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Alkaline hydrolysis of *N*-bromoiminothianthrene derivatives

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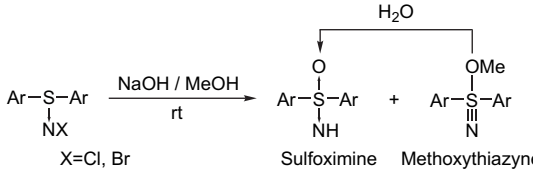
Abstract—5-(*N*-Bromo)iminothianthrene (**2**) and 5-(*N*-bromo)iminothianthrene 10-oxide (**5**) and 10,10-dioxide (**8**) were prepared and their alkaline hydrolyses were studied. The compound **2** and *cis*-5-(*N*-bromo)iminothianthrene 10-oxide (*cis*-**5**) afforded the corresponding sulfoximine exclusively. While, unexpectedly, both *trans*-5-(*N*-bromo)iminothianthrene 10-oxide (*trans*-**5**) and **8** afforded mainly de-brominated products, *trans*-5-iminothianthrene 10-oxide (*trans*-**4**) and 5-iminothianthrene 10,10-dioxide (**7**), respectively. In these cases, 5-iminothianthrene 5,10-dioxide (**6**) (*Z*- and *E*-mixture) and 5-iminothianthrene 5,10,10-trioxide (**9**) and further de-iminated products were also formed respectively as minor products. The stereochemical considerations on the S_N reactions are described in view of the steric effect and 'flip-flap' motion of the thianthrene framework.

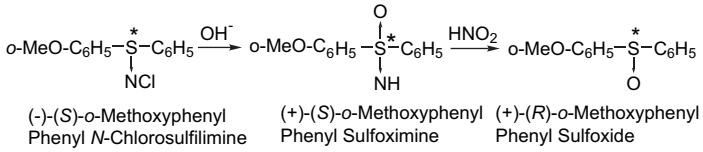
1. Introduction

N-Halosulfilimines are interesting derivatives that can be obtained easily by treating the corresponding *N*-unsubstituted sulfilimines with halogenating reagents.[1–4] However, their reactivities have been left still uncovered. It is reported that alkaline hydrolysis of diaryl *N*-halosulfilimines with sodium hydroxide in methanol afforded diaryl sulfoximine.[1–3,5] This reaction is synthetically useful for the preparation of diaryl sulfoximines. In 1987, from the results of stereochemical study using optically active (−)-(*S*)-*o*-methoxyphenyl phenyl *N*-chlorosulfilimine and other observations, Oae et al. suggested that the alkaline hydrolyses proceed by a nucleophilic attack of hydroxide ion with the retention of configuration on the sulfur atom (Scheme 1).[3]

In 1989 Yoshimura et al. have found that the novel intermediate diaryl methoxythiazyne, having a unique SN triple bond, incipiently formed in this reaction, and this intermediate is finally hydrolyzed to give diaryl sulfoximines (Scheme 2).[6] They fully examined the kinetic behavior of alkaline hydrolysis of diaryl *N*-halosulfilimines in MeOH/H_2O solution under various kinetic conditions and concluded that the alkaline hydrolysis of these derivatives proceeds via two concurrent mechanisms, the S_N1 mechanism involving nitridosulfonium cation $(Ph_2S{=}N)^+$ as an intermediate and the S_N2' mechanism with the transition state in which the N–X bond cleavage progressed more than the S–O bond formation with nucleophiles (HO^- and MeO^-).[7]



Scheme 2. Formation of diaryl methoxythiazyne and its conversion to diaryl sulfoximine.



Scheme 1. Hydrolysis of *o*-methoxyphenyl phenyl *N*-chlorosulfilimine and the determination of the stereochemical reaction course.

Keywords: Thianthrene; Sulfilimine; *N*-Bromosulfilimine; Sulfoximine; S_N reaction on sulfur; Steric hindrance; 'Flip-flap' motion.
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In order to extend this study in the thianthrene system and to obtain a clue for the hydrolysis mechanism of *N*-halosulfilimines and particularly for the formation of *N*-unsubstituted sulfilimines, we carried out the alkaline hydrolysis of **2** and its oxides at 10-*S*-position, such as *cis*-**5**, *trans*-**5**, and **8**.

