2e, 7515-17-5; 2f, 71797-96-1; 2g, 42122-44-1; 2h, 109034-23-3; 2i, 109034-24-4; 2j, 6824-26-6; 2k, 109034-25-5; 2l, 109034-26-6; 2m, 2216-94-6; 2n, 62497-24-9; 3a, 637-44-5; 3b, 4843-44-1; 4a, 7299-58-3; 4b, 109034-48-2; 4c, 109034-49-3; 4d, 21985-04-6; 5a, 109034-27-7; 5b, 80151-28-6; 5c, 37614-59-8; 5d, 1194-13-4; 6a, 109034-28-8; 6b, 74929-23-0; 6c, 90696-21-2; 7a, 15814-32-1; 7b, 109034-29-9; 7c, 109034-30-2; 7d, 109034-31-3; 7e, 109034-32-4; 7f, 62679-57-6; 7g, 109034-33-5; 7h, 109034-50-6; 8a, 15814-30-9; 8b, 109034-34-6; 8c, 109034-35-7; 8d, 109034-36-8; 8e, 109034-37-9; 8f, 54668-28-9; 8g, 109034-38-0; 8h, 109034-39-1; 9, 109034-40-4; 10a, 109034-41-5; 10b, 109034-42-6; 10c, 109034-43-7; 10d, 109034-44-8; 10e, 109034-45-9; 10f, 109034-46-0; 10g, 109034-47-1; 2,4,6-$Me_3C_6H_3$, 108-67-8; PhH, 71-43-2; 2,6-$Me_2C_6H_4$, 108-38-3; 4-$MeOC_6H_5$, 100-66-3; 2,5-$(MeO)_2C_6H_4$, 150-78-7; 4-F-$C_6H_5$, 462-06-6; 2,5-$F_2C_6H_4$, 540-36-3; 2-$MeOC_{10}H_7$, 93-04-9; 2,4-$(MeO)_2C_6H_4$, 151-10-0; 4-*t*-$BuC_6H_5$, 98-06-6; 3,4-$(MeO)_2C_6H_4$, 91-16-7; PhC≡CHO, 2579-22-8; $Me_3SiC{\equiv}CLi$, 54655-07-1; *t*-$BuMe_2SiO(CH_2)_3C{\equiv}CLi$, 61600-82-6; PhC≡CH, 536-74-3; $Me_3SiC{\equiv}CH$, 1066-54-2; $Me_3SiC{\equiv}CPH$, 2170-06-1; thiophene, 110-02-1; tetrachlorocyclopropane, 6262-42-6.

# Synthesis of New Cyclic Sulfur Ylides 9-Alkyl-10-cyano-9-thiaphenanthrenes and Their Novel Addition Reactions with Acetylenic Electrophiles

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*Received January 26, 1987*

Novel cyclic sulfur ylides 9-alkyl-10-cyano-9-thiaphenanthrenes **5** were synthesized in good yield by proton abstraction from the corresponding 10*H*-9-thiaphenanthrenium salts **4** with triethylamine in ethanol. 10-Cyano-9-methyl-9-thiaphenanthrene (**5a**) was treated with dimethyl or diethyl acetylenedicarboxylate in benzene to afford three 1:1 adducts, novel spiro compounds **7a,b**, dibenzothiocin derivatives **8a,b**, and benzothiocinium ylide derivatives **9a,b**. On the contrary, treatment of 9-ethylthiaphenanthrene derivative **5b** with the above acetylenic compounds afforded dibenzothiepin derivatives **16a,b** as major products together with dibenzothiocinium ylide derivatives **17a,b**. 10-Cyano-10-methyl-10*H*-9-thiaphenanthren-9-ium 9-methanide (D), generated from 10-cyano-9,10-dimethyl-10*H*-9-thiaphenanthrenium salt **10** by deprotonation with sodium hydride, rearranged to afford the two isomeric spiro compounds **11** and **12**. On heating at 200 °C, the spiro compounds **7a,b** underwent 1,5-sigmatropic rearrangement to afford dibenzothionin derivatives **14a,b** in high yield. On the other hand, pyrolysis of the spiro compounds **11** and **12** under similar conditions caused 1,3-rearrangement to give dibenzothiepin derivative **15**. Reaction of **5a** with methyl propiolate afforded 1:2 adduct **18**. Mechanisms for the above reactions are also discussed.

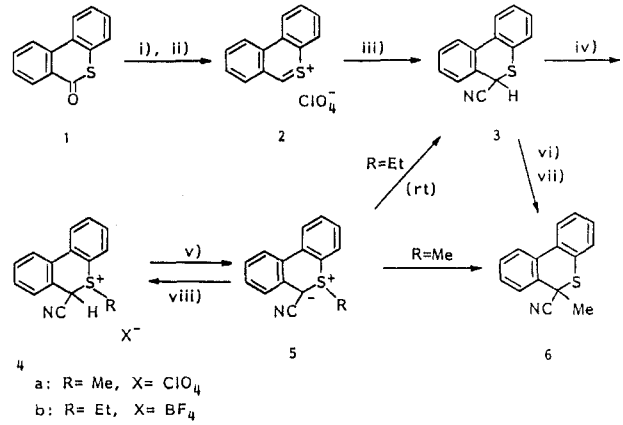
In conjunction with our interest in the chemistry of cyclic sulfur ylides, we have already reported the synthesis and reactions of 1- or 2-thianaphthalene derivatives[1] and 10-thiaanthracene derivatives,[2] in which ylide bond forms part of a cyclic conjugated ring system containing six $\pi$-electrons. In the reactions with various kinds of electrophiles, especially, unusual addition reactions occurred to provide a number of novel sulfur-containing heterocyclic compounds. This prompted us to investigate the synthesis and reactions with electrophiles of other new types of stable cyclic sulfur ylides.

We report here the synthesis and the novel addition reactions with acetylenic electrophiles of new cyclic sulfur ylides, 9-alkyl-10-cyano-9-thiaphenanthrenes **5**, which are considered to have the skeletons of both 1- and 2-thianaphthalenes. Addition products were quite unique compared with those observed from 1- or 2-thianaphthalenes.

## Results and Discussion

**Synthesis and Thermal Stability of 9-Alkyl-10-cyano-9-thiaphenanthrenes.** The four-step synthesis of the title compounds was performed as shown in Scheme I.

**Scheme I**[a]




[a] Reagents: (i) $LiAlH_4$, ether; (ii) 70% $HClO_4$; (iii) NaCN, ClC-$H_2CH_2Cl$; (iv) RI, AgX, $CH_2Cl_2$; (v) $Et_3N$, EtOH; (vi) NaH, THF; (vii) MeI; (viii) HX.

I. 9-Thiaphenanthrenylium perchlorate (**2**) was already synthesized by Lüttringhaus et al. in 1961.[3] However, their method requires five steps, and the yield in the Pschorr cyclization step is poor. Therefore, we investigated the improvement of the steps number and the yield. 3,4-Benzothiocoumarin (**1**) was easily synthesized by

(1) (a) Hori, M.; Kataoka, T.; Shimizu, H.; Narita, K.; Ohno, S.; Aoki, H. *Chem. Lett.* **1974**, 1101. (b) Hori, M.; Kataoka, T.; Shimizu, H.; Aoki, H.; *Heterocycles* **1979**, *5*, 413. (c) Hori, M.; Kataoka, T.; Shimizu, H.; Ohno, S.; Narita, K.; Koyama, H. *J. Chem. Soc., Chem. Commun.* **1981**, 364.

(2) Hori, M.; Kataoka, T.; Shimizu, H.; Ohno, S. *J. Org. Chem.* **1980**, *45*, 2468.

