HETEROCYCLES, Vol 27, No 10, 1988

PHOTOCHEMISTRY OF THE N-ACYLLACTAM AND ACYCLIC THIOIMIDE SYSTEMS. COMPETITION BETWEEN PATERNO-BÜCHI TYPE AND NORRISH TYPE I REACTIONS[1]

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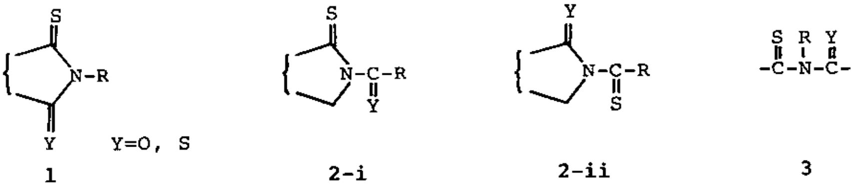
Abstract — Irradiation of semicyclic- (4) and acyclic thioimides (9) gave thietanes (6, 7, and 10) and/or α-cleavaged products (8 and 11), formations of those were explained in terms of Paterno-Büchi type and Norrish type I processes.

As a part of our continuing program to investigate imide photochemistry,[2] we have explored photoreactions of thioimide systems,[3] a new amalgamation of imide and sulfur. Generally, thioimides are classified into three structural classes; cyclic (1), N-acyllactam (semicyclic, 2), and acyclic (3) systems (Scheme 1). Although the photochemistry of the thioimides has been extensively studied, most of the reports have been concerned with that of the cyclic thioimides (1)[3] except for the work of Omote et al.[4] We have found that the photochemical behavior of the cyclic thioimides is strikingly different from that of the imides, the oxygen counterparts; i.e., these thioimides exclusively undergo photocycloaddition with olefins, and are substantially inert to Norrish type I (α-cleavage) and II processes.[3] Recently, it has been found that certain cyclic thioimides having a benzylic hydrogen at the γ, δ, and ε-positions in the side chains, as a special case, undergo Norrish type II reaction to give cyclized products.[5]

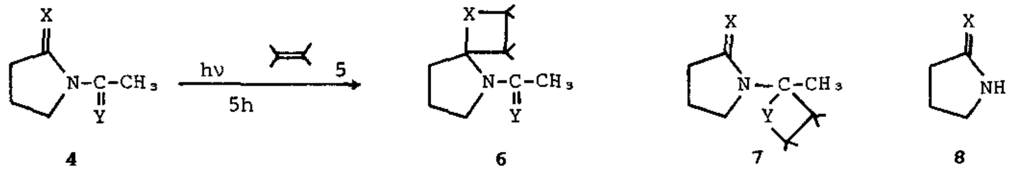


Scheme 1

In order to systematically investigate the scope and limitation of the photoreaction, the generality of the intermolecular photocycloaddition with olefin in N-acyllactam (4) and acyclic thioimide (9) systems were *studied and the results are reported in this paper.*

Photolyses of the thioimides (**4a-c**) in benzene were carried out in the presence of an excess of 2,3-dimethyl-2-butene (**5**). The results are listed in Table 1. Photolysis of N-acetylthiopyrrolidone **4a** gave spiro-thietane (**6**, 38%), and a small amount of thiopyrrolidone (**8a**, 5%), an α-cleavage product. Thioacetylpyrrolidone **4b** gave also an addition product (**7**, 24%) having a thietane located in the N-side chain. However, in the case of N-thioacetylthiopyrrolidone **4c**, *no cycloaddition products* due to the Paterno-Büchi type reaction were isolated, while only thiopyrrolidone (**8c**=**8a**), the α-cleavage product, was obtained in 82% yield.

Table 1 Photoreaction of **4**

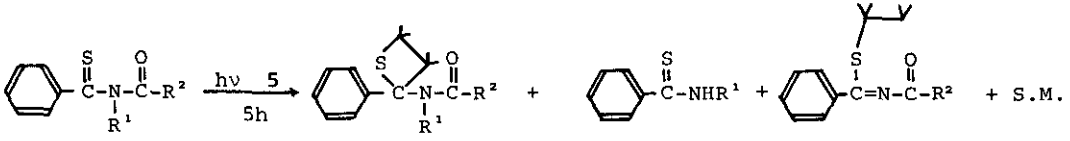


	6	**7**	**8**
a: X=S, Y=O	38 %	——	5 %
b: X=O, Y=S	——	24 %	26 %
c: X=Y=S	——	——	82 %

—— Not detected.

