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# Polar Cycloaddition of 9-Thiaphenanthrenium Salt with 1,3-Dienes

**Hiroshi Shimizu,* Shojiro Miyazaki, and Tadashi Kataoka**

*Gifu Pharmaceutical University, 6-1, Mitahora-higashi 5-chome, Gifu 502, Japan*

**Abstract**: Treatment of 9-thiaphenanthrenium salt **1** with conjugated dienes underwent regio- and stereospecific [2+4]-type polar cycloaddition to afford the corresponding sulfonium salt adducts **2** in good yields. Nucleophilic attack of some alcohols to the cycloadduct **2a** led to the two kinds of ring-opened compounds **3** and **4**. Reactions of compound **2a** with a variety of bases yielded the vinylcyclopropane derivative **5** and the ring-opened product **6**. Treatment of compound **2a** with LDA in the presence of methyl acrylate afforded the compound **7** which is believed to derive from Michael-addition of a reactive ylide intermediate to an α,β-unsaturated ester. Reductive cleavage of compound **2a** with $NaBH_4$ or $SmI_2$ afforded the ring-opened product **8**.

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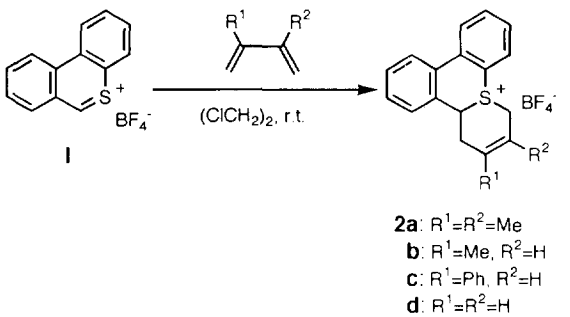
In our previous papers,[1] we reported interesting [2+4]-type polar cycloadditions of 1- and 2-benzothiopyrylium salts with several 1,3-dienes, affording the corresponding benzo-fused bicyclic sulfonium salts in high yields. In continuing works on the development of thiopyrylium ions as new dienophiles, we investigated the polar cycloaddition of 9-thiaphenanthrenium salt. In this paper, we describe polar cycloaddition of 9-thiaphenanthrenium salt **1** with several 1,3-dienes, and ring transformation of the cycloadducts obtained with alcohols, bases and reducing agents.

## Results and Discussion

Addition of 9-thiaphenanthrenium tetrafluoroborate **1** to a solution of 2 mol equiv. of 1,3-butadienes in dry 1,2-dichloroethane at room temperature and stirring of the mixture for 10-20 min afforded the corresponding cycloadducts **2** in fairly good yields (Scheme 1). The reaction conditions and product yields are summarized in Table 1. Cycloaddition of unsymmetrical 1,3-dienes such as isoprene (entry 2) or 2-phenyl-1,3-butadiene (entry 3) proceeded regiospecifically to give only a single regioisomer. The reaction of butadiene (entry 4) was rather slow and required longer reaction time (20 min.) to give a satisfactory yield. The structural assignment of the cycloadducts was based on the spectroscopic evidence (see Experimental section). In particular, the regiochemistry of the 9,10-buteno moieties in the cycloadducts **2b** and **2c** was determined mainly from the $^1H$ NMR spectra showing no coupling between the methylene protons of the allyl group attached to C-10 and the



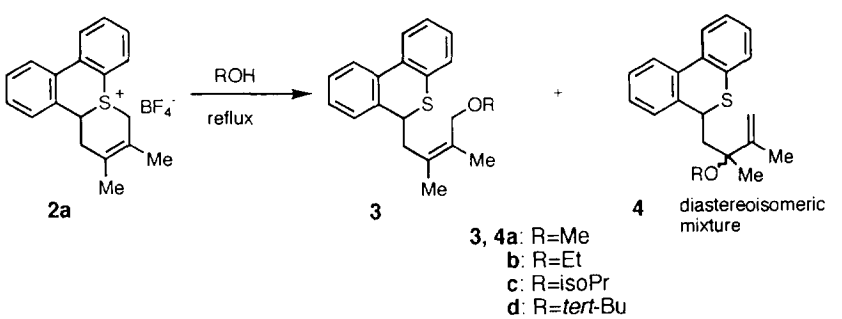

**Scheme 1**

Table 1. Cycloaddition of 9-Thiaphenanthrenium Salt **1** with 1,3-Dienes

| Entry | 1,3-Diene | | Time (t/min) | Product | |
|---|---|---|---|---|---|
| | $R^1$ | $R^2$ | | Compound | Yield (%) |
| 1 | Me | Me | 10 | **2a** | 86 |
| 2 | Me | H | 10 | **2b** | 80 |
| 3 | Ph | H | 10 | **2c** | 71 |
| 4 | H | H | 20 | **2d** | 71 |

olefinic proton.

We next focussed on an investigation of the reactivity of the cycloadducts obtained above in the hope of observing formation of novel sulfur-containing heterocyclic compounds, because the cycloadducts have reactive sulfonium ion structures. We performed the reaction of the cycloadduct **2a** with alcohols. The reaction results are summarized in Scheme 2 and Table 2. The cycloadduct **2a** underwent an easy cleavage of the sulfur-carbon




**Scheme 2**

bond by attack of alcohols to give ring-opened products, **3** and **4**. The latter compounds **4** were obtained as an inseparable diastereoisomeric mixtures in the ratios shown in Table 2. The product ratio of **3** and **4** was remarkably influenced by the bulkiness of an alcohol, *i.e.*, isopropyl- and *t*-butyl alcohol afforded only the

