

## Photochemical Reactions of Quinoxalin-2-ones and Related Compounds

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Irradiation of the quinoxalin-2-ones (**1a–c**, **e–g**, and **i**) in the presence of amines gave reductive dimers, the dihydro dimers (**3a–c**, **e–g**, and **i**) of quinoxalin-2-ones, while irradiation of the quinoxalin-2-ones (**1d**, **h**, and **j**), which possess a phenyl group at the 3-position, under similar conditions gave the reduced products, the 3,4-dihydroquinoxalin-2-ones (**4d**, **h**, and **j**). Irradiation of the 1,4-benzoxazin-2-ones (**2a–c**) in the presence of amines also yielded the reductive dimers, the dihydromers (**5a–c**) of 1,4-benzoxazin-2-ones. [2 + 2] Photocycloaddition reactions of the quinoxalin-2-ones (**1b**, **c**, **f**, **g** and **k**) with electron-poor alkenes were also examined.

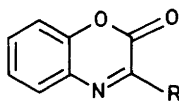
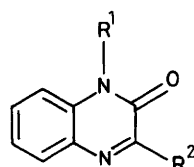
The photochemical reactions of compounds containing the C=N double bond have been extensively investigated,<sup>1</sup> but their photochemistry has not developed as rapidly as that of carbonyl compounds. The reason generally invoked is the low reactivity of the excited imino group due to the rapid radiationless decay which results from twisting around the C=N double bond (*syn–anti*-isomerization). Accordingly, it is possible that with cyclic molecules the energy-wasting *syn–anti* isomerization could be prevented. The major reaction generally observed in the photoreaction of the N=C–C=O chromophore of cyclic molecules is [2 + 2] cycloaddition with alkenes across the C=N double bond.<sup>2–4</sup> Ketimines (C=N–C=O), aza analogues of  $\alpha,\beta$ -unsaturated ketones, have been shown to undergo photo-reduction, hydrogen abstraction, and [2 + 2] photocycloaddition.<sup>1</sup> Recently, we have also found that the quinoxalin-2-ones (**1**) and the 1,4-benzoxazin-2-ones (**2**), which include the ketimine chromophore in the ring, undergo [2 + 2] photocycloaddition with alkenes to give tricyclic azetidine deriv-

atives.<sup>5–8</sup> These photocycloadditions proceeded with high regioselectivity. On the other hand, oxazinones failed to undergo [2 + 2] photocycloaddition with alkenes, but on carrying out the irradiation in propan-2-ol dimers were obtained.<sup>9</sup> The formation of reductive dimers was ascribed to hydrogen abstraction from the solvent by the low-lying  $n-\pi^*$  triplet state of the oxazinone. We report here the photochemical reductive dimerization of the quinoxalin-2-ones (**1**) and the 1,4-benzoxazin-2-ones (**2**) in the presence of amines<sup>10</sup> and [2 + 2] photocycloaddition of the quinoxalin-2-ones (**1**) with electron-poor alkenes.

### Results and Discussion

**Photochemical Reactions of the Quinoxalin-2-ones (1) and the Benzoxazin-2-ones (2) in the Presence of Amines.**—When a solution of 1,3-dimethylquinoxalin-2(1*H*)-one (**1e**) in propan-2-ol was irradiated in a Pyrex vessel with a high-pressure mercury lamp under argon for 15 h at room temperature, the reductive dimer (**3e**) was obtained in 4% yield, along with unchanged starting quinoxalin-2-one (**1e**) (93%). Irradiation of (**1e**) in other solvents such as methanol, benzene, tetrahydrofuran (THF), acetone, and acetonitrile under the same conditions also gave the reductive dimer (**3e**), but in low yields (see Table 1). When the quinoxalin-2-one (**1e**) was irradiated in benzene in the presence of triethylamine for 5 h, the yield of the reductive dimer (**3e**) increased considerably to 49%. The structure of (**3e**) was elucidated on the basis of its spectral data and elemental analysis. The mass spectra (chemical ionization) of (**3e**) showed a molecular ion peak at  $m/z$  351 ( $M^+ + 1$ ) and displayed a characteristic fragment at  $m/z$  176 [ $(M^+ + 1) - C_{10}H_{11}N_2O$ ]. In the <sup>13</sup>C NMR spectrum of (**3e**) a new quaternary carbon peak was present at  $\delta$  63.8 (s) and the peak due to the imino carbon in the starting compound had disappeared. Consequently, we concluded that compound (**3e**) is joined at the C-3,3' positions. Similarly, irradiation of the quinoxalin-2-ones (**1a–c**, **f**, **g**, and **i**) in the presence of triethylamine gave the corresponding reductive dimers (**3a–c**, **f**, **g**, and **i**) in 22–78% yields. The reductive dimers (**3f**, **g**, and **i**) were also obtained, though in rather low yields, when the photoreaction was carried out in benzene in the absence of triethylamine.

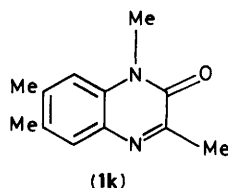
Irradiation of the quinoxalin-2-ones (**1d**, **h**, and **j**), which have a phenyl group at C-3, in benzene in the presence of triethylamine under the same conditions as described above gave the reduced products, the 3,4-dihydroquinoxalin-2-ones (**4d**, **h**, and **j**) in 40–99% yields and the corresponding reductive dimers were not detected. The structure of the reduced products



	R <sup>1</sup>	R <sup>2</sup>
( <b>1a</b> )	H	Me
( <b>1b</b> )	H	Bu
( <b>1c</b> )	H	Pen <sup>i</sup>
( <b>1d</b> )	H	Ph
( <b>1e</b> )	Me	Me
( <b>1f</b> )	Me	Bu
( <b>1g</b> )	Me	Pen <sup>i</sup>
( <b>1h</b> )	Me	Ph
( <b>1i</b> )	Et	Me
( <b>1j</b> )	Et	Ph

Pen<sup>i</sup> = isopentyl.

( <b>2a</b> )	Me
( <b>2b</b> )	Bu
( <b>2c</b> )	Pen <sup>i</sup>
( <b>2d</b> )	Ph

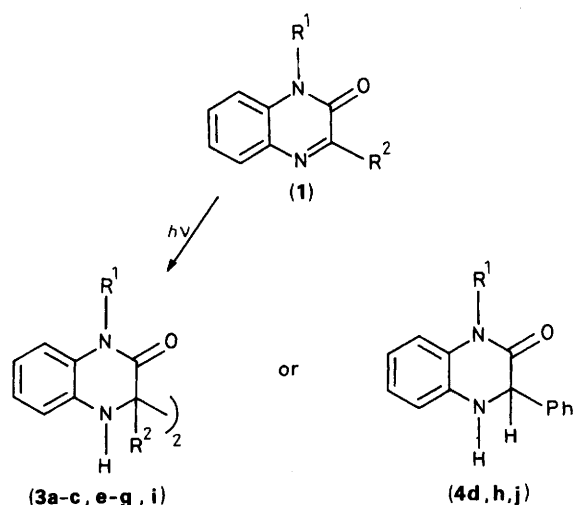


(**1k**)

