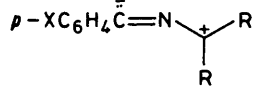
Photochemistry of 4-Acyloxy-2-azabuta-1,3-dienes. A Novel Photochemical 1,2-Acyl Migration in an Enol Ester. The Synthesis of 2,5-Dihydro-oxazole Derivatives

Diego Armesto,* Maria J. Ortiz, and Rafael Perez-Ossorio
Departamento de Quimica Organica, Facultad de Ciencias Quimicas, Universidad Complutense, 28040-Madrid, Spain
William M. Horspool
Department of Chemistry, The University, Dundee, DD1 4HN, Scotland

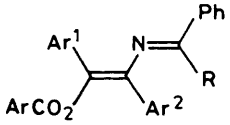
The facile photorearrangement of 4-acyloxy-2-azabuta-1,3-dienes to novel dihydro-oxazoles is described. For example 4-benzoyloxy-1,1,3,4-tetraphenyl-2-azabuta-1,3-diene (**2e**) rearranges into 5-benzoyl-2,2,4,5-tetraphenyl-2,5-dihydro-oxazole (**3e**). It is proposed that the rearrangement occurs *via* a [1,2]-aroyl migration related to the oxa-di-π-methane process of β,γ-unsaturated ketones.

Although hydro-oxazoles have been known since 1932,[1] their synthesis has not been well developed until recent times. Schmid[2] and Padwa[3] pioneered a synthetic route to this class of compound utilizing the photochemical generation of the ylides (**1**) and resultant trapping by suitable dipolarophiles to afford several novel examples of these compounds. There is little doubt that the Schmid-Padwa approach is versatile and usually proceeds in high yield. Alternative routes have been reported using more conventional ground state processes such as the cyclization of suitably substituted carbamates[4] or more recently by the trapping by imines of the carbene from 1-diazo-2-oxo-1,2-diphenylethane.[5]

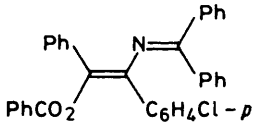
Here, we report a novel route to 2,5-dihydro-oxazoles utilizing the photochemical conversion[6] of the readily synthesized 4-aroyloxy-2-azabuta-1,3-dienes (**2**).



(**1**)



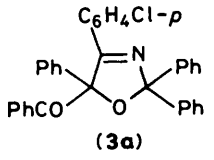
(**2**)



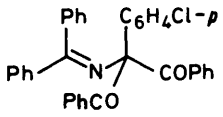
(**2a**)

Results and Discussion

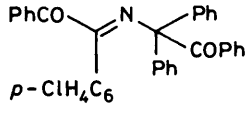
The preparative irradiations of the azadiene (**2a**) were carried out in an immersion well apparatus with a Pyrex filter and a 400 W medium-pressure Hg arc lamp. The irradiation brought about a rapid (15—30 min) colour change and the formation of a single photoproduct, as demonstrated by t.l.c. The colourless crystalline compound was isolated by conventional column chromatography on silica gel and further purification was achieved by crystallization. The ^{1}H n.m.r. spectrum was unhelpful while the i.r. spectrum indicated the absence of the ester carbonyl group (1 730 cm^{-1}) of the starting material and its replacement by a typical aryl keto group at 1 670 cm^{-1}. The mass spectrum of the photoproduct proved it to be isomeric with the starting material and also showed two sequential losses of PhCO fragments. Several possibilities were proposed for the structure of the compound exhibiting the above features. However, the most serious contenders were considered to be the dihydro-oxazole (**3a**), the [1,3]-migration product (**4**), and the [1,5]-migration product (**5**). This last compound does not, however, fit the available i.r. data and was rejected. A detailed examination of the mass spectrum of the product failed to eliminate conclusively either (**3a**) or (**4**). However, the fragmentation of the molecular ion of the product could follow the path shown in Scheme 1.



