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Tetrahedron 63 (2007) 7708–7716
Tetrahedron

Photo SN-bond cleavage and related reactions of thianthrene sulfilimine derivatives

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Received 21 March 2007; revised 1 May 2007; accepted 1 May 2007
Available online 7 May 2007

Abstract—Several 1- and 2-substituted thianthrene sulfilimine derivatives were prepared and the selectivity toward oxidation and N-tosylimination under several conditions was studied. In the photolysis of *trans*-5-(*N*-*p*-tosyl)iminothianthrene 10-oxide (*trans*-**10**), photo isomerization to *cis*-**10** was observed. Further, photoimino-transfer reaction of sulfilimines and their 10-mono- and -dioxide derivatives to sulfides was intensively studied to make clear the ability as nitrene precursors.

1. Introduction

According to the thianthrene sulfilimines there have been limited works, contrary to the ordinary sulfilimine derivatives.[1] Therefore, it is interesting to study the physical property and chemical reactivity of thianthrene sulfilimines, because thianthrene has inherently an interesting structure that is existing as two configurational isomers, due to the 'flip–flap' motion around S–S axis of their 1,4-dithiin frame-work with two fused-benzene rings.[2–6] In addition, the structure of its molecule is boat-form, therefore, the interaction between the 5- and 10-position sulfur atom and its substituents is interesting and also the substituent effects between the 1- or 2-substituent and the attacking site of the reagents on the regioselectivity for oxidation or N-tosylation reaction. Previously, We have reported the physical properties and chemical reactivities of several 5,10-disubstituted thianthrene sulfilimine derivatives with the X-ray crystallographic structural determinations.[7] Furthermore, the thermal behavior of these compounds was reported.[7]

Optically active sulfilimines are known to undergo thermal racemization through the pyramidal inversion substantially at around 70–100 °C.[8] Mislow and co-workers studied the thermal racemization of sulfoxides in detail at high temperature, generally at around 180–240 °C.[9]

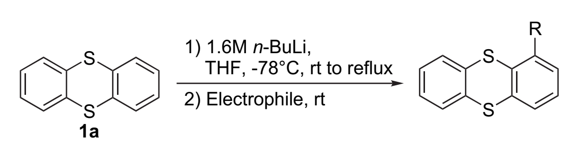
Concerning thianthrene sulfilimines and sulfoxides, we have studied and reported the thermal *cis–trans* isomerization between *cis*- and *trans*-5-(*N*-*p*-tosyl)iminothianthrene 10-oxide via pyramidal inversion on sulfur atom bearing NTs group.[7]

About the photolytic behavior of thianthrene sulfilimines there have been no report so far. About the photolysis of aliphatic and aromatic sulfilimine derivatives a few reports were appeared focused on the generation of nitrenes.[10] Therefore, in order to compare the photolytic behavior, various thianthrene derivatives were prepared and the reactivities under photolytic conditions were studied.

2. Results and discussion

2.1. Synthesis of thianthrene derivatives

Lithiation of thianthrene at C-1 followed by the reactions with various electrophiles provides easily various 1-substituted thianthrenes, i.e., 1-methylthianthrene (**1b**), 1-trimethylsilylthianthrene (**1c**), and 1-formylthianthrene (**1d**) as shown in Scheme 1.[11]



Scheme 1. Synthesis of 1-substituted thianthrenes.

Other substituted thianthrenes are prepared by the direct reaction of thianthrene with electrophile by the Friedel–Crafts type reaction. 2-Bromothianthrene (**1e**) was obtained by the

Keywords: Thianthrene; Sulfilimine; Nitrene; Photolysis; Photoisomerization.
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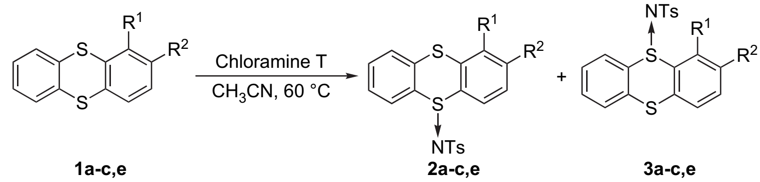
doi:10.1016/j.tet.2007.05.004

Table 1. Tosylimination of thianthrene derivatives



Entry		R^1	R^2	Yield[a] (%)	
				2	**3**
1	**1a**	H	H	94 (**2a**)	—
2	**1b**	Me	H	72 (**2b**)	24 (**3b**)
3	**1c**	TMS	H	67 (**2c**)	Trace (**3c**)
4[b]	**1e**	H	Br	30 (**2e**)	18 (**3e**)

[a] Isolated yield.
[b] Starting material of 27% was recovered.

reaction of thianthrene and 2.0 equiv of bromine in acetic acid at 80 °C, and 2,7- and 2,8-dibromothianthrene (**1f** and **1f′**) was obtained as a mixture in a similar reaction with 4.0 equiv of bromine.[12]

5-(*N*-*p*-Tosyl)iminothianthrene (**2a**)[7,13] and several 1- or 2-substituted 5- and 10-(*N*-*p*-tosyl)iminothianthrene derivatives, i.e., 1-methyl-5-(*N*-*p*-tosyl)iminothianthrene (**2b**), 1-methyl-10-(*N*-*p*-tosyl)iminothianthrene (**3b**), 1-trimethylsilyl-5-(*N*-*p*-tosyl)iminothianthrene (**2c**), 1-trimethylsilyl-10-(*N*-*p*-tosyl)iminothianthrene (**3c**), 2-bromo-5-(*N*-*p*-tosyl)-iminothianthrene (**2e**) and 2-bromo-10-(*N*-*p*-tosyl)iminothianthrene (**3e**) were obtained by the reaction of the corresponding thianthrene (**1a**) and thianthrene derivatives **1a**–**c**,**e** with chloramine T[14] in acetonitrile at 60 °C. These results are summarized in Table 1.

On S-tosylimination with chloramine T, interesting results were observed concerning the regioselectivity. In entry 2, 1-methylthianthrene (**1b**) afforded **2b** and **3b** in 72 and 24% yields, respectively; the ratio of S-tosylimination at 5- versus 10-position was 3:1. In contrast, 2-bromothianthrene (**1e**), which has no substituent at *peri* position and is supposed to be free from the steric effect, showed selectivity with even low ratio as 5:3 (entry 4). These results suggest that the product distribution of S-tosylimination for the 1- or 2-substituted thianthrene derivatives is not simply accounted for by the steric effect only. In the 2-bromo substituent (entry 4) electronic effect through benzene ring seems to be operating greatly; electron-donating effect by *para* position for 5-S-position and electron-withdrawing effect by *meta* position for 10-S-position.

