Photocycloaddition of Quinoxalin-2-ones and Benzoxazin-2-ones to Aryl Alkenes

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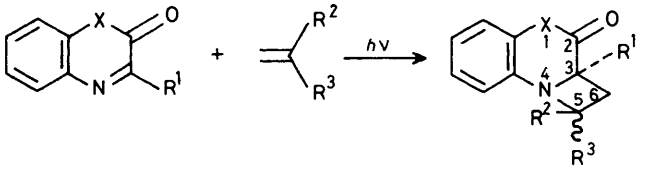
Photocycloadditions of quinoxalin-2-ones and benzoxazin-2-ones to arylalkenes are examined. Irradiation of quinoxalin-2-ones (**1**) in the presence of arylalkenes (**3**) such as 1,1-diphenylethylene, styrene, 2- or 4-vinylpyridine, *etc*, gave the azetidines (**4**)—(**22**) *via* [2 + 2]cycloaddition of the carbon–nitrogen double bond of (**1**) to the alkene. This photoreaction occurs from the excited triplet state of (**1**). Benzoxazin-2-ones (**2**) also added photochemically to arylalkenes to yield the corresponding azetidines (**23**)—(**28**).

While [2 + 2]photocycloadditions of alkenes to other alkenes,[1,2] to ketones,[2,3] and thioketones[4] to yield the expected four-membered ring compounds are well characterized and often employed in organic synthesis, similar cycloadditions to imines are relatively rare. The reason generally invoked is the poorer reactivity of the excited imino group due to the rapid radiationless decay which results by twisting around the carbon–nitrogen double bond. Intermolecular photocycloadditions of imines to alkenes are known only for cyclic systems which are conjugated with electron-withdrawing groups such as



(**1**) (**3**) (**4**)-(**28**)

	X	R^1		R^2	R^3
(**1a**)	NMe	Me	(**3a**)	Ph	Ph
(**1b**)	NEt	Me	(**3b**)	Me	Ph
(**1c**)	NMe	H	(**3c**)	H	Ph
(**1d**)	NMe	Bu	(**3d**)	H	*p*-MeC_6H_4
(**1e**)	NMe	Pent^i	(**3e**)	H	*p*-ClC_6H_4
(**1f**)	NMe	Ph	(**3f**)	H	*p*-$MeOC_6H_4$
(**1g**)	NEt	Ph	(**3g**)	Me	Me
(**1h**)	NPh	Me	(**3h**)	H	2-Pyridyl
			(**3i**)	H	4-Phridyl
(**2a**)	O	Me			
(**2b**)	O	Bu			
(**2c**)	O	Pent^i			
(**2d**)	O	Ph			

Scheme 1.

imino,[5] carbonyl,[6–9] cyano,[10] and amide[11] on both nitrogen and carbon atoms, and a hetero atom such as nitrogen[5,7] and oxygen[12] on the nitrogen atom. Swenton and Hyatt[7] and Szilágy and Wahmhoff[9] have reported that irradiation of the N=C–C=O chromophore of 1,3-dimethyl-6-azauracil results in [2 + 2]cycloaddition of alkenes to the C=N double bond. During the course of our studies dealing with the photochemical reactivities of cyclic conjugated nitrogen–carbonyl systems such as pyrimidinones[13] and pyrazinones,[14] a novel [2 + 2]-photocycloaddition[8] of the C=N double bond of the quinoxalin-2-ones (**1**) and the benzoxazin-2-ones (**2**) with electron-deficient alkenes was discovered. We have investigated the photocycloaddition of quinoxalin-2-ones (**1**) and then 1,4-benzoxazin-2-ones (**2**) to aryl alkenes because of its utility in the synthesis of the unique tricyclic system and here we report the results in details.

Results and Discussion

Irradiation of 1,3-dimethylquinoxalin-2-one (**1a**) with a 300 W high-pressure mercury lamp with a Pyrex filter in benzene or acetonitrile in the presence of 1,1-diphenylethylene (**3a**) (2 equiv.) at room temperature for 15 h, gave the azetidine (**4**) as the sole [2 + 2]photocycloadduct, in 22—24% isolated yields. A mixture of (**1a**) and (**3a**) in benzene in the dark for an equivalent period of time failed to react. The structure of the azetidine (**4**) was established by spectroscopic and microanalysis data, the latter indicating that it was a 1:1-adduct of (**1a**) and (**3a**).

The i.r. spectrum of (**4**) showed an absorption at 1 650 cm^{-1} characteristic of amide carbonyl. The most compelling evidence for the assigned structure was given by the n.m.r. spectrum, the ^1H n.m.r. spectrum of (**4**) showing two singlets at δ 1.58 (3 H, Me) and 3.10 (3 H, NMe), and two doublets at δ 2.65 (1 H) and 3.97 (1 H) assignable to methylene protons of the four-membered ring in addition to aromatic protons. The ^{13}C n.m.r. spectrum displayed signals at δ_C 26.5 (q, Me), 28.6 (q, NMe), 170.2 (s, CO), and newly formed signals at 46.3 (t), 60.3 (s), and 76.0 (s) due to azetidine methylene and quaternary carbons. Similarly, irradiation of the quinoxalin-2-ones (**1a**—**h**) in benzene under the same conditions to those described above in the presence of 1,1-diphenylethylene (**3a**), α-methylstyrene (**3b**), styrene (**3c**), *p*-methylstyrene (**3d**), and *p*-chlorostyrene (**3e**) gave the corresponding azetidines (**4**)—(**8**), (**12**)—(**14**), (**16**), and (**18**)—(**21**) in each case as the sole product in 14—98% isolated yield (Table 1). The azetidines thus obtained were assigned structures on the basis of their spectroscopic properties and elemental analyses (see Table 3 and the Experimental section). Characteristically, in their i.r. spectra they show amide carbonyl stretching at 1 650—1 685 cm^{-1} and the absence of a carbon–nitrogen double bond stretching band. The photoaddition proceeds regioselectively to give exclusively the head-to-tail adducts. The assignment of the regiochemistry was based upon the chemical shifts and splitting patterns in their n.m.r. spectra of the azetidine ring protons. The n.m.r. spectrum of the azetidine (**13**) indicated that the methylene protons at δ 2.65—3.49 (6-H_2, m) were coupled with two methine protons at δ 4.63 (3-H dd, *J* 4.4, 9.8 Hz) and 4.99 (5-H, br t, *J* 8.3 Hz), respectively, consistent with the regiochemistry assigned to the cycloadduct (**13**). In no case could the alternative head-to-head regioisomer (**29**) be detected. The quinoxalin-2-one (**1a**) also added photo-