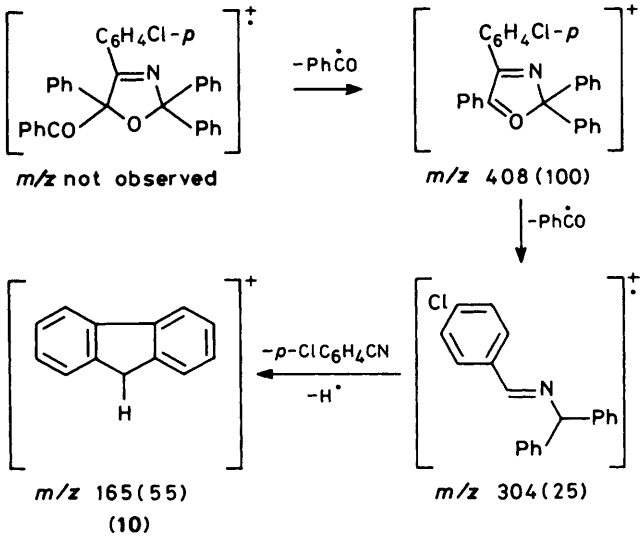
(**3a**)



(**4**)



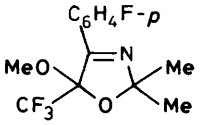
(**5**)



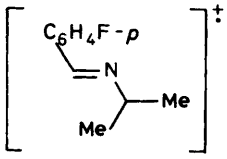
Scheme 1.

It is clear from the work of Schmid and his co-workers[7] that the 2,5-dihydro-oxazoles synthesized by them fragment in a similar way. For example, the compound (**6**) fragments by the

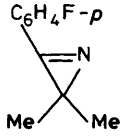
loss of MeO and CF_3CO to afford the ion (**7**) corresponding to the ylide from the azirine (**8**). Further substantiation for the fragmentation pattern proposed above is obtained from the reported fragmentation of the azirine (**9**) by loss of PhCN and H to afford the ion (**10**).[8] It should of course be borne in mind that the mass spectral fragmentation of compound (**4**) would give a fragment ion of the same mass but not necessarily the same identity.



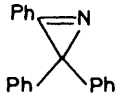
(**6**)



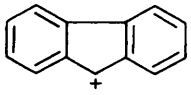
(**7**)



(**8**)



(**9**)



(**10**)

The ^{13}C n.m.r. spectrum of the product eliminates compound (**4**) from consideration and identifies the structure as (**3a**). Resonances occurred at δ 99.15 (C-2 or C-5), 111.79 (C-2 or C-5), 167.35 (C-4), and 197.95 (C=O) along with a complicated group of lines for the aryl carbons. The values are broadly in agreement with those reported by Schmid *et al.*[2b] for compounds of type (**6**). Discrepancies between our values and those of Schmid can be readily attributed to the differences in substituents around the ring. Final confirmation that the photoproduct was a novel 5-acyl-2,5-dihydro-oxazole was obtained from an *X*-ray diffraction structure determination compound (**3a**). This was carried out on a Nonius CAD 4F system and showed the crystal to be orthorhombic with a space group P_{abc} where $a = 16\,354(7)$, $b = 17\,464(9)$, $c = 18\,559(9)$ Å, $V = 5\,263$ Å, $Z = 8$, $F(000) = 2\,144$. The atomic parameters were refined by least squares analysis including 1 171 of the observed refractions to an *R* value of 0.054. The structure obtained was in complete agreement with that proposed for compound (**3a**) and full details are published elsewhere.[9]

The generality of the reaction was demonstrated for the azadiene esters (**2**). All of the esters were rapidly and easily converted by direct irradiation through Pyrex in methylene chloride solution into a single colourless crystalline photoproduct in high yield in each case (Table 1). The identity of the photoproducts as the 2,5-dihydro-oxazole derivatives (**3**) was based on the comparison of the physical data collected for the products with that of the conclusively identified product (**3a**). Thus, all the products exhibit carbonyl and imine groups in the i.r. spectrum in accordance with the proposed structure (Table 1).

