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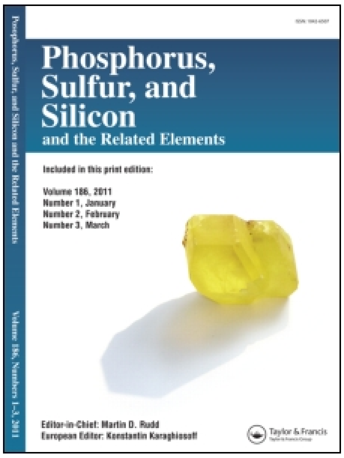

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THE [4 + 2]CYCLOADDITION REACTIONS OF AROMATIC THIONES WITH MALEIC ANHYDRIDE, NORBORNENE, AND NORBORNADIENE

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(*Received September 18, 1982; in final form December 15, 1982*)

The reactions of aryl 1-naphthyl thiones and aryl 2-naphthyl thiones with maleic anhydride, norbornene, and norbornadiene gave the 1,4-cycloadducts containing 3,4-dihydro-2*H*-thiopyran rings. 7*H*-Benz[*de*]anthracene-7-thione also reacted with norbornene and norbornadiene to give similar 1,4-cycloadducts. In the reaction of aryl phenyl thiones with norbornene, initially formed cycloadducts rearranged to aromatized compounds.

In these reactions, the aromatic thiones reacted with the olefins as a heterodiene system.

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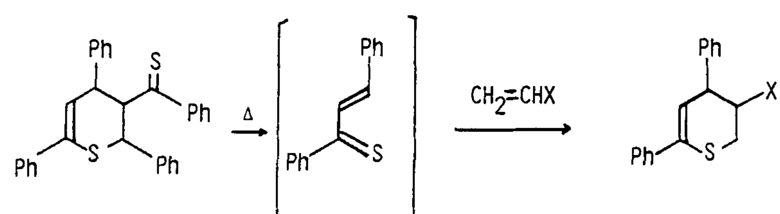
INTRODUCTION

The cycloaddition reactions of α,β-unsaturated thiones **2** derived from thiochalcone dimer **1** and 2-arylmethylenetetralin-1-thione dimer with dienophiles lead to the formation of 3,4-dihydro-2*H*-thiopyran **3** and 5,6-dihydro-2*H*-benzo[*h*]thiochroman derivatives, respectively.[1] In these reactions the thiones are acting as reactive heterodienes.



1 **2** **3**

X = CN, $CONH_2$, Ph, $COCH_3$

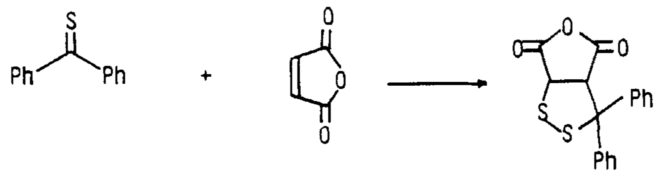
In the reactions of heterocyclic thiones with maleic anhydride and norbornene, we reported[2] that these thiones also reacted as heterodienes to give [4 + 2]cycloadducts. These reactions provide one of the useful methods for the preparation of some S-containing condensed heterocycles. However, little attention has been paid to [4 + 2]cycloaddition reactions of aromatic thiones with dienophilic olefins or acetylenes. Previous investigations have dealt almost exclusively with the reaction of thiobenzophenone with some acetylenic compounds.[3,4]

Accordingly, we have now studied the cycloaddition reactions of aryl phenyl thiones **4**, aryl 1-naphthyl thiones **6**, aryl 2-naphthyl thiones **8**, and 7*H*-

benz[*de*]anthracene-7-thione **14** with maleic anhydride, norbornene, and norbornadiene.

RESULTS AND DISCUSSION

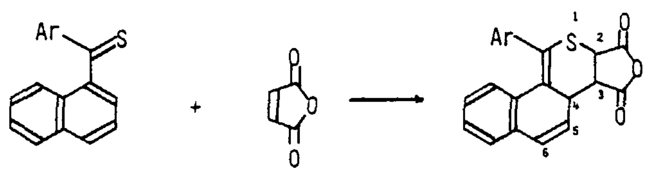
When the reaction of thiobenzophenone **4a** and maleic anhydride was carried out in refluxing dry xylene under a nitrogen atmosphere, an unexpected product **5** was obtained.



4a **5**

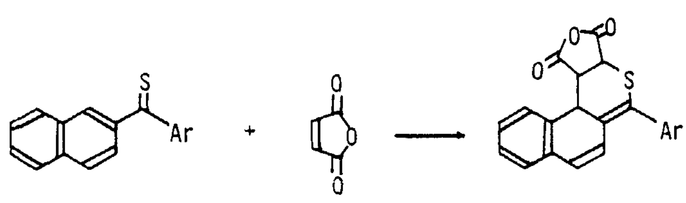
The IR spectrum of **5** showed bands at 1865 and 1790 cm^{-1} due to the anhydride linkage. The ^{1}H-NMR spectrum showed signals at δ 4.44 (d), 4.68 (d), and 7.20–7.35 (m, Ar—H). The ^{13}C-NMR spectrum showed the three alkyl carbon lines at δ 53.1 (d), 57.9 (d), and 80.4 (s). These data are consistent with the proposed **5** structure of a 1,2-dithiolane derivative.

