Thermal and Lewis Acid-Promoted Hetero Diels–Alder Reactions of $\alpha,\beta:\gamma,\delta$-Unsaturated Carbodithioic Esters and Carbothioic *O*-Esters; 5,6-Dihydro-2*H*-naphtho[1,2-*b*]thiopyran-3-carbodithioates and -carbothioic *O*-Esters

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Synopsis. Phenyl esters of 2-substituted 5,6-dihydro-2*H*-naphtho[1,2-*b*]thiopyran-3-carbodithioic acids (**2**) reacted with 2-norbornene, dimethyl acetylenedicarboxylate, diethyl azodicarboxylate, *N*-phenylmaleimide, dimethyl fumarate, 2-chloroacrylonitrile, methyl acrylate, and styrene in refluxing benzene to give the [4+2]cycloadducts, while the thermal cycloaddition reaction of *O*-methyl esters of 2-substituted 5,6-dihydro-2*H*-naphtho[1,2-*b*]thiopyran-3-carbothioic acids (**3**) was successful only with the triple-bonded dienophiles such as dimethyl acetylenedicarboxylate and ethyl propiolate. In the presence of a Lewis acid ($AlCl_3$ or $EtAlCl_2$), the reactions of both **2** and **3** were found to proceed efficiently even at room temperature.

Although many studies have been made on α,β-unsaturated thioketones[1,2] little attention has been paid to unsaturated carbodithioic esters and carbothioic *O*-esters. α,β-Unsaturated carbodithioic esters which can exist stably in the monomeric forms, seem to be limited to those bearing a bulky group around the dithioester group[3] or a hetero atom function such as an amino group at an appropriate position.[4] In certain cases α,β-unsaturated carbodithioic esters readily dimerize at ambient temperature[5] or are trapped *in situ* by dienophiles as [4+2]cycloadducts.[6] As for $\alpha,\beta:\gamma,\delta$-unsaturated carbodithioic esters, there is only one example reporting that methyl 2,4-pentadienedithioate, generated by flash vacuum thermolysis, readily cyclizes to the 2*H*-thiopyran derivative via electrocyclization.[7]

In the course of our study on β-phenylthio α,β-unsaturated thioketone **1** (Chart 1), we have recently synthesized the $\alpha,\beta:\gamma,\delta$-unsaturated carbodithioic esters **2**, viz., phenyl esters of 2-substituted 5,6-dihydro-2*H*-naphtho[1,2-*b*]thiopyran-3-carbodithioic acids, which could be isolated as stable monomers.[8] The corresponding carbothioic *O*-esters **3** could also be obtained stably.[9] In this study we have investigated the reactivity of **2** and **3** in the thermal and Lewis acid-promoted hetero Diels–Alder (HDA) reactions.

Results and Discussion

When the reactions of **2a**—**c** with 2-norbornene (NOR) were done in refluxing benzene, the [4+2]cycloadducts **4a**—**c** were obtained in good yields (Table 1) (Chart 2). The more congested carbodithioic ester **2d** ($R^1=R^2=Me$) did not react under the same reaction conditions. This reluctance in undergoing the HDA reaction is probably due to the steric repulsion between the two methyl groups and the phenylthio group encountered in the required *s-cis* conformation of the C=C–C=S moiety in **2d**.[10] Stereochemistry of **4** was proved to be *trans*(*exo*)-*trans*(*exo*) with respect to the norbornane skeleton and the framework originated from the (*C-12a*)–(*C-12b*) bond formation with the thiabutadiene system.[11] The reaction of **2c** with dimethyl acetylenedicarboxylate (DMAD), diethyl azodicarboxylate (DAD), *N*-phenylmaleimide (MI), and dimethyl fumarate (DF) similarly afforded the cycloadducts, **5**, **6**, (**7** and **7′**), and (**8** and **8′**), respectively. With the unsymmetrical dienophiles such as 2-chloroacrylonitrile (CAN), methyl acrylate (MA), and styrene (ST), the reaction gave the cycloadducts, (**9** or **9′**), (**10** and **10′**), and (**11** and **11′**) highly regioselectively (Chart 3). The electron-rich dienophiles such as butyl vinyl ether and enamine did not react under these thermal conditions.

