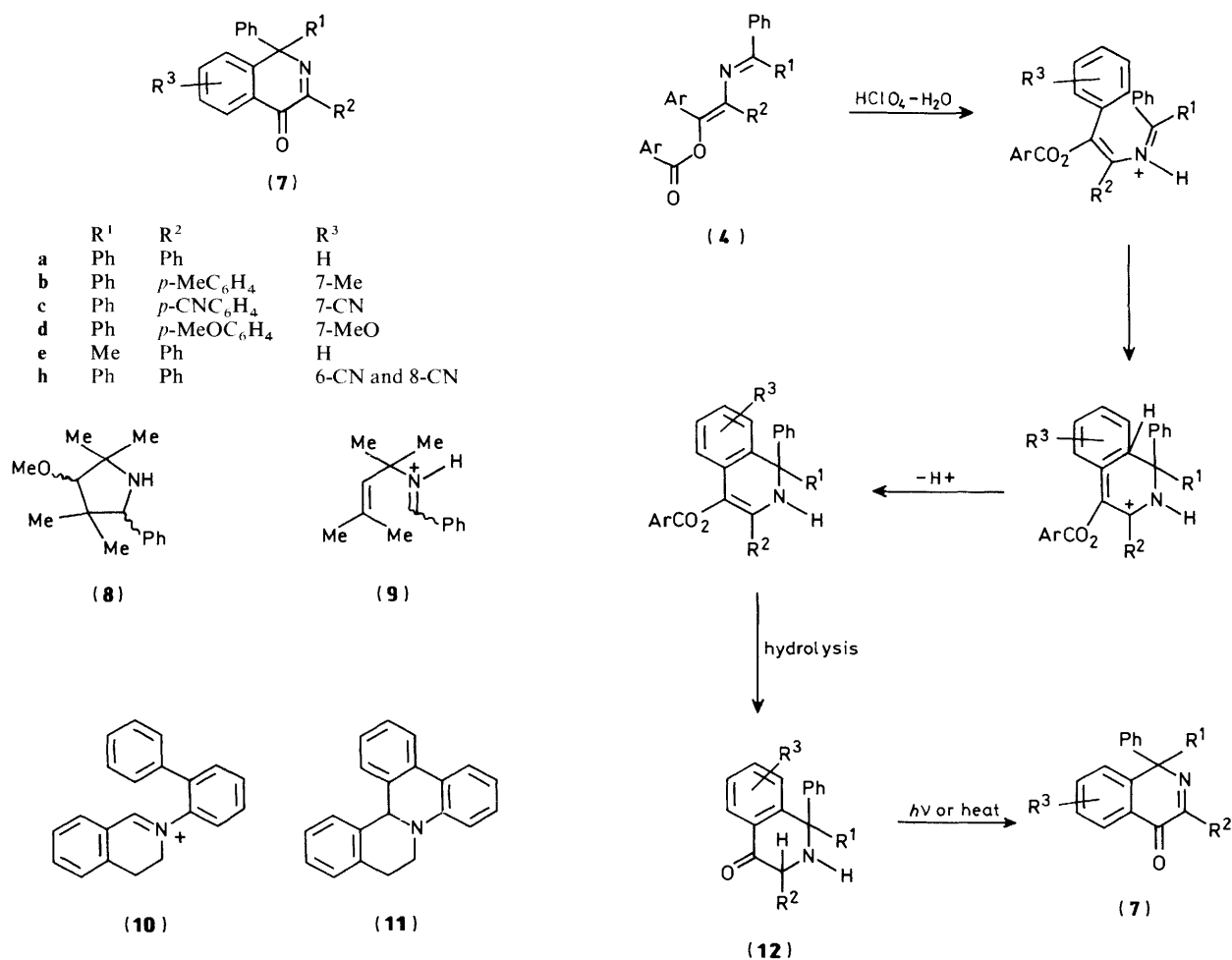
(6)

the presence of perchloric acid and boron trifluoride-diethyl ether where the nitrogen lone pair is either protonated or complexed with BF<sub>3</sub>.

### Results and Discussion

The azadienes required for the study were synthesized according to the previously described method.<sup>6,8</sup> In addition three new azadienes were prepared by the same method. This involves the reaction of the anion of the imine (5) with 2 equiv. of an acid chloride. In this manner the azadienes (4f–h) were synthesized.

