Reactions of 2-[(Phenylthio)methylene]tetralin-1-thione

Satoshi MORIYAMA and Shinichi MOTOKI*
Department of Chemistry, Faculty of Science, Science University of Tokyo,
Kagurazaka, Shinjuku-ku, Tokyo 162
(Received March 17, 1992)

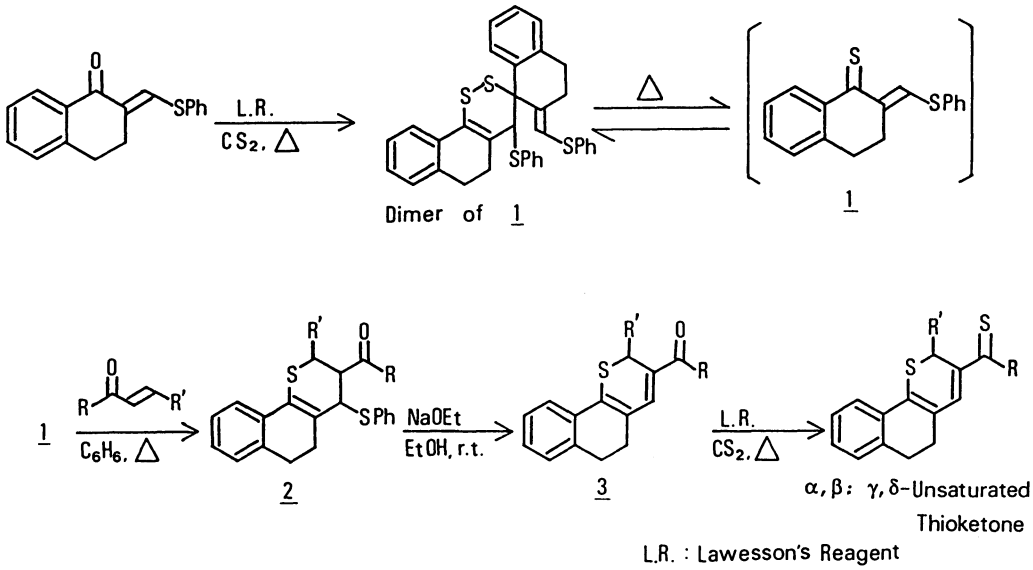
Hetero Diels–Alder reactions of 2-[(phenylthio)methylene]tetralin-1-thione (**1**) with methyl acrylate, methyl vinyl ketone, acrylonitrile, and other electron-poor dienophiles afford the corresponding cycloadducts (**2**), from which thiophenol is eliminated by the treatment with sodium alkoxide to give the corresponding 2*H*-thiopyran derivatives (**3**). The cycloadducts **2** with styrene and indene do not undergo elimination. The reactions of thioketone **1** with cycloalkenones give both the cycloadducts and the elimination products, even in the absence of a base. The reactions of **1** with acryloyl, crotonoyl, cinnamoyl, and 3-methyl-2-butenoyl chlorides give dienecarbothioic *S*-esters, in good yields, which are converted into stable dienecarbodithioic esters by the treatment with Lawesson's reagent. In the reaction of **1** with methyl 2-bromoacrylate, elimination of sulfenyl bromide takes place to afford the elimination product **3**.

Previously, synthesis of stable conjugated $\alpha,\beta:\gamma,\delta$-unsaturated thioketones starting from 2-[(phenylthio)-methylene]tetralin-1-thione **1** were reported (Scheme 1).[1,2] An important point concerning the syntheses is that the treatment of cycloadducts **2** with sodium ethoxide produces conjugated dienones **3** along with an elimination of thiophenol. Interest in this key step of the synthesis has led us to further investigate the hetero Diels–Alder reaction of **1** with other dienophiles and the subsequent elimination of **2** (Scheme 2).

Results and Discussion

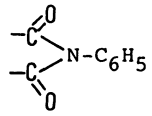
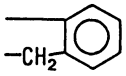
Reactions of β-phenylthio α,β-unsaturated thioketone **1**, generated by the thermolysis of its dimer, with electron-poor dienophiles, viz., methyl acrylate, methyl vinyl ketone, acrylonitrile, acrylaldehyde, crotonaldehyde, cinnamaldehyde, 3-methyl-2-butenal, dimethyl fumarate, and *N*-phenylmaleimide, were carried out in refluxing benzene for 1 to 5 h to give the cycloadducts **2a**—**i** (Table 1). Styrene and indene also gave similar adducts, **2j**,**k**.

