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Received June 3, 1996

Photochemical reactions of 1-methyl-4,6-diaryl-2(1*H*)pyrimidinones **1a-b** in the presence of thiols **2** are described. Irradiation of 1-methyl-4,6-diaryl-2(1*H*)-pyrimidinones **1a-b** in benzene in the presence of thiols **2** gave the unexpected 2:1-adducts, 3-methyl-4,6-diaryl-5-arylthio-6-(1'-methyl-4',6'-diaryldihydropyrimidin-2-on)yl-1,3-diazabicyclo[2.2.0]hexan-2-ones **3-6**, of **1** and **2**, whereas irradiation of **1a-b** alone in benzene resulted in recovery of the unchanged **1a-b**.

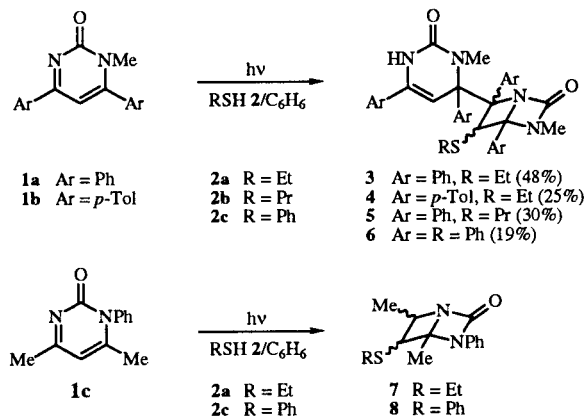
*J. Heterocyclic Chem.*, **34**, 143 (1997).

In course of our studies on the photochemical reactivities of cyclic conjugated nitrogen-carbonyl systems such as 2(1*H*)-pyrimidinones [1-9] and 2(1*H*)-pyrazinones [10-14], we found that upon irradiation 2(1*H*)-pyrimidinones undergo various types of photochemical reactions depending on the substituents in the 1-, 4-, and 6-positions [1-9]. For examples, 1,4,6-trisubstituted 2(1*H*)pyrimidinones undergo valence isomerization to yield 1,3-diazabicyclo[2.2.0]hex-5-ene-2-ones (Dewar pyrimidinones) [2-3]. Irradiation of *N*-aryl-2(1*H*)-pyrimidinones gave arylimine derivatives [4-6], which are produced by initial Norrish-type I cleavage of ArN-CO bond of 2(1*H*)-pyrimidinones; in alcohols 1-alkoxycarbonylamino-3-arylimino-1-propenes derivatives [4-5] and in the presence of amines 1-(*N'*-alkylureido)-3-arylimino-1-propenes [6] were produced. These are analogous to conjugated cyclohexanones [15] and 2-pyrones [16]. Inter- and intramolecular hydrogen abstraction reactions by nitrogen of the imino group of 2(1*H*)-pyrimidinones were also observed [7-9]. In this context, we report here the photochemical reactions of 1-methyl-4,6-diaryl-2(1*H*)-pyrimidinones **1** in the presence of thiols **2**, which formed the unexpected 2:1 adducts **3-6** of **1** and **2**.

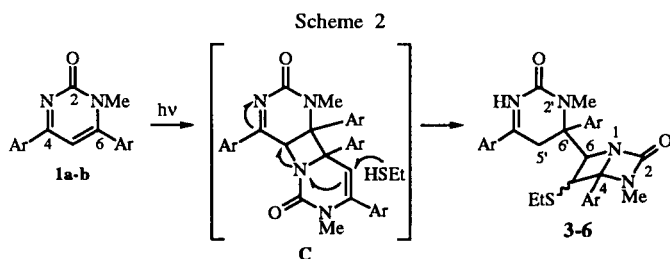
Photolysis of 1-methyl-4,6-diaryl-2(1*H*)-pyrimidinones **1** alone in benzene or methanol resulted in recovery of the starting materials **1** [7]. However, irradiation of 1-methyl-4,6-diphenyl-2(1*H*)-pyrimidinone **1a** in benzene in the presence of ethanethiol **2a** in a Pyrex vessel with a high-pressure mercury lamp under argon for 15 hours at room temperature gave a complex mixture of products from which a white crystalline solid, mp 175-176°, was isolated when the reaction mixture was purified through a silica gel column chromatography. This compound had the molecular formula C<sub>36</sub>H<sub>34</sub>N<sub>4</sub>O<sub>2</sub>S, which was equivalent to the 2:1 adduct **3** of the 2(1*H*)-pyrimidinone **1a** and ethanethiol **2a**. The ir spectrum of **3** showed absorptions at 3400 and 3300 cm<sup>-1</sup> due to amino group, 1785 cm<sup>-1</sup> due to typical of Dewar pyrimidinones [2,17], and 1680 and 1660 cm<sup>-1</sup> due to amide carbonyls. <sup>1</sup>H nmr spectrum of **3** displayed a singlet at δ 4.92 (1H) and a broad singlet at δ 5.23 (2H, 1H disappeared by treatment of deuterium oxide), which were assigned to methine at C-5 and olefinic at C-5' and amino protons, respectively. <sup>13</sup>C nmr spectrum of **3**