Previously it was demonstrated that irradiation of the azadienes (4) in methylene dichloride affords the dihydro-oxazoles (6) by what is formally a 1,2-benzoyl migration.<sup>6</sup> An X-ray structure determination<sup>9</sup> of the aza diene (4a) showed that the molecule was twisted to 40° in the crystal. Our reasoning was that this twist brought the lone pair on nitrogen into overlap with the enol ester part of the molecule. This should result in an increase of the electron density of the double bond. Excitation of this led to an electron transfer into the ester group which ultimately brought about the novel migration and cyclization. In an effort to establish whether or not an electron transfer was involved the reaction of the aza diene (4a) was carried out in the presence of perchloric acid. Irradiation of this for a brief time led to the formation of a yellow product. The reaction described is truly photochemical and dark control reactions gave recovered starting material. The compound from this reaction showed that the ester group of the diene had been replaced by an oxo group at 1 670 cm<sup>-1</sup>. Furthermore the <sup>13</sup>C spectrum showed the presence of a C=O at 175.9 and a C=N at 160.3 p.p.m. These data along with microanalytical evidence identified the compound as the isoquinolinone (7a).<sup>10</sup> Thus the reaction path for the azadiene (4a) in the presence of perchloric acid is completely different to that for the irradiation of the azadiene (4a) in methylene dichloride. The reason for this major difference is



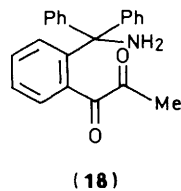
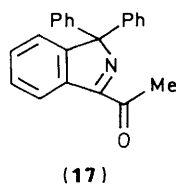
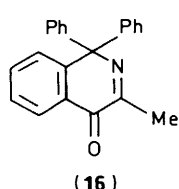
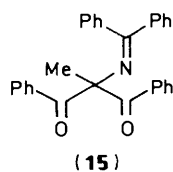
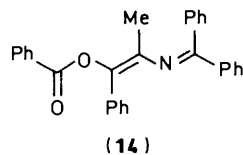
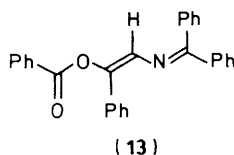
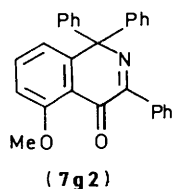
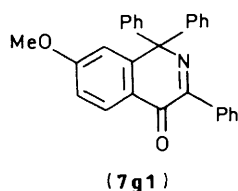
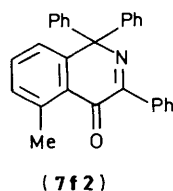
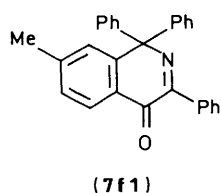
Scheme.

most likely due to protonation of the nitrogen lone pair of the azadiene (**4a**) to afford an iminium salt. This protonation will suppress an electron transfer step and instead the molecule follows a different reaction path, that of cyclization between the iminium carbon and a neighbouring aryl group. The photochemistry of iminium salts has been studied extensively by Mariano and his co-workers and has been reviewed.<sup>11</sup> A common reaction in such systems is cyclization of the iminium carbon to a non-conjugated double bond as in the formation of the heterocycle (**8**) from the iminium salt (**9**). In our example, the reaction again involves cyclization but the iminium carbon attacks the *ortho* position on a neighbouring aryl ring in a process akin to a Mannich reaction.<sup>12</sup> As far as we are aware there are very few examples of such a cyclization path but one such is the conversion of the salt (**10**) affording the heterocycle (**11**).<sup>13</sup> Thus the cyclization of the protonated azadiene (**4a**) follows the path shown in the Scheme involving the formation of the dihydro intermediate (**12**) following upon the conversion of the benzoate into a ketone. The method by which the removal of the benzoate occurs is presumably by the addition of water to the double bond followed by elimination of the benzoic acid. Indeed benzoic acid is isolated from the reaction mixture in yields comparable to those for the isoquinolinone. The dihydro compound (**12**) is not detected and presumably undergoes facile oxidation, either photochemical or thermal, to afford the final product. The suggestion that oxidation of (**12**) is facile is substantiated by the report<sup>14</sup> that dihydroquinoxalines are readily converted into the corresponding quinoxalones under similar conditions.