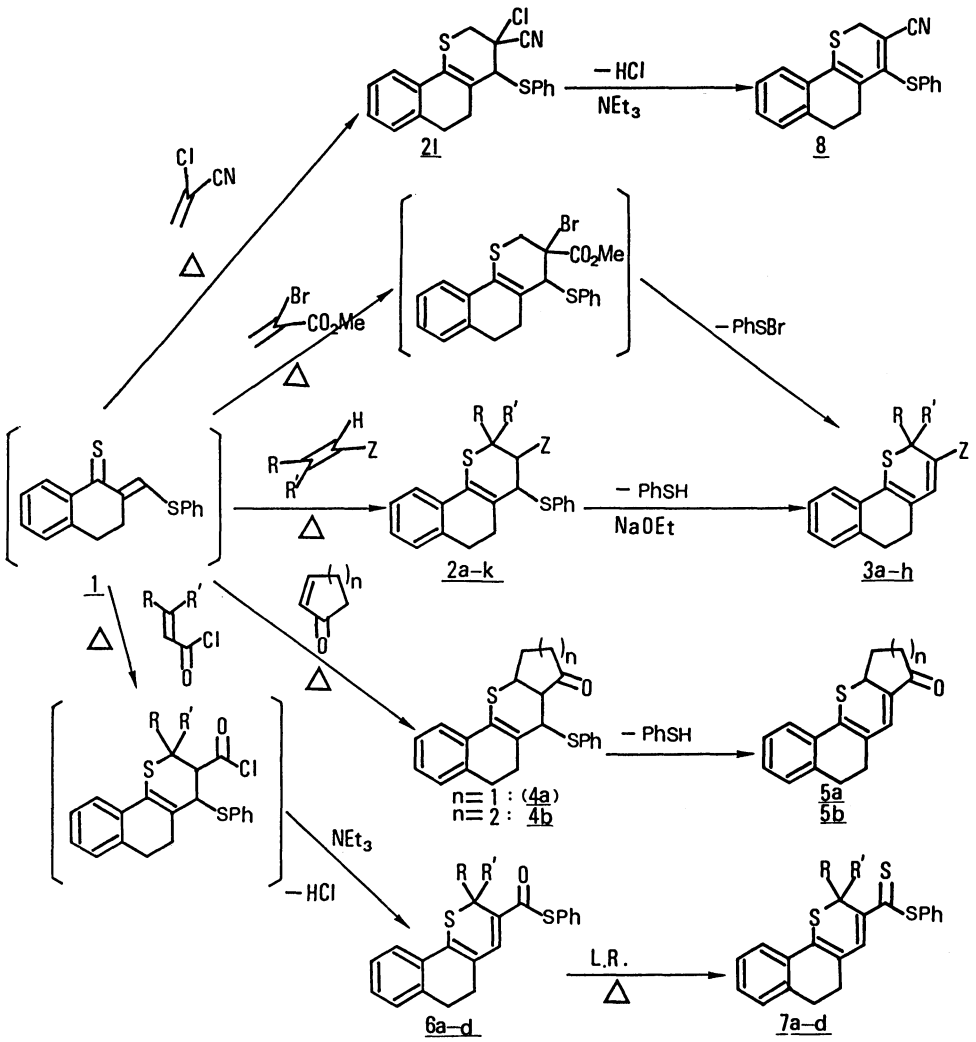
The ^{1}H NMR spectrum of **2a** exhibited four signals of the 3,4-dihydro-2*H*-thiopyran ring protons (Fig. 1). The signals at δ=3.56 and 3.14 were assigned to *H-2a* and *H-2e*, respectively. The former signal due to *H-2a* showed a large vicinal axial–axial coupling with *H-3* (J=12.2 Hz) as well as a geminal coupling with *H-2e* (J=12.9 Hz); the latter signal of *H-2e* showed a W-lattice long range coupling with *H-4* (J=2.0 Hz) in addition to the coupling with *H-3* (J=3.3 Hz) and *H-2a* (J=12.9 Hz). The small coupling constant (J=2.6 Hz) between *H-3* and *H-4* indicates that these protons are situated in the axial-equatorial positions; **2a** is therefore considered to be an *endo*-adduct (*H-3* and *H-4* are in *cis*-relationship). Analysis of the ^{1}H NMR spectra of the other adducts proved that **2b**—**h** were also *endo*-adducts. The adduct **2j** (with styrene) showed an ambiguous ^{1}H NMR spectrum; its structure (*endo*-adduct) was thus determined by conversion into the corresponding sul-



Scheme 1.

Table 1. Cycloaddition Reactions of Thioketone **1** with Dienophiles and Subsequent Elimination Reactions of Thiophenol from the Cycloadducts **2**

	Dienophile			Cycloadduct **2**				Elimination product **3**		
	R	R′	Z	Reaction time/h	Yield/%	Mp/°C	IR/cm^{-1}	Yield/%	Mp/°C	IR/cm^{-1}
a	H	H	CO_2CH_3	1	88	100—102	1748 (C=O)	89	80—81	1698 (C=O)
b	H	H	$COCH_3$	1	85	129—130	1706 (C=O)	92	116—117	1651 (C=O)
c	H	H	CN	1	77	113—114	2240 (C≡N)	82	70—71	2204 (C≡N)
d	H	H	CHO	3	90	140—141	1724 (C=O)	96	74—75	1674 (C=O)
e	CH_3	H	CHO	2.5	48	92—93	1728 (C=O)	92	Oil	1660 (C=O)
f	C_6H_5	H	CHO	3	85	135—136	1724 (C=O)	96	Oil	1662 (C=O)
g	CH_3	CH_3	CHO	5	76	126—127	1714 (C=O)	56	87—88	1672 (C=O)
h	CO_2CH_3	H	CO_2CH_3	1	83	149—150	1736 (C=O)	75	65—66	1742 (C=O) 1706 (C=O)
i	H			1	88	199—200	1735 (C=O)	—	—	—
j	H	H	C_6H_5	2	54	135—137	—	—	—	—
k	H			1.5	57	140—142	—	—	—	—



Scheme 2.

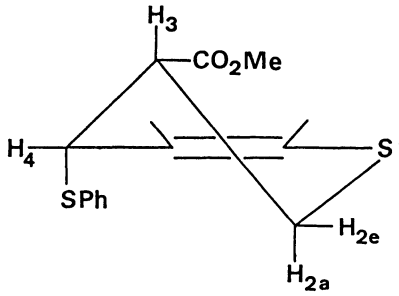


Fig. 1.

foxide **2j'**. The adducts, **2i** and **2k**, (with *N*-phenylmaleimide and indene) showed large (*H-2*)-(*H-3*) coupling constants (J=9.2 and 8.9 Hz) respectively. This suggests that the 3,4-dihydro-2*H*-thiopyran rings of **2i** and **2k** possess a boat form rather than a half-chair form, unlike in the case of **2a**—**h**. No *regio*- and *stereo*-isomers were formed in detectable amounts in these reactions.

The treatment of the adducts **2a**—**h** with sodium methoxide (or sodium ethoxide) at room temperature overnight afforded the corresponding 2*H*-thiopyran derivatives **3a**—**h** in high yields as the result of an elimination of thiophenol. The reaction of **2i** with sodium ethoxide gave an unidentified decomposition product. However, adducts **2j** and **2k** did not undergo elimination, even upon using stronger bases, such as KOBu^t, NaH, or BuLi. This result indicates that the presence of an electron-withdrawing group at position-3 in **2** is necessary for the facile elimination of thiophenol.

On the contrary, when **1** was heated with 2-cyclohexen-1-one, cycloaddition followed by the elimination of thiophenol took place concurrently to give the cycloadduct **4b** and elimination product **5b**. 2-Cyclopenten-1-one gave only elimination product **5a**; an attempt to obtain the cycloadduct **4a** by carrying out the reaction at lower temperature was unsuccessful. The dienone **5b** was also obtained by treatment of **4b** with sodium ethoxide at room temperature for a short reaction time. Although there is no experimental evidence for the readiness of the elimination reaction of **4**, it is likely that the PhS group and *H-3* in **4** are rigidly placed in the *trans*-diaxial conformation of their fused-ring.

