CHEMISTRY LETTERS, pp. 1397-1398, 1983. © The Chemical Society of Japan

PHOTOCHEMICAL REACTIONS OF N-THIOAROYLUREAS AND N-THIOAROYLTHIOUREAS

Hiromu AOYAMA,* Masami SAKAMOTO, and Yoshimori OMOTE Department of Chemistry, The University of Tsukuba, Sakura-mura, Ibaraki 305

Irradiation of N-thioaroylureas and N-thioaroylthioureas gave imidazolidinones and imidazolidinethiones, respectively both via intramolecular hydrogen abstraction by the thioaroyl groups; the photoproducts were easily converted to the imidazolones and imidazolthiones on treatment with trifluoroacetic acid.

Photochemical hydrogen abstraction of thicketones¹⁾ and thicesters²⁾ are well studied. However, that of nitrogen-containing thiocarbonyl compounds such as thioamides or thioimides has not been reported except for thiouracil derivatives.³⁾ We now report that of N-thioaroylureas and N-thioaroylthioureas. This reaction provides a useful synthetic method of some imidazolones (3) and imidazolthiones (6).



Table 1. Photolysis of 1 (Yield/%)						Tabl	Table 2. Photolysis of $\underline{4}$ (Yield/9							
	R ¹	R ²	R ³	R ⁴	2	<u>3</u> a)		Rl	R ²	R3	R ⁴		5	<u>6</u> a)
a:	Ph	Н	Н	Me	-	_	a:	Ph	Н	Н	Me		-	-
b:	Ph	Me	Н	Et	-	-	b:	Ph	Me	н	Et		-	-
c:	Ph	Me	Me	Pr ⁱ	-	-	c:	Ph	Me	Me	Pr^{i}	(51	-
d:	Ph	Ph	Н	PhCH ₂	68	92	d:	Ph	Ph	H	PhCH ₂	!	56	84
e:p-	MeOPh	Ph	Н	PhCH ₂	56	86	e:p-	-MeOPh	Ph	н	PhCH ₂	2	15	99
f:p-	ClPh	Ph	н	PhCH ₂	54	84	f:p-	ClPh	Ph	н	PhCH ₂		73	99
a) Yields from 2.						a) Y	a) Yields from 4.							

N', N'-Dialkyl-N-methyl-N-thiobenzoylureas $(\underline{1a}-\underline{c})$ were unreactive toward photolysis. On the other hand, when N', N'-dibenzyl-N-methyl-N-thiobenzoylurea (ld) was irradiated with a high pressure mercury lamp under argon, 1-benzyl-4,5-diphenyl-4-mercapto-3-methylimidazolidin-2-one (2d) was obtained in 68%. The NMR spectrum of the product indicated that it was a mixture of two stereoisomers. The separation of them was not achieved because they are unstable and converted to the imidazolone

 $(\underline{3d})$ gradually by spontaneous elimination of hydrogen sulfide at room temperature. Treatment of $\underline{2d}$ with trifluoroacetic acid in benzene gave $\underline{3d}$ in an excellent yield. The structure of $\underline{3d}$ was confirmed by the independent synthesis⁴ shown in Scheme 2. Similarly, imidazolidinones ($\underline{2e}$ and $\underline{2f}$) were obtained from N-thioaroylureas ($\underline{1e}$ and $\underline{1f}$) and converted to imidazolones ($\underline{3e}$ and $\underline{3f}$) in good yields (Table 1).



The photolysis of N-thioaroylthioureas $(\underline{4c}-\underline{f})$ gave the corresponding imidazolidinethiones $(\underline{5c}-\underline{f})$, while $\underline{4a}$ and $\underline{4b}$ were inert as in the case of $\underline{1a}$ and $\underline{1b}$. The products $(\underline{5d}-\underline{f})$ were also converted to the imidazolthiones $(\underline{6d}-\underline{f})$ by the acid-catalyzed elimination of hydrogen sulfide (Table 2).



The formation of 2 and 5 is reasonably explained in terms of hydrogen abstraction by the thioaroyl group via seven membered cyclic transition states and subsequent cyclization of the resulting 1,5-diradical (7). This reaction provides the first example of hydrogen abstraction of acyclic nitrogen-containing thiocarbonyl compounds, and is of interest in view of the fact that cyclic dithioimides

such as dithiosuccinimides do not undergo hydrogen abstraction.⁵⁾ Furthermore, these reactions provide a useful synthetic method of some imidazolones and imidazolthiones, since the synthesis of the starting materials (1 and 4) are easy.⁶⁾

References

- Y. Ohnishi and A. Ohno, Bull. Chem. Soc. Jpn., <u>46</u>, 3868(1973); A. Couture, J. Gómez, and P. de Mayo, J. Org. Chem., <u>46</u>, 2010(1981), and references cited therein.
- 2) S. Achmatwicz, D. H. R. Barton, P. D. Magnus, G. A. Poulton, and P. L. West, J. Chem. Soc., Perkin Trans. 1, <u>1973</u>, 1567 and 1580; Y. Ogata, K. Takagi, and S. Ihda, ibid., 1975, 1725.
- 3) J. L. Fourrey, G. Henry, and P. Jouin, Tetrahedron Lett., 1976, 2375.
- G. Holzmann, B. Kreig, H. Lautenschläger, and P. Konieczny, J. Heterocyclic Chem., <u>16</u>, 983(1979).
- 5) K. Oda, E. Yoshida, S. Wakao, M. Matsuda, and Y. Kanaoka, The 11th Symposium on Organic Sulfur and Phosphorus Chemistry, Tsukuba, Japan, 1983, 125.
- 6) Thioaroylureas $(\underline{la}-\underline{f})$ were synthesized in good yields by the reaction of the corresponding N-aroylureas with Lowesson's reagent, and N-thioaroylthioureas $(\underline{4a}-\underline{f})$ were obtained from N-aroylthioureas in the same manner.

(Received June 28, 1983)