

PHOTOCYCLOADDITIONS OF N-METHYLMONOTHIOPHTHALIMIDE WITH STYRENE
DERIVATIVES ACCOMPANIED BY 1,2-DITHIANE FORMATION¹

Minoru Machida,* Kazuaki Oda, Eiichi Yoshida, Shuji Wakao,
and Kosei Ohno

Faculty of Pharmaceutical Sciences, Higashi-Nippon-Gakuen
University, Ishikari-Tobetsu, Hokkaido 061-02, Japan

Yuichi Kanaoka*

Faculty of Pharmaceutical Sciences, Hokkaido University,
Sapporo 060, Japan

Abstract — Photolysis of N-methylmonothiophthalimide (1)
with styrene analogs (2) gave thietane derivatives (3)
accompanied by dithiane derivatives (4). The stereochemistry
of thietanes was determined by spectroscopies.

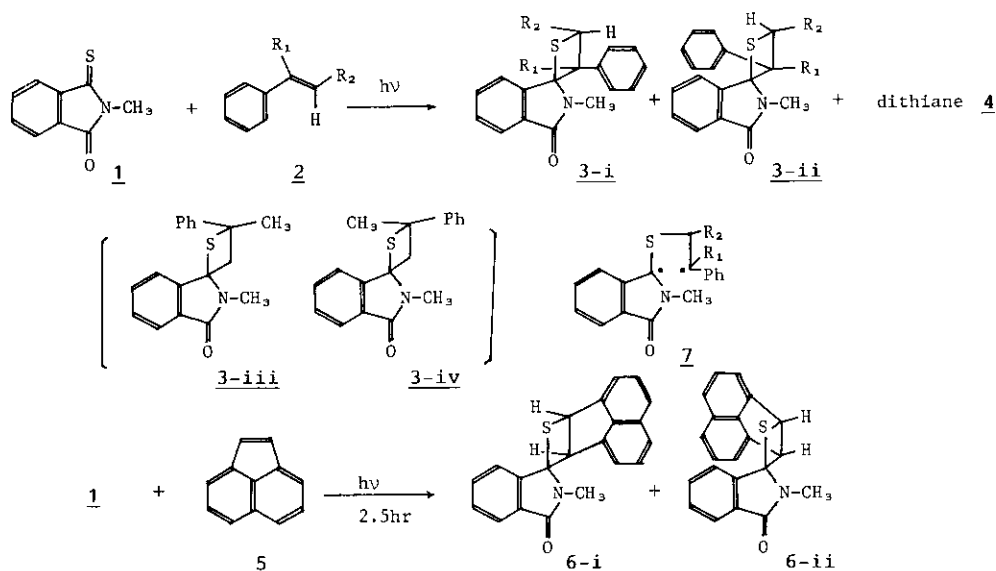
To develop a frontier of organic photochemistry, we have explored photoreactions
of thioimide systems^{1a} as one of extension of the imide photochemistry.²

It was found that aliphatic and aromatic thioimides undergo efficient [2 + 2]
photocyclization with olefins to give various thietanes.^{1a} In the course of
systematic studies on the thioimide photochemistry, we wish to report here the
photocycloaddition of N-methylmonothiophthalimide (1) with variously substituted
styrenes (2), and concomitant formation of dithiane derivatives (4).

A solution of 1 (5 mmol) and 2 (25 mmol) in benzene was irradiated with 500 W
high-pressure mercury lamp (Pyrex filter) for 1-10 h under a nitrogen atmosphere
and the results are listed in Table 1. In the most cases, thietanes (3) were
obtained accompanied by compounds consisting of two molecules of the thioimide
and one molecule of the styrene, which turned out to be the dithiane derivatives
(4), often in comparable yields.

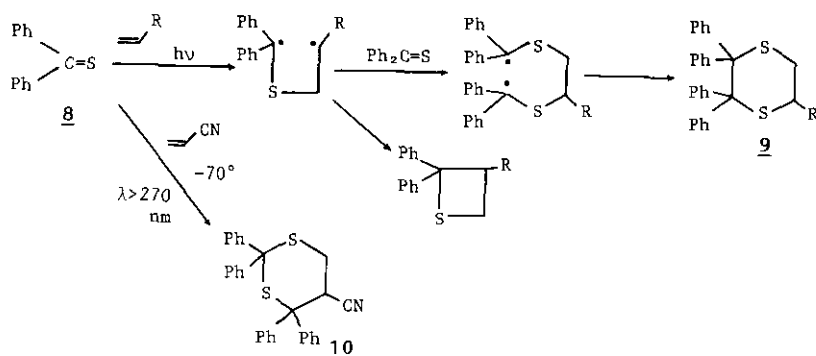
To obtain reference compounds to study the stereochemistry of 3, a mixture of 1
and acenaphthylene (5) was irradiated for 2.5 h. As expected, only two isomers³
of 6-i (anti) and 6-ii (syn) were obtained in 25 and 26% yields, respectively,
and could be easily distinguished by the chemical shifts of N-CH₃ protons (2.16

ppm for 6-i and 3.60 ppm for 6-ii) due to anisotropic effects of the naphthalene ring. Although four stereoisomers (3-i, 3-ii, 3-iii and 3-iv) are possible for the structure of 3b, two regioisomers (3-iii and 3-iv) were excluded based on the mass spectra of 3-i and 3-ii, which showed a peak corresponding to the loss of thioformaldehyde from the molecular ion. The stereochemistry of 3-i and 3-ii was determined on the basis of the anisotropic effects of the aromatics on the ¹H-NMR spectra of the N-methyl groups of 6 (N-CH₃: 2.72-2.89 ppm for 3a,b-i and 3.28-3.44 ppm for 3a,b-ii). This regioselectivity in forming the imide-thietanes 3 is reasonably explained by a mechanism in that the photoexcited thioimide initially attacks the β-carbon of styrene 2 giving the stabilized intermediate diradical 7.