(3) Lüttringhaus, A.; Kolb, A. *Z. Naturforsch., B. Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1961**, *16B*, 762.

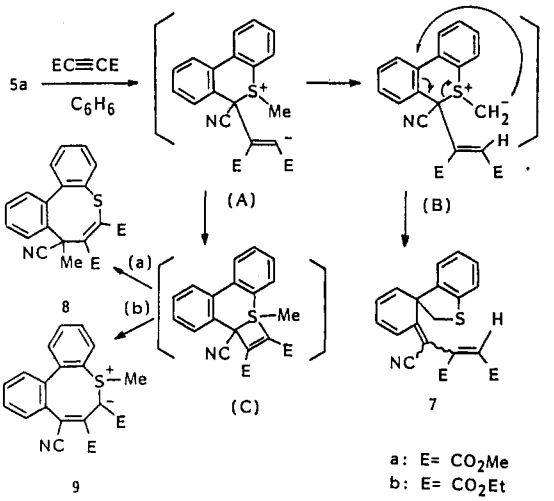
0022-3263/87/1952-3668$01.50/0 

treatment of dibenzothiophene with lithium, followed by carboxylation with carbon dioxide, as described by Gilman et al.[4] Reduction of **1** with $LiAlH_4$ in THF gave 10-hydroxy-10*H*-9-thiaphenanthrene, which was dissolved in dry ether and treated with 70% perchloric acid to yield **2** in 60% yield. Treatment of the perchlorate **2** with sodium cyanide in 1,2-dichloroethane and a small amount of water afforded 10-cyano-10*H*-9-thiaphenanthrene (**3**) in 86% yield. The cyano compound **3** was alkylated with alkyl iodides in the presence of silver salts to give the corresponding 10-cyano-9-methyl- (**4a**) or 10-cyano-9-ethyl-10*H*-9-thiaphenanthrenium salt (**4b**) in yield of 92% or 86%, respectively. These 9-thiaphenanthrenium salts were obtained as an inseparable mixture of cis and trans isomers. The cis–trans ratio was determined by $^1H$ NMR spectral data as 1:3 for **4a** and 1:5 for **4b**. Deprotonation of **4a** or **4b** with triethylamine in ethanol at 0 °C yielded 10-cyano-9-methyl- (**5a**) or 10-cyano-9-ethyl-9-thiaphenanthrene (**5b**) as yellow prisms in 94% or 100% yield, respectively. The absorption band of the cyano group in the IR spectra of **5a** and **5b** is stronger and shifts to lower wavenumber (2170 $cm^{-1}$ for **5a**, 2160 $cm^{-1}$ for **5a**) than that of ordinary cyano group, which indicates delocalization of the carbanion electron of **5a** and **5b** to the cyano group. The thiaphenanthrene **5** was treated with perchloric acid or tetrafluoroboric acid to give the corresponding thiaphenanthrenium salt **4a** or **4b**, respectively. The above spectral and chemical observations reveal the ylidic property of the thiaphenanthrene.

We next examined the thermal stability of the thiaphenanthrenes **5a** and **5b** and found that **5a** is much more stable than **5b**. The 9-methyl derivative **5a** is stable in solution at room temperature at least for 1 month, while the 9-ethyl derivative gradually decomposes at room temperature to give **3** by $\beta$-elimination. However, on heating a benzene solution of **5a** for 8 h, 1,2-rearrangement occurred to give 10-cyano-10-methyl-10*H*-9-thiaphenanthrene (**6**) in 47% yield. The 1,2-rearrangement of **5a** was also performed on irradiation with high-pressure Hg lamp to give **6** in quantitative yield. The structure of **6** was easily determined by $^1H$ NMR spectrum and further confirmed by an independent synthesis of the sample. Treatment of **3** with NaH in THF under nitrogen, followed by addition of methyl iodide yielded **6** in high yield.

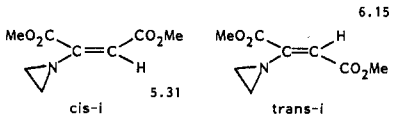
**Reaction of 10-Cyano-9-methyl-9-thiaphenanthrene (5a) with Dialkyl Acetylenedicarboxylate.** 10-Cyano-9-methyl-9-thiaphenanthrene (**5a**) reacted with dimethyl acetylenedicarboxylate (DMAD) in benzene at room temperature to give three 1:1 adducts, spiro compound **7a**, mp 140–141 °C, ring-expanded eight-membered compound **8a**, as an oil, and eight-membered ylidic compound **9a**, mp 154–157 °C dec, in yields of 31%, 17%, and 11%, respectively (Scheme II). The structures of these 1:1-adducts were established mainly on the basis of spectral evidence. Elemental analyses and mass spectral data (*m/z*, 379 ($M^+$)) indicate a molecular formula of $C_{21}H_{17}NO_4S$ corresponding to a 1:1-adduct of **5a** and DMAD for these products. The IR spectrum of **7a** showed characteristic absorption bands at 2197 $cm^{-1}$ for the cyano group and at 1735 $cm^{-1}$ for the two ester groups. The $^1H$ NMR spectrum (400 MHz) of **7a** showed clearly characteristic signals at $\delta$ 6.01 (dd, $J$ = 9.3, 5.8 Hz), 6.24 (d, $J$ = 9.3 Hz), 6.53 (dd, $J$ = 10.7, 5.8 Hz), and 7.00 (d, $J$ = 10.7 Hz) attributable to the four olefinic protons of the cyclohexadiene ring with the two methylene proton signals at $\delta$ 3.34 and 3.81 (each d, $J$ = 12.2 Hz). Further, owing to the low $\delta$ value (5.20) of the vinyl proton signal, the ester groups are assumed to be cis, for the corresponding signals for protons of the maleate and fumarate isomers of i[5] appear at $\delta$ 5.31 and 6.15, respectively. The $^{13}C$ NMR spectrum of **7a** showed the quaternary carbon signal ($\delta$ 57.23) assignable to the spiro carbon atom. The geometry of exocyclic double bond cannot be specified. The structure of compound **8a** was established by the $^{13}C$ NMR spectral data showing the quaternary carbon signal at $\delta$ 51.1, which becomes a multiplet by the gated decoupling technique in NOE mode, indicating that carbon has methyl group. The ylide structure of the compound **9a**[7] was especially supported by the characteristic IR absorption bands of the

**Scheme II**



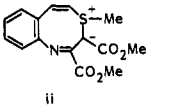

(4) (a) Gilman, H.; Esmay, D. L. *J. Am. Chem. Soc.* **1953**, *75*, 2947. (b) Gilman, H.; Dietrich, J. J. *J. Org. Chem.* **1957**, *22*, 851.

(5) Dolfini, J. E. *J. Org. Chem.* **1965**, *30*, 1298. The $\delta$ values here were used for the determination of several maleate and fumarate structures.[2,6]

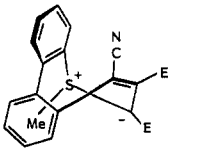



(6) (a) Acheson, R. M.; Wright, N. D.; Tasker, P. A. *J. Chem. Soc., Perkin Trans. 1* **1972**, 2918. (b) Wade, J. J. *J. Org. Chem.* **1979**, *44*, 1816.

