

## THE NORRISH TYPE II REACTION OF THE CYCLIC THIOIMIDES WITH A BENZYLIC HYDROGEN<sup>1</sup>

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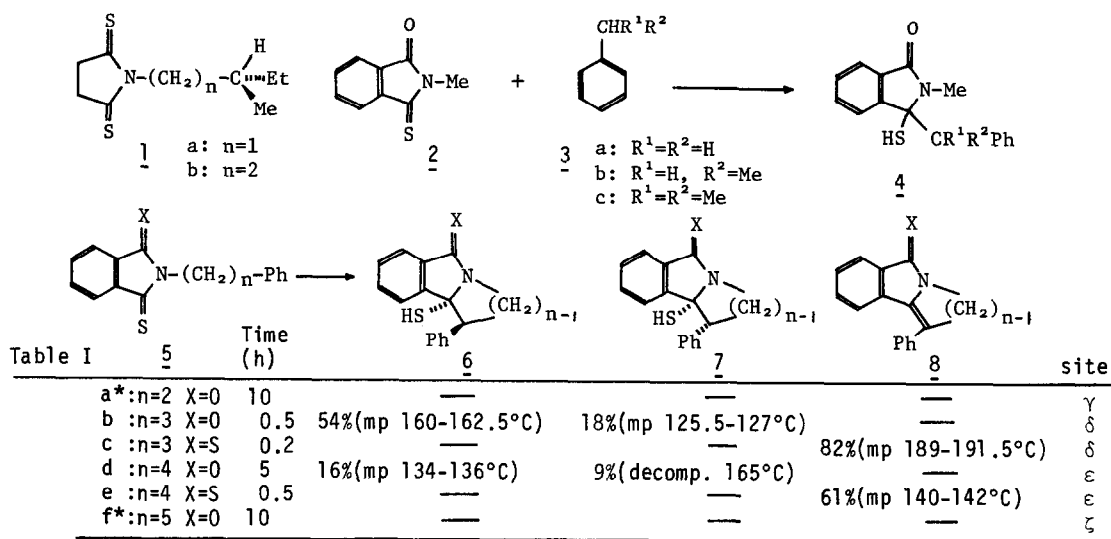
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**Abstract:** On irradiation cyclic thioimides with N- $\omega$ -phenylalkyl substituents undergo the Norrish type II cyclization when benzylic hydrogen is available at the  $\delta$ - or  $\epsilon$ -position of the thiocarbonyl group.

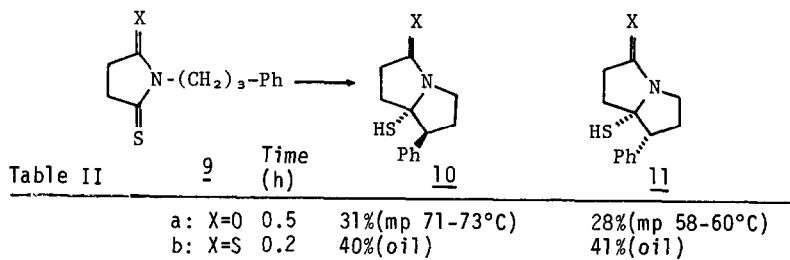
Intramolecular hydrogen abstraction in excited carbonyl compounds, the Norrish type II reaction, is among the more extensively studied of photoreactions.<sup>2</sup> Also in the photochemistry of thiones, the sulfur analogs, the related reaction has been well established.<sup>3</sup> In our general study of the photochemistry of the thioimide function, we have found some instances of behavior strikingly different from that of the imides,<sup>4</sup> the oxygen counterparts; i.e., the thioimides efficiently undergo photocycloaddition,<sup>5</sup> but seem substantially inert to the Norrish type I and II processes.<sup>5,6</sup> However, use of a thioimide with a chiral center at the  $\delta$ -position **1b** results in partial racemization suggestive of potential occurrence of the hydrogen abstraction.<sup>5a</sup> In addition, such abstraction has recently been reported with thioaroylurea, acyclic thioimide-like derivatives.<sup>7</sup> The work to be described here reports some limited but first example of the Norrish type II reaction of certain cyclic thioimides.

In preliminary experiments, N-methylmonothiophthalimide **2** was irradiated<sup>8</sup> in presence of alkylbenzenes **3**. The addition products **4**,<sup>9</sup> apparently resulting from hydrogen abstraction from the benzylic position followed by coupling as seen in a precedent with phthalimides,<sup>10</sup> were obtained in the yields in parallel with the relative reactivity of the hydrogens [ $1^\circ$  (0%) <  $2^\circ$  (25%) <  $3^\circ$  (64%)], suggestive of involvement of radical intermediates.

The irradiation of a series of N- $\omega$ -phenylalkyl-thio- or dithio-phthalimides **5** results in the formation of products **6-8** which are expected from the type II cyclization initiated by  $\delta$ - or  $\epsilon$ -hydrogen abstraction (Table I). It is noteworthy that the  $\gamma$ -hydrogen definitely reactive in the ketones<sup>2</sup> is inert in the thioimide system, compatible with the observed lack of racemization in recovered **1a**.<sup>5a</sup> Similar irradiation of the analogous thiosuccinimides **9** gave the cyclized products, a mixture of isomeric pyrrolizidinethiols **10**, **11** (Table II). Thus, these results demonstrate that cyclic thioimides undergo the Norrish type II cyclization at least if a benzylic hydrogen is available at the  $\delta$ - or  $\epsilon$ -position of the thiocarbonyl group.<sup>11</sup> Since no cyclobutane due to  $\gamma$ -abstraction nor type II  $\beta$ -fission products appear to accompany, the pyrrolizidine- and indolizidine-thiol formation of synthetic utility is a major course in the type II processes of this particular thioimides system.



\* : Substrate was recovered quantitatively.



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#### References and Notes

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- a) M. Machida, K. Oda, E. Yoshida, and Y. Kanaoka, *J. Org. Chem.*, **50**, 1681 (1985); b) For example, a series of dithio-succinimides and -phthalimides with N-alkyl substituents unchanged on irradiation.<sup>5a</sup>
- Some monothio-phthalimides were reported to be inactive; J. D. Coyle and P. A. Rapley, *Tetrahedron Lett.*, **25**, 2247 (1984).
- a) H. Aoyama, M. Sakamoto, and Y. Omote, *Chem. Lett.*, 1397 (1983); b) M. Sakamoto, H. Aoyama, and Y. Omote, *J. Org. Chem.*, **49**, 1837 (1984).
- A substrate (10 mM) in benzene (500 ml) [containing **3** (30 eq.)] was irradiated for 1-5 h with a 1 KW high-pressure mercury lamp through Pyrex.
- All new compounds gave satisfactory elemental analytical and spectral data.
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- The preponderance of the thiocarbonyl over the carbonyl in the photoreactions may be due to the much more intensive absorption of the former chromophore under the irradiation conditions.

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