The route to the synthesis of isoquinolinones is quite general and a series of cyclizations has been studied. Thus all the

azadienes (**4b–e**) undergo the cyclization. The yields of products (**7b–e**) are variable but are generally > 50% even in the example (**4e**) where there is a 1-methyl substituent. Only the azadiene (**4d**) gave a low yield (23%) which could be due to the influence of the *p*-methoxy substituent inhibiting the cyclization step. The influence of *m*-substitution on the 3- and 4-aryl groups was also investigated using the azadienes (**4f–h**). Again cyclization took place but the efficiency of the reaction was poorer than the preceding examples. Furthermore the cyclization gave an inseparable mixture of isomeric products (**7f–h**). Because of the substituents on the azadienes (**4f**) and (**4g**) it was possible to identify the two isomeric products as (**7f1**) and (**7f2**) and (**7g1**) and (**7g2**) in each case using <sup>1</sup>H and <sup>13</sup>C n.m.r. spectroscopy. In these two cases the isomers were present in a ratio of 7:3. The dicyanoisoquinolinone (**7h**) did not have the facility for identification of the isomers. It is also interesting to note that the cyclization can be carried out by replacing perchloric acid with BF<sub>3</sub>·OEt<sub>2</sub>. This was tried for one azadiene (**4b**) and the yield of isoquinolinone obtained was superior to that for the perchloric acid reaction.

In addition to the cyclization of the protonated azadienes (**4a–h**) into the isoquinolinones (**7a–h**) the recovered azadienes (**4**) all were shown by <sup>1</sup>H n.m.r. spectroscopy to have undergone *trans-cis*-isomerization but no attempt was made to isolate the *cis*-isomers. In our previous study<sup>6</sup> of the photochemical reactions of the azadienes (**4**) by direct irradiation no evidence for *trans-cis*-isomerization was obtained. Only in the case of the azadiene (**13**) did *trans-cis*-isomerization occur.<sup>7</sup> In



this case it was argued that the lack of a 3-substituent permitted the azadiene to be flat and to behave as a normal diene on direct excitation.

The above study has been extended to include the methyl substituted azadiene (14). Previously it was demonstrated that the direct irradiation of this molecule in methylene dichloride brought about a 1,3-benzoyl migration to afford the 1,3-diketone (15).<sup>7</sup> The azadiene (14) suffered extensive decomposition with perchloric acid and in this case  $\text{BF}_3 \cdot \text{OEt}_2$  was used. Irradiation of this mixture gave a high yield (92%) of the isoquinolinone (16). Interestingly in this case the isoquinolinone (16) proved to be less stable than those isolated previously. On recrystallization or acid hydrolysis (16) was converted quantitatively into the isomeric product (17). Presumably this arises by hydrolysis of the imine C=N bond to afford a diketone (18) which recyclizes to the isoindole (17).

Finally, the irradiation of the azadiene (13) was carried out using  $\text{BF}_3 \cdot \text{OEt}_2$ . This, however, failed to yield cyclized product and gave only recovered starting material. This is an important observation since we have already established that this diene (13) is flat. All of the others (4) and (14) have been shown to be twisted around the (3)-N bond and this feature appears to be critical for the success of the isoquinolinone synthesis.

The above route is a useful synthetic path for the formation of previously unknown isoquinolinone derivatives. Currently research is aimed at the synthesis of less heavily substituted derivatives which might be of value as starting materials in the synthesis of naturally occurring compounds such as the protoberberine alkaloids.

## Experimental

M.p.s were determined on a Buchi 510D apparatus in open capillaries and are uncorrected. I.r. spectra were recorded as KBr discs unless otherwise stated using a Perkin-Elmer 257 spectrophotometer and band positions are reported in wave-numbers. N.m.r. spectra were recorded in deuteriochloroform solution unless otherwise stated using a Varian T-60A spectrometer for protons and a Bruker WP 60FT for carbon with chemical shifts ( $\delta$ ) expressed in p.p.m. downfield from internal  $\text{Me}_4\text{Si}$ . U.v./visible spectra were recorded in methylene dichloride solution using a Perkin-Elmer 550 spectrometer. Mass spectra were determined on a VG Micromass 16F. 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 in anhydrous methylene dichloride (400 ml) were purged for 1 h with de-oxygenated nitrogen and irradiated under a positive pressure of nitrogen. After completion of the irradiation solid  $\text{Na}_2\text{CO}_3$  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 chloroform layer was washed with water, dried ( $\text{MgSO}_4$ ), filtered, and evaporated to dryness under reduced pressure. The resultant oil was separated by chromatography on a column of silica gel using mixtures of ethyl acetate-hexane as eluant.

