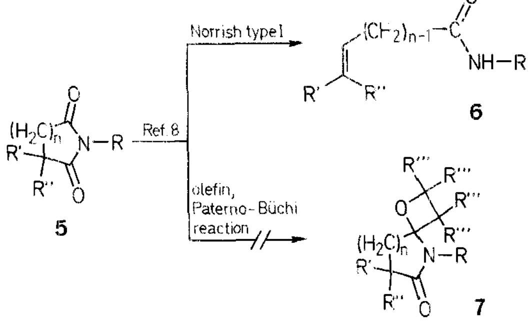
We had previously reported that succinimides (**5**) with substituents on C-3 of the imide ring undergo the Norrish type I reaction to give alkenamides **6**, but no Paterno-Büchi products (**7**) were obtained (Scheme **B**)[8].



Scheme **B**

By contrast, we have now found that photolysis of ring-substituted dithiosuccinimides gives rise to thietanes which correspond to Paterno-Büchi type products.

Intermolecular Photocycloaddition of Ring-Substituted Cyclic Dithioimides with 2,3-Dimethyl-2-butene: A Facile Synthesis of Spiro-Thietanes[1]

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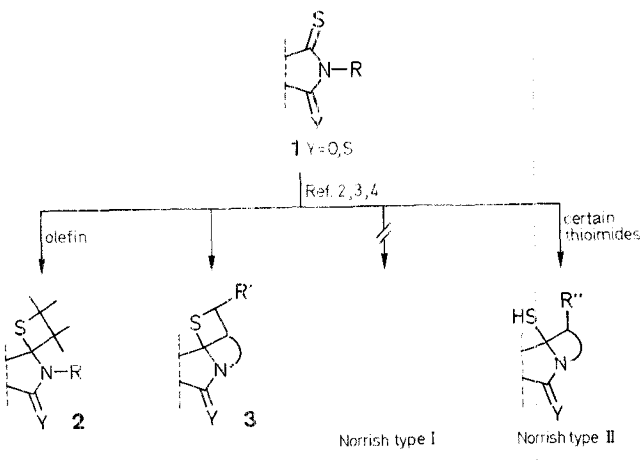
Upon irradiation, unsymmetrically 3-substituted and symmetrical bicyclic dithiosuccinimides undergo photocycloaddition with 2,3-dimethyl-2-butene to give various spiro-thietanes, including highly strained multicycles.

The photoreactions of cyclic thioimides (**1**) have recently been extensively studied[2,3,4]. Most dithioimides are inert to both the Norrish type I (α-cleavage) and Norrish type II (hydrogen abstraction) reactions in contrast to the behavior of their oxygen analogs (imides)[5] and nitrogen-lacking counterparts (thiones)[6,7]. However, many aliphatic and aromatic di- and mono-thioimides undergo both inter-[2,3] and intramolecular[1,4] photocycloaddition (Paterno-Büchi type reaction) with olefins to afford imide-thietanes (**2** and **3**) (Scheme **A**).



Scheme **A**

As part of our photochemical synthetic studies dealing with nitrogen-thiocarbonyl systems[1], we now report the facile synthesis of spiro-thietanes by the photocycloaddition of unsymmetrically 3-substituted and symmetrical bicyclic dithiosuccinimides with olefins.

Dithiosuccinimides (**10a–e** and **13**) were prepared from the corresponding imides (**8a–e** and **9**) and phosphorus(V) sulfide[9]. Photolysis of the dithioimides in benzene was carried out in the presence of an excess of 2,3-dimethyl-2-butene. The reaction of 1,3-dimethyldithiosuccinimide (**10a**) gave two regioisomers (**11a** and **12a**), one of these consists of two stereoisomers (**11a–i** and **11a–ii**), which are formed by the preferential cycloaddition at the less-hindered thiocarbonyl group[2]. The other product is a single stereoisomer (**12a**). The reaction of unsymmetrically ethyl-substituted dithioimide **10b** also gave thietanes **11b–i** and **11b–ii** in 30 and 12% yields, respectively, accompanied by a mixture of two unseparable stereoisomers **12b**. Irradiation of dimethyl-substituted dithioimide **10c** produced only thietane **11c** in 54% yield as a single regioisomer along with recovered starting material (25%).

Table 1. Dithioimides **10a–e**, **13** Prepared

Dithioimide No.	Yield [%]	b.p. [°C]/torr	Molecular Formula[a]
10a	68	143–146/12	$C_6H_9NS_2$ (159.3)
10b	62	152–158/12	$C_7H_{11}NS_2$ (173.3)
10c	54	160–162/12	$C_7H_{11}NS_2$ (173.3)
10d	69	m.p. 80–81 °C	$C_{10}H_{15}NS_2$ (213.3)
10e	52	128–134/8	$C_7H_9NS_2$ (171.3)
13	51	149–155/10	$C_7H_9NS_2$ (171.3)