The carbothioic *O*-esters **3a**—**d**[9] underwent the thermal HDA reaction, but the reaction required longer reaction times or a higher temperature (Table 2). The reaction with NOR, MI, DF, MA, ST, and DAD did not proceed even in refluxing xylene.

It is well-known that a Lewis acid is an effective catalyst for the Diels–Alder reaction. We examined the reaction of the carbodithioic ester **2c** with DMAD in the presence of $AlCl_3$ (Table 3). Surprisingly the reaction (Entry 3; 1.1 equiv $AlCl_3$) was completed within 5 min at room temperature to give **5** in an excellent yield. A catalytic amount of $AlCl_3$ (Entry 2) was also effec-

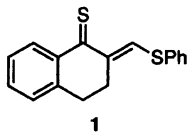

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Chart 1.

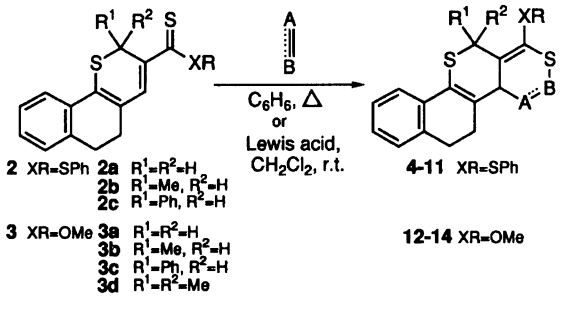

Chart 2.

Table 1. Thermal HDA Reaction of **2** at 80 °C in Benzene

Entry	Dithioester	Dienophile	React. time/h	Product	Yield %	Ratio[a] *cis* : *trans*
1	**2a**	NOR	4	**4a**	70	0 : 100[b]
2	**2b**	NOR	5	**4b**	80	0 : 100[b]
3	**2c**	NOR	7.5	**4c**	75	0 : 100[b]
4	**2c**	DMAD	3	**5**	98	—
5	**2c**	DAD	3	**6**	95	—
6	**2c**	MI	1.5	**7 7′**	62	58 : 42
7	**2c**	DF	7	**8 8′**	75	66 : 34[d]
8	**2c**	CAN	4	**9** or **9′**	95	[c]
9	**2c**	MA	5	**10 10′**	98	85 : 15[d]
10	**2c**	ST	7	**11 11′**	73	43 : 57

a) Determined by ^{1}H NMR (270 MHz) spectroscopy. b) With respect to the positions *12a*, *12b*. c) Unclear. d) The *trans* adduct was not isolated.

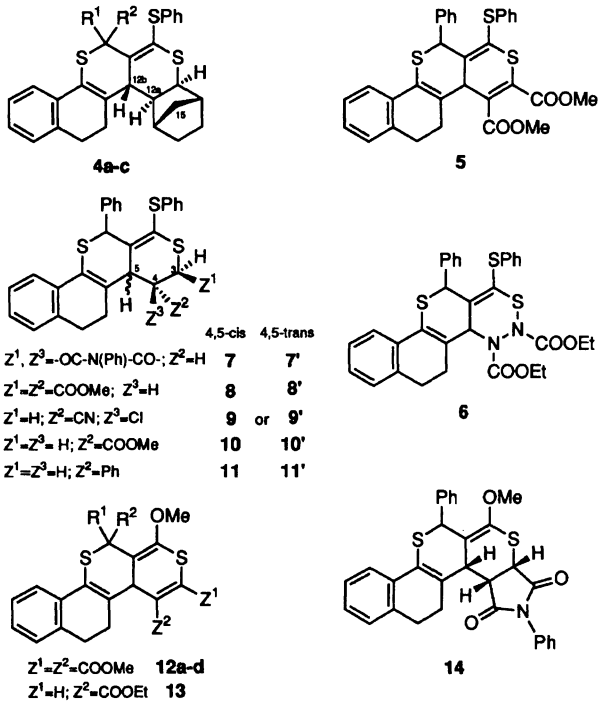

Chart 3.

tive for the reaction. The use of the excess Lewis acid (Entries 4 and 5) severely decreased the yield probably due to decomposition of **2c** by the action of the excess Lewis acid. $EtAlCl_2$ (1.1 equiv) showed good results, while BF_3·OEt_2 and $ZnCl_2$ (1.1 equiv) were less effective for the rate acceleration. With the other dienophiles (Entries 9—12) under suitable conditions (1.1 equiv $AlCl_3$), the reactions were also promoted by the Lewis acid except for DAD. The Lewis acid also affected the diastereoselectivity to enhance the *cis*(*endo*)-selectivity in the cases of Entries 10—12 compared with the thermal reaction (Table 1, Entries 6, 7, and 9).