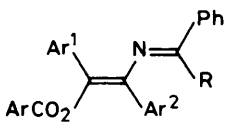
The tabulated mass spectral fragmentation patterns (Table 2) all show the same basic tendency to eliminate two aroyl groups followed by an aryl nitrile. This is shown by all the compounds (**3a**—**g**). The less heavily substituted compound (**3h**) also exhibits loss of two acyl groups but is somewhat different in the final fragmentations.

The ^{13}C n.m.r. line positions are also tabulated (Table 1) and clearly indicate the similarity in the spectral positions for the C=O and C=N carbon atoms. The resonances around 111 and 99 p.p.m. are assigned to the C-2 and C-5 carbons of the oxazoline ring but neither calculations nor comparison with the other ^{13}C n.m.r. data for 2,5-dihydro-oxazoles allows us to establish which is which. The oxazoline (**3h**) was synthesized in an attempt to solve this problem. However, the replacement of one phenyl group in (**3e**) by a methyl group does not significantly affect the chemical shift of the C-2 atom.

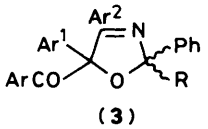
The overall rearrangement involves a [1,2]-aroyl migration and cyclization. There are, however, a few ways of bringing this about and these are outlined in Scheme 2. Based on literature precedence it is possible to make some reasoned judgements as to the applicability of some or all of these routes.

The oxirane path involving a novel class of vinyl oxirane (**11**) can be discounted on the basis that the ring-opening of the oxirane might be expected to follow a variety of paths leading to several products including isomeric dihydro-oxazoles. It is clear from the work of Jeger *et al.*[10] on the all carbon analogues that such multi-path behaviour is common for oxiranes. Furthermore no evidence was obtained for the intermediacy of any compound in the conversion or, for that matter, for the presence of other photoproducts such as an isomeric dihydro-oxazoles [*e.g.* (**12**)]. Thus, we are left with two reasonable possibilities: (i) Norrish Type I fission yielding radical pair (**13**), cyclization to radical (**14**) and selective bond formation between (**14**) and ArCO, or (ii) an oxa-di-π-methane type process involving intermediate biradicals (**15**) and (**16**) and clean cyclization to the observed products without the intermediacy of an oxirane.

The absence of isomeric dihydro-oxazoles appears to favour a process of the oxa-di-π-methane type. Such behaviour of an enol ester is unprecedented. The photochemistry of enol esters is dominated by the [1,3]-acyl shift.[11] This rearrangement appears to be independent of the ester and is exemplified in Scheme 3 for the conversion of aryl esters *via* the Photo-Fries reaction,[12] and for vinyl benzoates.[13] The literature is devoid of alternative reaction paths such as the [1,2]-acyl migration, a