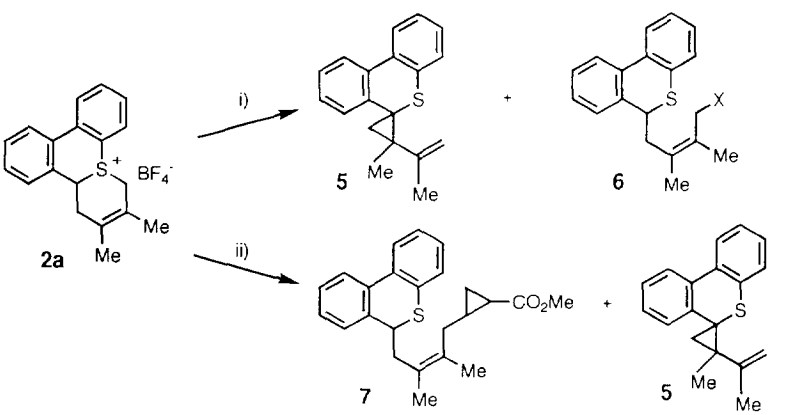
Table 2. Reactions of Cycloadduct **2a** with Alcohols

| Entry | Alcohol | Time (t/min) | Products | | | | |
|---|---|---|---|---|---|---|---|
| | | | R | **3** | Yield (%) | **4** | Yield (%) (diastereoisomeric ratio)[a] |
| 1 | MeOH | 10 | Me | **3a** | 77 | **4a** | 21 (1:1.7) |
| 2 | EtOH | 10 | Et | **3b** | 86 | **4b** | 10 (1:1.5) |
| 3 | isoPrOH | 10 | isoPr | **3c** | 89 | **4c** | - |
| 4 | *tert*-BuOH | 20 | *tert*-Bu | **3d** | 84 | **4d** | - |

[a] Determined by $^1$H NMR spectroscopy.

products **3** which might be formed *via* $S_N2$ reaction.

We next tried the ring transformation of the cycloadduct **2a** with a variety of organic and inorganic bases. The results are summarized in Scheme 3 and Table 3. Treatment of the cycloadduct **2a** with strong and non-nucleophilic bases such as LDA, NaH, DBU, and $K_2CO_3$ afforded vinyl cyclopropane derivative **5** (entries 1-3 and 8), while upon treatment with weak and nucleophilic bases such as alkylamines and KOAc, the cycloadduct



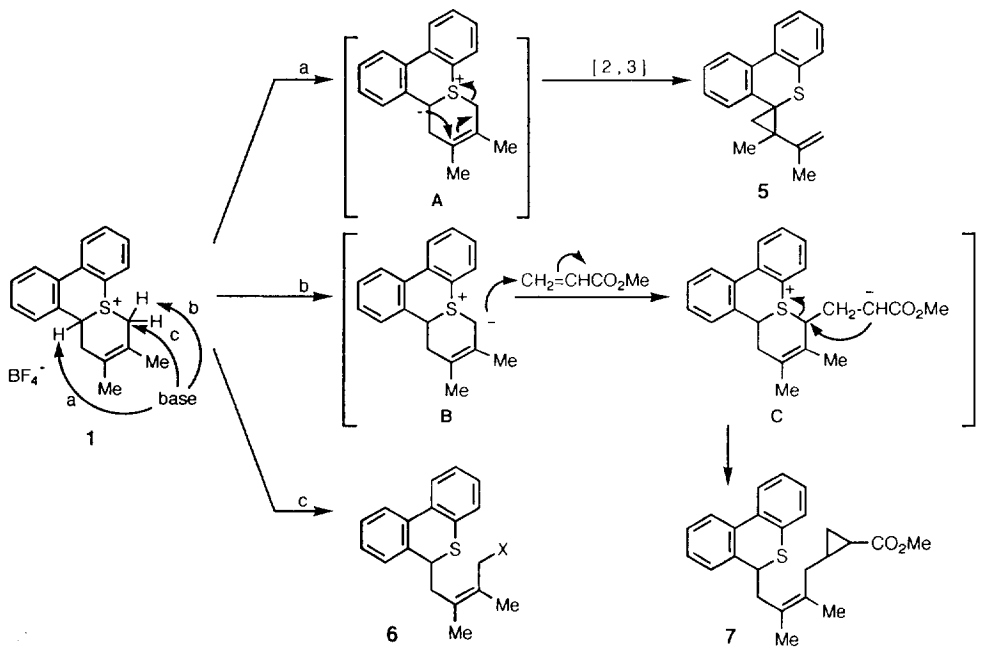

**Scheme 3** *Reagents and conditions*: i) base, ii) a) LDA, THF, b) $CH_2$=$CHCO_2Me$, THF, $N_2$, -78-0 °C

Table 3. Reactions of Cycloadduct **2a** with Various Bases

| Entry | Base | Solvent | Temp (°C) | Products (%yield) | | | |
|---|---|---|---|---|---|---|---|
| | | | | **5** | **6**(X) | | |
| 1 | LDA | THF | -78-0 | 33 | - | | |
| 2 | NaH | DMF | 0 | 45 | - | | |
| 3 | DBU | THF | 0 | 72 | - | | |
| 4 | NaOEt | EtOH | 0 | 78 | **3b** | trace | (OEt) |
| 5 | $Et_3N$ | $(CH_2Cl)_2$ | RT | - | **6e** | 94 | ($NEt_3BF_4$) |
| 6 | $Et_2NH$ | $(CH_2Cl)_2$ | RT | - | **6f** | 86 | ($NEt_2$) |
| 7 | AcOK | $(CH_2Cl)_2$ | RT | - | **6g** | 95 | (OAc) |
| 8 | $K_2CO_3$ | acetone | RT | 58 | | | |

**2a** produced only ring-opened products **6** *via* $S_N2$ reaction in high yields (entries 5-7). A strong base, NaOEt also afforded mainly the compound **5**, but nucleophilically attacked product **3b** in a trace amount. It is worthy to note that extremely strong bases, LDA and NaH afforded very low yield of the product **5**, suggesting the formation of another reactive intermediate which might be decomposed to undetermined complex products. Therefore, we carried out the reaction in the presence of methyl acrylate as a Michael-acceptor. Treatment of **2a** with LDA, followed by addition of methyl acrylate afforded the adduct **7** in 37% yield together with vinylcyclopropane derivative **5** in 25% yield as shown in Scheme 3.