**Table 1.** Yields of the quinoxalin-2-one dimers (3) and the 3,4-dihydroquinoxalin-2-ones (4).

Quinoxalin-2-one (1)	Amine	Solvent	Irrad. time/h	% Yield <sup>b</sup>		
				(3)	(4)	Recovered (1)
<b>a</b>	—	M <sup>c</sup>	15	— <sup>d</sup>	—	15
	Et <sub>3</sub> N (7.5) <sup>a</sup>	M	15	78	—	trace
<b>b</b>	—	M	15	—	—	ca. 100
	Et <sub>3</sub> N	M	15	26	—	45
<b>c</b>	—	M	15	—	—	ca. 100
	Et <sub>3</sub> N	M	15	30	—	68
<b>d</b>	—	M	15	—	—	ca. 100
	Et <sub>3</sub> N	M	15	—	99	—
<b>e</b>	—	Pr <sup>i</sup> OH	15	4	—	93
	—	MeOH	15	trace	—	ca. 100
	—	C <sub>6</sub> H <sub>6</sub>	15	10	—	70
	—	THF	15	6	—	85
	—	Me <sub>2</sub> CO	15	4	—	80
	—	MeCN	15	trace	—	ca. 100
	Et <sub>3</sub> N	C <sub>6</sub> H <sub>6</sub>	5	49	—	43
	Et <sub>3</sub> N	MeOH	5	79	—	21
	Et <sub>3</sub> N	MeCN	5	62	—	34
	PhNMe <sub>2</sub> (7.1)	C <sub>6</sub> H <sub>6</sub>	15	50	—	30
	Et <sub>2</sub> NH (8.01)	C <sub>6</sub> H <sub>6</sub>	15	40	—	15
	PrNH <sub>2</sub> (8.78)	C <sub>6</sub> H <sub>6</sub>	15	14	—	60
	Bu <sup>t</sup> NH <sub>2</sub> (8.64)	C <sub>6</sub> H <sub>6</sub>	15	10	—	70
<b>f</b>	—	C <sub>6</sub> H <sub>6</sub>	15	trace	—	60
	Et <sub>3</sub> N	C <sub>6</sub> H <sub>6</sub>	15	68	—	trace
<b>g</b>	—	C <sub>6</sub> H <sub>6</sub>	15	trace	—	99
	Et <sub>3</sub> N	C <sub>6</sub> H <sub>6</sub>	15	22	—	40
<b>h</b>	—	C <sub>6</sub> H <sub>6</sub>	15	—	—	ca. 100
	Et <sub>3</sub> N	C <sub>6</sub> H <sub>6</sub>	15	—	79	trace
<b>i</b>	—	C <sub>6</sub> H <sub>6</sub>	15	16	—	80
	Et <sub>3</sub> N	C <sub>6</sub> H <sub>6</sub>	15	68	—	trace
<b>j</b>	—	C <sub>6</sub> H <sub>6</sub>	15	—	—	ca. 100
	Et <sub>3</sub> N	C <sub>6</sub> H <sub>6</sub>	15	—	40	35

<sup>a</sup> Ionization potential (in eV) given in parentheses; D. W. Turner, *Adv. Phys. Org. Chem.*, 1966, **4**, 47. <sup>b</sup> Isolated yield. <sup>c</sup> Methylene dichloride-methanol (2:5). <sup>d</sup> Not detected.



(4d, h, and j) was confirmed on the basis of their physical properties and elemental analyses. The IR spectra of (4) showed absorptions at 3 320–3 325 and 1 655–1 665  $\text{cm}^{-1}$  characteristic of an amino group at C-4 and amide carbonyl, respectively. The C-3 methine proton of (4) appeared as a doublet ( $J$  2.0 Hz) coupled with the amino proton at *ca.*  $\delta$  5 in the  $^1\text{H}$  NMR spectrum. The  $^{13}\text{C}$  NMR spectra of (4) displayed a methine carbon at C-3 at *ca.*  $\delta$  60 as a doublet.

The photoreaction of 1,3-dimethylquinoxalin-2-one (1e) was

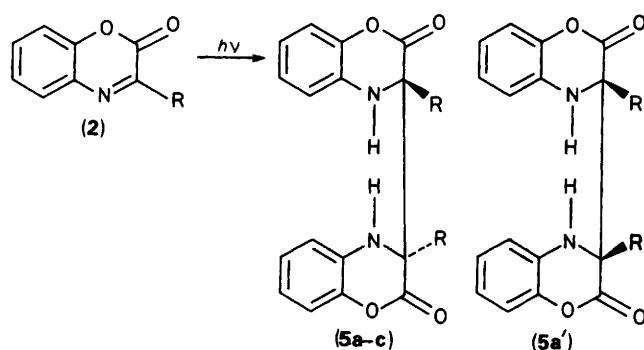
examined in the presence of various amines and in various solvents in the presence of triethylamine (see Table 1). The reductive dimer (3e) is formed in higher yields in polar solvents than in non-polar solvents. Amines possessing lower ionization potentials favour the formation of the reductive dimer (3e). These results suggest that the formation of the reductive dimers (3) involves an intermediate anion radical resulting from electron transfer from the amine to the excited quinoxalin-2-one (1), analogous to the photoreaction of ketone triplets with amines, which generally proceeds *via* an electron transfer followed by transfer of the  $\alpha$ -hydrogen atom of the amine and formation of radicals.<sup>11</sup> Then the anion radical abstracts a proton from the amine cation radical to produce radical pairs and leads ultimately to dimerization.

Similar results were obtained in the photoreaction of 1,4-benzoxazin-2-ones (2), which contain a cyclic keto-imine unit (Table 2). Irradiation of the 1,4-benzoxazin-2-ones (2a–c) in the presence of amines yielded the reductive dimers (5) in moderate yields. In the case of the 3-methyl compound (2a), two stereoisomeric reductive dimers, (5a) and (5a') were isolated. In the  $^1\text{H}$  NMR spectrum of (5a) the methyl protons ( $\delta$  1.58) appeared at higher field than those ( $\delta$  1.66) in (5a') and this shift may be due to the shielding effect of the aromatic ring. The  $^{13}\text{C}$  NMR spectra of (5a) also showed quaternary and methyl carbon signals at higher field than those in (5a'). As Dreiding models show that the methyl protons of the ( $\pm$ )-isomer of the dimer are more shielded by the aromatic ring than in the *meso*-isomer, we tentatively assigned the dimer (5a) as the ( $\pm$ )-isomer and the dimer (5a') as the *meso*-isomer.  $^1\text{H}$  NMR spectroscopy

