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PHOTOREACTION OF N-SUBSTITUTED MONOTHIOPHTHALIMIDES WITH STYRENE DERIVATIVES. AN EXAMPLE OF FORMATION AND FISSION OF THE THIETANE RING[1]

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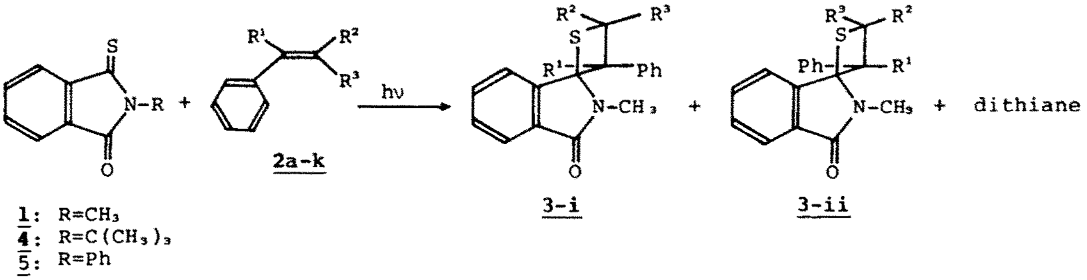
Abstract— Photolysis of N-methylmonothiophthalimide (1) in the presence of various styrene derivatives (2) afforded efficiently spiro-thietanes (3). The stereochemistry and the chemical conversion of the thietanes were discussed.

As a logical extension of the imide photochemistry[2] which has been extensively studied, we have recently initiated studies on thioimide systems,[3] a new amalgamation of the imide and sulfur. The major photochemical processes of the thioimides are limited to photocycloaddition (Paterno-Büchi type reaction) with olefins in contrast to the diverse behavior of their oxygen analogs (imides[2]) and nitrogen-lacking counterparts (thiones[4]). During the course of systematic studies on such thioimide photochemistry, we have found that aromatic monothioimides (1) undergo efficient [2+2] photocycloaddition (Paterno-Büchi type) with styrene derivatives (2) in which the resulting thietanes (3) are accompanied by various dithianes, often in comparable yields (Scheme 1).[5] The present report is a detailed account of this work including some chemical behavior of the thietane ring.



Scheme 1

In order to explore the solvent effects on the photocycloaddition, irradiation of 1 in the presence of trans-stilbene (2e) or cinnamonitrile (2f) was examined using various solvents (Table 1). Whereas photoreaction of 1 with 2e in acetonitrile afforded thietane 3, the reaction proceeded more cleanly in benzene to form the thietane along with improved recovery of 1. Photoreaction of 1 in acetonitrile containing various amounts of 2e was also examined (Table 2).

From the results of these preliminary experiments, general photolysis of 1 in the presence of 2 was carried out as follows. A solution of 1 (5 mmol) and 2 (25 mmol) in benzene was irradiated with a 500 W high-pressure mercury lamp (Pyrex filter) for 1-10 h under a nitrogen atmosphere (Scheme 1). The results

Table 1. Photoreaction of 1 with 2e or 2f in various solvents.

Solvent	Olefin[a]	React. time (h)	Thietane (%)[b] 3e	3f
CH_3CN	2e	0.25	40	
CH_3CN	2f	1		21
Benzene	2e	0.25	23	
Benzene	2f	1		28
Acetone	2e	0.25	30	
Acetone	2f	1		17
CH_3OH	2e	0.25	17	
CH_3OH	2f	1		14

a: Reactant ratio, 1 (1, imide) : 5 (2, olefin).
b: Estimated by gas chromatography.

2e: R^2=Ph, R^1=R^3=H
2f: R^2=CN, R^1=R^3=H

Table 2. Photoreaction of 1 in the presence of various amounts of 2e.

1[a] (mmole)	2e[a] (mmole)	Thietane 3e (%)[b]
0.1	0.05	10
0.1	0.10	24
0.1	0.20	29
0.1	0.30	38
0.1	0.50	43
0.1	0.75	46

a: Reaction time, 30 min; solvent, acetonitrile.
b: Estimated by gas chromatography.

Table 3. Photoproducts (3, 6 and 7).