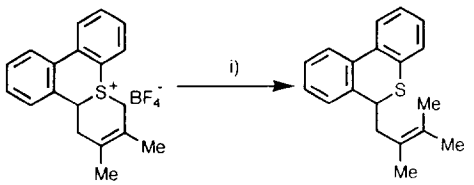
A possible mechanistic interpretation for the ring transformation of cycloadduct **2a** caused by various bases is depicted in Scheme 4. Three different paths a, b, and c for each product will be considered. In path a, the




Scheme 4

bases abstract the acidic benzylic proton adjacent to the positively charged sulfur atom to lead to an ylidic intermediate **A**. Intermediate **A** degrades then *via* a 2,3-sigmatropic rearrangement to form a cyclopropane ring and afford compound **5**. In path b, the bases abstract another acidic proton of the sulfonium compound **2a** to form the ylidic intermediate **B**. Intermediate **B** then adds to methyl acrylate to give the intermediate **C**, which cyclizes to construct a cyclopropane ring together with the fission of S-C bond and afford the final adduct **7**. In path c, nucleophilic bases attack on the allylic carbon adjacent to sulfur atom along with the fission of the carbon-sulfur bond to give the ring-opened compounds **6**.

Finally, we attempted the reduction of the cycloadduct **2a** with sodium borohydride and also with a single-electron transfer reducing agent, samarium diiodide expecting the formation of a sulfur-containing ten-membered ring by the reductive cleavage of the S-$C_{10}$ bond. However, both of the reducing agents cleaved the bond between sulfur and allylic carbon to give the ring-opened product **8** in good yield as shown in Scheme 5.




2a 8

Scheme 5 *Reagents and conditions*; i), $SmI_2$, MeOH, THF, room temp. or $NaBH_4$, EtOH, room temp

## Experimental

Melting points were measured on a Yanagimoto micromelting point apparatus, and are uncorrected. IR spectra were measured on a JASCO A-1 spectrophotometer. $^1$H-NMR spectra were recorded on a Hitachi R-20B (60 MHz) or a JEOL GX-270 (270 MHz) spectrometer using tetramethylsilane as internal standard. The chemical shifts are in δ units (ppm) with coupling constants J in Hz. $^{13}$C NMR spectra were obtained using a JEOL GX-270 spectrometer. Mass spectra were obtained using a JEOL JMS-D 300 spectrometer with a direct-insertion probe at 70 eV. High-resolution mass determination was conducted on a JMA 2000 on-line system. Elemental analyses were performed at the Microanalytical Laboratory of Gifu Pharmaceutical University. Analytical and preparative TLC (PLC) were performed on Merk silica gel 60PF-254 plates.

### 9-Thiaphenanthrenium Tetrafluoroborate 1

Triphenylcarbenium tetrafluoroborate [4] (6.965 g, 21.1 mmol) was added to a stirred solution of 9, 10-dihydro-9-thiaphenanthrene [5] (3.803 g, 19.18 mmol) in dry nitromethane (20 ml) and the mixture was stirred for 30 min at room temperature. To the reaction mixture was added dry ether to precipitate 4.105 g (75.3%) of **1** as orange crystals after recrystallization from nitromethane-dry ether: mp 165 °C (dec.) IR (KBr): 1120-1030 ($BF_4^-$) cm$^{-1}$. $^1$H-NMR ($CD_3CN$) δ: 8.10-8.29 (3H, m, ArH), 8.51-8.63 (3H, m, ArH), 9.11-9.20 (2H, m, ArH), 11.08 (1H, s, 10-H). $^{13}$C-NMR ($CD_3CN$) δ: 126.4 (d), 127.7 (d), 130.6 (d), 131.0 (s), 131.6 (s), 131.9 (d), 132.2 (d), 134.2 (s), 135.2 (d), 136.1 (d), 138.5 (s), 143.4 (d), 175.1 (d). Anal. Calcd for $C_{13}H_9BF_4S$: C, 54.96; H, 3.19. Found: C, 54.75; H, 3.19.

### General Procedure for the Reaction of 1 with Several 1,3-Butadienes

9-Thiaphenanthrenium salt **1** (1 mmol) was added portionwise to a stirred solution of an appropriate substituted 1,3-butadiene (2 mmol) in 1,2-dichloroethane (10 ml) at room temperature, and the mixture was stirred for an appropriate time. In the case of 1,3-butadiene, butadiene gas was bubbled into a stirred suspension of the salt **1** (1 mmol) in 1,2-dichloroethane (10 ml) for 5 min at room temperature, and the mixture was stirred for an appropriate time. Ether was added to the reaction mixture to precipitate the product.

**9,10-(2,3-Dimethyl-2-buteno)-9,10-dihydro-9-thiaphenanthrenium tetrafluoroborate 2a** (86%), colorless columns (acetonitrile-ether), mp 144.5-145.5 °C (dec.). IR (KBr): 1100-1030 ($BF_4^-$) cm$^{-1}$. $^1$H-NMR ($CD_3CN$) δ: 1.74 (6H, s, 2xMe), 2.81 (1H, dd, J=19.0, 5.9 Hz, CHC*H*$_2$), 2.92 (1H, br d, J=19.0 Hz, CHC*H*H), 3.79 and 4.06 (each 1H, each br d, J=17.1 Hz, $S^+$-$CH_2$), 5.00 (1H, t, J=5.9 Hz, C*H*$CH_2$), 7.49-7.68 (4H, m, ArH), 7.83-7.89 (2H, m, ArH), 7.95-7.98 (1H, m, ArH), 8.10-8.13 (1H, m, ArH). $^{13}$C-NMR ($CD_3CN$) δ: 19.4 (q), 20.0 (q), 31.7 (t), 36.0 (t), 44.5 (d), 116.7 (s), 118.0 (s), 128.5 (d), 128.6 (s), 128.7 (s), 128.8 (d), 129.0 (s), 131.0 (d), 131.4 (d), 131.5 (d), 131.7 (s), 135.7 (d). Anal. Calcd for $C_{19}H_{19}BF_4S$: C, 62.31; H, 5.23. Found: C, 62.19; H, 5.30.