Although the carbothioic *O*-esters **3** were less reactive than **2** under the thermal conditions as described

Table 2. Thermal HDA Reaction of **3** at 80 °C in Benzene

Entry	*O*-Thioester	Dienophile	React. time/h	Product	Yield %
1	**3a**	DMAD	5	**12a**	95
2	**3b**	DMAD	6	**12b**	96
3	**3c**	DMAD	7	**12c**	91
4	**3d**	DMAD	10	**12d**	78
5	**3c**	EP	9[a]	**13**	93
6	**3c**	MI	20[a]	**14**	Trace

a) At 110 °C in toluene.

above, the use of a Lewis acid effectively promoted the reaction of **3c** with DMAD, ethyl propiolate (EP), and MI to provide excellent results as well (Table 4). The reaction with MI highly effectively, stereoselectively gave the *cis*(*endo*) adduct **14** in good yield (Entry 9) in contrast to the uncatalyzed reaction (Table 2, Entry 6).

We have described the first example of HDA reaction of $\alpha,\beta:\gamma,\delta$-unsaturated carbodithioic esters and carbothioic *O*-esters and it is noteworthy that the reaction can be effectively promoted by the suitable use of a Lewis acid regardless of the presence of the Lewis acid-susceptible thiocarbonyl group.[12]

Experimental

The same instruments as those stated in our previous paper[10] were used for measurements of IR, MS, and NMR spectra and for elemental analysis. The ^{1}H (270 MHz) and ^{13}C NMR spectra were measured in $CDCl_3$ solvent. The ^{13}C NMR spectral data of the compounds **3**—**14** are deposited as Document No. 67055 at the Office of the Editor of Bull. Chem. Soc. Jpn. The procedures for the thermal reactions[13] and the Lewis acid-promoted reactions[12] were done as described in our previous papers.

***cis- transoid-* 12a, 12b- 9, 10, 11, 12, 12a, 12b, 13, 14-Octahydro-7-phenylthio-9,12-methano-6*H*,8a*H*-5,8-dithiabenzo[*c*]chrysene (4a):** Pale yellow cubes; mp 162—163 °C; MS (70 eV) *m/z* (rel intensity) 446 (M^+; 14), 413 (4), 243 (100); ^{1}H NMR δ=1.17—1.25 (3H, m), 1.56—1.59 (2H, m), 2.19—2.33 (3H, m), 2.47—2.63 (3H, m), 2.78—3.04 (4H, m), 3.24 (1H, dd, J=1.0, 14.2 Hz), 4.22 (1H, d, J=14.2 Hz), 7.15—7.36 (8H, m), 7.63 (1H, d, J=7.6 Hz). Found: C, 72.59; H, 6.06%. Calcd for $C_{27}H_{26}S_3$: C, 72.60; H, 5.87%.

***cis- transoid-* 12a, 12b- 9, 10, 11, 12, 12a, 12b, 13, 14-Octahydro-7-phenylthio-9,12-methano-6-methyl-6*H*, 8a*H*-5,8-dithiabenzo[*c*]chrysene (4b):** Pale yellow cubes; mp 179—180 °C; MS *m/z* 460 (M^+; 15), 427 (3), 257 (100); ^{1}H NMR δ=1.12—1.24 (3H, m), 1.30 (3H, d, J=6.9 Hz), 1.51—1.59 (2H, m), 2.18—2.23 (2H, m), 2.29—2.35 (1H, m), 2.45—2.71 (3H, m), 2.80—3.11 (4H, m), 4.50 (1H, q, J=6.9 Hz), 7.16—7.87 (8H, m), 7.67 (1H, d, J=7.3 Hz). Found: C, 73.10; H, 6.14%. Calcd for $C_{28}H_{28}S_3$: C, 72.99; H, 6.13%.

