Syntheses and Reactions of Conjugated Dienic Thioketones

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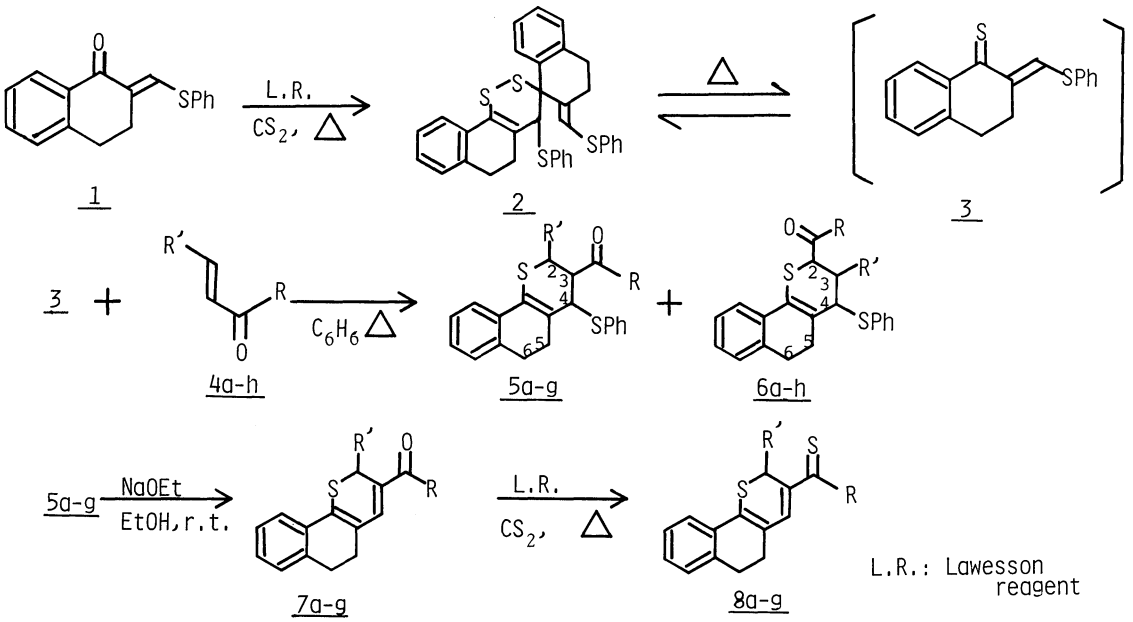
5,6-Dihydro-2-phenyl-3-thiobenzoyl-2*H*-naphtho[1,2-*b*]thiin (**8a**) and the related dienic thioketones were synthesized in 3 steps starting from 2-(phenylthio)methylenetetralin-1-thione with chalcone, 4′-chrolochalcone, 4′-methoxychalcone, 2-cinnamoylthiophen, 2-cinnamoylfuran, 1-phenyl-2-buten-1-one, and acrylophenone respetively. Similarly, 3-thiobenzoyl-2,6-diphenyl-2*H*-thiin (**8i**) was synthesized from 1-phenyl-3-phenylthio-2-propene-1-thione. All of these dienic thioketones were found to exist in stable monomeric form. The conjugated dienic thioketone (**8a**) reacted as α, β-unsaturated thioketone with 2-norbornene, 2,5-norbornadiene, diethyl azodicarboxylate, diphenyl fumarate, *N*-phenyl- and *N*-(*p*-tolyl)maleimides, 2-chloroacrylonitrile, methyl methacrylate, acrylonitrile, and styrene to give the corresponding [4+2]cycloadducts. The thioketone (**8i**) also reacted with 2-norbornene to give the corresponding cycloadduct. The reaction provides a useful method for the syntheses of various sulfur-containing heterocycles.

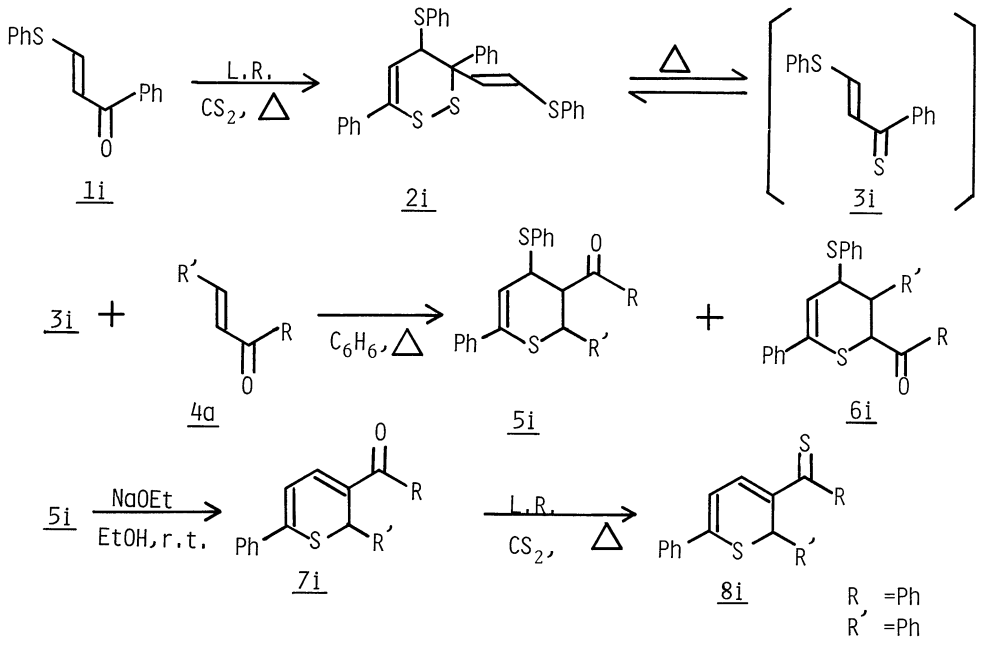
During the course of an investigation of the properties of α, β-unsaturated thioketones,[1] we have been interested in the chemistry of more highly unsaturated thioketones, viz conjugated dienic thioketones. However, so far as we know, there has been apparently no case in which the thioketone is isolated. Only a few literatures with reference to their transient generation are known. For example, Brandsma et al.[2] reported that conjugated dienic thioketones were derived as unstable intermediates from allenic thioketones formed by the thio-Claisen rearrangement of 2-alkynyl vinyl sulfides. Thioionone derivatives and 4,6-dimethyl-3,5-heptadiene-2-thione were formed from the corresponding ketones but these thioketones were unstable and readily cyclized to 2*H*-thiin derivatives.[3] Transformation of 1,5-diphenyl-2,4-pentadien-1-one to the corresponding thioketone was also unsuccessful.[4] Recently, we reported the synthesis of a stable conjugated dienic thioketone, viz 5,6-dihydro-2-phenyl-3-thiobenzoyl-2*H*-naphto[1,2-*b*]thiin **8a** in a preliminary communication.[5] This interesting result has led us to investigate the scope of the synthesis and the reaction of such dienic thioketones.

Results and Discussion

Syntheses of Conjugated Dienic Thioketones. 2-(Phenylthio)methylene-1-tetralone **1** was prepared from 1-tetralone, ethyl formate and thiophenol. Reaction of the ketone **1** with Lawesson reagent gave the dimer **2** of the corresponding thioketone **3**, whose structure was confirmed by the ^{1}H and ^{13}C NMR spectra. The thioketone monomer **3** generated by retro Diels–Alder reaction of **2** reacted with chalcone **4a** to give the cycloadduct **5a** and its regioisomer **6a**. In the ^{1}H NMR



Scheme 1.