On the other hand, the reaction of phenyl 1-naphthyl thione **6a** and maleic anhydride afforded the normal cycloadduct **7a**. In the ^{1}H-NMR spectrum, the multiplet at δ 3.64–3.78, the double-doublet at δ 4.01, the doublet at δ 4.40, and double-doublet at δ 6.20 are assigned to H-4, H-3, H-2, and H-5, respectively. The signal of H-6 was overlapped with those of aromatic protons. The coupling constant between H-2 and H-3 ($J_{2,3}$ = 9.6 Hz) indicates that the product has a 2,3 cis configuration.



6a, Ar=Phenyl
b, Ar=mesityl

7



8a, Ar=p-CH$_3$O-Ph
b, Ar=mesityl

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TABLE I

Reaction of the thiones with maleic anhydride

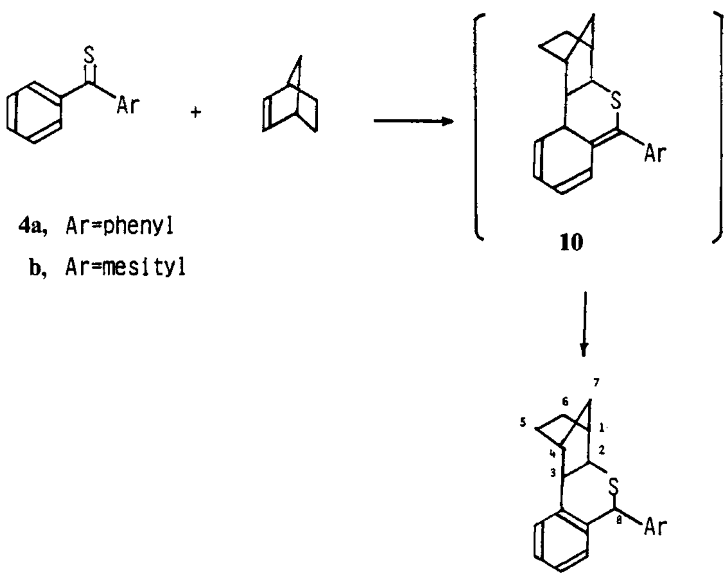
Thione	Product	Ar	Reaction time, h[a]	Mp, °C	Yield, %[b]
4a	**5**	phenyl	5	83–86	18
6a	**7a**	phenyl	27[c]	158–160 (dec.)	51
6b	**7b**	mesityl	6	100–102	43
8a	**9a**	*p*-CH_3O-Ph	3	145–148	91
8b	**9b**	mesityl	5	189–191 (dec.)	31

[a] The reactions were carried out in refluxing dry xylene except for **6a**.
[b] Based on the thione.
[c] The reaction was carried out in refluxing dry benzene.

The reaction of mesityl 1-naphthyl thione **6b**, *p*-methoxyphenyl 2-naphthyl thione **8a**, and mesityl 2-naphthyl thione **8b** with maleic anhydride gave the similar cycloadducts **7b**, **9a**, and **9b**, respectively. The results are presented in Table I.

In these aryl naphthyl thiones, the reaction took place across the 1,2-bond of the naphthalene ring and thiocarbonyl group as expected.

When the reaction of thiobenzophenone **4a** and norbornene was carried out in refluxing xylene under a nitrogen atmosphere, the product **11a** was obtained. In the ^{1}H-NMR spectrum, the doublet at δ 2.68 and the double-doublet at δ 3.66 are attributed to H-2 or H-3. The singlet at δ 4.73 is assigned to H-8 and the two broad singlets at δ 2.26 and 2.94 are attributed to H-1 or H-4. The coupling constant between H-2 and H-3 is 8.0 Hz; this value indicates the 2,3 cis configuration. The mass spectrum, IR spectrum, and elemental analysis are in agreement with the proposed structure **11a**.



4a, Ar=phenyl
b, Ar=mesityl

10

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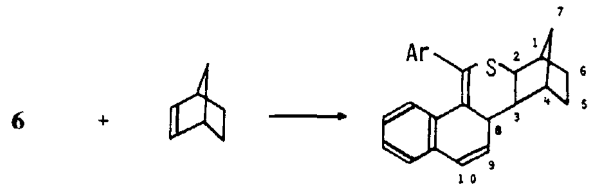
It seems probable that the thione reacted with norbornene by a formal [4 + 2]cycloaddition reaction to give initial adduct **10a** which rearranged to **11a** owing to its tendency to restore the aromatic system. The reaction of mesityl phenyl thione **4b** with norbornene gave the similar product **11b**.

On the other hand, the reaction of aryl 1-naphthyl thione **6** and aryl 2-naphthyl thione **8** with norbornene gave only the initial cycloadducts **12** and **13**, respectively, in place of aromatized adducts. For example, the ^{1}H-NMR spectrum of **12b** showed



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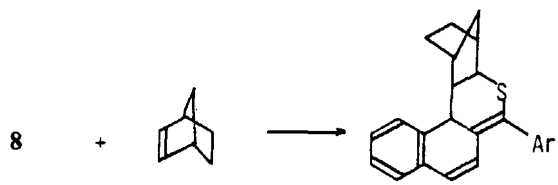