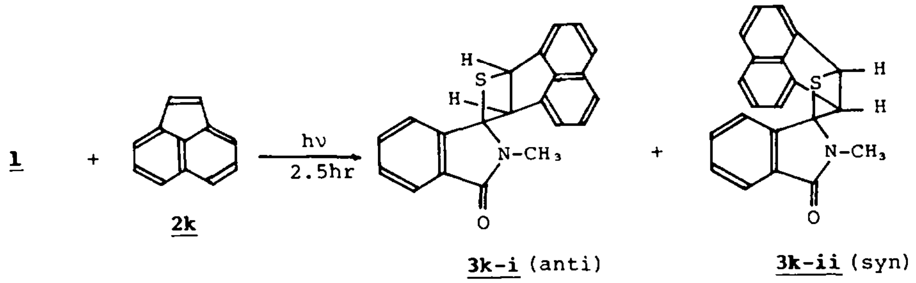
Imide	Olefin 2	R^1	R^2	R^3	Time (h)	Thietane (%)			Dithiane (%)
1						3-i	3-ii		
R=CH_3	a	H	H	H	10.0	14	13	(mixture)[a]	65
	b	CH_3	H	H	5.0	41	15		31
	c	Ph	H	H	10.0	34			-
	d	H	CH_3	H	1.5	50	3		37
	e	H	Ph	H	1.0	36	44	(mixture)[a]	15
	f	H	CN	H	7.0	33	13	(mixture)[a]	43
	g	H	$COCH_3$	H	2.5	33	17	(mixture)[a]	37
	h	H	$COOCH_3$	H	6.0	41	17		35
	i	H	H	Ph	1.0	36[b]	44[b]	(mixture)[a]	15
	j	$-(CH_2)_4-$		H	7.0	25	37		-
4						6-i	6-ii		
R=t-Bu	b	CH_3	H	H	22.0	32	-		-
	e	H	Ph	H	9.0	15	60		-
	k	acenaphthylene			6.0	31	50		-
5						7-i	7-ii		
R=Ph	b	CH_3	H	H	12.0	55	32		-
	e	H	Ph	H	1.5	41	52		-
	k	acenaphthylene			4.5	24	55		-

a: A mixture of two stereoisomers estimated by ^{1}H-NMR spectroscopy.
b: Be identical with the products from 2e.

with the simple monothiophthalimide 1 and various styrene derivatives are listed in Table 3.

Further, in order to see the structural requirements in forming the imide-thietane, the reaction of monothiophthalimides (4,5) having a t-butyl or a phenyl group as the N-substituent with styrene derivatives (2b,e,k) was tested. Progress of the photolysis was monitored by thin-layer chromatography until the imide (4,5) disappeared. Although the stereoselectivity in forming the thietane (6,7) was influenced little by N-substituents in their side chain, with *t*-stilbene (2e) the starting materials (1,5) disappeared more rapidly than with other styrene analogs giving thietanes (3e,7e) in good yields.

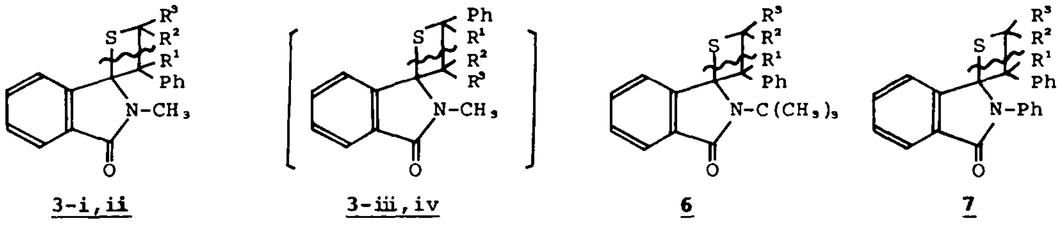
As reference compounds to study the stereochemistry of these thietanes 3, thietanes 3k-i and 3k-ii were prepared from 1 and acenaphthylene (2k), in which a naphthalene ring is rigidly fused and the geometric isomerism can not exist. These isomers (3k-i and 3k-ii) could be easily distinguished by the chemical shifts of N-CH$_3$ protons in the ^{1}H-NMR spectra. For 3k-ii, the peak due to N-CH$_3$ showed a lowfield shift at 3.60 ppm compared with that at 2.16 ppm for 3k-i, as a result of anisotropic effects of the naphthalene ring. Vicinal protons on the thietane ring appeared as two doublets with a coupling constant of 7 Hz at 5.12 and 5.50 ppm. The observed vicinal coupling constant has a value close to one^6 for the assignment to the *cis* protons (Scheme 2).



Scheme 2

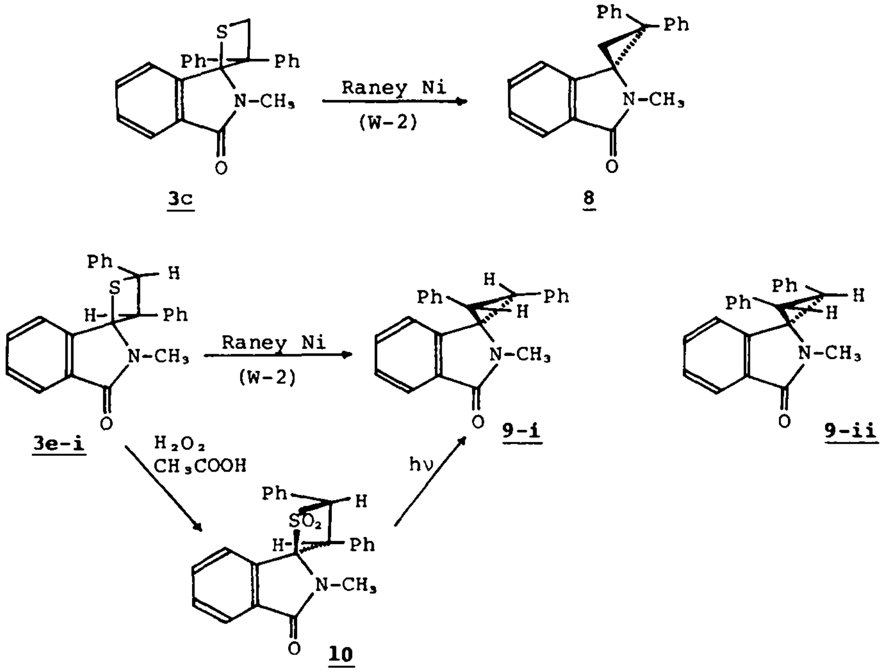
Since a pair of stereoisomers of the thietanes were isolated in the many cases above (Table 3), the stereochemistry of them 3 was easily determined on the basis of the values of the vicinal couplig constants, the chemical shifts of N-CH$_3$, and the mass spectra. Thus the 3-i series in Table 3 are of the *anti*, while the 3-ii series are of the *syn* isomers. Interestingly, in all the mass spectra of the thietane derivatives (3) obtained in this study, the loss of R^{2}R^{3}C=S from the molecular ion was observed as a characteristic fragmentation pattern, indicating that the R^2 and R^3 groups are attached to the carbon adjacent to sulfur in the thietane ring, which was used to distinguish the regioisomerism excluding a possible involvement of the other isomers 3-iii,iv (Scheme 3).^{3a,7} Similarly the structures of 6 and 7 were determined on the basis of the spectroscopy.