(7) The low $\delta$ values for $S^+$–Me groups of ylide structure ($\delta$ 1.89 for **9a** and $\delta$ 1.87 for **9b**) in their $^1H$ NMR spectra are not surprising, because the $S^+$–Me group of the analogous eight-membered ylide ii[8] resonates at $\delta$ 1.97, whose structure was determined by the comparison with the analogous compound confirmed by X-ray structure determination by Grant et al.[9] It is apparent from use of Dreiding models that the orientation of the $S^+$–Me group of the eight-membered ylides is just under the benzene ring as shown below, which is very similar to the conformation of analogous compound confirmed by X-ray structure determination.[9] Therefore, these low $\delta$ values of $S^+$–Me groups might be explained in terms of significant anisotropic effects of benzene ring to the $S^+$–Me group.



ii

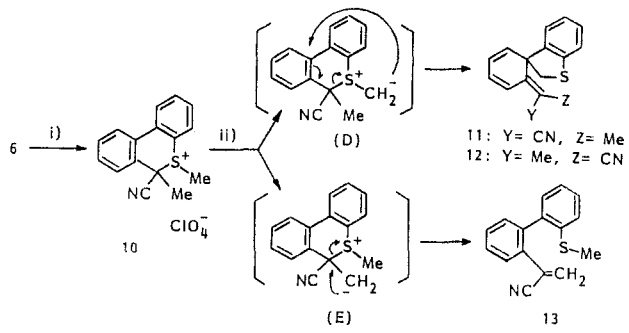


Conformation of 9

(8) Shimizu, H.; Matsuo, K.; Kataoka, T.; Hori, M. *Chem. Pharm. Bull.* **1984**, *32*, 4360.

(9) Grant, R. D.; Rees, C. W.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1982**, 1060.

**Scheme III**[a]



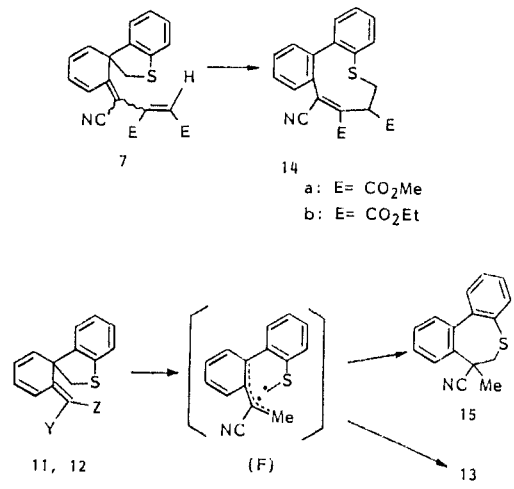

[a] Reagents: (i) MeI, $AgBF_4$, $CH_2Cl_2$; (ii) NaH, THF.

cyano and ester carbonyl groups: a stronger and shift to a lower wavenumber (2190 $cm^{-1}$ for CN, 1640 $cm^{-1}$ for one of $CO_2Et$) than those of ordinary cyano or ester carbonyl groups, indicating delocalization of the ylide carbanion electrons of **9a** to the conjugated cyano and carbonyl groups. A similar reaction of **5a** with diethyl acetylenedicarboxylate (DEAD) gave the corresponding three 1:1 adducts, **7b**, **8b**, and **9b**[7] in 23.2%, 22.5%, and 15% yields, respectively.

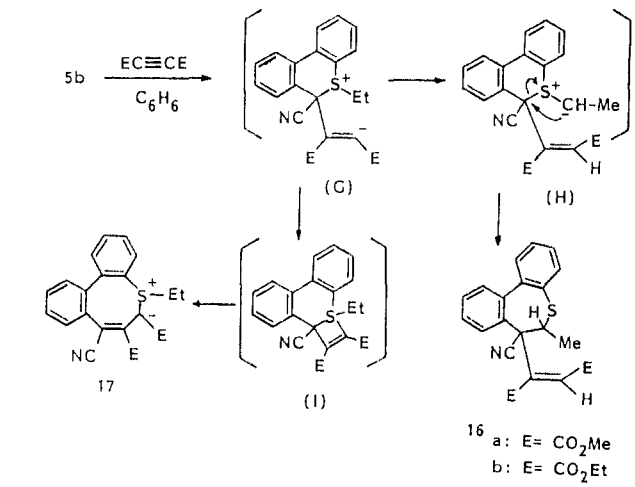
A plausible mechanism for the formation of **7**, **8**, and **9** is also presented in Scheme II. Nucleophilic attack of **5a** on the electron-deficient acetylenes (DMAD, DEAD) forms the switterionic intermediate A, which leads to the sulfonium ylide intermediate B by an intramolecular proton abstraction from the proximate *S*-methyl group. Attack of the carbanion of the ylide intermediate B on the aromatic carbon (C-4a) accompanied by cleavage of the C-10–S bond gives **7** (Sommelet–Hauser-type rearrangement). On the other hand, the intermediate A gives rise to the $\sigma$-sulfurane intermediate C, which collapses to **8** by bonding between C-10 and methyl group (path a) or to **9** by heterolytic cleavage of C-10–S bond (path b). To our knowledge, the formation of spiro compounds analogues to **7** has not previously been observed in the reactions of cyclic sulfur ylides with electrophiles.

In order to investigate the generality of the formation of spiro compounds, we carried out the generation of exocyclic methylide corresponding to the intermediate B as shown in Scheme III. As a model compound, we selected the methylide D which is considered to be easily generated from 10-cyano-9,10-dimethyl-10*H*-9-thiaphenanthrenium salt (**10**) by treatment with strong base, because two hydrogen atoms of position 10 are blocked with two substituents (CN and Me). Compound **10** was readily prepared from the reaction of **6** with methyl iodide in the presence of silver tetrafluoroborate in refluxing dichloromethane. The salt **10** was obtained as an inseparable mixture of trans and cis isomers (ratio of 2:1). When a suspension of **10** in THF was treated with NaH, a yellow color appeared but immediately faded to result in the formation of two isomeric spiro compounds **11** and **12** in 29% and 16% yields, respectively, together with a 6% yield of $\beta$-elimination product **13** as shown in Scheme III. Assignments for the geometries of exo-methylene parts of the compounds **11** and **12** are based on the chemical shifts of the methyl groups in their $^1H$ NMR spectra, the methyl group of **11** being more shielded ($\delta$ 1.71) than that of **12** ($\delta$ 2.10) by the proximate benzene ring, because the studies of Dreiding model of **11** show the methyl group oriented just over the benzene ring. Thus, it is established that the exo-ylides such as B and D undergo easily Sommelet–Hauser-type rearrangement to afford spiro compounds and subsequently the mechanism for the formation of spiro compounds discussed above was also confirmed.

**Scheme IV**



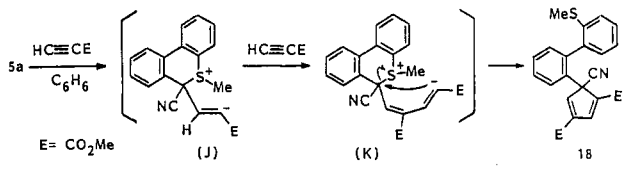

**Scheme V**




We next examined the thermal reaction of the spiro compounds **7a**,**b**, **11**, and **12** in order to investigate their ring-expansion reactions into new sulfur-containing heterocycles. On heating a benzene solution in a sealed tube up to 200 °C for 4 h, **7a** underwent a thermal 1,5-rearrangement to afford the ring-expanded product **14a** in 95% yield. A similar 1,5-rearrangement of the spiro compound **7b** under the same conditions yielded a 90% yield of the corresponding ring-expanded product **14b** (Scheme IV). On the other hand, when a solution of **11** or **12** in benzene was heated in a sealed tube at 200 °C for 7 h, the 1,3-rearrangement was completed to afford dibenzothiepin derivative **15** in high yield along with the formation of ring-opened product **13**. Mechanistically, the above 1,5-rearrangement is approved to be a sigmatropic rearrangement. However, the 1,3-rearrangement observed for the spiro compounds **11** and **12** is forbidden on the basis of orbital-control theory. Therefore, the formation of the dibenzothiepin **15** is probably explained by the mechanism via the biradical intermediate F formed by the homolytic fission between spiro carbon and methylene. The methylene radical of the intermediate F is stabilized by the participation of the adjacent sulfur atom. The intermediate F is strongly supported by the isolation of ring-opened product **13**, which might be derived from the hydrogen radical abstraction from methyl group by methylene radical of the intermediate F.