**Table 2.** Yields of the benzoxazin-2-one dimers (5).

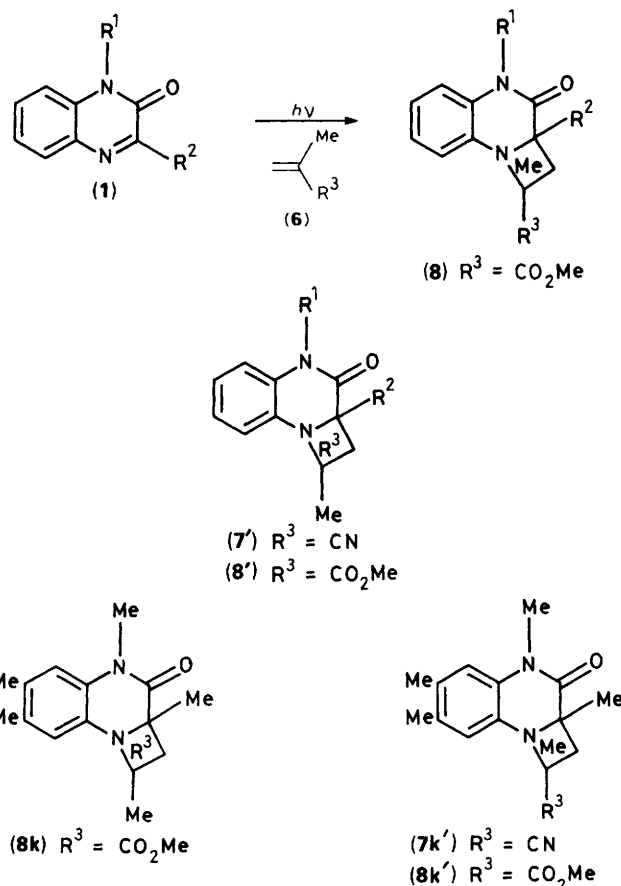
Oxazin-2-one (2)	Amine	Solvent	Irrad. time/h	% Yield <sup>a</sup>		
				(5)	(5')	Recovered (2)
<b>a</b>	—	C <sub>6</sub> H <sub>6</sub> <sup>b</sup>	15	6	—	50
	—	C <sub>6</sub> H <sub>6</sub> <sup>b</sup>	3	—	—	ca. 100
	—	MeOH	15	16	—	35
	Et <sub>3</sub> N	C <sub>6</sub> H <sub>6</sub>	3	33	46	trace
	Et <sub>3</sub> N	MeOH	3	10	11	12
	Et <sub>3</sub> N	MeCN	3	45	53	trace
	Et <sub>3</sub> N	C <sub>6</sub> H <sub>6</sub> <sup>b</sup>	3	44	30	trace
	PhNMe <sub>2</sub>	C <sub>6</sub> H <sub>6</sub>	3	44	—	30
	Et <sub>2</sub> NH	C <sub>6</sub> H <sub>6</sub>	3	8	—	38
	PrNH <sub>2</sub>	C <sub>6</sub> H <sub>6</sub>	3	trace	—	trace
	BP <sup>c,e</sup>	C <sub>6</sub> H <sub>6</sub> <sup>b</sup>	3	3	—	82
	MK <sup>d,e</sup>	C <sub>6</sub> H <sub>6</sub> <sup>b</sup>	3	38	—	20
<b>b</b>	—	C <sub>6</sub> H <sub>6</sub>	15	2	—	73
	Et <sub>3</sub> N	C <sub>6</sub> H <sub>6</sub>	15	18	—	—
	MK	C <sub>6</sub> H <sub>6</sub> <sup>b</sup>	3	25	—	40
<b>c</b>	—	C <sub>6</sub> H <sub>6</sub>	15	1	—	73
	Et <sub>3</sub> N	C <sub>6</sub> H <sub>6</sub>	15	20	—	9
	MK	C <sub>6</sub> H <sub>6</sub> <sup>b</sup>	3	26	—	50
<b>d</b>	—	C <sub>6</sub> H <sub>6</sub>	15	—	—	ca. 100
	Et <sub>3</sub> N	C <sub>6</sub> H <sub>6</sub>	15	f	—	—

<sup>a</sup> Isolated yield. <sup>b</sup> Irradiation with 366 nm light. <sup>c</sup> BP = Benzophenone. <sup>d</sup> MK = Michler's ketone. <sup>e</sup> BP and MK absorbed more than 95% of the incident light. <sup>f</sup> Intractable mixture.



using a chiral shift reagent led to no conclusions about the stereochemistry. The reductive dimers (5) were also produced, albeit in low yields, on carrying out the irradiation without amines as an electron donor. The photoreaction did not proceed in the presence of a triplet sensitizer such as benzophenone. On the other hand, the addition of Michler's ketone increased the reaction rate and yield of the reductive dimers (5), probably owing to the electron-donating nature of Michler's ketone. Irradiation of 3-phenyl-1,4-benzoxazin-2-one (2d) gave an intractable mixture. The formation of the reductive dimers (5) can be explained in terms of a sequential electron-proton transfer mechanism, analogous to the photoreaction of the quinoxalin-2-ones (1).

[2 + 2] Photocycloaddition of the Quinoxalin-2-ones (1) with Electron-poor Alkenes.—Recently, we reported that several quinoxalin-2-ones (1) reacted photochemically with electron-poor alkenes<sup>5</sup> or aryl alkenes<sup>7</sup> to yield the [2 + 2] cycloadducts, azetidine derivatives. In order to study the generality of this photochemical synthesis of azetidines, we examined the photoreaction of the quinoxalin-2-ones (1b, c, f, g, and k) with electron-poor alkenes such as methacrylonitrile (6a) and methyl methacrylate (6b). When the quinoxalin-2-ones (1b, c, f, and g)—which have hydrogen atoms in the side chain



at C-3 which could be abstracted by the carbonyl oxygen or imino nitrogen atom—were irradiated, intramolecular hydrogen abstraction was not observed and the starting

**Table 3.** Yields of the 1:1 cycloadducts (7) and (8).

Quinoxalin-2-one (1)	Alkene (6), R <sup>3</sup>	Solvent	Yield (%) <sup>a</sup>	
			(7), (8)	(7'), (8')
<b>b</b>	CN	M <sup>b</sup>	(7b) — <sup>c</sup>	(7b') 86
	CO <sub>2</sub> Me	M	(8b) 40	(8b') 60
<b>c</b>	CN	M	(7c) —	(7c') 99
	CO <sub>2</sub> Me	M	(8c) 45	(8c') 55
<b>f</b>	CN	C <sub>6</sub> H <sub>6</sub>	(7f) —	(7f') 95
	CO <sub>2</sub> Me	C <sub>6</sub> H <sub>6</sub>	(8f) 29	(8f') 62
<b>g</b>	CN	C <sub>6</sub> H <sub>6</sub>	(7g) —	(7g') 99
	CO <sub>2</sub> Me	C <sub>6</sub> H <sub>6</sub>	(8g) 40	(8g') 33
<b>k</b>	CN	C <sub>6</sub> H <sub>6</sub>	(7k) —	(7k') 99
	CO <sub>2</sub> Me	C <sub>6</sub> H <sub>6</sub>	(8k) 52	(8k') 45

<sup>a</sup> Isolated yield. <sup>b</sup> Methylene dichloride–methanol (5:2). <sup>c</sup> Not detected.

materials were recovered quantitatively. Irradiation of the quinoxalin-2-ones (**1b**, **c**, **f**, **g**, and **k**) in methylene dichloride–methanol or benzene in the presence of methacrylonitrile (**6a**) with a high-pressure mercury lamp through a Pyrex filter under argon gave the [2 + 2] photocycloadducts, the azetidine derivatives (7b', c', f', g', and k') in excellent yields (Table 3). Irradiation of the quinoxalin-2-ones (**1b**, **c**, **f**, **g**, and **k**) in the presence of methyl methacrylate (**6b**) yielded two stereoisomeric azetidine derivatives, (8b, c, f, g, and k) and (8b', c', f', g', and k'). The structure of the photoproducts (7) and (8) was determined by their elemental analyses and spectral data, in particular the close similarity of their <sup>1</sup>H and <sup>13</sup>C NMR spectra to those of the reported azetidine derivatives.<sup>5,7</sup> The regiochemistry of the photoproducts and non-stereospecificity of the cycloaddition are compatible with those in the previous work.<sup>5,7</sup> Consequently, the formation of the [2 + 2] photocycloadducts, the azetidine derivatives (7) and (8), could be explained in terms of the more stable 1,4-diradical intermediate<sup>5–7</sup> and, in spite of the substituents at C-3 and the aromatic ring of (1), the [2 + 2] photocycloaddition of the quinoxalin-2-ones (1) with electron-poor alkenes proceeded.