To further confirm the structures of these thietanes, 3c-i was treated with Raney nickel, reductive desufurization which is of importance in identifying the structure of thietane.^{7,8,9} As expected, ring constraction took place to afford a cyclopropane product 8 in 54% yield as a sole product together with recovery of 3c-i (17%). Similar treatment of 3e-i with Raney nickel gave two spiro cyclopropane isomers 9-i and 9-ii in 20 and 27% yields, respectively together with recovery of 3e-i (29%). The structures of these desulfurized products were determined on the basis of elemental analysis and spectral data. The mass spectrum of 8 showed a molecular ion peak at m/e 325, which corresponds to the



Scheme 3

loss of sulfur from the molecular ion of 3c-i. Similarly, both the mass spectra of 9-i and 9-ii also showed a molecular ion peak at m/e 325. In the ^{1}H-NMR spectrum of 9-i, two doublets with a coupling of J=9 Hz appeared at 3.37 and 3.75 ppm, indicating the presence of two benzylic hydrogens which are trans configuration to each other. By contrast, in the ^{1}H-NMR spectrum of 9-ii, two benzylic proton signal superimposed on a singlet at 3.56 ppm each other, indicating the cis configuration, which was further supported by the ^{13}C-NMR spectroscopy. In the off-resonance decoupled ^{13}C-NMR spectrum, two doublets due to benzylic carbons in 9-i appeared at 31.2 and 35.5 ppm compared with a singlet at 30.6 for 9-ii, which has cis configuration.



Scheme 4

Imide-thietanes, a spiro system containing both sulfur and nitrogen, have structural features as potential intermediates for various chemical transformations. For example, hydrogen peroxide oxidation of 3e-i produced a cyclic sulfone 10, which, on irradiation, gave a cyclopropane derivative as a result of extrusion reaction of a sulfone moiety. Interestingly the reaction took a stereospecific course leading to a sole product 9-i in a quantitative yield, again confirming the trans configuration of the substrate thietane 3e-i. Thus reaction will provide a stereoselective preparative method of such spiro cyclopropane system.

As shown in Fig. 1, N-methylmonothiophthalimide 1 in methylcyclohexane possesses a low-intensity band at 493 nm (ε=24), and more intensive bands at 296 nm (ε=13,400) and 326 nm (ε=9,500), which showed red shifts in comparison with that of N-methyldithiosuccinimide[3a]. In more polar solvent such as ethanol, the band at 493 nm shifted to 488 nm, to be attributed to a n,π^* transition. Although the fluorescence of 1 was not observed, the strong phosphorescence with a life-time of 2-3 msec appeared at 551 nm (excited, 386 nm, 77°K, in ethanol). A wavelengthdependence curve of the formation of 3e was close to the longer wavelength region in the absorption spectrum of 1 (Fig. 1).

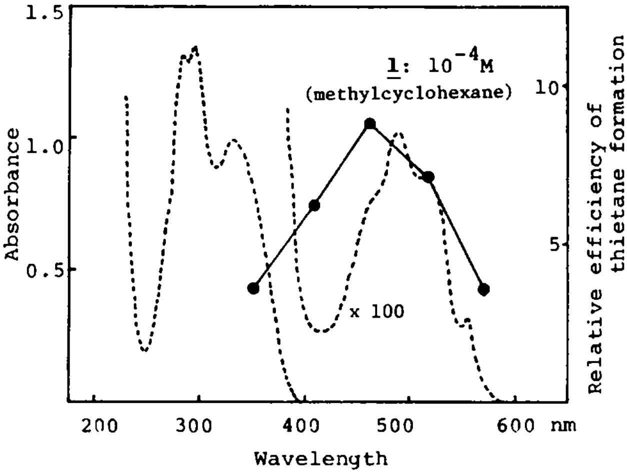
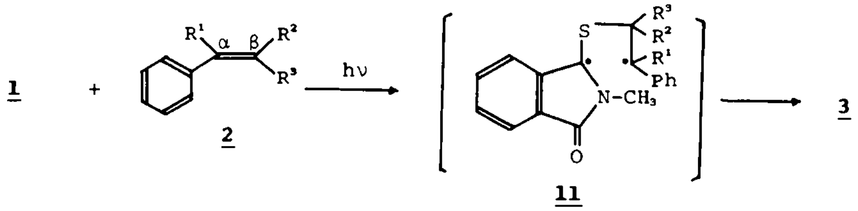


Fig. 1. Absorption spectrum and wavelength dependency of the thietane 3e formation: (---) absorption spectrum of 1, (—●—) relative efficiency of thietane formation 3e/1 .