13

a multiplet at δ 1.34–1.80 for H-3, H-5, H-6, and H-7, three singlets at δ 1.90, 2.30, and 2.34 for the methyl hydrogens in the mesityl group, and two broad singlets at δ 2.20–2.40 and 2.71 for H-4 and H-1, respectively. A doublet at δ 2.70 ($J_{2,3}$ = 8.6 Hz), a multiplet at δ 3.08–3.28, and two double-doublets at δ 6.28 and 6.52 ($J_{8,9}$ = 4.0 Hz, $J_{9,10}$ = 10.0 Hz, and $J_{8,10}$ = 1.5 Hz (long range)) are assigned to H-2, H-8, H-9, and H-10, respectively. A multiplet at δ 6.68–7.16 (6 H) is assigned to aromatic protons. The mass spectrum showed ion peaks at m/e 384 (M^+) and 290 (M^+-norbornene). These data are consistent with the proposed structure **12b**. The reaction of 7*H*-benz[*de*]anthracene-7-thione **14** with norbornene gave the cycloadduct **15**. The results are presented in Table II.

TABLE II

Reaction of thiones with norbornene

Thione	Product	Ar	Reaction time, h[a]	Mp, °C	Yield, %[b]
4a	**11a**	phenyl	9	108–110	44
4b	**11b**	mesityl	3	164–166	28
6a	**12a**	phenyl	8	145–147	64
6b	**12b**	mesityl	1	126–127	66
8a	**13a**	*p*-CH_3O-Ph	1	150–154	51
8b	**13b**	mesityl	8	203–204	75
14	**15**	—	3	145–147	58

[a] The reactions were carried out in refluxing dry xylene.
[b] Based on the thione.

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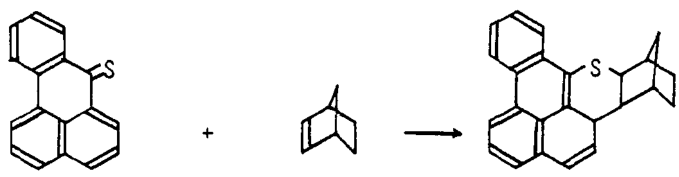
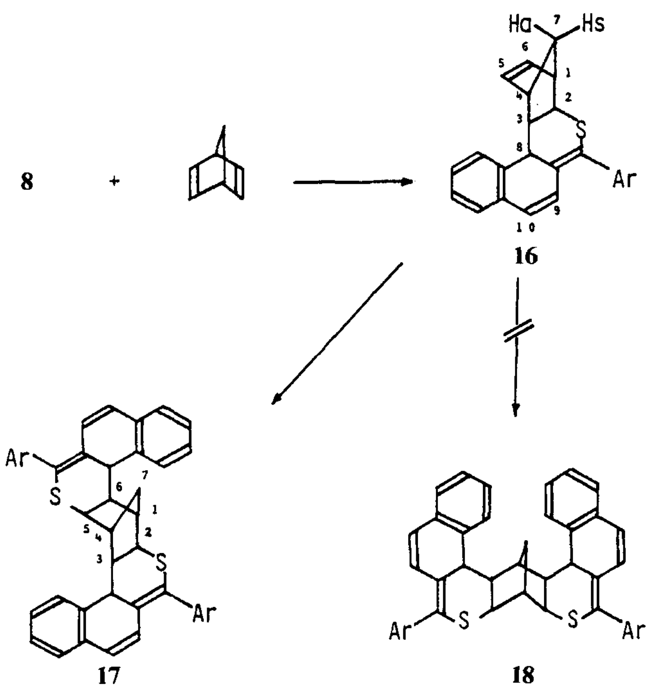


14 15

The endo-exo configuration of 2-substituted norbornane is proved by the ^{13}C-NMR spectrum. Namely, it has been reported[5] that the exo-2 group usually shields the C-7 carbon in the ^{13}C-NMR spectrum and the resonance of the C-7 carbon is thus upfield 1.3–4.4 ppm from the one in norbornane itself. In the off-resonance-decoupled spectra of **11a** and **12a**, the signals corresponding to the C-7 carbons appeared at 34.4 and 34.6 ppm, respectively. These signals are shifted 4.3 and 4.1 ppm upfield, respectively, in comparison with that of norbornane. Therefore, it may be reasonable to assume that the products **11a** and **12a** have exo configurations. Similarly, the cis-exo configurations of the products **11b**, **12b**, **13**, and **15** are supported by means of ^{1}H- and ^{13}C-NMR spectroscopy.

As is shown in Tables I and II, replacement of a phenyl group by a mesityl group in **4** and **6**, and of a mesityl group by a *p*-methoxyphenyl group in **8** accelerate the reaction. 7*H*-Benz[*de*]anthracene-7-thione **14** has a condensed ring system relative to **6a** but reacts more readily. Its high reactivity results from the formation of a stable phenanthrene nucleus in the product **15**.