## Experimental

M.p.s and b.p.s are uncorrected and were measured with a Yanaco micro-melting point apparatus (MP-J3) and Büchi kugelrohr distillation apparatus (KR-3), respectively. IR spectra were determined with a Hitachi 260-30 spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured with a JEOL FX-100 (100 MHz) spectrometer using tetramethylsilane as an internal standard, and were recorded for solutions in [<sup>2</sup>H<sub>6</sub>]dimethyl sulphoxide unless otherwise noted. UV spectra were recorded on a JASCO UVIDEDEC-505 spectrophotometer and mass spectra were obtained with a Hitachi M-80 spectrometer. Silica gel (Merck Kieselgel 60 or Wakogel C-300 for flash chromatography) was used for column chromatography.

**Starting Materials.**—Quinoxalin-2-ones (**1a**, **d–j**)<sup>5</sup> and benzoxazin-2-ones (**2a–d**)<sup>7</sup> were prepared according to methods previously described in the literature and (**1b**), (**1c**), and (**1k**) were prepared by a modification of these methods. A solution of *o*-phenylenediamine (1 mmol) and the corresponding  $\alpha$ -keto ester (1.2 mmol) in EtOH (30 ml) was heated under reflux for 2 h. After evaporation the residue was recrystallized from chloroform–hexane to give the quinoxalin-2-ones (**1b**) and (**1c**). To a stirred solution of 3,6,7-trimethylquinoxalin-2-one (1 mmol) and sodium methoxide [from sodium (1 mmol) and MeOH (5 ml)] in MeOH (25 ml) dimethyl sulphate (2 mmol) was added in drops at room temperature and the

reaction mixture was then heated under reflux for 1 h. Usual work-up gave the quinoxalin-2-one (**1k**).

**3-Butylquinoxalin-2-(1H)-one (1b)** had m.p. 154.5–155.5 °C (Found: C, 71.0; H, 6.95; N, 13.9. C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>O requires C, 71.25; H, 6.95; N, 13.85%);  $\nu_{\max}$ (KBr) 3 150 and 1 660 cm<sup>-1</sup>;  $\delta_{\text{H}}$  1.01 (3 H, t), 1.35–1.95 (4 H, m), 2.89 (2 H, t), 7.25–7.85 (4 H, m), and 12.41 (1 H, br s);  $\delta_{\text{C}}$  13.9 (q), 22.1 (t), 28.3 (t), 32.5 (t), 115.2 (d), 128.1 (d), 129.3 (d), 131.8 (s), 154.7 (s), and 161.9 (s).

**3-Isopentylquinoxalin-2-(1H)-one (1c)** had m.p. 170–171 °C (Found: C, 72.95; H, 7.9; N, 12.15. C<sub>13</sub>H<sub>16</sub>N<sub>2</sub>O requires C, 73.0; H, 7.85; N, 12.15%);  $\nu_{\max}$ (KBr) 3 150 and 1 665 cm<sup>-1</sup>;  $\delta_{\text{H}}$  1.02 (6 H, d, *J* 6.8 Hz), 1.5–1.85 (3 H, m), 2.89 (2 H, t, *J* 7.8 Hz), 7.25–7.65 (3 H, m), and 7.80 (1 H, d, *J* 7.8 Hz);  $\delta_{\text{C}}$  22.5 (q), 27.6 (d), 30.8 (t), 35.2 (t), 115.2 (d), 123.0 (d), 128.0 (d), 129.3 (d), 131.7 (s), 154.6 (s), and 162.1 (s).

**1,3,6,7-Tetramethylquinoxalin-2(1H)-one (1k)** had m.p. 163–164 °C (Found: C, 71.0; H, 6.95; N, 13.75. C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>O requires C, 71.25; H, 6.95; N, 13.85%);  $\nu_{\max}$ (KBr) 1 640 and 1 620 cm<sup>-1</sup>;  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) 2.32 (3 H, s), 2.38 (3 H, s), 2.54 (3 H, s), 3.63 (3 H, s), 6.99 (1 H, s), and 7.49 (1 H, s);  $\delta_{\text{C}}$ (CDCl<sub>3</sub>) 19.1 (q), 20.4 (q), 21.4 (q), 28.8 (q), 114.0 (d), 129.3 (d), 130.9 (s), 131.0 (s), 132.2 (s), 139.0 (s), 155.0 (s), and 156.8 (s).

**General Procedure for the Photochemical Reactions of the Quinoxalin-2-ones (1) and Benzoxazin-2-ones (2) in the Presence or the Absence of an Amine.**—A solution of (1) [or (2)] (200 mg) in dry solvent (70 ml) in the presence of excess of amine (0.2–1 ml) in a Pyrex vessel was irradiated with a high-pressure mercury lamp (300 W) under argon at room temperature for 3–15 h. After removal of the solvent, the residue was chromatographed with benzene–ethyl acetate [50:1–4:1 for (1)] or benzene–hexane [50:1–2:1 for (2)] as eluant to yield the photoproducts. The photochemical reactions of (1) and (2) in the absence of amine were carried out under similar conditions for 15 h.

The *dihydrodimer* (**3a**) of 3-methylquinoxalin-2-one [bis(2-methyl-3-oxo-1,2,3,4-tetrahydroquinoxalin-2-yl)] had m.p. 241 °C (decomp.) (Found: C, 66.75; H, 5.6; N, 17.25. C<sub>18</sub>H<sub>18</sub>N<sub>4</sub>O<sub>2</sub> requires C, 67.05; H, 5.6; N, 17.49%);  $\nu_{\max}$ (KBr) 3 320, 3 190, 1 650, and 1 620 cm<sup>-1</sup>;  $\delta_{\text{H}}$  1.56 (6 H, s), 6.12 (2 H, br s), 6.55–6.95 (8 H, m), and 10.33 (2 H, br s);  $\delta_{\text{C}}$  21.7 (q), 63.7 (s), 112.8 (d), 114.3 (d), 117.3 (d), 122.9 (d), 125.0 (s), 132.9 (s), and 168.3 (s).

The *dihydrodimer* (**3b**) of 3-butylquinoxalin-2-one had m.p. 148.5–150 °C (Found: C, 70.95; H, 7.2; N, 13.65. C<sub>24</sub>H<sub>30</sub>N<sub>4</sub>O<sub>2</sub> requires C, 70.9; H, 7.45; N, 13.8%);  $\nu_{\max}$ (KBr) 3 375, 3 210, 1 670, and 1 615 cm<sup>-1</sup>;  $\delta_{\text{H}}$  0.97 (6 H, t), 1.0–1.8 (8 H, m), 2.2–2.5 (4 H, m), 5.66 (2 H, br s), 6.40–6.85 (8 H, m), and 10.17 (2 H, br s);  $\delta_{\text{C}}$  14.2 (q), 22.8 (t), 26.7 (t), 34.5 (t), 69.2 (s), 111.6 (d), 113.9 (d), 116.1 (d), 122.6 (d), 124.2 (s), 133.6 (s), and 166.9 (s).