Table 1. Yield of azetidine derivatives (**4**)—(**28**)[a]

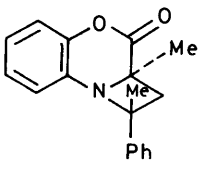
Product	X	R^1	R^2	R^3	Yield (%)[b] Azetidine	Yield (%)[b] Recovered (**1**)
(**4**)	NMe	Me	Ph	Ph	24 (22)[c]	63 (50)[c]
(**5**)	NMe	Me	Me	Ph	22	68
(**6**)	NMe	Me	H	Ph	63	Trace
(**7**)	NMe	Me	H	*p*-MeC_6H_4	46	40
(**8**)	NMe	Me	H	*p*-ClC_6H_4	40	29
(**9**)	NMe	Me	Me	Me	13 (19)[d]	60 (50)[d]
(**10**)	NMe	Me	H	2-Pyridyl	69	15
(**11**)	NMe	Me	H	4-Pyridyl	86	Trace
(**12**)	NEt	Me	Ph	Ph	14	64
(**13**)	NMe	H	H	Ph	52	13
(**14**)	NMe	Bu	Ph	Ph	26	73
(**15**)	NMe	Bu	H	4-Pyridyl	98	Trace
(**16**)	NMe	Pent[i]	Ph	Ph	27	65
(**17**)	NMe	Pent[i]	H	4-Pyridyl	70	Trace
(**18**)	NMe	Ph	Ph	Ph	78	Trace
(**19**)	NMe	Ph	Me	Ph	80	20
(**20**)	NEt	Ph	Ph	Ph	70	10
(**21**)	NPh	Me	Ph	Ph	34	65
(**22**)	NPh	Me	H	4-Pyridyl	85	Trace
(**23**)	O	Me	Ph	Ph	50	25
(**24a**)[e]	O	Me	Me	Ph	30	25
(**24b**)[e]	O	Me	Ph	Me	10	
(**25**)	O	Me	H	Ph	47	15
(**26**)	O	Bu	Ph	Ph	42	17
(**27**)	O	Pent[i]	Ph	Ph	56	Trace
(**28**)	O	Ph	Ph	Ph	39	60

[a] Irradiation was carried out in benzene for 15 h. [b] Isolated yield. [c] Acetonitrile was used as solvent. [d] Acetone was used as solvent. [e] Stereoisomer.

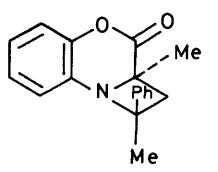
Table 2. Yield of azetidine (**6**) obtained from 1,3-dimethylquinoxalin-2-one (**1**) and styrene (**3c**) under various conditions[a]

Run	Solvent	Conditions	Yield (%)[b] Azetidine (**6**)	Yield (%)[b] Recovered (**1a**)
1	Benzene	N_2, HP[c]	44 (63)[d]	44 (<1)[d]
2	Acetone	N_2, HP	34	42
3	MeOH	N_2, HP	55	25
4	CH_3CN	N_2, HP	34	43
5	Benzene	O_2, HP	7	65
6	Benzene	N_2, 313 nm,[e] *m*-methoxyacetophenone[f]	43	46
7	Benzene	N_2, 336 nm[g]	63	<1
8	Benzene	N_2, 336 nm, *trans*-stilbene[h]	3	78

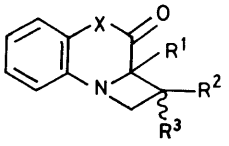
[a] Irradiation time: 3 h. [b] Isolated yield. [c] High-pressure mercury lamp (300 W). [d] Irradiation time: 15 h. [e] A Pyrex glass filter and an aqueous solution of K_2CrO_4 (0.54 g l^{-1}) and Na_2CO_3 (2 g l^{-1}) was used to isolate the 313 nm region. [f] *m*-Methoxyacetophenone absorbed >95% of the incident light. [g] A Pyrex glass filter and a methanol solution of naphthalene (5 g l^{-1}) was used to isolate the 366 nm region. [h] U.v. spectrum of *trans*-stilbene showed no absorption at 366 nm when 10 mol equiv. *trans*-stilbene was used.



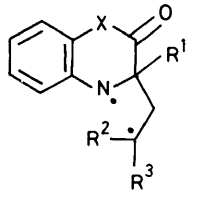
(**24a**)



(**24b**)



(**29**)



(**30**)

chemically to isobutene (**3g**), to give the azetidine (**9**), but in low yield (13%); it did not, however, react with hex-1-ene. Irradiation of quinoxalin-2-one (**1a**) with *p*-methoxystyrene (**3f**) gave an intractable mixture, whilst with the 1,2-disubstituted alkene, β-methylstyrene, it was recovered quantitatively. The success of the photocycloadditions of the quinoxalin-2-ones (**1**) to arylalkenes prompted us to examine the reaction with heteroaromatic alkenes such as vinylpyridines and *N*-vinylcarbazoles. Irradiation of the quinoxalin-2-ones (**1a**, **d**, **e**, **h**) in benzene in the presence of 2- or 4-vinylpyridine (**3h**, i) yielded the 1:1-cycloadducts, the azetidines (**10**), (**11**), (**15**), (**17**), and (**22**) in high yields. The head-to-tail regiochemistry was assigned on the basis of the n.m.r. spectrum. For example, the methine proton of (**10**) in the azetidine ring adjacent to nitrogen appeared as the X part of on ABX pattern (*J* 7.5, 8.8 Hz) at δ 4.95 with coupling to the adjacent methylene protons at δ 2.54 (A of ABX, *J* 7.5, 11.4 Hz) and 3.33 (B of ABX, *J* 8.8, 11.4 Hz). Irradiation of the quinoxalin-2-one (**1a**) in benzene in the presence of vinyl carbazole, however, gave small amounts of inseparable mixtures, no azetidine being detected.