When the reaction of *p*-methoxyphenyl 2-naphthyl thione **8a** and norbornadiene was carried out in refluxing benzene under a nitrogen atmosphere, the 2 : 1 adduct **17a** was obtained. The mass spectrum of **17a** showed ion peaks at m/e 648 (M^+) and



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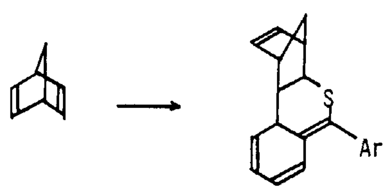
370 (M^+-thione). In this case two regioisomeric structures **17a** and **18a** can be considered as the structure of the product. However, no difference between the chemical shifts of H-1 and H-4 [δ 2.48 (broad s, 2 H)] indicates that the product is **17a**. On the other hand, the reaction of mesityl 2-naphthyl thione **8b** with norbornadiene gave both 1 : 1 adduct **16b** and 2 : 1 adduct **17b**. When the reaction was carried out at room temperature, **16b** was obtained as only the isolable product. The IR spectrum of **16b** showed bands at 2975 and 2950 (C—H) cm^{-1}. The mass spectrum showed ion peaks at m/e 382 (M^+) and 290 (M^+-norbornadiene). The ^{1}H-NMR spectrum showed three singlets at δ 2.03, 2.10, and 2.28 for the methyl groups, two broad singlets at δ 2.92 and 3.32 for H-4 and H-1, two doublets at δ 2.72 (J_{gem} = 8.6 Hz) and 3.85 ($J_{3,8}$ = 10.7 Hz) for H-7s and H-8, two multiplets at δ 1.60–1.85 (J_{gem} = 8.6 Hz) and 1.80–2.10 ($J_{2,3}$ = 7.7 Hz and $J_{3,8}$ = 10.7 Hz) for H-7a and H-3, a double–doublet at δ 2.85 ($J_{2,3}$ = 7.7 Hz and $J_{2,7a}$ = 1.6 Hz) for H-2, two doublets at δ 5.92 ($J_{9,10}$ = 9.5 Hz) and 6.22 ($J_{9,10}$ = 9.5 Hz) for H-9 and H-10, and a multiplet at δ 6.02–6.22 for the olefinic protons of H-5 and H-6, respectively. These assignments were based on the spin-decoupling experiments.

The mass spectrum of **17b** showed ion peaks at m/e 672 (M^+), 382 (M^+-thione), and 290 (thione) and there was no difference between the chemical shifts of H-1 and H-4 [δ 2.44 (broad s, 2 H)] in the ^{1}H-NMR spectrum.

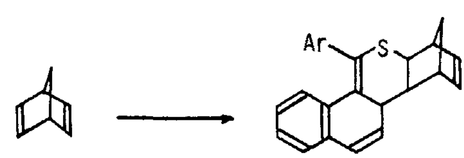
The reactions of mesityl phenyl thione **4b**, mesityl 1-naphthyl thione **6b**, and 7*H*-benz[*de*]anthracene-7-thione **14** with norbornadiene gave only the 1 : 1 adducts **19b**, **20b**, and **21**, respectively. The results are presented in Table III.

4b +



19b

6b +



20b

14 +

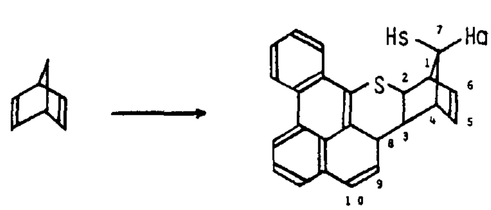


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TABLE III

Reaction of thiones with norbornadiene

Thione	Product	Ar	Reaction time, h[a]	Mp, °C	Yield, %[b]
4b	**19b**	mesityl	12	142–143 (dec.)	39
6b	**20b**	mesityl	1	122–124	61
8a	**17a**	p-CH_3O-Ph	5	238–239 (dec.)	87
8b	**16b**	mesityl	1	195–197	64
	17b	mesityl		251–254	10
8b	**16b**	mesityl	1 week[c]	195–197	54
14	**21**	—	3	185–186 (dec.)	58

[a] The reactions were carried out in refluxing dry benzene.
[b] Based on the thione.
[c] The reaction was carried out in benzene at room temperature.

As a result of the present work, it has been found that the conjugated system made up of a thiocarbonyl group and the bond of an aromatic ring in aromatic thiones can function as α,β-unsaturated thiones and react with various olefins to give the corresponding cycloadducts. The reactions also can be utilized for the syntheses of dihydrobenzothiopyran and dihydronaphthothiopyran derivatives.

EXPERIMENTAL

All the melting points are uncorrected. ^{1}H-NMR spectra and ^{13}C-NMR spectra were recorded on a JEOL JNM-FX 100 spectrometer in $CDCl_3$ solution using Me_4Si as internal standard at 100 MHz or 25 MHz, respectively. IR spectra were obtained on a Hitachi Model 260-10 infrared spectrometer. Mass spectra were obtained with Hitachi double-focusing mass spectrometers, Model RMU-7M and M-80 operating at 70 eV. Silica gel (Wako gel C-200) was used for column chromatography.

Preparation of starting materials. 7*H*-Benz[*de*]anthracen-7-one was obtained commercially. All other ketones were prepared by the Friedel-Crafts reaction. The thiones were prepared according to the method of Lawesson[6] by the reaction of the corresponding ketone and Lawesson's reagent [2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide].

A solution of the ketone (10 mmol) and Lawesson's reagent (6 mmol) in dry toluene (10 ml) was refluxed under a nitrogen atmosphere until all the ketone had been consumed as evidenced by TLC analysis. The solvent was evaporated and the residue was chromatographed on Florisil gel (100–200 mesh) using benzene-hexane (1 : 2) as the eluent. The solvent was evaporated and the residue was recrystallized to give the thione. In aryl mesityl ketone, the two ortho methyl groups prevent the attack of thionation reagent on the carbonyl carbon, so the reaction was carried out in refluxing dry xylene.