Acryloyl, crotonoyl, cinnamoyl, and 3-methyl-2-butenoyl chlorides were allowed to react readily with **1** in refluxing benzene to give the corresponding cycloadducts. 3-Methyl-2-butenoyl chloride was so less reactive that prolonged heating was required. As these adducts were too unstable to be separated by column chromatography, they were successively treated with triethylamine. Instead of dienecarboxylic acid chloride, dienecarbothioic *S*-esters **6a**—**d** were obtained in fairly good yields. As is well known, acid chlorides containing α-hydrogen readily undergo dehydrohalogenation with tertiary amines to yield ketenes. The formation of **6** thus presumably proceeded via conversion of the initially formed cycloadducts into ketene derivatives, followed by an intramolecular nucleophilic attack (rearrangement) of the PhS group onto the central ketene carbon. The dienecarbothioic *S*-esters **6** were readily converted into conjugated dienecarbodithioic esters **7a**—**d** by the treatment with Lawesson's reagent. Except for some examples,[3,4] conjugated dithioesters are generally unstable and dimerize by a self-cycloaddition reaction.[5,6] However, highly conjugated dithioesters **7a**—**d** were found to be very stable and in the monomeric forms, as like as α,β: γ,δ-unsaturated thioketones reported previously.[2]

Interesting results were obtained in the reaction of **1** with α-halo dienophiles. With 2-chloroacrylonitrile, the product was an inseparable mixture of *endo*- and *exo*-adducts **2l**. Upon the treatment of **2l** with triethyl-

Table 2. Reactions of Thioketone **1** with Cycloalkenones

	Cycloalkenone	Reaction temp/°C	Reaction time/h	Cycloadduct **4**			Elimination Product **5**		
				Yield/%	Mp/°C	IR/cm^{-1}	Yield/%	Mp/°C	IR/cm^{-1}
a	2-Cyclopenten-1-one	65	2	0	—	—	54	154—155	1694 (C=O)
b	2-Cyclohexen-1-one	65	2	37	130—131	1714 (C=O)	20	108—109	1664 (C=O)
b	2-Cyclohexen-1-one	80	1	32	130—131	1714 (C=O)	10	108—109	1664 (C=O)

Table 3. Reactions of Thioketone **1** with Acid Chloride and Subsequent Conversion of the Products **6** into Dithioesters **7**

	Acid chloride	*S*-Phenyl thioester **6**			Dithioester **7**			
		Reaction time	Yield/%	Mp/°C	Reaction temp/°C	Reaction time/h	Yield/%	Mp/°C
a	Acryloyl chloride	5 min	57	160—162	110	7	68	146—147
b	Crotonoyl chloride	15 min	59	148—149	110	7	72	154—155
c	Cinnamoyl chloride	15 min	70	139—141	110	10	72	134—135
d	3-Methyl-2-butenoyl chloride	5 h	66	111—112	140	10	50	Red oil

amine, elimination of hydrogen chloride took place, giving 3-cyano-4-phenylthio-2*H*-thiopyran derivative **8**. In contrast, heating **1** with methyl 2-bromoacrylate afforded the same 3-methoxycarbonyl-2*H*-thiopyran derivative as did the elimination product **3a**, as the result of elimination of sulfenyl bromide from the adduct. Although it is well known that sulfenyl halides add smoothly to alkenes to give β-chloro sulfides,[7] only a few examples concerning the elimination of sulfenyl halides giving alkenes have been reported.[8] The contrast between these two reactions with different α-halo dienophiles are under further investigation.

Experimental

All melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were determined on a JEOL JNM FX-100 (100 MHz) or EX-270 (270 MHz) spectrometer in $CDCl_3$ solvent. Tetramethylsilane was used as an internal standard. IR spectra (KBr disk) were measured with a Hitachi 270-30. Mass spectra were measured on a Hitachi mass spectrometer RMU-7M (70 eV) with a data-proceeding system M-003. Elemental analysis was performed using a Yanagimoto Model MT-3 CHN corder.

A Typical Procedure for the Cycloaddition Reaction of 2-[(Phenylthio)methylene]tetralin-1-thione 1 with Dienophiles. A solution of the dimer (3.55 mmol/monomer) of the thioketone **1** and methyl acrylate (10.6 mmol) in dry benzene (50 cm^3) was refluxed for 1 h under a nitrogen atmosphere. The solvent was removed and the residue was chromatographed on Wakogel C-200 with ethyl acetate–hexane (1 : 8) to give the cycloadduct **2a**, which was recrystallized from hexane.

3,4,5,6-Tetrahydro-4-phenylthio-3-methoxycarbonyl-2*H*-naphto [1,2-*b*] thiopyran (2a): Colorless plates; MS *m/z* 368 (M^+; 0.3), 258 (M^+−PhSH; 35), 243 (72), 199 (100), 165 (37), 152 (13), 115 (19), 110 (74); ^{1}H NMR δ=2.33—2.47 (1H, m), 2.67—2.87 (3H, m), 3.14 (1H, ddd, *J*=2.0, 3.3, 12.9 Hz), 3.19 (3H, s), 3.24 (1H, ddd, *J*=2.6, 3.3, 12.2 Hz), 3.56 (1H, dd, *J*=12.2, 12.9 Hz), 4.29 (1H, dd, *J*=2.0, 2.6 Hz), 7.10—7.32 (6H, m), 7.39—7.51 (3H, m); ^{13}C NMR δ=22.9 (t), 28.4 (t), 30.4 (t), 44.9 (d), 51.3 (q), 53.1 (d), 171.2 (C=O; s). Found: C, 68.71; H, 5.43%. Calcd for $C_{21}H_{20}O_2S_2$: C, 68.44; H, 5.47%.

3,4,5,6-Tetrahydro-4-phenylthio-3-acetyl-2*H*-naphto[1,2-*b*]thiopyran (2b): Colorless needles; MS *m/z* 352 (M^+; 0.3), 242 (M^+−PhSH; 20), 199 (100), 165 (24), 110 (45), 43 (79); ^{1}H NMR δ=1.83 (3H, s), 2.35—2.58 (1H, m), 2.79—2.91 (3H, m), 3.07 (1H, ddd, *J*=1.7, 2.6, 12.9 Hz), 3.19 (1H, ddd, *J*=2.6, 3.0, 11.9 Hz), 3.46 (1H, dd, *J*=11.9, 12.9 Hz), 4.20 (1H, dd, *J*=1.7, 3.0 Hz), 7.11—7.33 (5H, m), 7.40—7.52 (4H, m); ^{13}C NMR δ=22.8 (t), 28.4 (2C; t, q), 30.6 (t), 52.5 (d), 53.4 (d), 206.0 (C=O; s). Found: C, 71.32; H, 5.63%. Calcd for $C_{21}H_{20}OS_2$: C, 71.55; H, 5.72%.