Irradiation of 1,3-dimethylquinoxalin-2-one (**1a**) in the presence of styrene (**3c**) under a variety of conditions (Table 2) gave the azetidine (**6**) in 34—55% yield, depending on the solvent. There was almost no formation of the azetidine (**6**) in the presence of the triplet quenchers oxygen and *trans*-stilbene (E_T = 50 kcal mol^{-1}). The isolated amount of the azetidine (**6**) was almost the same as that from direct irradiation of (**1a**) and (**3c**) with monochromatic light of 313 nm in the presence of a triplet sensitizer such as *m*-methoxyacetophenone (E_T = 72.4 kcal mol^{-1}) where >95% of the incident light was absorbed. These results suggest that the photocycloaddition occurs from the excited triplet state of the quinoxalin-2-one (**1a**).

The regiochemistry of the cycloaddition seems to be determined here, as in other cases,[15] by formation of the more stable biradical intermediate (**30**). Similar photocycloadditions were observed with 1,4-benzoxazin-2-ones (**2a**—**d**) which upon irradiation in benzene in the presence of arylalkenes such as 1,1-diphenylethylene (**3a**), α-methylstyrene (**3b**), and styrene (**3c**) yielded the azetidines (**23**)—(**28**) in 39—56% yields. Structural assignments were made on the basis of the similarity of the n.m.r. spectra with those of the azetidines derived from the quinoxalin-2-ones (**1**) with arylalkenes (**3**). In the reaction of 2-methyl-1,4-benzoxazin-2-one (**2a**) with α-methylstyrene (**3b**), two stereoisomers of the azetidine (**24a**) and (**24b**) were obtained. The stereochemistry was tentatively assigned as shown on the basis of the n.m.r. spectra. The 5-methyl protons (δ 1.53) of (**24a**) appeared at higher field than those (δ 1.96) of an alternative stereoisomer (**24b**) due to the anisotropic effect of the benzene ring. The 5-methyl carbon (24.0 p.p.m.) of the azetidine (**24a**) appeared upfield from the corresponding signal (31.9 p.p.m.) of an alternative stereoisomer (**24b**). Irradiation of the benzoxazin-2-ones (**2a**—**d**) in the presence of 4-vinylpyridine gave small amounts of inseparable mixtures, along with unchanged (**2**) (>50%) but none of the corresponding

Table 3. N.m.r. spectral data of azetidine derivatives (**4**)—(**28**)