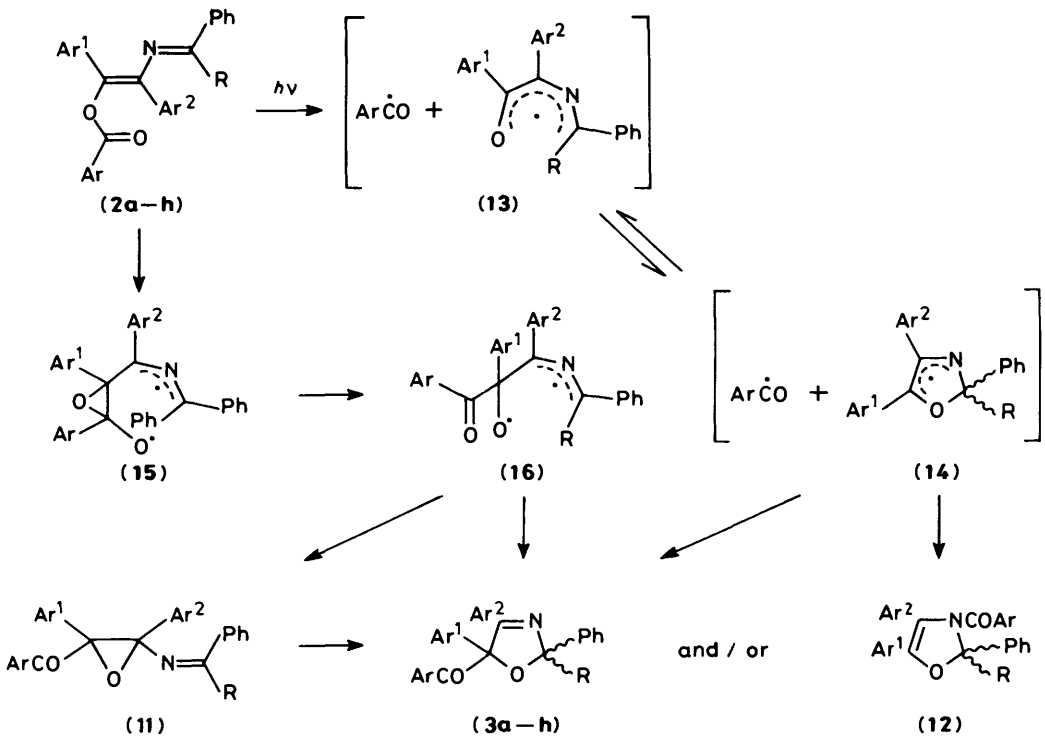


(**2**)



(**3**)

(**2a**); (**3a**) Ar = Ar^1 = R = Ph, Ar^2 = *p*-ClC_6H_4
(**2b**); (**3b**) Ar = Ar^1 = R = Ph, Ar^2 = *p*-MeC_6H_4
(**2c**); (**3c**) Ar = Ar^1 = R = C_6H_5, Ar^2 = *p*-$MeOC_6H_4$
(**2d**); (**3d**) Ar = *m*-BrC_6H_4, Ar^1 = Ar^2 = R = Ph
(**2e**); (**3e**) Ar = Ar^1 = Ar^2 = R = Ph
(**2f**); (**3f**) Ar = Ar^1 = Ar^2 = *p*-$MeOC_6H_4$, R = Ph
(**2g**); (**3g**) Ar = Ar^1 = Ar^2 = *p*-CNC_6H_4, R = Ph
(**2h**); (**3h**) Ar = Ar^1 = Ar^2 = Ph, R = Me



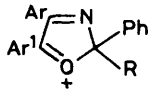
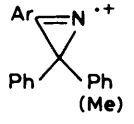
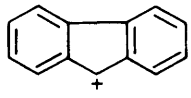
Scheme 2.

Table 1. Yield (%) and relevant spectroscopic data for 2,5-dihydro-oxazoles (3)

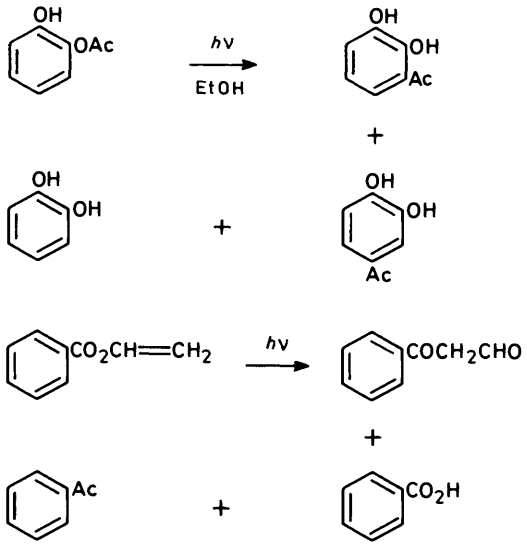
Compound	Isolated yield (%)	I.r.[a] C=O	I.r.[a] C=N	^{13}C n.m.r.[b] C=O	^{13}C n.m.r.[b] C=N	^{13}C n.m.r.[b] C-2 or C-5[c]	^{13}C n.m.r.[b] C-2 or C-5[c]
(3a)	59	1 670	1 630	197.9	167.3	111.8	99.1
(3b)	71	1 670	1 625	198.0	168.3	112.0	99.3
(3c)	62	1 670	1 630	198.1	167.3	111.7	99.1
(3d)	30	1 680	1 620	196.9	167.9	111.9	99.0
(3e)	60	1 670	1 625	197.6	168.1	111.8	99.2
(3f)	30	1 680	1 630	196.5	167.6	111.3	98.8
(3g)	33	1 685	1 630	195.9	165.6	113.5	98.3
(3h)	31	1 675	1 625	198.7	167.4	110.9	99.0