3-Cyano-3,4,5,6-tetrahydro-4-phenylthio-2*H*-naphto[1,2-*b*]thiopyran (2c): Colorless needles; MS *m/z* 335 (M^+; 13), 225 (M^+−PhSH; 100), 193 (22), 165 (22), 152 (11), 115 (18), 110 (36); ^{1}H NMR δ=2.26—2.40 (1H, m), 2.72—2.89 (3H, m), 3.17 (1H, ddd, *J*=2.0, 2.0, 12.5 Hz), 3.47 (1H, ddd, *J*=2.0, 3.3, 12.2 Hz), 3.60 (1H, dd, *J*=12.2, 12.5 Hz), 3.89 (1H, dd, *J*=2.0, 3.3 Hz), 7.12—7.41 (7H, m), 7.65—7.70 (2H, m); ^{13}C NMR δ=25.0 (t), 28.1 (t), 30.3 (t), 33.3 (d), 52.1 (d). Found: C, 71.46; H, 5.13; N, 4.09%. Calcd for $C_{20}H_{17}NS_2$: C, 71.60; H, 5.11; N, 4.18%.

3-Formyl-3,4,5,6-tetrahydro-4-phenylthio-2*H*-naphto[1,2-*b*]thiopyran (2d): Pale yellow needles; MS *m/z* 228 (M^+−PhSH; 43), 199 (100), 165 (16), 110 (59); ^{1}H NMR δ=2.11—2.28 (4H, m), 2.95—3.54 (3H, m), 4.24 (1H, d, *J*=3.0 Hz), 6.01—5.56 (9H, m), 9.46 (1H, bs); ^{13}C NMR δ=21.9 (t), 28.4 (t), 30.3 (t), 52.0 (d), 52.6 (d), 198.7 (H-C=O; d). Found: C, 70.97; H, 5.22%. Calcd for $C_{20}H_{18}OS_2$: C, 70.97; H, 5.36%.

3-Formyl-3,4,5,6-tetrahydro-2-methyl-4-phenylthio-2*H*-naphto[1,2-*b*]thiopyran (2e): Pale yellow cubes; MS *m/z* 352 (M^+; 1), 243 (M^+−PhS; 100), 227 (19), 213 (60), 199 (37), 165 (26), 117 (57), 110 (30); ^{1}H NMR δ=1.48 (3H, d, *J*=6.6 Hz), 2.26—2.38 (1H, m), 2.43—2.82 (4H, m), 4.01 (1H, dq, *J*=6.6, 10.9 Hz), 4.12 (1H, d, *J*=3.6 Hz), 7.10—7.46 (9H, m), 9.77 (1H, d, *J*=3.0 Hz); ^{13}C NMR δ=19.1 (q), 28.1 (t), 29.3 (t), 31.8 (d), 53.0 (d), 56.8 (d), 201.3 (H-C=O; d). Found: C, 71.53; H, 5.90%. Calcd for $C_{21}H_{20}OS_2$: C, 71.53; H, 5.90%.

3-Formyl-3,4,5,6-tetrahydro-2-phenyl-4-phenylthio-2*H*-naphto[1,2-*b*]thiopyran (2f): Pale yellow crystals; MS *m/z* 275 (M^+−PhSH−CHO; 100), 241 (7), 110 (47); ^{1}H NMR δ=2.07—2.94 (4H, m), 3.38 (1H, ddd, *J*=3.0, 3.8, 11.8 Hz), 4.21 (1H, d, *J*=3.8 Hz), 5.06 (1H, d, *J*=11.8 Hz), 6.89—7.52 (14H, m), 9.46 (1H, d, *J*=3.0 Hz); ^{13}C NMR δ=28.3 (t), 29.4 (t), 41.8 (d), 54.1 (d), 55.3 (d), 201.5 (H-C=O; d). Found: C, 75.41; H, 5.25%. Calcd for $C_{26}H_{22}OS_2$: C, 75.32; H, 5.35%.

3-Formyl-3,4,5,6-tetrahydro-2,2-dimethyl-4-phenylthio-2*H*-naphto[1,2-*b*]thiopyran (2g): Pale yellow needles; MS *m/z* 366 (M^+; 0.2), 257 (M^+−PhS; 95), 229 (49), 227 (100), 213 (34), 187 (49), 165 (14), 117 (30), 110 (60), 65 (24); ^{1}H NMR δ=1.38 (3H, s), 1.44 (3H, s), 2.41 (1H, dd, *J*=4.6, 6.0 Hz), 2.50—2.68 (1H, m), 2.71—2.96 (3H, m), 4.23 (1H, d, *J*=6.0 Hz), 7.08—7.46 (9H, m), 9.64 (1H, d, *J*=4.6 Hz); ^{13}C NMR (DEPT) δ=27.1 (CH_3), 28.5 (CH_2), 28.7 (CH_2), 29.1 (CH_3), 42.6 (C), 51.8 (CH), 57.4 (CH), 200.1 (H-C=O). Found: C, 72.10; H, 6.12%. Calcd for $C_{22}H_{22}OS_2$: C, 72.09; H, 6.05%.

3,4,5,6-Tetrahydro-2,3-bis (methoxycarbonyl)-4-phenylthio-2*H*-naphto[1,2-*b*]thiopyran (2h): Colorless needles; MS *m/z* 426 (M^+; 0.2), 395 (M^+−OMe; 0.4), 363 (0.3), 335 (0.3), 317 (M^+−PhS; 37), 285 (32), 257 (100), 199 (16), 165 (10), 109 (10); ^{1}H NMR δ=2.37—2.72 (1H, m), 2.71—2.91 (3H, m), 3.14 (3H, s), 3.47 (1H, dd, *J*=3.3, 11.6 Hz), 3.80 (3H, s), 4.28 (1H, d, *J*=3.3 Hz), 4.71 (1H, d, *J*=11.6 Hz), 7.10—7.50 (9H, m); ^{13}C NMR (DEPT) δ=28.3 (CH_2), 30.0 (CH_2), 39.5 (CH), 42.8 (CH), 51.6 (CH_3), 52.7 (CH), 53.0 (CH_3), 170.5 (C=O), 171.1 (C=O). Found: C, 64.69; H, 5.49%. Calcd for $C_{23}H_{22}O_4S_2$: C, 64.76; H, 5.20%.

5,6,7,7a,9,11a-Hexahydro-9-phenyl-7-phenylthio-11-thia-9-azacyclopenta[*b*]phenanthrene-8,10-dione (2i): MS *m/z* 346 (M^+−PhS; 49), 226 (31), 198 (100), 165 (45), 110 (78); ^{1}H NMR δ=2.32—2.72 (4H, m), 3.81 (1H, dd, *J*=4.3, 9.2 Hz), 4.41 (1H, d, *J*=4.3 Hz), 4.41 (1H, d, *J*=9.2 Hz), 7.06—7.43 (13H, m), 7.63 (1H, d, *J*=7.3 Hz); ^{13}C NMR (DEPT) δ=27.8 (CH_2), 28.3 (CH_2), 43.6 (CH), 49.3 (CH), 52.4 (CH), 174.1 (C=O), 174.2 (C=O). Found: C, 70.59; H, 4.58; N, 3.14%. Calcd for $C_{27}H_{21}O_2NS$: C, 71.18; H, 4.65; N, 3.07%.