	^{1}H N.m.r. (δ in $CDCl_3$)		^{13}C N.m.r. (δ in $CDCl_3$)		
Compd.	Azetidine ring	Others	Azetidine ring	C=O	Others
(**4**)	2.65 (1 H, d, *J* 12.2 Hz), 3.97 (1 H, d, *J* 12.2 Hz)	1.58 (3 H, s), 3.10 (3 H, s), 6.56—6.96 (5 H, m), 7.05 (4 H, m), 7.23—7.64 (5 H, m)	46.3 (t), 60.3 (s), 76.0 (s)	170.2 (s)	26.5 (q), 28.6 (q), 114.4 (d), 122.7 (d), 123.2 (d), 126.3 (d), 126.6 (d), 127.2 (d), 128.1 (d), 131.2 (s), 134.2 (s), 139.2 (s), 148.4 (s)
(**5**)	2.49 (1 H, d, *J* 11.7 Hz), 3.07 (1 H, d, *J* 11.7 Hz)	1.52 (3 H, s), 1.55 (3 H, s), 3.41 (3 H, s), 6.66—6.98 (4 H, m), 7.18—7.72 (5 H, m)	48.6 (t), 59.5 (s), 68.1 (s)	170.1 (s)	24.0 (q), 27.4 (q), 29.0 (q), 114.8 (d), 121.1 (d), 122.6 (d), 123.2 (d), 124.9 (d), 126.7 (d), 128.3 (d), 131.5 (s), 133.6 (s), 148.3 (s)
(**6**)	2.38 (1 H, A of ABX, *J* 7.8, 11.2 Hz), 3.25 (1 H, B of ABX, *J* 8.3, 11.2 Hz), 4.80 (1 H, br t, *J* 7.8 Hz)	1.60 (3 H, s), 3.43 (3 H, s), 6.59—7.12 (4 H, m), 7.23—7.59 (5 H, m)	42.4 (t), 61.5 (s), 66.9 (d)	170.6 (s)	27.1 (q), 29.1 (q), 114.7 (d), 122.4 (d), 123.4 (d), 124.1 (d), 126.7 (d), 127.8 (d), 128.6 (d), 133.6 (s), 134.2 (s), 142.8 (s)
(**7**)	2.37 (1 H, A of ABX), 3.22 (1 H, B of ABX, *J* 8.3, 11.7 Hz), 4.77 (1 H, br t, *J* 8.3 Hz)	1.60 (3 H, s), 2.37 (3 H, s), 6.58—7.40 (4 H, m), 7.19 (2 H, d, *J* 7.8 Hz), 7.43 (2 H, *J* 7.8 Hz)	42.4 (t), 61.4 (s), 66.7 (d)	170.6(s)	21.1 (q), 27.0 (q), 28.9 (q), 114.6 (d), 122.3 (d), 123.3 (d), 123.9 (d), 126.6 (d), 129.2 (d), 133.4 (s), 134.1 (s), 137.4 (s), 139.7 (s)
(**8**)	2.32 (1 H, A of ABX, *J* 7.8, 11.5 Hz), 3.23 (B of ABX, *J* 7.8, 11.5 Hz), 4.77 (1 H, br t, *J* 7.8 Hz)	1.59 (3 H, s), 3.43 (3 H, s), 6.60 (1 H, br d, *J* 7.6 Hz), 6.75—7.14 (3 H, m), 7.41 (4 H, dd, *J* 8.8, 14.2 Hz)	42.4 (t), 61.5 (s), 66.2 (d)	170.4 (s)	26.9 (q), 29.0 (q), 114.7 (d), 122.7 (d), 123.4 (d), 124.3 (d), 128.1 (d), 128.7 (d), 133.6 (s), 133.7 (s), 141.3 (s)
(**9**)	2.31 (1 H, d, *J* 11.7 Hz), 2.73 (1 H, d, *J* 11.7 Hz)	1.08 (3 H, s), 1.47 (3 H, s), 1.51 (3 H, s), 3.36 (3 H, s), 6.68—7.03 (4 H, m)	46.0 (t), 59.2 (s), 63.8 (s)	170.6 (s)	24.4 (q), 27.9 (q), 28.8 (q), 32.3 (q), 114.5 (d), 122.1 (d), 122.7 (d), 123.1 (d), 131.3 (s), 133.7 (s)
(**10**)	2.54 (1 H, A of ABX, *J* 7.5, 11.4 Hz), 3.33 (1 H, B of ABX, *J* 8.8, 11.4 Hz), 4.95 (1 H, X of ABX, *J* 7.5, 8.8 Hz)	1.63 (3 H, s), 3.44 (3 H, s), 6.65—7.30 (5 H, m), 7.75—7.78 (8 H, m)	40.4 (t), 61.9 (s), 67.6 (d)	170.3 (s)	27.2 (q), 28.9 (q), 114.7 (d), 120.9 (d), 122.0 (d), 122.5 (d), 123.4 (d), 124.0 (d) 133.3 (s), 134.0 (s), 136.8 (d), 149.4 (d), 161.9 (s)
(**11**)	2.33 (1 H, A of ABX, *J* 7.9, 11.4 Hz), 3.29 (1 H, B of ABX, *J* 8.4, 11.4 Hz), 4.81 (1 H, br t, *J* 7.9 Hz)	1.60 (3 H, s) 6.60—7.18 (4 H, m), 7.48 (2 H, br d, *J* 5.7 Hz), 8.64 (2 H, br d, *J* 5.7 Hz)	41.8 (t), 61.9 (s), 65.5 (d)	170.2 (s)	27.0 (q), 29.0 (q), 114.9 (d), 121.5 (d), 122.3 (d), 123.6 (s), 123.6 (d), 124.6 (d), 133.6 (s), 150.2 (d), 151.6(s)
(**12**)	2.62 (1 H, d, *J* 12.2 Hz), 3.98 (1 H, d, *J* 12.2 Hz)	0.91 (3 H, s), 1.55 (3 H, s), 3.53—4.04 (2 H, m), 6.60—7.00 (4 H, m), 7.06 (4 H, s), 7.22—7.63 (6 H, m)	46.2 (t), 60.2 (s), 76.1 (s)	169.4 (s)	11.7 (q), 26.5 (q), 36.2 (t), 114.5 (d), 122.6 (d), 123.2 (d), 123.6 (d), 127.4 (d), 126.5 (d), 128.6 (d), 127.2 (d), 128.2 (d), 128.3 (d), 131.6 (s), 132.6 (s), 139.2 (s), 148.7 (s)