When the mixture of **1f** and **1f′**, which is not able to separate conveniently by column chromatography, was reacted with chloramine T under the similar conditions (but for sufficiently longer reaction time, 1 day), 2,7- and 2,8-dibromo-5-(*N*-*p*-tosyl)iminothianthrene (**2f** and **2f′**) were obtained in moderate yields after HPLC separation in 17 and 23% yields, respectively (Scheme 2).

This product ratio (1:1.4) also seems to indicate the yield ratio of **1f** versus **1f′** in the di-bromination reaction of thianthrene.

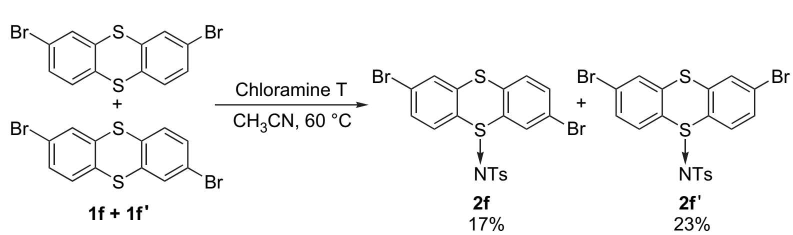
In this case, the exclusive formation of **2f′** in S-tosylimination of **1f′** is apparently due to both the electronic effect and the steric effect of two bromine atoms at both 2- and 8-position. The similar regioselectivity for 5- versus 10-position was also observed by the oxidation of **1a**–**c**,**e** with *m*-CPBA as shown in Table 2. However, in these cases, the observed selectivities were smaller than S-tosylimination.

5-(*N*-Substituted)iminothianthrenes, i.e., 5-(*N*-1-naphthylsulfonyl)iminothianthrene (**7α**), 5-(*N*-2-naphthylsulfonyl)-iminothianthrene (**7β**), 5-(*N*-acetyl)iminothianthrene (**8**), and 5-(*N*-benzoyl)iminothianthrene (**9**),were easily obtained in high yields by the reaction of 5-iminothianthrene (**6**)[15] with various acyl or sulfonyl halides (Scheme 3).

trans- and *cis*-5-(*N*-*p*-Tosyl)iminothianthrene 10-oxide (*trans*-**10** and *cis*-**10**), and 5-(*N*-*p*-tosyl)iminothianthrene 10,10-dioxide (**11**), successively, *trans*- and *cis*-5-iminothianthrene 10-oxide (*trans*-**12** and *cis*-**12**), and 5-iminothianthrene 10,10-dioxide (**13**) were prepared according to our previous report.[7]

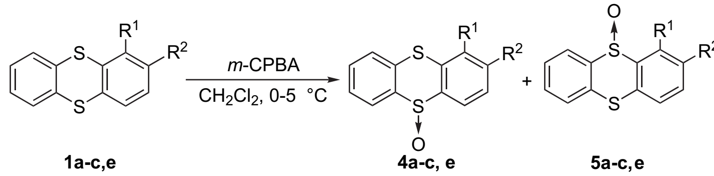
2.2. Photolysis of thianthrene *N*-tosylsulfilimine derivatives

The photolyses of **2a**, *cis*-**10**, *trans*-**10**, and **11** were carried out using a 400 W high-pressure mercury lamp with Pyrex filter in CH_2Cl_2, the results are summarized in Table 3.



Scheme 2. 5-Imination of 2,7- and 2,8-bromothianthrene.

Table 2. Oxidation of thianthrene derivatives with *m*-CPBA



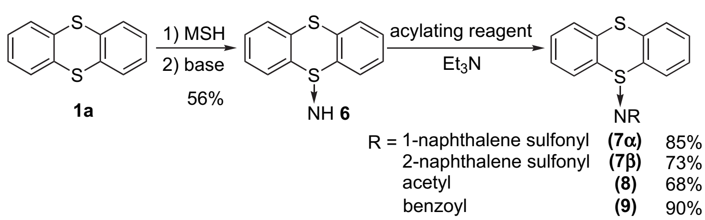
Entry		R^1	R^2	Yield[a] (%)	
				4	**5**
1	**1a**	H	H	89 (**4a**)	—
2	**1b**	Me	H	54 (**4b**)	30 (**5b**)
3	**1c**	TMS	H	50 (**4c**)	30 (**5c**)
4	**1e**	H	Br	48 (**4e**)	33 (**5e**)

[a] Isolated yield.

Although thianthrene itself is stable under the photochemical conditions, thianthrene sulfilimines and sulfoxides were found to photolyze to **1a**, **4a**, thianthrene 5,5-dioxide (**14**), and *p*-toluenesulfonamide (**15**).

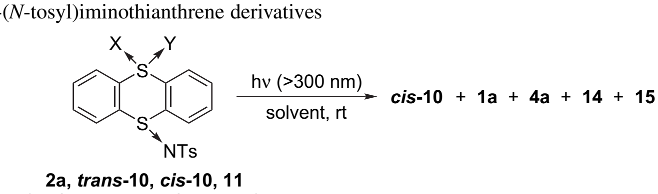
The photolysis of **2a** and **11** proceeded smoothly and exclusively via SN-bond cleavage. Compound **2a** afforded the de-iminated product **1a** and *p*-toluenesulfonamide (**15**) in 65 and 32% yields, respectively, with recovery of **2a** (entry 1), and **11** afforded the de-iminated **14** and **15**, in 78 and 70% yields, respectively (entry 2). However, *trans*-**10** and *cis*-**10** photolyzed in different ways. The reaction of *cis*-**10** proceeded to form **4a** in only 13% yield even after irradiation for 6 h (entry 3). This reason is considered to be due to no absorption of *cis*-**10** beyond 300 nm in the UV spectra as shown in Figure 1.

In contrast, *trans*-**10** proceeded readily to form **4a** and **1a** in 65 and 10% yields, respectively (entry 4). Compound **1a** seems to be formed by the further secondary photolysis of **4a**. However, in this case, *cis*-**10** was formed unexpectedly in 25% yield instead of the recovery of *trans*-**10**. This result



Scheme 3. Synthesis of 5-(*N*-substituted)iminothianthrenes.