[a] In KBr. [b] In $CDCl_3$ with chemical shift in p.p.m. relative to internal $SiMe_4$. [c] It has proved impossible to differentiate between resonances C-2 and C-5.

Table 2. Mass spectra for the dihydro-oxazoles (3)

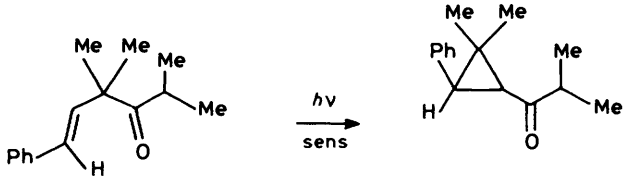
Compound	M^+			
(3a)	*a*	408 (100)	304 (25)	165 (98)
(3b)	493 (3)	338 (100)	283 (38)	165 (49)
(3c)	*a*	404 (100)	299 (20)	165 (42)
(3d)	559 (11)	374 (100)	269 (40)	165 (46)
(3e)	479 (12)	374 (100)	269 (42)	165 (50)
(3f)	569 (5)	434 (100)	299 (15)	165 (40)
(3g)	554 (13)	424 (100)	294 (86)	165 (90)
(3h)	417 (11)	312 (100)	207 (20)	

[a] Not observed.



Scheme 3.

rearrangement commonly found in the β,γ-unsaturated ketones [14] (Scheme 4). The suggested mechanism must, for the moment, remain speculative since thus far we have been unable to justify our claim. It does not seem unreasonable, however, to explain the departure from normality of these enol esters by involving the imino group in the reaction, perhaps *via* a charge transfer interaction. The final decision of which mechanism is operative awaits the results of a mechanistic study.



Scheme 4.

Experimental

Melting points 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 u.v. visible spectra were recorded on a Perkin-Elmer I 24 spectrophotometer. ^1H And ^{13}C N.m.r. spectra were recorded on Varian T-60 and Varian FT-80A spectrometers respectively. Samples were dissolved in $CDCl_3$ and chemical shifts are expressed in p.p.m. downfield from $SiMe_4$. Mass spectra were recorded on a Varian MAT-711 spectrometer. Elemental analysis were performed by the Consejo Superior de Investigaciones Cientificas, Madrid.

Synthesis of the Azadienes (**2**).—The azadienes (**2**) were synthesized by the method previously reported by us.[15]

Azadiene (**2d**). This was prepared from 3-aza-1,2,4,4-tetraphenylbut-2-en-1-one (3.37 g, 9 mmol) using NaH (540 mg, 18 mmol) in HMPA–THF (70 ml) as the base. The anion was trapped by the addition of *m*-bromobenzoyl chloride (11.2 mmol). The products were isolated in the manner described previously.[15] The azadiene (**2d**) (3.52 g, 70% from ethanol) had m.p. 122—123 °C; δ_H 6.7—8.0 (m, ArH); δ_C 122.54—140.61 (ArC), 164.10 (C=O), and 170.46 (C=N); $\nu_{max.}$(KBr) 3 050, 1 735, 1 620, 1 595, 1 570, 1 445, 1 240, 1 100, 740, and 700 cm^{-1}; $\lambda_{max.}(CH_2Cl_2)$ 238 (ε, 33 913 $dm^3\ mol^{-1}\ cm^{-1}$) 255 (26 087), 285 (21 739), and 302 nm (17 391); *m/z* (rel. intensity, %) 559 (M^+, 11%), 558 (4), 557 (11), 375 (30), 374 (100), 270 (12), 269 (48), 166 (17), 165 (57), and 105 (20) (Found: C, 73.0; H, 4.0; Br, 14.1; N, 2.6. $C_{34}H_{24}BrNO_2$ requires C, 73.11; H, 4.30; Br, 14.30; N, 2.51%).

