Photochemical Reductive Dimerization of Quinoxalin-2-ones and 1,4-Benzoxazin-2-one

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Irradiation of the quinoxalin-2-ones (**1a—d**) in the presence of amine gave the quinoxalin-2-one reductive dimers (**2a—d**), while irradiation of the 1,4-benzoxazin-2-one (**4**) under similar conditions gave two stereoisomeric reductive dimers [(**5a**) and (**5b**)].

The photochemistry of the C=N double bond has attracted much attention in recent years; however it has not developed as rapidly as that of carbonyl compounds.[1] 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. Swenton *et al.*[2] and Wamhoff *et al.*[3] have reported that irradiation of the N=C–C=O chromophore† of 1,3-dimethyl-6-azauracil results

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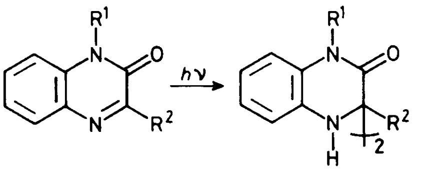
† Ketimines (C=N–C=O), aza-analogues of α,β-unsaturated ketones, have been shown to undergo photoreductions, hydrogen abstractions, and (2 + 2) photocycloadditions (ref. 1).

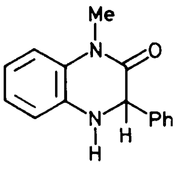
Table 1. Yield of the reductive dimers (**2**).

Quinoxalin-2-one (**1**)	Amine	Solvent	Irradiation time/h	Yield (%)[b] Dimer (**2**)	Yield (%)[b] Recovered (**1**)
a	—	Me_2CHOH	15	4	93
	—	MeOH	15	—	*ca.* 100
	—	C_6H_6	15	10	70
	Et_3N (7.5)[a]	C_6H_6	5	49	43
	Et_3N	MeOH	5	79	21
	Et_3N	MeCN	5	62	34
	$PhNMe_2$ (7.1)	C_6H_6	15	50	30
	Et_2NH (8.01)	C_6H_6	15	40	15
	$PrNH_2$ (8.78)	C_6H_6	15	14	60
	Bu^tNH_2 (8.64)	C_6H_6	15	10	70
b	—	C_6H_6	15	16	80
	Et_3N	C_6H_6	15	68	trace
c	—	C_6H_6	15	trace	60
	Et_3N	C_6H_6	15	36	43
d	—	C_6H_6	15	trace	99
	Et_3N	C_6H_6	15	22	40
e	—	C_6H_6	15	—	*ca.* 100
	Et_3N	C_6H_6	15	—	trace [79.90 (**3**)[c]]

[a] Ionization potential given in parentheses, D. W. Turner, 'Advances in Physical Organic Chemistry,' ed. V. Gold, Academic Press, London, 1966, vol. 4, p.47. [b] Isolated yield. [c] Reduced product.

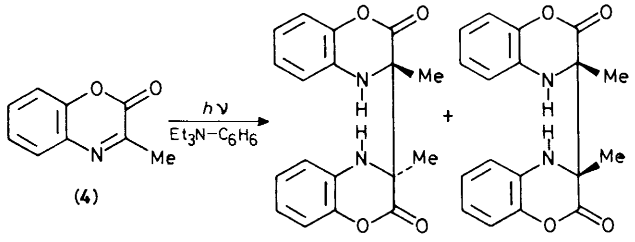


(1) (2)



(3)

a; $R^1 = Me$, $R^2 = Me$
b; $R^1 = Et$, $R^2 = Me$
c; $R^1 = Me$, $R^2 = Bu$
d; $R^1 = Me$, $R^2 = Me_2CHCH_2CH_2$
e; $R^1 = Me$, $R^2 = Ph$



(4) (5a) (5b)

in (2 + 2) photocyloaddition of olefins to the C=N double bond. We have also found that the quinoxalin-2-ones (**1**) undergo (2 + 2) photocycloaddition with electron-deficient olefins to give azetidine derivatives.[4] These photocycloadditions proceeded with high regiospecificity. However, oxazinone failed to undergo (2 + 2) photocycloaddition with olefins, but on carrying out the irradiation in propan-2-ol dimers were obtained.[5] The formation of reductive dimers was ascribed to hydrogen abstraction from the solvent by the low-lying n-π* triplet state of oxazinone. We report here the photochemical reductive dimerization of the quinoxalin-2-ones (**1**) and the 1,4-benzoxazin-2-one (**4**) in the presence of amine.

Irradiation of 1,3-dimethylquinoxalin-2-one (**1a**) in propan-2-ol in a Pyrex vessel with a high-pressure mercury lamp under nitrogen for 15 h at room temperature afforded the reductive dimer (**2a**) (4% yield) and unchanged starting material (**1a**) (93% yield)‡ [(**2a**) m.p. 199—200 °C; $\lambda_{max.}$ (EtOH) (ε) 214 (42 300), 227 (46 200), and 314 (7 300); ν(KBr) 3340, 1640, 1600, 1505, 1380, 1265, and 745 cm^{-1}; $\delta_H(CDCl_3)$ 1.52 (s, 6H), 3.35 (s, 6H), and 6.62—7.01 (m, 10H); $\delta_C(CDCl_3)$ 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 ionization) 351 (QM^+)]. The ^{13}C n.m.r. spectra of (**2a**) showed a quaternary carbon atom at δ 63.8 (s) and no imino carbon signal,§ so we concluded that this compound is joined at the C-3 positions. The reductive dimer (**2a**) was also obtained in 10% yield when (**1a**) was irradiated in benzene; but in the presence of excess of triethylamine irradiation for 5 h gave (**2a**) in 49% yield. Similarly, irradiation of the quinoxalin-2-ones (**1b**—**d**) in the presence of triethylamine gave the reductive dimers (**2b**—**d**) in 22—68% yields. The reductive dimers (**2b**—**d**) were also obtained, though in rather low yields, when the photoreaction was carried out in benzene. Irradiation of 1-methyl-3-phenylquinoxalin-2-one (**1e**) in benzene in the presence of triethylamine gave the reduced product (**3**) in high yield and the reductive dimer was not detected. Irradiation of the 1,4-benzoxazin-2-one (**4**) in benzene in the presence of triethylamine gave two stereoisomeric reductive dimers, (**5a**) and (**5b**), in 46 and 33% yields, respectively. Intramolecular hydrogen abstraction products involving the carbonyl oxygen or imino nitrogen atom were not detected when the quinoxalin-2-ones (**1c**, **d**), which possess hydrogen atoms which could be abstracted in the side chain at C-3, were irradiated in benzene. The photoreaction of (**1a**) was examined in the presence of various amines, and in various solvents in the presence of triethylamine. The results are summarized in Table 1 and they show that the reductive dimer (**2a**) is formed in higher yields in polar solvents than in non-polar solvents, and that amines with

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‡ Satisfactory elemental analyses were obtained for all new compounds.

§ ^{13}C.N.m.r. spectrum of (**1a**); $\delta_C(CDCl_3)$ 21.5 (q), 28.9 (q), 113.5 (d), 123.5 (d), 129.3 (d), 129.4 (d), 132.5 (s), 133.1 (s), 155.1 (s), and 158.2 (s).

lower ionization potential are more favourable for the formation of the reductive dimer. The mechanism of this photoreaction is not clear at present, but we tentatively postulate that the formation of the reductive dimers (**2**) 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 α-hydrogen atom of the amine and formation of radicals.[6]

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