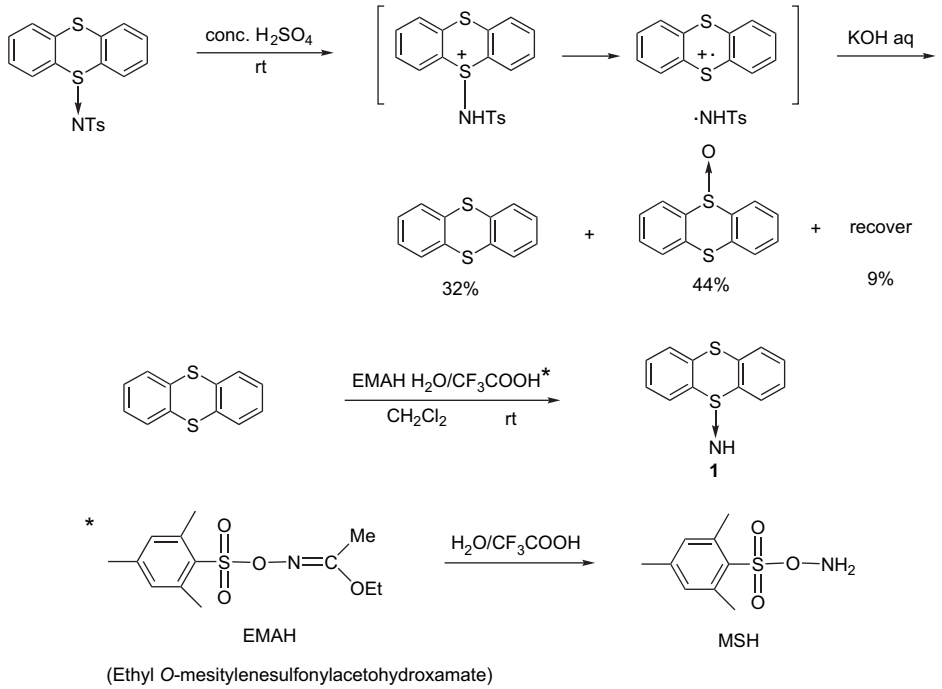
2. Results and discussion

For the preparation of 5-iminothianthrene (**1**), we tried the hydrolysis of thianthrene *N*-tosylsulfilimine in 95% concentrated sulfuric acid following the literature.[8,9] However, this reaction only afforded thianthrene and thianthrene 5-oxide probably via thianthrene cation radical. The desired *N*-unsubstituted thianthrene sulfilimine was successfully obtained by the reaction of thianthrene with *O*-(mesitylenesulfonyl)-hydroxylamine (MSH) obtained in situ by trifluoroacetic acid catalyzed hydrolysis of ethyl *O*-mesitylenesulfonylacetohydroxamate by the modified literature procedure[10] as shown in Scheme 3.

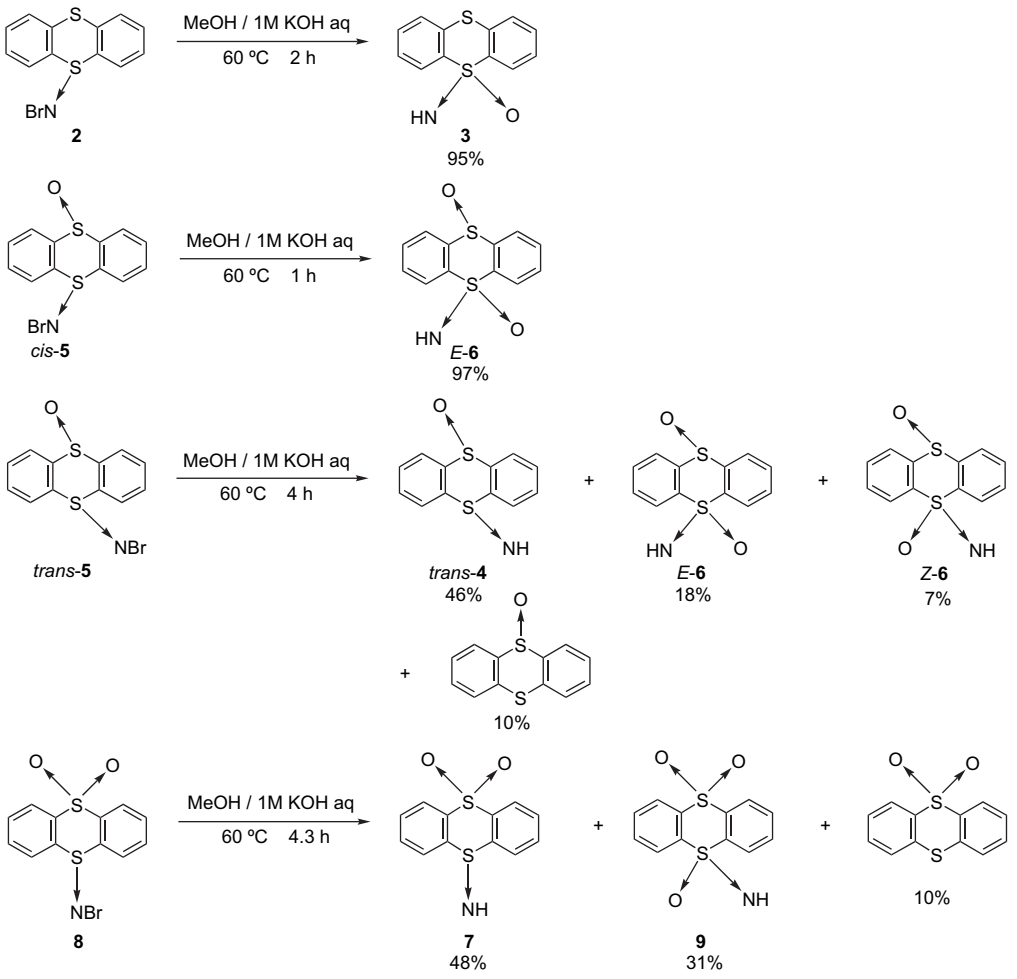
cis-5-Iminothianthrene 10-oxide (*cis*-**4**), *trans*-**4**, and 5-iminothianthrene 10,10-dioxide (**7**) were obtained by the hydrolysis reaction of the corresponding *N*-tosylsulfilimines with concentrated sulfuric acid.[11] Then, further *N*-bromination of the corresponding unsubstituted sulfilimines was performed with NBS to afford **2**, *cis*- and *trans*-**5**, and **8** in good yields.