(**13**)	2.65—3.49 (2 H, m), 4.63 (1 H, dd, *J* 4.4, 9.3 Hz), 4.99 (1 H, br t, *J* 8.3 Hz)	6.53—6.62 (1 H, m), 6.71—7.02 (2 H, m), 7.21—7.58 (5 H, m)	35.5 (t), 56.2 (d), 71.1 (d)	167.7 (s)	28.4 (q), 114.5 (d), 121.1 (d), 123.4 (d), 123.6 (d), 126.3 (d), 127.8 (d), 128.5 (d), 132.9 (s), 135.2 (s), 147.5 (s)
(**14**)	2.68 (1 H, d, *J* 12.2 Hz), 3.90 (1 H, d, *J* 12.2 Hz)	0.81 (3 H, br t), 1.15—1.42 (4 H, m), 1.73—2.04 (2 H, m), 6.53—6.97 (4 H, m), 7.03 (4 H, s), 7.21—7.65 (5 H, m)	45.0 (t), 63.6 (s), 75.9 (s)	169.9 (s)	13.9 (q), 22.8 (t), 25.8 (t), 28.6 (q), 40.8 (t), 114.4 (d), 122.6 (d), 122.8 (d), 123.1 (d), 126.4 (d), 126.7 (d), 127.2 (d), 128.1 (d), 128.3 (d), 132.4 (s), 134.3 (s), 139.6 (s), 148.5 (s)
(**15**)	2.50 (1 H, A of ABX, *J* 7.9, 11.4 Hz), 3.23 (1 H, B of ABX, *J* 7.8, 11.4 Hz), 4.73 (1 H, br t, *J* 7.9 Hz)	0.85 (3 H, br t), 1.29—1.43 (4 H, m), 1.80—2.07 (2 H, m), 3.45 (3 H, s), 6.67—7.08 (4 H, m), 7.44—7.51 (2 H, m), 8.61—8.68 (2 H, m)	40.9 (t), 64.8 (s), 65.5 (d)	169.7 (s)	13.7 (q), 22.7 (t), 25.2 (t), 28.7 (q), 40.2 (t), 114.7 (d), 121.3 (d), 121.8 (d), 123.4 (d), 124.3 (d), 133.6 (s), 134.8 (s), 150.0 (d), 151.6 (s)
(**16**)	2.69 (1 H, d, *J* 12.2 Hz), 3.91 (1 H, d, *J* 12.2 Hz)	0.80 (6 H, d, *J* 5.4 Hz), 1.10—1.60 (3 H, m), 1.66—2.08 (2 H, m), 6.52—7.03 (8 H, m), 7.18—7.64 (6 H, m)	45.1 (t), 63.5 (s), 75.9 (s)	169.8 (s)	22.3 (q), 22.5 (q), 28.1 (q), 28.6 (d), 32.4 (t), 38.8 (t), 114.3 (d), 122.6 (d), 122.7 (d), 122.9 (d), 126.4 (d), 126.6 (d), 127.1 (d), 128.0 (d), 128.2 (d), 128.3 (d), 132.3 (s), 134.2 (s), 139.0 (s), 148.4 (s)
(**17**)	2.35 (1 H, A of ABX, *J* 7.9, 11.4 Hz), 3.23 (1 H, B of ABX, *J* 8.8, 11.4 Hz), 4.79 (1 H, br t, *J* 7.9 Hz)	0.84 (6 H, d, *J* 6.2 Hz), 1.07—1.80 (3 H, m), 1.85—2.06 (2 H, m), 3.45 (3 H, s), 6.60—7.07 (4 H, m), 7.48 (2 H, d, *J* 4.4 Hz), 8.64 (2 H, br d)	40.2 (t), 64.9 (s), 65.6 (d)	169.8 (s)	22.3 (q), 28.1 (q), 28.8 (d), 31.9 (t), 39.0 (t), 114.7 (d), 121.3 (d), 121.7 (d), 123.4 (d), 124.3 (d), 133.5 (s), 134.8 (s), 150.1 (d), 151.7 (s)
(**18**)	2.91 (1 H, d, *J* 12.2 Hz), 4.37 (1 H, d, *J* 12.2 Hz)	3.01 (3 H, s), 6.50—6.60 (1 H, m), 6.67—6.95 (2 H, m), 7.04—7.60 (12 H, m), 7.62—7.70 (4 H, m)	47.3 (t), 68.4 (s), 76.4 (s)	168.3 (s)	29.1 (q), 114.9 (d), 122.9 (d), 123.7 (d), 124.1 (d), 125.5 (d), 126.6 (d), 126.8 (d), 127.3 (d), 128.2 (d), 128.3 (d), 131.9 (d), 135.0 (s), 139.1 (s), 142.7 (s), 148.2 (s)
(**19**)	2.78 (1 H, d, *J* 11.7 Hz), 3.48 (1 H, d, *J* 11.7 Hz)	1.65 (3 H, s), 6.82—7.01 (3 H, m), 7.05—7.43 (6 H, m), 7.54—7.70 (4 H, m)	49.8 (t), 64.1 (s), 68.5 (s)	168.1 (s)	23.8 (q), 29.4 (q), 115.0 (d), 121.2 (d), 123.2 (d), 123.3 (d), 125.3 (d), 126.8 (d), 127.2 (d), 128.2 (d), 128.3 (d), 131.9 (s), 134.3 (s), 143.1 (s), 147.6 (s)
(**20**)	2.86 (1 H, d, *J* 12.2 Hz), 4.37 (1 H, d, *J* 12.2 Hz)	0.78 (3 H, t), 3.33—4.02 (2 H, m), 6.55—6.69 (1 H, m), 6.76—7.70 (18 H, m)	47.1 (t), 64.6 (s), 76.4 (s)	167.4 (s)	11.5 (q), 36.5 (t), 114.8 (d), 122.7 (d), 124.0 (d), 125.4 (d), 126.6 (d), 126.8 (d), 127.3 (d), 127.5 (d), 128.2 (d), 128.3 (d), 128.5 (d), 132.2 (s), 133.3 (s), 139.2 (s), 142.7 (s), 148.4 (s)