Table 3. Photochemical behavior of 5-(*N*-tosyl)iminothianthrene derivatives



Entry	Compound	Solvent	Time (h)	*C* (mM)	Yield[a] (%)					
					cis-**10**[b]	**1a**	**4a**	**14**	**15**	Recovery
1	**2a**	CH_2Cl_2	5.0	12.5	—	65	—	—	32	16
2	**11**	CH_2Cl_2	5.0	12.5	—	0	0	78	70	0
3	*cis*-**10**	CH_2Cl_2	6.0	12.5	—	[c]	13	—	Trace	83
4	*trans*-**10**	CH_2Cl_2	3.0	12.5	25	10	65	—	Trace	0
5	*trans*-**10**	CH_2Cl_2	2.0	12.5	25	Trace	51	—	Trace	[c]
6	*trans*-**10**	CH_2Cl_2	2.0	25	26	Trace	51	—	Trace	[c]
7	*trans*-**10**	CH_2Cl_2	2.0	50	15	Trace	45	—	Trace	[c]
8	*trans*-**10**	CH_3CN	2.0	12.5	15	Trace	35	—	Trace	[c]
9	*trans*-**10**	CH_3CN	2.0	25	18	Trace	38	—	Trace	[c]
10	*trans*-**10**	MeOH	2.0	12.5	0	29	26	—	47	[c]

[a] Isolated yield.
[b] Isomerized product from *trans*-**4a**.
[c] Not determined (less than 10%).

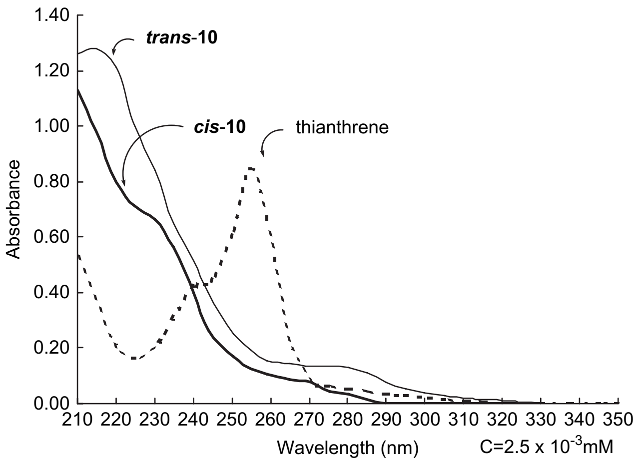


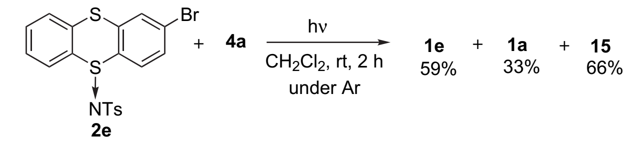
Figure 1. UV spectra of compounds *trans*-**10**, *cis*-**10**, and thianthrene (**1a**).

probably implies that *trans*-**10** absorbed UV light to lead to the photoexcited state, followed by the SN-bond cleavage to generate nitrene and to form the resultant sulfoxide **4a**. Then, *cis*-**10** was formed by the recombination of *N*-tosyl nitrene with **4a**. The reaction mechanism is depicted in Figure 2, together with several other probable pathways including photopyramidal inversion process.

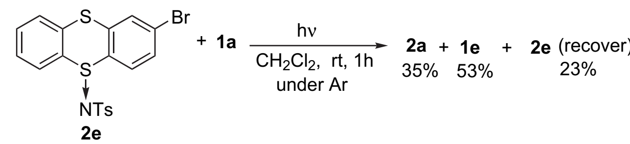
In order to determine whether the *N*-tosyl group migration is inter- or intramolecular, the cross-over experiment using a 1:1 mixture of **2e** and **4a** was carried out under the same photolytic conditions (Scheme 4). However, the phototransfer product of *N*-tosyl group to **4a**, i.e., *cis*-**10** or *trans*-**10**, was not obtained at all, despite the formation of de-iminated product **1e** and **15** in good yield.

To investigate the further photolytic behavior of thianthrene sulfilimine derivatives, irradiation of a 1:1 mixture of **2e** and thianthrene (**1a**) was carried out. The *N*-tosyl group transfer product **2a** and de-iminated product **1e** were formed expectedly in 35 and 53% yields, respectively (Scheme 5).

Further, the photoreaction of **3b** found to afford the isomerization product **2b** in rather good yields (Scheme 6). In this case, **2b** was formed predominantly, probably because direction for recombination of nitrene initially formed seems to be determined preferentially to the less hindered site

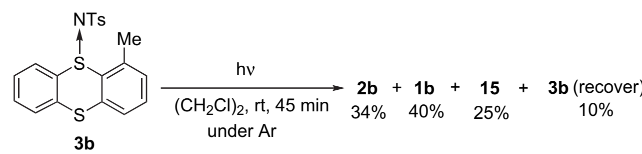


Scheme 4. Cross-over experiment between **2e** and **4a**.



Scheme 5. Cross-over experiment between **2e** and **1a**.

(5-position). This result was rationalized that compound **3b** was not obtained by the irradiation of **2b** under the same conditions.



Scheme 6.

All these results seem to describe that thianthrene sulfilimines decompose to generate nitrene under UV irradiation (>300 nm) and recombination of nitrene to the resultant thianthrene derivatives proceeded via the inter- and/or intramolecular pathway concurrently with the formation of **15** from tosyl nitrene, depending on the nature of sulfilimines and nitrene acceptor used in the cross-over experiments.

2.3. The effect of solvents and concentrations on the photolysis of *trans*-10

The effect of several solvents and concentrations was examined in the photolysis of *trans*-**10** in order to get further details of the photoreaction. The results are summarized in Table 3. This reaction was performed under the limited condition because of the limited solubility of *trans*-**10** in the common solvents.

