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Photoaddition of Olefins to Quinolin-, Isoquinolin-, and Phthalazin-thione Systems<sup>+,1)</sup>

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Irradiation of quinolin-2-, isoquinolin-1-, and phthalazin-1thiones 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 nitrogencarbony1<sup>2)</sup> and -thiocarbony1<sup>3)</sup> systems, we are exploring photochemical behavior of nitrogen-heteroaromatic thione systems.<sup>1)</sup> 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.<sup>4)</sup> In this paper we report photochemical behavior of the bicyclic homologues of such heteroaromatic thione systems as quinolin-2-thione 1, isoquinolin-1-thione <u>14a</u>, and phthalazin-1-thione <u>14b</u>.

Irradiation of quinolin-2-thione (<u>1</u>) (1.0 mmol) in acetonitrile in the presence of excess olefins (<u>2</u>) (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 (<u>3-7</u>), whose structures were determined as shown in Scheme 1 based on their spectral and analytical data, and the results are listed in Table 1.





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

Table 1. Yields of Photoproducts

Formation of all the photoproducts may be interpreted in terms of involvement of a thiyl biradical <u>9</u> derived from the common thietane intermediate <u>8</u> by secondary photolysis, but heterolytic cleavage of <u>8</u> involving a mercaptide <u>10</u> accompanied with proton transfer would also be possible. Hydrogen abstraction by the thiyl radical <u>9</u> (path A) and/or proton transfer from nitrogen to sulfur (path B) may give sulfide products <u>3</u>. Air oxidation of <u>3</u> affords disulfide products <u>4</u>, though a pathway (C) from <u>9</u> can not be ruled out. Addition of a second molecule of isobutene to <u>9a</u>, in which the thiyl radical center is less hindered (R<sub>1</sub>=R<sub>2</sub>=H), affords "two-fold addition" products <u>5</u><sup>4</sup> (path D). Desulfurized alkylated products (<u>6</u>,<u>7</u>), which were not observed in the case of the monocyclic pyridinthiones and pyrimidinthiones,<sup>4</sup> probably arise from unimolecular collapse of <u>9b</u> either by desulfurization (path E to <u>6</u>) or elimination of thioacetone (path F to <u>7</u>) (Scheme 2).<sup>5</sup>



Next, isoquinolin-1-thione (<u>14a</u>), an isomeric benzopyridin-2-thione of (<u>1</u>), was subjected to the similar photolysis in the presence of olefins (<u>2a-e</u>). In addition to the thiol <u>15</u> and sulfide <u>16</u>, unexpected tricyclic products <u>17</u> were obtained in the most cases (Scheme 3 and Table 2).<sup>6)</sup> Again the intermediacy of a thietane <u>18</u> is postulated, from which a normal photolysis (A) forms a thiyl radical <u>19</u> leading to <u>15</u> and <u>16</u> (Scheme 4). The formation of 8,9-dihydrothiopyrano[4,3,2ij]isoquinoline <u>17</u> 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 <u>peri</u>-position of the benzene ring (<u>21</u>) forming a new C-C bond, followed by oxidative aromatization ( $\underline{22} \rightarrow \underline{17}$ ).<sup>7</sup>



Table 2. Yields of Photoproducts

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



Scheme 4.

To see further applicability of this new photo-addition-cyclization, irradiation of phthalazin-1-thione (<u>14b</u>) was performed in the presence of olefins (<u>2a-d</u>). As expected, 8,8-dimethyl-, and 8,8,9-trimethyl-8,9-dihydrothiopyrano [4,3,2-ij]phthalazines (<u>17ba</u> and <u>17bd</u>) 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<sup>8)</sup> and the olefin-addition,<sup>9)</sup> 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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- 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 <u>9</u> favors these courses.
- 6) Spectral data and elemental analyses of <u>17aa</u>: MS m/z 215 (M<sup>+</sup>), 200 (base); NMR (CDCl<sub>3</sub>): δ 1.54 (6H, s, CH<sub>3</sub>), 3.10 (2H, s, CH<sub>2</sub>), 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<sub>13</sub>H<sub>13</sub>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 <u>19</u> leads to none of the isomeric thio heterocycles 23.
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