General Procedure for the Irradiation of 2-Azadienes (**2**).—The photolyses were carried out using an immersion well apparatus in conjunction with a Pyrex filter and a 400 W Hg arc lamp. Solutions of the azadienes (**2a**—**h**) (6 mmol) in methylene chloride (380 ml) were purged with purified nitrogen for 1 h prior to irradiation. The solutions were irradiated for 10—45 min. The solvent was removed under reduced pressure and the crude photolysates were chromatographed on a slurry packed silica gel column (3 × 100 cm) eluting with hexane–ether.

5-Benzoyl-4-(p-chlorophenyl)-2,2,5-triphenyl-2,5-dihydro-oxazole (**3a**). Irradiation time: 22 min, chromatography eluting with ether–hexane (5:95) gave a white solid (203 mg) which was recrystallized from ethanol to yield the *dihydro-oxazole* (**3a**) (180 mg, 59%), m.p. 228—229 °C; δ_H 7.0—7.9 (m, ArH); δ_C 99.15 (C-2 or C-5), 111.79 (C-2 or C-5), 124.37—144.06 (ArC), 167.35 (C=N), and 197.95 (C=O); $\nu_{max.}$(KBr) 3 060, 1 670, 1 630, 1 595, 1 490, 1 450, 1 200, 1 090, 990, 870, 770, 750, and 700 cm^{-1}; $\lambda_{max.}(CH_2Cl_2)$ 232 (22 400) and 257 nm (35 900); *m/z* 410 (37), 408 (M^+ − PhCO, 100), 304 (25), 166 (42), 165 (98), 164 (10), 105 (95), and 77 (23) (Found: C, 79.65; H, 4.7; Cl, 7.0; N, 2.85. $C_{34}H_{24}ClNO_2$ requires C, 79.45; H, 4.67; Cl, 6.91; N, 2.72%).

5-Benzoyl-4-(p-tolyl)-2,2,5-triphenyl-2,5-dihydro-oxazole (**3b**). Irradiation time: 18 min, chromatography eluting with ether–hexane (2:98) gave a white solid (231 mg) which was recrystallized from ethanol to yield the *dihydro-oxazole* (**3b**) (210 mg, 71%), m.p. 245—246 °C; δ_H 2.3 (3 H, s, Me), 6.9—7.5 (22 H, m, ArH), 7.6—7.9 (2 H, m, ArH); δ_C 21.37 (Me), 99.28 (C-2 or C-5), 111.98 (C-2 or C-5), 126.46—144.53 (ArC), 168.29 (C=N), and 197.99 (C=O); $\nu_{max.}$(KBr) 3 040, 1 670, 1 625, 1 610, 1 600, 1 450, 1 210, 1 095, 990, 870, 755, and 700 cm^{-1}; $\lambda_{max.}(CH_2Cl_2)$ 233 (62 666), 242 (40 000), and 281 nm (6 666); *m/z* 493 (M^+, 3), 388 (100), 283 (38), 243 (3), 202 (8), 165 (49), 105 (32), and 83 (18) (Found: C, 85.4; H, 5.6; N, 2.6. $C_{35}H_{27}NO_2$ requires C, 85.19; H, 5.40; N, 2.83%).