The structures of thietanes **6**, **7** were determined on the basis of analytical and spectral data. For a typical example, in the mass spectrum of **7** the molecular ion peak (M$^+$=227) indicated the addition of *olefin* **5** *to* **4b**. *The* ^{1}H-*nmr spectrum* showed signals due to five methyl groups at 1.25, 1.30, 1.35, 1.60, and 2.00 ppm, respectively. The ^{13}C-nmr spectrum showed the peaks due to a carbonyl, two dimethyl-substituted carbons , and a quaternary carbon adjacent to a sulfur and a nitrogen atoms at 173.9 (s), 53.5 (s), 46.1 (s), and 75.9 (s), respectively.

Table 2 Photoreaction of **9**



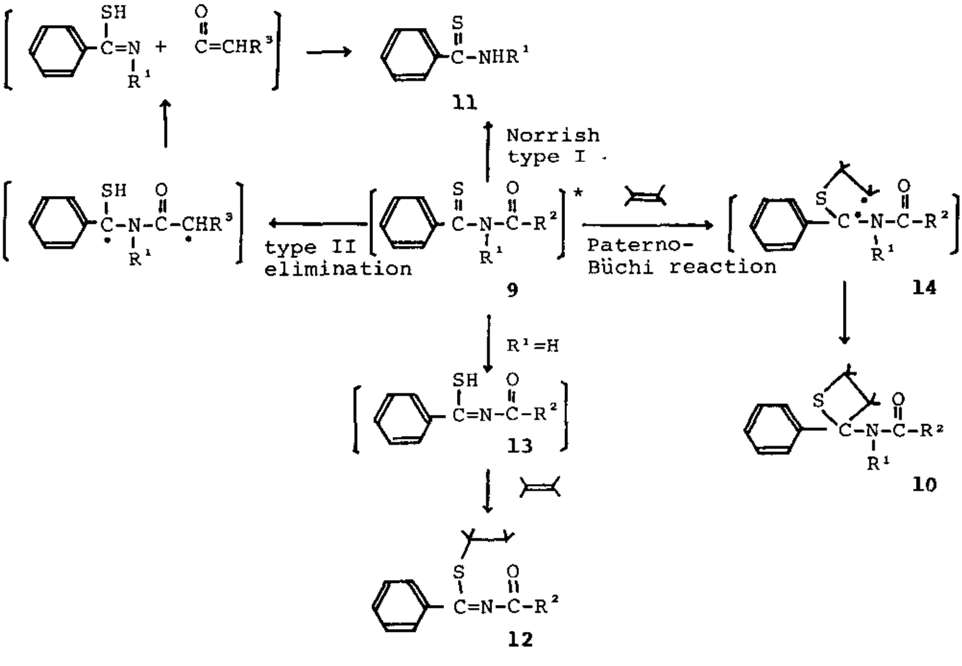
R¹	R²	**10**	**11**	**12**	(9)
a: H	CH₃	27 %	——	20 %	18 %
b: H	Ph	22 %	——	——	66 %
c: CH₃	CH₃	10 %	21 %	——	11 %
d: CH₃	Ph	21 %	12 %	——	16 %
e: Ph	CH₃	——	48 %	——	12 %
f: Ph	Ph	——	46 %	——	22 %

—— Not detected.

Next, in order to see photoreaction of acyclic thioimide system, photolyses of N-acylthiobenzamides (**9a-f**) were examined under the similar conditions. The results are listed in Table 2. In the photolysis of **9a** (R^1=H, R^2=CH_3), two adducts (**10a** and **12a**) were obtained, while **9b** gave only thietane (**10b**). In the cases of **9c,d** (R^1=CH_3), thietanes (**10c** and **10d**) and N-methylthiobenzamide (**11c=11d**) were obtained, respectively. Photolyses of **9e** and **9f** (when R^1=Ph) gave only the α-cleavage product, N-phenylthiobenzamide (**11e=11f**) in moderate yields, respectively.