In the case of hydrolysis of **2** with KOH in MeOH/H_2O at 60 °C for 2 h, the isolated products were 5-iminothianthrene 5-oxide (**3**, 95%). Under the same conditions for 1 h, *cis*-**5** led to (*E*)-5-iminothianthrene 5,10-dioxide (*E*-**6**) exclusively in 97% yield with the retention of configuration on sulfur atom at 5-*S*-position. However, *trans*-**5** afforded a rather complex reaction mixture even slowly (4 h), forming *trans*-**4**, *E*-**6**, *Z*-**6**, and thianthrene 5-oxide in 46%, 18%, 7%, and 10% yields, respectively. Similarly, in the reaction of **8**, the corresponding *N*-unsubstituted sulfilimine (**7**) was formed in 48%, with further de-iminated product thianthrene 5,5-dioxide in 10%, and the expected sulfoximine **9** in 31% yield. In both cases the de-brominated products *trans*-**4** and **7** are thought to be formed by nucleophilic attack of a nucleophile (HO^- or MeO^-) on bromine atom of *trans*-**5** or **8** with retention of configuration. Successively, *trans*-**4** and **7** were de-iminated partially to give the corresponding thianthrene 5-oxide and 5,5-dioxide. On the other hand, products *E*-**6**, *Z*-**6**, and **9** are apparently formed through nucleophilic attack of HO^- and/or MeO^- on sulfur atom at 5-*S*-position of *cis*- and *trans*-**5** and **8** (Scheme 4).

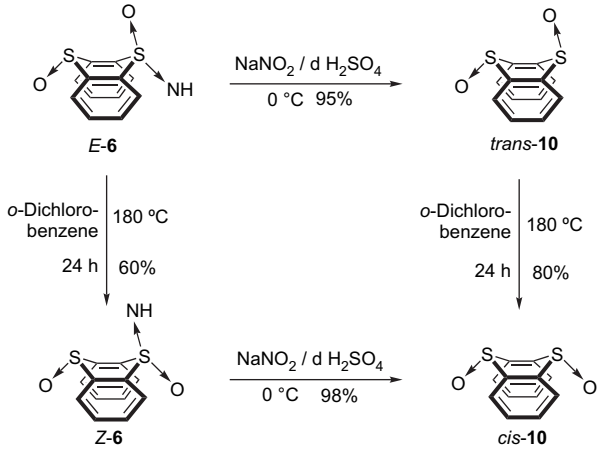
Concerning the stereochemistry of *E*- and *Z*-**6**, the determination of the configuration of NH group on sulfur atom at 5-*S*-position was performed by the de-imination procedure in the literature.[3] Thus, in order to distinguish between these two isomers, the de-imination reactions of *E*- or *Z*-**6** via diazotization with sodium nitrite in 45% aqueous sulfuric acid at 0 °C were carried out. The de-imination of compound *E*-**6** led to only *trans*-thianthrene 5,10-dioxide (*trans*-**10**) in 95% yield, while in the same procedure using compound *Z*-**6**, *cis*-thianthrene 5,10-dioxide (*cis*-**10**) was formed in 98% yield. According to the de-imination mechanism on sulfur atom with nitrous acid it has been known to proceed with the retention of configuration.[12–15] Thus, the stereochemical assignment for the de-imination from *E*-**6** and *Z*-**6** to *trans*-**10** and *cis*-**10**, respectively, in Scheme 5 was confirmed definitely as the results of product analysis depicted in Scheme 4.



Scheme 3. Reaction of 5-(*N*-*p*-tosyl)iminothianthrene with concd H_2SO_4 and imination of thianthrene with MSH.