From the above results, it seems that the thietanes 3, 6, and 7 arise from the triplet state of monothiophthalimide 1 in analogy with behavior of aliphatic thioimide systems.[3a] In addition, the formation of a pair of thietanes also supports a mechanism involving a biradical intermediate[3a] 11 arising from the triplet excited state. The regioselective formation of the thietanes 3 is explained in terms of initial attack of the excited thiocarbonyl to the β-carbon of styrene giving the stabilized biradical 11 (Scheme 5).

Thus, the monothiophthalimide undergoes efficient cycloaddition with styrene derivatives having a chromophore such as benzene ring to give spiro-thietanes, in contrast to the insufficient formation of spiro-thietanes in monothiosuccinimide system (aliphatic counterpart) with styrenes.[10] Thus by changing a key element in the imide systems from oxygen to sulfur, the resulting thioimides undergo preferencial cycloaddition to imide-thietanes, interesting spiro intermediates. In fact, formation of complex mixtures of dithianes (Table 3) must be ascribed to secondary transformations of the initially formed thietanes. The dithiane chemistry of the thietanes will be discussed in a separate paper.



Scheme 5

EXPERIMENTAL

All m.ps were determined on a Yamato m.p. apparatus (model MP-21) and are uncorrected. IR spectra were recorded on a JASCO-A-102 spectrometer. NMR spectra were taken on a Hitachi R-40 spectrometer and a JEOL FX-60 spectrometer or a JEOL JNM-FX-90Q spectrometer. Chemical shifts are reported in ppm (δ) relative to TMS (0.0 ppm) as an internal standard. The abbreviations used are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Mass spectra (MS) were obtained on a JEOL JMS-QH-100 mass spectrometer. UV spectra were measured with a Hitachi 228 spectrophotometer. Emission spectra were measured with a Hitachi 650-60 fluorescence spectrophotometer equipped with a Hitachi phosphoroscope attachment (650-0175). Preparative irradiations were conducted by using a 500 w high-pressure mercury lamp (Eikosha PIH-500) through Pyrex glass at room temperature. Stirring of the reaction mixture was effected by the introduction of stream of nitrogen at the bottom of the outer jacket. Wavelength-dependence experiments were carried out a JASCO CRM-FA spectroirradiator. Gas chromatographic analyses were performed on a Hitachi 163 gas chromatograph equipped with a flame ionization detector using a 2 m X 3 mm, 1.5% OV-17 on Chromosorb W, glass column. All column chromatography was conducted using silica gel (Merck, Kieselgel 60, 70-230 mesh). Thinchrographic analyses were performed on a Iatron TFG-10 thinchrograph.

Preparation of N-substituted monothiophthalimides (1, 4 and 5).

Monothioimides (1[11], 4,[11] 5,[12]) were prepared according to the reported procedures.

Imide 1: m.p. 91-92° (lit.[11], m.p. 89°).

Imide 4: m.p. 110-112°. IR (nujol): 1710 cm^{-1}. MS m/z: 219 (M^+). Found: C, 65.83; H, 6.04; N, 6.50; S, 14.71. Calc for $C_{12}H_{13}NOS$: C, 65.72; H, 5.97; N, 6.39; S, 14.62.

Imide 5: m.p. 131-132°. IR (nujol): 1740 cm^{-1}. MS m/z: 239 (M^+). Found: C, 70.37; H, 3.60; N, 5.78; S, 13.36. Calc for $C_{14}H_9NOS$: C, 70.27; H, 3.79; N, 5.85; S, 13.40.

Irradiation of N-methylmonothiophthalimide (1, 4 and 5) in the presence of olefin (2a-k): General procedure.

A solution of thioimide 1 (5 mmol) and olefin 2 (25 mmol) in 500 ml of benzene was irradiated for 1-10 h. After removal of the solvent in vacuo, the residue was chromatographed on a silica gel column and purified by recrystallization.

Thietane 3a-i, 3a-ii (a mixture of two stereoisomers): IR (nujol): 1685 cm^{-1}. MS m/z: 235 (M^+ - SCH_2). 3a-i: ^{1}H-NMR ($CDCl_3$): δ 2.89 (3H, s, N-Me), 3.32, 3.92 (2H, tx2, J=10 Hz, SCH_2), 5.36 (1H, t, J=10 Hz, CHPh), 6.5-8.1 (9H, m, Ar H), 3a-ii: ^{1}H-NMR:δ 3.28 (3H, s, N-Me), 3.29, 3.91 (2H, tx2, J=10 Hz, SCH_2), 5.19 (1H, t, J=10 Hz, CHPh), 6.5-8.1 (9H, m, Ar H).