Scheme 2.

spectrum of **5a**, signals at δ=4.13 (1H, d, J=2.8 Hz), 4.60 (1H, dd, J=2.8, 10.8 Hz), and 5.17 (1H, d, J=10.8 Hz) were assigned to the C-4, C-3, and C-2 protons, respectively. These coupling constants indicate that C-2 and C-3 protons are in axial–axial (trans) and C-3 and C-4 protons are in axial–equatorial (cis) relationships. The cycloadduct **5a** showed the signal of the C-2 proton at higher magnetic field than that of the regioisomer **6a** (δ=5.67) whereas the signal of the C-3 proton at lower field than that of **6a** (δ=4.05). The reaction of **3** with other α,β- unsaturated ketones **4b—e** gave the cycloadducts **5a—e** and their regioisomers **6e** and **6d**. All of these cycloadducts had the same steric relationships as those of **5a** with respect to their C-2, C-3, and C-4 protons. No other stereoisomer could not be obtained. Usually, the cycloadduct **5** was the major product, but in the reaction with benzal pinacolone **4h**, only the cycloadduct **6h** was formed. Presumably, the steric repulsion between phenylthio (-SPh) or C-5, C-6 ethylene groups and *t*-butyl group would prevent the formation of **5h**. The elimination of thiophenol easily took place by treatment of **5a** with sodium ethoxide at room temperature to give the dienone **7a** in nearly quantitative yield, but no reaction was observed in the case of **6a** under the same reaction conditions. The difference between the reactivity of **5a** and **6a** also indicates that electron-withdrawing benzoyl group is attached to the C-3 (not the C-2) in **5a** and thus promotes the elimination reaction. The IR absorption band of the carbonyl group of **7a** shifted to longer wavelengths region (about 50 cm^{-1}) than that of **5a** due to conjugation. Reaction of **7a** with Lawesson reagent gave the conjugated dienic thioketone **8a** as dark red crystals. The ^{1}H NMR spectrum of **8a** showed the signals at δ=2.17—2.83 (4H, m, -C<u>H</u>$_2$C<u>H</u>$_2$-), 6.23 (1H, s, Ph-C<u>H</u><), and 7.00—7.58 (15H, m, aromatic and olefinic protons). The ^{13}C NMR spectrum also showed the signals corresponding to two methylene carbons (δ=28.2, t, 28.6, t), one methine carbon (δ=42.9, d) and a thiocarbonyl carbon (δ=230.7, s). The characteristic band of the thiocarbonyl group appeared at 1148 cm^{-1} in the IR spectrum. On the basis of these data, **8a** was found to exist in monomeric form.

Similarly, other dienic thioketones **8b—g** were synthesized in relatively good yields. Starting from 1-phenyl-3-phenylthio-2-propene-1-thione **3h**,[6] monocyclic dienic thioketones **8i** was obtained.

All of these thioketones were red colored stable monomers. These results are shown in Tables 1 and 2.

Cycloaddition of Conjugated Dienic Thioketone 8a. As it has been found that the dienic thioketones **8** are unusually stable, we have examined the cycloaddition reaction of **8** to investigate whether the C=C–C=S or the C=C–C=C moiety is a reactive site.

The reaction of the dienic thioketone **8a** with 2-norbornene proceeded very slowly in benzene at room temperature. When the reaction mixture was refluxed for 4 h, the red color of the solution faded and a colorless product was obtained. The mass spectrum of the product showed the molecular ion peak of the 1:1 adduct at *m/z* 490 and the fragment ion peak corresponding to **8a** at *m/z* 396. The ^{13}C NMR spectrum of the product showed five signals of the methylene carbons, six signals of the methine carbons and sixteen signals of the unsaturated carbons but no signal of the thiocarbonyl carbon. In the ^{13}C NMR spectrum, the resonance for C-15 carbon shifted

Table 1. Yields, Melting Points, and IR Data of Cycloadducts **5** and **6**

	R	R′	Cycloadduct **5**			Cycloadduct **6**		
			Yield/%	Mp/°C	IR/cm^{-1}; C=O	Yield/%	Mp/°C	IR/cm^{-1}; C=O
a	C_6H_5	C_6H_5	63	178—181	1688	24	159—160	1690
b	*p*-ClC_6H_4	C_6H_5	83	173—175	1689	—	—	—
c	*p*-$CH_3OC_6H_4$	C_6H_5	47	158—161	1690	26	208—209	1678
d	2-Thienyl	C_6H_5	60	175—176	1665	27	144—145	1670
e	2-Furyl	C_6H_5	87	159—160	1675	—	—	—
f	C_6H_5	CH_3	55	52—55	1684	—	—	—
g	C_6H_5	H	96	142—144	1679	—	—	—
h	$(CH_3)_3C$	C_6H_5	—	—	—	71	117—119	1715
i	C_6H_5	C_6H_5	29	167—168	1695	32	119—120	1698

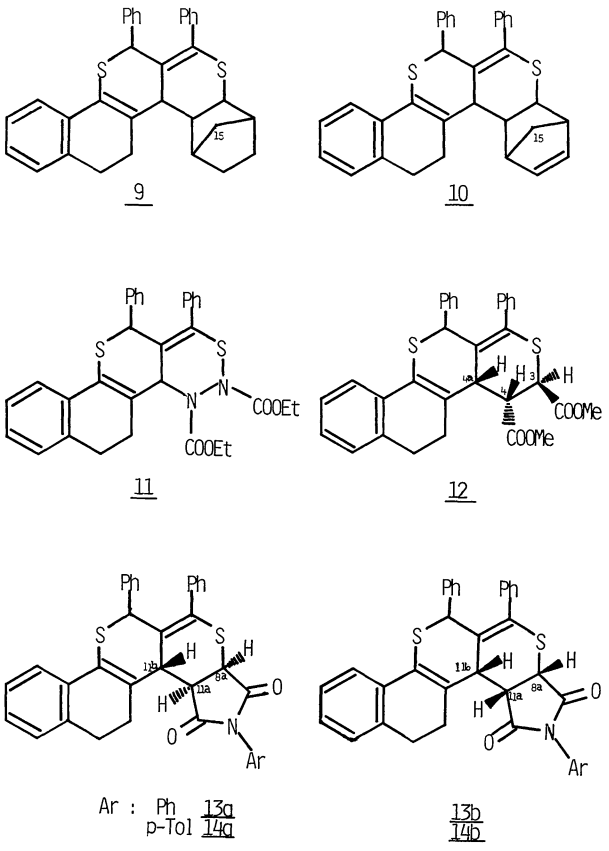
Table 2. Yields, Melting Points, and Analytical Data of Dienones **7** and Dienic Thioketones **8**

	Dienone **7**			Dienic thioketone **8**			
	Yield/%	Mp/°C	IR/cm^{-1}; C=O	Yield/%	Mp/°C	IR/cm^{-1}; C=S	^{13}C NMR/δ, C=S
a	90	123—124	1632	74	72—74	1148	230.7
b	73	153—155	1630	88	74—76	1148	228.2
c	83	102—103	1658	56	72—74	1147	237.5
d	83	126—127	1616	70	139—140	1142	217.0
e	79	Oil	1613	56	72—74	1145	208.8
f	100	Oil	1630	80	76—78	1148	229.9
g	60	106—107	1624	48	72—74	1144	229.7
i	90	146—147	1628	60	71—73	1156	231.9

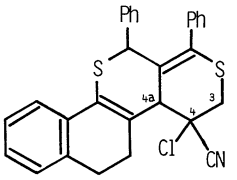
upfield by 4.8 ppm from that of C-7 carbon of norbornane (δ=38.7). Therefore, **9** would be *exo* with respect to the norbornyl skeleton.[7] These data supported that the product **9** was formed by the [4+2]cycloaddition reaction of norbornene with the C=C–C=S moiety of **8a**.

Similarly, thioketone **8a** reacted with 2,5-norbornadiene, diethyl azodicarboxylate (DAD), dimethyl fumarate, *N*-phenyl- and *N*-(*p*-tolyl)maleimides to give the corresponding cycloadducts **10—14**. In all cases, **8a** reacted as an α,β-unsaturated thioketone. The reaction with 2,5-norbornadiene also gave the *exo* cycloadduct **10**. In the ^{13}C NMR spectrum, the resonance of the C-15 carbon (δ=43.1) shifted upfield from that of the C-7 carbon of norbornene (δ=48.8).[7] In the cycloadduct **12**, the coupling constants of the C-3 proton (δ=4.29, J=2.1 Hz) and C-4a proton (δ=3.46, J=4.2 Hz) indicated that the C-3 and C-4 protons are in equatorial-equatorial (trans) and the C-4 and C-4a protons are in equatorial—axial (cis) relationships.

In the case of the reaction with *N*-phenylmaleimide, two stereoisomeric adducts, **13a** and **13b**, were obtained. The ^{1}H NMR spectrum of **13a** showed the signals at δ=3.47 (1H, d, J=10.2 Hz, C-11b proton), 3.75 (1H, dd, J=8.4 and 10.2 Hz, C-11a) and 4.60 (1H, d, J=8.4 Hz, C-8a),while, those of **13b** showed signals at δ=3.68 (1H, d, J=7.2 Hz), 3.95 (1H, dd, J=7.2 and 9.0 Hz), and 4.45 (1H, d, J=9.0 Hz), respectively. From these data, it seems reasonable to assume that **13a** has *exo* configuration and **13b** has *endo* one. The reaction with *N*-(*p*-tolyl)maleimide also gave two stereoisomeric adducts, **14a** and **14b**.