*Synthesis of Dienes the (4).*—The dienes (4a),<sup>6</sup> (4b),<sup>8</sup> (4c),<sup>8</sup> (4d),<sup>6</sup> (4e),<sup>8</sup> and (4i)<sup>8</sup> were synthesized as described previously. The new dienes (4f–h) were synthesized using the method described previously.<sup>9</sup>

4-(*m*-Toluoyloxy)-4-(*m*-tolyl)-1,1,3-triphenyl-2-azabuta-1,3-diene (4f). The imine (5) (2.0 g, 7.4 mmol) in THF (5 ml) added to sodium hydride 0.88 g, 36.9 mmol) in HMPA (60 ml) and *m*-toluoyl chloride (4.55 g, 29.5 mmol) was added to the solution of the resultant anion. Conventional work-up followed by chromatography on silica gel (100 g) using hexane-ethyl acetate (95:5) as eluant gave the following: the azadiene (4f) (2.9 g, 77%) as yellow crystals m.p. 193–195 °C, (ethanol);  $\nu_{\text{max}}$  (CDCl<sub>3</sub>) 1 735 and 1 620  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  7.9–7.5 (2 H, m, ArH) 7.5–6.7 (21 H, m, ArH), 2.3 (3 H, s, Me), and 2.2 (3 H, s, Me);  $\delta_{\text{C}}$  170.1 (C=N), 165.5 (COO), 139.7–124.3 (ArC), 21.4 (Me), and 21.00 (Me);  $\lambda_{\text{max}}$  (CH<sub>2</sub>Cl<sub>2</sub>) 240 ( $\epsilon = 34\,300 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) and 291 nm (23 800);  $m/z$  507 ( $M^+$ , 27%), 388 (100), 283 (38), and 165 (49) (Found: C, 84.9; H, 5.5; N, 2.9. C<sub>36</sub>H<sub>29</sub>NO<sub>2</sub> requires C, 85.21; H, 5.72; N, 2.76%).

4-(*m*-Methoxybenzoyloxy)-4-(*m*-methoxyphenyl)-1,1,3-triphenyl-2-azabuta-1,3-diene (4g). The imine (5) (2.0 g, 3.8 mmol) in THF (5 ml) was added to sodium hydride (0.88 g, 36.9 mmol) in HMPA (60 ml) and *m*-methoxybenzoyl chloride (4.98 g, 29.5 mmol) was added to the solution of the resultant anion. Conventional work-up followed by chromatography on silica gel (100 g) using hexane-ethyl acetate (9:1) as eluant gave the following: the azadiene (4g) (3.0 g, 75%) as yellow crystals m.p. 108–110 °C, (ethanol);  $\nu_{\text{max}}$  (KBr) 1 730 and 1 600  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  8.0–7.6 (2 H, m, ArH), 7.4–6.6 (21 H, m, ArH), 3.7 (3 H, s, MeO), and 3.5 (3 H, s, MeO);  $\delta_{\text{C}}$  170.3 (C=N), 165.2 (COO), 159.3, 159.0, 140.1–122.0 (ArC), 55.1 (MeO), and 54.7 (MeO);  $\lambda_{\text{max}}$  (CH<sub>2</sub>Cl<sub>2</sub>) 240 (34 300) and 291 nm (23 800);  $m/z$  539 ( $M^+$ , 18%), 404 (100), 299 (24), and 165 (39) (Found: C, 79.9; H, 5.5; N, 2.5. C<sub>36</sub>H<sub>29</sub>NO<sub>4</sub> requires C, 80.15; H, 5.38; N, 2.60%).

4-(*m*-Cyanobenzoyloxy)-4-(*m*-cyanophenyl)-1,1,3-triphenyl-2-azabuta-1,3-diene (**4h**). The imine (**5**) (1.0 g, 3.7 mmol) in THF (5 ml) added to sodium hydride (0.44 g, 18.5 mmol) in HMPA (40 ml) and *m*-cyanobenzoyl chloride (3.05 g, 18.5 mmol) was added to the solution of the resultant anion. Conventional work-up followed by chromatography on silica gel (80 g) using hexane-ethyl acetate (98:2) as eluant gave the following: the *azadiene* (**4h**) (1.1 g, 56%) as yellow crystals m.p. 220–222 °C, (ethanol);  $\nu_{\max}$  (KBr) 2 310, 1 740, and 1 600  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  8.3–6.9 (m, ArH);  $\delta_{\text{C}}$  170.0 (C=N), 164.9 (COO), 143.4–127.4 (ArC), 112.5 (CN), and 111.8 (CN);  $\lambda_{\max}$  (CH<sub>2</sub>Cl<sub>2</sub>) 248 (29 500), and 280 nm (19 200);  $m/z$  529 ( $M^+$ , 23%), 399 (100), 269 (42), and 165 (31) (Found: C, 81.5; H, 4.3; N, 8.1. C<sub>36</sub>H<sub>23</sub>N<sub>3</sub>O<sub>2</sub> requires C, 81.66; H, 4.35; N, 7.94%).