Thietane 3b-i: m.p. 159-160°. IR (nujol): 1685 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 1.90 (3H, s, Me), 2.72 (3H, s, N-Me), 2.92, 4.12 (2H, dx2, J=9 Hz, SCH_2), 6.5-6.7 (2H, m, Ar H), 7.0-7.3 (3H, m, Ar H), 7.4-8.0 (4H, m, Ar H). MS m/z: 249 (M^+ - SCH_2). Found: C, 73.20; H, 5.61; N, 4.74; S, 10.64. Calc for $C_{18}H_{17}NOS$: C, 73.19; H, 5.80; N, 4.74; S, 10.85.

Thietane 3b-ii: m.p. 194-195°. IR (nujol): 1685 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 1.93 (3H, s, N-Me), 3.00, 4.07 (2H, dx2, J=9 Hz, SCH_2), 3.44 (3H, s, N-Me), 6.5-6.7 (2H, m, Ar H), 6.8-7.2 (6H, m, Ar H), 7.5-7.7 (1H, m, Ar H). MS m/z: 295 (M^+), 249 (M^+ - SCH_2). Found: C, 73.12; H, 5.80; N, 4.76; S, 10.84. Calc for $C_{18}H_{17}NOS$: C, 73.19; H, 5.80; N, 4.74; S, 10.85.

Thietane 3c: m.p. 156-158°. IR (nujol): 1695 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 2.77 (3H, s, N-Me), 3.96, 4.23 (2H, dx2, J=11 Hz, SCH_2), 6.3-6.4 (1H, m, Ar H), 6.9-7.4 (12H, m, Ar H), 7.7-7.8 (1H, m, Ar H). MS m/z: 311 (M^+ - SCH). Found: C, 77.36; H, 5.32; N, 3.96; S, 9.07. Calc for $C_{23}H_{19}NOS$: C, 77.28; H, 5.36; N, 3.92; S, 8.97.

Thietane 3d-i: m.p. 180-183°. IR (nujol): 1695 cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 1.70 (3H, d, J=6 Hz, Me), 3.48 (3H, s, N-Me), 4.3-4.6 (1H, m, SCH), 4.66 (1H, d, J=10 Hz, CHPh), 6.6-7.7 (9H, m, Ar H). MS m/z: 295 (M^+), 235 (M^+ - SCHMe). Found: C, 73.08; H, 5.87; N, 4.69; S, 10.89. Calc for $C_{18}H_{17}NOS$: C, 73.19; H, 5.80, N, 4.74, S, 10.85.

Thietane 3d-ii: m.p. 192-195°. IR (nujol): 1695 cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 0.93 (3H, d, J=8 Hz, Me), 3.52 (3H, s, N-Me), 3.8-4.2 (1H, m, SCH), 4.62 (1H, d, J=10 Hz, CHPh), 7.1-8.1 (9H, m, Ar H). MS m/z: 235 (M^+ - SCHMe). Found: C, 73.08; H, 5.82; N, 4.75; S, 10.79. Calc for $C_{18}H_{17}NOS$: C, 73.19; H, 5.80; N, 4.69; S, 10.89.

Thietane 3e-i: m.p. 195-196°. IR (nujol): 1700 cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 3.00 (3H, s, N-Me), 5.34 (1H, d, J=10 Hz, CHPh), 5.47 (1H, d, J=10 Hz, CHPh), 6.6-6.8 (2H, m, Ar H), 7.0-7.9 (14H, m, Ar H), 8.0-8.2 (1H, m, Ar H). MS m/z: 235 (M^+ - SCHPh). Found: C, 77.40; H, 5.38; N, 3.94; S, 8.94. Calc for $C_{23}H_{19}NOS$: C, 77.28, H, 5.36; N, 3.92; S, 8.97.

Thietane 3e-ii: m.p. 206-209°. IR (nujol): 1700 cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 3.46 (3H, s, N-Me), 5.13 (1H, d, J=10 Hz, CHPh), 5.46 (1H, d, J=10 Hz, CHPh), 6.6-7.8 (14H, m, Ar H). MS m/z: 235 (M^+ - SCHPh). Found: C, 77.55; H, 5.31; N, 3.78; S, 8.88. Calc for $C_{23}H_{19}NOS$: C, 77.28; H, 5.36; N, 3.92; 8.97.

Thietane 3f-i: m.p. 175-176°. IR (nujol): 1690 cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 2.80 (3H, s, N-Me), 4.83 (1H, d, J=10 Hz, SCH), 5.57 (1H, d, J=10 Hz, CHPh), 6.6-6.8 (2H, m, Ar H), 7.1-7.3 (3H, m, Ar H), 7.4-7.9 (3H, m, Ar H), 7.9-8.1 (1H, m, Ar H). Found: C, 70.60; H, 4.53; N, 9.03; S, 10.27. Calc for $C_{18}H_{14}NOS$: C, 70.56; H, 4.61; N, 9.14; S, 10.46.