Cycloaddition reactions of **8a** with some unsymmetrical dienophiles such as 2-chloroacrylonitrile, methyl methacrylate, acrylonitrile and styrene resulted in the products **15—18** regioselectively in which the methylene carbons of the dienophiles combined to the sulfur atom of **8a**. The orientation of the addition of the dienophiles is the same as those of the reactions with thiochalcone or 2-arylmethylenetetralin-1-thione.[1] For example, the reaction with 2-chloroacrylonitrile gave an adduct **15**. In the ^{1}H NMR spectrum, the signal of the doublets at δ=3.56 and 3.72 (J=13.0 Hz) were assigned to the nonequivalent C-3 methylene protons, the singlet at δ=3.74 to the C-4a and the singlet at δ=4.90 to the C-12 protons respectively. The ^{1}H NMR spectrum of **16** showed the similar pattern to that of **15**, though long-range coupling (J=1.2 Hz) between the C-3 (axial) and C-4a protons was observed. But the spectrum of **17** was not clear to prove its stereochemistry. The reaction with styrene gave two products which could be separated by preparative TLC. These adducts were epimers to each other with respect to the C-4 carbon and the phenyl group is axial in **18a** and equatorial in **18b**.[8]



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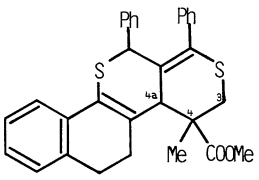

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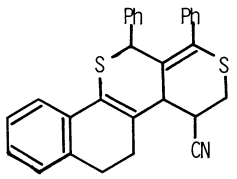

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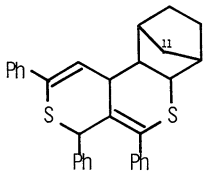

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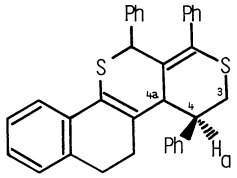
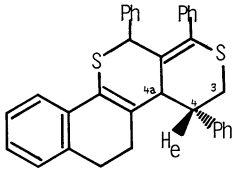


18a
H_a : axial



18b
H_e : equatorial

Thioketone **8a** did not react with electron-rich olefins, such as butyl vinyl ether, and 1-morpholino-1-cyclohexene.

The monocyclic dienic thioketone **8i** also reacted with 2-norbornene to give the corresponding adduct **19** which had *exo* configuration similar to **9**. The reaction proceeded more rapidly than that of **8a** to give the adduct in higher yield. In these cycloaddition reactions, no regioisomer or stereoisomer was not obtained except for the adducts **13**, **14**, and **18**. These results are shown in Table 3.

Previously, we reported that the cycloaddition reaction of α,β-and $\alpha,\beta,\alpha',\beta'$-unsaturated thioketones afforded dihydrothiin[1] and tetrahydro-1-benzothiin derivatives.[9] The present syntheses starting from **8** provide the third useful synthetic method for the preparation of a different type of sulfur-containing heterocycles, viz dihydro-2,7-dithianaphthalene derivatives. Another remarkable result is that all of the dienic thioketones **8** were obtained in monomeric form as stable crystals.

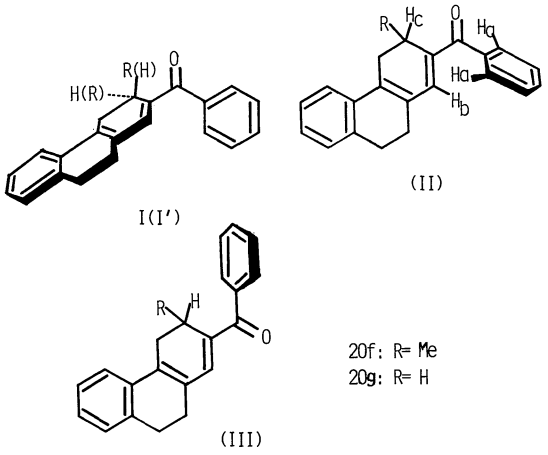
Three kinds of stable α, β-unsaturated thioketones have been known in the literatures. The first group are β-amino α,β-unsaturated thioketones[10] which are stabilized by electron-donating resonance effect of β-amino groups. The second group are 3-arylmethylenebornane-2-thiones[11] in which C=C–C=S moiety in the molecule are sterically blocked by bulky neighboring groups. The third category of stable α,β-unsaturated thioketones are 2-cyclohexene-1-thione and relat-

Table 3. Cycloaddition Reactions of Dienic Thioketones with Dienophiles

Entry	Dienophile	Reaction time	Product	Yield	Mp	IR
		h		%	°C	cm^{-1}
1	2-Norbornene	4	**9**	50	226—227	—
2	2,5-Norbornadiene	4	**10**	45	228—230	—
3	DAD	4	**11**	59	170—171	1740, 1305 (COO–)
4	Dimethyl fumarate	5	**12**	73	158—160	1731 (C=O)
5	*N*-Phenylmaleimide	2	**13a**	42	147—148	1784, 1720 (C=O)
			13b	47	228—229	1784, 1720 (C=O)
6	*N*-(*p*-Tol)maleimide	2	**14a**	43	189—192	1784, 1717 (C=O)
			14b	44	248—251	1784, 1718 (C=O)
7	2-Chloroacrylonitrile	7	**15**	46	189—191	—
8	Methyl methacrylate	3	**16**	84	202—203	1748, 1168 (COO–)
9	Acrylonitrile	3	**17**	56	208—209	2244 (C≡N)
10	Styrene	3	**18a**	56	109—111	—
			18b	21	101—102	—
11	2-Norbornene (**8i**)	1	**19**	70	209—211	—

ed *exo*-cyclic thioketones.[12] In these compounds, C=C and C=S bonds are constrained in a *transoid* form, so they do not take part in dimerization and exist in monomeric form. Previously, we have considered that **8a** is the stable thioketone belonged to the third category[5] but the stability of **8g** and **8i** could not be explained well by such concept.

Accordingly, the conformational analysis of **8** was performed by the calculation of molecular mechanics using the MM2PP program.[13] Since necessary parameters for the calculation of **8** could not be obtained, dienic ketones 2-benzoyl-3-methyl-3,4,9,10-tetrahydrophenanthrene **20f** and 2-benzoyl-3,4,9,10-tetrahydrophenanthrene **20g** were selected as model



molecules. The result of the calculation for **20g** revealed that there are three stable conformations I, II, and III with the rotation about the =C–CO– and –CO–Ph bonds. In the most stable conformation I, the tetrahydrophenanthrene ring is nearly perpendicular to the benzoyl group. In the *transoid* conformation II (less stable) and *cisoid* conformation III (the least stable), phenyl group is out of a plane of the other part of the molecule. Difference of the energy between the conformations I and III and the energy barrier for the conversion from I to III were estimated as 2.0 and 5.7 kcal mol^{-1}. In the dienic ketone **20f**, there exist two stable conformations (I and I′) having nearly the same stability. However, differences of the energy between the conformation I (I′) and III increased to 4.9 kcal mol^{-1} and the energy barriers for the conversion from I to III and from I′ to III were 5.5 and 7.7 kcal mol^{-1}, respectively.[14] These results clearly indicate that the conformation I becomes more stable in the methyl substituted dienic ketone **20f** than in non-substituted compound **20g**. The result can be explained by considering that the tetrahydrophenanthrene ring, carbonyl, and phlenyl group in **20** can not be coplanar due to the steric replusion between the hydrogen atom H_a and H_b, H_c or methyl group, and in three conformations I (I′), II, and III, the conformations I and I′ would gain the largest stabilization from the resonance between the carbonyl and phenyl group.

These results would be approximately applicable to dienic thioketones **8f** and **8g** and also **8a—e**. No tendency for dimerization and low reactivity towards dienophiles of **8** are thus reasonably recognized by such nonplanar C=C–C=S system and the energy barrier between the cisoid (III) and stable (I (I′)) conformations.