***cis- transoid-* 12a, 12b- 9, 10, 11, 12, 12a, 12b, 13, 14-Octahydro-6-phenyl-7-phenylthio-9,12-methano-6*H*, 8a*H*-5,8-dithiabenzo[*c*]chrysene (4c):** Pale yellow cubes; mp 175—176 °C; MS *m/z* 522 (M^+; 18), 489 (9),

Table 3. Lewis Acid-Promoted HDA Reaction of **2c**[a)]

Entry	Dienophile	Lewis acid	Equiv	React. time	Product	Yield %	Ratio[b)] *cis* : *trans*
1	DMAD	None	—	5 d	**5**	90	—
2	DMAD	$AlCl_3$	0.5	10 min	**5**	88	—
3	DMAD	$AlCl_3$	1.1	5 min	**5**	98	—
4	DMAD	$AlCl_3$	2.0	5 min	**5**	32	—
5	DMAD	$AlCl_3$	3.0	5 min	**5**	22	—
6	DMAD	$EtAlCl_2$	1.1	10 min	**5**	89	—
7	DMAD	BF_3·OEt_2	1.1	4 h	**5**	95	—
8	DMAD	$ZnCl_2$	1.1	2 d	**5**	94	—
9	DAD	$AlCl_3$	1.1	2 d	**6**	95	—
10	MI	$AlCl_3$	1.1	5 min	**7 7′**	90	61 : 39
11	DF	$AlCl_3$	1.1	5 min	**8 8′**	90	72 : 28
12	MA	$AlCl_3$	1.1	5 min	**10 10′**	99	93 : 7

a) In ratio of **2c** : dienophile : Lewis acid=1.0 : 3.0 : 0—3.0 in CH_2Cl_2 at ca. 18 °C. b) Determined by ^1H NMR (270 MHz) spectroscopy.

Table 4. Lewis Acid-Promoted HDA Reaction of **3c**[a)]

Entry	Dienophile	Lewis acid	Equiv	React. time	Product	Yield %
1	DMAD	None	—	10 d	**12c**	78
2	DMAD	$AlCl_3$	0.5	10 min	**12c**	94
3	DMAD	$AlCl_3$	1.1	5 min	**12c**	96
4	DMAD	$AlCl_3$	2.0	5 min	**12c**	58
5	DMAD	$AlCl_3$	3.0	5 min	**12c**	55
5	DMAD	$EtAlCl_2$	1.1	10 min	**12c**	92
6	DMAD	BF_3·OEt_2	1.1	1 d	**12c**	82
7	DMAD	$ZnCl_2$	1.1	5 d	**12c**	77
8	EP	$AlCl_3$	1.1	5 min	**13**	94
9	MI	$AlCl_3$	1.1	40 min	**14**	92

a) In ratio of **3c** : dienophile : Lewis acid=1.0 : 3.0 : 0—3.0 in CH_2Cl_2 at ca. 18 °C.

319 (100); ^1H NMR δ=1.17—1.30 (3H, m), 1.55—1.61 (3H, m), 2.24—2.62 (6H, m), 2.82—2.95 (1H, m), 3.05 (1H, d, J=7.6 Hz), 3.18 (1H, d, J=10.6 Hz), 5.67 (1H, s), 7.00—7.49 (14H, m). Found: m/z 522.1532. Calcd for $C_{33}H_{30}S_3$: M, 522.1510.

5,6-Dihydro-3,4-bis(methoxycarbonyl)-12-phenyl-1-phenylthio-4a*H*,12*H*-2,11-dithiachrysene (5): Pale yellow solids; mp 56—58 °C; IR (KBr) 1730 cm^{-1} (C=O); MS m/z 570 (M^+; 4), 537 (6), 461 (100); ^1H NMR δ=2.35—2.58 (2H, m), 2.69—2.91 (2H, m), 3.72 (3H, s), 3.79 (3H, s), 4.23 (1H, s), 5.73 (1H, s), 7.07—7.37 (13H, m), 7.52—7.55 (1H, m). Found: m/z 570.1001. Calcd for $C_{32}H_{26}O_4S_3$: M, 570.0993.