Thietane 3f-ii (unseparable from 3f-i): ^{1}H-NMR (CDCl$_3$): δ 3.46 (3H, s, N-Me), 4.81 (1H, d, J=10 Hz, SCH), 5.38 (1H, d, J=10 Hz, CHPh), 6.6-6.9 (2H, m, Ar H), 7.0-7.8 (7H, m, Ar H).

Thietane 3g-i: m.p. 142-144°. IR (nujol): 1690 cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 2.38 (3H, s, COMe), 2.86 (3H, s, N-Me), 4.83 (1H, d, J=9 Hz, SCH), 5.60 (1H, d, J=9 Hz, CHPh), 6.6-6.7 (2H, m, Ar H), 7.1-8.0 (7H, m, Ar H). MS m/z: 323 (M^+), 235 (M^+ - SCHCOMe). Found: C, 70.50; H, 5.17; N, 4.22; S, 9.74. Calc for $C_{19}H_{17}NOS$: C, 70.56; H, 4.61; N, 9.14; S, 10.46.

Thietane 3g-ii (unseparable from 3g-i): ^{1}H-NMR (CDCl$_3$): δ 2.33 (3H, s, COMe), 3.36 (3H, s, N-Me), 4.45 (3H, d, J=10 Hz, SCH), 5.40 (3H, d, J=10 Hz, CHPh), 6.5-8.0 (9H, m, Ar H).

Thietane 3h-i, 3h-ii (a mixture of two stereoisomers): IR (nujol): 1710 cm^{-1}. MS m/z: 339 (M^+), 235 (M^+ - SCHCOOMe). 3h-i: ^{1}H-NMR (CDCl$_3$): δ 2.82 (3H, s, N-Me), 3.83 (3H, s, OMe), 4.82 (1H, d, J=9 Hz, SCH), 5.62 (1H, s, J=9 Hz, CHPh), 6.5-8.2 (9H, m, Ar H). 3h-ii: ^{1}H-NMR: δ 3.43 (3H, s, N-Me), 3.81 (3H, s, OMe), 4.78 (1H, d, J=9 Hz, SCH), 5.44 (1H, d, J=9 Hz, CHPh), 6.5-8.2 (9H, m, Ar H). Found: C, 67.05; H, 4.99; N, 4.16; S, 9.33. Calc for $C_{19}H_{17}NOS$: C, 67.24; H, 5.05; N, 4.13; S, 9.45.

Thietane 3j-i: m.p. 167-168°. IR (nujol): 1700 cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 1.4-2.3 (8H, m, $-(CH_2)_4-$), 2.83 (3H, s, N-Me), 4.8-5.0 (1H, m, SCH), 6.8-8.1 (9H, m, Ar H). MS m/z: 335 (M^+). Found: C, 75.21; H, 6.29; N, 4.03; S, 9.51. Calc for $C_{21}H_{21}NOS$: C, 75.19; H, 6.31; N, 4.18; S, 9.56.

Thietane 3j-ii: m.p. 175-176°. IR (nujol): 1700 cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 1.5-2.3 (3H, m, $-(CH_2)_4-$), 3.47 (3H, s, N-Me), 4.9-5.1 (1H, m, SCH), 6.6-7.9 (9H, m, Ar H). MS m/z: 335 (M^+). Found: C, 75.09; H, 6.44; N, 4.00; S, 9.68. Calc for $C_{21}H_{21}NOS$: C, 75.19; H, 6.31; N, 4.18; S, 9.68.

Thietane 3k-i: m.p. 218-221°. IR (nujol): 1690 cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 2.16 (3H, s, N-Me), 5.12 (1H, d, J=7 Hz, SCHCH), 5.50 (1H, d, J=7 Hz, SCH), 7.0-7.1 (1H, m, Ar H), 7.3-7.8 (8H, m, Ar H), 8.1-8.2 (1H, m, Ar H). MS m/z: 297 (M^+ - S). Found: C, 76.70; H, 4.52; N, 4.34; S, 9.72. Calc for $C_{21}H_{15}NOS$: C, 76.57; H, 4.59; N, 4.25; S, 9.73.

Thietane 3k-ii: m.p. 217-219°. IR (nujol): 1690 cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 3.60 (3H, s, N-Me), 5.17 (1H, d, J=7 Hz, SCHCH), 5.28 (1H, d, J=7 Hz, SCH), 6.0-6.2 (1H, m, Ar H), 6.4-6.5 (1H, m, Ar H), 6.9-7.8 (8H, m, Ar H). MS m/z: 297 (M^+ - S). Found: C, 76.61; H, 4.66; N, 4.26; S, 9.81. Calc for $C_{21}H_{15}NOS$: C, 76.57; H, 4.59; N, 4.25; S, 9.73.

Thietane 6b-i: m.p. 154-155°. IR (nujol): 1690 cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 1.40 (9H, s, N-CMe$_3$), 1.65 (3H, s, Me), 2.95 (1H, d, J=9 Hz, SCH), 4.19 (1H, 7.0-8.0 (9H, m, Ar H). MS m/z: 291 (M^+ - SCH$_2$). Found: C, 74.76; H, 6.94; N, 4.08; S, 9.65. Calc for $C_{21}H_{23}NOS$: C, 74.74; H, 6.87; N, 4.15; S, 9.50.