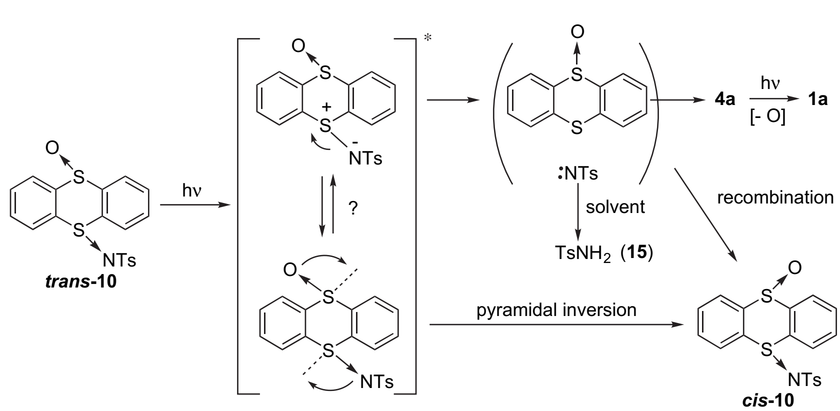
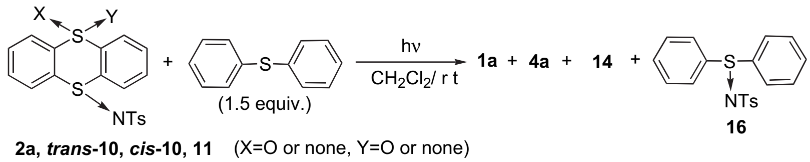


Figure 2. Plausible mechanisms of photolysis of **10**.

Table 4. Photolysis of 5-(*N*-*p*-tosyl)iminothianthrene derivatives in the presence of diphenyl sulfide



Entry	Compound	Time (h)	Yield[a] (%)				
			Recover	**1a**	**4a**	**14**	**16**
1	**2a**	5	11	61			33
2	**11**	5	0	0	0	88	70
3	*trans*-**10**	3	0	11	83		44
4	*cis*-**10**	6	82	Trace	17		Trace

[a] Isolated yield.

In dichloromethane, the product distribution revealed to be almost the same and there was no significant change in the product ratio, forming **4a** and *cis*-**10** in 51 and ca. 25% yield, when the concentration was changed from 12.5 to 50 mM (entries 5–7). When the concentration was increased to 50 mM, the yields of both **4a** and *cis*-**10a** were decreased substantially, however, the reason is not clear at present. Similarly, when the photolysis was carried out in CH_3CN, almost the same result was observed (entries 8 and 9). However, in a protic solvent such as methanol, **15** was obtained as a major products, and *cis*-**10** was not formed at all (entry 10). These results suggest that this photoreaction of *trans*-**10** under UV irradiation generated *N*-tosyl nitrene, and it was converted to **15** readily, but in aprotic solvent, such as CH_2Cl_2 and acetonitrile, the formation of **15** was decreased. Concerning the generation of nitrene in the photoreaction of dimethyl-(*N*-*p*-tosyl)sulfilimine in methanol, Hayashi and Swern reported that the nitrene generation was occurred by photoinduced SN-bond breaking.[10a]

2.4. Photolysis of 5-(*N*-*p*-tosyl)iminothianthrene derivatives in the presence of diphenyl sulfide: trapping experiment of generated *N*-tosyl nitrene

Further, photoreaction of 5-(*N*-*p*-tosyl)iminothianthrenes **2a**, *trans*-**10**, *cis*-**10**, and **11** in the presence of diphenyl sulfide was studied. As shown in Table 4, the expected trapped product, diphenyl-(*N*-*p*-tosyl)sulfilimine **16**, was formed in moderate yields, except for the reaction of *cis*-**10**. The control experiments revealed that **16** was stable and does not decompose practically under the same conditions.

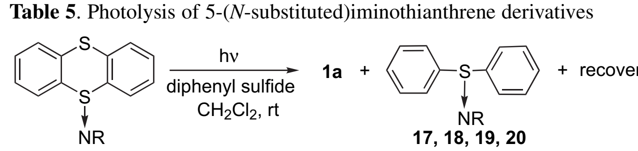
The photolysis of **2a** in the presence of 1.5 equiv of diphenyl sulfide afforded **1a** and **16**[16] in 61 and 33% yields, respectively (entry 1). When the reaction of **2a** was carried out using 5.0 equiv of diphenyl sulfide, the yields of products were almost the same (35%). In the case of **11**, **16** was obtained in 70% yield (entry 2). In the case of *trans*-**10**, the trapped product **16** was also formed in moderate yield, however, contrary to the results without diphenyl sulfide (cf. entries 4 and 5 in Table 3), the photoisomerized product *cis*-**10** was not formed at all (entry 3). In the case of *cis*-**10** (entry 4), similar result was observed as when without diphenyl sulfide (cf. entry 3 in Table 3). When comparing the results whether in the absence or presence of diphenyl sulfide as in Tables 3 and 4, only the distinct difference is the formation of the *N*-tosyl nitrene-transfer product **16** instead of the formation of **15** that is formed in the presence of diphenyl sulfide. The conversions (%) to *N*-tosyl nitrene, which was estimated on the basis of the yields of **16**, **1a**, **4a** and **14** after correction according to the recovery of the starting materials, decrease in the order of **11**, *trans*-**10**, and **2a** as ca. 70, 44 and 37%, respectively. As mentioned previously, *cis*-**10** revealed to show the persistence under the photolytic conditions in contrast with the other *N*-tosyliminothianthrenes.

2.5. Photolysis of other thianthrene sulfilimines

Photolyses of 5-(*N*-substituted)iminothianthrene derivatives under the same conditions were also studied, in order to study the effect of *N*-substituent on the photo SN-bond cleavage. These results are summarized in Table 5.

On photolysis 5-iminothianthrene (**6**), 5-(*N*-acetyl)iminothianthrene (**8**), and 5-(*N*-benzoyl)iminothianthrene (**9**) decomposed to form **1a** in high yields of 94, 89, and 80%,

Table 5. Photolysis of 5-(*N*-substituted)iminothianthrene derivatives



Entry	R	Compound	Ph_2S (equiv)	Time (h)	Yield[a] (%)		
					1a	**17–20**	Recover
1	H	**6**	None	0.5	94	—	0
2	Acetyl	**8**	None	1	89	—	0
3	Benzoyl	**9**	None	2	80	—	7
4	NTs	**2a**	None	4	59	—	26
5	α-Naphthalene sulfonyl	**7α**	None	1	33	—	58
6	β-Naphthalene sulfonyl	**7β**	None	1	43	—	57
7	β-Naphthalene sulfonyl	**7β**	5.0	1	49	10 (**18**)	10
8	Acetyl	**8**	5.0	0.5	83	10 (**19**)	0
9	Benzoyl	**9**	5.0	0.5	11	20 (**20**)	50
10	H	**6**	5.0	0.5	91	0 (**17**)	0

[a] Isolated yield.

respectively (entries 1–3). However, on photolysis both 5-(N-α- and -β-naphthalenesulfonyl)iminothianthrene **7α** and **7β** found to resist to decompose to **1a** compared to **2a**, but resulted in poor yield (33 and 43% yield, respectively) with ca. 60% recoveries of the starting materials after 1 h (entries 5 and 6). As a result, practically no difference in the effect was observed in the cases of substitution of sulfonyl group, such as α- and β-naphthyl (**7α** and **7β**) and phenyl substituent (**2a**).