3,4-Bis(ethoxycarbonyl)-3,4,5,6-tetrahydro-12-phenyl-1-phenylthio-4a*H*,12*H*-2,11-dithia-3,4-diazachrysene (6): Colorless cubes; mp 151—153 °C; IR (KBr) 1740, 1724 cm^{-1} (C=O); MS m/z 602 (M^+; 4), 428 (2), 320 (100); ^1H NMR δ=1.17—1.25 (6H, m), 2.16—2.23 (1H, m), 2.71—2.83 (3H, m), 4.11—4.21 (4H, m), 5.32 (1H, s), 6.31 (1H, s), 7.15—7.62 (14H, m). Found: C, 63.57; H, 4.85; N, 4.69%. Calcd for $C_{32}H_{30}O_4N_2S_3$: C, 63.76; H, 5.02; N, 4.65%.

***cis*-*cisoid*-11a,11b-9,10,11,12,12a,12b,13,14-Octahydro-6,10-diphenyl-7-phenylthio-6*H*-5,8-dithia-10-azacyclopenta[*c*]chrysene-9,11-dione (7):** Pale orange cubes; mp 222—223 °C; IR (KBr) 1716 cm^{-1} (C=O); MS m/z 601 (M^+; 1), 428 (31), 319 (100); ^1H NMR δ=2.33—2.72 (3H, m), 3.01—3.44 (1H, m), 3.60 (1H, d, J=6.6 Hz), 3.90 (1H, d, J=6.6, 9.6 Hz), 4.20 (1H, d, J=9.6 Hz), 5.81 (1H, s), 7.02—7.27 (15H, m), 7.34—7.50 (4H, m). Found: C, 71.79; H, 4.60; N, 2.35%. Calcd for $C_{36}H_{27}O_2NS_3$: C, 71.85; H, 4.52; N, 2.33%.

***cis*-*transoid*- (7′):** Pale orange solid; mp 101—102 °C; IR (KBr) 1720 cm^{-1} (C=O); MS m/z 601 (M^+; 0.1), 428 (17), 319 (100); ^1H NMR δ=2.27—2.53 (3H, m), 3.11—3.24 (1H, m), 3.47 (1H, d, J=10.6 Hz), 3.70 (1H, d, J=8.9, 10.6 Hz), 4.40 (1H, d, J=8.9 Hz), 5.79 (1H, s), 6.96—7.54 (19H, m). Found: m/z 601.1204. Calcd for $C_{36}H_{27}O_2NS_3$: M, 601.1204.

(3*R,4*R**,4a*R**)-4,4a,5,6-Tetrahydro-3,4-bis(methoxycarbonyl)-12-phenyl-1-phenylthio-3*H*,12*H*-2,11-dithiachrysene (8):** Pale orange cubes; mp 150—151 °C; IR (KBr) 1732 cm^{-1} (C=O); MS m/z 572 (M^+; 0.3), 463 (4), 113 (100); ^1H NMR δ=2.16—2.27 (1H, m), 2.43—2.87 (3H, m), 3.51 (1H, d, J=4.3 Hz), 3.61 (3H, s), 3.80 (3H, s), 3.85 (1H, dd, J=2.3, 4.3 Hz), 4.28 (1H, d, J=2.3 Hz), 5.98 (1H, s), 7.08—7.48 (14H, m). Found: C, 66.85; H, 4.79%. Calcd for $C_{32}H_{28}O_4S_3$: C, 67.10; H, 4.93%.

(3*R,4*R**,4a*S**)- (8′):** ^1H NMR δ=3.51 (3H, s), 3.70 (3H, s), 6.04 (1H, s). These signals marked the difference from **8**.

4-Chloro-4-cyano-4,4a,5,6-tetrahydro-12-phenyl-1-phenylthio-3*H*,12*H*-2,11-dithiachrysene (9) or (9′): Pale orange cubes; mp 144—145 °C; MS m/z 515 (M^+; 2), 479 (11), 319 (100); ^1H NMR δ=2.17—2.55 (2H, m), 2.73—2.95 (2H, m), 3.32 (1H, d, J=13.5 Hz), 3.56 (1H, d, J=13.5 Hz), 3.71 (1H, s), 5.85 (1H, s), 7.04—7.28 (8H, m), 7.29—7.41 (5H, m), 7.53—7.56 (1H, m). Found: C, 67.52; H, 4.29; N, 2.69%. Calcd for $C_{29}H_{22}NS_3Cl$: C, 67.48; H, 4.30; N, 2.71%.

