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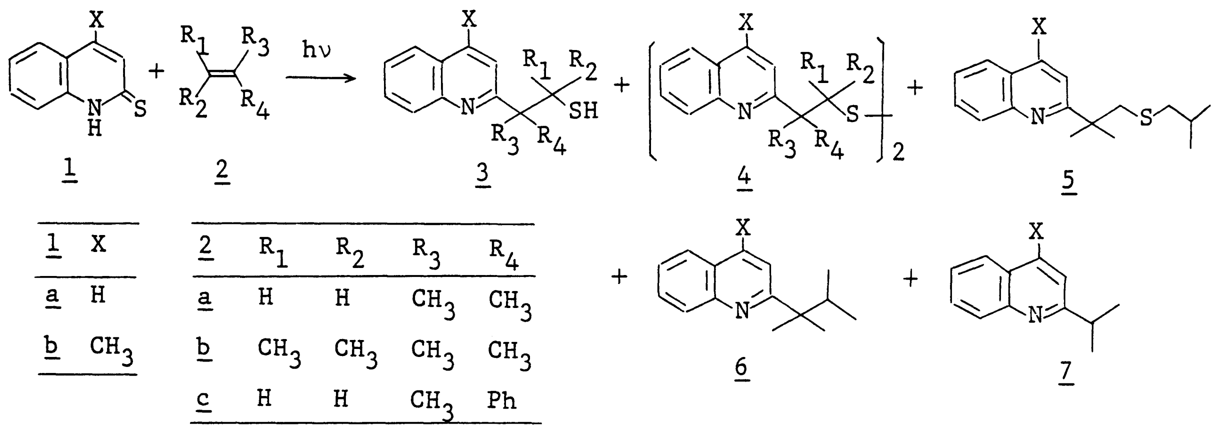
Photoaddition of Olefins to Quinolin-, Isoquinolin-, and Phthalazin-thione Systems[†,1)]

Eisuke SATO, Yoshiya IKEDA, and Yuichi KANAOKA*
Faculty of Pharmaceutical Sciences, Hokkaido University,
Kita-12, Nishi-6, Kitaku, Sapporo 060

Irradiation of quinolin-2-, isoquinolin-1-, and phthalazin-1-thiones with olefins afforded photoaddition products: substituted quinolines, isoquinolines and phthalazines at the thiocarbonyl carbon. A new addition-cyclization was found producing tricyclic thiopyrano-isoquinolines and -phthalazines.

In an extention of our systematic studies of the photochemistry of nitrogen-carbonyl$^{2)}$ and -thiocarbonyl$^{3)}$ systems, we are exploring photochemical behavior of nitrogen-heteroaromatic thione systems.$^{1)}$ Our initial work showed that the major photoreactions of 2-thiopyridone and 2-thiopyrimidone, the simplest members of the family, in the presence of olefins, are [2+2]addition predominantly localized at the C=S bond.$^{4)}$ In this paper we report photochemical behavior of the bicyclic homologues of such heteroaromatic thione systems as quinolin-2-thione 1, isoquinolin-1-thione 14a, and phthalazin-1-thione 14b.

Irradiation of quinolin-2-thione (1) (1.0 mmol) in acetonitrile in the presence of excess olefins (2) (10 mmol) with a 500 W high-pressure mercury lamp through a Pyrex filter for 0.75-3 h under argon atmosphere gave a series of 2-substituted quinolines (3-7), whose structures were determined as shown in Scheme 1 based on their spectral and analytical data, and the results are listed in Table 1.