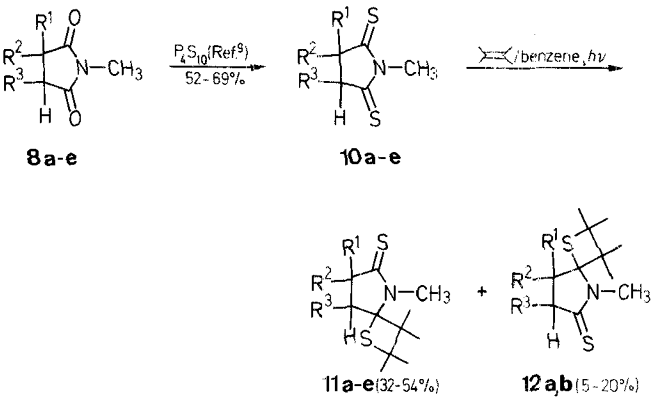
[a] The microanalyses were in good agreement with the calculated values: C ±0.17, H ±0.24, N ±0.13.

Table 2. Synthesis of Spirothietanes **11**, **12**, **14**

Substrate	Irradiation[a] [h]	Photo Product	Yield [%]	m.p. [°C]	Molecular Formula[b]	MS m/e (M⁺)	¹H-NMR ($CDCl_3$)[c] δ [ppm]	¹³C-NMR ($CDCl_3$)[c] δ [ppm]
10a	3.0	**11a-i**	22	89–90.5	$C_{12}H_{21}NS_2$ (243.4)	243	1.15 (s, 3H, CH_3); 1.20 (s, 3H, CH_3); 1.30 (d, 3H, J = 7 Hz, CH_3); 1.50 (s, 6H, 2CH_3); 2.3–3.2 (m, 3H); 3.55 (s, 3H, NCH_3)	16.8; 20.8; 21.0; 23.4; 27.0; 34.4; 42.0; 42.3; 45.0; 56.2; 79.4; 206.8
		11a-ii	18	115–117	$C_{12}H_{21}NS_2$ (243.4)	243	1.15 (s, 6H, 2CH_3); 1.30 (d, 3H, J = 7 Hz, CH_3); 1.40 (s, 3H, CH_3); 1.55 (s, 3H, CH_3); 1.6–3.4 (m, 3H); 3.45 (s, 3H, NCH_3)	17.2; 21.3; 23.6; 25.0; 26.8; 34.6; 40.8; 44.8; 44.8; 56.0; 83.1; 207.0
		12a	5	54–56	$C_{12}H_{21}NS_2$ (243.4)	243	0.95 (d, 3H, J = 7 Hz, CH_3); 1.10 (s, 3H, CH_3); 1.20 (s, 3H, CH_3); 1.40 (s, 3H, CH_3); 1.50 (s, 3H, CH_3); 2.7–3.0 (m, 3H); 3.45 (s, 3H, NCH_3)	15.8; 20.7; 20.8; 24.6; 27.0; 34.4; 35.8; 45.8; 47.0; 55.4; 87.4; 200.1
10b	2.5	**11b-i**	30	65–67	$C_{13}H_{23}NS_2$ (257.5)	257	0.8 (t, 3H, J = 7 Hz); 1.5–1.9 (m, 5H); 1.10 (s, 3H, CH_3); 1.15 (s, 3H, CH_3); 1.35 (s, 3H, CH_3); 1.45 (s, 3H, CH_3); 3.40 (s, 3H, NCH_3)	15.6; 15.9; 21.3; 23.6; 24.4; 32.8; 34.4; 42.4; 42.6; 45.4; 56.2; 78.3; 206.9
		11b-ii	12	82–83.5	$C_{13}H_{23}NS_2$ (257.5)	257	1.10 (t, 3H, CH_3); 1.15 (s, 3H, CH_3); 1.20 (s, 3H, CH_3); 1.50 (s, 6H, 2CH_3); 1.5–1.9 (m, 5H); 3.50 (s, 3H, NCH_3)	15.9; 18.9; 21.1; 22.8; 24.4; 32.8; 34.8; 40.4; 40.4; 44.9; 56.1; 78.8; 207.6
		12b	20				(a mixture of two stereoisomers)	
10c	2.0	**11c**	54	77–79	$C_{13}H_{23}NS_2$ (257.5)	257	1.10 (s, 3H, CH_3); 1.15 (s, 3H, CH_3); 1.25 (s, 3H, CH_3); 1.30 (s, 6H, 2CH_3); 1.35 (s, 3H, CH_3); 1.8 (d, 1H, J = 12 Hz); 2.3 (d, 1H, J = 12 Hz); 3.55 (s, 3H, NCH_3)	22.7; 25.5; 27.6; 29.0; 29.7; 36.8; 36.8; 46.1; 48.3; 49.6; 56.4; 80.2; 212.6
10d	1.0	**11d**	50	114–117	$C_{16}H_{27}NS_2$ (297.5)	297	1.10 (s, 3H, CH_3); 1.20 (s, 3H, CH_3); 1.50 (s, 6H, 2CH_3); 0.8–2.1 (m, 10H); 1.95 (d, 1H, J = 12 Hz); 3.15 (d, 1H, J = 12 Hz); 3.55 (s, 3H, NCH_3)	22.8; 23.4; 23.4; 23.5; 24.3; 25.0; 25.5; 27.4; 30.4; 36.8; 41.9; 48.4; 55.1; 56.4; 80.2; 206.1
10e	3.0	**11e**	32	85–87	$C_{13}H_{21}NS_2$ (255.5)	255	1.00 (s, 3H, CH_3); 1.20 (s, 3H, CH_3); 1.35 (s, 3H, CH_3); 1.55 (s, 3H, CH_3); 1.5–2.8 (m, 6H); 3.1 (s, 3H, CH_3)	21.7; 23.7; 23.8; 26.4; 27.0; 30.4; 36.8; 41.5; 47.2; 52.1; 57.0; 85.8; 206.7
13	0.5	**14**	64	60–62	$C_{13}H_{21}NS_2$ (255.5)	255	1.15 (s, 3H, CH_3); 1.30 (s, 3H, CH_3); 1.35 (s, 3H, CH_3); 1.55 (s, 3H, CH_3); 1.5–2.8 (m, 6H); 3.1 (s, 3H, NCH_3)	18.4; 18.9; 25.5; 27.5; 28.8; 29.4; 30.8; 32.8; 45.4; 50.8; 56.2; 80.4; 212.8