**9,10-(3-Methyl-2-buteno)-9,10-dihydro-9-thiaphenanthrenium tetrafluoroborate 2b** (80%), colorless prisms (acetonitrile-ether), mp 148.5-149.5 °C (dec.). IR (KBr): 1100-1030 ($BF_4^-$) $cm^{-1}$. $^1$H-NMR ($CD_3CN$) δ: 1.79 (3H, s, Me), 2.73 (1H, dd, J=19.0, 5.9 Hz, CHC*H*H), 2.90 (1H, br d, J=19.0 Hz, CHCH*H*), 3.89 and 4.17 (each 1H, each br d, J=17.1 Hz, $S^+$-$CH_2$), 5.04 (1H, t, J=5.9 Hz, C*H*$CH_2$), 5.57 (1H, br s, $S^+$-$CH_2$C*H*=C), 7.53-7.67 (4H, m, ArH), 7.83-7.89 (2H, m, ArH), 7.95-7.97 (1H, m, ArH), 8.09-8.12 (1H, m, ArH). $^{13}$C-NMR ($CD_3CN$) δ: 24.2 (q), 30.21 (t), 32.6 (t), 45.1 (d), 111.5 (d), 116.5 (s), 128.5 (d),128.6 (d), 128.9 (d), 130.9 (d), 131.3 (d), 131.4 (d), 131.9 (s), 135.6 (d), 135.8 (s), 137.5 (s). Anal. Calcd for $C_{18}H_{17}BF_4S$: C, 61.39; H, 4.87. Found: C, 61.18; H, 4.83.

**9,10-(3-Phenyl-2-buteno)-9,10-dihydro-9-thiaphenanthrenium tetrafluoroborate 2c** (71.4%), colorless columns (acetonitrile-ether), mp 154.5-156.5 °C (dec.), IR (KBr): 1110-1040 ($BF_4^-$) $cm^{-1}$. $^1$H-NMR ($CD_3CN$) δ: 3.18 (1H, ddd, J=19.0, 6.8, 1.5 Hz, CHC*H*H), 3.37 (1H, ddd, J=19.0, 5.4, 2.0 Hz, CHCH*H*), 4.19 (1H, dt, J=18.1, 1.5 Hz, $S^+$-C*H*H), 4.44 (1H, dt, J=18.1, 2.0 Hz, $S^+$-CH*H*), 5.18 (1H, dt, J=18.1, 1.5 Hz, C*H*$CH_2$), 6.11-6.14 (1H, m, $S^+$-$CH_2$C*H*=C), 7.35 (5H, br s, ArH), 7.54-7.55 (2H, m, ArH), 7.59-7.69 (2H, m, ArH), 7.83-7.89 (2H, m, ArH), 7.97 (1H, br d, J=7.8 Hz, ArH), 8.10 (1H, br d, J=7.8 Hz, ArH). $^{13}$C-NMR ($CD_3CN$) δ: 28.7 (t), 33.2 (t), 45.3 (d), 114.5 (d), 116.4 (s), 126.5 (d), 128.6 (d), 128.8 (d), 129.0 (s), 129.0 (d), 129.6 (d), 131.1 (d), 131.5 (d), 131.8 (d), 132.0 (s), 135.6 (d), 135.8 (s), 139.2 (s), 140.5 (s). Anal. Calcd for $C_{23}H_{19}BF_4S$: C, 66.68; H, 4.62. Found: C, 66.54; H, 4.63.

**9,10-(2-Buteno)-9,10-dihydro-9-thiaphenanthrenium tetrafluoroborate 2d** (71%), colorless columns (acetonitrile-ether), mp 163-164 °C (dec.). IR (KBr): 1100-1030 ($BF_4^-$) $cm^{-1}$. $^1$H-NMR ($CD_3CN$) δ: 2.72-2.81 (1H, m, CHC*H*H), 2.92-2.99 (1H, m, CHCH*H*), 3.93-4.01 (1H, m, $S^+$-C*H*H), 4.21-4.29 (1H, m, $S^+$-CH*H*), 5.03 (1H, t, J=5.9 Hz, C*H*$CH_2$), 5.82-5.87 (1H, m, $S^+$-$CH_2$C*H*=CH), 6.02-6.08 (1H, m, $S^+$-$CH_2$CH=C*H*), 7.54-7.67 (4H, m, ArH), 7.83-7.88 (2H, m, ArH), 7.93-7.96 (1H, m, ArH), 8.09-8.11 (1H, m, ArH). $^{13}$C-NMR ($CD_3CN$) δ: 25.7 (t), 32.2 (t), 44.7 (d), 116.6 (s), 117.3 (d), 128.6 (d), 128.8 (d), 128.9 (d), 129.1 (s), 131.0 (d), 131.4 (d), 131.7 (d), 132.0 (s), 135.6 (d), 135.9 (s). Anal. Calcd for $C_{17}H_{15}BF_4S$: C, 60.38; H, 4.47. Found: C, 60.15; H, 4.46.

**Reactions of Cycloadduct 2a with Alcohols.**

A mixture of the cycloadduct **2a** (183 mg, 0.5 mmol) and appropriate dry alcohol (5 ml) was refluxed for 10-20 min. To the reaction mixture was added saturated aq. $NaHCO_3$ and the mixture was extracted with dichloromethane. The organic layer was washed with water, dried over $MgSO_4$, and evaporated off to dryness. The residual oil was subjected to PLC on silica gel with hexane-ethyl acetate (10:1) to afford the products.

**10-(4-Methoxy-2,3-dimethylbut-2-enyl)-9,10-dihydro-9-thiaphenanthrene 3a** (76.8%) from the reaction with methanol; colorless oil, $^1$H-NMR ($CDCl_3$) δ: 1.62 (6H, s, 2xMe), 2.42 and 2.47 (each 1H, each dd, J=13.7, 7.8 Hz, CHC$H_2$), 3.00 (3H, s, OMe), 3.25 and 3.45 (each 1H, each d, J=11.2 Hz, C$H_2$OMe), 3.86 (1H, t, J=7.8 Hz, C*H*$CH_2$), 7.06-7.08 (1H, m, ArH), 7.19-7.37 (4H, m, ArH), 7.38-7.42 (1H, m, ArH), 7.67-7.70 (1H, m, ArH), 7.79-7.82 (1H, m, ArH). $^{13}$C-NMR ($CDCl_3$) δ: 16.6 (q), 19.1 (q), 39.3 (t), 43.2 (d), 57.4 (q), 72.4 (t), 125.1 (d), 126.0 (d), 126.2 (d), 127.0 (d), 127.6 (d), 127.9 (d), 129.3 (d), 129.5 (s), 129.6 (s), 131.6 (s), 132.9 (s), 133.7 (s), 136.7 (s). MS *m/z*: 310 ($M^+$), 197 (base). Anal. Calcd for $C_{20}H_{22}OS$: C, 77.38; H, 7.14. Found: C, 77.14; H, 7.21.