**Irradiation of Dienes (4).**—**Synthesis of 1,1,3-triphenylisoquinolin-4(1H)-one (7a).** The diene (**4a**) (0.5 g, 1.04 mmol), perchloric acid (0.52 g, 5.20 mmol), and sodium carbonate (0.55 g, 5.2 mmol) were irradiated for 15 min. Work-up yielded an orange oil (0.48 g) which was chromatographed on silica gel (40 g) using hexane-ethyl acetate (9:1). This yielded the following in order of elution: the *isoquinolinone* (**7a**) (0.2 g, 52%) as yellow crystals, m.p. 188–190 °C (ethanol);  $\delta_{\text{H}}$  6.9–7.3 (m, ArH) and 7.4–8.0 (m, ArH);  $\delta_{\text{C}}$  175.9 (C=O), 160.3 (C=N), 148.3, 145.2, 135.0, 132.5, 130.3–127.2 (ArC), and 71.8 (quaternary C);  $\nu_{\max}$  1 670 and 1 600  $\text{cm}^{-1}$ ;  $m/z$  373 ( $M^+$ , 15%), 315 (20), 270 (82), and 201 (100) (Found: C, 87.1; H, 5.1; N, 3.45. C<sub>27</sub>H<sub>19</sub>NO requires C, 86.86; H, 5.09; N, 3.75%); recovered diene (**4a**) as a mixture of *cis-trans*-isomers (0.21 g, 42%); and benzoic acid (0.07 g, 41%).

**Synthesis of 1,1-diphenyl-3-(*p*-tolyl)isoquinolin-4(1H)-one (7b).** The diene (**4b**) (0.3 g, 0.60 mmol), perchloric acid (0.306 g, 3.0 mmol), and sodium carbonate (0.35 g, 3.0 mmol) were irradiated for 17 min. Work-up yielded an orange oil (0.30 g) which was chromatographed on silica gel (30 g) using hexane-ethyl acetate (95:5). This yielded the following in order of elution: the *isoquinolinone* (**7b**) (0.15 g, 65%) as yellow crystals m.p. 187–188 °C (ethanol);  $\delta_{\text{H}}$  8.3–8.1 (1 H, m, ArH), 7.9–7.8 (2 H, d, ArH), 7.5–7.0 (15 H, m, ArH), and 2.3 (3 H, s, Me);  $\delta_{\text{C}}$  176.2 (C=O), 160.3 (C=N), 148.5, 145.3, 140.4, 132.8–127.0 (ArC), 71.8 (quaternary C), and 21.4 (Me);  $\nu_{\max}$  1 670 and 1 595  $\text{cm}^{-1}$ ;  $\lambda_{\max}$  (CH<sub>2</sub>Cl<sub>2</sub>) 238 (41 000) and 274 nm (28 500);  $m/z$  387 ( $M^+$ , 16%), 270 (100), 241 (24), and 239 (16) (Found: C, 87.1; H, 5.4; N, 3.5. C<sub>28</sub>H<sub>21</sub>NO requires C, 86.82; H, 5.42; N, 3.61%); recovered diene (**4b**) as a mixture of *cis-trans*-isomers (0.08 g, 27%); and benzoic acid (0.03 g, 41%).

**Irradiation of the azadiene (4b) with BF<sub>3</sub>·OEt<sub>2</sub>.** The azadiene (**4b**) (0.3 g, 0.60 mmol) and BF<sub>3</sub>·OEt<sub>2</sub> (0.2 ml, 1.8 mmol) were irradiated for 17 min. Work-up gave the same products as above: the *isoquinolinone* (**7b**) (0.10 g, 45%), recovered diene (**4b**) (0.15 g, 50%), and benzoic acid (0.2 g, 28%).