3,4,5,6-Tetrahydro-3-phenyl-4-phenylthio-2*H*-naphto[1,2-*b*]thiopyran (2j): Colorless cubes; MS *m/z* 386 (M^+; 1), 276 (M^+−PhSH; 100), 244 (12), 199 (24), 110 (35); ^{1}H NMR δ=2.32—2.45 (1H, m), 2.71—2.85 (3H, m), 3.08 (1H, ddd, *J*=1.7, 1.7, 11.6 Hz), 3.67—3.86 (3H, m), 6.75—6.80 (2H, m), 6.93—7.04 (3H, m), 7.10—7.28 (8H, m), 7.46—7.51 (1H, m); ^{13}C NMR δ=26.3 (t), 28.5 (t), 30.7 (t), 44.6 (d), 59.6 (d). Found: C, 77.94; H, 5.37%. Calcd for $C_{25}H_{22}S_2$: C, 77.67; H,

5.37%.

5,6,7,7a,12,12a-Hexahydro-7-phenylthio-13-thiaindeno[3,2-*b*]phenanthrene (2k): MS *m/z* 398 (M^+; 0.2), 289 (M^+−PhS; 100), 255 (21), 239 (9), 205 (22), 174 (11), 161 (10), 141 (19), 128 (33), 115 (45), 110 (48), 77 (24), 65 (35), 39 (43), 28 (60); ^{1}H NMR δ=2.19—2.27 (1H, m), 2.37—2.71 (3H, m), 3.44—3.48 (2H, m), 3.91 (1H, dd, *J*=4.0, 8.9 Hz), 4.17 (1H, ddd, *J*=2.0, 8.9, 17.5 Hz), 4.30 (1H, d, *J*=4.0 Hz), 6.68—7.38 (12H, m), 7.59—8.00 (1H, m); ^{13}C NMR (DEPT) δ=28.1 (CH_2), 29.5 (CH_2), 42.5 (CH), 42.7 (CH_2), 51.8 (CH), 57.9 (CH). Found: C, 78.42; H, 5.29%. Calcd for $C_{26}H_{22}S_2$: C, 78.35; H, 5.56%.

Oxidation of the Cycloadduct 2j. A solution of *m*-chloroperbenzoic acid (1.88 mmol, 80%; Nakarai Tesk) in CH_2Cl_2 (30 cm^3) was added dropwise to a solution of the cycloadduct **2j** (1.25 mmol) in CH_2Cl_2 (30 cm^3) at −15 °C under a nitrogen atmosphere. After stirring for 4 h at room temperature, the reaction mixture was washed with a $NaHCO_3$ aqueous solution and water, and then dried over anhydrous $MgSO_4$. The solvent was removed and the residue was chromatographed on Wakogel C-200 with CH_2Cl_2 to give sulfoxide **2j'**, which was recrystallized from CH_2Cl_2–hexane (yield 56%).

3,4,5,6-Tetrahydro-3-phenyl-4-phenylthio-2*H*-naphto[1,2-*b*]thiopyran 1-oxide (2j'): Colorless cubes; mp 208—210 °C; IR; 1030 cm^{-1} (S=O); MS *m/z* 402 (M^+; 1), 385 (M^+−O−H; 67), 293 (M^+−PhS; 17), 275 (20), 244 (87), 189 (100), 165 (15), 128 (35), 115 (38), 109 (29), 91 (49); ^{1}H NMR δ=2.46—2.61 (1H, m), 2.77—2.95 (3H, m), 3.40 (1H, dd, *J*=2.3, 13.5 Hz), 3.51 (1H, dd, *J*=12.5, 13.5 Hz), 3.87 (1H, d, *J*=3.3 Hz), 4.46 (1H, ddd, *J*=2.3, 3.3, 12.5 Hz), 6.70—7.34 (13H, m), 7.97 (1H, d, *J*=7.3 Hz); ^{13}C NMR (DEPT) δ=27.7 (CH_2), 30.6 (CH_2), 34.1 (CH), 45.8 (CH_2), 60.1 (CH). Found: C, 74.62; H, 5.42%. Calcd for $C_{25}H_{22}OS_2$: C, 74.59; H, 5.51%.

A Typical Procedure for the Elimination of Thiophenol from the Cycloadducts 2. To a solution of the cycloadduct **2a** (2.47 mmol) in benzene (50 cm^3) was added a sodium methoxide solution (sodium metal (13.0 mmol) in methanol (50 cm^3)). After stirring for 1 d, water was added to the mixture. The product was extracted with ether and dried over anhydrous $MgSO_4$. The solvent was removed and the residue was chromatographed on Wakogel C-200 with ethyl acetate–hexane (1 : 8) to give 2*H*-thiopyran **3a**, which was recrystallized from ether–hexane.

5,6-Dihydro-3-methoxycabonyl-2*H*-naphto[1,2-*b*]thiopyran (3a): Yellow plates; MS *m/z* 258 (M^+; 48), 243 (83), 227 (6), 199 (100), 197 (23), 165 (29), 115 (13), 59 (5); ^{1}H NMR δ=2.51—2.57 (2H, m), 2.82—2.87 (2H, m), 3.68 (2H, s), 3.82 (3H, s), 7.15—7.29 (4H, m), 7.54—7.60 (1H, m); ^{13}C NMR (DEPT) δ=24.3 (CH_2), 28.0 (CH_2), 28.4 (CH_2), 52.0 (CH_3), 166.6 (C=O). Found: C, 69.81; H, 5.65%. Calcd for $C_{15}H_{14}O_2S$: C, 69.74; H, 5.46%.

5,6-Dihydro-3-methylcarbonyl-2*H*-naphto[1,2-*b*]thiopyran (3b): Orange cubes; MS *m/z* 242 (M^+; 31), 199 (100), 165 (10); ^{1}H NMR δ=2.40 (3H,s), 2.44—2.97 (4H, m), 3.67 (2H, s), 7.01 (1H, s), 7.06—7.29 (3H, m), 7.46—7.60 (1H, m); ^{13}C NMR δ=22.9 (t), 25.2 (q), 28.0 (t), 28.5 (t), 196.0 (C=O; s). Found: C, 74.50; H, 5.82%. Calcd for $C_{15}H_{14}OS$: C, 74.34; H, 5.82%.