Experimental

All melting points were uncorrected. ^{1}H NMR spectra were determined on a JEOL JNM PMX 60SI, FX-100 or Varian PX-400 spectrometer in $CDCl_3$ solvent and ^{13}C NMR spectra were recorded on a JEOL JNM FX-100 spectrometer in $CDCl_3$. TMS was used as an internal standard. IR and UV spectra were measured with Hitachi 270-30 and 320. Mass spectra were measured on a Hitachi mass spectrometer RMU-7M (70 eV) or M-80 with a data processing system M-003. Elemental analyses were performed using a Yanagimoto Model MT-3 CHN corder.

2-(Phenylthio)methylene-1-tetralone **1** was prepared from 1-tetralone, ethyl formate, and thiophenol by the methods which were virtually identical with those of Kochetkov[15] and of Engelhard.[16] (**1**) : Yellow needles; mp 59—60 °C; MS *m/z* 266 (M^+; 100), 233 (19), 189 (67), 157 (19); IR (KBr) 1651 cm^{-1} (C=O); ^{1}H NMR δ=2.92 (4H,s), 7.03—7.63 (7H,m), 7.77—8.20 (2H,m). Found: C, 76.50; H, 5.31%. Calcd for $C_{17}H_{14}OS$: C, 76.66; H, 5.30%. Similarly, 1-phenyl-3-phenylthio-2-propen-1-one (**1i**) was prepared according to the method of Engelhard.[16] Chalcone, 4′-chlorochalcone, 4′-methoxychalcone, 2-cinnamoylthiophene, 2-cinnamoylfuran, benzal pinacolone, and 1-phenyl-2-buten-1-one were prepared by aldol condensation, respectively. Acrylophenone[17] was prepared by elimination of HCl from 3-chloropropiophenone. Lawesson reagent was prepared by the method given in the literature.[18]

Thionation of 1. A suspension of the ketone **1** (15.0 mmol) and Lawesson reagent (8.66 mmol) in carbon disulfide (100 cm^3) was refluxed for 5 h under a nitrogen atmosphere. The reaction mixture was passed through a short column of Florisil gel using benzene–hexane (1:1) as an eluent, and the solvent was removed. The colorless needles were recrystallized from benzene/hexane in a freezer.

2-(Phenylthio)methylenetetralin-1-thione Dimer (2): Colorless needles; mp 120—122 °C; yield 46%; MS *m/z* 282 (M^+/2;7), 205 (100), 171 (7); ^{1}H NMR δ=2.10—3.05 (8H, m), 4.77 (1H, s), 6.40 (1H, s), 6.63—7.97 (18H, m); ^{13}C NMR δ=25.6 (t), 28.2 (t), 29.7 (t), 30.6 (t), 57.3 (s), 64.2 (d). Found: C, 72.41; H, 4.81%. Calcd for $C_{34}H_{28}S_4$: C, 72.30; H, 5.00%

A Typical Procedure for the Cycloaddition of Thione 3 with Ketones 4. A solution of the thioketone dimer **2** (3.55 mmol/monomer) and chalcone **4** (3.90 mmol) in benzene (10 cm^3) was refluxed for 2 h under a nitrogen atmosphere. The reaction mixture was chromatographed on Wakogel C-200 with benzene–hexane (1:1) as an eluent. The desired dihydrothiin **5a** and its regioisomer **6a** were separated by recrystallization from ethanol.

3-Benzoyl-3,4,5,6-tetrahydro-2-phenyl-4-phenylthio-2*H*-naphto[1,2-*b*]thiin (5a); Colorless needles; MS *m/z* 380 (M^+-PhSH; 5), 275 (29), 205 (100), 131 (15), 110 (12), 105 (22);

^{1}H NMR δ=2.22—2.98 (4H,m), 4.13 (1H, d, *J*=2.8 Hz), 4.60 (1H, dd *J*=2.8, 10.8 Hz), 5.17 (1H, d, *J*=10.8 Hz), 6.88—7.47 (19H, m); ^{13}C NMR δ=28.5 (t), 30.2 (t), 42.5 (d), 50.7 (d), 54.8 (d), 192.3 (s; C=O). Found: C, 78.40; H, 5.36%. Calcd for $C_{32}H_{26}OS_2$: C, 78.33; H, 5.34%

2-Benzoyl-3,4,5,6-tetrahydro-3-phenyl-4-phenylthio-2*H*-naphto[1,2-*b*]thiin (6a): Colorless cubes; MS *m/z* 380 (M^+-PhSH; 7), 275 (100), 241 (8), 205 (38), 110 (53), 105 (34); ^{1}H NMR δ=2.30—2.83 (4H, m), 3.87 (1H, d, *J*=2.8 Hz), 4.05 (1H, dd, *J*=2.8, 10.8 Hz), 5.67 (1H, d, *J*=10.8 Hz), 6.87—7.44 (17H, m), 7.83—7.93 (2H, m); ^{13}C NMR δ=28.2 (t), 30.2 (t), 43.5 (d), 45.3 (d), 59.0 (d), 194.5 (s; C=O). Found: C, 78.32; H, 5.35%. Calcd for $C_{32}H_{26}OS_2$: C, 78.33; H, 5.34%.

3-(*p*-Chlorobenzoyl)-3,4,5,6-tetrahydro-2-phenyl-4-phenylthio-2*H*-naphto[1,2-*b*]thiin (5b): MS *m/z* 415 (M^+-PhS; 9), 275 (29), 241 (28), 205 (100), 139 (30), 110 (10); ^{1}H NMR δ=2.45—3.15 (4H, m), 4.18 (1H, d, *J*=3.2 Hz), 4.61 (1H, dd, *J*=3.2, 11.0 Hz), 5.22 (1H, d, *J*=11.0 Hz), 6.83—7.60 (18H, m). Found: C, 73.20; H, 4.75%. Calcd for $C_{32}H_{25}OS_2Cl$: C, 73.19; H, 4.80%.

3-(*p*-Anisoyl)-3,4,5,6,-tetrahydro-2-phenyl-4-phenylthio-2*H*-naphto[1,2-*b*]thiin (5c): MS *m/z* 411 (M^+-PhS; 17), 282 (61), 275 (27), 238 (54), 205 (100), 135 (54), 110 (15); ^{1}H NMR δ=2.55—2.93 (4H, m), 3.77 (3H, s), 4.20 (1H, d, *J*=2.4 Hz), 4.60 (1H, dd, *J*=2.4, 10.0 Hz), 5.20 (1H, d, *J*=10.0 Hz), 6.62—7.57 (18H, m). Found: C, 76.16; H, 5.42%. Calcd for $C_{33}H_{28}O_2S_2$: C, 76.12; H, 5.42%.

2-(*p*-Anisoyl)-3,4,5,6-tetrahydro-3-phenyl-4-phenylthio-2*H*-naphto[1,2-*b*]thiin (6c): MS *m/z* 411 (M^+-PhS; 70), 275 (100), 241 (7), 238 (6), 205 (15), 135 (44), 110 (26); ^{1}H NMR δ=2.22—2.92 (4H, m), 3.77 (3H, s), 3.90 (1H, d, *J*=3.2 Hz), 4.13 (1H, dd, *J*=3.2, 11.2 Hz), 5.67 (1H, d, *J*=11.2 Hz), 6.38—7.65 (16H, m), 8.00 (2H, d, *J*=9.0 Hz). Found: C, 76.12; H, 5.41%. Calcd for $C_{33}H_{28}OS_2$: C, 76.12; H, 5.42%.

3,4,5,6,-Tetrahydro-2-phenyl-4-phenylthio-3-(2-thenoyl)-2*H*-naphto[1,2-*b*]thiin (5d): MS *m/z* 387 (M^+-PhS; 6), 275 (100), 241 (6), 213 (6), 205 (15), 111 (48), 110 (29); ^{1}H NMR δ=2.63—2.98 (4H, m), 3.95 (1H, d, *J*=3.2 Hz), 4.46 (1H, dd, *J*=3.2, 10.0 Hz), 5.18 (1H, d, *J*=10.0 Hz), 6.83—7.52 (17H, m). Found: C, 72.27; H, 4.85%. Calcd for $C_{30}H_{24}OS_3$: C, 72.54; H, 4.87%.