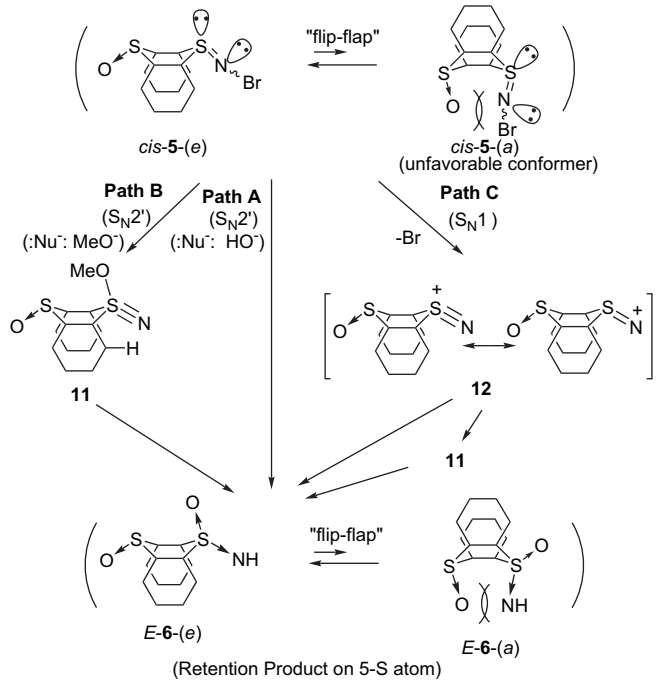
Scheme 4. Product analysis for the reaction of 5-(*N*-bromo)iminothianthrenes in KOH/(MeOH–H_2O) solution.



Scheme 5. Determination of the stereochemistry of sulfoximines *E*- and *Z*-**6** and the thermal conversion of *E*-**6** to *Z*-**6**.

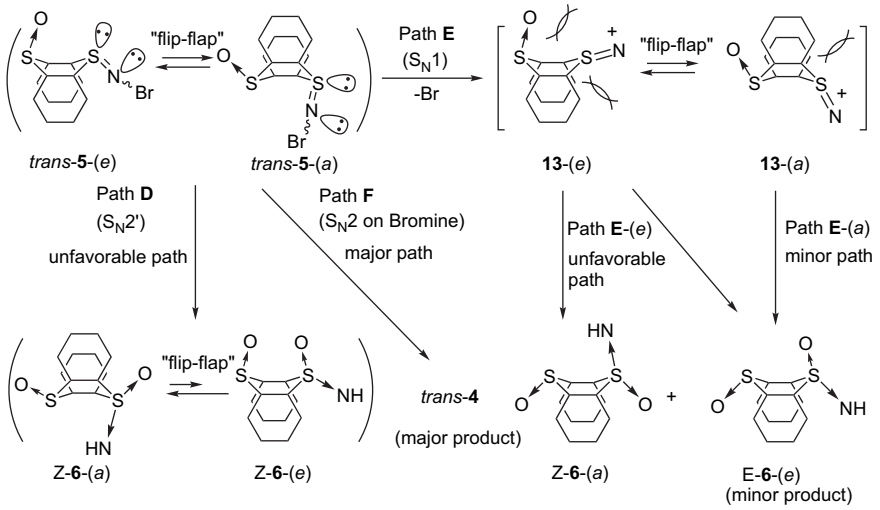
In Scheme 5, the result of thermal isomerization from *E*-**6** to *Z*-**6** (via thermal pyramidal inversion at 10-*S*-atoms, followed by successive 'flip-flap' motion, or vice versa) was also presented together with the *trans*- to *cis*-**10** isomerization.[11] This result seems to suggest that *Z*-**6** is more thermodynamically stable than *E*-**6** in *o*-dichlorobenzene and hence, unsubstituted sulfilimino group (–S–NH) is more stable at axial than equatorial position. However, the reason is unclear. According to the stability of these two conformations, the ab initio MO calculation will be performed in near future.

The confirmed configurational assignment of the products *E*- and *Z*-**6**, is suggestive to explain the mechanistic pathway on the stereochemistry in the alkaline hydrolysis of *trans*- and *cis*-**5**. In the alkaline hydrolysis of *cis*-**5**, the mechanistic aspect will be discussed as follows as illustrated in Scheme 6. In the thianthrene system, there is a possibility to exist as the mixture of 'flip-flap' inter-convertible confomers around S–S axis of the dithiin framework. Therefore, *cis*-**5** will exist as a mixture of two comformers of *cis*-**5**-(*e*) and *cis*-**5**-(*a*) (*e*: equatorial SN bond, *a*: axial SN bond). Comparison between these two conformers indicates clearly that *cis*-**5**-(*a*) is less stable than *cis*-**5**-(*e*) due to the 1,4-diaxial interaction between SO and *N*-bromosulfimide groups. Hence, HO^- attacks 5-*S*-position of *cis*-**5**-(*e*) more preferentially than *cis*-**5**-(*a*) via the S_N2' mechanism (Path **A**), resulting in the formation of *E*-**6**. Methoxide nucleophile also attacks 5-*S*-position of *cis*-**5**-(*e*) similarly (Path **B**), resulting in the concurrent formation of the intermediate methoxythiazyne **11** that is hydrolyzed rapidly to *E*-**6** spontaneously. Another possible route to *E*-**6** is via S_N1 mechanism (Path **C**) that leads to nitridosulfonium cation intermediate **12** initially,