Thietane 6e-i, 6e-ii (a mixture of two stereoisomers): IR (nujol): 1700 cm^{-1}. 6e-i: ^{1}H-NMR (CDCl$_3$): δ 1.52 (9H, s, N-CMe$_3$), 5.39 (1H, d, J=10 Hz, CHPh), 5.64 (1H, d, J=10 Hz, CHPh), 6.9-7.8 (14H, m, Ar H). 6e-ii: ^{1}H-NMR: δ 1.98 (9H, s, N-CMe$_3$), 5.59 (1H, d, J=7 Hz, CHPh), 6.7-7.8 (14H, m, Ar H). MS m/z: 277 (M^+ - SCHPh). Found: C, 78.09; H, 6.24; N, 3.41; S, 7.84. Calc for $C_{26}H_{25}NOS$: C, 78.16; H, 6.31; N, 3.51; S, 8.02.

Thietane 6k-i: m.p. 192-193°. IR (nujol): 1690 cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 1.06 (9H, s, N-CMe$_3$), 5.31, 5.44 (1Hx2, dx2, J=7 Hz, SC$\underline{\mathrm{H}}$C$\underline{\mathrm{H}}$), 7.1-7.3 (2H, m, Ar H), 7.3-7.9 (6H, m, Ar H), 8.0-8.3 (2H, m, Ar H). MS m/z: 371 (M$^+$). Found: C, 77.63; H, 5.66; N, 3.59; S, 8.40. Calc for $C_{24}H_{21}NOS$: C, 77.60; H, 5.70; N, 3.77; S, 8.63.

Thietane 6k-ii: m.p. 210-212°. IR (nujol): 1690 cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 2.12 (9H, s, N-CMe$_3$), 5.15 (1H, d, J=7 Hz, SCHC$\underline{\mathrm{H}}$), 5.71 (1H, d, J=7 Hz, SCH), 5.7-6.0 (1H, m, Ar H), 6.3-6.5 (1H, m, Ar H), 6.6-7.8 (6H, m, Ar H). MS m/z: 371 (M$^+$). Found: C, 77.83; H, 5.70; N, 3.88; S, 8.58. Calc for $C_{24}H_{21}NOS$: C, 77.60; H, 5.70; N, 3.88; S, 8.63.

Thietane 7b-i: m.p. 189-191°. IR (nujol): 1695 cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 1.97 (3H, s, Me), 2.61, 3.33 (2H, d, J=9 Hz, SCH$_2$), 6.2-8.1 (14H, m, Ar H). MS m/z: 357 (M$^+$), 311 (M$^+$ - SCH$_2$). Found: C, 77.33; H, 5.32; N, 3.79; S, 9.03. Calc for $C_{23}H_{19}NOS$: C, 77.33; H, 5.32; N, 3.79; S, 9.03.

Thietane 7b-ii: m.p. 179-182°. IR (nujol): 1695 cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 1.52 (3H, s, Me), 2.87, 4.08 (2H, dx2, J=9 Hz, SCH$_2$), 6.6-7.8 (14H, m, Ar H). MS m/z: 357 (M$^+$), 311 (M$^+$ - SCH$_2$). Found: C, 77.24; H, 5.42; N, 4.28; S, 8.96. Calc for $C_{23}H_{19}NOS$: C, 77.28; H, 5.36; ;N, 3.92; S, 8.97.

Thietane 7e-i, 7e-ii (a mixture of two stereoisomers): IR (nujol): 1710 cm^{-1}. 7e-i: ^{1}H-NMR (CDCl$_3$): δ 4.74 (1H, d, J=11 Hz, SCHC$\underline{\mathrm{H}}$), 5.48 (1H, d, J=11 Hz, SCH), 6.3-8.2 (19H, m, Ar H). 7e-ii: ^{1}H-NMR: δ 5.20, 5.28 (1Hx2, dx2, J=11 Hz, SC$\underline{\mathrm{H}}$C$\underline{\mathrm{H}}$), 6.3-8.2 (19H, m, Ar H). MS m/z: 311 (M$^+$ - SCHPh). Found: C, 80.11; H, 5.01; N, 3.36; S, 7.61. Calc for $C_{28}H_{21}NOS$: C, 80.16; H, 5.05; N, 3.34; S, 7.64.

Thietane 7k-i: m.p. 171-173°. IR (nujol): 1710 cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 4.92 (1H, d, J=7 Hz, SCHC$\underline{\mathrm{H}}$), 5.65 (1H, d, J=7 Hz, SCH), 6.4-8.0 (14H, m, Ar H), 8.0-8.3 (1H, m, Ar H). MS m/z: 391 (M$^+$). Found: C, 79.80; H, 4.23; N, 3.35; S, 8.24. Calc for $C_{26}H_{17}NOS$: C, 79.77; H, 4.38; N, 3.58; S, 8.19.

Thietane 7k-ii: m.p. 208-211°. IR (nujol): 1710 cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 4.55 (1H, d, J=7 Hz, SCHC$\underline{\mathrm{H}}$), 5.22 (1H, d, J=7 Hz, SCH), 6.1-6.3 (1H, m, Ar H), 6.4-6.6 (1H, m, Ar H), 6.8-7.9 (13H, m, Ar H). MS m/z: 391 (M$^+$). Found: C, 79.64; H, 4.20; N, 3.52; S, 8.25. Calc for $C_{26}H_{17}NOS$: C, 79.77; H, 4.38; N, 3.58; S, 8.19.