Table 3 (*continued*)

Compd.	^{1}H N.m.r. (δ in $CDCl_3$) Azetidine ring	^{1}H N.m.r. (δ in $CDCl_3$) Others	^{13}C N.m.r. (δ in $CDCl_3$) Azetidine ring	^{13}C N.m.r. (δ in $CDCl_3$) C=O	^{13}C N.m.r. (δ in $CDCl_3$) Others
(**21**)	2.67 (1 H, d, *J* 12.2 Hz), 4.01 (1 H, d, *J* 12.2 Hz)	1.71 (3 H, s), 5.96 (1 H, dd, *J* 1.5, 7.8 Hz), 6.21—6.87 (3 H, m), 7.01—7.68 (5 H, m)	45.6 (t), 61.1 (s), 76.4 (s)	170.1 (s)	24.6 (q), 116.8 (q), 122.9 (d), 123.2 (d), 123.9 (d), 126.4 (d), 126.9 (d), 127.3 (d), 127.6 (d), 128.2 (d), 128.5 (d), 129.6 (d), 130.7 (s), 135.7 (s), 137.7 (s), 139.4 (s), 148.7 (s)
(**22**)	2.37 (1 H, A of ABX, *J* 7.9, 11.4 Hz), 3.35 (1 H, B of ABX, *J* 8.4, 11.4 Hz), 5.98 (1 H, br t, *J* 8.4 Hz)	1.73 (3 H, s), 6.21—6.33 (1 H, m), 6.63—6.89 (3 H, m), 7.21—7.64 (7 H, m), 8.63—8.70 (2 H, m)	41.6 (t), 62.4 (s), 65.8 (d)	170.1 (s)	26.9 (q), 116.9 (d), 121.4 (d), 122.4 (d), 123.6 (d), 128.2 (d), 128.6 (d), 129.1 (d), 130.0 (d), 132.9 (d), 134.8 (s), 137.4 (s), 150.2 (d), 151.5 (s)
(**23**)	2.75 (1 H, d, *J* 12.7 Hz), 4.00 (1 H, d, *J* 12.7 Hz)	1.66 (3 H, s), 6.73—6.85 (4 H, m), 7.09 (5 H, br s), 7.30—7.61 (6 H, m)	46.0 (t), 59.4 (s), 76.7 (s)	169 4 (s)	26.3 (q), 116.7 (d), 123.0 (d), 123.6 (d), 124.2 (d), 126.2 (d), 127.0 (d), 127.6 (d), 127.9 (d), 128.2 (d), 128.3 (d), 138.6 (s), 146.0 (s), 148.0 (s)
(**24a**)	2.57 (1 H, d, *J* 11.7 Hz), 3.06 (1 H, d, *J* 11.7 Hz)	1.53 (3 H, s), 1.64 (3 H, s), 6.74—7.02 (4 H, m), 7.24—7.70 (5 H, m)	48.1 (t), 58.7 (s), 68.9 (s)	169.6 (s)	24.0 (q), 26.4 (q), 117.1 (d), 121.9 (d), 123.6 (d), 124.8 (s), 124.8 (d), 127.0 (d), 128.5 (d), 146.2 (s), 147.5 (s)
(**24b**)	2.64 (1 H, d, *J* 12.2 Hz), 3.58 (1 H, d, *J* 12.2 Hz)	1.65 (3 H, s), 1.96 (3 H, s), 6.68—6.94 (4 H, m), 7.03—7.41 (5 H, m)	45.1 (t), 59.2 (s), 70.0 (s)	169.6 (s)	26.8 (q), 31.9 (q), 116.8 (d), 122.8 (d), 123.4 (d), 124.5 (d), 124.9 (s), 126.1 (d), 127.6 (d), 128.2 (d), 128.6 (d)
(**25**)	2.42 (1 H, A of ABX, *J* 8.3, 11.7 Hz), 3.24 (1 H, B of ABX, *J* 8.3, 11.7 Hz), 4.77 (1 H, br t, *J* 8.3 Hz)	1.66 (3 H, s,), 6.60—7.05 (4 H, m), 7.29—7.58 (5 H, m)	41.7 (t), 60.5 (s), 67.8 (d)	169.5 (s)	26.1 (q), 117.1 (d), 122.4 (d), 124.6 (d), 124.9 (d), 126.5 (d), 128.0 (d), 128.6 (d), 131.6 (s), 141.7 (s), 145.8 (s)
(**26**)	2.73 (1 H, d, *J* 12.2 Hz), 3.94 (1 H, d, *J* 12.2 Hz)	0.83 (3 H, br t), 1.10—1.55 (4 H, m), 1.82—2.10 (2 H, m), 6.72—6.84 (5 H, m), 7.04—7.09 (4 H, m), 7.29—7.62 (5 H, m)	44.8 (t), 62.7 (s), 76.5 (s)	169.1 (s)	13.8 (q), 22.7 (t), 25.8 (t), 40.5 (t), 116.6 (d), 122.5 (d, 123.4 (d), 124.1 (d), 126.2 (d), 127.0 (d), 127.7 (d), 127.9 (d), 128.3 (d), 129.3 (d) 138.9 (s), 146.0 (s), 147.8 (s)
(**27**)	2.78 (1 H, d, *J* 12.2 Hz), 3.94 (1 H, d, *J* 12.2 Hz)	0.81 (6 H, d, *J* 5.9 Hz), 1.15—1.58 (3 H, m), 1.86—2.06 (2 H, m), 6.78—6.82 (4 H, m), 7.08 (4 H, br s), 7.23—7.61 (5 H, m)	44.9 (t), 62.7 (s), 76.4 (s)	169.1 (s)	22.3 (q), 22.4 (q), 28.0 (d), 32.2 (t), 38.7 (t), 116.6 (d), 122.5 (d), 123.4 (d), 124.1 (d), 126.2 (d), 127.0 (d), 127.7 (d), 127.9 (d), 128.3 (d), 129.3 (s), 138.9 (s), 146.0 (s), 147.8 (s)
(**28**)	3.00 (1 H, d, *J* 12.2 Hz), 4.39 (1 H, d, *J* 12.2 Hz)	6.72—7.67 (19 H, m)	4.27 (t), 64.1 (s), 77.1 (s)	167.5 (s)	116.9 (d), 123.2 (d), 124.3 (d), 125.4 (d), 126.3 (d), 127.1 (d), 128.0 (d), 128.3 (d), 128.7 (d), 128.9 (d), 138.5 (s), 140.1 (s), 146.7 (s), 147.6 (s)

azetidines. The formation of the azetidines (**23**)—(**28**) could be also explained in terms of the 1,4-diradical intermediate (**30**; X = O). In view of these results, it is interesting to note that the photocycloaddition of the quinoxalin-2-ones (**1**) and the benzoxazin-2-ones (**2**) with arylalkenes (**3**) is regiospecific, giving the four-membered ring products, azetidines (**4**)—(**28**), and that the additional conjugation with an electron-withdrawing group such as a carbonyl imino,[5] cyano,[10] or amide[11] is important for the [2 + 2]photocycloaddition of alkene to carbon–nitrogen double bonds.

Experimental

M.p.s and b.p.s are uncorrected and were measured with a Yanaco micro-melting point apparatus (MP-J3) and Buchi Kugelrohr distillation apparatus (KR-3), respectively. U.v. spectra were recorded on JASCO UVIDEC-505 spectrophotometer. I.r. spectra were determined with Hitachi 260-30 spectrophotometer. ^{1}H and ^{13}C N.m.r. spectra were measured with JEOL FX-100 (100 MHz) spectrometer using tetramethylsilane as an internal standard and $CDCl_3$ as solvent. 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**—**c**, **f**—**h**)[8,16] and benzoxazin-2-ones (**2a**—**d**)[8,17,18] were prepared according to methods previously described in the literature and (**1d**) and (**1e**) were prepared by a modification of these methods.