The *dihydrodimer* (**3c**) of 3-isopentylquinoxalin-2-one had m.p. 171–173 °C (Found: C, 71.55; H, 7.85; N, 12.65. C<sub>26</sub>H<sub>34</sub>N<sub>4</sub>O<sub>2</sub> requires C, 71.85; H, 7.9; N, 12.9%);  $\nu_{\max}$ (KBr) 3 380, 1 660, and 1 625 cm<sup>-1</sup>;  $\delta_{\text{H}}$  0.90 (12 H, br d), 1.2–1.9 (8 H, m), 2.3–2.6 (2 H, m), 5.63 (2 H, br s), 6.2–6.85 (8 H, m), and 10.20 (2 H, br s);  $\delta_{\text{C}}$  22.6 (q), 28.1 (d), 32.5 (t), 33.3 (t), 69.3 (s), 111.6 (d), 113.8 (d), 116.1 (d), 122.6 (d), 124.2 (s), 133.6 (s), and 166.8 (s).

The *dihydrodimer* (**3e**) of 1,3-dimethylquinoxalin-2-one had m.p. 199–200 °C (Found: C, 68.35; H, 6.3; N, 15.9. C<sub>20</sub>H<sub>22</sub>N<sub>4</sub>O<sub>2</sub> requires C, 68.55; H, 6.3; N, 16.0%);  $\nu_{\max}$ (KBr) 3 340 and 1 640 cm<sup>-1</sup>;  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) 1.52 (6 H, s), 3.35 (6 H, s), and 6.6–7.05 (10 H, m);  $\delta_{\text{C}}$ (CDCl<sub>3</sub>) 19.8 (q), 29.3 (q), 63.8 (s), 114.1 (d), 114.5 (d), 118.5 (d), 124.2 (d), 127.1 (s), 134.2 (s), and 169.1 (s); *m/z* (chemical ionisation, CI) 351 (*M*<sup>+</sup> + 1) and 176 (*M*<sup>+</sup> + 1 – C<sub>10</sub>H<sub>11</sub>N<sub>2</sub>O, 100%).

The *dihydrodimer* (**3f**) of 1-methyl-3-butylquinoxalin-2-one had m.p. 100–102 °C (Found: C, 71.7; H, 7.75; N, 12.75. C<sub>26</sub>H<sub>34</sub>N<sub>4</sub>O<sub>2</sub> requires C, 71.85; H, 7.9; N, 12.9%);  $\nu_{\max}$ (KBr)



3 360, 1 655, and 1 640  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}(\text{CDCl}_3)$  0.74 (6 H, t), 0.95–1.7 (8 H, m), 2.40 (4 H, br t), 3.23 (6 H, s), 5.26 (2 H, br s), and 6.35–7.0 (8 H, m);  $\delta_{\text{C}}(\text{CDCl}_3)$  14.0 (q), 23.0 (t), 26.7 (t), 28.8 (q), 36.0 (t), 68.9 (s), 112.4 (d), 113.9 (d), 117.4 (d), 124.0 (d), 126.0 (s), 134.1 (s), and 167.4 (s).

The *dihydrodimer* (**3g**) of 1-methyl-3-isopentylquinoxalin-2-one had m.p. 130–131 °C (Found: C, 72.4; H, 8.25; N, 11.8.  $\text{C}_{28}\text{H}_{38}\text{N}_4\text{O}_2$  requires C, 72.7; H, 8.25; N, 12.1%;  $\nu_{\text{max}}(\text{KBr})$  3 360, 1 655, and 1 640  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}(\text{CDCl}_3)$  0.69 (12 H, d,  $J$  5.4 Hz), 0.95–1.8 (8 H, m), 2.25–2.4 (2 H, m), 3.25 (6 H, s), 5.25 (2 H, br s), and 6.45–7.0 (8 H, m);  $\delta_{\text{C}}(\text{CDCl}_3)$  22.5 (q), 28.2 (q), 28.9 (d), 33.2 (t), 34.1 (t), 68.9 (s), 112.5 (d), 113.9 (d), 117.5 (d), 124.1 (d), 126.1 (s), 134.3 (s), and 167.5 (s).

The *dihydrodimer* (**3i**) of 1-ethyl-3-methylquinoxalin-2-one had m.p. 209.5–210 °C (Found: C, 69.5; H, 6.85; N, 14.65.  $\text{C}_{22}\text{H}_{26}\text{N}_4\text{O}_2$  requires C, 69.8; H, 6.9; N, 14.8%;  $\nu_{\text{max}}(\text{KBr})$  3 330 and 1 640  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}(\text{CDCl}_3)$  1.28 (6 H, t), 1.51 (6 H, s), 3.75–4.36 (4 H, m), and 6.65–7.05 (10 H, m);  $\delta_{\text{C}}(\text{CDCl}_3)$  12.5 (q), 19.4 (q), 37.3 (t), 63.4 (s), 113.8 (d), 115.0 (d), 118.5 (d), 124.1 (d), 125.8 (s), 134.4 (s), and 168.6 (s);  $m/z$  (CI) 379 ( $M^+ + 1$ ) and 190 ( $M^+ + 1 - \text{C}_{11}\text{H}_{13}\text{N}_2\text{O}$ , 100%).

3-Phenyl-3,4-dihydroquinoxalin-2-one (**4d**) had m.p. 194–196 °C (Found: C, 74.75; H, 5.35; N, 12.5.  $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}$  requires C, 75.0; H, 5.4; N, 12.5%;  $\nu_{\text{max}}(\text{KBr})$  3 320, 3 190, and 1 665  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}(\text{CDCl}_3)$  5.08 (1 H, d,  $J$  2.0 Hz), 6.55–7.05 (5 H, m), 7.35–7.75 (5 H, m), and 10.85 (1 H, br s);  $\delta_{\text{C}}$  59.5 (d), 113.4 (d), 114.9 (d), 117.7 (d), 123.1 (d), 125.4 (s), 127.0 (d), 127.6 (d), 128.3 (d), 133.9 (s), 140.4 (s), and 166.0 (s).

1-Methyl-3-phenyl-3,4-dihydroquinoxalin-2-one (**4h**) had m.p. 145–147 °C (Found: C, 75.3; H, 5.85; N, 11.7.  $\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}$  requires C, 75.6; H, 5.9; N, 11.75%;  $\nu_{\text{max}}(\text{KBr})$  3 320 and 1 660  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}(\text{CDCl}_3)$  3.36 (3 H, s), 4.40 (1 H, br s), 5.02 (1 H, d,  $J$  2.0 Hz), 6.65–6.95 (4 H, m), and 7.2–7.4 (5 H, m);  $\delta_{\text{C}}(\text{CDCl}_3)$  29.2 (q), 60.8 (d), 113.9 (d), 114.7 (d), 119.4 (d), 123.7 (d), 128.2 (d), 128.6 (d), 129.5 (s), 134.4 (s), 139.0 (s), and 166.0 (s).

1-Ethyl-3-phenyl-3,4-dihydroquinoxalin-2-one (**4j**) had m.p. 103.5–104 °C (Found: C, 76.05; H, 6.4; N, 11.05.  $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}$  requires C, 76.15; H, 6.4; N, 11.1%;  $\nu_{\text{max}}(\text{KBr})$  3 325 and 1 655  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}(\text{CDCl}_3)$  1.24 (3 H, t), 3.99 (2 H, q), 4.39 (1 H, br s), 4.98 (1 H, d,  $J$  2.0 Hz), 6.65–7.0 (4 H, m), and 7.2–7.45 (5 H, m);  $\delta_{\text{C}}(\text{CDCl}_3)$  12.4 (q), 37.1 (t), 60.6 (d), 114.4 (d), 114.5 (d), 119.4 (d), 123.5 (d), 127.0 (d), 127.0 (s), 128.1 (d), 128.6 (d), 134.6 (s), 139.0 (s), and 165.3 (s).