As described above, the major products from the addition reaction of 9-methylthiaphenanthrene (**5a**) with DMAD or DEAD were novel spiro compounds **7**. The

**Scheme VI**




9-ethyl derivative **5b**, however, resulted in a different reaction course (Scheme V). Treatment of **5b** with DMAD in benzene afforded a 38% yield of a dibenzothiepin derivative **16a** together with eight-membered ylidic product **17a** (12% yield). A spiro compound was not isolated. The $^1$H NMR spectrum of **16a** showed characteristic doublet signal ($J$ = 7 Hz) attributable to the methyl protons at $\delta$ 1.58 and also showed a quartet signal ($J$ = 7 Hz) assignable to the methine proton at $\delta$ 4.09. The $^{13}$C NMR signals supporting the structure of **16a** appear at $\delta$ 52.43 as a doublet (methine carbon) and at $\delta$ 57.21 as a singlet (quaternary carbon). The structure of compound **17a** was determined by the spectral data on the analogy with compound **9a**. Similar results were obtained from the reaction with DEAD to give **16b** and **17b** in 19% and 12% yields, respectively. The fumarate structure of **16a** and **16b** was determined by $^1$H NMR chemical shifts ($\delta$ 6.06 for **16a**, $\delta$ 6.10 for **16b**)[5,6] of the olefinic proton, although the reason why the fumarate compounds were yielded preferentially in these cases is not clear at present. All attempts to convert the dibenzothiepin derivative **16** into nine-membered compound corresponding to **14** through 1,3-rearrangement were unsuccessful.

The formation of **16a,b** and **17a,b** can be rationalized by the mechanism depicted in Scheme V. The intermediate H undergoes Stevens-type 1,2-rearrangement to result in the formation of the ring-expansion product **16**, probably because of the steric effect of more bulky S-substituent (Et) preventing the ylidic carbanion from attacking the aromatic ring. This Stevens-type ring-expansion reaction was observed in the thermal reaction of analogous exocyclic ylides by Benati group.[10] The product **17** is formed via the $\sigma$-sulfurane intermediate I.

Finally, we carried out the reaction of **5a** with methyl propiolate (MP). Treatment of **5a** with MP in benzene did not yield any 1:1 adduct but ring-opened product **18** as a 1:2-adduct of the ylide and MP in 19% yield, as shown in Scheme VI, which also shows a plausible mechanism for the formation of **18**. The structure of **18** was determined by spectral data. Microanalytical and mass spectral data ($M^+$, $m/z$ 405) indicate a molecular formula $C_{23}H_{19}NO_4S$ corresponding to a 1:2 adduct of **5a** and MP. It showed $^1$H NMR peaks at $\delta$ 2.52 (SMe), 3.68 (OMe), 3.85 (OMe), 6.37 (olefinic H), 7.91 (olefinic H), and 7.13–7.90 (Ar H) and $^{13}$C NMR peaks at $\delta$ 49.64 attributable to a quaternary carbon atom of cyclopentadiene ring. IR absorptions appear at 2240 (CN) and 1700 cm$^{-1}$ (ester).

## Experimental Section

Melting points were determined by using a Yanagimoto micromelting apparatus and are uncorrected. Elemental analyses were performed at the Microanalytical Laboratory of Gifu Pharmaceutical University. $^1$H nuclear magnetic resonance ($^1$H NMR) spectra were run on a Hitachi R-20B, JEOL FX-100, and GX-270 and Bruker WH-400 spectrometers. $^{13}$C nuclear magnetic resonance ($^{13}$C NMR) spectra were determined with a JEOL FX-100 or GX-270 spectrometer. Chemical shifts are expressed in parts per million (ppm) with respect to tetramethylsilane as an internal standard. Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet. Infrared (IR) spectra were determined on a JASCO IR A-1 infrared spectrometer and are expressed in reciprocal centimeters. Mass spectra (MS) were obtained with a JEOL JMS-D300 spectrometer with a direct-insertion probe at an ionization voltage of 70 eV. Exact mass determination was conducted on the JMA 2000 on-line system. Analytical and preparative thin-layer chromatography (preparative TLC) were performed by using E. M. Merck silica gel 60PF-254.

**9-Thiaphenanthrenylium Perchlorate (2).** Lithium aluminum hydride (178 mg) was slowly added to an ice-cooled solution of 3,4-benzothiocoumarin (**1**, 1 g) in dry THF (10 mL), and the mixture was stirred for 2 h at room temperature. After an excess lithium aluminum hydride was decomposed by treatment with a water-saturated ether, the mixture was acidified with a diluted hydrochloric acid and extracted with ether. The ether layer was washed with water, dried over anhydrous $MgSO_4$, and concentrated to dryness to leave 9-hydroxy-10*H*-9-thiaphenanthrene as pale yellow crystals in quantitative yield, which were used in the successive reaction without further purification: IR (KBr) 3450 cm$^{-1}$ (OH); $^1$H NMR ($CDCl_3$) $\delta$ 2.05 (1 H, br s, OH), 4.95 (1 H, s, 10-H), 7.08–7.30 (5 H, m, Ar H), 7.80–8.21 (3 H, m, Ar H). The hydroxy compound was dissolved in dry ether (50 mL) and cooled in an ice-bath, and 70% perchloric acid (5 mL) was added with stirring. The precipitated yellow crystals were collected and washed thoroughly with acetic acid and dry ether to give 0.852 g (61%) of **2**, which was absolutely identical with the sample prepared by the method of Lüttringhaus.[3]

**10-Cyano-10*H*-9-thiaphenanthrene (3).** Powdered **2** (5.6 g) was added by portions with vigorous stirring to a solution of sodium cyanide (1.48 g), water (5 mL), and 1,2-dichloroethane (100 mL), and the mixture was further stirred at room temperature for 2 h. The organic layer was separated, washed with water, and dried over anhydrous $MgSO_4$. The solvent was evaporated off under reduced pressure to give 3.6 g (85.7%) of **3**, which was recrystallized from hexane–$CH_2Cl_2$ to form colorless prisms: mp 120 °C; IR (KBr) 2200 cm$^{-1}$ (CN); $^1$H NMR ($CDCl_3$) $\delta$ 4.78 (1 H, s, 10-H), 7.24–8.00 (8 H, m, Ar H). Anal. Calcd for $C_{14}H_9NS$: C, 75.31; H, 4.06; N, 6.27. Found: C, 75.26; H, 4.06; N, 6.09.

**10-Cyano-9-methyl-10*H*-9-thiaphenanthrenium Perchlorate (4a).** To an ice-cooled solution of **3** (2.5 g) and methyl iodide (16 g) in 1,2-dichloroethane (60 mL) was added silver perchlorate (2.4 g) portionwise with stirring. After 7 h, the precipitate was filtered and washed thoroughly with hot acetone. The filtrate and the washings were combined and diluted with ether to precipitate 3.5 g (92%) of **4a**. Recrystallization from acetone–ether afforded colorless prisms, which were mixtures of inseparable cis and trans stereoisomers: mp 153 °C dec; IR (KBr) 1100 cm$^{-1}$ ($ClO_4^-$); $^1$H NMR ($CF_3CO_2H$) $\delta$ 3.05 (s, Me) and 6.14 (s, 10-H) [attributable to one of the isomers], 3.12 (s, Me) and 6.44 (s, 10-H) [assignable to another isomer]. Anal. Calcd for $C_{15}H_{12}ClO_4S \cdot {}^1/_2CH_3COCH_3$: C, 54.03; H, 4.12; N, 3.82. Found: C, 53.95; H, 4.05; N, 3.67.