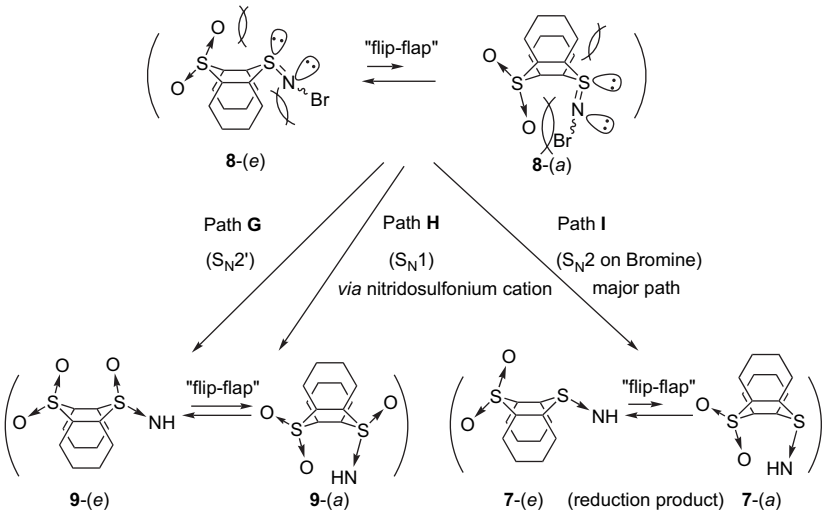


Scheme 6. Reaction mechanism of *cis*-**5** in KOH/(MeOH–H_2O) solution.

and successively to give *E*-**6**. Consequently, in the hydrolysis of *cis*-**5** under the conditions only the product *E*-**6** with retention of configuration was formed. In the alkaline hydrolysis of *trans*-**5**, the reaction path will be accounted for as follows. Similar to the cis-isomer, *trans*-**5** will exist as two conformers of *trans*-**5**-(*e*) and *trans*-**5**-(*a*) (*e* and *a* notations are the same as in case of cis-isomer), that have almost the same stability because of the absence of 1,4-diaxial interaction between SO and *N*-bromosulfimide groups (Scheme 7). However, contrary to *cis*-**5**, it is suggested that the attacking site of nucleophiles in *trans*-**5**-(*e*) was hindered substantially by SO group at 10-*S*-position, and further, *trans*-**5**-(*a*) has the steric hindrance due to *peri*-hydrogens on the fused benzene rings. Therefore, in the S_N2' mechanism the attack of HO^- or MeO^- ion at 5-*S*-position is prevented greatly to afford *Z*-**6** (Path **D**). This path **D** seems to be less important. Another possible route to S_N products *E*- and *Z*-**6** is via S_N1 mechanism. Ionization of *trans*-**5** leads to nitridosulfonium cation intermediates **13**-(*e*) and **13**-(*a*), and successively to give *E*-**6** and *Z*-**6**, as depicted in Scheme 7. In this case, the less-hindered nitridosulfonium cation intermediate **13**-(*a*) seems to be more favorable for attack of H_2O or MeOH than **13**-(*e*), resulting in the formation of *E*-**6** (18%) via path **E**-(*a*) preferentially than *Z*-**6** (7%) via path **E**-(*e*). The de-brominated product *trans*-**4** is formed as the main product in 46% yield, by the attack of HO^- and/or MeO^- on bromine atom, because this route is apparently the most favorable with absence of steric hindrance (Path **F**).



Scheme 7. Reaction route of *trans*-**5** in KOH/(MeOH–H_2O) solution.



Scheme 8. Reaction mechanism of **8** in KOH/(MeOH–H_2O) solution.

However, the precise mechanism of this de-bromination process is not clear at present. Further, these results suggest that S_N2' on sulfur proceeds (Path **D**) faster than both solvolysis (S_N1 process: Path **E**) and de-bromination (S_N2 reaction on bromine atom: Path **F**). *cis*-**5** (1 h; only S_N product, *E*-**6**) was found to react faster than *trans*-**5** (4 h) in which case sterically preferable S_N1 product ratio (via Path **E**) is quite small compared with the de-brominated product, *trans*-**4** (via Path **F**).