**Synthesis of 7-cyano-3-(*p*-cyanophenyl)-1,1-diphenylisoquinolin-4(1H)-one (7c).** The diene (**4c**) (0.7 g, 1.26 mmol), perchloric acid (0.63 g, 6.3 mmol), and sodium carbonate (0.67 g, 6.3 mmol) were irradiated for 25 min. Work-up yielded an orange oil (0.68 g) which was chromatographed on silica gel (60 g) using hexane-ethyl acetate (17:3). This yielded the following in order of elution: the *isoquinolinone* (**7c**) (0.30 g, 56%) as yellow crystals, m.p. 256–257 °C (ethanol);  $\delta_{\text{H}}$  8.2–7.0 (m, ArH);  $\delta_{\text{C}}$  174.0 (C=O), 158.2 (C=N), 148.7, 143.4, 138.2, 133.9–127.4 (ArC), 116.3 (CN), 113.9 (CN), and 71.6 (quaternary C);  $\nu_{\max}$  2 230, 1 675, and 1 600  $\text{cm}^{-1}$ ;  $\lambda_{\max}$  (CH<sub>2</sub>Cl<sub>2</sub>) 267 nm (22 800);  $m/z$  423 ( $M^+$ , 37%), 295 (61), and 149 (100) (Found: C, 81.7; H, 4.4; N, 9.6. C<sub>29</sub>H<sub>17</sub>N<sub>3</sub>O requires C, 82.27; H, 4.02; N, 9.93%); recovered diene (**4c**) as a mixture of *cis-trans*-isomers (0.24 g, 34%); and *p*-cyanobenzoyl acid (0.085 g, 46%).

**Synthesis of 7-methoxy-3-(*p*-methoxyphenyl)-1,1-diphenylisoquinolin-4(1H)-one (7d).** The diene (**4d**) (0.45 g, 0.79 mmol), perchloric acid (0.39 g, 3.95 mmol) and sodium carbonate (0.42

g, 3.95 mmol) were irradiated for 90 min. Work-up yielded an orange oil (0.49 g) which was chromatographed on silica gel (40 g) using hexane-ethyl acetate (4:1). This yielded the following in order of elution: the *isoquinolinone* (**7d**) (0.08 g, 23%) as yellow crystals, m.p. 196–198 °C (ethanol);  $\delta_{\text{H}}$  8.2–6.8 (17 H, m, ArH), 3.7 (3 H, s, MeO), and 3.6 (3 H, s, MeO);  $\delta_{\text{C}}$  175.3 (C=O), 160.2 (C=N), 143.2–127.1 (ArC), 113.2, 112.5, 71.5 (quaternary C), 55.3 (MeO), and 54.8 (MeO);  $\nu_{\max}$  1 670 and 1 600  $\text{cm}^{-1}$ ;  $\lambda_{\max}$  (CH<sub>2</sub>Cl<sub>2</sub>) 242 (24 550) and 312 nm (16 300);  $m/z$  433 ( $M^+$ , 27%), 300 (64), 238 (66), and 135 (100) (Found: C, 80.2; H, 5.1; N, 3.4. C<sub>29</sub>H<sub>23</sub>NO<sub>3</sub> requires C, 80.37; H, 5.31; N, 3.23%); recovered diene (**4d**) as a mixture of *cis-trans*-isomers (0.23 g, 51%); and *p*-methoxybenzoic acid (0.01 g, 8%).

**Synthesis of 1-methyl-1,3-diphenylisoquinolin-4(1H)-one (7e).** The diene (**4e**) (0.7 g, 1.7 mmol), perchloric acid (0.84 g, 8.4 mmol), and sodium carbonate (0.89 g, 8.4 mmol) were irradiated for 20 min. Work-up yielded an orange oil (0.66 g) which was chromatographed on silica gel (80 g) using hexane-ethyl acetate (98:2). This yielded the following in order of elution: the *isoquinolinone* (**7e**) (0.32 g, 62%) as yellow crystals, m.p. 94–96 °C (ethanol);  $\delta_{\text{H}}$  7.5–8.1 (11 H, m, ArH), 6.7–7.3 (3 H, m, ArH), and 1.9 (3 H, s, Me);  $\delta_{\text{C}}$  175.6 (C=O), 160.1 (C=N), 151.1, 143.4, 135.5, 133.1, 130.6–126.0 (ArC), 64.7 (quaternary C), and 29.7 (Me);  $\nu_{\max}$  1 670 and 1 600  $\text{cm}^{-1}$ ;  $\lambda_{\max}$  (CH<sub>2</sub>Cl<sub>2</sub>) 273 nm (15 400);  $m/z$  311 ( $M^+$ , 25%), 283 (21), and 208 (100) (Found: C, 85.2; H, 5.2; N, 4.6. C<sub>22</sub>H<sub>17</sub>NO requires C, 84.89; H, 5.47; N, 4.50%); recovered diene (**4e**) as a mixture of *cis-trans*-isomers (0.08 g, 11%); and benzoic acid (0.7 g, 34%).