**10-Cyano-9-ethyl-10*H*-9-thiaphenanthrenium Tetrafluoroborate (4b).** A mixture of **3** (1 g), ethyl iodide (7 g), and silver tetrafluoroborate (973 mg) in $CH_2Cl_2$ (20 mL) was stirred under reflux for 12 h. The reaction mixture was filtered off, and the filtrate was diluted with ether. The precipitates were collected and recrystallized from $CH_2Cl_2$–ether to give 1.3 g (85.5%) of **4b** as colorless prisms (inseparable mixture of cis and trans stereoisomers): mp 139–141 °C; IR (KBr) 2230 (CN), 1030–1120 cm$^{-1}$ ($BF_4^-$); $^1$H NMR ($CF_3CO_2H$) $\delta$ 1.45 (t, $J$ = 7.5 Hz, $CH_2CH_3$), 1.54 (t, $J$ = 7.5 Hz, $CH_2CH_3$), 3.00–3.75 (4 H, m, $CH_2CH_3$), 6.18 (s, 10-H), 6.50 (s, 10-H), 7.58–8.43 (m, Ar H). Anal. Calcd for $C_{16}H_{14}BF_4NS$: C, 56.66; H, 4.16; N, 4.13. Found: C, 56.53; H, 4.24; N, 4.09.

**10-Cyano-9-methyl-9-thiaphenanthrene (5a).** A solution of triethylamine (2.2 g) in EtOH (5 mL) was added to a stirred suspension of **4a** (3.5 g) in EtOH (60 mL) at 0 °C, and the mixture was further stirred at the same temperature for 5 h. The reaction mixture was poured into water and extracted with $CH_2Cl_2$. The extract was washed three times with water, dried over anhydrous $MgSO_4$, and evaporated off to dryness under reduced pressure. The residual oil was triturated with ether to give 2.25 g (93.7%) of **5a** as yellow prisms after recrystallization from $CH_2Cl_2$–ether: mp 97 °C dec; IR (KBr) 2170 cm$^{-1}$ (CN); $^1$H NMR ($CDCl_3$) $\delta$ 2.20 (3 H, s, Me), 6.96–8.15 (8 H, m, Ar H); mass spectrum, $m/z$ 237

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($M^+$), 222 (base), 190. Anal. Calcd for $C_{15}H_{11}NS$: C, 75.92; H, 4.67; N, 5.90. Found: C, 75.54; H, 4.74; N, 5.73.

**10-Cyano-9-ethyl-9-thiaphenanthrene (5b).** Triethylamine (417 mg) was added to a stirred suspension of **4b** (700 mg) in EtOH (40 mL) at 0 °C. The mixture was stirred at 0 °C for 4 h. Workup as described for **5a** afforded 518 mg (quantitative) of **5b** as yellow prisms after recrystallization from $CH_2Cl_2$–hexane: mp 102–105 °C; IR (neat) 2160 $cm^{-1}$ (CN); $^1H$ NMR ($CDCl_3$) $\delta$ 1.02 (3 H, t, $J$ = 7 Hz, $CH_2CH_3$), 2.07–2.96 (2 H, m, $CH_2CH_3$), 6.90–8.07 (8 H, m, Ar H); mass spectrum, $m/z$ 251 ($M^+$). Anal. Calcd for $C_{16}H_{13}NS$: C, 76.46; H, 5.21; N, 5.57. Found: C, 76.72; H, 5.21; N, 5.57.

**Thermal Rearrangement of 5a.** A solution of **5a** (85 mg) in benzene (30 mL) was refluxed for 8 h. The solvent was evaporated off, and the residue was subjected to preparative TLC on silica gel using hexane–ethyl acetate (3:1) and successive microdistillation to give 40 mg (47.2%) of 10-cyano-10-methyl-10*H*-9-thiaphenanthrene (**6**) as yellow crystals: mp 84–85 °C.

**10-Cyano-10-methyl-10*H*-9-thiaphenanthrene (6).** Sodium hydride (110 mg, 60% dispersion in mineral oil) was added by portions under nitrogen to a stirred solution of **3** (418 mg) in dry THF (25 mL), and the mixture was stirred at room temperature for 30 min. To this red solution was added methyl iodide (268 mg) and stirred at room temperature for 1 h. The reaction mixture was poured into water and extracted with $CH_2Cl_2$. The extract was washed with water, dried over anhydrous $MgSO_4$, and concentrated to dryness. The residual oil was purified by preparative TLC on silica gel using hexane–ethyl acetate (3:1) as the developing solvent to give 432 mg (97.2%) of **6**, which was further purified by distillation to afford colorless crystals: mp 84–85 °C; IR (KBr) 2240 $cm^{-1}$ (CN); $^1H$ NMR ($CDCl_3$) $\delta$ 2.02 (3 H, s, Me), 7.20–7.95 (8 H, m, Ar H). Anal. Calcd for $C_{15}H_{11}NS$: C, 75.92; H, 4.67; N, 5.90. Found: C, 76.13; H, 4.63; N, 5.59.

**Reaction of 5a with Dimethyl Acetylenedicarboxylate.** A mixture of **5a** (400 mg) and dimethyl acetylenedicarboxylate (240 mg) in dry benzene (20 mL) was stirred at room temperature for 20 h. The reaction mixture was concentrated under reduced pressure to leave a red brown oil. The oil was separated by preparative TLC on silica gel using hexane–$CH_2Cl_2$ (1:3) as the developing solvent. The first fraction afforded 200 mg (31.3%) of 6-[1-cyano-2,3-bis(methoxycarbonyl)-2-propenylidene]-2,4-cyclohexadiene-1-spiro-3′-(2,3-dihydrobenzo[*b*]thiophene) (**7a**), which was recrystallized from hexane–$CH_2Cl_2$ to form pale yellow prisms: mp 140–141 °C; IR (KBr) 2197 (CN), 1735 $cm^{-1}$ (ester); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 3.34 (1 H, d, $J$ = 12.2 Hz, $CH_2$), 3.81 (1 H, d, $J$ = 12.2 Hz, $CH_2$), 3.68 (3 H, s, OMe), 3.75 (3 H, s, OMe), 5.20 (1 H, s, olefinic H of maleate), 6.01 (1 H, dd, $J$ = 9.3, 5.8 Hz, olefinic H), 6.24 (1 H, d, $J$ = 9.3 Hz, olefinic H), 6.53 (1 H, dd, $J$ = 10.7, 5.8 Hz, olefinic H), 7.00 (1 H, d, $J$ = 10.7 Hz, olefinic H), 6.87–7.20 (8 H, m, Ar H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 45.42 (t), 52.14 (q), 52.97 (q), 57.23 (s), 107.30 (s), 164.29 (s), 164.44 (s); mass spectrum, $m/z$ 379 ($M^+$). Anal. Calcd for $C_{21}H_{17}NO_4S$: C, 66.48; H, 4.52; N, 3.69. Found: C, 66.44; H, 4.42; N, 3.65. The second fraction gave 109 mg (17%) of 8-cyano-6,7-bis(methoxycarbonyl)-8-methyl-8*H*-dibenzo[*b*,*d*]thiocin (**8a**) as a pale yellow oil: $^1H$ NMR ($CDCl_3$) $\delta$ 2.04 (3 H, s, Me), 3.75 (3 H, s, OMe), 3.90 (3 H, s, OMe), 7.08–8.10 (8 H, m, Ar H); high-resolution mass spectrum, $m/z$ 379.0855 (calcd for $C_{21}H_{17}NO_4S$, 379.0857). The third fraction gave a pale brown crystal, which was not pure and then further subjected to preparative TLC on silica gel using ethyl acetate–$CH_2Cl_2$ (1:1) to afford 73 mg (11.4%) of 8-cyano-6,7-bis(methoxycarbonyl)-5-methyl-6*H*-dibenzo[*b*,*d*]thiocinium 6-anion (**9a**) as yellow columns after recrystallization from hexane–$CH_2Cl_2$: mp 154–157 °C dec; IR (KBr) 2190 (CN), 1730 (ester), 1640 $cm^{-1}$ (ester); $^1H$ NMR ($CDCl_3$) $\delta$ 1.89 (3 H, s, Me), 3.67 (3 H, s, OMe), 3.81 (3 H, s, OMe), 7.26–8.10 (8 H, m, Ar H); mass spectrum, $m/z$ 379 ($M^+$); $^{13}C$ NMR ($CDCl_3$) $\delta$ 33.01 (q), 51.33 (q), 52.79 (q), 95.41 (s), 119.99 (s), 123.84 (s), 165.22 (s). Anal. Calcd for $C_{21}H_{17}NO_4S$: C, 66.48; H, 4.52; N, 3.69. Found: C, 66.23; H, 4.48; N, 3.72.