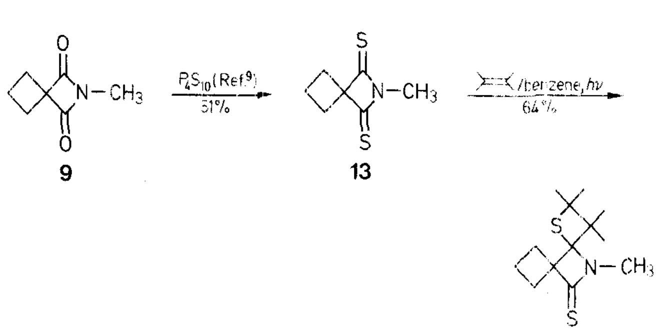
[a] 1 kW High-pressure mercury lamp (Pyrex filter).
[b] The microanalyses were in good agreement with the calculated values: C ±0.23, H ±0.20, N ±0.18, S ±0.12.
[c] JEOL FX 90 Q spectrometer.

Although the stereochemistry of the isomers is not known, the regioisomers could easily be distinguished on the basis of the chemical shifts of the thiocarbonyl C-atoms in the ¹³C-NMR spectra. For a typical example (**11a**), the signal of the thiocarbonyl C-atom is located at δ = 206–207 ppm relative to that of **12a** (200 ppm), thus indicating the presence of a methyl substituent at the α-position with respect to the thiocarbonyl group.



8a-e 10a-e 11a-e (32-54%) 12a,b (5-20%)

8, 10, 11, 12	R^1	R^2	R^3
a	CH_3	H	H
b	C_2H_5	H	H
c	CH_3	CH_3	H
d	$-(CH_2)_5-$		H
e	H	$-CH_2-CH_2-$	



9 13 14

Scheme C

In order to prove the structural requirements of the Paterno-Büchi processes, the photolysis of some bicyclic dithioimides (**10d, 10e,** and **13**) was examined. As expected for the 3,3-spiro-substituted dithioimide **10d**, thietane **11d** was obtained *via* selective reaction with the less hindered thiocarbonyl group.

The reaction of symmetrically substituted cyclic dithioimides (**10e, 13**) readily produced strained ring compounds, *i.e.*, tricyclic monospiro (**11e**) and dispiro (**14**) systems, respectively (Scheme **C**). These imide-thietanes (**11, 12, 14**) represent spiro systems which contain both sulfur and nitrogen and which are otherwise unaccessible; they possess structural features of interest as intermediates for various synthetic transformations[2,3,4]. Thus, the photocycloaddition of thioimides may provide a novel synthetic route to new N- and S-containing multiheterocyclic systems.

Imides:
The imides **8a**[10], **8b**[11], **8c**[12], **8d**[13], **8e**[14], and **9**[8], were prepared following the reported procedures.

Dithioimides:
Dithioimides (**10a–e** and **13**) were prepared from the corresponding imides and phosphorus(V) sulfide by the procedure of Ref.[9], and purified by column chromatography (Table 1).

Irradiation of Dithioimides; General Procedure:
A solution of the dithioimide (5 mmol) and 2,3-dimethyl-2-butene (2.11 g, 25 mmol) in benzene (500 ml) is irradiated through Pyrex glass at room temperature using a 1 kW high-pressure mercury lamp. After removal of the solvent *in vacuo*, the products are separated by column chromatography on silica gel (using benzene as solvent), and purified by recrystallization (Table 2).

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[1] (a) Photochemistry of the Nitrogen-Thiocarbonyl Systems; 6. Part 5: Machida, M., Oda, K., Kanaoka, Y. *Tetrahedron Lett.* **1985**, *26*, 5173.
(b) Photoinduced Reactions; 81. Part 80: Ref. 1a.
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