3,4,5,6-Tetrahydro-3-phenyl-4-phenylthio-2-(2-thenoyl)-2*H*-naphto[1,2-*b*]thiin (6d): MS *m/z* 387 (M^+-PhS; 7), 275 (40), 241 (3), 213 (35), 205 (31), 110 (100); ^{1}H NMR δ=2.32—2.88 (4H, m), 3.93 (1H, dd, *J*=2.8, 10.8 Hz), 4.13 (1H, d, *J*=2.8 Hz), 5.58 (1H, d, *J*=10.8 Hz), 6.82—7.50 (15H, m), 7.65 (1H, d *J*=6.0 Hz), 7.93 (1H, d, *J*=4.0 Hz). Found: C, 72.57: H, 4.72%. Calcd for $C_{30}H_{24}OS_3$: C, 72.54; H 4.87%.

3-(2-Furoyl)-3,4,5,6-tetrahydro-2-phenyl-4-phenylthio-2*H*-naphto[1,2-*b*]thiin (5e): MS *m/z* 371 (M^+-PhS; 10), 275 (100), 249 (23), 242 (7), 205 (33), 197 (16), 110 (41), 95 (31); ^{1}H NMR δ=2.43—3.13 (4H, m), 4.33 (1H, d, *J*=2.8 Hz), 4.48 (1H, dd, *J*=2.8, 10.8 Hz), 5.17 (1H, d, *J*=10.8 Hz), 6.23 (1H, dd, *J*=1.6, 3.2 Hz), 6.65 (1H, d, *J*=3.2 Hz), 6.97—7.52 (15H, m). Found: C, 74.84; H, 4.94%. Calcd for $C_{30}H_{24}O_2S_2$: C, 74.97; H, 5.03%.

3-Benzoyl-3,4,5,6-tetrahydro-2-methyl-4-phenylthio-2*H*-naphto[1,2-*b*]thiin (5f): MS *m/z* 428 (M^+; 1), 318 (4), 303 (3), 218 (12), 213 (19), 110 (100), 105 (31); ^{1}H NMR δ=1.55 (3H, d, *J*=7.4 Hz), 2.28—3.15 (4H, m), 3.88—4.99 (3H, m), 6.97—7.78 (14H, m). Found: C 75.65, H 5.30%. Calcd for $C_{27}H_{24}OS_2$: C, 75.66; H, 5.64%.

3-Benzoyl-3,4,5,6-tetrahydro-4-phenylthio-2*H*-naphto[1,2-*b*]thiin (5g): MS *m/z* 304 (M^+-PhSH; 25), 199 (65), 110 (33), 105 (100); ^{1}H NMR δ=2.20—2.92 (4H, m), 3.12 (1H, ddd, *J*=2.0, 2.0, 13.0 Hz), 3.68 (1H, dd, *J*=11.5, 13.0 Hz), 4.00—4.28 (2H, m), 6.84—7.62 (14H, m); ^{13}C NMR δ=23.4 (t), 28.4 (t), 30.6 (t), 47.3 (d), 53.8 (d), 198.6 (s; C=O). Found: C, 75.16; H, 5.36%. Calcd for $C_{26}H_{22}OS_2$: C, 75.32; H, 5.35%.

3,4,5,6-Tetrahydro-3-phenyl-4-phenylthio-2-pivaloyl-2*H*-naphto[1,2-*b*]thiin (6h): MS *m/z* 470 (M^+; 2), 361 (55), 275 (8), 205 (39), 131 (100), 110 (16); ^{1}H NMR δ=1.17 (9H, s), 2.22—2.88 (4H, m), 3.82—4.05 (2H, m), 5.17 (1H, d, *J*=12.0 Hz), 7.05—7.47 (14H, m); ^{13}C NMR δ=26.8 (q), 28.0 (t), 30.1 (t), 43.6 (d), 44.6 (s), 46.3 (d), 57.9 (d), 210.4 (s; C=O). Found: C, 76.63; H, 6.46%. Calcd for $C_{30}H_{30}OS_2$; C, 76.55; H, 6.42%.

3-Benzoyl-3,4-dihydro-2,6-diphenyl-4-phenylthio-2*H*-thiin (5i): MS *m/z* 355 (M^+-PhS; 16), 249 (17), 233 (8), 105 (100); ^{1}H NMR δ=4.32 (1H, dd, *J*=2.3, 6.2 Hz), 4.51 (1H, dd, *J*=2.3, 11.0 Hz), 4.95 (1H, d, *J*=11.0 Hz), 6.18 (1H, d, *J*=6.2 Hz), 6.90—7.75 (20H, m). Found: C, 77.70; H, 5.19%. Calcd for $C_{30}H_{24}OS_2$: C, 77.55; H, 5.21%.

2-Benzoyl-3,4-dihydro-3,6-diphenyl-4-phenylthio-2*H*-thiin (6i): MS *m/z* 355 (M^+-PhS; 42), 339 (7), 249 (42), 208 (26), 179 (71), 109 (20), 105 (100); ^{1}H NMR δ=4.00 (1H, dd, *J*=4.8, 8.0 Hz), 4.51 (1H, dd, *J*=4.8, 5.0 Hz), 5.17 (1H, d, *J*=8.0 Hz), 6.20 (1H, d, *J*=5.0 Hz), 7.60—7.10 (18H, m), 7.80—8.00 (2H, m). Found: C, 77.36; H, 5.70%. Calcd for $C_{30}H_{24}OS_2$: C, 77.55; H, 5.21%.

A Typical Procedure for the Elimination of Benzenethiol from the Cycloadducts 5. To a solution of the cycloadduct **5** (2.04 mmol) in benzene (20 cm^3) was added sodium ethoxide (sodium metal 10.9 mmol in ethanol 30 cm^3). After stirring overnight, water was added to the mixture, and the product was extracted with diethyl ether. The solvent was removed and the residue was chromatographed on Wakogel C-200 with ethyl acetate–hexane (1:4). The dienone **7a** of yellow cubes was recrystallized from diethyl ether–hexane.

3-Benzoyl-5,6-dihydro-2-phenyl-2*H*-naphto[1,2-*b*]thiin (7a): MS *m/z* 380 (M^+; 3), 303 (1), 275 (100), 241 (5), 218 (10), 109 (10), 105 (10); ^{1}H NMR δ=2.23—2.80 (4H, m), 5.57 (1H, s), 6.98—7.68 (15H, m). ^{13}C NMR δ=28.1 (t), 28.6 (t), 39.3 (d), 195.6 (s). UV (cyclohexane) 259 nm (log ε, 4.05), 306 (4.07), 427 (4.12). Found: C, 81.93; H, 5.22%. Calcd for $C_{26}H_{20}OS$: C, 82.07; H, 5.30%.

3-(*p*-Chlorobenzoyl)-5,6-dihydro-2-phenyl-2*H*-naphto[1,2-*b*]thiin (7b): MS *m/z* 414 (M^+; 3), 337 (6), 275 (100), 241 (4), 139 (9); ^{1}H NMR δ=2.22—3.05 (4H, m), 5.55 (1H, s), 6.99—7.64 (14H, m); ^{13}C NMR δ=28.0 (t), 28.5 (t), 39.3 (d), 194.1 (s). Found: C, 75.12; H, 4.78%. Calcd for $C_{26}H_{19}OSCl$: C, 75.26; H, 4.62%.

3-(*p*-Anisoyl)-5,6-dihydro-2-phenyl-2*H*-naphto[1,2-*b*]thiin (7c): MS *m/z* 410 (M^+; 6), 333 (1), 275 (100), 241 (5), 135 (87); ^{1}H NMR δ=2.18—3.17 (4H, m), 3.80 (3H, s), 5.48 (1H, s), 6.87 (2H, d, *J*=9.6 Hz), 6.98 (1H, s), 7.03—7.48 (9H, m), 7.65 (2H, d, *J*=9.6 Hz); ^{13}C NMR δ=28.1 (t), 28.7 (t), 39.7 (d), 55.4 (q), 194.4 (s). Found: C, 79.05; H, 5.25%. Calcd for $C_{27}H_{22}O_2S$: C, 78.99; H, 5.40%.

5,6-Dihydro-2-phenyl-3-(2-thenoyl)-2*H*-naphto[1,2-*b*]thiin (7d): MS *m/z* 386 (M^+; 6), 275 (100), 241 (4), 111 (8); ^{1}H NMR δ=2.40—3.07 (4H, m), 5.50 (1H, s), 7.00—7.70 (13H, m). ^{13}C NMR δ=28.1 (t), 28.7 (t), 40.0 (d), 186.2 (s). Found: C, 74.57; H, 4.69%. Calcd for $C_{24}H_{18}OS_2$: C, 74.58; H, 4.69%.