In the ir spectrum of **12a**, the peaks at 1600 and 1680 cm^{-1} suggested the presence of a carbon-nitrogen double bond and an amide moiety, respectively. In the mass spectrum, the molecular ion peak (M^+=263) indicated the adduct of **9a** to **5**, and in addition the fragment peak with m/z 178 indicated elimination of $C(CH_3)_2$-$CH(CH_3)_2$ group from the sulfide **12a**. Further, the ^{13}C-nmr spectrum of **12a** showed the peaks due to an amide carbonyl, two dimethyl-substituted carbons, and a carbon of carbon-nitrogen double bond at 167.1 (s), 57.3 (s), 35.7 (d), and 182.5 (s) ppm, respectively.

In conclusion, although endo (in a lactam moiety) and exo (in an acyl moiety) thiocarbonyl groups in semicyclic monothioimides (**4a** and **4b**) are both essentially photoreactive to olefin, the dithioimide (**4c**) having two thiocarbonyl groups rather undergoes formal α-cleavage reaction in competition with cycloaddition to olefin to give thiopyrrolidone (**8c**). The formation of the thiopyrrolidone seems to take dual pathways, Norrish type I and type II elimination processes, on the analogy of photochemical behavior of hemicyclic imides (the oxygen counterparts).[6] However, no simple explanation for this preferential



Scheme 2

formation of **8c** in the case of **4c** can be offered at the present time. Likewise, involvement of this formal α-cleavage reaction was observed also with acyclic monothioimides **9** (Scheme 2). In the case of **9f** (R^1=R^2=Ph) lacking a hydrogen in accessible locations, a possiblity of α-cleavage via the Norrish type II process due to hydrogen abstraction is excluded. Therefore, the formation of **8** and **11** may be explained in terms of the Norrish type I reaction. In N-unsubstituted acyclic thioimides (**9a,b**, R^2=H), none of α-cleavage products were isolated, therefore N-substituents seem to enhance the reactivity to α-cleavage. On the other hand, in the thione photochemistry, involvement of α-cleavage has been limited to strained systems such as cyclobutanethiones[7] and to thioesters.[8] Recently, Omote et al.[9] found that thioxo-β-lactams (four membered monothioimides), which were produced by ring opening reaction of thiazine ring of β-lactams, undergo α-cleavage. Thus, α-cleavage in thioimides also would seem restricted to internally strained systems. However, as shown in Scheme 2, processes of α-cleavage (**9**→**11**) were observed with unstrained acyclic thioimides (**9**) in contrast with inertness of the cyclic thioimides[3] to the Norrish type I reaction. An addition of olefin (**9**→**13**→**12**) is also an interesting example of the thioimide photoreactions.[10] It is noteworthy that in unstrained thioimide systems such as **4** and **9**, the Norrish type I α-cleavage (**9**→**11**) occurs in competition with Paterno-Büchi type reaction (**9**→**14**→**10**), which is representative in the cyclic thioimide systems.[3]

EXPERIMENTAL

All melting points were determined on Yamato melting point apparatus model MP-21 and are uncorrected. Ir spectra were recorded on a Shimadzu IR-400 spectrometer. Nmr spectra were taken on a Hitachi R-40 spectrometer and a JEOL-FX 90Q spectrometer. Chemical shifts are reported in part per million (δ) relative to tetramethylsilane (TMS, 0.0ppm) as an internal standard. The abbreviations used are as follows : s, singlet; d, doublet; t, triplet; q, quartet; sep, septet; m, multiplet. Mass spectra were determined with a JEOL JMS-QH 100 gas chromatograph-mass spectrometer with a direct inlet system.

General Procedure for Prepration of Thioimides (4 and 9)

The Thioimides **4a-c**,[12] **9a,b**,[13] **9c-f**,[14] were prepared according to the reported procedures.

General Procedure for Irradiation of Thioimides (4 and 9)

A solution of the thioimide (5 mmol) and 2,3-dimethyl-2-butenes (2.1g, 25 mmol) in benzene (500ml) was irradiated through a Pyrex filter in a nitrogen atmosphere at room temparature using a 1kW high-pressure mercury lamp. After removal of the solvent in vacuo, the products were separated by column chromatography on silica gel (using benzene as solvent). The spectral data were listed in Table 3.