3-Butyl-1-methylquinoxalin-2-one (**1d**). M.p. 142—144 °C (Found: C, 72.05; H, 7.35; N, 13.05. $C_{13}H_{16}N_2O$ requires C, 72.2; H, 7.45; N, 12.95%); $\lambda_{max.}$(EtOH) 229 (ε 21 900), 278 (6 000), 330sh (6 900), and 337 nm (7 000); $\nu_{max.}$(KBr) 1 635 cm^{-1} (C=O); δ_H 0.97 (3 H, t, Me), 1.29—1.93 (4 H, m, CH_2), 2.95 (2 H, br t, CH_2), 3.69 (3 H, s, Me), 7.21—7.60 (3 H, m), and 7.77—7.87 (1 H, m) (ArH); δ_C 13.9 (q, Me), 22.7 (t), 28.9 (t), 34.0 (t) (CH_2), 28.9 (q, Me), 113.4 (d), 123.3 (d), 129.3 (d), 129.5 (d), 132.6 (s), 132.9 (s) (ArC), 154.8 (s, C=N), and 161.2 (s, C=O).

3-Isopentyl-1-methylquinoxalin-2-one (**1e**). B.p. 145 °C at 2 mmHg; m.p. 44.5—45 °C (Found: C, 72.95; H, 7.9; N, 12.15. $C_{14}H_{18}N_2O$ requires C, 73.0; H, 7.85; N, 12.15%); $\nu_{max.}$(KBr) 1 645 cm^{-1} (C=O); δ_H 0.99 (6 H, d, Me, *J* 5.9 Hz), 1.56—1.76 (3 H, m, CH_2 and CH), 2.86—3.02 (2 H, m, CH_2), 3.69 (3 H, s, Me), 7.21—7.59 (3 H, m), 7.70—7.80 (1 H, m) (ArH); δ_C 22.5 (q, Me), 28.2 (d, CH), 28.9 (q, Me), 32.4 (t), 35.7 (t) (CH_2), 113.4 (d), 123.4 (d), 129.3 (d), 129.5 (d), 137.2 (s), 133.0 (s) (ArC), 154.8 (s, C=N), and 161.5 (s, C=O).

General Procedure for the Photochemical Reactions of the Quinoxalin-2-ones (**1a**—**h**) *and the Benzoxazin-2-ones* (**2a**—**d**) *with Alkenes* (**3**).—A solution of the quinoxalin-2-one (200 mg) or the benzoxazin-2-one (200 mg) and the alkene (2 mol equiv.) in dry solvent (70 ml) in a Pyrex vessel was irradiated with a high-pressure mercury lamp (300 W) under argon for 3—15 h at room temperature. After removal of the solvent, the residue was chromatographed on a silica gel column with benzene–ethyl acetate (50:1—4:1) as eluant to yield the photoproducts. N.m.r. spectra of azetidines (**4**)—(**28**) are summarized in Table 3.

Azetidine (**4**). M.p. 130—131 °C (Found: C, 81.3; H, 6.3; N, 7.9. $C_{24}H_{22}N_2O$ requires C, 81.3; H, 6.25; N, 7.9%); $\nu_{max.}$(KBr) 1 650 cm^{-1} (C=O).

Azetidine (**5**). B.p. 150 °C at 2 mmHg (decomp.) (Found: C, 77.85; H, 6.95; N, 9.5. $C_{19}H_{20}N_2O$ requires C, 78.05; H, 6.9; N, 9.6%); $\nu_{max.}$(film) 1 665 cm^{-1} (C=O); *m/z* (c.i.) 293 ($M^+ + 1$).

Azetidine (**6**). M.p. 85.5—87 °C (Found: C, 77.5; H, 6.45; N, 10.0. $C_{18}H_{18}N_2O$ requires C, 77.65; H, 6.5; N, 10.05%); $\nu_{max.}$(KBr) 1 670 cm^{-1} (C=O).

Azetidine (**7**). M.p. 112—113 °C (Found: C, 77.75; H, 6.85; N, 9.55. $C_{19}H_{20}N_2O$ requires C, 78.05; H, 6.9; N, 9.6%); $\nu_{max.}$(KBr) 1 665 cm^{-1} (C=O).

Azetidine (**8**). M.p. 114—114.5 °C (Found: C, 69.05; H, 5.45; N, 8.95. $C_{18}H_{17}N_2O$ requires C, 69.1; H, 5.45; N, 8.95%); $\nu_{max.}$(KBr) 1 665 cm^{-1} (C=O).

Azetidine (**9**). B.p. 120 °C at 2 mmHg (Found: C, 72.8; H, 7.85; N, 12.1. $C_{14}H_{18}N_2O$ requires C, 73.0; H, 7.85; N, 12.15%); $\nu_{max.}$(film) 1 660 cm^{-1} (C=O).

Azetidine (**10**). M.p. 74.5—75.5 °C (Found: C, 72.8; H, 6.15; N, 14.95. $C_{17}H_{17}N_3O$ requires C, 73.1; H, 6.15, N, 15.05%); $\nu_{max.}$(KBr) 1 660 cm^{-1} (C=O).

Azetidine (**11**). M.p. 152—153 °C (Found: C, 72.75; H, 6.15; N, 14.95. $C_{17}H_{17}N_3O$ requires C, 73.1; H, 6.15; N, 15.05%); $\nu_{max.}$(film) 1 660 cm^{-1} (C=O).

Azetidine (**12**). B.p. 145 °C at 2 mmHg (decomp.); $\nu_{max.}$(film) 1 660 cm^{-1} (C=O); *m/z* (c.i.) 365 ($M^+ + 1$).