1	X
a	H
b	CH_3

2	R_1	R_2	R_3	R_4
a	H	H	CH_3	CH_3
b	CH_3	CH_3	CH_3	CH_3
c	H	H	CH_3	Ph

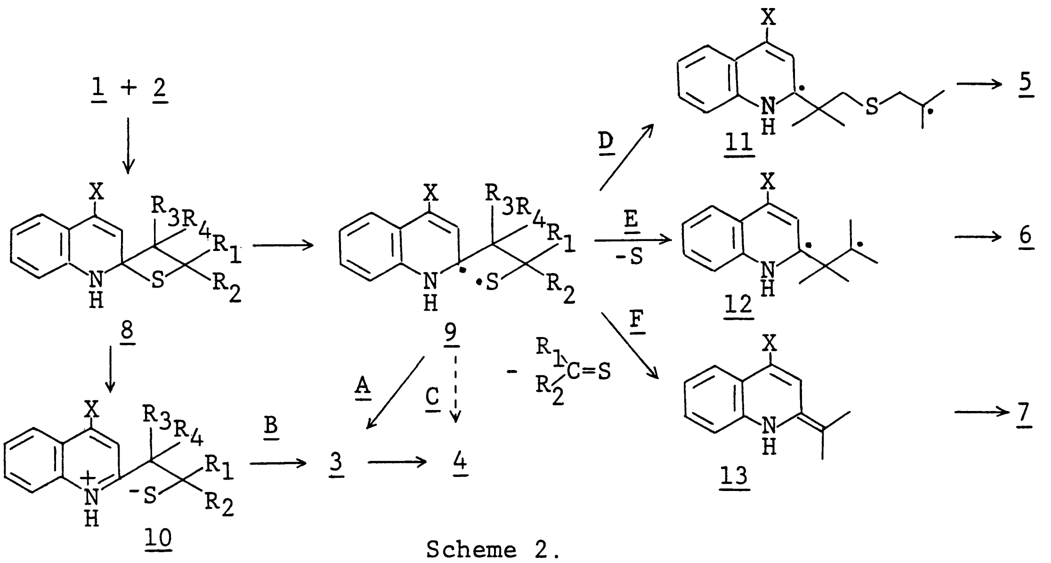
Scheme 1.

[†] This contribution is dedicated to Professor Teruaki Mukaiyama on the occasion of his 60th birthday.

Table 1. Yields of Photoproducts

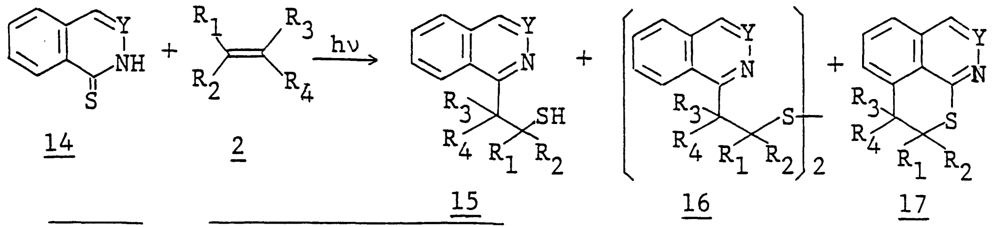
Thione (mmol)	Olefin (mmol)	Time h	Product yield / % 3	4	5	6	7
1a(1)	2a(10)	2	9	14	5	-	-
1a(1)	2b(10)	3	27	14	-	8	8
1a(1)	2c(5)	3/4	20	24	-	-	-
1b(1)	2a(10)	2	15	24	10	-	-
1b(1)	2b(10)	3	33	7	-	7	trace

Formation of all the photoproducts may be interpreted in terms of involvement of a thiyl biradical 9 derived from the common thietane intermediate 8 by secondary photolysis, but heterolytic cleavage of 8 involving a mercaptide 10 accompanied with proton transfer would also be possible. Hydrogen abstraction by the thiyl radical 9 (path A) and/or proton transfer from nitrogen to sulfur (path B) may give sulfide products 3. Air oxidation of 3 affords disulfide products 4, though a pathway (C) from 9 can not be ruled out. Addition of a second molecule of isobutene to 9a, in which the thiyl radical center is less hindered (R_1=R_2=H), affords "two-fold addition" products 5⁴⁾ (path D). Desulfurized alkylated products (6,7), which were not observed in the case of the monocyclic pyridinthiones and pyrimidinthiones,4) probably arise from unimolecular collapse of 9b either by desulfurization (path E to 6) or elimination of thioacetone (path F to 7) (Scheme 2).5)



Scheme 2.

Next, isoquinolin-1-thione (14a), an isomeric benzopyridin-2-thione of (1), was subjected to the similar photolysis in the presence of olefins (2a-e). In addition to the thiol 15 and sulfide 16, unexpected tricyclic products 17 were obtained in the most cases (Scheme 3 and Table 2).6) Again the intermediacy of a thietane 18 is postulated, from which a normal photolysis (A) forms a thiyl radical 19 leading to 15 and 16 (Scheme 4). The formation of 8,9-dihydrothiopyrano[4,3,2-ij]isoquinoline 17 is interesting from a synthetic view point, and may be explained by an alternative photolysis (B) to form a "non-thiyl" biradical 20, whose side chain radical end attacks the neighboring peri-position of the benzene ring (21) forming a new C-C bond, followed by oxidative aromatization (22→17).$^{7)}$