The ( $\pm$ )-*dihydrodimer* (**5a**) of 3-methyl-1,4-benzoxazin-2-one [bis(3-methyl-2-oxo-3,4-dihydro-1,4-benzoxazin-3-yl)] had m.p. 196–197 °C (Found: C, 66.75; H, 5.0; N, 8.6.  $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_4$  requires C, 66.65; H, 4.95; N, 8.65%;  $\lambda_{\text{max}}(\text{EtOH})$  291 nm ( $\epsilon$  8 800);  $\nu_{\text{max}}(\text{KBr})$  3 390, 1 740, 1 725, and 1 615  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  1.58 (6 H, s), 6.40 (2 H, br s), 6.5–7.0 (8 H, m);  $\delta_{\text{C}}$  21.9 (q), 63.9 (s), 114.3 (d), 115.4 (d), 117.6 (d), 124.6 (d), 131.1 (s), 139.1 (s), and 166.6 (s);  $m/z$  (CI) 325 ( $M^+ + 1$ ) and 163 ( $M^+ + 1 - \text{C}_9\text{H}_8\text{NO}_2$ , 100%).

The meso-*dihydrodimer* (**5a'**) of 3-methyl-1,4-benzoxazin-2-one had m.p. 178–179 °C (Found: C, 66.4; H, 4.95; N, 8.55.  $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_4$  requires C, 66.65; H, 4.95; N, 8.65%;  $\lambda_{\text{max}}(\text{EtOH})$  244 sh ( $\epsilon$  7 200) and 299 nm ( $\epsilon$  600);  $\nu_{\text{max}}(\text{KBr})$  3 350, 3 320, 1 740, 1 725, and 1 620  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  1.66 (6 H, s), 6.28 (2 H, dd,  $J$  2.0, 7.3 Hz), 6.45–6.8 (6 H, m), and 6.92 (2 H, dd,  $J$  2.0, 7.3 Hz);  $\delta_{\text{C}}$  23.1 (q), 65.8 (s), 113.5 (d), 114.9 (d), 116.8 (d), 124.5 (d), 131.9 (s), 139.6 (s), and 164.3 (s);  $m/z$  (CI) 325 ( $M^+ + 1$ ) and 163 ( $M^+ + 1 - \text{C}_9\text{H}_8\text{NO}_2$ , 100%).

The ( $\pm$ )-*dihydrodimer* (**5b**) of 3-butyl-1,4-benzoxazin-2-one had m.p. 123–123.5 °C (Found: C, 70.7; H, 6.9; N, 6.85.  $\text{C}_{24}\text{H}_{28}\text{N}_2\text{O}_4$  requires C, 70.55; H, 6.9; N, 6.85%;  $\nu_{\text{max}}(\text{KBr})$  3 370, 1 735, and 1 620  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  0.75 (6 H, t), 0.95–1.9 (10 H, m), 2.15–2.5 (2 H, m), 5.12 (2 H, s), and 6.45–7.05 (8 H, m);  $\delta_{\text{C}}$  13.7 (q), 22.7 (t), 26.5 (t), 36.5 (t), 68.6 (s), 113.6 (d), 116.2 (d), 118.7 (d), 125.8 (d), 131.2 (s), 138.6 (s), and 166.8 (s).

The ( $\pm$ )-*dihydrodimer* (**5c**) of 3-isopentyl-1,4-benzoxazin-2-one had m.p. 128.5–129 °C (Found: C, 71.45; H, 7.4; N, 6.35.  $\text{C}_{26}\text{H}_{32}\text{N}_2\text{O}_4$  requires C, 71.55; H, 7.4; N, 6.4%;  $\nu_{\text{max}}(\text{KBr})$  3 380, 1 730, and 1 620  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}(\text{CDCl}_3)$  0.71 (12 H, d,  $J$  4.9 Hz), 0.95–1.7 (8 H, m), 2.1–2.6 (2 H, m), 5.06 (2 H, s), and 6.6–7.1 (8 H, m);  $\delta_{\text{C}}(\text{CDCl}_3)$  22.3 (q), 28.1 (d), 33.1 (t), 34.5 (t), 68.8 (s), 113.6 (d), 116.1 (d), 118.7 (d), 125.8 (d), 131.3 (s), 138.7 (s), and 166.8 (s).

*General Procedure for the [2 + 2] Photocycloadditions of the Quinoxalin-2-ones (1b–c, f, g, and k) with the Alkenes (6).*—A solution of (**1**) (200 mg) and a large excess of alkene (**6**) (*ca.* 1 ml) in dry solvent (70 ml) was irradiated under the same conditions as described above for 15 h. After removal of the solvent, the residue was chromatographed with benzene–ethyl acetate (9:1–4:1) as eluant to yield the [2 + 2] cycloadducts (**7**) and (**8**).

The [2 + 2] cycloadduct (**7b'**) had m.p. 163.5–164.5 °C (Found: C, 71.4; H, 7.1; N, 15.6.  $\text{C}_{16}\text{H}_{16}\text{N}_3\text{O}$  requires C, 71.35; H, 7.1; N, 15.6%;  $\nu_{\text{max}}(\text{KBr})$  3 250, 2 215, 1 675, and 1 640  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}(\text{CDCl}_3)$  0.82 (3 H, t), 1.0–1.6 (4 H, m), 1.8–2.0 (2 H, m), 1.77 (3 H, s), 2.55 (1 H, A of ABq,  $J$  12.2 Hz), 3.27 (1 H, B of ABq,  $J$  12.2 Hz), 6.75–7.15 (4 H, m), and 9.26 (1 H, br s);  $\delta_{\text{C}}(\text{CDCl}_3)$  13.8 (q), 22.7 (t), 25.0 (t), 28.4 (q), 40.4 (t), 42.0 (t), 59.9 (s), 65.0 (s), 116.4 (d), 119.5 (s), 122.7 (d), 124.1 (d), 126.0 (d), 129.3 (s), 132.2 (s), and 170.3 (s).

The [2 + 2] cycloadduct (**8b**) had m.p. 114.5–115.5 °C (Found: C, 67.5; H, 7.4; N, 9.2.  $\text{C}_{17}\text{H}_{22}\text{N}_2\text{O}_3$  requires C, 67.5; H, 7.35; N, 9.25%;  $\nu_{\text{max}}(\text{KBr})$  3 220, 1 745, 1 675, and 1 155  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}(\text{CDCl}_3)$  0.80 (3 H, t), 1.0–1.4 (4 H, m), 1.35 (3 H, s), 1.7–2.05 (2 H, m), 2.86 (2 H, ABq,  $J$  12.2, 22.5 Hz), 3.84 (3 H, s), 6.75–7.2 (4 H, m), and 9.58 (1 H, br s);  $\delta_{\text{C}}(\text{CDCl}_3)$  13.9 (q), 21.3 (q), 22.7 (t), 25.2 (t), 40.6 (t), 40.7 (t), 52.4 (q), 63.5 (s), 66.7 (s), 115.6 (d), 122.9 (d), 123.8 (d), 129.8 (s), 131.5 (s), 171.7 (s), and 174.8 (s).