5-Benzoyl-4-(p-methoxyphenyl)-2,2,5-triphenyl-2,5-oxazole (**3c**). Irradiation time: 25 min, chromatography eluting with ether–hexane (8:92) gave a white solid (220 mg) which was recrystallized from ethanol to yield the *dihydro-oxazole* (**3c**) (190 mg, 62%), m.p. 220—221 °C; δ_H 3.7 (3 H, s, MeO), 6.6—7.4 (22 H, m, ArH), and 7.6—7.8 (2 H, m, ArH); δ_C 55.2 (MeO), 99.15 (C-2 or C-5), 111.72 (C-2 or C-5), 113.30—161.30 (ArC), 167.29 (C=N), and 198.11 cm^{-1} (C=O); $\nu_{max.}$(KBr) 3 060, 1 670, 1 630, 1 610, 1 570, 1 450, 1 310, 1 260, 1 180, 980, 770, 760, and 700 cm^{-1}; $\lambda_{max.}(CH_2Cl_2)$ 230 (22 300), 265 (27 000), and 280 nm (24 110); *m/z* 405 (32), 404 (M^+ − PhCO, 100), 299 (20), 284 (10), 166 (17), 165 (42), 105 (21), and 77 (9) (Found: C, 82.25; H, 5.35; N, 2.85. $C_{35}H_{27}NO_3$ requires C, 82.51; H, 5.30; N, 2.75%).

5-(m-Bromobenzoyl)-2,2,4,5-tetraphenyl-2,5-dihydro-oxazole (**3d**). Irradiation time: 26 min, chromatography eluting with ether–hexane (5:95) gave a white solid (134 mg) which was recrystallized from ethanol to afford the *dihydro-oxazole* (**3d**) (105 mg, 30%), m.p. 131—132 °C; δ_H 6.98—7.97 (m, ArH); δ_C 98.98 (C-2 or C-5), 111.87 (C-2 or C-5), 122.10—143.80 (ArC), 167.95 (C=N), and 196.89 (C=O); $\nu_{max.}$(KBr) 3 080, 1 680, 1 620, 1 600, 1 490, 1 420, 1 240, 1 220, 1 000, 750, and 700 cm^{-1}; $\lambda_{max.}(CH_2Cl_2)$ 233 (26 600), 251 nm (32 200); *m/z* 559, 557 (M^+, 11), 374 (100), 375 (20), 270 (9), 269 (40), 166 (15), 165 (46), and 105 (20) (Found: C, 73.2; H, 4.0; Br, 14.1; N, 2.75. $C_{34}H_{24}BrNO_2$ requires C, 73.11; H, 4.30; Br, 14.30; N, 2.51%).

5-Benzoyl-2,2,4,5-tetraphenyl-2,5-dihydro-oxazole (**3e**). Irradiation time: 25 min, chromatography eluting with ether–hexane (3:97) gave a white solid (193 mg) which was recrystallized from ethanol to yield the *dihydro-oxazole* (**3e**) (150 mg, 60%), m.p. 194—

195 °C; δ_H 6.8—7.9 (m, ArH); δ_C 99.20 (C-2 or C-5), 111.85 (C-2 or C-5), 125.13—143.20 (ArC), 168.15 (C=N), and 197.60 (C=O); $\nu_{max.}$(KBr) 3 060, 1 670, 1 625, 1 600, 1 450, 1 260, 1 070, 1 010, 860, 750, and 700 cm^{-1}; $\lambda_{max.}$(CH_2Cl_2) 234 (17 500) and 254 nm (23 500); *m/z* 479 (M^+, 12), 374 (100), 269 (42), 165 (50), 105 (45), and 77 (10) (Found: C, 85.4; H, 5.25; N, 3.0. $C_{34}H_{25}NO_2$ requires C, 85.17; H, 5.21; N, 2.92%).