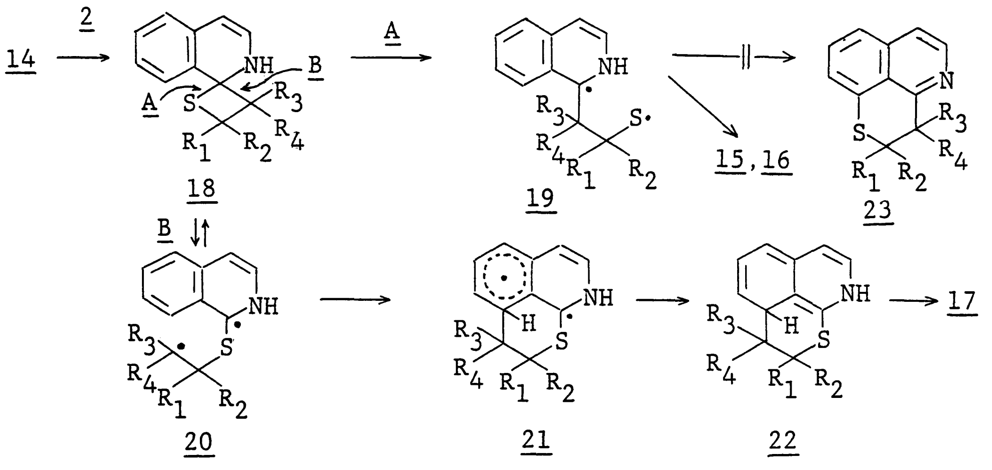
14	Y
a	CH
b	N

2	R_1	R_2	R_3	R_4
a	H	H	CH_3	CH_3
b	CH_3	CH_3	CH_3	CH_3
d	H	CH_3	CH_3	CH_3
e	H	H	CH_3	CN

Scheme 3.

Table 2. Yields of Photoproducts

Thione (mmol)	Olefin (mmol)	Time h	Product yield / % 15	16	17
14a(1)	2a(10)	2	64	-	9
14a(1)	2b(10)	2	-	17	26
14a(1)	2d(10)	2	-	-	37
14a(1)	2e(10)	2	68	-	-
14b(1)	2a(10)	2	-	-	51
14b(1)	2d(10)	2	-	-	25



Scheme 4.

To see further applicability of this new photo-addition-cyclization, irradiation of phthalazin-1-thione (14b) was performed in the presence of olefins (2a-d). As expected, 8,8-dimethyl-, and 8,8,9-trimethyl-8,9-dihydrothiopyrano[4,3,2-ij]phthalazines (17ba and 17bd) were obtained, respectively, as a sole product.

The reactive sites of the excited states of aza-aromatic carbonyl systems such as 2-quinolone and 1-isoquinolone, including the dimerization[8)] and the olefin-addition,[9)] are well known to be the 3,4-double bond within the aza-aromatic ring. By contrast, photoaddition of olefins to the bicyclic aza-aromatic thione systems occurs predominantly at the C=S group, leading to various aza-aromatics with substituents introduced at the thiocarbonyl carbon. Bicyclic structures may impart more resonance stabilization to the relevant intermediate biradicals than in the monocyclic counterparts, and one interesting variation is the novel addition-cyclization reaction involving the peri-position of the azanaphthalenes 14 leading to new tricyclic aza-thio systems 17.

References

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2) Y. Kanaoka, Acc. Chem. Res., 11, 407 (1978); H. Takechi, M. Machida, and Y. Kanaoka, Liebigs Ann. Chem., 1986, 859, and papers cited therein.
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4) Y. Kanaoka, M. Hasebe, T. Nishio, Y. Ikeda, and E. Sato, submitted.
5) Apparently extended conjugation of the bicyclic nature of the radical intermediate 9 favors these courses.
6) Spectral data and elemental analyses of 17aa: MS m/z 215 (M^+), 200 (base); NMR ($CDCl_3$): δ 1.54 (6H, s, CH_3), 3.10 (2H, s, CH_2), 7.54-7.42 (4H, m, aromatic), 8.45 (1H, d, J=6 Hz, aromatic); Found: C, 72.60; H, 6.06; N, 6.41; S, 15.01%. Calcd for $C_{13}H_{13}NS$: C, 72.51; H, 6.09; N, 6.51; S, 14.89%.
7) It is worth noting that, if this mechanism is correct, the thiyl radical 19 leads to none of the isomeric thio heterocycles 23.
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