Thiobenzophenone **4a** [mp 49–50°C (lit.[6] 53°C)]. Mesityl phenyl thione **4b** [blue oil (lit.[7] blue oil)]. Phenyl 1-naphthyl thione **6a** [mp 106–108°C (lit.[8] 112°C)]. Mesityl 1-naphthyl thione **6b** [blue crystals (recrystallized from ethanol); mp 139–141°C; IR (KBr) 1600, 1275, 1230, 850, 800, and 780 cm^{-1}; MS m/e 290 (M^+, 100), 171 ($C_{10}H_7$—C=S + , 57), and 163 (mesityl—C=S + , 17)]. p-Methoxyphenyl 2-naphthyl thione **8a** [blue leaflets (recrystallized from CH_2Cl_2–hexane); mp 128–130°C; IR (KBr) 3050, 2830, 1600, 1500, and 1260 cm^{-1}; MS m/e 278 (M^+, 100), 171 ($C_{10}H_7$—C=S + , 29), and 151 (p-CH_3O—Ph—C=S + , 49)]. Mesityl 2-naphthyl thione **8b** [blue oil; IR (neat) 3050, 2980, 1280, 1220, and 1195 cm^{-1}; MS m/e 290 (M^+, 100), 171 ($C_{10}H_7$—C=S + , 35), and 163 (mesityl—C=S + , 27)]. 7*H*-Benz[*de*]anthracene-7-thione **14** [mp 136–138°C (lit.[9] 132°C)].

Cycloaddition reactions of the aromatic thiones with dienophiles. General procedure. A solution of the thione (5 mmol) and dienophile (5 mmol or slightly excess) in dry benzene or xylene (5 ml) was refluxed under a nitrogen atmosphere until all the thione had been consumed as indicated by TLC. The solvent was evaporated and the residue was chromatographed on Silica gel (Wako gel C-200). The solvent was evaporated and the residue was recrystallized to give the cycloadduct.

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5: chromatographed by eluting with benzene–ligroin (2 : 1); colorless prisms (from benzene–ligroin); IR (KBr) 1865 (C=O) and 1790 (C=O) cm^{-1}; ^{1}H-NMR δ 4.44 (d, J = 7.5 Hz, 1 H), 4.68 (d, J = 7.5 Hz, 1 H), and 7.20–7.35 (m, 10 H); MS m/e 328 (M^+, 44), 264 (13), 220 (100), 198 (thione, 3), 192 (55), and 165 (27). Anal. Calcd for $C_{17}H_{12}O_3S_2$: C, 62.17; H, 3.68; S, 19.52. Found: C, 62.07; H, 3.85; S, 19.35.

7a: chromatographed by eluting with benzene–hexane (2 : 1); colorless crystals (from benzene); IR (KBr) 1865 (C=O) and 1785 (C=O) cm^{-1}; ^{1}H-NMR δ 3.64–3.78 (m, 1 H), 4.01 (dd, J = 9.6 and 4.7 Hz, 1 H), 4.40 (d, J = 9.6 Hz, 1 H), 6.20 (dd, J = 9.3 and 4.3 Hz, 1 H), and 6.60–7.48 (m, 10 H); MS m/e 346 (M^+, 4), 247 (100), 215 (6), and 171 (17). Anal. Calcd for $C_{21}H_{14}O_3S$: C, 72.82; H, 4.07; S, 9.26. Found: C, 72.67; H, 4.29; S, 9.38.

7b: chromatographed by eluting with benzene–ligroin (3 : 1); red crystals (from benzene–hexane); IR (KBr) 2955 (C—H), 1865 (C=O), and 1790 (C=O) cm^{-1}; ^{1}H-NMR δ 1.85 (s, 3 H), 2.26 (s, 3 H), 2.29 (s, 3 H), 3.56 (dd, J = 4.0 and 3.2 Hz, 1 H), 3.97 (dd, J = 10.4 and 3.2 Hz, 1 H), 4.18 (d, J = 10.4 Hz, 1 H), 6.10 (dd, J = 10.0 and 4.0 Hz, 1 H), 6.62–7.58 (m, 7 H, olefinic and aromatic protons); MS m/e 388 (M^+, 17), 315 (10), 290 (thione, 100), 275 (24), 257 (20), and 242 (17). Anal. Calcd for $C_{24}H_{20}O_3S$: C, 74.20; H, 5.19; S, 8.25. Found: C, 74.39; H, 5.10; S, 8.45.

9a: red crystals (from benzene); IR (KBr) 2840 (OCH_3), 1860 (C=O), and 1790 (C=O) cm^{-1}; ^{1}H-NMR δ 3.84 (s, 3 H), 4.10 (dd, J = 4.2 and 0.6 Hz, 1 H), 4.34 (d, J = 4.2 Hz, 1 H), 4.38 (d, J = 4.2 Hz, 1 H), 6.45 (d, J = 12.0 Hz, 1 H), 6.59 (d, J = 12.0 Hz, 1 H), 6.82–6.95 (m, 2 H), 7.23–7.44 (m, 6 H); MS m/e 376 (M^+, 1), 304 (1), 278 (100), 245 (73), 202 (20), and 151 (38). Anal. Calcd for $C_{22}H_{16}O_4S$: C, 70.20; H, 4.28; S, 8.52. Found: C, 70.29; H, 4.41; S, 8.65.