The product distribution from **8** under the same conditions also will be accounted for by the similar explanation as in the case of *trans*-**5**, as depicted in Scheme 8. The displacement reaction on sulfur atom to the product **9** via Path **G** (S_N2' mechanism) seems to be difficult. The attacking site for a nucleophile to **8**-(*e*) is sterically hindered by one SO group at 10-*S*-position and also **8**-(*a*) has the steric hindrance against nucleophile by interaction with *peri*-hydrogens on two benzene rings. Therefore, the possible route to **9** seems to be via S_N1 mechanism forming nitridosulfonium cation intermediates via path **H**, subsequently to lead to the product **9** as in the case of *trans*-**5** (Scheme 7). The compound **7** is formed as the major product by the attack of HO^- and/or MeO^- on bromine atom via S_N2 mechanism (Path **I**). The rather slow reaction time (4.3 h), compared to the result of hydrolysis of *cis*-**5** (see Scheme 6), also seems to suggest that S_N1 proceeds more slowly than S_N2'. The mechanism for the further de-imination steps for thianthrene 5-oxide and 5,5-dioxide from *trans*-**4** and **7**, respectively, is not clear at present.

3. Conclusion

The nucleophilic reaction on *N*-halosulfilimine among trivalent sulfur compounds involves many complex viewpoints mechanistically as follows. (1) Attacking site of nucleophile onto sulfur or halogen. (2) Types of transition state (usually trigonal bipyramidal; in this case attacking direction of nucleophile and leaving direction of leaving group are crucial to reflect to the change of the resulting stereochemistry of the products). (3) Berry pseudo-rotation (turnstile rotation) and so on.[16,17] However, in the thianthrene system with rather rigid dibenzodithiin framework these considerations are thought to be restricted greatly, in the direction of both nucleophile and leaving group in the transition state, and particularly in pseudo-rotation behavior. As a consequence, all the discussions shown above seem to explain the difference of the reactivities and the product distribution for **2**, *cis*- and *trans*-**5**, and **8** under the alkaline hydrolysis conditions in MeOH/H_2O.

4. Experimental

4.1. General

All the melting points were uncorrected. The ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded in $CDCl_3$ using TMS as an internal standard. 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 the reagents were of the highest quality and were further purified by distillation or recrystallization. The solvents were further purified by general methods.

4.1.1. 5-Iminothianthrene (1). Thianthrene (300 mg, 1.39 mmol) was dissolved in 25 mL of CH_2Cl_2 and into this solution 0.27 mL (3.47 mmol) of trifluoroacetic acid and 50 μl (2.77 mmol) of H_2O were added. To this solution was added ethyl *O*-mesitylenesulfonylacetohydroxamate (514.5 mg, 1.80 mmol) in CH_2Cl_2. After stirring for one day at rt, the reaction mixture was basified with aqueous $NaHCO_3$, and then extracted with $CHCl_3$. The chloroform layer was washed with brine, dried over anhydrous $MgSO_4$, and removed at reduced pressure to give **1** (245.7 mg, 76%),[18] that was recrystallized from CH_2Cl_2–hexane (colorless crystal). Mp 152–156 °C (dec 153 °C, lit.[18]); ^1H NMR ($CDCl_3$): δ=7.38–7.42 (m, 2H), 7.52–7.56 (m, 2H),

7.58–7.61 (m, 2H), 8.00–8.03 (m, 2H); IR (KBr): ν= 934 cm^{-1}.

4.1.2. 5-(*N*-Bromo)iminothianthrene (2). To a solution of **1** (217.2 mg, 0.939 mmol) in 25 mL of acetone, *N*-bromosuccinimide (178 mg, 1.13 mmol) in 5 mL of acetone was added at 5 °C. After 15 min, into the reaction mixture sufficient ice-water was added to form yellow precipitate, that was collected by filtration, washed with water to remove the succinimide formed, and dried at reduced pressure to give **2** (243.4 mg, 84.5%) followed by recrystallization from CH_2Cl_2–hexane (yellow crystal). Mp 121–123 °C (dec); ^1H NMR ($CDCl_3$): δ=7.48–7.53 (m, 2H), 7.57–7.66 (m, 4H), 8.00–8.08 (m, 2H); IR (KBr): ν=1437, 881, 757 cm^{-1}. Anal. Calcd for $C_{12}H_8NOS_2Br$: C, 46.46; H, 2.60; N, 4.51. Found: C, 46.58; H, 2.60; N, 4.53.