**10-(2-Methoxy-2,3-dimethylbut-3-enyl)-9,10-dihydro-9-thiaphenanthrene 4a** (21.3%) as an inseparable mixture of diastereoisomers in a ratio 1:1.7 from the reaction with methanol; colorless oil, MS *m/z*: 310 ($M^+$), 197 (base). High resolution mass spectrum, *m/z*, 310.1410 (calcd for $C_{20}H_{22}OS$, 310.1392).

$^1$H-NMR ($CDCl_3$) for the major isomer of **4a**. δ: 1.24 (3H, s, Me), 1.61 (br s, $CH_2$=C*Me*), 1.96 (1H, dd, J=14.7, 5.4 Hz, CHC*H*H), 2.12(1H, dd, J=14.7, 4.9 Hz, CHCH*H*), 3.00 (3H, s, OMe), 3.92 (1H, dd, J=6.4, 5.4 Hz, C*H*$CH_2$), 4.90 and 5.00 (each 1H, each br s, C=$CH_2$), 7.18-7.36 (m, ArH), 7.40-7.44 (m, ArH), 7.66-7.69 (m, ArH). $^{13}$C-NMR ($CDCl_3$) for the major isomer of **4a**. δ: 18.8 (q), 21.4 (q), 39.6 (d), 43.1 (t), 49.7 (q), 79.1 (s), 114.0 (t), 125.1 (d), 125.2 (d), 126.3 (d), 126.4 (d), 126.6 (d), 127.4 (d), 127.8 (d), 129.5 (d), 131.7 (s), 133.1 (s), 134.5 (s), 138.6 (s), 147.2 (s). $^1$H-NMR of the minor isomer of **4a**. δ: 1.26 (3H, s, Me), 1.64 (3H, br s, $CH_2$=C*Me*), 1.94 (1H, dd, J=14.7, 4.9, CHC*H*H), 2.06 (1H, dd, J=14.7, 6.8 Hz, CHCH*H*), 2.99 (3H, s, OMe), 3.84 (1H, dd, J=6.8, 4.9 Hz, C*H*$CH_2$), 5.02 and 5.05 (each 1H, each br s, C=$CH_2$), 7.18-7.36 (m, ArH), 7.40-7.44 (m, ArH), 7.66-7.69 (m, ArH), 7.78-7.81 (m, ArH). $^{13}$C-NMR ($CDCl_3$) for the minor isomer of **4a.** δ: 18.9 (q), 21.4 (q), 39.8 (d), 43.0 (t), 49.5 (q), 79.5 (s), 114.3 (t), 126.3 (d), 126.4 (d), 126.6 (d), 127.4 (d), 127.8 (d), 129.5 (d), 131.6 (s), 133.1 (s), 134.7 (s), 138.6 (s), 146.7 (s).

**10-(4-Ethoxy-2,3-dimethylbut-2-enyl)-9,10-dihydro-9-thiaphenanthrene** **3b** (86.4%) from the reaction with ethanol; colorless oil, $^1$H-NMR ($CDCl_3$) δ: 1.03 (3H, t, J=6.8 Hz, $OCH_2$*Me*), 1.62 and 1.64 (each 3H, each s, 2xMe), 3.10 and 3.13 (each 1H, each dq, J=12.7, 6.8 Hz, O*C*$H_2$Me), 3.29 and 3.48 (each 1H, each d, J=10.7 Hz, $OCH_2$-), 3.86 (1H, t, J=7.3 H Hz, C*H*$CH_2$), 7.05-7.08 (1H, m, ArH), 7.18-7.42 (5H, m, ArH), 7.67-7.70 (1H, m, ArH), 7.78-7.82 (1H, m, ArH). $^{13}$C-NMR ($CDCl_3$) δ: 15.0 (q), 16.4 (q), 19.1 (q), 39.3 (t), 43.2 (d), 65.0 (t), 70.3 (t), 125.1 (d), 126.0 (d), 126.2 (d), 127.0 (d), 127.6 (d), 127.9 (d), 129.2 (s), 129.2 (d), 129.8 (s), 131.4 (s), 132.9 (s), 133.7 (s), 136.8 (s). MS *m/z* 324 ($M^+$), 197 (base). Anal. Calcd for $C_{21}H_{24}OS$: C, 77.73; H, 7.46. Found: C, 77.52; H, 7.55.

**10-(2-Ethoxy-2,3-dimethylbut-3-enyl)-9,10-dihydro-9-thiaphenanthrene** **4b** (9.9%) as an inseparable mixture of diastereoisomers in a ratio 1:1.5 from the reaction with ethanol; colorless oil, MS *m/z*, 324 ($M^+$), 197 (base). $^1$H-NMR ($CDCl_3$) for the major isomer of **4b**. δ: 1.10 (3H, t, J=6.8 Hz, $OCH_2$*Me*), 1.25 (3H, s, Me), 1.62 (3H, s, Me), 1.97 (1H, dd, J=14.7, 5.4 Hz, CHC*H*H), 2.13 (1H, dd, J=14.7, 6.4 Hz, CHCH*H*), 3.02-3.29 (2H, m, O*C*$H_2$Me), 3.92 (1H, dd, J=6.4, 5.4 Hz, C*H*$CH_2$), 4.90 (1H, br s, C=C*H*H), 4.98-4.99 (1H, m, C=CH*H*), 7.18-7.73 (m, ArH), 7.66-7.69 (m, ArH), 7.78-7.82 (m, ArH). $^1$H-NMR ($CDCl_3$) δ: 1.08 (3H, t, J=6.8 Hz, $OCH_2$*Me*), 1.28 (3H, s, Me), 1.64 (3H, s, Me), 1.94 (1H, dd, J=14.7, 4.9 Hz, CHC*H*H), 2.08 (1H, dd, J=14.7, 6.8 Hz, CHCH*H*), 3.84 (1H, dd, J=6.8, 4.9 Hz, C*H*$CH_2$), 5.01 (1H, br s, C=C*H*H), 5.04-5.05 (1H, m, C=CH*H*),7.18-7.73 (m, ArH), 7.66-7.69 (m, ArH), 7.78-7.82 (1H, m, ArH).