3-Cyano-5,6-dihydro-2*H*-naphto[1,2-*b*]thiopyran (3c): MS *m/z* 225 (M^+; 100), 210 (8), 197 (10), 190 (25), 165 (28), 152 (10), 115 (18), 32 (21); ^{1}H NMR δ=2.35—2.61 (2H, m), 2.75—2.95 (2H, m), 3.46 (2H, s), 5.76 (1H, s), 6.04—6.32 (3H, m), 6.40—6.58 (1H, m); ^{13}C NMR δ=26.0 (t), 27.7 (t), 28.1 (t), 95.1 (C–C≡N; s), 118.8 (C≡N; s). Found: C, 74.54; H, 4.89; N, 5.91%. Calcd for $C_{14}H_{11}NS$: C, 74.63; H, 4.92; N, 6.22%.

3-Formyl-5,6-dihydro-2*H*-naphto[1,2-*b*]thiopyran (3d): Orange plates; MS *m/z* 228 (M^+; 49), 199 (M^+−CHO; 100), 165 (15), 115 (16); ^{1}H NMR δ=2.48—3.00 (4H, m), 3.66 (2H, s), 6.85 (1H, s), 7.08—7.36 (3H, m), 7.49—7.65 (1H, m), 9.45 (1H, s); ^{13}C NMR δ=21.9 (t), 28.0 (t), 28.3 (t), 190.5 (C=O; d). Found: C, 73.77; H, 5.10%. Calcd for $C_{14}H_{12}OS$; C, 73.65; H, 5.30%.

3-Formyl-5,6-dihydro-2-methyl-2*H*-naphto[1,2-*b*]thiopyran (3e): Orange cubes; MS *m/z* 242 (M^+; 30), 227 (M^+−Me; 33), 213 (100), 197 (5), 178 (6), 165 (15), 128 (3), 115 (6); ^{1}H NMR δ=1.23 (3H, d, *J*=6.9 Hz), 2.44—2.55 (1H, m), 2.63—2.98 (3H, m), 8.37 (1H, q, *J*=6.9 Hz), 6.82 (1H, s), 7.16—7.29 (3H, m), 7.61—7.67 (1H, m), 9.55 (1H, s); ^{13}C NMR (DEPT) δ=21.0 (CH_3), 28.1 (CH_2), 28.4 (CH_2), 30.0 (CH), 190.8 (C=O). Found: C, 64.52; H, 5.09%. Calcd for $C_{15}H_{14}OS$: C, 64.54; H, 5.10%.

3-Formyl-5,6-dihydro-2-phenyl-2*H*-naphto[1,2-*b*]thiopyran (3f): Orange oil; MS *m/z* 304 (M^+; 7), 275 (100), 262 (9), 241 (7), 165 (7), 115 (13); ^{1}H NMR δ=2.38—3.03 (4H, m), 5.32 (1H, s), 7.05 (1H, s), 6.88—7.71 (9H, m), 9.63 (1H, s); ^{13}C NMR δ=28.0 (t), 28.4 (t), 37.7 (d), 190.9 (C=O; d). Found: *m/z* 304.0925. Calcd for $C_{20}H_{16}OS$: M, 304.0922.

3-Formyl-5,6-dihydro-2,2-dimethyl-2*H*-naphto[1,2-*b*]thiopyran (3g): Yellow cubes; MS *m/z* 256 (M^+; 10), 227 (100), 212 (4), 178 (10), 165 (8), 128 (7), 115 (10), 28 (10); ^{1}H NMR δ=1.65 (6H, s), 2.54—2.60 (2H, m), 2.84—2.89 (2H, m), 6.72 (1H, s), 7.16—7.37 (3H, m), 7.59—7.62 (1H, m), 9.51 (1H, s); ^{13}C NMR (DEPT) δ=27.7 ($2CH_3$), 28.0 (CH_2), 28.0 (CH_2), 43.7 (C), 192.0 (H–C=O). Found: C, 74.77; H, 6.45%. Calcd for $C_{16}H_{16}OS$: C, 74.96; H, 6.29%.

5,6-Dihydro-2,3-dimethoxycarbonyl-2*H*-naphto[1,2-*b*]-thiopyran (3h): Yellow crystals; MS *m/z* 316 (M^+; 1), 257 (M^+−COOMe; 100), 197 (18), 165 (6), 28 (3); ^{1}H NMR δ=2.42—2.53 (1H, m), 2.60—2.96 (3H, m), 3.69 (3H, s), 3.84 (3H, s), 4.83 (1H, s), 7.16—7.29 (3H, m), 7.41 (1H, s), 7.58—7.61 (1H, m); ^{13}C NMR (DEPT) δ=27.9 (CH_2), 28.5 (CH_2), 38.4 (CH), 52.3 (CH_3), 53.0 (CH_3), 166.2 (C=O), 170.4 (C=O). Found: C, 64.52; H, 5.09%. Calcd for $C_{17}H_{16}O_4S$: C, 64.54, H, 5.10%.

A Typical Procedure for the Reaction of the Thioketone 1 with Cycloalkenones. A solution of the dimer (5.00 mmol/monomer) of the thioketone **1** and 2-cyclopenten-1-one (10.0 mmol) in dry THF (50 cm^3) was refluxed for 2 h under a nitrogen atmosphere. The solvent was removed and the residue was chromatographed on Wakogel C-200 with ethyl acetate–hexane (1 : 8) to give the elimination product **5a**, which was recrystallized from ether–hexane.

5,6,10,11-Tetrahydro-11-thiacyclopenta[*b*]phenanthren-8(9*H*)-one (5a): Yellow cubes; MS *m/z* 254 (M^+; 25), 226 (67), 212 (100), 197 (25), 178 (25), 165 (29); ^{1}H NMR δ=1.93—3.22 (8H, m), 4.08—4.73 (1H, m), 6.66—7.07 (1H, m), 7.17—7.88 (4H, m); ^{13}C NMR δ=27.0 (t), 28.0 (t), 28.4 (t), 37.4 (t), 38.5 (d), 202.8 (C=O; s). Found: C, 75.68; H, 5.39%. Calcd for $C_{16}H_{14}OS$: C, 75.55; H, 5.55%.

5,6,7,7a,9,10,11,11a-Octahydro-7-phenylthio-8*H*-12-thiabenz[*a*]anthracen-8-one (4b): Pale yellow needles; MS *m/z* 378 (M^+; 1), 269 (M^+−PhS; 100), 212 (65), 110 (51); ^{1}H NMR δ=1.88—2.88 (10H, m), 2.96 (1H, dd, *J*=2.0, 4.0 Hz), 4.34 (1H, d, *J*=2.0 Hz), 4.44—4.48 (1H, m), 7.04—7.47 (9H, m); ^{13}C NMR δ=22.5 (t), 28.3 (t), 29.0 (t), 30.2 (t), 38.0 (d), 40.3 (t), 50.3 (d), 52.0 (d), 206.8 (C=O; s). Found: C, 72.75; H, 5.86%. Calcd for $C_{23}H_{22}OS$: C, 72.97; H, 5.86%.