**Synthesis of 6- and 8-methyl-1,1,3-triphenylisoquinolin-4(1H)-one (7f).** The diene (**4f**) (0.5 g, 0.98 mmol), perchloric acid (0.5 g, 4.9 mmol), and sodium carbonate (0.52 g, 4.9 mmol) were irradiated for 20 min. Work-up yielded an orange oil (0.47 g) which was chromatographed on silica gel (50 g) using hexane-ethyl acetate (95:5). This yielded the following in order of elution: the *isoquinolinone* (**7f**) (0.15 g, 40%) as yellow crystals m.p. 214–216 °C (ethanol);  $\delta_{\text{H}}$  8.0–6.9 (18 H, m, ArH), 2.4 (s, Me), and 1.7 (s, Me) (total 3 H in a ratio of 7:3);  $\delta_{\text{C}}$  176.1 (C=O), 160.4 (C=N), 147.5–125.8 (ArC), 72.0 (quaternary C), 71.7 (quaternary C), 22.7 (Me), and 20.9 (Me);  $\nu_{\max}$  1 665, 1 605, and 1 595  $\text{cm}^{-1}$ ;  $\lambda_{\max}$  (CH<sub>2</sub>Cl<sub>2</sub>) 274 nm (13 400);  $m/z$  387 ( $M^+$ , 23%), 284 (100), and 241 (25) (Found: C, 86.5; H, 5.5; N, 3.4. C<sub>20</sub>H<sub>21</sub>NO requires C, 86.82; H, 5.43; N, 3.62%); recovered diene (**4f**) as a mixture of *cis-trans*-isomers (0.23 g, 46%); and *m*-methylbenzoic acid (0.04 g, 30%).

**Synthesis of 6- and 8-methoxy-1,1,3-triphenylisoquinolin-4(1H)-one (7g).** The diene (**4g**) (0.6 g, 1.11 mmol), perchloric acid (0.56 g, 5.6 mmol), and sodium carbonate (0.59 g, 5.6 mmol) were irradiated for 35 min. Work-up yielded an orange oil (0.56 g) which was chromatographed on silica gel (60 g) using hexane-ethyl acetate (9:1). This yielded the following in order of elution: the *isoquinolinone* (**7g**) (0.20 g, 45%) as yellow crystals m.p. 156–158 °C (ethanol);  $\delta_{\text{H}}$  8.3–7.9 (2 H, m, ArH), 7.4–6.6 (15 H, m, ArH), 3.8 (s, MeO), and 3.7 (s, MeO) (total 3 H in a ratio of 7:3);  $\delta_{\text{C}}$  175.0 (C=O), 161.0 (C=N), 145.4–113.1 (ArC), 71.5 (quaternary C), 69.5 (quaternary C), 55.2 (MeO), and 55.1 (MeO);  $\nu_{\max}$  1 670 and 1 610  $\text{cm}^{-1}$ ;  $\lambda_{\max}$  (CH<sub>2</sub>Cl<sub>2</sub>) 277 (11 800) and 345 nm (2 800);  $m/z$  403 ( $M^+$ , 26%), 386 (23), 300 (100), and 257 (21) (Found: C, 83.0; H, 5.3; N, 3.2. C<sub>28</sub>H<sub>21</sub>NO<sub>2</sub> requires C, 83.37; H, 5.21; N, 3.47%); recovered diene (**4g**) as a mixture of *cis-trans*-isomers (0.28 g, 47%); and *m*-methoxybenzoic acid (0.05 g, 30%).

**Synthesis of 6- and 8-cyano-1,1,3-triphenylisoquinolin-4(1H)-one (7h).** The diene (**4h**) (0.5 g, 0.94 mmol), perchloric acid (0.48 g, 4.7 mmol), and sodium carbonate (0.50 g, 4.7 mmol) were irradiated for 40 min. Work-up yielded an orange oil (0.40 g) which was chromatographed on silica gel (50 g) using hexane-ethyl acetate (4:1). This yielded the following in order of elution: the *isoquinolinone* (**7h**) (0.06 g, 16%) as yellow crystals, m.p.