The [2 + 2] cycloadduct (**8b'**) had b.p. 190 °C at 2 mmHg (Found: C, 67.6; H, 7.35; N, 9.25.  $\text{C}_{17}\text{H}_{22}\text{N}_2\text{O}_3$  requires C, 67.5; H, 7.35; N, 9.25%;  $\nu_{\text{max}}(\text{film})$  3 190, 1 725, 1 670, and 1 155  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}(\text{CDCl}_3)$  0.83 (3 H, t), 1.1–1.55 (4 H, m), 1.73 (3 H, s), 1.5–2.05 (2 H, m), 2.33 (1 H, A of ABq,  $J$  11.7 Hz), 3.22 (1 H, B of ABq,  $J$  11.7 Hz), 3.36 (3 H, s), 6.65–7.0 (4 H, m), and 9.65 (1 H, br s);  $\delta_{\text{C}}(\text{CDCl}_3)$  13.8 (q), 22.7 (t), 25.0 (t), 26.3 (q), 40.0 (t), 41.5 (t), 51.5 (q), 64.2 (s), 69.6 (s), 115.7 (d), 120.2 (d), 123.3 (d), 131.3 (s), 170.4 (s), and 172.2 (s).

The [2 + 2] cycloadduct (**7c'**) had m.p. 187–188 °C (Found: C, 71.95; H, 7.45; N, 14.8.  $\text{C}_{17}\text{H}_{21}\text{N}_3\text{O}$  requires C, 72.05; H, 7.45; N, 14.8%;  $\nu_{\text{max}}(\text{KBr})$  3 250, 2 220, 1 680, and 1 645  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}(\text{CDCl}_3)$  0.82 (6 H, d,  $J$  6.4 Hz), 1.1–1.75 (4 H, m), 1.77 (3 H, s), 1.8–2.0 (1 H, m), 2.55 (1 H, A of ABq,  $J$  11.7 Hz), 3.27 (1 H, B of ABq,  $J$  11.7 Hz), 6.8–7.2 (4 H, m), and 9.45 (1 H, br s);  $\delta_{\text{C}}(\text{CDCl}_3)$  22.4 (q), 28.0 (q), 28.3 (d), 31.5 (t), 38.3 (t), 41.8 (t), 59.9 (s), 64.5 (s), 116.4 (d), 119.4 (s), 122.6 (d), 124.0 (d), 126.0 (d), 129.2 (s), 132.1 (s), and 170.4 (s).

The [2 + 2] cycloadduct (**8c**) had b.p. 160 °C at 2 mmHg (Found: 68.3; H, 7.7; N, 8.85.  $\text{C}_{18}\text{H}_{24}\text{N}_2\text{O}_3$  requires C, 68.35; H, 7.65; N, 8.85%;  $\nu_{\text{max}}(\text{film})$  3 175, 1 740, 1 670, and 1 150  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}(\text{CDCl}_3)$  0.90 (6 H, d,  $J$  6.3 Hz), 1.1–1.6 (3 H, m), 1.35 (3 H, s), 1.7–2.05 (2 H, m), 2.99 (2 H, ABq,  $J$  12.2, 22.9 Hz), 3.84 (3 H, s), 6.75–7.3 (4 H, m), and 9.98 (1 H, br s);  $\delta_{\text{C}}(\text{CDCl}_3)$  21.1 (q), 22.3 (q), 27.9 (d), 31.7 (t), 38.6 (t), 40.6 (t), 53.3 (q), 63.3 (s), 66.5 (s), 115.6 (d), 122.7 (d), 123.6 (d), 128.1 (d), 129.6 (s), 131.5 (s), 171.8 (s), and 174.7 (s).

The [2 + 2] cycloadduct (**8c'**) had b.p. 165 °C at 2 mmHg (Found: C, 68.15; H, 7.75; N, 8.8.  $\text{C}_{18}\text{H}_{24}\text{N}_2\text{O}_3$  requires C, 68.35; H, 7.65; N, 8.85%;  $\nu_{\text{max}}(\text{film})$  3 200, 1 735, 1 675, and 1 160  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}(\text{CDCl}_3)$  0.83 (6 H, d,  $J$  5.9 Hz), 1.15–1.6 (3 H, m), 1.73 (3 H, s), 1.7–2.05 (2 H, m), 2.33 (1 H, A of ABq,  $J$  11.7 Hz), 3.32 (1 H, B of ABq,  $J$  11.7 Hz), 3.34 (3 H, s), 6.65–6.95 (4 H, m), and 9.87 (1 H, br s);  $\delta_{\text{C}}(\text{CDCl}_3)$  22.4 (q), 26.2 (q), 28.1 (d), 31.6 (t), 39.6 (t), 39.9 (t), 51.4 (q), 64.2 (s), 69.6 (s), 115.7 (d), 120.1 (d),

123.2 (d), 128.2 (d), 131.0 (s), 131.2 (2), 170.5 (s), and 172.1 (s).

The [2 + 2] cycloadduct (**7f'**) had b.p. 165 °C at 2 mmHg (Found: C, 71.8; H, 7.5; N, 14.65.  $C_{17}H_{21}N_3O$  requires C, 72.05; H, 7.45; N, 14.8%;  $\nu_{\max}(\text{film})$  2 230 and 1 670  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}(\text{CDCl}_3)$  0.81 (3 H, t), 1.1–1.45 (4 H, m), 1.74 (3 H, s), 1.6–1.95 (2 H, m), 2.53 (1 H, A of ABq,  $J$  12.2 Hz), 3.18 (1 H, B of ABq,  $J$  12.2 Hz), 3.42 (3 H, s), and 6.85–7.3 (4 H, m);  $\delta_{\text{C}}(\text{CDCl}_3)$  13.7 (q), 22.5 (t), 25.0 (t), 27.9 (q), 28.9 (q), 40.1 (t), 42.4 (t), 59.5 (s), 64.6 (s), 115.4 (d), 119.4 (s), 123.3 (d), 123.6 (d), 126.1 (d), 130.2 (s), 135.2 (s), and 169.0 (s).

The [2 + 2] cycloadduct (**8f**) had b.p. 160 °C at 2 mmHg (Found: C, 68.15; H, 7.65; N, 8.9.  $C_{18}H_{24}N_2O_3$  requires C, 68.35; H, 7.65; N, 8.85%;  $\nu_{\max}(\text{film})$  1 735, 1 665, and 1 160  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}(\text{CDCl}_3)$  0.79 (3 H, t), 1.31 (3 H, s), 1.15–1.35 (4 H, m), 1.55–2.05 (2 H, m), 2.83 (2 H, ABq,  $J$  12.2, 23.9 Hz), 3.39 (3 H, s), 3.82 (3 H, s), and 6.8–7.25 (4 H, m);  $\delta_{\text{C}}(\text{CDCl}_3)$  13.7 (q), 20.9 (q), 22.1 (t), 25.2 (t), 28.7 (q), 40.7 (t), 40.9 (t), 52.2 (q), 62.8 (s), 66.2 (s), 114.4 (d), 122.9 (d), 123.3 (d), 123.5 (d), 130.7 (s), 134.1 (s), 169.7 (s), and 174.5 (s).

The [2 + 2] cycloadduct (**8f'**) had b.p. 135 °C at 2 mmHg (Found: C, 68.1; H, 7.7; N, 8.85.  $C_{18}H_{24}N_2O_3$  requires C, 68.35; H, 7.65; N, 8.85%;  $\nu_{\max}(\text{film})$  1 730, 1 670, and 1 160  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}(\text{CDCl}_3)$  0.83 (3 H, t), 1.1–1.4 (4 H, m), 1.72 (3 H, s), 1.65–1.95 (2 H, m), 2.33 (1 H, A of ABq,  $J$  12.2 Hz), 3.23 (1 H, B of ABq,  $J$  12.2 Hz), 3.35 (3 H, s), 3.39 (3 H, s), and 6.65–7.1 (4 H, m);  $\delta_{\text{C}}(\text{CDCl}_3)$  13.7 (q), 22.7 (t), 25.1 (t), 26.2 (q), 28.7 (q), 40.5 (t), 41.4 (t), 51.5 (q), 63.8 (s), 69.2 (s), 114.4 (d), 120.4 (d), 122.9 (d), 123.1 (d), 132.4 (s), 133.7 (s), 168.6 (s), and 172.1 (s).