9b: chromatographed by eluting with benzene; colorless silky needles (from benzene–hexane); IR (KBr) 1865 (C=O) and 1790 (C=O) cm^{-1}; ^{1}H-NMR δ 2.03 (s, 3 H), 2.13 (s, 3 H), 2.30 (s, 3 H), 4.02 (d, J = 3.0 Hz, 1 H), 4.32 (d, J = 9.0 Hz, 1 H), 4.50 (dd, J = 9.0 and 3.0 Hz, 1 H), 5.99 (d, J = 9.0 Hz, 1 H), 6.36 (d, J = 9.0 Hz, 1 H), 6.80–6.90 (m, 2 H), and 7.16–7.44 (m, 4 H); MS m/e 388 (M^+, 24), 290 (thione, 100), 275 (20), 257 (81), and 243 (49). Anal. Calcd for $C_{24}H_{20}O_3S$: C, 74.20; H, 5.19; S, 8.25. Found: C, 74.32; H, 5.23; S, 8.27.

11a: chromatographed by eluting with benzene: colorless crystals (from ethanol); IR (KBr) 3070, 3050, 3020, 2980 (C—H), and 2895 (C—H) cm^{-1}; ^{1}H-NMR δ 1.04–1.92 (m, 6 H), 2.26 (broad s, 1 H), 2.68 (d, J = 8.0 Hz, 1 H), 2.94 (broad s, 1 H), 3.66 (dd, J = 8.0 and 1.8 Hz, 1 H), 4.73 (s, 1 H), and 6.50–7.48 (m, 9 H); MS m/e 292 (M^+, 100), 259 (6), 198 (thione, 28), 147 (29), and 91 (17). Anal. Calcd for $C_{20}H_{20}S$: C, 82.14; H, 6.89; S, 10.96. Found: C, 82.11; H, 6.93; S, 11.00.

11b: chromatographed by eluting with hexane: slightly yellow crystals (from ethanol); IR (KBr) 2960 (C—H), 1490, and 1455 cm^{-1}; ^{1}H-NMR δ 1.05–2.40 (m, 7 H), 2.12 (s, 3 H), 2.28 (s, 3 H), 2.36 (s, 3 H), 2.68 (d, J = 7.0 Hz, 1 H), 2.84–2.95 (m, 1 H), 3.65 (dd, J = 7.0 and 0.5 Hz, 1 H), 5.28 (s, 1 H), and 6.65–7.54 (m, 6 H); MS m/e 334 (M^+, 81), 240 (16), 207 (42), 132 (100), and 67 (12). Anal. Calcd for $C_{23}H_{26}S$: C, 82.58; H, 7.83; S, 9.58. Found: C, 82.71; H, 7.88; S, 9.81.

12a: slightly yellow crystals (from ethanol); IR (KBr) 3050 (Ar—H) and 2950 (C—H) cm^{-1}; ^{1}H-NMR δ 1.04–2.00 (m, 7 H), 2.32 (broad s, 1 H), 2.92–3.08 (m, 1 H), 3.02 (broad s, 1 H), 3.86 (d, J = 8.0 Hz, 1 H), 5.28–5.60 (m, 1 H), 6.30–6.55 (m, 1 H), and 6.68–7.95 (m, 9 H); MS m/e 342 (M^+, 100), 248 (thione, 19), 229 (15), and 215 (15). Anal. Calcd for $C_{24}H_{22}S$: C, 84.17; H, 6.47; S, 9.36. Found: C, 83.87; H, 6.53; S, 9.50.

12b: light yellow crystals (from ethanol); IR (KBr) 2960 (C—H) and 1460 cm^{-1}; ^{1}H-NMR δ 1.34–1.80 (m, 7 H), 1.90 (s, 3 H), 2.30 (s, 3 H), 2.34 (s, 3 H), 2.20–2.40 (1 H), 2.70 (d, J = 8.6 Hz, 1 H), 2.71 (broad s, 1 H), 3.08–3.28 (m, 1 H), 6.28 (dd, J = 10.0 and 4.0 Hz, 1 H), 6.52 (dd, J = 10.0 and 1.5 Hz, 1 H), and 6.68–7.16 (m, 6 H); MS m/e 384 (M^+, 35), 290 (thione, 100), 275 (14), 257 (12), 242 (12), and 171 (16). Anal. Calcd for $C_{27}H_{28}S$: C, 84.33; H, 7.34; S; 8.34. Found: C, 84.30; H, 7.37; S, 8.36.

13a: chromatographed by eluting with benzene–hexane (1 : 1); slightly yellow crystals (from ethanol); IR (KBr) 2950 (C—H), 2875, and 1600 cm^{-1}; ^{1}H-NMR δ 0.90–1.80 (m, 6 H), 2.26–2.48 (m, 2 H), 2.56–2.76 (m, 2 H), 3.48 (d, J = 10.8 Hz, 1 H), 3.80 (s, 3 H), 6.30 (d, J = 9.1 Hz, 1 H), 6.48 (d, J = 9.1 Hz, 1 H), 6.76–6.92 (m, 2 H), and 7.08–7.50 (m, 6 H); MS m/e 372 (M^+, 21), 278 (thione, 100), 245 (33), 202 (5), and 151 (13). Anal. Calcd for $C_{25}H_{24}OS$: C, 80.61; H, 6.49; S, 8.61. Found: C, 80.32; H, 6.42; S, 8.52.