3-(2-Furoyl)-5,6-dihydro-2-phenyl-2*H*-naphto[1,2-*b*]thiin (7e): MS *m/z* 370 (M^+; 6), 341 (1), 275 (100), 241 (37); ^{1}H NMR δ=2.40—3.10 (4H, m), 5.58 (1H, s), 6.52 (1H, dd, *J*=1.6, 3.2 Hz), 7.06—7.75 (12H, m); ^{13}C NMR δ=28.1 (t), 28.8 (t), 39.1 (d), 180.3 (s). Found: C, 77.84; H, 5.18%. Calcd for $C_{24}H_{18}O_2S$: C, 77.81; H, 4.90%.

3-Benzoyl-5,6-dihydro-2-methyl-2*H*-naphto[1,2-*b*]thiin (7f): MS *m/z* 318 (M^+; 14), 303 (13), 213 (100), 178 (9), 165 (12), 115 (9), 105 (27); ^{1}H NMR δ=1.34 (3H, d, *J*=7.0 Hz), 2.20—2.96 (4H, m), 4.38 (1H, q, *J*=7.0 Hz), 6.76 (1H, s), 6.07—6.72 (9H, m); ^{13}C NMR δ=20.6 (q), 28.1 (t), 28.6 (t), 32.1 (d), 195.4 (s). Found: *m/z* 318.1083. Calcd for $C_{21}H_{18}OS$: M, 318.1074.

3-Benzoyl-5,6-dihydro-2*H*-naphto[1,2-*b*]thiin (7g): MS *m/z* 304 (M^+; 23), 199 (100), 165 (12), 105 (39); ^{1}H NMR δ=2.39—2.60 (2H, m), 2.73—2.95 (2H, m), 3.82 (2H, s), 6.78 (1H, s), 7.08—7.74 (9H, m); ^{13}C NMR δ=24.6 (t), 28.0 (t), 28.4 (t), 195.1 (s). Found: C, 78.72; H, 5.44%. Calcd for $C_{20}H_{16}OS$: C, 78.91; H, 5.30%.

3-Benzoyl-2,6-diphenyl-2*H*-thiin (7i): MS *m/z* 354 (M^+; 4), 249 (100), 121 (9), 105 (29), 77 (26); ^{1}H NMR δ=5.68 (1H, s), 6.68 (1H, d, *J*=8.0 Hz), 7.19 (1H, d, *J*=8.0 Hz), 7.20—7.83 (15H, m); ^{13}C NMR δ=39.8 (d), 116.5 (d), 126.3 (d), 126.7 (d, 2C), 127.7 (d, 2C), 128.1 (d, 2C), 128.4 (d, 2C), 128.5 (d, 2C), 128.8 (d, 2C), 129.9 (d), 131.2 (d), 136.8 (s), 138.5 (s), 138.8 (d), 141.3 (s), 144.0 (s), 195.5 (s). UV (cyclohexane) 401 nm (log ε, 4.09). Found: C, 81.27; H, 5.30%. Calcd for $C_{24}H_{18}OS$: C, 81.32; H, 5.12%.

A Typical Procedure for the Thionation of Dienones 7. A suspension of the dienone **7a** (1.84 mmol) and Lawesson reagent (1.24 mmol) in carbon disulfide (50 cm^3) was refluxed for 5 h under a nitrogen atmosphere. The solvent was removed and the residue was passed through a short column of Florisil gel using benzene–hexane (1:1) as an eluent. After the evaporation of the first red fraction, dienic thioketone **8a** was recrystallized from hexane.

5,6-Dihydro-2-phenyl-3-thiobenzoyl-2*H*-naphto[1,2-*b*]thiin (8a): Red rhombics; MS *m/z* 396 (M^+; 100), 393 (69), 287 (28), 275 (69), 241 (23), 198 (9), 121 (39); ^{1}H NMR δ=2.17—2.83 (4H, m), 6.23 (1H, s), 7.00—7.58 (15H, m); ^{13}C NMR δ=28.2 (t), 28.6 (t), 42.9 (d), 230.7 (s). UV (cyclohexane) 271 nm (log ε, 3.96), 338 (3.96), 498 (4.08). Found: 78.59; H, 5.16%. Calcd for $C_{26}H_{20}S_2$: C, 78.74; H, 5.08%.

3-(*p*-Chrolothiobenzoyl)-5,6-dihydro-2-phenyl-naphto-[1,2-*b*]thiin (8b): Red rhombics; MS *m/z* 430 (M^+; 69), 428 (69), 397 (25), 351 (17), 307 (25), 275 (100), 154 (22); ^{1}H NMR δ=2.33—2.90 (4H, m), 6.23 (1H, s), 7.10—7.60 (14H, m); ^{13}C NMR δ=28.1 (t), 28.5 (t), 42.9 (d), 228.2 (s). Found: C, 72.47; H, 4.44%. Calcd for $C_{26}H_{19}S_2Cl$: C, 72.45; H, 4.44%.

5,6-Dihydro-2-phenyl-3-(*p*-thioanisoyl)-2*H*-naphto[1,2-*b*]-thiin (8c): Red crystals; MS *m/z* 426 (M^+; 100), 394 (48), 349 (8), 318 (9), 305 (20), 286 (22), 275 (16), 151 (59), 121 (13); ^{1}H NMR δ=1.99—2.99 (4H, m), 3.89 (3H, s), 6.15 (1H, s), 6.81 (2H, d, *J*=9.6 Hz), 7.00—7.37 (10H, m), 7.55 (2H, d, *J*=9.6 Hz); ^{13}C NMR δ=36.0 (t), 36.4 (t), 51.7 (d), 63.3 (q), 237.5 (s). Found: *m/z* 426.1119. Calcd for $C_{27}H_{22}OS_2$: M, 426.1107.

5,6-Dihydro-2-phenyl-3-(2-thiothenoyl)-2*H*-naphto[1,2-*b*]-thiin (8d): Red plates; MS *m/z* 402 (M^+; 20), 368 (68), 275 (100); ^{1}H NMR δ=2.37—2.88 (4H, m), 5.93 (1H, s), 6.95—7.37 (11H, m), 7.43 (1H, dd, *J*=1.2, 4.0 Hz), 7.58 (1H, dd, *J*=1.2, 5.6 Hz); ^{13}C NMR δ=28.2 (t), 28.6 (t), 44.8 (d), 217.0 (s). Found: C, 71.63; H, 4.64%. Calcd for $C_{24}H_{18}S_3$: C, 71.60; H, 4.51%.

5,6-Dihydro-2-phenyl-3-(2-thiofuroyl)-2*H*-naphto[1,2-*b*]-thiin (8e): Red crystals; MS *m/z* 386 (M^+; 25), 384 (23), 355 (25), 352 (11), 275 (71), 33 (100); ^{1}H NMR δ=2.28—2.98 (4H, m), 5.99 (1H, s), 6.50 (1H, dd, *J*=1.8, 3.5 Hz), 6.84—7.60 (10H, m), 7.45 (1H, s), 7.68 (1H, dd, *J*=0.8, 1.8 Hz); ^{13}C NMR δ=28.2 (t), 28.7 (t), 44.0 (d), 208.8 (s). Found: *m/z* 386.0811. Calcd for $C_{24}H_{18}OS_2$: M 386.0795.

5,6-Dihydro-2-methyl-3-thiobenzoyl-2*H*-naphto[1,2-*b*]thiin (8f): Red crystals; MS *m/z* 334 (M^+; 46), 318 (17), 301 (40), 213 (100); ^{1}H NMR δ=1.36 (3H, d, *J*=6.5 Hz), 2.20—2.97 (4H, m), 5.06 (1H, q, *J*=6.5 Hz), 6.87 (1H, s), 7.02—7.73 (9H, m); ^{13}C NMR δ=19.9 (q), 28.1 (t), 28.5 (t), 35.6 (d), 229.9 (s). Found: C, 75.05; H, 5.02%. Calcd for $C_{21}H_{18}S_2$: C, 75.40; H, 5.42%.

5,6-Dihydro-3-thiobenzoyl-2*H*-naphto[1,2-*b*]thiin (8g): Red crystals; MS *m/z* 320 (M^+; 100), 287 (39), 199 (88), 165 (27), 121 (83); ^{1}H NMR δ=2.37—2.60 (2H, m), 2.66—2.95 (2H, m), 4.22 (2H, s), 6.84 (1H, s), 7.00—7.74 (9H, m); ^{13}C NMR δ=28.1 (t), 28.5 (t), 28.8 (t), 229.7 (s). Found: *m/z* 320.0672. Calcd for $C_{20}H_{16}S_2$: M, 320.0690.