(4*R, 4a*R**)-4, 4a, 5, 6-Tetrahydro-4-methoxycarbonyl-12-phenyl-1-phenylthio-3*H*, 12*H*-2, 11-dithiachrysene (10):** Colorless needles; mp 73—74 °C; IR (KBr) 1732 cm^{-1} (C=O); MS m/z 514 (M^+; 7), 481 (8), 319 (100); ^1H NMR δ=2.01—2.07 (1H, m), 2.28—2.35 (1H, m), 2.59—2.76 (2H, m), 3.18 (1H, dd, J=4.6, 12.8 Hz), 3.31 (1H, d, J=4.6 Hz), 3.37 (1H, dd, J=5.2, 12.8 Hz), 3.59 (1H, ddd, J=4.6, 4.6, 5.2 Hz), 3.63 (3H, s), 6.09 (1H, s), 7.08—7.50

(14H, m). Found: m/z 514.1093. Calcd for $C_{30}H_{26}O_2S_3$: M, 514.1095.

(4*R,4a*S**)- (10′):** ^{1}H NMR δ=3.71 (3H, s), 6.27 (1H, s).

(4*R,4a*R**)-4,4a,5,6-Tetrahydro-4,12-diphenyl-1-phenylthio-3*H*,12*H*-2,11-dithiachrysene (11):** Pale orange cubes; mp 216—218 °C; MS m/z 532 (M^+; 0.2), 428 (26), 104 (100); ^{1}H NMR δ=1.80—2.10 (2H, m), 2.18—2.31 (1H, m), 2.34—2.49 (1H, m), 2.82 (1H, dd, J=3.6, 12.7 Hz), 3.38 (1H, d, J=5.6 Hz), 3.63 (1H, dd, J=3.9, 12.7 Hz), 3.87 (1H, ddd, J=3.6, 3.9, 5.6 Hz), 6.38 (1H, s), 7.02—7.89 (19H, m). Found: m/z 532.1332. Calcd for $C_{34}H_{28}S_3$: M, 532.1353.

(4*R,4a*S**)- (11′):** Pale oragne solids; mp 68—69 °C; MS m/z 532 (M^+; 1), 428 (45), 319 (100); ^{1}H NMR δ=1.54—1.64 (2H, m), 1.80—2.21 (2H, m), 3.08 (1H, dd, J=6.3, 12.9 Hz), 3.20 (1H, dd, J=6.6, 12.9 Hz), 3.44 (1H, d, J=7.6 Hz), 3.60 (1H, ddd, J=6.3, 6.6, 7.6 Hz), 6.01 (1H, s), 6.89—7.51 (19H, m). Found: m/z 532.1333.

5,6-Dihydro-1-methoxy-3,4-bis(methoxycarbonyl)-4a*H*,12*H*-2,11-dithiachrysene (12a): Colorless cubes; mp 141—142 °C; IR (KBr) 1722 cm^{-1} (C=O); MS m/z 416 (M^+; 22), 401 (10), 385 (100); ^{1}H NMR δ=2.41—2.52 (2H, m), 2.75—2.86 (2H, m), 3.36 (1H, d, J=1.3, 13.5 Hz), 3.70 (3H, s), 3.73 (3H, s), 3.74 (1H, d, J=1.3 Hz), 3.85 (1H, d, J=13.5 Hz), 3.87 (3H, s), 7.10—7.26 (3H, m), 7.58—7.61 (1H, m). Found: C, 60.84; H, 4.77%. Calcd for $C_{21}H_{20}O_5S_2$: C, 60.56; H, 4.84%.

5,6-Dihydro-1-methoxy-3,4-bis(methoxycarbonyl)-12-methyl-4a*H*,12*H*-2,11-dithiachrysene (12b): Colorless cubes; mp 109—110 °C; IR (KBr) 1730 cm^{-1} (C=O); MS m/z 430 (M^+; 17), 415 (5), 399 (100); ^{1}H NMR δ=1.42 (3H, d, J=6.9 Hz), 2.33—2.49 (2H, m), 2.63—2.91 (2H, m), 3.70 (3H, s), 3.74 (3H, s), 3.86 (3H, s), 3.88 (1H, s), 4.30 (1H, q, J=6.9 Hz), 7.10—7.24 (3H, m), 7.55—7.64 (1H, m). Found: C, 61.35; H, 5.13%. Calcd for $C_{22}H_{22}O_5S_2$: C, 61.37; H, 5.15%.