4.1.3. *cis*-5-(*N*-Bromo)iminothianthrene 10-oxide (*cis*-5). To a solution of *cis*-**4**[10] (203.0 mg, 0.82 mmol) in 34 mL of CH_2Cl_2 was added *N*-bromosuccinimide (173.6 mg, 0.98 mmol) in 17 mL of CH_2Cl_2 at rt. After 30 min the solvent was removed, and the residue was washed with water. Yellow crystalline material was dissolved again in CH_2Cl_2 and dried over anhydrous $MgSO_4$. The solvent was removed at reduced pressure to give *cis*-**5** (261.0 mg, 97%) that was recrystallized from CH_2Cl_2–hexane (yellow crystal). Mp 154–176 °C (dec); ^1H NMR ($CDCl_3$): δ=7.80–7.86 (m, 4H), 8.12–8.15 (m, 4H); ^{13}C NMR ($CDCl_3$): δ=125.0, 127.4, 129.4, 130.8, 131.6, 138.7; IR (KBr): ν=1075, 890 cm^{-1}. Anal. Calcd for $C_{12}H_8NOS_2Br$: C, 44.18; H, 2.47; N, 4.29. Found: C, 44.14; H, 2.42; N, 4.27.

4.1.4. *trans*-5-(*N*-Bromo)iminothianthrene 10-oxide (*trans*-5). To a solution of *trans*-**4**[10] (501.1 mg, 2.03 mmol) in 34 mL of CH_2Cl_2 was added *N*-bromosuccinimide (432.8 mg, 2.43 mmol) in 23 mL of CH_2Cl_2 at rt. After 30 min the solvent was removed, and the residue was washed with water. Yellow crystalline material was dissolved again in CH_2Cl_2 and dried over anhydrous $MgSO_4$. The solvent was removed at reduced pressure to give *trans*-**5** (591 mg, 89%) that was recrystallized from CH_2Cl_2–hexane (yellow crystal). Mp 168–177 °C (dec); ^1H NMR ($CDCl_3$): δ= 7.71–7.75 (m, 2H), 7.81–7.86 (m, 2H), 8.04–8.06 (m, 2H), 8.24–8.26 (m, 2H); ^{13}C NMR ($CDCl_3$): δ=129.8, 130.1, 131.4, 132.4, 136.2, 140.7; IR (KBr): ν=1025, 885 cm^{-1}. Anal. Calcd for $C_{12}H_8NOS_2Br$: C, 44.18; H, 2.47; N, 4.29. Found: C, 44.16; H, 2.16; N, 4.40.

4.1.5. 5-(*N*-Bromo)iminothianthrene 10,10-dioxide (8). To a solution of **7**[11] (150.7 mg, 0.57 mmol) in 5 mL of CH_2Cl_2 was added *N*-bromosuccinimide (123.4 mg, 0.69 mmol) in 14 mL of CH_2Cl_2 at rt. After 30 min the solvent was removed, and the residue was washed with water. Yellow crystalline material was dissolved again in CH_2Cl_2 and dried over anhydrous $MgSO_4$. The solvent was removed at reduced pressure to give **8** (182.0 mg, 93%) that was recrystallized from CH_2Cl_2–hexane (yellow crystal). Mp 180–190 °C (dec); ^1H NMR ($CDCl_3$): δ=7.79–7.83 (m, 2H), 7.87–7.91 (m, 2H), 8.17–8.19 (m, 2H), 8.24–8.27 (m, 2H); ^{13}C NMR ($CDCl_3$): δ=126.2, 128.3, 131.4, 133.0, 136.1, 139.4; IR (KBr): ν=1320, 1165, 890 cm^{-1}. Anal. Calcd for $C_{12}H_8NO_2S_2Br$: C, 42.11; H, 2.35; N, 4.09. Found: C, 42.17; H, 2.06; N, 4.14.

4.1.6. Hydrolysis of 2. To a suspension of **2** (46.5 mg, 0.15 mmol) in 6 mL of methanol was added 3 mL of 1 M aqueous KOH solution. After stirring for 2 h at 60 °C, the solution was neutralized with aqueous ammonium chloride and extracted with $CHCl_3$. The chloroform layer was washed with water and dried over anhydrous $MgSO_4$, and removed at reduced pressure to give 5-iminothianthrene 5-oxide (**3**, 39.2 mg, 95%) that was recrystallized from acetone–hexane (colorless crystal). Mp 117–118 °C; ^1H NMR ($CDCl_3$): δ=7.49–7.56 (m, 4H), 7.63–7.67 (m, 2H), 8.12–8.27 (m, 2H); IR (KBr): ν=3292, 1232, 978, 755 cm^{-1}. Anal. Calcd for $C_{12}H_9NO_2S_2$: C, 58.27; H, 3.67; N, 5.66. Found: C, 58.11; H, 3.74; N, 5.57.