3-Thiobenzoyl-2,6-diphenyl-2*H*-thiin (8i): Red crystals; MS *m/z* 370 (M^+; 100), 338 (86), 294 (89), 261 (23), 121 (48), 77 (18); ^{1}H NMR δ=6.27 (1H, s) 6.64 (1H, d, *J*=10.0 Hz), 7.18 (1H, d, *J*=10.0 Hz), 6.83—7.60 (15H, m); ^{13}C NMR δ=43.5 (d), 118.0 (d), 126.9 (d), 127.5 (d, 2C), 127.7 (d, 2C), 127.8 (d, 2C),128.2 (d, 2C), 128.4 (d, 2C), 128.7 (d, 2C), 129.8 (d), 130.2 (d), 134.8 (s), 136.0 (s), 136.9 (d), 140.7 (s), 146.5 (s), 148.8 (s), 231.9 (s). UV (cyclohexane) 328 nm (log ε, 4.15), 473 (4.24). Found: C, 77.80; H, 4.97%. Calcd for $C_{24}H_{18}S_2$; C, 77.80; H, 4.90%.

A Typical Procedure for the Cycloaddition of Dienic Thioketone 8a with Dienophiles. A solution of the thioketone **8a** (0.505 mmol) and norbornene (2.53 mmol) in benzene (10 cm^3) was refluxed for 4 h under a nitrogen atmosphere. The solvent was removed and the residue was chromatographed on Wakagel C-200 to give the cycloadduct **9** which was recrystallized from hexane.

9,10,11,12,12a,12b,13,14-Octahydro-6,7-diphenyl-9,12-methano-6*H*,8a*H*-5,8-dithiabenzo[*c*]chrysene (9): MS *m/z* 490 (M^+; 45), 457 (63), 397 (100), 363 (57), 287 (20), 275 (35), 241 (12); ^{1}H NMR δ=1.13—1.17 (6H, m), 2.13—3.68 (7H, m), 3.08—3.30 (2H, m), 4.82 (1H, s), 6.86—7.39 (14H, m); ^{13}C NMR δ=28.0 (t), 29.4 (t), 29.9 (t), 32.2 (t), 33.9 (t), 41.9 (d), 43.5 (d), 49.1 (d), 50.9 (d), 52.9 (d), 57.8 (d). Found: C, 81.07; H, 6.30% Calcd for $C_{33}H_{30}S_2$: C, 80.77; H, 6.16%.

9,12,12a,12b,13,14-Hexahydro-6,7-diphenyl-9,12-methano-6*H*,8a*H*-5,8-dithiabenzo[*c*]chrysene (10): Colorless cubes; MS *m/z* 488 (M^+; 29), 422 (56), 396 (20), 390 (100), 363 (23), 331 (22), 275 (15); ^{1}H NMR δ=1.62—1.79 (1H, m), 2.34—3.10 (8H, m), 3.36—3.52 (2H, m), 4.86 (1H, s), 6.10—6,20 (2H, m), 6.92—7.38 (14H, m). ^{13}C NMR δ=27.9 (t), 31.9 (t), 43.1 (t), 47.0 (d), 48.0 (d), 49.2 (d), 51.2 (d), 52.0 (d), 55.2 (d). Found: C, 81.01; H, 5.78%. Calcd for $C_{33}H_{28}S_2$: C, 81.10; H, 5.77%.

Diethyl 3,4,5,6-Tetrahydro-1,12-diphenyl-4a*H*,12*H*-2,11-dithia-3,4-diazochrysene-3,4-dicarboxylate (11): Colorless rhombics; MS *m/z* 482 (M^+–NCOOEt–H; 2), 396 (16), 363 (14), 287 (4), 275 (13), 121 (15), 29 (100); ^{1}H NMR δ=1.20 (6H, t, *J*=6.5 Hz), 2.07—2.95 (4H, m), 4.15 (2H, q, *J*=6.5 Hz), 4.18 (2H, q, *J*=6.5 Hz), 5.14 (1H, s), 5.30 (1H, s), 7.32—7.98 (14H, m); ^{13}C NMR δ=14.4 (q), 25.4 (t), 28.1 (t), 46.2 (d), 55.5 (d), 153.8 (s; C=O), 155.9 (s; C=O). Found: C, 67.16; H, 5.55; N,

4.88%. Calcd for $C_{32}H_{30}O_4N_2S_2$: C, 67.34; H, 5.30; N, 4.91%.

Dimethyl 4,4a,5,6-Tetrahydro-1,12-diphenyl-3*H*,12*H*-2,11-dithiachrysene-3,4-dicarboxylate (12): Colorless needles; MS *m/z* 540 (M^+; 4), 507 (2), 418 (4), 396 (92), 363 (76), 287 (28), 275 (63), 241 (22), 121 (38), 113 (100); ^1H NMR δ=1.98—3.06 (4H, m), 3.46 (1H, d, *J*=4.2 Hz), 3.56 (3H, s), 3.71—3.89 (1H, m), 3.79 (6H, s), 4.29 (1H, d, *J*=2.1 Hz), 4.94 (1H, s), 6.80—7.45 (14H, m); ^{13}C NMR δ=28.2 (t), 28.4 (t), 41.5 (d), 43.1 (d), 43.6 (d), 50.0 (d), 52.5 (q), 53.0(q), 170.2 (s; C=O), 171.5 (s; C=O). Found: C, 71.36; H, 5.10%. Calcd for $C_{32}H_{28}O_4S_2$: C, 71.08; H, 5.22%.

***cis-transoid*-11a,11b-8a,9,10,11,11a,11b,12,13-Octahydro-6,7,10-traiphenyl-6*H*-5,8-dithia-10-azoacyclopenta[*c*]chrysene-9,11-dione (13a):** Colorless needles; less polar than (**13b**); MS *m/z* 569 (M^+; 1), 535 (7), 396 (70), 363 (49), 287 (21), 275 (51), 241 (17), 173 (100), 129 (26); ^1H NMR δ=2.28—2.64 (3H, m), 2.96—3.32 (1H, m), 3.47 (1H, d, *J*=10.2 Hz), 3.75 (1H, dd, *J*=8.4, 10.2 Hz), 4.60 (1H, d, *J*=8.4 Hz), 4.92 (1H, s), 6.82—7.56 (19H, m); ^{13}C NMR δ=27.5 (t), 31.4 (t), 47.0 (d), 49.4 (d), 49.7 (d), 51.3 (d), 172.9 (s; C=O), 173.9 (s; C=O). Found: C, 76.13; H, 4.94; N, 2.46%. Calcd for $C_{36}H_{27}O_2NS_2$: C, 75.89; H, 4.78; N, 2.46%

***cis-cisoid*-11a,11b-8a,9,10,11,11a,11b,12,13-Octahydro-6,7,10-triphenyl-6*H*-5,8-dithia-10-azoacyclopenta[*c*]chrysene-9,11-dione (13b):** Colorless cubes; MS *m/z* 569 (M^+; 6), 535 (3), 396 (100), 363 (81), 287 (29), 275 (66), 241 (24), 173 (96), 129 (27), 121 (46),; ^1H NMR δ=2.45—2.80 (3H, m), 2.91—3.19 (1H, m), 3.68 (1H, d, *J*=7.2 Hz), 3.95 (1H, dd, *J*=7.2, 9.0 Hz), 4.45 (1H, d, *J*=9.0 Hz), 4.91 (1H, s), 6.93—7.38 (19H, m); ^{13}C NMR δ=27.9 (t), 28.9 (t), 46.5 (d), 47.0 (d), 48.3 (d), 50.6 (d), 172.0 (s; C=O), 174.2 (s; C=O). Found: C, 75.64; H, 4.72; N, 2.26%. Calcd for $C_{36}H_{27}O_2NS_2$: C, 75.89; H, 4.78; N, 2.46%.