5,6,9,10,11,11a-Hexahydro-8*H*-12-thiabenz[*a*]anthracen-8-one (5b): Yellow plates; MS *m/z* 268 (M^+; 26), 212 (100), 197 (10); ^{1}H NMR δ=1.83—3.13 (10H, m) 3.83—4.20 (1H, m), 6.87—7.63 (5H, m); ^{13}C NMR δ=20.7 (t), 27.9 (2C; t), 28.1 (t), 38.6 (t), 38.7 (d), 196.8 (C=O; s). Found: *m/z* 268.0915. Calcd for $C_{17}H_{16}OS$: M, 268.0923.

Eliminatioin of Thiophenol from the Cycloadduct 4b. To a solution of the cycloadduct **4b** (2.80 mmol) in benzene (30 cm^3) was added to a sodinum ethoxide solution (sodium metal (14.0 mmol) in ethanol (30 cm^3)). After stirring for 30 min, water was added to the reaction mixture. The product was extracted with ether and dried over anhydrous $MgSO_4$. The solvent was removed and the residue was chromatographed on Wakogel C-200 with ethyl acetate–hexane (1 : 4) to give the elimination product **5b** which was recrystallized from ether. The yield was 79%.

A Typical Procedure for the Reaction of Thioketone 1 with Acid Chlorides. A solution of the dimer (3.72 mmol/monomer) of the thioketone **1** and acryloyl chloride (4.10 mmol) in dry benzene (50 cm^3) was refluxed for 5 min under a nitrogen atmosphere. Et_3N (37.2 mmol) was added to the reaction mixture after cooling to 0 °C; the solution was again refluxed for 2 h. The reaction mixture was poured into water, and the product was extracted with ether. The extract was dried over anhydrous $MgSO_4$. The solvent was removed and the residue was chromatographed on Wakogel C-200 with benzene–hexane (1 : 2) to give the dienecarbothioic ester **6a**, which was recrystallized from ether–hexane.

***S*-Phenyl 5,6-Dihydro-2*H*-naphto[1,2-*b*]thiopyran-3-carbothioate (6a):** Orange cubes; MS *m/z* 336 (M^+; 5), 227 (M^+−PhS; 100), 199 (29), 197 (10), 109 (8), 39 (8), 28 (4); ^{1}H NMR δ=2.57—2.91 (4H, m), 3.73 (2H, s), 7.17—7.61 (10H, m); ^{13}C NMR (DEPT) δ=24.5 (CH_2), 28.0 (CH_2), 28.5 (CH_2), 187.9 (C=O). Found: C, 71.31; H, 4.60%. Calcd for $C_{20}H_{16}OS_2$: 71.39; H, 4.79%.

***S*-Phenyl 5,6-Dihydro-2-methyl-2*H*-naphto[1,2-*b*]thiopyran-3-carbothioate (6b):** Yellow cubes; MS *m/z* 350 (M^+; 4), 241 (100), 213 (9), 109 (4), 39 (4), 28 (11); ^{1}H NMR δ=1.28 (3H, d, *J*=6.8 Hz), 2.47—2.98 (4H, m), 4.20 (1H, q, *J*=6.8 Hz), 7.16—7.66 (10H, m); ^{13}C NMR (DEPT) δ=20.7 (CH_3), 28.1 (CH_2), 28.6 (CH_2), 32.4 (CH), 188.0 (C=O). Found: C, 71.79; H, 5.31%. Calcd for $C_{21}H_{18}OS_2$: C, 71.96; H, 5.18%.

***S*-Phenyl 5,6-Dihydro-2-phenyl-2*H*-naphto[1,2-*b*]thiopyran-3-carbothioate (6c):** Orange cubes; MS *m/z* 412 (M^+; 3), 303 (M^+−PhS; 100), 275 (90), 197 (3), 109 (12), 39 (2), 28 (17); ^{1}H NMR δ=2.39—2.99 (4H, m), 5.36 (1H, d, *J*=2.3 Hz), 7.13—7.61 (15H, m); ^{13}C NMR (DEPT) δ=28.1 (CH_2), 28.6 (CH_2), 39.8 (CH), 188.3 (C=O). Found: C, 75.88; H, 4.77%. Calcd for $C_{26}H_{20}OS_2$: C, 75.69; H, 4.89%.

***S*-Phenyl 5,6-Dihydro-2,2-dimethyl-2*H*-naphto[1,2-*b*]thiopyran-3-carbothioate (6d):** Orange cubes; MS *m/z* 364 (M^+; 3), 255 (M^+−PhS; 100), 227 (29), 211 (6), 197 (2), 109 (13), 39 (6), 28 (3); ^{1}H NMR δ=1.59 (6H, s), 2.55—2.91 (4H, m), 7.17—7.61 (10H, m); ^{13}C NMR (DEPT) δ=27.3 ($2CH_3$), 28.1 (CH_2), 28.2 (CH_2), 44.6 (C), 189.0 (C=O). Found: C, 72.61; H, 5.42%. Calcd for $C_{22}H_{20}OS_2$: C, 72.49; H, 5.53%.

A Typical Procedure for the Formation of Dithioesters with Lawesson's Reagent. A suspension of thioester **6a** (1.00 mmol) and Lawesson's reagent (0.75 mmol) in dry toluene (30 cm^3) was refluxed for 6 h under a nitrogen atmosphere. The solvent was removed and the reaction mixture was passed through a short column of Florisil using benzene–hexane (1 : 2) as an eluent, and the solvent was removed. Dithioester **7a** was recrystallized from ether–hexane.

Phenyl 5,6-Dihydro-2*H*-naphto[1,2-*b*]thiopyran-3-carbodithioate (7a): Red plates; MS *m/z* 352 (M^+; 27), 243 (M^+−PhS; 100), 199 (15), 197 (9), 165 (26), 109 (13), 39 (13); ^{1}H NMR δ=2.64—2.93 (4H, m), 4.16 (2H, s), 7.17—7.63 (10H, m); ^{13}C NMR (DEPT) δ=28.2 (CH_2), 28.8 (CH_2), 29.4 (CH_2), 221.0 (C=S). Found: *m/z* 352.0404. Calcd for $C_{20}H_{16}S_3$: M, 352.0414.