**10-(4-Isopropoxy-2,3-dimethylbut-2-enyl)-9,10-dihydro-9-thiaphenanthrene** **3c** (88.8%) from the reaction with isopropyl alcohol; colorless oil, $^1$H-NMR ($CDCl_3$) δ: 0.92 and 0.97 (each 3H, each s, J=5.9 Hz, OCH*Me*$_2$), 1.62 and 1.64 (each 3H, each s, 2xMe), 2.40 and 2.57 (each 1H, each dd, J=13.7, 7.8 Hz, CHC*H*$_2$), 3.23 (1H, m, J=5.9 Hz, OC*H*Me$_2$), 3.25 and 3.44 (each 1H, each d, J=10.7 Hz, $OCH_2$), 3.86 (1H, t, J=7.8 Hz, C*H*$CH_2$), 7.05-7.08 (1H, m,, ArH), 7.18-7.42 (5H, m, ArH), 7.67-7.70 (1H, m, ArH), 7.78-7.81 (1H, m, ArH). $^{13}$C-NMR ($CDCl_3$) δ: 16.9 (q), 19.0 (q), 21.8 (q), 21.9 (q), 39.4 (t), 43.2 (d), 67.9 (t), 70.4 (d), 125.1 (d), 126.0 (d), 126.1 (d), 127.0 (d), 127.6 (d), 127.9 (d), 128.9 (s0, 129.3 (d), 130.0 (s), 131.4 (s), 132.9 (s), 133.7 (s), 136.8 (s). Anal. Calcd for $C_{22}H_{26}OS$: C, 78.06; H, 7.74. Found: C, 77.79; H, 7.88.

**10-(2,3-Dimethyl-4-tert-butoxybut-2-enyl)-9,10-dihydro-9-thiaphenanthrene** **3d** (83.5%) from the reaction with *tert*-butyl alcohol; colorless oil, $^1$H-NMR ($CDCl_3$) δ: 0.99 (9H, s, $OCMe_3$), 1.64 (6H, s, 2xMe), 2.40 and 2.48 (each 1H, each dd, J=13.2, 7.8 Hz, CHC*H*$_2$), 3.11 and 3.32 (each 1H, each d, J=10.3 Hz, $OCH_2$), 3.87 (1H, t, J=7.8 Hz, C*H*$CH_2$), 7.06-7.09 (1H, m, ArH), 7.19-7.42 (5H, m, ArH), 7.68-7.71

(1H, m, ArH), 7.78-7.81 (1H, m, ArH). $^{13}$C-NMR ($CDCl_3$) δ: 16.9 (q), 19.0 (q), 27.3 (q), 39.6 (t), 43.1 (d), 61.8 (t), 72.3 (s), 125.1 (d), 125.9 (d), 126.1 (d), 127.1 (d), 127.6 (d), 127.9 (d), 128.4 (s), 129.3 (d), 130.4 (s), 131.5 (s), 132.9 (s), 133.7 (s), 136.9 (s). MS *m/z*: 352 ($M^+$), 197 (base). Anal. Calcd for $C_{23}H_{28}OS$: C, 78.36; H, 8.01. Found: C, 78.30; H, 8.10.

**Reactions of Cycloadduct 2a with a Variety of Bases.** The results including reaction conditions and yields are summarized in Table 3.

**(a) With Lithium Diisopropylamide (LDA).** Butyllithium (1.62M solution in hexane; 0.75 ml, 1.2 mmol) was added with stirring to diisopropylamine (200 mg, 1.98 mmol) in dry THF (10 ml) at -30 °C under nitrogen. After 30 min, the cycloadduct **2a** (366 mg, 1 mmol) was added at -78 °C to the mixture, which was then stirred for 1 h before being allowed to warm to 0 °C. An aq. $NH_4Cl$ solution was added to the reaction mixture which was then extracted with dichloromethane. The extract was washed with water, dried over $MgSO_4$, and evaporated to afford a residue which was subjected to PLC on silica gel with hexane-dichloromethane (10:1) to give 91 mg (32.7%) of 2'-isopropenyl-2'-methylspiro[9,10-dihydro-9-thiaphenanthrene-10,1'-cyclopropane] **5** as colorless needles after recrystallization from methanol, mp 97-98 °C, $^1$H-NMR ($CDCl_3$) δ: 0.81 and 1.21 (each 3H, each s, 2xMe), 1.44 and 1.65 (each 1H, each d, J=6.8 Hz, $CH_2$), 4.76 and 4.92 (each 1H, each br s, C=$CH_2$), 7.14-7.37 (6H, m, ArH), 7.69-7.72 (1H, m, ArH), 7.81-7.84 (1H, m, ArH). $^{13}$C-NMR ($CDCl_3$) δ: 19.5 (t), 19.8 (q), 20.6 (q), 33.1 (s), 38.3 (s), 113.3 (t), 124.5 (d), 125.6 (d), 126.0 (d), 126.4 (d), 126.9 (d), 127.3 (d), 128.0 (d), 134.5 (s), 135.8 (s), 136.5 (s), 146.2 (s). MS *m/z* 278 ($M^+$), 263 (base). Anal. Calcd for $C_{19}H_{18}S$: C, 81.97; H, 6.52. Found: C, 81.79; H, 6.55.

**(b) With Sodium Hydride.** Sodium hydride (60% dispersion in mineral oil; 25 mg, 0.6 mmol) was added with stirring to an ice-cooled solution of the cycloadduct **2a** (183 mg, 0.5 mmol) in dry DMF (5 ml) under nitrogen, and the mixture was stirred for 30 min. The reaction mixture was poured into ice-water and extracted with dichloromethane. The organic layer was washed with water, dried over $MgSO_4$ and evaporated off to dryness. The residual oil was purified by PLC on silica gel as above to afford 63 mg (45%) of **5**.

**(c) With 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU).** The cycloadduct **2a** (183 mg, 0.5 mmol) was added with stirring to an ice-cooled solution of DBU (91 mg, 0.6 mmol) in dry DMF (5 ml) under nitrogen and the mixture was stirred for 30 min at 0 °C. The reaction mixture was poured into water and extracted with ethyl acetate. Work-up as above gave 101 mg (72%) of **5**.