Further in order to study the efficiency of nitrene transfer to sulfide, the photolyses of 5-(*N*-substituted)iminothianthrenes in the presence of diphenyl sulfide were carried out under the same conditions. In the case of β-naphthyl substituent, compared to the case of **2a** (entry 1 in Table 4) the nitrene-transfer efficiency seems to be low and product **18** was obtained in only 10% yield after 90% starting material was decomposed (entry 7). In the case of carbonyl substituents, **8** decomposed completely very quickly to afford **1a** in 83% yield, but **19**[17] in poor yield of 10% (entry 8), and **9** decomposed rather slowly to afford **20**[17] in 20% yield after 50% decomposition (entry 9).

Concerning the rather low yield of the nitrene-trapped product, **18–20**, in the photolyses of **7β**, **8**, and **9**, compared to **2a**, under the similar conditions, the stability (life time) and the nature (singlet or triplet state) of the nitrene generated seem to be influenced greatly by the *N*-substituents. Particularly, in case of the nitrene without any electron-withdrawing substituents generated from iminothianthrene (**6**), the nature of nitrene (:NH) may be very unstable, so that the trapped product was not formed in the presence of diphenyl sulfide, but de-iminated product **1a** was formed in high yield (entry 10).

3. Conclusion

Thianthrene sulfilimines were readily prepared by the reaction of substituted thianthrene derivatives with chloramine T or *O*-mesitylenesulfonylhydroxylamine (MSH). On N-tosylation or oxidation of 1- or 2-substituted thianthrene derivatives, the regioselectivities toward the attacking site of the reagents whether 5- or 10-position of sulfur atom were observed as ca. 3:1 and 1.8 to 1.5:1, respectively. The photolysis of thianthrene sulfilimines and their oxides occurred as SN- and SO-bond cleavage to afford the corresponding thianthrene derivatives, and in the photolysis of *trans*-**10**, trans–cis isomerization was observed. Isomerization mechanism is proposed to be via the recombination between thianthrene oxide and nitrene that is initially formed after several mechanistic studies. The photolysis of **2a** was also carried out in the presence of diphenyl sulfide to afford imino-transfer product **16**. Further, the substituent effects of 1- or 2-substituted thianthrene on the photoimino-transfer reaction in the presence of diphenyl sulfide were investigated, and also the *N*-iminoacyl substituent and oxidized state (mono- or dioxide) effects on the same reaction conditions were studied. In conclusion, the photolyses of various 5-(*N*-substituted)iminothianthrenes under UV irradiation with high-pressure mercury lamp with Pyrex filter found to generate nitrenes and to produce imino-transfer products in the presence of diphenyl sulfides.

4. Experimental

4.1. General

All the melting points were uncorrected. The ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded in $CDCl_3$ using TMS as an internal standard. The IR spectra were recorded on a HORIBA FT-71 spectrometer. The elemental analyses were performed at Microanalytical Laboratory of the Department of Material Systems Engineering and Life Science, University of Toyama. All the reactions were monitored with TLC using Silica Gel 60 F_{254} TLC plates and the products were separated by column chromatography using Silica Gel 60 and also by preparative layer chromatography using Silica Gel 60 PF_{254} with UV detection. All reagents were of the highest quality and were further purified by distillation or recrystallization. The solvents were further purified by general methods.

4.2. General procedure of N-tosylimination of thianthrene derivatives with chloramine T

To a stirred solution of 1.3 equiv chloramine T in acetonitrile was added thianthrene derivatives **1** in acetonitrile at 60 °C. After enough time by monitoring the reaction by TLC, the colorless suspension was evaporated and dried under reduced pressure. The residue was extracted with chloroform. The chloroform layer was washed with water and brine, and dried over anhydrous $MgSO_4$. After removal of solvent under reduced pressure, purification was carried out by column chromatography on silica gel, eluting with hexane–ethyl acetate (1:1) to yield the corresponding 5- or 10-*S*-tosyliminothianthrene derivatives.

4.2.1. N-Tosylimination of 1-methylthianthrene (1b). The above procedure was employed by using **1b** (150.3 mg, 0.65 mmol) in acetonitrile (2 ml) and chloramine T (243.8 mg, 0.87 mmol) in acetonitrile (10 ml) to afford 186.6 mg of 1-methyl-5-(*N*-*p*-tosyl)iminothianthrene (**2b**) and 61.3 mg of 1-methyl-10-(*N*-*p*-tosyl)iminothianthrene (**3b**) in 72 and 24% yields, respectively (reaction time: 4 h). Compound **2b**: mp 136–139 °C (colorless crystals from chloroform–hexane); ^{1}H NMR ($CDCl_3$) δ 2.39 (s, 3H), 2.90 (s, 3H), 7.25–7.28 (m, 2H), 7.33–7.41 (m, 2H), 7.44–7.52 (m, 2H), 7.66–7.67 (m, 1H), 7.75–7.77 (m, 1H), 7.89–7.94 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 20.1, 21.4, 123.5, 125.7, 126.3, 128.6, 129.0, 129.5, 129.7, 130.3, 130.9, 132.2, 133.9, 134.5, 138.3, 141.1, 142.1; IR (KBr) ν=1430, 1280, 1140, 1080, 950 cm^{-1}. Anal. Calcd for $C_{20}H_{17}NS_3O_2$: C, 60.12; H, 4.29; N, 3.51. Found: C, 60.06; H, 4.24; N, 3.35. Compound **3b**: mp 205–207 °C (colorless crystals from chloroform–hexane); ^{1}H NMR ($CDCl_3$) δ 2.34 (s, 3H), 2.59 (s, 3H), 7.08 (d, J=8.0 Hz, 2H), 7.21 (d, J=7.6 Hz, 1H), 7.31–7.38 (m, 2H), 7.49 (dt, J_1=7.8 Hz, J_2=1.4 Hz, 2H), 7.59–7.65 (m, 3H), 7.70 (dd, J_1=7.8, J_2=1.4 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 19.8, 21.3, 126.2, 126.8, 126.9, 127.2, 127.5, 128.7, 128.8, 130.0, 131.3, 131.6, 132.2, 136.3, 136.4, 140.6, 141.3, 141.5; IR (KBr) ν=1430, 1260, 1120, 1080, 930 cm^{-1}. Anal. Calcd for $C_{20}H_{17}NS_3O_2$: C, 60.12; H, 4.29; N, 3.51. Found: C, 60.14; H, 4.38; N, 3.28.