**Reaction of 5a with Diethyl Acetylenedicarboxylate.** A mixture of **5a** (395 mg) and diethyl acetylenedicarboxylate (283.3 mg) in dry benzene (20 mL) was stirred at room temperature for 2.5 days under nitrogen atmosphere. The solvent was evaporated off, and the residual oil was separated by preparative TLC on silica gel using hexane–ethyl acetate (3:1) as the developing solvent to afford following three products.

6-[1-Cyano-2,3-bis(ethoxycarbonyl)-2-propenylidene]-2,4-cyclohexadiene-1-spiro-3′-(2,3-dihydrobenzo[*b*]thiophene) (**7b**) (159 mg, 23.4%): yellow oil; IR (neat) 2200 (CN), 1730 (ester), 1635 $cm^{-1}$ (C=C); $^1H$ NMR ($CDCl_3$) $\delta$ 1.22 (3 H, t, $J$ = 7 Hz, $CH_2CH_3$), 1.26 (3 H, t, $J$ = 7 Hz, $CH_2CH_3$), 3.55 (2 H, AB q, $J$ = 12.2 Hz, $CH_2$), 4.08 (2 H, q, $J$ = 7 Hz, $CH_2CH_3$), 4.16 (2 H, q, $J$ = 7 Hz, $CH_2CH_3$), 5.06 (1 H, s, olefinic H), 5.78–6.83 (4 H, m, olefinic H), 6.85–7.20 (4 H, m, Ar H); mass spectrum, $m/z$ 407 ($M^+$), 260 (base); high-resolution mass spectrum, $m/z$ 407.1169 (calcd for $C_{23}H_{21}NO_4S$, 407.1171).

8-Cyano-6,7-bis(ethoxycarbonyl)-8-methyl-8*H*-dibenzo[*b*,*d*]-thiocin (**8b**) (153 mg, 22.5%): colorless prisms after recrystallization from hexane–$CH_2Cl_2$; mp 113–115 °C; IR (KBr) 2240 (CN), 1735, 1720 (ester), 1620 $cm^{-1}$ (C=C); $^1H$ NMR ($CDCl_3$) $\delta$ 1.23 (3 H, t, $J$ = 7 Hz, $CH_2CH_3$), 1.38 (3 H, t, $J$ = 7 Hz, $CH_2CH_3$), 2.02 (3 H, s, Me), 4.19 (2 H, q, $J$ = 7 Hz, $CH_2CH_3$), 4.33 (2 H, q, $J$ = 7 Hz, $CH_2CH_3$), 7.32–7.96 (8 H, m, Ar H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 13.86 (q), 15.85 (q), 51.14 (s), 62.23 (t), 62.55 (t), 117.1 (s), 165.03 (s), 166.41 (s); mass spectrum, $m/z$ 407 ($M^+$), 258 (base). Anal. Calcd for $C_{23}H_{21}NO_4S$: C, 67.79; H, 5.19; N, 3.44. Found: C, 67.95; H, 5.23; N, 3.49.

8-Cyano-6,7-bis(ethoxycarbonyl)-5-methyl-6*H*-dibenzo[*b*,*d*]-thiocinium 6-anion (**9b**) (102 mg, 15%): yellow plates after recrystallization from hexane–$CH_2Cl_2$: mp 145–147 °C dec; IR (KBr) 2190 (CN), 1730, 1640 $cm^{-1}$ (ester); $^1H$ NMR ($CDCl_3$) $\delta$ 1.23 (3 H, t, $J$ = 7 Hz, $CH_2CH_3$), 1.34 (3 H, t, $J$ = 7 Hz, $CH_2CH_3$), 1.87 (3 H, s, SMe), 4.17 (2 H, q, $J$ = 7 Hz, $CH_2CH_3$), 4.28 (2 H, q, $J$ = 7 Hz, $CH_2CH_3$), 7.39–7.96 (8 H, m, Ar H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 13.74 (q), 14.51 (q), 32.89 (q), 60.08 (t), 62.04 (t), 95.56 (s), 119.97 (s), 124.06 (s), 167.40 (s); mass spectrum, $m/z$ 407 ($M^+$). Anal. Calcd for $C_{23}H_{21}NO_4S \cdot {}^1/_2CH_2Cl_2$: C, 61.39; H, 4.70; N, 3.11. Found: C, 61.13; H, 4.82; N, 3.05.

**10-Cyano-9,10-dimethyl-10*H*-9-thiaphenanthrenium Perchlorate (10).** Silver perchlorate (418 mg, 90% purity) was added portionwise to a stirred solution of **6** (430 mg) and methyl iodide (2.57 g) in 1,2-dichloroethane (20 mL). The mixture was stirred at room temperature for 12 h. Workup as described for **4a** gave 260 mg (40.8%) of **10** which was recrystallized from acetone–ether to form colorless prisms as an inseparable mixture of cis and trans isomers: mp 191–193 °C dec; IR (KBr) 1110 $cm^{-1}$ ($ClO_4^-$); $^1H$ NMR ($CF_3CO_2H$) $\delta$ 2.20 (s, 10-Me) and 3.18 (s, 9-Me) [attributable to one of the isomers], 2.63 (s, 10-Me) and 2.99 (s, 9 -Me) [assignable to another isomer]. Anal. Calcd for $C_{16}H_{14}ClNO_4S$: C, 54.63; H, 4.01; N, 3.98. Found: C, 54.65; H, 4.02; N, 3.93.

**Treatment of 10 with Sodium Hydride.** Sodium hydride (60%, 45.6 mg) was added under nitrogen to a stirred suspension of **10** (400 mg) in dry THF (10 mL). After being stirred for 5 h at room temperature, the reaction mixture was poured into water and extracted with $CH_2Cl_2$. The extract was washed with water, dried over anhydrous $MgSO_4$, and evaporated off to dryness. The residue was separated by preparative TLC on silica gel using hexane–ethyl acetate (3:1) as the developing solvent to give three products.