Azetidine (**13**). B.p. 145 °C at 2 mmHg (decomp.); $\nu_{max.}$(film) 1 665 cm^{-1} (C=O); *m/z* (c.i.) 265 ($M^+ + 1$).

Azetidine (**14**). B.p. 125 °C at 2 mmHg (decomp.); $\nu_{max.}$(film) 1 660 cm^{-1} (C=O); *m/z* (c.i.) 397 ($M^+ + 1$). The azetidines (**12**)—(**14**) did not give satisfactory microanalytical data since these compounds decomposed on distillation to give the quinoxalin-2-ones (**1b**—**d**).

Azetidine (**15**). M.p. 105—106 °C (Found: C, 74.4; H, 7.2; N, 12.95. $C_{20}H_{23}N_3O$ requires C, 74.7; H, 7.2; N, 13.0%); $\nu_{max.}$(KBr) 1 665 cm^{-1} (C=O).

Azetidine (**16**). B.p. 138 °C at 2 mmHg (decomp.); $\nu_{max.}$(film) 1 660 cm^{-1} (C=O); *m/z* (c.i.) 411 ($M^+ + 1$). This product did not give satisfactory microanalytical data since it decomposed on distillation to give the quinoxalin-2-one (**1e**).

Azetidine (**17**). M.p. 117—118 °C (Found: C, 75.1; H, 7.55; N, 12.5. $C_{21}H_{25}N_3O$ requires C, 75.2; H, 7.5; N, 12.5%); $\nu_{max.}$(KBr) 1 660 cm^{-1} (C=O).

Azetidine (**18**). M.p. 171.5—172.5 °C (Found: C, 83.65; H, 5.75; N, 6.65. $C_{29}H_{24}N_2O$ requires C, 83.6; H, 5.8; N, 6.7%); $\nu_{max.}$(KBr) 1 660 cm^{-1} (C=O).

Azetidine (**19**). M.p. 193.5—195 °C (Found: C, 81.0; H, 6.2; N, 7.7. $C_{24}H_{22}N_2O$ requires C, 81.3; H, 6.25; N, 7.9%); $\nu_{max.}$(KBr) 1 665 cm^{-1} (C=O).

Azetidine (**20**). M.p. 147—148 °C (Found: C, 83.4; H, 6.1; N, 6.45. $C_{30}H_{26}N_2O$ requires C, 83.7; H, 6.1; N, 6.45%); $\nu_{max.}$(KBr) 1 665 cm^{-1} (C=O).

Azetidine (**21**). M.p. 156.5—157.5 °C (Found: C, 83.35; H, 5.8; N, 6.65. $C_{29}H_{24}N_2O$ requires C, 83.6; H, 5.8; N, 6.7%); $\nu_{max.}$(KBr) 1 685 cm^{-1} (C=O).

Azetidine (**22**). M.p. 169—170 °C (Found: C, 77.5; H, 5.6; N, 12.15. $C_{22}H_{19}N_3O$ requires C, 77.4; H, 5.6; N, 12.3%); $\nu_{max.}$(KBr) 1 680 cm^{-1} (C=O).

Azetidine (**23**). M.p. 168.5—169.5 °C (Found: C, 80.7; H, 5.6; N, 4.05. $C_{23}H_{19}NO_2$ requires C, 80.9; H, 5.6; N, 4.1%); $\nu_{max.}$(KBr) 1 775 cm^{-1} (C=O).

Azetidine (**24a**). M.p. 81.5—82 °C (Found: C, 77.6; H, 6.1; N, 4.95. $C_{18}H_{17}NO_2$ requires C, 77.4; H, 6.15; N, 5.0%); $\nu_{max.}$(KBr) 1 770 cm^{-1} (C=O).

Azetidine (**24b**). B.p. 135 °C at 2 mmHg (Found: C, 77.25; H, 6.3; N, 4.9. $C_{18}H_{17}NO_2$ requires C, 77.4; H, 6.15; N, 5.0%); $\nu_{max.}$(film) 1 760 cm^{-1} (C=O).

Azetidine (**25**). M.p. 72—73 °C (Found: C, 76.9; H, 5.7; N, 5.2. $C_{17}H_{15}NO_2$ requires C, 76.95; H, 5.7; N, 5.25%); $\nu_{max.}$(KBr) 1 760 cm^{-1} (C=O).

Azetidine (**26**). M.p. 117.5—118 °C (Found: C, 81.35; H, 6.55; N, 3.6. $C_{26}H_{25}NO_2$ requires C, 81.45; H, 6.55; N, 3.65%); $\nu_{max.}$(KBr) 1 775 cm^{-1} (C=O).

Azetidine (**27**). M.p. 126—127 °C (Found: C, 81.35; H, 6.85; N, 3.5. $C_{27}H_{27}NO_2$ requires C, 81.6; H, 6.85; N, 3.5%); $\nu_{max.}$(KBr) 1 775 cm^{-1} (C=O).

Azetidine (**28**). M.p. 166—166.5 °C (Found: C, 83.55; H, 5.25; N, 3.4. $C_{28}H_{21}NO_2$ requires C, 83.35; H, 5.25; N, 3.45%); $\nu_{max.}$(KBr) 1 775 cm^{-1} (C=O).

Sensitization.—A solution of the quinoxalin-2-one (**1a**) (200 mg) and styrene (**3c**) (2 mol equiv.) in benzene (70 ml) in the presence of *m*-methoxyacetophenone (in such a ratio that the sensitizer absorbs >95% of the incident light) was irradiated at 313 nm under the same conditions to those described above. Work-up gave the azetidine (**6**) along with the starting quinoxalin-2-one (**1a**).

Quenching.—A solution of the quinoxalin-2-one (**1a**) (200 mg) and styrene (**3c**) (2 mol equiv.) in benzene (70 ml) in the presence of *trans*-stilbene (10 mol equiv.) was irradiated at 366 nm under the same conditions. Work-up gave the azetidine (**6**) together with (**1a**).

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