**(d) With Sodium Ethoxide.** Sodium hydride (30 mg, 0.75 mmol) was added to dry ethanol (5 ml) and the mixture was stirred for 10 min. The cycloadduct **2a** (183 mg, 0.5 mmol) was added with stirring to the above solution with cooling. After the mixture was stirred for 30 min, it was poured into an ice-water and extracted with ether. Work-up as usual afforded a residue which was subjected to PLC on silica gel with hexane-ethyl acetate (15:1) to afford 139 mg (78.4%) of **5** and a trace ammount of **3b**.

**(e) With Triethylamine.** The cycloadduct **2a** (183 mg, 0.5 mmol) was added with stirring to a solution of triethylamine (101 mg, 1 mmol) in 1,2-dichloroethane ( 5 ml), and the mixture was stirred for 4 h at room temperature. Ether was added to the reaction mixture to precipitate 221 mg (94.4%) of 2,3-dimethyl-4-(9,10-dihydro-9-thiaphenanthren-10-yl)but-2-enyltriethylammonium tetrafluoroborate **6e** as colorless powder after recrystallization from chloroform-ether; mp 138-139.5 °C. IR (KBr): 1100-1031 ($BF_4^-$) cm$^{-1}$, $^1$H-NMR ($CDCl_3$) δ: 10.1 (9H, t, J=7.3 Hz, 3x$CH_2$Me), 1.81 and 1.84 (each 3H, each s, 2xMe), 2.35 (1H, dd, J=13.7, 5.9 Hz, CHC*H*H), 2.48 (1H, dd, J=13.7, 9.3 Hz, CHCH*H*), 2.88-3.01 (6H, m, 3xC*H*$_2$Me), 3.11 and 3.27 (each 1H, each d, J=14.2 Hz, C*H*$_2$N$^+$-Et$_3$), 3.98 (1H, dd, J=9.3, 5.9 Hz, C*H*$CH_2$), 7.16-7.19 (1H, m, ArH), 7.28-7.46 (5H, m, ArH), 7.73-7.76 (1H, m, ArH), 7.84-7.87 (1H, m, ArH). $^{13}$C-NMR ($CDCl_3$) δ: 7.8 (q),

19.9 (q), 20.5 (q), 40.0 (t), 42.3 (d), 53.2 (t), 59.7 (t), 120.6 (s), 125.4 (d), 126.3 (d), 126.8 (d), 127.0 (d), 128.3 (d), 128.4 (d), 128.8 (d), 129.5 (d), 130.6 (s), 132.2 (s), 133.5 (s), 135.9 (s), 142.3 (s). Anal. Calcd for $C_{25}H_{34}BF_4NS$: C, 64.24; H, 7.33; N, 3.00. Found: C, 64.01; H, 7.28; N, 3.07.

**(f) With Diethylamine.** A mixture of the cycloadduct **2a** (183 mg, 0.5 mmol) and diethylamine (75 mg, 1 mmol) in 1,2-dichloroethane (5 ml) was stirred at room temperature for 30 min. The reaction mixture was poured into water and extracted with dichloromethane. The organic layer was washed with water, dried over $MgSO_4$ and evaporated off to dryness. The residual oil was purified by PLC on silica gel with chloroform-methanol (20:1) to afford 152 mg (86.4%) of 10-(4-diethylamino-2,3-dimethylbut-2-enyl)-9,10-dihydro-9-thiaphenanthrene **6f** as a colorless oil. $^1$H-NMR ($CDCl_3$) δ: 0.81 (6H, t, J=7.3 Hz, 2x$CH_2$*Me*), 1.61 (6H, s, 2xMe), 2.09-2.22 (4H, m, 2x$CH_2$Me), 2.27 and 2.50 (each 1H, each d, $CH_2NEt_2$), 2.45 (2H, d, J=7.8 Hz, CHC$H_2$), 3.89 (1H, t, J=7.8 Hz, C*H*$CH_2$), 7.05-7.08 (1H, m, ArH), 7.19-7.42 (5H, m, ArH), 7.67-7.70 (1H, m, ArH), 7.78-7.81 (1H, m, ArH). $^{13}$C-NMR ($CDCl_3$) δ: 11.5 (q), 17.5 (q), 19.3 (q), 39.4 (t), 43.3 (d), 46.2 (t), 55.3 (t), 125.2 (d), 126.0 (d), 126.1 (d), 127.0 (d), 127.4 (s), 127.6 (d), 127.9 (d), 129.4 (d), 131.1 (s), 131.6 (s), 133.2 (s), 133.9 (s), 137.0 (s). MS *m/z*: 351 ($M^+$), 197 (base). Anal. Calcd for $C_{23}H_{29}NS$: C, 78.58; H, 8.31; N, 3.98. Found: C, 78.32; H, 8.25; N, 3.98.

**(g) With Potassium Acetate.** A mixture of the cycloadduct **2a** (183 mg, 0.5 mmol) and potassium acetate (98 mg, 1 mmol) in 1,2-dichloroethane (5 ml) was stirred for 30 min at room temperature. After dilution with water, the reaction mixture was extracted with dichloromethane and worked up as above to afford a crude oil, which was purified by PLC on silica gel with hexane-ethyl acetate (8:1) to afford 160 mg (94.7%) of 10-(4-acetoxy-2,3-dimethylbut-2-enyl)-9,10-dihydro-9-thiaphenanthrene **6g** as a colorless oil. IR (neat) 1725 (ester) cm$^{-1}$. $^1$H-NMR ($CDCl_3$) δ: 1.60 and 1.63 (each 3H, each s, 2xMe), 1.94 (3H, s, OCOMe), 2.46 (2H, br d, J=7.8 Hz, CHC$H_2$), 3.85 (1H, t, J=7.8 Hz, C*H*$CH_2$), 3.86 and 4.13 (each 1H, each d, J=12.2 Hz, C$H_2$OAc), 7.05-7.08 (1H, m, ArH), 7.20-7.41 (5H, m, ArH), 7.68-7.71 (1H, m, ArH), 7.80-7.84 (1H, m, ArH). $^{13}$C-NMR ($CDCl_3$) δ: 16.4 (q), 19.3 (q), 20.9 (q), 39.3 (t), 43.1 (d), 64.7 (t), 125.3 (d), 126.1 (d), 126.4 (d), 126.9 (d), 127.0 (s), 127.6 (d), 127.7 (d), 128.0 (d), 129.2 (d), 131.0 (s), 131.2 (s), 132.9 (s), 133.6 (s), 136.4 (s), 170.8 (s). MS *m/z*: 338 ($M^+$), 197 (base). Anal. Calcd for $C_{21}H_{22}O_2S$: C, 74.52; H, 6.55. Found: C, 74.28; H, 6.66.