6-[(*E*)-1-Cyanoethylidene]-2,4-cyclohexadiene-1-spiro-3′-(2,3-dihydrobenzo[*b*]thiophene) (**11**) (84 mg, 29.4%): colorless leaflets after recrystallization from hexane–benzene; mp 144–145 °C; IR (KBr) 2200 $cm^{-1}$ (CN); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 1.71 (3 H, s, Me), 3.34 (1 H, d, $J$ = 11.7 Hz, $CH_2$), 3.60 (1 H, d, $J$ = 11.7 Hz, $CH_2$), 5.90 (1 H, dd, $J$ = 9.4, 5.8 Hz, olefinic H), 6.11 (1 H, d, $J$ = 9.4 Hz, olefinic H), 6.21 (1 H, dd, $J$ = 9.8, 5.8 Hz, olefinic H), 6.87 (1 H, d, $J$ = 9.8 Hz, olefinic H), 6.87–7.26 (4 H, m, Ar H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 18.8 (q), 46.2 (t), 57.2 (s), 109.7 (s), 117.6 (d), 119.3 (s), 122.5 (d), 125.4 (d), 125.5 (d), 125.7 (d), 127.2 (d), 128.7 (d), 135.7 (d), 140.4 (s), 142.5 (s), 155.4 (s); mass spectrum, $m/z$ 251 ($M^+$), 184 (base). Anal. Calcd for $C_{16}H_{13}NS$: C, 76.46; H, 5.21; N, 5.57. Found: C, 76.56; H, 5.19; N, 5.48.

6-[(*Z*)-1-Cyanoethylidene]-2,4-cyclohexadiene-1-spiro-3′-(2,3-dihydrobenzo[*b*]thiophene) (**12**) (46 mg, 16.1%): colorless prisms after recrystallization from ether; mp 128–130 °C; IR (KBr) 2195 $cm^{-1}$ (CN); $^1H$ NMR (200 MHz, $CDCl_3$) $\delta$ 2.09 (3 H, s, Me), 3.37 (1 H, d, $J$ = 11.4 Hz, $CH_2$), 3.90 (1 H, d, $J$ = 11.4 Hz, $CH_2$), 6.97 (1 H, ddd, $J$ = 10.0, 6.2, 1.2 Hz, olefinic H), 6.26 (1 H, dd, $J$ = 10.0, 1.2 Hz, olefinic H), 6.27 (1 H, ddd, $J$ = 10.0, 6.2, 1.2 Hz, olefinic H), 6.58 (1 H, dd, $J$ = 10.0, 1.2 Hz, olefinic H), 6.83–7.25 (4 H, m, Ar H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 17.70 (q), 49.29 (t), 57.9 (s),

106.39 (s), 117.7 (d), 119.2 (s), 122.1 (d), 122.4 (d), 125.3 (d), 125.7 (d), 128.1 (d), 128.7 (d), 137.3 (d), 142.0 (s), 143.9 (s), 155.4 (s); mass spectrum, $m/z$ 251 ($M^+$), 184 (base). Anal. Calcd for $C_{16}H_{13}NS$: C, 76.46; H, 5.21; N, 5.57. Found: C, 76.20; H, 5.22; N, 5.51.

2-(1-Cyanovinyl)-2′-(methylthio)biphenyl (**13**) (18 mg, 6.3%): an oil; IR (neat) 2210 $cm^{-1}$ (CN); $^1H$ NMR ($CDCl_3$) $\delta$ 2.35 (3 H, s, Me), 5.73 (1 H, s, $=CH_aH_b$), 5.93 (1 H, s, $=CH_aH_b$), 7.05–7.63 (8 H, m, Ar H); mass spectrum, $m/z$ 251 ($M^+$), 204 (base); high-resolution mass spectrum, $m/z$ 251.0764 (calcd for $C_{16}H_{13}NS$, 251.0766).

**Thermal Rearrangement of the Spiro Compound 7a.** A solution of **7a** (125 mg) in benzene (20 mL) was heated at 195–200 °C in a sealed tube for 4 h. The reaction mixture was concentrated to dryness to give 119 mg (95.2%) of 9-cyano-7,8-bis(methoxycarbonyl)-6,7-dihydrodibenzo[*b*,*d*]thionin (**14a**) as colorless columns after recrystallization from ether: mp 154–155 °C; IR (KBr) 2205 (CN), 1745, 1730 $cm^{-1}$ (ester); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 2.95 (1 H, dd, $J$ = 15.4, 9.2 Hz, 6-H), 3.51 (1 H, dd, $J$ = 15.4, 1.1 Hz, 6-H), 3.67 (1 H, dd, $J$ = 9.2, 1.1 Hz, 7-H), 3.75 (3 H, s, OMe), 3.67 (3 H, s, OMe), 7.26–7.71 (8 H, m, Ar H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 34.9 (t), 51.9 (d), 52.7 (q), 115.8 (s), 122.4 (s), 126.6 (d), 128.6 (d), 129.6 (d), 129.7 (d), 129.8 (d), 129.9 (d), 132.7 (s), 133.2 (s), 137.6 (d), 143.5 (s), 144.8 (s), 146.0 (s), 163.9 (s), 170.3 (s); mass spectrum, $m/z$ 379 ($M^+$), 261 (base). Anal. Calcd for $C_{23}H_{21}NO_4S$: C, 66.48; H, 4.52; N, 3.69. Found: C, 66.65; H, 4.51; N, 3.74.

**Thermal Rearrangement of the Spiro Compound 7b.** A solution of **7b** (70 mg) in benzene (10 mL) was heated under the same reaction conditions and worked up as for **7a**. The residual oil was purified by preparative TLC on silica gel using hexane–ethyl acetate (3:1) to afford 63 mg (90%) of 9-cyano-7,8-bis(ethoxycarbonyl)-6,7-dihydrodibenzo[*b*,*d*]thionin (**14b**) as a colorless oil: IR (neat) 2215 (CN), 1742, 1720 (ester), 1620 $cm^{-1}$ (C=C); $^1H$ NMR ($CDCl_3$) $\delta$ 1.20 (3 H, t $J$ = 7 Hz, $CH_2CH_3$), 1.23 (3 H, t, $J$ = 7 Hz, $CH_2CH_3$), 2.92 (1 H, dd, $J$ = 15, 9 Hz, 6-H), 3.50 (1 H, dd, $J$ = 15, 1.7 Hz, 6-H), 3.61 (1 H, dd, $J$ = 9, 1.7 Hz, 7-H), 4.07 (2 H, q, $J$ = 7 Hz, $CH_2CH_3$), 4.16 (2 H, q, $J$ = 7 Hz, $CH_2CH_3$), 7.18–7.72 (8 H, m, Ar H); mass spectrum, $m/z$ 407 ($M^+$), 260 (base); high-resolution mass spectrum, $m/z$ 407.1202 ($M^+$) (calcd for $C_{23}H_{21}NO_4S$, 407.1201).

**Thermal Rearrangement of the Spiro Compounds 11 and 12.** A solution of **11** (45 mg) in benzene (20 mL) was heated at 195–200 °C in a sealed tube for 8 h. The reaction mixture was filtered and concentrated to dryness to leave an oil, which was separated by preparative TLC on silica gel using hexane–ethyl acetate (3:1) as the developing solvent to give 38 mg (84.4%) of 7-cyano-7-methyl-6,7-dihydrodibenzo[*b*,*d*]thiepin (**15**) as colorless columns after recrystallization from hexane–ether and 5 mg (11.1%) of **13**. **15**: mp 111–112 °C; IR (KBr) 2210 $cm^{-1}$ (CN); $^1H$ NMR ($CDCl_3$) $\delta$ 1.88 (3 H, s, Me), 3.12 (1 H, d, $J$ = 13 Hz, 6-H), 4.03 (1 H, d, $J$ = 13 Hz, 6-H), 7.12–7.89 (8 H, m, Ar H); mass spectrum, $m/z$ 251 ($M^+$). Anal. Calcd for $C_{16}H_{13}NS$: C, 76.46; H, 5.21; N, 5.57. Found: C, 76.68; H, 5.31; N, 5.49.

