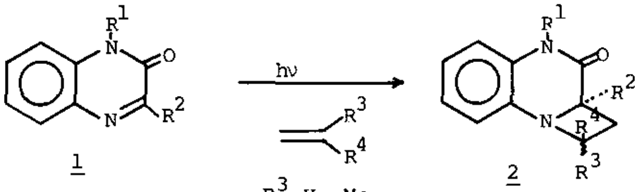
HETEROCYCLES, Vol. 23, No. 1, 1985

PHOTOCHEMICAL REACTIONS OF QUINOXALIN-2-THIONES

Takehiko Nishio and Yoshimori Omote
Department of Chemistry, University of Tsukuba,
Sakura-mura, Niihari-gun, Ibaraki, 305, Japan

Abstract —— In contrast with their oxo-analogues (1), quinoxalin-2-thiones (3) undergo photo-induced addition to cyclohexene (4a), methacrylonitrile (4b), and methyl methacrylate (4c) to give 2-substituted quinoxalines (6-14).

It has been demonstrated that a variety of thiones can undergo photo-induced addition to various olefins.[1,2] However, the photochemical properties of thioamides[3] and thioimides[4] have been scarcely studied. Thus, we report on investigation of the photochemical reactions of quinoxalin-2-thiones (3) which illustrates an example of the dramatic difference in the photochemical behaviors of carbonyl[5] and thiocarbonyl compounds. Recently, we reported that on irradiation quinoxalin-2-ones (1) reacted regioselectively with electron-deficient olefins to afford the 1:1-adducts of C=N double bond of 1 and olefin, azetidine derivatives (2).[5]



1

2

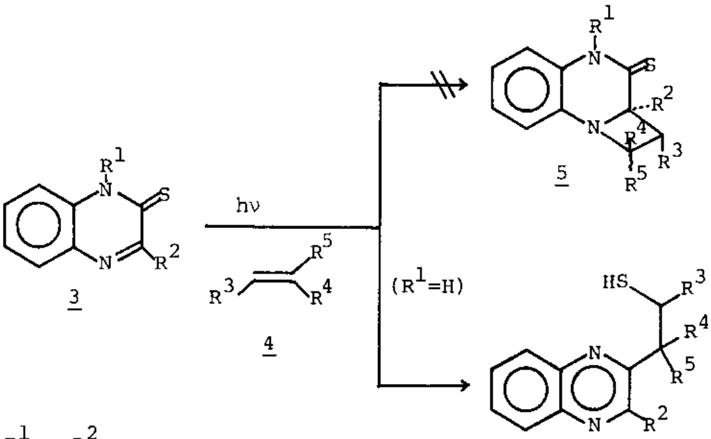
R^1, R^2=H, Me, Ph

R^3=H, Me

R^4=CN, CO_2Me, $CO_2CH=CH_2$

Irradiation of 3-methylquinoxalin-2-thione [3a; λ_{max}(EtOH) 218 (ε=16400), 275 (9800), and 392 nm (6200)] (200 mg) in ethylene glycol dimethyl ether (50 ml) in the presence of large excess cyclohexene (∿1 ml) with a high pressure mercury lamp (Eikosha EHB-300 W) through a Pyrex filter under nitrogen for 10 h gave 2-(2-mercaptocyclohexyl)-3-methylquinoxaline (6) [mp 101-102°C; λ_{max}(EtOH) 205 (ε=35000), 237 (30500), 312 (sh, 7000), and 318 nm (8300); ν_{max}(KBr) 2555, 1557, 1485, 1100, and 763 cm^{-1};

δ_H($CDCl_3$) 1.25-2.63 (m, 8H), 1.60 (d, 1H, J=5.9 Hz), 2.75 (s, 3H), 3.39-3.73 (m, 2H), 7.45-7.71 (m, 2H), and 7.88-8.13 (m, 2H); δ_C($CDCl_3$) 21.1(t), 22.5(q), 24.6(t), 25.2(t), 34.5(t), 40.0(d), 45.3(d), 128.0(d), 128.5(d), 128.9(d), 140.3(s),140.4 (s), 152.3(s), and 156.9(s); m/e (chemical ionozation) 259 (QM$^+$)] in 48% isolated yield, along with the unchanged thione (3a). The structure of 6 was elucidated on the basis of spectral properties and elemental analysis.[6] Oguchi and his co-workers described that irradiation of a mixture of 3-methylquinoxalin-2-thione (3a) and cyclohexene (4a) gave 2-cyclohexylthio-3-methylquinoxaline (16) and 2-(3-methylquinoxalyl)disulfide (17) via radical mechanism.[7] The ^{13}C-n.m.r. spectrum of 6 showed two tertiary carbons at δ 40.0(d) and 45.3(d) and four secondary carbons at δ 21.1(t), 24.6(t), 25.2(t), and 34.5(t) and no thiocarbonyl carbon signal,[8] so we concluded that the photoproduct thus obtained is 2-(2-mercaptocyclohexyl)-3-methylquinoxaline (6). Similarly, irradiation of the quinoxalin-2-thiones (3b-c) in the presence of cyclohexene (4a) gave the corresponding 2-substituted quinoxaline (7-8).