showed a olefinic carbon at δ 105.1 (d, C-5'), three quaternary carbons at δ 68.5 (s, C-6 or C-6'), 77.7 (s, C-6' or C-6) and 80.9 (s, C-4), and two ureido carbonyl carbons at δ 154.2 (s), and 159.9 (s). Thus, the photoproduct was characterized as 3-methyl-4,6-diphenyl-5-ethylthio-6-(1'-methyl-4',6'-diphenyldihydropyrimidin-2-on)yl-1,3-diazabicyclo[2.2.0]hexan-2-one **3**. Similarly, irradiation of 1-methyl-4,6-diaryl-2(1*H*)pyrimidinones **1a-b** in benzene in the presence of thiols **2** under the same conditions as described above gave the corresponding 2:1 adducts **4-6** of **1a-b** and **2** in 19-30% yields. The structure of 2:1 adducts **4-6** was elucidated on the basis of their spectroscopic properties and elemental analyses (see Experimental section).

Scheme 1



On the other hand, irradiation of 1-phenyl-4,6-dimethyl-2(1*H*)pyrimidinone **1c** in benzene in the presence of thiols **2a,c** gave the 1:1 adduct, 5-arylthio-4,6-dimethyl-3-phenyl-1,3-diazabicyclo[2.2.0]hexan-2-ones **7-8** [4] of Dewar pyrimidinone, which was formed by photochemical electrocyclozation of **1c** [2], and thiols **2**. Although the mechanism for the formation of 2:1 adducts **3-6** of the 2(1*H*)-pyrimidinones **1** and thiols **2** is unclear at present, we postulate the reaction path as shown in Scheme 2 that involves [2π + 2π] photodimerization between N3-C4 and C5-C6 bonds leading to cyclobutane **C**, which produces the final product by the addition of thiol followed by ring opening of cyclobutane.



## EXPERIMENTAL

Melting points were measured with Yanaco micro melting point apparatus (MP-3J) and are uncorrected. The ir spectra were recorded on a Hitachi 260-30 spectrophotometer (in potassium bromide and are in  $\text{cm}^{-1}$ ). The uv spectra were recorded on a JASCO UVDEC-505 spectrophotometer (in ethanol and in nm).  $^1\text{H}$  and  $^{13}\text{C}$  nmr spectra were run on a JEOL FX-100 spectrometer (100 MHz) in deuteriochloroform using TMS as an internal standard ( $\delta$  in ppm, J in Hz).

General Procedure for the Photochemical Reactions of the 2(1H)-Pyrimidinones **1** in the Presence of Thiols **2**.

A solution of the pyrimidinone **1** (1 mmole) in benzene (50 ml) in the presence of an excess of the thiol (*ca* 0.5 ml) was irradiated in a Pyrex vessel with a high-pressure mercury lamp (300 W) under an argon atmosphere for 15 hours at room temperature. After removal of the solvent, the residue was chromatographed on a silica gel column with benzene/ethyl acetate (19:1) as eluant to give 5-aralkylthio-6-(pyrimidin-2'-on)yl-1,3-diazabicyclo[2.2.0]hexan-2-ones **3-6**.

3-Methyl-4,6-diphenyl-5-ethylthio-6-(1'-methyl-4',6'-diphenyldihydropyrimidin-2'-on)yl-1,3-diazabicyclo[2.2.0]hexan-2-one (**3**).

This compound had mp 175-176°; uv:  $\lambda$  274 ( $\epsilon$   $6.2 \times 10^3$ ); ir:  $\nu$  3400, 3300 (NH), 1785, 1680, 1660 (CO);  $^1\text{H}$  nmr:  $\delta$  1.49 (t, 3H, J = 7.3,  $\text{CH}_3$ ), 2.51 (s, 3H, NMe), 2.79 (s, 3H, NMe), 2.89 (q, 2H, J = 7.3,  $\text{CH}_2$ ), 4.92 (s, 1H, CH), 5.23 (br s, 2H, NH and =CH, 1H disappeared by addition of deuterium oxide), 6.45-6.55 (2H, m, aromatic), 6.99-7.35 (16H, m, aromatic), 7.48-7.61 (m, 2H, aromatic);  $^{13}\text{C}$  nmr:  $\delta$  14.7 (q,  $\text{CH}_3$ ), 27.8 (q, NMe), 28.5 (t,  $\text{CH}_2$ ), 32.3 (q, NMe), 55.4 (d, CH), 65.8 (s, quaternary C), 77.7 (s, quaternary C), 80.9 (s, quaternary C), 105.1 (d, =CH), 154.2 (s, CO), 159.9 (s, CO) in addition to aromatic carbon peaks.