Raney nickel reductive desulfurization of thietanes 3c and 3e-i: Preparation of 8 and 9.

To a solution of 3c (175 mg, 0.5 mmol) in 5 ml of ab. ethanol was added Raney nickel (W-2, prepared from 2.5 g Raney nickel aluminium alloy). The solution was refluxed for 3 h. The residual oil obtained from the filtrate was chromatographed on silica gel to give spiro-cyclopropane 8, m.p. 190-191°. IR (nujol): 1690 cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 2.23, 2.53 (1Hx2, dx2, J=7 Hz, CH$_2$), 2.25 (3H, s, N-Me), 5.5-5.9 (1H, m, Ar H), 6.9-7.5 (12H, m, Ar H), 7.8-7.9 (1H, m, Ar H). ^{13}C-NMR (CDCl$_3$): δ 21.3, 27.3, 27.4, 42.2, 53.7, 121.6, 123.1, 127.1, 127.3, 128.5, 128.9, 129.1, 131.7, 141.4, 144.6, 169.4. MS m/z: 325 (M$^+$). Found: C, 85.07; H, 5.87; N, 4.21. Calc for $C_{23}H_{19}NO$: C, 84.89; H, 5.88; N, 4.30.

Similar procedure was used for the reduction of 3e-i. Separation by column chromatography gave 9-i and 9-ii in 20 and 27% yields, respectively.

Compound 9-i: m.p. 122-124°. IR (nujol): 1690 cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 2.45 (3H, s, N-Me), 3.37 (1H, d, J=9 Hz, CHPh), 3.75 (1H, d, J=9 Hz), 6.1-6.3 (1H, m, Ar H). 7.0-7.5 (12H, m, Ar H), 7.7-8.0 (1H, m, Ar H). ^{13}C-NMR (CDCl$_3$): δ 27.0, 31.2, 35.5, 54.1, 120.3, 123.4, 127.2, 127.5, 127.8, 128.3, 128.6, 128.8, 129.6, 130.7, 131.6, 135.4, 135.5, 144.2, 168.9. MS m/z: 325 (M$^+$). Found: C, 84.73; H, 5.95; N, 4.10;. Calc for $C_{23}H_{19}NO$: C, 84.89; H, 5.88; N, 4.30.

Compound 9-ii: m.p. 175-177°. IR (nujol): 1670 cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 3.11 (3H, s, N-Me), 3.56 (2H, s, C$\underline{\mathrm{H}}$C$\underline{\mathrm{H}}$Ph), 5.8-6.0 (1H, m, Ar H), 6.9-7.4 (12H, m, Ar H), 7.8-8.0 (1H, m, Ar H). ^{13}C-NMR (CDCl$_3$): δ 24.3, 30.6, 52.8, 123.2, 125.3, 127.1, 127.2, 128.1, 128.4, 128.8, 129.2, 131.2, 132.7, 133.0, 141.1, 168.0. MS m/z: 325 (M$^+$). Found: C, 84.65; H, 5.85; N, 4.51. Calc for $C_{23}H_{19}NO$: C, 84.89; H, 5.88; N, 4.30.

Oxidation of thietane (3e-i) to sulfone (10).

A mixture of thietane (3e-i; 179 mg, 0.5 mmol) in 20 ml of acetone, 3 ml of acetic acid and 3 ml of 30% aqueous hydrogen peroxide was refluxed for 5 h. After removal of the solvent, the residual oil was triturated with dichloromethane. The solution was dried and concentrated in vacuo to give 129 mg (66%) of sulfone (10), m.p. 148-150°. IR (nujol): 1710 cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 2.86 (3H, s, N-Me), 5.1-5.2 (2H, m, C$\underline{\mathrm{H}}$C$\underline{\mathrm{H}}$Ph), 6.5-8.0 (14H, m, Ar H). MS m/z: 325 (M$^+$- SO$_2$). Found: C, 70.60; H, 5.21; N, 3.34; S, 7.39. Calc for $C_{23}H_{19}NO_3S$: C, 70.93; H, 4.92; N, 3.60; S, 7.23.

Irradiation of sulfone (10).

A solution of sulfone (10; 195 mg) in 5 ml of acetone was irradiated for 6 h. After removal of the solvent in vacuo, the residue was recrystallized from ethanol to give 9-i quantitatively.

Wavelength-dependence experiments for formation of thietane (3e). Irradiation at various wavelengths.

A solution of 1 (1 mmol) and 2e (5 mmol) in 100 ml of acetonitrile was prepared. A 5 ml portion of this solution was placed into each of five Vycol tubes, which were then attached to a high-vacuum line, degassed with a series of five freeze-pump-thaw cycles, and sealed. Each sample was irradiated at 356, 410, 463, 516, and 570 nm for 1 h by spectroirradiator. Yields for thietane 3e formation at various wavelengths were determined by thinchrographic analysis by using N-t-butylphthalimide as an internal standard.

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