Phenyl 5,6-Dihydro-2-methyl-2*H*-naphto[1,2-*b*]thiopyran-3-carbodithioate (7b): Red cubes; MS *m/z* 366 (M^+; 24), 257 (M^+−PhS; 100), 213 (10), 197 (5), 165 (13), 109 (16), 39 (10); ^{1}H NMR δ=1.32 (3H, d, *J*=6.9 Hz), 2.55—2.97 (4H, m), 4.89 (1H, q, *J*=6.9 Hz), 7.17—7.67 (10H, m); ^{13}C NMR (DEPT) δ=20.3 (CH_3), 28.3 (CH_2), 28.8 (CH_2), 36.6 (CH), 220.9 (C=S). Found: C, 68.94; H, 5.00%. Calcd for $C_{21}H_{18}S_3$: C, 68.81; H, 4.95%.

Phenyl 5,6-Dihydro-2-phenyl-2*H*-naphto[1,2-*b*]thiopyran-3-carbodithioate (7c): Red cubes; MS *m/z* 428 (M^+; 33), 319 (M^+−PhS; 100), 275 (46), 197 (4), 165 (7), 109 (15), 39 (10); ^{1}H NMR δ=2.56—2.97 (4H, m), 6.14 (1H, s), 7.13—7.57 (15H, m); ^{13}C NMR (DEPT) δ=28.3 (CH_2), 28.7 (CH_2), 43.6 (CH), 221.3 (C=S). Found: C, 72.76; H, 4.80%. Calcd for $C_{26}H_{20}S_3$: C, 72.85; H, 4.70%.

Phenyl 5,6-Dihydro-2,2-dimethyl-2*H*-naphto[1,2-*b*]thiopyran-3-carbodithioate (7d): Red oil; MS *m/z* 380 (M^+; 8), 271 (M^+−PhS; 100), 255 (20), 227 (58), 178 (8), 165 (7), 109 (16), 65 (15), 39 (16); ^{1}H NMR δ=1.70 (6H, s), 2.56—2.96 (4H, m), 6.72 (1H, s), 7.16—7.60 (9H, m); ^{13}C NMR (DEPT) δ=27.0 ($2CH_3$), 28.1 ($2CH_2$), 45.3 (C), 226.8 (C=S). Found: *m/z* 380.0717. Calcd for $C_{22}H_{20}S_3$: M, 380.0727.

Reaction of the Thioketone 1 with 2-Chloroacrylonitrile. A solution of the dimer (3.58 mmol/monomer) of thioketone **1** and 2-chloroacrylonitrile (17.9 mmol) in dry benzene (50 cm^3) was refluxed for 1 h under a nitrogen atmosphere. The solvent was removed and the residue was chromatographed on Wakogel C-200 with ethyl acetate–hexane (1 : 8) to give the cycloadduct **2l**, which was recrystallized from ether (Yield 69%).

3-Chloro-3-cyano-3,4,5,6-tetrahydro-2*H*-naphto[1,2-*b*]-thiopyran (2l): Pale yellow cubes; *endo-exo* mixture (major product : minor product=ca. 7 : 3); mp 143—145 °C; MS *m/z* 369 (M^+; 3), 260 (M^+−PhS; 100), 224 (57), 190 (22), 109 (39); ^{1}H NMR (major product) δ=2.29—2.50 (1H, m), 2.69—2.89 (3H, m), 3.29 (1H, dd, *J*=2.3, 13.5 Hz), 3.90 (1H, *J*=2.3 Hz), 4.02 (1H, d, *J*=13.5 Hz), 7.13—7.43 (6H, m), 7.55—7.67 (3H, m); (minor product) δ=2.29—2.50 (1H, m), 2.69—2.89 (3H, m), 3.33 (1H, dd, *J*=2.3, 12.7 Hz), 4.01 (1H, d, *J*=12.7 Hz), 4.16 (1H, d, *J*=2.3 Hz), 7.13—7.43 (6H, m), 7.55—7.67 (3H, m); ^{13}C NMR (DEPT) (major product) δ=28.0 (CH_2), 30.6 (CH_2), 33.3 (CH_2), 55.8 (C), 58.6 (CH), 117.6 (C≡N); (minor product) δ=28.0 (CH_2), 30.9 (CH_2), 32.5 (CH_2), 59.2 (C), 60.8 (CH), 116.8 (C≡N). Found: C, 64.84; H, 4.22; N, 3.63%. Calcd for $C_{20}H_{16}NS_2Cl$: C, 64.94; H, 4.36; N, 3.79%.

Elimination of Thiophenol from the Cycloadduct 2l. A solution of the cycloadduct mixture **2l** (1.30 mmol) and Et_3N (13.0 mmol) in dry benzene (50 cm^3) was refluxed for 2 h under a nitrogen atmosphere. The reaction mixture was poured into water and extracted with ether. The ether extract was then dried over anhydrous $MgSO_4$. The solvent was removed and the residue was chromatographed on Wakogel C-200 to give 2*H*-thiopyran **8**, which was recrystallized from ether–hexane (Yield 94%).

3-Cyano-5,6-dihydro-2*H*-naphto[1,2-*b*]thiopyran (8): Yel-

low cubes; mp 142—143 °C; IR 2198 cm^{-1} (C≡N); MS *m/z* 333 (M^+; 92), 275 (M^+−CN−S; 10), 256 (M^+−Ph; 100), 224 (37), 190 (43), 165 (27), 134 (26), 91 (40), 28 (73); ^1H NMR δ=2.23—2.28 (2H, m), 2.53—2.59 (2H, m), 3.49 (2H, s), 7.02—7.05 (1H, m), 7.14—7.27 (7H, m), 7.57—7.61 (1H, m); ^{13}C NMR (DEPT) δ=26.4 (CH_2), 27.6 (CH_2), 28.1 (CH_2), 100.0 (C–C≡N), 118.1 (C≡N). Found: C, 72.05; H, 4.46; N, 4.39%. Calcd for $C_{20}H_{15}NS_2$: C, 72.04; H, 4.53; N, 4.20%.

Reaction of the Thioketone 1 with Methyl 2-Bromoacrylate. A solution of the dimer (3.35 mmol) of thioketone **1** and methyl 2-bromoacrylate (5.02 mmol) in dry benzene (50 cm^3) was refluxed for 1 h under a nitrogen atmosphere. The reaction mixture was washed with a $NaHCO_3$ aqueous solution and extracted with ether. The ether extract was then dried over anhydrous $MgSO_4$. The solvent was removed and the residue was chromatographed on Wakogel C-200 with benzene–hexane (1 : 2) as an eluent to give elimination product **3a**. The yield was 56%. When the reaction mixture was refluxed in the presence of Et_3N (33 mmol) for 1 h, the yield was increased to 74%.

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