185–187 °C (ethanol);  $\delta_{\text{H}}$  8.5 (1 H, s, ArH), 8.2–7.9 (2 H, m, ArH), and 7.8–7.0 (15 H, m, ArH);  $\delta_{\text{C}}$  174.1 (C=O), 159.7 (C=N), 152.3–127.8 (ArC), 117.3 (C≡N), 112.3 (C≡N), 71.9 (quaternary C), and 68.5 (quaternary C);  $\nu_{\text{max}}$  2 230, 1 675, and 1 600  $\text{cm}^{-1}$ ;  $\lambda_{\text{max}}$  (CH<sub>2</sub>Cl<sub>2</sub>) 257 (19 000) and 296 nm (6 900);  $m/z$  398 ( $M^+$ , 21%), 295 (100), 252 (24), 149 (18), 91 (13), and 77 (32) (Found: C, 84.8; H, 4.4; N, 6.8. C<sub>28</sub>H<sub>18</sub>N<sub>2</sub>O requires C, 84.42; H, 4.52; N, 7.047%); recovered diene (**4h**) as a mixture of *cis-trans*-isomers (0.27 g, 54%); and *m*-cyanobenzoic acid (0.02 g, 14%).

**Synthesis of 3-methyl-1,1-diphenylisoquinolin-4(1H)-one (16).** 4-Benzoyloxy-3-methyl-1,1,4-tetraphenyl-2-azabuta-1,3-diene (**14**) (300 mg, 0.72 mmol) and BF<sub>3</sub>·OEt<sub>2</sub> (0.3 ml, 2.16 mmol) were irradiated for 30 min. Work-up yielded an oil (0.28 g) which was chromatographed silica gel (50 g) using hexane–ethyl acetate (95:5). This gave the *title compound* (**16**) (0.21 g, 92%) as yellow crystals, m.p. 107–109 °C;  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) 8.2–8.4, 7.2–7.6 (14 H, m, ArH), and 2.4 (3 H, s, Me);  $\delta_{\text{C}}$ (CDCl<sub>3</sub>) 175.6 (C=O), 162.5 (C=N), 149.2, 144.6, 132.6, 130.2, 127.0–128.7 (ArC), 71.6 (quaternary C), and 20.4 (Me);  $\nu_{\text{max}}$ (CHCl<sub>3</sub>) 1 670 and 1 640  $\text{cm}^{-1}$ ;  $\lambda_{\text{max}}$ (CH<sub>2</sub>Cl<sub>2</sub>) 230 (8 400) and 262 nm (7 000);  $m/z$  311 ( $M^+$ , 18%), 270 (100), 241 (20), and 165 (14) (Found:  $M^+$ , 311.13124. C<sub>22</sub>H<sub>17</sub>NO requires  $M^+$ , 311.1306).

**Thermal Transformation of the Isoquinolinone (16).**—Chromatography of (**16**), attempted recrystallization from ethanol or hydrolysis with THF–H<sub>2</sub>SO<sub>4</sub> (dil. 20% by vol.) afforded the *isoindole* (**17**), m.p. 110–111 °C;  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) 8.3–8.4 (m), 7.3–7.7 (14 H, m, ArH), and 2.8 (3 H, s, Me);  $\nu_{\text{max}}$ (CHCl<sub>3</sub>) 1 700  $\text{cm}^{-1}$ ;  $\lambda_{\text{max}}$ (CH<sub>2</sub>Cl<sub>2</sub>) 260 (2 000) and 265 nm (1 700);  $m/z$  311 ( $M^+$ , 90%), 268 (100), 190 (12), and 165 (25) (Found:  $M^+$ , 311.13111. C<sub>22</sub>H<sub>17</sub>NO requires  $M^+$ , 311.1306).

**Irradiation of the Diene (13).**—4-Benzoyloxy-1,1,4-triphenyl-2-azabuta-1,3-diene (0.3 g, 0.74 mmol) and BF<sub>3</sub>·OEt<sub>2</sub> (0.3 ml, 2.2 mmol) were irradiated for a total of 4 h. During the irradiation samples were examined by t.l.c. at 30 min, 1 h, and 2 h but only starting material was observed. After 4 h the reaction was worked up conventionally to yield, using hexane–ethyl acetate (93:7) as eluant: the azadiene (**13**) (0.22 g, 74%), benzophenone (0.5 g, 37%), and highly polar material (0.03 g).

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