4.2.2. N-Tosylimination of 1-trimethylsilylthianthrene (1c). The above procedure was employed by using **1c**

(161.1 mg, 0.56 mmol) in acetonitrile (4 ml) and chloramine T (200.0 mg, 0.71 mmol) in acetonitrile (5 ml) to afford 1-trimethylsilyl-5-(*N*-*p*-tosyl)iminothianthrene (**2c**) (169.9 mg) and 1-trimethylsilyl-10-(*N*-*p*-tosyl)iminothianthrene (**3c**) (40.0 mg) in 67 and 16% yields, respectively (reaction time: 1 h). Compound **2c**: mp 197–199 °C (colorless crystals from chloroform–hexane); ^{1}H NMR ($CDCl_3$) δ 0.44 (s, 9H), 2.39 (s, 3H), 7.26–7.28 (m, 2H), 7.44–7.53 (m, 3H), 7.59–7.61 (m, 1H), 7.65–7.68 (m, 1H), 7.91–7.96 (m, 4H); ^{13}C NMR ($CDCl_3$) δ −0.3, 21.4, 125.4, 126.2, 126.3, 128.1, 129.0, 129.4, 129.5, 130.3, 130.9, 135.1, 135.6, 136.2, 136.7, 141.0, 142.0, 142.1; IR (KBr) ν=1280, 1140, 1080, 980 cm^{-1}. Anal. Calcd for $C_{22}H_{23}NSiS_3O_2$: C, 57.73; H, 5.06; N, 3.06. Found: C, 57.96; H, 4.86; N, 3.14.

4.2.3. N-Tosylimination of 2-bromothianthrene (1e). The above procedure was employed by using **1e** (291.5 mg, 0.99 mmol) in acetonitrile (5 ml) and chloramine T (331.2 mg, 1.12 mmol) in acetonitrile (8 ml) to afford 2-bromo-5-(*N*-*p*-tosyl)iminothianthrene (**2e**) (136.8 mg) and 2-bromo-10-(*N*-*p*-tosyl)iminothianthrene (**3e**) (83.5 mg) in 30 and 18% yields, respectively, with recovery (77.7 mg, 27%) of starting material (reaction time: 1 day). Compound **2e**: mp 220–223 °C (dec) (colorless crystals from chloroform–hexane); ^{1}H NMR ($CDCl_3$) δ 2.41 (s, 3H), 7.29 (d, *J*=8.4 Hz, 2H), 7.47–7.55 (m, 2H), 7.61–7.67 (m, 2H), 7.73 (d, *J*=8.4 Hz, 1H), 7.81 (d, *J*=2.0 Hz, 1H), 7.89–7.94 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 21.5, 125.6, 125.9, 126.3, 126.3, 127.0, 129.3, 129.5, 129.6, 129.6, 131.2, 132.1, 133.4, 133.9, 140.8, 142.4; IR (KBr) ν=1430, 1290, 1140, 1090, 970 cm^{-1}. Anal. Calcd for $C_{19}H_{14}NS_3O_2Br$: C, 49.14; H, 3.04; N, 3.02. Found: C, 49.14; H, 3.08; N, 3.05. Compound **3e**: mp 197–201 °C (colorless crystals from chloroform–hexane); ^{1}H NMR ($CDCl_3$) δ 2.42 (s, 3H), 7.31 (d, *J*=8.0 Hz, 2H), 7.49–7.58 (m, 4H), 7.65 (dd, J_1=7.2 Hz, J_2=1.4 Hz, 1H), 7.82 (d, *J*=2.0 Hz, 1H), 7.92–7.95 (m, 3H). ^{13}C NMR ($CDCl_3$) δ 21.5, 123.3, 125.9, 126.3, 128.4, 129.3, 129.3, 129.6, 129.7, 129.9, 130.7, 131.2, 133.8, 134.1, 136.1, 140.8, 142.6; IR (KBr) ν=1440, 1290, 1150, 1090, 960 cm^{-1}. Anal. Calcd for $C_{19}H_{14}NS_3O_2Br$: C, 49.14; H, 3.04; N, 3.02. Found: C, 49.20; H, 3.00; N, 3.14.

4.2.4. N-Tosylimination of mixture of 2,7- and 2,8-dibromothianthrene (1f and 1f′). The above procedure was employed by using **1f**, **1f′** (161.7 mg, 0.43 mmol) in acetonitrile (10 ml), and chloramine T (150.6 mg, 0.54 mmol) in acetonitrile (5 ml). The reaction mixture was separated by HPLC using methanol–water (10:1) as the eluant to afford 2,7-dibromo-5-(*N*-*p*-tosyl)iminothianthrene **2f** (39.1 mg) and 2,7-dibromo-10-(*N*-*p*-tosyl)iminothianthrene **2f′** (53.7 mg) in 17 and 23% yields, respectively (reaction time: 1 day). Compound **2f**: mp 199–201 °C (colorless crystals); ^{1}H NMR ($CDCl_3$) δ 2.42 (s, 3H), 7.31 (d, *J*=8.0 Hz, 2H), 7.49 (d, *J*=8.0 Hz, 1H), 7.58 (dd, J_1=8.2 Hz, J_2=2.2 Hz, 1H), 7.65 (dd, J_1=8.4 Hz, J_2=2.0 Hz, 1H), 7.76 (d, *J*=8.4 Hz, 1H), 7.80–7.82 (m, 2H), 7.91–7.94 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 21.5, 123.7, 125.9, 126.3, 127.1, 128.6, 129.7, 130.8, 131.8, 132.3, 132.4, 133.0, 134.4, 136.0, 140.7, 142.8; IR (KBr) ν=1430, 1300, 1150, 1090, 970 cm^{-1}. Anal. Calcd for $C_{19}H_{13}NS_3O_2Br_2$: C, 42.00; H, 2.41; N, 2.58. Found: C, 42.25; H, 2.14; N, 2.36. Compound **2f′**: mp 245–250 °C (dec) (colorless crystals); ^{1}H NMR ($CDCl_3$) δ 2.42 (s, 3H), 7.29 (d, *J*=8.4 Hz, 2H), 7.65 (dd, J_1=8.6 Hz, J_2=1.8 Hz, 2H), 7.73 (d, *J*=8.4 Hz, 2H), 7.81 (d, *J*=1.6 Hz, 2H), 7.91 (d, *J*=8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 21.5, 125.9, 126.3, 127.1, 129.6, 131.4, 132.3, 132.4, 133.2, 140.6, 142.6; IR (KBr) ν=1430, 1300, 1150, 1090, 970 cm^{-1}. Anal. Calcd for $C_{19}H_{13}NS_3O_2Br_2$: C, 42.00; H, 2.41; N, 2.58. Found: C, 42.24; H, 2.48; N, 2.86.