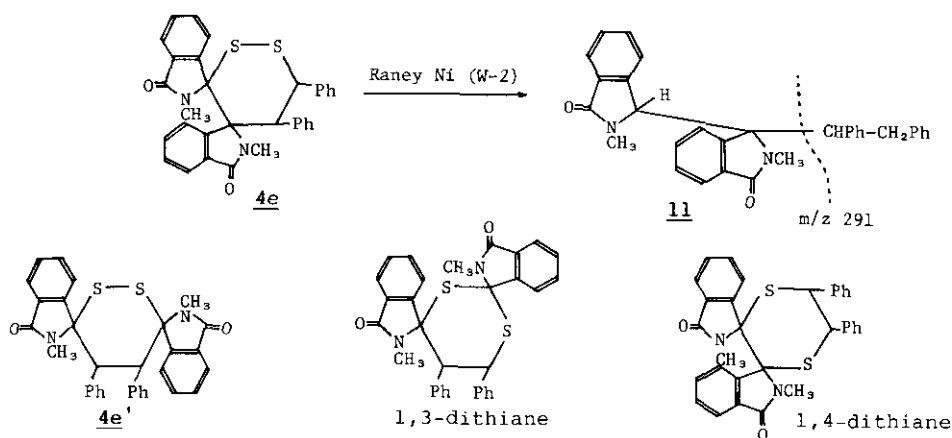
Scheme I

Compounds 4 were obtained as a mixture of stereoisomers, which were difficult to be separated, and their total yields are listed in Table 1. Their mass spectra indicated that the compound 4 consists of two molecules of 1 and one molecule of 2, suggestive of dithiane in analogy with the reactions of thiones, which undergo photocycloaddition to a variety of olefins to give thietanes and 1,4-dithianes.⁴ The formation of dithianes is one of characteristics of the thione photochemistry which differs from that of ketones, and the typical pathway from thiobenzophenone 8 is shown in Scheme II. By contrast, excitation into a high singlet state S₂ at



-70°C leads to the formation of a 1,3-dithiane 10.^{4b}

These compounds 4 were obtained in a form of complex mixture consisting presumably of regio- and stereoisomers of dithianes.⁵ Desulfurization of a sample of 4e, which contain two isomers after repeated column chromatography, was performed by refluxing with Raney-Ni in ethanol, and the product was purified with column chromatography giving rise to a mixture of diastereoisomers 11, the structure of which was determined on the basis of spectral data.⁶ From these results the compound 4e is deduced to be a 1,2-dithiane 4e, since 1,3- and 1,4-dithianes should lead to different desulfurized products. A possibility of the other 1,2-dithiane 4e' is excluded in view of the structure of the desulfurized product 11 (Scheme III).



Although the stereochemistry of 4 is yet unknown, this seems to be the first example of the formation of 1,2-dithiane in the photochemistry of thione derivatives.

More detailed studies of the photoreactions of the imide-thietanes and the dithianes will be reported elsewhere.

Table 1. Photoproducts from Thioimide 1 and Styrene Derivatives 2

<u>2</u>	R ₁	R ₂	Time (hr)	Thietane ^a		Dithiane <u>4</u> ^b Yield %
				<u>3-i</u>	Yield % (mp °C) <u>3-ii</u>	
<u>a</u>	H	H	10.0	14 ^c	13 ^c	65
<u>b</u>	CH ₃	H	5.0	41 (159-160)	15 (194-195)	31
<u>c</u>	Ph	H	10.0	34 (156-158)		--
<u>d</u>	H	CH ₃	1.5	50 (180-183)	3 (192-195)	37
<u>e</u>	H	Ph	1.0	36 (195-196)	44 (206-209)	15
<u>f</u>	H	CN	7.0	33 (175-176)	13 ^c	43
<u>g</u>	H	COMe	2.5	33 (142-144)	17 ^c	37

a All products showed reasonable analytical and spectral data (IR, Mass, ¹H- and ¹³C-NMR). The ratios of 3-i and 3-ii were determined by ¹H-NMR spectroscopy.

b Total yields of 1,2-dithiane and other dithianes.

c A mixture of 3-i and 3-ii estimated from ¹H-NMR.

REFERENCES AND NOTES

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- a) Y. Kanaoka, *Acc. Chem. Res.*, **11**, 407 (1978); b) M. Machida, K. Oda, and Y. Kanaoka, *Chem. Pharm. Bull.*, **32**, 75 (1984); c) Idem, *ibid.*, **32**, 950 (1984).
- Compounds 6-i (mp 218-221°C), 6-ii (mp 217-219°C) both gave satisfactory elemental analyses and spectral data (IR, Mass, ¹H- and ¹³C-NMR).
- a) A. Ohno, Y. Ohnishi, and G. Tsuchihashi, *J. Am. Chem. Soc.*, **91**, 5038 (1969);
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- For example, the dithianes 4e consist of a mixture of eight isomers based on eight N-Me peaks in their ¹H-NMR spectra.
- Compound 11 (mp 229-231°C) gave satisfactory elemental analysis and spectral data; MS m/z: 326, 291 (M⁺-stilbene). ¹³C-NMR (δ) (-CH^a-C^b(Ph)-CH^c-CH₂^dPh),
 C_a 63.3 (d), C_b 72.7 (s), C_c 52.6 (d), C_d 36.2 (t), respectively.

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