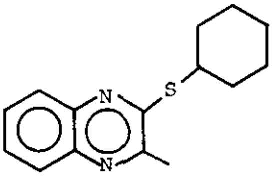


3 4 5 6-14

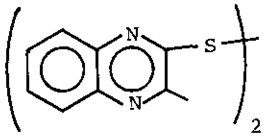
	R1	R2
3a	H	Me
3b	H	Ph
3c	H	H
3d	Me	Me

	R3	R4	R5
4a	$-(CH_2)_4-$		H
4b	H	Me	CN
4c	H	Me	CO_2Me

Furthermore, 2-substituted quinoxalines (9-14) were obtained in 35-63% yields when the quinoxalin-2-thione (3a-c) was irradiated in the presence of electron-deficient olefins such as methacrylonitrile (4b) and methyl methacrylate (4c) under the same conditions as described above. On the other hand, 1,3-dimethylquinoxalin-2-thione



16



17

(3d) was inert to the photolysis in ethylene glycol dimethyl ether in the presence of olefins (4a-c) under the similar conditions

Table. Yield of the 2-Substituted Quinoxalines (6-14)

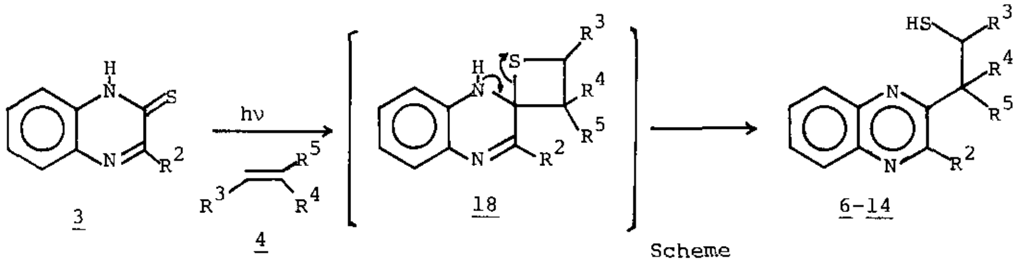
					Yield (%)[a]		
Compd.	R^2	R^3	R^4	R^5	Product	Recovered (3)	
6	Me	$-(CH_2)_4-$		H	48	5	
7	Ph	$-(CH_2)_4-$		H	50	∿0	
8	H	$-(CH_2)_4-$		H	43	25	(15)[b] 32
9	Me	H	Me	CN	54	23	
10	Ph	H	Me	CN	35	trace	
11	H	H	Me	CN	35	trace	
12	Me	H	Me	CO_2Me	59	trace	
13	Ph	H	Me	CO_2Me	35	15	
14	H	H	Me	CO_2Me	63	trace	

[a] Isolated yield. [b] The yield of 3-phenylquinoxalin-2-one (15)

A reasonable mechanism for the formation of 2-substituted quinoxalines (6-14) is presented in Scheme, which the thietane (18), formed initially by the photochemical [2+2]cycloaddition of thiocarbonyl to olefin,[9] undergoes aromatization to give the final products (6-14). This ready mode of carbon-carbon bond formation described here would provide a convenient method for the preparation of the 2-substituted quinoxalines.

REFERENCES AND FOOTNOTES

1. P.de Mayo, *Acc. Chem. Res.*, 1976, **9**, 52
2. A. Ohno, "Organic Chemistry of Sulfur", ed. S. Oae, Plenum Press, New York, 1977, p. 189.



Scheme

3. a) C. Marazono, J.L. Fourrey, and B.C. Das, J. Chem. Soc. Chem. Commun., 1977, 742.

b) P.de Mayo, L.K. Sydnes, and G. Wenska, J. Org. Chem., 1980, 45, 1549.

c) M. Machida, K. Oda, and Y. Kanaoka, Tetrahedron Lett., 1984, 25, 409.

4. a) J.D. Coyle and P.A. Raply, ibid., 1984, 25, 2247.

b) Y. Kanaoka, M. Hasebe, and E. Sato, "Abstract of Symposium on Photochemistry", (Sapporo), 1981, p.79.

c) K. Oda, S. Wakao, M. Machida, Y. Hatanaka, and Y. Kanaoka, ibid., 1981, p. 95.

d) T. Yonezawa, M. Matsumoto, Y. Matumura, and H. Kato, Bull. Chem. Soc. Jpn., 1969, 42, 2323.

e) H. Gotthardt and S. Niebrel, Chem. Ber., 1978, 109, 2871.

f) P. Jouin and J.L. Fourrey, Tetrahedron Lett., 1975, 1329 and references cited therein.

5. T. Nishio, J. Org. Chem., 1984, 49, 827.

6. Satisfactory elemental analyses have been obtained for all new compounds.

7. M. Hoshino, K. Suzuki, and S. Oguchi, Bull. Tokyo Gakugei University, Ser. IV, 1975, 27, 134.

8. ^{13}C-n.m.r. spectrum of 3a; δ_H (DMSO-D_6) 24.7(q), 115.7(d), 125.6(d), 128.0(d), 130.1(d), 131.6(s), 134.9(s), 161.4(s), and 175.1(s).

9. The regiochemistry of photocycloaddition is in accord with the previously published works in thioamide[3a] and thioimide[4b,f] photochemistry.

Received, 17th September, 1984