***cis-transoid*-11a,11b-8a,9,10,11,11a,11b,12,13-Octahydro-6,7-diphenyl-10-(*p*-tolyl)-6*H*-5,8-dithia-10-azoacyclopenta[*c*]chrysene-9,11-dione (14a):** MS *m/z* 583 (M^+; 1), 550 (5), 396 (30), 362 (25), 287 (10), 275 (26), 241 (19), 187 (100); ^1H NMR δ=2.38 (3H, s), 2.17—2.64 (3H, m), 2.93—3.32 (1H, m), 3.46 (1H, d, *J*=10.6 Hz), 3.70 (1H, d, *J*=8.3, 10.6 Hz), 4.61 (1H, d, *J*=8.3 Hz), 4.93 (1H, s), 6.75—7.42 (18H, m); ^{13}C NMR δ=21.3 (t), 27.5 (t), 31.4 (t), 47.0 (d), 49.5 (d), 49.7 (d), 51.3 (d), 173.1 (s; C=O), 174.1 (s; C=O). Found: C, 75.85; H, 4.99; N, 2.22%. Calcd for $C_{37}H_{29}O_2NS_2$: C, 76.12; H, 5.01; N, 2.40%.

***cis-cisoid*-11a,11b-8a,9,10,11,11a,11b,12,13-Octahydro-6,7-diphenyl-10-(*p*-tolyl)-6*H*-5,8-dithia-10-azoacyclopenta[*c*]chrysene-9,11-dione (14b):** MS *m/z* 583 (M^+; 4), 549 (1), 429 (3), 396 (92), 362 (76), 287 (28), 275 (59), 241 (33), 187 (100); ^1H NMR δ=2.31 (3H, s), 2.34—2.80 (3H, m), 2.85—3.20 (1H, m), 3.61 (1H, d, *J*=7.3 Hz), 3.92 (1H, dd, *J*=7.3, 9.0 Hz), 4.39 (1H, d, *J*=9.0 Hz), 4.89 (1H, s), 6.88—7.22 (18H, m); ^{13}C NMR δ=21.3 (q), 28.0 (t), 28.9 (t), 46.6 (d), 47.1 (d), 48.4 (d), 50.6 (d), 172.2 (s; C=O), 174.4 (s; C=O). Found: C, 76.24; H, 4.87; N, 2.22%. Calcd for $C_{37}H_{29}O_2NS_2$: C, 76.12; H, 5.01; N, 2.40%.

4-Chloro-4-cyano-4,4a,5,6-tetrahydro-1,12-diphenyl-3*H*,12*H*-2,11-dithiachrysene (15): Colorless crystals; MS *m/z* 483 (M^+; 10), 447 (29), 414 (57), 396 (100), 363 (22), 287 (40), 121 (93); ^1H NMR δ=2.05—3.06 (4H, m), 3.56 (1H, d, *J*=13.0 Hz), 3.72 (1H, d, *J*=13.0 Hz), 3.74 (1H, s), 4.90 (1H, s), 6.91—7.46 (14H, m); ^{13}C NMR δ=27.7 (t), 31.4 (t), 44.8 (t), 48.3 (d), 55.2 (d), 63.0 (s), 117.1 (s; C≡N). Found: C, 71.89; H, 4.55; N, 2.86%. Calcd for $C_{29}H_{22}NS_2Cl$: C, 71.95; H, 4.58; N, 2.89%.

Methyl 4,4a,5,6-Tetrahydro-4-methyl-1,12-diphenyl-3*H*,12*H*-2,11-dithiachrysene-4-carboxylate (16): Pale orange rhombics; MS *m/z* 496 (M^+; 2), 396 (100), 363 (70), 287 (24), 275 (56), 241 (20), 121 (34), 100 (22); ^1H NMR δ=1.51 (3H, s), 2.01—2.80 (4H, m), 3.01 (1H, dd, *J*=1.4, 13.2 Hz), 3.24 (1H, d, *J*=13.2 Hz), 3.68 (3H, s), 3.73 (1H, d, *J*=1.4 Hz), 4.92 (1H, s), 6.88—7.60 (14H, m); ^{13}C NMR δ=24.6 (q), 25.9 (t), 28.4 (t), 33.1 (t), 43.9 (s), 47.2 (d), 49.8 (d), 52.4 (q), 176.6 (s; C=O). Found: C, 74.75; H, 5.67%. Calcd for $C_{31}H_{28}O_2S_2$; C, 74.96; H, 5.68%.

4-Cyano-4,4a,5,6-tetrahydro-1,12-diphenyl-3*H*,12*H*-2,11-dithiachrysene (17): Pale yellow needles; MS *m/z* 449 (M^+; 19), 416 (14), 396 (100), 363 (59), 286 (28), 275 (50), 121 (55); ^1H NMR δ=2.10—2.90 (4H, m), 3.04—3.18 (2H, m), 3.35 (1H, d, *J*=6.0 Hz), 3.44—3.64 (1H, m), 5.00 (1H, s), 6.02—6.48 (14H, m); ^{13}C NMR δ=28.0 (t), 28.3 (t), 29.4 (t), 31.1 (d), 43.4 (d), 47.9 (d), 119.9 (s; C≡N). Found: C, 77.17; H, 5.10; N, 2.92%. Calcd for $C_{29}H_{23}NS_2$; C, 77.46; H, 5.16; N, 3.12%.

***rel*-(4*R*,4a*R*)-4,4a,5,6-Tetrahydro-1,4,12-triphenyl-3*H*,12*H*-2,11-dithiachrysene (18a):** Colorless cubes; MS *m/z* 500 (M^+; 1), 396 (41), 363 (23), 287 (9), 275 (14), 241 (6), 121 (11), 104 (100); ^1H NMR (400 MHz) δ=1.63—1.69, (1H, m), 1.86—1.99 (2H, m), 2.12—2.18 (1H, m), 3.25 (1H, dd, *J*=7.0, 12.5 Hz, (-S-C<u>H</u>$_2$-)), 3.34 (1H, dd, *J*=6.0, 12.5 Hz, (-S-C<u>H</u>$_2$-)), 3.58 (1H, m, (-CH$_2$-C<u>H</u>(Ph)-)), 3.47 (1H, d, *J*=8.0 Hz, (-CH(Ph)-C<u>H</u><)), 5.04 (1H, s, (-S-C<u>H</u>(Ph)-), 6.85—7.43 (19H, m); ^{13}C NMR δ=27.2 (t), 30.3 (t), 35.7 (t), 46.7 (d), 48.8 (d), 49.9 (d). Found: C, 81.23, H, 5.52%. Calcd for $C_{34}H_{28}S_2$: C, 81.56; H, 5.64%.

***rel*-(4*S*,4a*R*)-4,4a,5,6-Tetrahydro-1,4,12-triphenyl-3*H*,12*H*-2,11-dithiachrysene (18b):** Colorless crystals; MS *m/z* 500 (M^+; 2), 465 (9), 396 (100), 363 (49), 335 (13), 287 (18), 275 (46), 241 (111), 205 (21), 121 (20), 104 (26); ^1H NMR (400 MHz) δ=1.94—2.12 (2H, m), 2.23—2.31 (1H, m), 2.41—2.51 (1H, m), 2.90 (1H, dd, *J*=4.0, 13.0 Hz, (-S-C<u>H</u>$_2$-)), 3.40 (1H, d, *J*=6.0 Hz, (-CH(Ph)-C<u>H</u><)), 3.68 (1H, dd, *J*=4.0, 13.0 Hz, (-S-C<u>H</u>$_2$-)), 3.92 (1H, m, (-CH$_2$-C<u>H</u>(Ph)-)), 5.23 (1H, s (-S-C<u>H</u>(Ph)-), 6.96—7.75 (19H, m); ^{13}C NMR δ=28.0 (t), 28.3 (t), 35.6 (t), 39.6 (d), 41.5 (d), 45.9 (d). Found: C, 81.87; H, 5.76%. Calcd for $C_{34}H_{28}S_2$: C, 81.56; H, 5.64%.

5,8-Methano-1,3,10-triphenyl-4a,4b,6,7,8,8a-hexahydro-1*H*,5*H*-2,9-dithiaphenanthrene (19): Colorless cubes; MS *m/z* 464 (M^+; 83), 431 (81), 370 (64), 338 (65), 261 (23), 249 (38), 121 (100); ^1H NMR δ=1.18—1.78 (5H, m), 1.94—2.66 (4H, m), 3.13—3.34 (2H, m), 4.96 (1H, s), 6.61 (1H, d, *J*=6.5 Hz), 7.01—7.39 (15H, m); ^{13}C NMR δ=29.1 (t), 29.8 (t), 34.1 (t), 42.7 (d), 43.0 (d), 43.5 (d), 47.9 (d), 51.8 (d), 58.0 (d). Found: C, 80.16; H, 5.97%. Calcd for $C_{31}H_{28}S_2$: C, 80.13; H, 6.07%.

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