4.3. General procedure of oxidation of thianthrene derivatives with *m*-CPBA

To a stirred solution of thianthrene derivatives **1** in dichloromethane (2 ml), 1.1 equiv *m*-CPBA dissolved in dichloromethane (4 ml) was added under ice cooling. After 2 h, the reaction mixture was washed with saturated solution of sodium bicarbonate to remove *m*-chlorobenzoic acid and *m*-CPBA, washed with water, and dried over anhydrous $MgSO_4$. After removal of solvent under reduced pressure, purification was made by chromatography on silica gel eluting with ethyl acetate–hexane (1:3) to afford the corresponding thianthrene sulfoxides **4** and **5** as colorless crystals.

4.3.1. 1-Methylthianthrene 5-oxide (4b). Yield 54%; mp 128–129 °C (colorless solid from chloroform–hexane); ^{1}H NMR ($CDCl_3$) δ 2.51 (s, 3H), 7.28 (d, *J*=7.6 Hz, 1H), 7.37–7.44 (m, 2H), 7.51 (dt, J_1=7.6 Hz, J_2=1.2 Hz, 1H), 7.61 (dd, J_1=7.2 Hz, J_2=0.4 Hz, 1H), 7.76 (d, *J*=7.6 Hz), 7.89 (dd, J_1=7.6 Hz, J_2=1.2 Hz, 1H); ^{13}C NMR δ 20.0, 122.1, 124.3, 128.0, 128.4, 129.2, 129.7, 131.1, 137.3, 137.5, 141.2, 141.3, 141.6; IR (KBr) ν=1445, 1073, 1047, 1035 cm^{-1}. Anal. Calcd for $C_{13}H_{10}OS_2$: C, 63.38; H, 4.09; N, 0.00. Found: C, 63.24; H, 3.87; N, 0.00.

4.3.2. 1-Methylthianthrene 10-oxide (5b). Yield 30%; mp 145–146 °C (colorless crystals from chloroform–hexane); ^{1}H NMR ($CDCl_3$) δ 2.83 (s, 3H), 7.24–7.26 (m, 1H), 7.35 (t, *J*=7.6 Hz, 1H), 7.46–7.53 (m, 2H), 7.56–7.58 (m, 1H), 7.72–7.74 (m, 1H), 7.98–8.00 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 19.5, 126.9, 127.4, 128.5, 130.0, 130.1, 130.5, 131.4, 133.1, 133.3, 136.0, 136.8, 139.7; IR (KBr) ν=1443, 1053, 1021 cm^{-1}. Anal. Calcd for $C_{13}H_{10}OS_2$: C, 63.38; H, 4.09; N, 0.00. Found: C, 63.12; H, 3.74; N, 0.00.

4.3.3. 1-Trimethylsilylthianthrene 5-oxide (4c). Yield 50%; mp 118–120 °C (colorless crystals from chloroform–hexane); ^{1}H NMR ($CDCl_3$) δ 0.46 (s, 9H), 7.42 (dt, J_1=7.4 Hz, J_2=1.2 Hz, 1H), 7.50–7.58 (m, 3H), 7.62–7.64 (m, 1H), 7.92 (dt, J_1=8.6 Hz, J_2=1.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ −0.2, 124.1, 125.0, 127.6, 128.5, 128.6, 129.0, 129.7, 134.5, 135.6, 141.1, 142.2, 142.7; IR (KBr) ν=1360, 1230, 1060, 1030 cm^{-1}. Anal. Calcd for $C_{15}H_{16}OS_2Si$: C, 59.17; H, 5.30; N, 0.00. Found: C, 58.93; H, 5.16; N, 0.00.

4.3.4. 2-Bromothianthrene 5-oxide (4e). Yield 48%; mp 121–123 °C (colorless crystals from dichloromethane–hexane); ^{1}H NMR ($CDCl_3$) δ 7.45 (dt, J_1=7.6 Hz, J_2=1.2 Hz, 1H), 7.57 (dt, J_1=7.6 Hz, J_2=1.2 Hz, 1H), 7.61–7.64 (m, 1H), 7.67 (dd, J_1=8.2 Hz, J_2=1.8 Hz, 1H), 7.76–7.78 (m, 2H), 7.91–7.93 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 124.1, 124.5, 125.8, 127.7, 128.7, 129.1, 130.0, 130.4, 131.5, 131.6, 140.7, 141.2; IR (KBr) ν=1420, 1060 cm^{-1}.

Anal. Calcd for $C_{12}H_7BrOS_2$: C, 46.31; H, 2.27; N, 0.00. Found: C, 46.21; H, 2.33; N, 0.00.

4.3.5. 2-Bromothianthrene 10-oxide (5e). Yield 33%; mp 159–160 °C (colorless crystals from dichloromethane–hexane); ^{1}H NMR ($CDCl_3$) δ 7.43–7.49 (m, 2H), 7.55–7.64 (m, 3H), 7.91–7.94 (m, 1H), 8.04 (d, J=2.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 122.9, 124.5, 127.3, 127.5, 128.1, 128.7, 129.1, 130.0, 130.3, 132.9, 141.0, 143.6; IR (KBr) ν=1430, 1080 cm^{-1}. Anal. Calcd for $C_{12}H_7BrOS_2$: C, 46.31; H, 2.27; N, 0.00. Found: C, 45.84; H, 2.50; N, 0.00.

4.4. General procedure for sulfonylation or acylation of 5-iminothianthrene (6)

To a stirred solution of **6** in dichloromethane (3 ml) and 1.2 equiv triethylamine, 1.2 equiv electrophiles was added at room temperature. After 1 h stirring, the reaction mixture was washed with water, dried over anhydrous $MgSO_4$, and condensed under reduced pressure. The residue was recrystallized from dichloromethane–hexane to afford thianthrene sulfilimines **7–9**.