**(h) With Potassium Carbonate.** A mixture of the cycloadduct **2a** (183mg, 0.5 mmol) and potassium carbonate (138 mg, 1 mmol) in acetone (5 ml) was stirred for 3 h at room temperature. After addition of water, the mixture was extracted with dichloromethane. Work-up as usual afforded 80 mg (57.6%) of **5**.

**Reaction of Cycloadduct 2a with LDA in the Presence of Methyl Acrylate.**

The cycloadduct **2a** (183 mg, 0.5 mmol) was added with stirring at -78 °C to a LDA solution prepared from diisopropylamine (103 mg, 1.02 mmol), *n*-butyllithium (0.3 ml of 1.68 *N* hexane solution) in dry THF (5 ml) as in (a). After the mixture was stirred for 10 min, a solution of methyl acrylate (60 mg, 0.7 mmol) in THF (1 ml) was added to the mixture, which was then stirred for 1 h at -78 °C before being allowed to warm up to 0 °C. The oily residue obtained after work-up as in (a) was subjected to PLC on silica gel with hexane-ethyl acetate (15:1) to give 67 mg (36.8%) of 10-[3-(2-methoxycarbonylcyclopropyl)-2-methylbut-2-enyl]-9,14-dihydro-9-thiaphenanthrene **7** and 34 mg (24.5%) of **5**. Compound **7**: colorless plates (hexane-dichloromethane), mp 107-109.5 °C. IR (KBr): 1725 (ester) cm$^{-1}$. $^1$H-NMR ($CDCl_3$) δ: 0.92 (1H, ddd, J=8.3, 6.8, 4.4 Hz, cyclopropane H), 1.06 (1H, dt, J=4.9, 4.4 Hz, cyclopropane H), 1.29 (3H, s, Me), 1.52 (1H, ddd, J=8.3, 4.9, 4.4 Hz, cyclopropane H), 1.60 (3H, s, Me), 1.76 (1H, ddd, J=6.8, 4.9, 4.4 Hz, cyclopropane H), 2.46 and 2.61 (each 1H, each dd, J=13.7, 7.8 Hz, CHC$H_2$), 3.64 (3H, s, OMe), 3.92 (1H,

t, J=7.8 Hz, C*H*$CH_2$), 7.07-7.10 (1H, m, ArH), 7.21-7.35 (4H, m, ArH), 7.40-7.43 (1H, m, ArH), 7.67-7.70 (1H, m, ArH), 7.81-7.85 (1H, m, ArH). $^{13}$C-NMR ($CDCl_3$) δ: 13.9 (q), 14.2 (t), 19.3 (d), 20.1 (q), 24.9 (d), 39.4 (t), 43.2 (d), 51.6 (q), 125.4 (d), 126.0 (d), 126.3 (d), 126.9 (d), 127.6 (d), 127.8 (s), 127.9 (d), 128.7 (s), 129.2 (d), 131.3 (s), 133.0 (s), 133.8 (s), 136.9 (s), 174.3 (s). MS *m/z*: 364 ($M^+$), 197 (base). Anal. Calcd for $C_{23}H_{24}O_2S$: C, 75.55; H, 6.72. Found: C, 75.79; H, 6.64.

**Reduction of Cycloadduct 2a with Sodium Borohydride.** Sodium borohydride (19 mg, 0.5 mmol) was added in one portion to a stirred suspension of the cycloadduct **2a** (183 mg, 0.5 mmol) in ethanol (5 ml) and the mixture was stirred for 20 min. The reaction mixture was poured into water, and extracted with dichloromethane. The extract was washed with water, dried over $MgSO_4$, and evaporated off. The residue was subjected to PLC on silica gel with hexane-ethyl acetate (4:1) to afford 131 mg (93.6%) of 10-(2,3-dimethylbut-2-enyl)-9,10-dihydro-9-thiaphenanthrene **8** as a colorless oil. $^1$H-NMR ($CDCl_3$) δ: 1.21 (3H, s, Me), 1.55 (6H, s, 2xMe), 2.38 (2H, d, J=7.8 Hz, CHC*H*$_2$), 3.85 (1H, t, J=7.8 Hz, C*H*$CH_2$), 7.03-7.06 (1H, m, ArH), 7.16-7.33 (4H, m, ArH), 7.38-7.42 (1H, m, ArH), 7.65-7.68 (1H, m, ArH), 7.76-7.80 (1H, m, ArH). $^{13}$C-NMR ($CDCl_3$) δ: 18.8 (q), 20.0 (q), 20.6 (q), 39.8 (t), 43.1 (d), 123.8 (s), 125.1 (d), 125.9 (d), 126.1 (d), 127.0 (d), 127.5 (d), 127.8 (d), 128.0 (s), 129.3 (d), 131.7 (s), 133.1 (s), 133.9 (s), 137.1 (s). MS *m/z*: 280 ($M^+$), 197 (base). Anal. Calcd for $C_{19}H_{20}S$: C, 81.38; H, 7.19. Found: C, 81.20; H, 7.22.

**Reduction of Cycloadduct 2a with Samarium Diiodide ($SmI_2$).** A mixture of Sm (1.504 g, 10 mmol) and 1,2-diiodoethane (1.409 g, 5 mmol) in dry THF (50 ml) was refluxed with stirring for 30 min under nitrogen, and was further continued to stirr overnight. This $SmI_2$ solution (10 ml, 1 mmol) was dropwise added to a stirred suspension of the cycloadduct **2a** (183 mg, 0.5 mmol) in dry THF (5 ml) at room temperature under nitrogen, and the mixture was stirred for 15 min. To the reaction mixture was added dil. hydrochloric acid (1 *N*, 10 ml) and the whole was extracted with diethyl ether. The ether layer was washed successively with sat. aq. $NaHCO_3$, water, 10% $Na_2S_2O_3$ and water, dried ($MgSO_4$) and evaporated. The residue was purified by PLC on silica gel with hexane-ethyl acetate (15:1) to give the compound **8** (87 mg, 62%).

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