The [2 + 2] cycloadduct (**7g'**) had m.p. 110–111.5 °C (Found: C, 72.65; H, 7.8; N, 14.1.  $C_{18}H_{23}N_3O$  requires C, 72.7; H, 7.8; N, 14.1%;  $\nu_{\max}(\text{KBr})$  2 220 and 1 655  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}(\text{CDCl}_3)$  0.80 (6 H, d,  $J$  5.9 Hz), 1.0–1.6 (3 H, m), 1.74 (3 H, s), 1.65–1.95 (2 H, m), 2.53 (1 H, A of ABq,  $J$  12.2 Hz), 3.19 (1 H, B of ABq,  $J$  12.2 Hz), 3.43 (3 H, s), and 6.85–7.2 (4 H, m);  $\delta_{\text{C}}(\text{CDCl}_3)$  22.3 (q), 28.0 (q), 29.1 (d), 31.7 (t), 38.2 (t), 42.3 (t), 59.6 (s), 65.0 (s), 115.0 (d), 119.5 (s), 123.5 (d), 123.6 (d), 126.2 (d), 130.2 (s), 135.2 (s), and 169.1 (s).

The [2 + 2] cycloadduct (**8g**) had b.p. 165 °C at 2 mmHg (Found: C, 69.0; H, 7.95; N, 8.6.  $C_{19}H_{26}N_2O_3$  requires C, 69.05; H, 7.95; N, 8.45%;  $\nu_{\max}(\text{film})$  1 740, 1 670, and 1 160  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}(\text{CDCl}_3)$  0.79 (3 H, d,  $J$  6.4 Hz), 0.80 (3 H, d,  $J$  6.4 Hz), 0.95–1.6 (3 H, m), 1.31 (3 H, s), 1.7–2.0 (2 H, m), 2.83 (2 H, ABq,  $J$  12.2, 23.9 Hz), 3.40 (3 H, s), 3.83 (3 H, s), and 6.85–7.25 (4 H, m);  $\delta_{\text{C}}(\text{CDCl}_3)$  20.9 (q), 22.3 (q), 27.9 (q), 28.7 (d), 31.8 (t), 38.6 (t), 40.7 (t), 52.1 (q), 62.8 (s), 66.1 (s), 114.4 (d), 122.9 (d), 132.2 (d), 123.5 (d), 130.6 (s), 134.1 (s), 169.6 (s), and 174.5 (s).

The [2 + 2] cycloadduct (**8g'**) had b.p. 170 °C at 2 mmHg (Found: C, 68.9; H, 7.95; N, 8.45.  $C_{19}H_{26}N_2O_3$  requires C, 69.05; H, 7.95; N, 8.45%;  $\nu_{\max}(\text{film})$  1 735, 1 665, and 1 160  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}(\text{CDCl}_3)$  0.82 (6 H, d,  $J$  5.9 Hz), 1.05–1.6 (3 H, m), 1.72 (3 H, s), 1.7–2.0 (2 H, m), 2.32 (1 H, A of ABq,  $J$  11.7 Hz), 3.22 (1 H, B of ABq,  $J$  11.7 Hz), 3.34 (3 H, s), 3.39 (3 H, s), and 6.65–

7.05 (2 H, m);  $\delta_{\text{C}}(\text{CDCl}_3)$  22.4 (q), 26.2 (q), 28.0 (q), 28.7 (d), 31.7 (t), 39.5 (t), 40.3 (t), 51.5 (q), 63.6 (s), 69.1 (s), 114.5 (d), 120.4 (d), 122.9 (d), 123.1 (d), 132.3 (s), 133.7 (s), 168.6 (s), and 172.1 (s).

The [2 + 2] cycloadduct (**7k'**) had m.p. 146–148 °C (Found: C, 71.1; H, 7.1; N, 15.55.  $C_{16}H_{19}N_3O$  requires C, 71.35; H, 7.1; N, 15.6%;  $\nu_{\max}(\text{KBr})$  2 210, 1 655, and 1 610  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}(\text{CDCl}_3)$  1.47 (3 H, s), 1.74 (3 H, s), 2.20 (3 H, s), 2.26 (3 H, s), 2.47 (1 H, A of ABq,  $J$  12.2 Hz), 3.23 (1 H, B of ABq,  $J$  12.2 Hz), 3.39 (3 H, s), 6.69 (1 H, s), and 6.80 (1 H, s);  $\delta_{\text{C}}(\text{CDCl}_3)$  19.0 (q), 19.8 (q), 26.4 (q), 28.1 (q), 29.1 (q), 44.2 (t), 59.7 (s), 61.8 (s), 116.8 (d), 119.5 (s), 125.1 (d), 126.5 (s), 131.9 (s), 132.9 (s), 134.7 (s), and 169.3 (s).

The [2 + 2] cycloadduct (**8k**) had m.p. 99–100 °C (Found: C, 67.55; H, 7.35; N, 9.25.  $C_{17}H_{22}N_2O_3$  requires C, 67.5; H, 7.35; N, 9.25%;  $\nu_{\max}(\text{KBr})$  1 740, 1 655, 1 610, and 1 165  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}(\text{CDCl}_3)$  1.31 (3 H, s), 1.50 (3 H, s), 2.19 (3 H, s), 2.55 (3 H, s), 2.82 (2 H, ABq,  $J$  11.7, 24.6 Hz), 3.37 (3 H, s), 3.83 (3 H, s), 6.71 (1 H, s), and 6.95 (1 H, s);  $\delta_{\text{C}}(\text{CDCl}_3)$  19.0 (q), 19.6 (q), 20.4 (q), 26.7 (q), 28.9 (q), 42.3 (t), 52.3 (q), 59.9 (s), 66.1 (s), 115.9 (d), 124.8 (d), 127.0 (s), 131.7 (s), 132.0 (s), 132.1 (s), 170.3 (s), and 174.8 (s).

The [2 + 2] cycloadduct (**8k'**) had m.p. 78–78.5 °C (Found: C, 67.3; H, 7.35; N, 9.25.  $C_{17}H_{22}N_2O_3$  requires C, 67.5; H, 7.35; N, 9.25%;  $\nu_{\max}(\text{KBr})$  1 735, 1 665, 1 615, and 1 165  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}(\text{CDCl}_3)$  1.50 (3 H, s), 1.72 (3 H, s), 2.14 (3 H, s), 2.20 (3 H, s), 2.28 (1 H, A of ABq,  $J$  11.7 Hz), 3.26 (1 H, B of ABq,  $J$  11.7 Hz), 3.36 (3 H, s), 3.40 (3 H, s), 6.53 (1 H, s), and 6.67 (1 H, s);  $\delta_{\text{C}}(\text{CDCl}_3)$  18.9 (q), 19.5 (q), 26.8 (q), 27.8 (q), 28.8 (q), 42.2 (t), 51.5 (q), 60.6 (s), 68.9 (s), 115.9 (d), 122.3 (d), 128.7 (s), 131.0 (s), 131.4 (s), 169.1 (s), and 172.3 (s).

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