5,6-Dihydro-1-methoxy-3,4-bis(methoxycarbonyl)-12-phenyl-4a*H*,12*H*-2,11-dithiachrysene (12c): Pale yellow oil; IR (NaCl) 1728 cm^{-1} (C=O); MS m/z 492 (M^+; 38), 461 (100), 433 (5); ^{1}H NMR δ=2.26—2.55 (2H, m), 2.60—2.89 (2H, m), 3.56 (3H, s), 3.72 (3H, s), 3.86 (3H, s), 4.14 (1H, s), 5.35 (1H, s), 7.06—7.42 (8H, m), 7.55—7.58 (1H, m). Found: m/z 492.1065. Calcd for $C_{27}H_{24}O_5S_2$: M, 492.1065.

5,6-Dihydro-1-methoxy-3,4-bis(methoxycarbonyl)-12,12-dimethyl-4a*H*,12*H*-2,11-dithiachrysene (12d): Pale yellow solids; mp 40—42 °C; IR (KBr) 1726 cm^{-1} (C=O); MS m/z 444 (M^+; 29), 413 (100), 385 (8); ^{1}H NMR δ=1.53 (3H, s), 1.75 (3H, s), 2.44—2.50 (2H, m), 2.75—2.96 (2H, m), 3.96 (6H, s), 3.75 (1H, s), 3.84 (3H, s), 7.11—7.25 (3H, m), 7.59—7.72 (1H, m). Found: m/z 444.1062. Calcd for $C_{23}H_{24}O_5S_2$: M, 444.1065.

4-Ethoxycarbonyl-5,6-dihydro-1-methoxy-12-phenyl-4a*H*,12*H*-2,11-dithiachrysene (13): Pale yellow oil; IR (NaCl) 1710 cm^{-1} (C=O); MS m/z 448 (M^+; 8), 448 (37), 29 (100); ^{1}H NMR δ=1.28 (3H, t, J=6.9 Hz), 2.20—2.48 (2H, m), 2.74—2.99 (2H, m), 3.39 (3H, s), 4.20 (1H, dq, J=6.9, 10.9 Hz), 4.27 (1H, dq, J=6.9, 10.9 Hz), 4.72 (1H, s), 5.47 (1H, s), 7.03—7.49 (7H, m), 7.49—7.65 (2H, m), 7.72 (1H, s). Found: m/z 448.1165. Calcd for $C_{26}H_{24}O_3S_2$: M, 448.1167.

***cis-cisoid*-11a,11b-9,10,11,12,12a,12b,13,14-Octahydro-7-methoxy-6,10-diphenyl-6*H*-5,8-dithia-10-azacyclopenta[*c*]chrysene-9,11-dione (14):** Colorless cubes; mp 150—151 °C; IR (KBr)1720 cm^{-1} (C=O); MS m/z 523 (M^+; 3), 509 (12), 335 (100); ^{1}H NMR δ=2.33—2.72 (3H, m), 3.05—3.18 (1H, m), 3.47 (1H, d, J=6.9 Hz), 3.70 (3H, s), 3.73 (1H, d, J=6.9, 8.9 Hz), 4.33 (1H, d, J=8.9 Hz), 5.28 (1H, s), 7.02—7.48 (14H, m). Found: C, 70.96; H, 4.63; N, 2.46%. Calcd for $C_{31}H_{25}O_3NS_2$: C, 71.10; H, 4.81; N, 2.67%.

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9) According to the procedure reported in our previous paper,[8] **3a**—**d** were newly prepared by sulfurization of the corresponding esters starting from **1** and methyl acrylate, methyl crotonate, cinnamoyl chloride, and 3-methyl-2-butenoyl chloride, respectively; **3a**: bright red cubes; mp 51—52 °C; MS 274 (M^+); **3b**: mp 86—88 °C; MS 288 (M^+); **3c**: mp 133—134 °C; MS 350 (M^+); **3d**: bright red oil; MS 302 (M^+).

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11) The resonance of the *C-15* carbon (δ=33.8) in the ^{13}C NMR spectra of **4a**—**c** appeared upfield compared to that of the *C-7* carbon of norbornane (δ=38.7), suggesting a *trans(exo)* configuration with respect to the norbornane skeleton. The coupling constant $J_{12a-12b}$=10.6 Hz in the ^{1}H NMR spectrum of **4c** suggests that **4** is the *trans(exo)* adduct.

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