5-(p-*Methoxybenzoyl*)-4,5-(*di*-p-*methoxyphenyl*)-2,2-*diphenyl*-2,5-*dihydro-oxazole* (**3f**). Irradiation time: 30 min, chromatography eluting with ether–hexane (20:80) gave a white solid (153 mg) which was recrystallized from ethanol to afford the *dihydro-oxazole* (**3f**) (100 mg, 30%), m.p. 238—239 °C; δ_H 3.73 (3 H, s, MeO), 3.76 (3 H, s, MeO), 3.83 (3 H, s, MeO), and 6.66—8.00 (22 H, m, ArH); δ_C 55.18 (2 × Me), 55.35 (Me), 98.85 (C-2 or C-5), 111.28 (C-2 or C-5), 113.10—163.21 (ArC), 167.61 (C=N), and 196.53 (C=O); $\nu_{max.}$(KBr) 3 080, 1 680, 1 630, 1 610, 1 600, 1 510, 1 450, 1 305, 1 260, 1 180, 990, 840, 775, and 700 cm^{-1}; $\lambda_{max.}$(CH_2Cl_2) 230 (34 800), and 289 nm (44 800); *m/z* 569 (M^+, 5), 435 (44), 434 (100), 299 (15), 248 (8), 166 (16), 165 (40), 136 (6), 135 (64), 105 (3), and 77 (9) (Found: C, 77.85; H, 2.65; N, 5.4. $C_{37}H_{31}NO_5$ requires C, 78.03; H, 2.46; N, 5.44%).

5-(p-*Cyanobenzoyl*)-4,5-(*di*-p-*cyanophenyl*)-2,2-*diphenyl*-2,5-*dihydro-oxazole* (**3g**). Irradiation time: 30 min, chromatography eluting with ether–hexane (20:80) gave a white solid (120 mg) which was recrystallized from ethanol to afford the *dihydro-oxazole* (**3g**) (110 mg, 33%), m.p. 238—239 °C; δ_H 7.0—8.0 (m, ArH); δ_C 98.34 (C-2 or C-5), 113.54 (C-2 or C-5), 116.74 (C=N), 117.59 (C=N), and 117.94 (C=N), 125.81—142.53 (ArC), 165.60 (C=N), and 195.92 (C=O); $\nu_{max.}$(KBr) 3 060, 2 215, 1 685, 1 630, 1 610, 1 450, 1 250, 1 000, 770, and 700 cm^{-1}; $\lambda_{max.}$(CH_2Cl_2) 233 (12 700), 248 (16 100), and 256 (14 000) nm; *m/z* 554 (M^+, 13), 424 (100), 294 (86), 166 (37), 165 (90), and 130 (60) (Found: C, 80.0; H, 3.9; N, 10.0. $C_{37}H_{22}N_4O_2$ requires C, 80.14; H, 3.88; N, 10.10%).

5-*Benzoyl*-2-*methyl*-2,3,5-*triphenyl*-2,5-*dihydro-oxazole* (**3h**). Irradiation time: 30 min, chromatography eluting with ether–hexane (10:90) gave a white solid (118 mg) which was recrystallized from ethanol to afford the *dihydro-oxazole* (**3h**) (80 mg, 31%), m.p. 125—126 °C; δ_H 2.4 (3 H, s, Me) and 6.8—7.7 (20 H, m, ArC); δ_C 30.05 (Me), 99.04 (C-2 or C-5), 110.90 (C-2 or C-5), 125.56—144.46 (ArC), 167.36 (C=N), and 198.73 (C=O); $\nu_{max.}$(KBr) 3 080, 1 675, 1 625, 1 600, 1 450, 1 260, 1 220, 860, 760, 700, and 670 cm^{-1}; $\lambda_{max.}$(CH_2Cl_2) 251 nm (17 369); *m/z* 417 (M^+, 11), 313 (25), 312 (100), 207 (20), 206 (12), 165 (5), 105 (46), and 77 (16) (Found: C, 83.65; H, 5.4; N, 3.45. $C_{29}H_{23}NO_2$ requires C, 83.45; H, 5.51; N, 3.36%).

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