13b: yellow needles (from benzene); IR (KBr) 2960 (C—H), 1610, 1480, and 1450 cm^{-1}; ^{1}H-NMR δ 0.92–1.80 (m, 6 H), 2.05 (s, 3 H), 2.20 (s, 3 H), 2.28 (s, 3 H), 2.10–2.48 (2 H), 2.64 (dd, J = 10.0 and 1.0 Hz, 1 H), 2.75–2.90 (m, 1 H), 3.56 (d, J = 10.0 Hz, 1 H), 5.95 (d, J = 9.0 Hz, 1 H), 6.24 (d, J = 9.0 Hz, 1 H), 6.80–6.88 (m, 2 H), and 7.08–7.38 (m, 4 H); MS m/e 384 (M^+, 33), 290 (thione, 100), 275 (57), and 242 (19). Anal. Calcd for $C_{27}H_{28}S$: C, 84.33; H, 7.34; S, 8.34. Found: C, 84.29; H, 7.34; S, 8.37.

15: orange crystals (from benzene–hexane); IR (KBr) 3050, 2965, 2875, 1595, 830, and 760 cm^{-1}; ^{1}H-NMR δ 1.05–1.95 (m, 6 H), 2.25–2.55 (m, 3 H), 2.78 (broad s, 1 H), 3.28–3.50 (m, 1 H), 6.40 (dd, J = 9.6 and 3.9 Hz, 1 H), 6.76 (dd, J = 9.6 and 1.6 Hz, 1 H), 7.16–7.64 (m, 4 H), and 8.32–8.62 (m, 3 H); MS m/e 340 (M^+, 21), 246 (M^+-norbornene, 100), and 202 (14). Anal. Calcd for $C_{24}H_{20}S$: C, 84.66; H, 5.92; S, 9.42. Found: C, 84.96; H, 6.04; S, 9.52.

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16b: chromatographed by eluting with benzene–hexane (1 : 1); colorless crystals (from benzene–ethanol); IR (KBr) 2975, 2950 (C—H), and 1610 cm^{-1}; ^1H-NMR δ 1.60–1.85 (m, J = 8.6 Hz, 1 H), 1.80–2.10 (m, J = 10.7 and 7.7 Hz, 1 H), 2.03 (s, 3 H), 2.10 (s, 3 H), 2.28 (s, 3 H), 2.72 (d, J = 8.6 Hz, 1 H), 2.85 (dd, J = 7.7 and 1.6 Hz, 1 H), 2.92 (broad s, 1 H), 3.32 (broad s, 1 H), 3.85 (d, J = 10.7 Hz, 1 H), 5.92 (d, J = 9.5 Hz, 1 H), 6.02–6.22 (m, 2 H), 6.22 (d, J = 9.5 Hz, 1 H), 6.75–6.90 (m, 2 H), and 6.98–7.40 (m, 4 H); MS m/e 382 (M^+, 96), 315 (66), 290 (100), 257 (55), 242 (28), and 197 (14). Anal. Calcd for $C_{27}H_{26}S$: C, 84.77; H, 6.85; S, 8.38. Found: C, 84.97; H, 7.01; S, 8.36.

17a: chromatographed by eluting with benzene–hexane (1 : 1); slightly yellow crystals (from benzene–ethanol); IR (KBr) 2850 (OCH_3), 1610, 1510, and 1260 cm^{-1}; ^1H-NMR δ 1.48–1.92 (m, 2 H), 2.48 (broad s, 2 H), 2.50–2.60 (m, 2 H), 2.85–2.92 (m, 2 H), 3.66 (d, J = 10.7 Hz, 2 H), 3.78 (s, 6 H, OCH_3), 6.32 (d, J = 8.0 Hz, 2 H), 6.45 (d, J = 8.0 Hz, 2 H), and 6.70–7.30 (m, 16 H); MS m/e 648 (M^+, 1), 370 (21), 278 (100), 245 (41), 202 (7), and 151 (15). Anal. Calcd for $C_{43}H_{36}O_2S_2$: C, 79.59; H, 5.59; S, 9.88. Found: C, 79.84; H, 5.73; S, 10.08.

17b: colorless crystals (from benzene–ethanol); IR (KBr) 2975, 2925 (C—H), and 1610 cm^{-1}; ^1H-NMR δ 1.65–1.97 (m, 2 H), 2.04 (s, 6 H), 2.10 (s, 6 H), 2.26 (s, 6 H), 2.44 (broad s, 2 H), 2.55–2.65 (m, 2 H), 2.88–3.00 (m, 2 H), 3.74 (d, J = 10.8 Hz, 2 H), 5.92 (d, J = 9.2 Hz, 2 H), 6.25 (d, J = 9.2 Hz, 2 H), 6.82 (broad s, 4 H), and 6.98–7.45 (m, 8 H); MS m/e 672 (M^+, 1), 382 (41), 315 (48), 290 (100), 257 (70), and 242 (49). Anal. Calcd for $C_{47}H_{44}S_2$: C, 83.88; H, 6.59; S, 9.53. Found: C, 83.62; H, 6.82; S, 9.43.