Table 3. Photoproducts

Compound	Appearance mp (°C) (Solvent)	ir (cm^{-1})	mass (M$^+$)	^{1}H-nmr (δppm)	^{13}C-nmr (δppm)	Formula	Analyses (%) Calcd	Analyses (%) Found
6	oil	1660	227	1.15(3H,s,Me),1.25(3H,s,Me),1.30(3H,s,Me),1.50(3H,s,Me),2.10(3H,s,COMe),2.3-3.0(4H,m),3.6-3.8(2H,m).	21.4(t),22.4(q),23.4(q),24.8(q),26.4(q),30.1(q),41.8(t),45.4(s),48.7(t),55.5(s),71.8(s),170.1(s).	$C_{12}H_{21}NOS$	C: 63.39 H: 9.31 N: 6.16	63.48 9.11 6.20
7	oil	1720	227	1.25(3H,s,Me),1.30(3H,s,Me),1.35(3H,s,Me),1.60(3H,s,Me),2.00(3H,s,Me),1.9-2.5(3H,m),3.0-4.0(3H,m).	18.8(t),21.2(q),22.6(q),26.1(q),27.6(q),30.1(q),33.3(t),46.1(s),48.8(t),53.5(s),75.9(s),173.9(s).	$C_{12}H_{21}NOS$	C: 63.39 H: 9.31 N: 6.16	63.31 9.52 6.20
10a	171-173 (n-Hexane)	1680	263	0.80(3H,s,Me),1.30(6H,s,2xMe),1.70(3H,s,Me),1.95(3H,s,COMe),7.1(1H,br s,NH),7.2-7.6(5H,m,Ar H).	20.4(q),23.1(q),24.8(q),26.8(q),29.6(q),40.1(s),50.8(s),70.9(s),126.2(d),127.1(dx2),127.6(dx2),143.2(s),168.0(s).	$C_{15}H_{21}NOS$	C: 68.40 H: 8.04 N: 5.32	68.50 8.31 5.33
12a	oil	1680 1600	263	1.00(6H,d,J=6Hz,CH$\underline{\mathrm{Me}}_2$),1.50(6H,s,2xMe),1.90(3H,s,COMe),2.30(1H,sep,J=6Hz,C$\underline{\mathrm{H}}$Me$_2$),7.0-7.4(5H,m,Ar H).	18.9(qx2),24.8(qx2),25.8(q),35.7(d),57.3(s),127.4(dx2),128.5(dx2),130.8(d),137.4(s),167.1(s),182.5(s).	$C_{15}H_{21}NOS$	C: 68.40 H: 8.04 N: 5.32	68.39 8.17 5.45
10b	123-124.5 (n-Hexane)	1680	325	0.80(3H,s,Me),0.90(3H,s,Me),1.10(3H,s,Me),1.40(3H,s,Me),7.1(1H,br s,NH),7.2-8.3(10H,m,Ar H).	23.1(q),24.8(q),27.9(q),35.3(q),43.9(s),53.4(s),76.8(s),128.1(dx2),128.5(dx2),128.8(d),129.8(dx2),130.0(d),131.8(dx2),138.5(s),142.0(s),172.2(s).	$C_{20}H_{23}NOS$	C: 73.81 H: 7.12 N: 4.30	73.93 7.36 4.38
10c	oil	1680	277	1.10(3H,s,Me),1.20(3H,s,Me),1.30(3H,s,Me),1.65(3H,s,Me),1.95(3H,s,COMe),2.75(3H,s,N-Me),7.2-8.0(5H,m,Ar H).	20.8(q),22.5(q),23.9(q),25.5(q),28.6(q),30.1(q),45.8(s),52.3(s),73.8(s),125.5(d),127.1(dx2),127.8(dx2),144.1(s),169.0(s).	$C_{16}H_{23}NOS$	C: 69.27 H: 8.36 N: 5.05	69.18 8.40 5.31
10d	118.5-120 (n-Hexane)	1680	339	1.20(3H,s,Me),1.30(3H,s,Me),1.40(3H,s,Me),1.80(3H,s,Me),2.65(3H,s,N-Me),7.1-8.3(10H,m,Ar H).	22.5(q),23.5(q),26.5(q),28.4(q),35.7(q),45.3(s),55.8(s),78.5(s),127.5(dx2),127.5(dx2),127.8(d),128.4(dx2),129.8(d),131.2(dx2),138.0(s),141.5(s),171.7(s).	$C_{21}H_{25}NOS$	C: 74.29 H: 7.42 N: 4.13	74.32 7.18 4.01

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Received, 27th May, 1988