Anal. Calcd. for  $\text{C}_{36}\text{H}_{34}\text{N}_4\text{O}_2\text{S}$  (586.742): C, 73.69; H, 5.84; N, 9.55. Found: C, 73.31; H, 5.81; N, 9.46.

3-Methyl-4,6-diphenyl-5-propylthio-6-(1'-methyl-4',6'-diphenyldihydropyrimidin-2'-on)yl-1,3-diazabicyclo[2.2.0]hexan-2-one (**4**).

This compound had mp 168-169°; uv:  $\lambda$  275 ( $\epsilon$   $5.9 \times 10^3$ ); ir:  $\nu$  3420, 3300 (NH), 1790, 1680, 1660 (CO);  $^1\text{H}$  nmr:  $\delta$  1.16 (t, 3H, J = 7.3,  $\text{CH}_3$ ), 1.75-1.96 (m, 2H,  $\text{CH}_2$ ), 2.51 (s, 3H, NMe), 2.79 (s, 3H, NMe), 2.84 (t, 2H, J = 7.8,  $\text{CH}_2$ ), 4.98 (s, 1H, CH), 5.23 (br s, 2H, NH and =CH), 6.44-6.53 (m, 2H, aromatic), 7.02-7.36 (m, 16H, aromatic), 7.42-7.60 (m, 2H, aromatic);  $^{13}\text{C}$  nmr:  $\delta$  13.5 (q,  $\text{CH}_3$ ), 23.0 (t,  $\text{CH}_2$ ), 27.8 (q, NMe), 32.3 (q, NMe), 36.5 (t,  $\text{CH}_2$ ), 55.7 (d, CH), 65.7 (s, quaternary C), 77.7 (s, quaternary C), 80.9 (s, quaternary C), 105.0 (d, =CH), 154.0 (s, CO), 159.9 (s, CO) in addition to aromatic carbon peaks.

Anal. Calcd. for  $\text{C}_{37}\text{H}_{36}\text{N}_4\text{O}_2\text{S}$  (600.768): C, 73.97; H, 6.04; N, 9.32. Found: C, 73.58; H, 6.00; N, 9.19.

3-Methyl-4,6-diphenyl-5-phenylthio-6-(1'-methyl-4',6'-diphenyldihydropyrimidin-2'-on)yl-1,3-diazabicyclo[2.2.0]hexan-2-one (**5**).

This compound had mp 167.5-168.5°; uv:  $\lambda$  258 ( $\epsilon$   $1.08 \times 10^4$ ); ir: 3430, 3300 (NH), 1790, 1680, 1660 (sh) (CO).  $^1\text{H}$  nmr:  $\delta$  2.58 (s, 3H, NMe), 2.77 (s, 3H, NMe), 5.23 (br s, 2H, NH and =CH), 5.42 (s, 1H, CH), 6.44-6.53 (m, 2H, aromatic), 7.06-7.68 (m, 23H, aromatic).

Anal. Calcd. for  $\text{C}_{40}\text{H}_{34}\text{N}_4\text{O}_2\text{S}$  (634.782): C, 75.68; H, 5.40; N, 8.64. Found: C, 75.36; H, 5.29; N, 8.73.

3-Methyl-4,6-di-tolyl-5-ethylthio-6-(1'-methyl-4',6'-ditolyldihydropyrimidin-2'-on)yl-1,3-diazabicyclo[2.2.0]hexan-2-one (**6**).

This compound had mp 155-156°; uv:  $\lambda$  220 (sh,  $\epsilon$   $4.07 \times 10^4$ ), 272 ( $\epsilon$   $6.7 \times 10^3$ ); ir:  $\nu$  3420, 3260 (NH), 1785, 1675, 1660 (CO).  $^1\text{H}$  nmr:  $\delta$  1.47 (t, 3H, J = 7.8,  $\text{CH}_3$ ), 2.26 (s, 3H, Me), 2.28 (s, 3H, Me), 2.32 (s, 3H, 2 x Me), 2.50 (s, 3H, NMe), 2.78 (s, 3H, NMe), 2.85 (q, 2H, J = 7.8,  $\text{CH}_2$ ), 4.87 (s, 1H, CH), 5.18 (br s, 2H, NH and =CH), 6.47 (d, 2H, J = 7.8, aromatic), 6.87-7.42 (m, 14H, aromatic).

Anal. Calcd. for  $\text{C}_{40}\text{H}_{42}\text{N}_4\text{O}_2\text{S}$  (642.846): C, 74.73; H, 6.58; N, 8.71. Found: C, 74.55; H, 6.59; N, 8.56.

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