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PHOTOCHEMICAL REACTIONS OF N-THIOAROYLUREAS AND N-THIOAROYLTHIOUREAS

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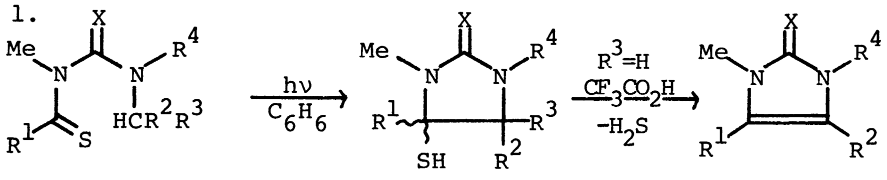
Irradiation of N-thioaroylureas and N-thioaroylthioureas gave imidazolidinones and imidazolidinethiones, respectively both via intramolecular hydrogen abstraction by the thioaroyl groups; the photoproducts were easily converted to the imidazolones and imidazolthiones on treatment with trifluoroacetic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

Photochemical hydrogen abstraction of thioketones$^{1)}$ and thioesters$^{2)}$ 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).

Scheme 1.



1:X=O
4:X=S

2:X=O
5:X=S

3:X=O
6:X=S

Table 1. Photolysis of 1 (Yield/%)

	R^1	R^2	R^3	R^4	2	3$^{a)}$
a:	Ph	H	H	Me	-	-
b:	Ph	Me	H	Et	-	-
c:	Ph	Me	Me	Pr^i	-	-
d:	Ph	Ph	H	$PhCH_2$	68	92
e:	p-MeOPh	Ph	H	$PhCH_2$	56	86
f:	p-ClPh	Ph	H	$PhCH_2$	54	84

a) Yields from 2.

Table 2. Photolysis of 4 (Yield/%)

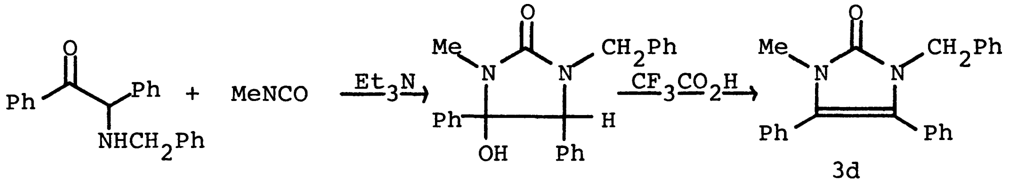
	R^1	R^2	R^3	R^4	5	6$^{a)}$
a:	Ph	H	H	Me	-	-
b:	Ph	Me	H	Et	-	-
c:	Ph	Me	Me	Pr^i	61	-
d:	Ph	Ph	H	$PhCH_2$	56	84
e:	p-MeOPh	Ph	H	$PhCH_2$	45	99
f:	p-ClPh	Ph	H	$PhCH_2$	73	99

a) Yields from 4.

N',N'-Dialkyl-N-methyl-N-thiobenzoylureas (1a-c) were unreactive toward photolysis. On the other hand, when N',N'-dibenzyl-N-methyl-N-thiobenzoylurea (1d) 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

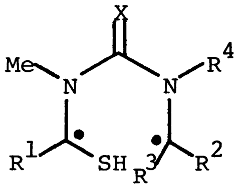
(3d) gradually by spontaneous elimination of hydrogen sulfide at room temperature. Treatment of 2d with trifluoroacetic acid in benzene gave 3d in an excellent yield. The structure of 3d was confirmed by the independent synthesis4) shown in Scheme 2. Similarly, imidazolidinones (2e and 2f) were obtained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

Scheme 2



3d

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



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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

1) Y. Ohnishi and A. Ohno, Bull. Chem. Soc. Jpn., 46, 3868(1973); A. Couture, J. Gómez, and P. de Mayo, J. Org. Chem., 46, 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, 1973, 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.
4) G. Holzmann, B. Kreig, H. Lautenschläger, and P. Konieczny, J. Heterocyclic Chem., 16, 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 (1a-f) were synthesized in good yields by the reaction of the corresponding N-aroylureas with Lowesson's reagent, and N-thioaroylthioureas (4a-f) were obtained from N-aroylthioureas in the same manner.

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