4.4.1. 5-(*N*-α-Naphthalenesulfonyl)iminothianthrene (7α). Yield 85%; mp 219–220 °C (colorless crystals from chloroform–hexane); ^{1}H NMR ($CDCl_3$) δ 7.33–7.42 (m, 4H), 7.50 (t, J=8.0 Hz, 1H), 7.58–7.62 (m, 3H), 7.73 (dt, J_1=7.8 Hz, J_2=1.2 Hz, 1H), 7.83 (dd, J_1=7.8 Hz, J_2=1.2 Hz, 2H), 7.92 (d, J=8.0 Hz, 1H), 7.99 (d, J=8.4 Hz, 1H), 8.36 (dd, J_1=7.6 Hz, J_2=1.2 Hz, 1H), 9.18 (d, J=8.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 124.2, 126.0, 126.3, 126.6, 127.5, 127.7, 128.4, 128.7, 128.9, 129.4, 130.3, 130.9, 133.2, 133.9, 134.3, 138.8; IR (KBr) ν=1300, 1110, 950 cm^{-1}. Anal. Calcd for $C_{22}H_{15}NO_2S_3$: C, 62.68; H, 3.59; N, 3.32. Found: C, 62.53; H, 3.37; N, 3.50.

4.4.2. 5-(*N*-β-Naphthalenesulfonyl)iminothianthrene (7β). Yield 73%; mp 224–225 °C (colorless crystals from chloroform–hexane); ^{1}H NMR ($CDCl_3$) δ 7.43–7.49 (m, 4H), 7.57–7.65 (m, 4H), 7.89–7.97 (m, 5H), 8.09 (dd, J_1=9.4 Hz, J_2=1.6 Hz, 1H), 8.59 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 122.5, 125.8, 126.9, 127.2, 127.8, 128.2, 129.0, 129.3, 129.5, 130.3, 131.0, 132.3, 133.9, 134.4, 140.6; IR (KBr) ν=1300, 1150, 970 cm^{-1}. Anal. Calcd for $C_{22}H_{15}NO_2S_3$: C, 62.68; H, 3.59; N, 3.32. Found: C, 62.76; H, 3.48; N, 3.42.

4.4.3. 5-(*N*-Acetyl)iminothianthrene (8). Yield 68%; mp 160–162 °C (colorless crystals from chloroform–hexane); ^{1}H NMR ($CDCl_3$) δ 2.37 (s, 3H), 7.47–7.56 (m, 4H), 7.68–7.70 (m, 2H), 7.91–7.93 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 24.9, 127.3, 128.6, 129.4, 130.8, 132.1, 132.2, 184.0; IR (KBr) ν=1560, 1300 cm^{-1}. Anal. Calcd for $C_{14}H_{11}NOS_2$: C, 61.51; H, 4.06; N, 5.12. Found: C, 61.72; H, 4.38; N, 4.94.

4.4.4. 5-(*N*-Benzoyl)iminothianthrene (9). Spectral data: yield 90%; mp 180–182 °C (colorless crystals from chloroform–hexane); ^{1}H NMR ($CDCl_3$) δ 7.46–7.56 (m, 7H), 7.69–7.71 (m, 2H), 7.98–8.00 (m, 2H), 8.39–8.41 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 126.9, 128.0, 128.7, 129.2, 129.4, 130.6, 131.3, 131.6, 133.1, 136.1, 178.2; IR (KBr) ν=1600, 1320, 1280 cm^{-1}. Anal. Calcd for $C_{19}H_{13}NOS_2$: C, 68.03; H, 3.91; N, 4.18. Found: C, 68.25; H, 4.18; N, 4.54.

4.4.5. Diphenyl-(*N*-β-naphthalenesulfonyl)sulfilimine (18). Spectral data: yield 72%; mp 127–128 °C (colorless crystals from chloroform–hexane); ^{1}H NMR ($CDCl_3$) δ 7.39–7.58 (m, 8H), 7.58–7.64 (m, 4H), 7.77–7.88 (m, 4H), 8.38–8.41 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 122.6, 126.6, 126.9, 127.2, 127.7, 127.9, 128.8, 129.0, 129.8, 132.1, 132.3, 134.2, 136.3, 141.1; IR (KBr) ν=1301, 1148, 1127, 965 cm^{-1}. Anal. Calcd for $C_{22}H_{17}NO_2S_2$: C, 67.49; H, 4.38; N, 3.58. Found: C, 67.13; H, 4.11; N, 3.77.

4.5. General photolysis procedure

A solution of thianthrene derivatives in a solvent was placed in a Pyrex tube equipped with a rubber septum. The solvent was used after removal of O_2 by passing Ar or N_2 bubbling for 30 min. Irradiation of samples was carried out using a 400 W high-pressure mercury lamp under Ar atmosphere at room temperature. The reaction progress was monitored by HPLC, TLC, or ^{1}H NMR spectroscopy. After UV irradiation, the solvent was evaporated and the residue was purified by column chromatography or preparative thin layer chromatography on silica gel, and the products were characterized by IR and NMR spectral data.

4.5.1. General photolysis procedure of 5-iminothianthrene derivatives 2a, 3b, and 6–11 in the absence or presence of diphenyl sulfide. The solution of 5-iminothianthrene derivatives in CH_2Cl_2 (concentration=25 mM) was placed in a Pyrex tube equipped with a rubber septum. The photolyses in the presence of diphenyl sulfide were performed under the same conditions as the general photolysis procedure after addition of the sulfide. The workup, separation, purification, and identification procedures were followed as the general photolysis procedure.

4.6. Cross-over experiment between 2e and 4a and between 2e and 1a

The solution of **2e** (28.6 mg, 0.061 mmol) and **4a** (14.2 mg, 0.061 mmol) in 25 ml of dichloromethane was irradiated under the same conditions for 2 h. In the case between **2e** and **1a**, the solution of **2e** (49.7 mg, 0.107 mmol) and thianthrene **1a** (23.4 mg, 0.108 mmol) in CH_2Cl_2 (42 ml) was irradiated under the same conditions for 1 h. After removal of the solvent, this residue was chromatographed on silica gel preparative plate using ethyl acetate–hexane (1:3) as the eluant. The products were identified by ^{1}H NMR data.

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