4.1.7. Hydrolysis of *cis*-5. To a suspension of *cis*-**5** (50.2 mg, 0.15 mmol) in 6 mL of methanol was added 3 mL of 1 M aqueous KOH solution. After stirring for 1 h at 60 °C, the solution was neutralized with aqueous H_2SO_4 and extracted with $CHCl_3$. The chloroform layer was washed with water and dried over anhydrous $MgSO_4$, and removed at reduced pressure to give *E*-**6** (39.2 mg, 97%) that was recrystallized from EtOAc–hexane (colorless crystal). Mp 225–227 °C; ^1H NMR ($CDCl_3$): δ=3.52 (s, 1H), 7.64–7.68 (m, 2H), 7.70–7.75 (m, 2H), 8.11–8.14 (m, 2H), 8.18–8.20 (m, 2H); ^{13}C NMR ($CDCl_3$): δ=124.8, 125.7, 130.3, 132.3, 136.6, 147.2; IR (KBr): ν=3170, 1240, 1095, 1050, 950 cm^{-1}. Anal. Calcd for $C_{12}H_9NO_2S_2$: C, 54.73; H, 3.44; N, 5.31. Found: C, 54.42; H, 3.26; N, 5.34.

4.1.8. Hydrolysis of *trans*-5. To a suspension of *cis*-**5** (50.3 mg, 0.15 mmol) in 20 mL of methanol was added 10 mL of 1 M aqueous KOH solution. After stirring for 4 h at 60 °C, the solution was neutralized with aqueous H_2SO_4 and extracted with $CHCl_3$. The chloroform layer was washed with 3% aqueous H_2SO_4 and water, and dried over anhydrous $MgSO_4$, and removed at reduced pressure and then the residue was purified by preparative layer chromatography (silica gel; EtOAc–$CHCl_3$=1:20) to give *E*-**6** (7.5 mg, 18%), (*Z*)-5-iminothianthrene 5,10-dioxide (*Z*-**6**, 3.0 mg, 7%), and thianthrene 5-oxide (3.5 mg, 10%). Neutralization of aqueous H_2SO_4 layer gave *trans*-**4** (17.4 mg, 46%). Compound *Z*-**6** (colorless crystal): mp 239–241 °C (recrystallization from EtOAc–hexane); ^1H NMR ($CDCl_3$): δ=7.66–7.70 (m, 2H), 7.73–7.77 (m, 2H), 8.11–8.15 (m, 4H); ^{13}C NMR ($CDCl_3$): δ=125.1, 126.1, 130.4, 132.5, 136.5, 146.8; IR (KBr): ν=3190, 1240, 1095, 1070, 980 cm^{-1}. Anal. Calcd for $C_{12}H_9NO_2S_2$: C, 54.73; H, 3.44; N, 5.31. Found: C, 54.34; H, 3.48; N, 5.27.

4.1.9. Hydrolysis of 8. To a suspension of **8** (50.8 mg, 0.15 mmol) in 14 mL of methanol was added 7 mL of 1 M aqueous KOH solution. After stirring for 4.3 h at 60 °C, the solution was neutralized with aqueous sulfuric acid and extracted with $CHCl_3$. The chloroform layer was washed with 3% aqueous H_2SO_4 and water and dried over anhydrous $MgSO_4$, and removed at reduced pressure and then the residue was purified by preparative layer chromatography (silica gel; EtOAc–Hexane=1:1) to give **9** (13.0 mg, 31%) and thianthrene 5,5-dioxide (3.6 mg, 10%). Neutralization of aqueous H_2SO_4 layer gave **7** (18.9 mg, 48%). Compound **9** (colorless crystal): mp 262–266 °C (dec); ^1H NMR ($CDCl_3$): δ=7.77–7.84 (m, 4H), 8.24–8.27 (m, 2H), 8.28–8.30 (m, 2H); ^{13}C NMR ($CDCl_3$): δ=125.7, 125.8, 133.0,

133.8, 138.4, 142.4; IR (KBr): ν=3210, 1315, 1250, 1165, 980 cm^{-1}. Anal. Calcd for $C_{12}H_9NO_3S_2$: C, 51.60; H, 3.25; N, 5.01. Found: C, 51.74; H, 3.31; N, 4.93.

4.1.10. De-imidation of *E*-6 to *trans*-10. To a solution of *E*-**6** (50.2 mg, 0.19 mmol) in 7 mL of 45% aqueous H_2SO_4 was added sodium nitrite (27.6 mg, 0.40 mmol) in 1.5 mL of water at 0 °C. After 30 min the solution was extracted with $CHCl_3$. The chloroform layer was washed with water and dried over anhydrous $MgSO_4$ and the solvent was removed at reduced pressure to give *trans*-**10**[11] (44.9 mg, 95%) that was identified by ^1H NMR and IR spectral data.

4.1.11. De-imidation of *Z*-6 to *cis*-10. To a solution of *Z*-**6** (40.1 mg, 0.15 mmol) in 4 mL of 45% aqueous H_2SO_4 was added sodium nitrite (22.4 mg, 0.32 mmol) in 1.5 mL of water at 0 °C. After 30 min the solution was extracted with $CHCl_3$. The chloroform layer was washed with water and dried over anhydrous Mg_2SO_4 and the solvent was removed at reduced pressure to give *cis*-**10**[11] (37.0 mg, 98%) that was identified by ^1H NMR and IR spectral data.

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