Pyrolysis of **12** (53 mg) was performed under the same conditions as above and worked up to afford 26 mg (49.1%) of **15** and 10 mg (18.9%) of **13**.

**Reaction of 5b with Dimethyl Acetylenedicarboxylate.** A mixture of **5b** (420 mg) and dimethyl acetylenedicarboxylate (237 mg) in dry benzene (15 mL) was stirred at room temperature for 10 h under nitrogen. The solvent was evaporated off to dryness, and the residual oil was separated by preparative TLC on silica gel using hexane–ethyl acetate (3:1) as the developing solvent to give 250 mg (38%) of 7-cyano-7-[(*E*)-1,2-bis(methoxycarbonyl)-vinyl]-6-methyl-6,7-dihydrodibenzo[*b*,*d*]thiepin (**16a**) as colorless prisms after recrystallization from hexane–$CH_2Cl_2$: mp 113 °C; IR (KBr) 2240 (CN), 1750, 1735 (ester), 1635 $cm^{-1}$ (C=C); $^1H$ NMR ($CDCl_3$) $\delta$ 1.58 (3 H, d, $J$ = 7 Hz, $CHCH_3$), 3.60 (3 H, s, OMe), 3.62 (3 H, s, OMe), 4.09 (1 H, q, $J$ = 7 Hz, $CHCH_3$), 6.06 (1 H, s, olefinic H), 7.18–7.90 (8 H, m, Ar H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 52.16 (q), 52.43 (d), 52.63 (q), 57.21 (s), 117.39 (s), 163.98 (s), 165.20 (s); mass spectrum, $m/z$ 393 ($M^+$), 211 (base). Anal. Calcd for $C_{22}H_{19}NO_4S$: C, 67.16; H, 4.87; N, 3.56. Found: C, 67.07; H, 5.04; N, 3.47. Extraction of the original point with $CH_2Cl_2$ gave 79 mg (12%) of 8-cyano-6,7-bis(ethoxycarbonyl)-5-ethyl-6*H*-dibenzo[*b*,*d*]thiocinium 6-anion (**17a**) as yellow prisms after recrystallization from hexane–$CH_2Cl_2$: mp 155–157 °C dec; IR (KBr) 2185 (CN), 1735, 1660 $cm^{-1}$ (ester); $^1H$ NMR ($CDCl_3$) $\delta$ 0.93 (3 H, t, $J$ = 7.5 Hz, $CH_2CH_3$), 1.63–2.40 (2 H, m, $CH_2CH_3$), 3.69 (3 H, s, OMe), 3.85 (3 H, s, OMe), 7.25–7.98 (8 H, m, Ar H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 9.71 (t), 43.40 (t), 51.24 (q), 52.74 (q), 94.94 (s), 120.17 (s), 121.57 (s), 165.73 (s), 168.03 (s); mass spectrum, $m/z$ 393 ($M^+$). Anal. Calcd for $C_{22}H_{19}NO_4S$: C, 67.16; H, 4.87; N, 3.56. Found: C, 66.98; H, 4.85; N, 3.54.

**Reaction of 5b with Diethyl Acetylenedicarboxylate.** A mixture of **5b** (445 mg) and diethyl acetylenedicarboxylate (301 mg) in dry benzene (20 mL) was stirred at room temperature for 2.5 days under nitrogen stream. The reaction mixture was concentrated under reduced pressure and ether was added to the residual oil. Precipitated crystals were filtered and recrystallized from hexane–$CH_2Cl_2$ to give 91 mg (12.2%) of 8-cyano-6,7-bis(ethoxycarbonyl)-5-ethyl-6*H*-dibenzo[*b*,*d*]thiocinium 6-anion (**17b**) as pale yellow plates: mp 148–149 °C dec; IR (KBr) 2180 (CN), 1730, 1660 $cm^{-1}$ (ester); $^1H$ NMR ($CDCl_3$) $\delta$ 0.92 (3 H, t, $J$ = 7 Hz, $CH_2CH_3$), 1.24 (3 H, t, $J$ = 7 Hz, $CH_2CH_3$), 1.36 (3 H, t, $J$ = 7 Hz, $CH_2CH_3$), 1.63–2.40 (2 H, m, $CH_2CH_3$), 4.16 (2 H, q, $J$ = 7 Hz, $CH_2CH_3$), 4.31 (2 H, q, $J$ = 7 Hz, $CH_2CH_3$), 7.22–7.97 (8 H, m, Ar H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 9.79 (q), 13.66 (q), 14.44 (q), 43.35 (t), 59.97 (t), 61.93 (t), 94.97 (s), 120.14 (s), 121.84 (s), 165.57 (s), 167.51 (s); mass spectrum, $m/z$ 421 ($M^+$). Anal. Calcd for $C_{24}H_{23}NO_4S$: C, 68.39; H, 5.50; N, 3.32. Found: C, 68.30; H, 5.49; N, 3.31. The filtrate was subjected to preparative TLC on silica gel using hexane–ethyl acetate (3:1) to give 92 mg (12.3%) of 7-cyano-7-[(*E*)-bis(ethoxycarbonyl)vinyl]-6-ethyl-6,7-dihydrodibenzo[*b*,*d*]thiepin (**16b**) as colorless plates after recrystallization from hexane–$CH_2Cl_2$: mp 105–106 °C; IR (KBr) 1730 $cm^{-1}$ (ester); $^1H$ NMR ($CDCl_3$) $\delta$ 1.09 (3 H, t, $J$ = 7 Hz, $CH_2CH_3$), 1.20 (3 H, t, $J$ = 7 Hz, $CH_2CH_3$), 1.57 (3 H, d, $J$ = 6.9 Hz, $CHCH_3$), 3.91–4.30 (5 H, m, 2 × $CH_2CH_3$ and $CHCH_3$), 7.15–7.98 (8 H, m, Ar H); mass spectrum, $m/z$ 421 ($M^+$). Anal. Calcd for $C_{24}H_{23}NO_4S$: C, 68.39; H, 5.50; N, 3.32. Found: C, 68.15; H, 5.40; N, 3.35.

**Reaction of 5a with Methyl Propiolate.** A solution of **5a** (150 mg) and methyl propiolate (374 mg) in dry benzene (20 mL) was stirred at 50–60 °C for 6 h. The reaction mixture was concentrated under reduced pressure to dryness. The residual oil was separated by preparative TLC on silica gel using hexane–ether as the developing solvent to give 48.9 mg (19.1%) of 2-[1-cyano-2,4-bis(methoxycarbonyl)-2,4-cyclopentadien-1-yl]-2′-(methylthio)biphenyl (**18**) as colorless prisms after recrystallization from hexane–$CH_2Cl_2$: mp 219–221 °C: IR (KBr) 2240 (CN), 1700 $cm^{-1}$ (ester); $^1H$ NMR ($CDCl_3$) $\delta$ 2.52 (3 H, s, SMe), 3.68 (3 H, OMe), 3.85 (3 H, s, OMe), 6.37 (1 H, s, olefinic H), 7.91 (1 H, s, olefinic H), 7.13–7.90 (8 H, m, Ar H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 17.74 (q), 49.64 (s), 52.25 (q), 52.60 (q), 118.24 (s), 119.56 (s), 120.50 (d), 120.68 (d), 126.05 (d), 125.84 (d), 128.13 (s), 128.66 (d), 128.93 (d), 129.96 (d), 139.99 (s), 140.11 (d), 141.76 (s), 142.05 (s), 151.24 (d), 140.11 (s), 164.39 (s), 165.33 (s); mass spectrum, $m/z$ 405 ($M^+$). Anal. Calcd for $C_{23}H_{19}NO_4S$: C, 68.13; H, 4.72; N, 3.45. Found: C, 68.26; H, 4.72; N, 3.34.