19b: chromatographed by eluting with benzene–ligroin (1 : 2); colorless crystals (from ethanol); IR (KBr) 3040 (Ar—H), 2975, 2950 (C—H), and 1610 cm^{-1}; ^1H-NMR δ 1.48–2.10 (m, 3 H), 2.07 (s, 3 H), 2.13 (s, 3 H), 2.26 (s, 3 H), 2.58 (dd, J = 7.8 and 1.4 Hz, 1 H), 2.85 (broad s, 1 H), 2.95–3.25 (m, 2 H), 5.54–6.36 (m, 6 H, olefinic protons), and 6.72–6.92 (m, 2 H); MS m/e 332 (M^+, 80), 265 (100), 240 (thione, 91), 206 (55), 192 (31), and 163 (33). Anal. Calcd for $C_{23}H_{24}S$: C, 83.08; H, 7.28; S, 9.64. Found: C, 82.89; H, 7.08; S, 9.55.

20b: chromatographed by eluting with benzene–hexane (1 : 2); slightly yellow crystals (from ethanol); IR (KBr) 3060, 3040 (Ar—H), 2975, 2950 (C—H), 1650, and 1485 cm^{-1}; ^1H-NMR δ 1.91 (s, 3 H), 1.40–2.05 (m, 2 H), 2.29 (s, 3 H), 2.32 (s, 3 H), 2.20–2.72 (m, 2 H), 2.80 (d, J = 7.1 Hz, 1 H), 3.05–3.52 (m, 2 H), 6.00–6.65 (m, 4 H), and 6.68–7.15 (m, 6 H); MS m/e 382 (M^+, 75), 316 (100), 315 (98), 290 (thione, 74), 275 (14), 242 (17), 197 (21), and 171 (22). Anal. Calcd for $C_{27}H_{26}S$: C, 84.77; H, 6.85; S, 8.38. Found: C, 84.48; H, 6.88; S, 8.23.

21: yellow needles (from CH_2Cl_2); IR (KBr) 3080, 3045, 2995, 760, and 700 cm^{-1}; ^1H-NMR δ 1.62–1.80 (m, J_{gem} = 9.3, $J_{2,7a}$ = 1.4, and $J_{3,7a}$ = 1.4 Hz, 1 H, H-7a), 1.75–2.02 (m, $J_{2,3}$ = 8.6 and $J_{3,8}$ = 9.6 Hz, 1 H, H-3), 2.60–2.75 (m, J_{gem} = 9.3 Hz, 1 H, H-7s), 2.66 (d, $J_{2,3}$ = 8.6 Hz, 1 H, H-2), 3.02 (broad s, 1 H, H-4), 3.26 (broad s, 1 H, H-1), 3.52–3.76 (m, $J_{3,8}$ = 9.6 and $J_{8,9}$ = 3.6 Hz, 1 H, H-8), 6.00–6.28 (m, 2 H, H-5 and H-6), 6.42 (dd, $J_{9,10}$ = 10.1 and $J_{8,9}$ = 3.6 Hz, 1 H, H-9), 6.78 (dd, $J_{9,10}$ = 10.1 and $J_{8,10}$ = 1.8 Hz, 1 H, H-10), 7.28–7.68 (m, 4 H), and 8.30–8.67 (m, 3 H); MS m/e 338 (M^+, 37), 271 (100), 246 (thione, 94), and 202 (27). Anal. Calcd for $C_{24}H_{18}S$: C, 85.17; H, 5.36; S, 9.47. Found: C, 85.26; H, 5.45; S, 9.29.

^{13}C-NMR spectral data

5: δ 53.1 (d), 57.9 (d), 80.4 (s), 126.8, 127.9, 128.0, 128.3, 128.5, 138.5 (s), 142.0 (s), 166.6 (s), 169.4 (s).

7b: δ 16.9 (q), 20.1 (q), 21.1 (q), 22.6 (d), 42.8 (d), 52.1 (d), 125.5, 126.5, 127.9, 128.2, 128.3, 128.7, 129.2, 129.5, 131.5, 132.1, 134.0, 134.8 (s), 135.2 (s), 136.7 (s), 138.5 (s), 169.2 (s), 170.1 (s).

11a: δ 29.2 (t), 29.8 (t), 34.4 (t), 42.4 (d), 43.5 (d), 46.3 (d), 47.4 (d), 50.8 (d), 124.4, 125.6, 126.5, 127.4, 128.0, 128.6, 128.9, 139.3 (s), 139.7 (s), 141.9 (s).

11b: δ 20.9 (q), 21.0 (q), 21.7 (q), 28.8 (t), 30.6 (t), 34.6 (t), 41.5 (d), 42.7 (d), 44.2 (d), 46.2 (d), 50.6 (d), 124.4, 125.5, 126.2, 128.9, 129.0, 131.1, 132.4, 136.5, 136.8, 138.5, 139.3.

12a: δ 29.3 (t), 29.9 (t), 34.6 (t), 42.4 (d), 43.3 (d), 46.6 (d), 51.7 (d), 58.3 (d), 124.5, 125.1, 125.6, 126.6, 127.9, 128.7, 131.8 (s), 139.3 (s).

12b: δ 19.6 (q), 20.5 (q), 21.1 (q), 29.0 (t), 29.8 (t), 33.7 (t), 39.7 (d), 42.2 (d), 44.3 (d), 50.3 (d), 59.3 (d), 125.7, 126.5, 126.6, 127.1, 127.4, 128.7, 129.0, 130.6, 131.0, 131.3, 133.2, 134.6, 136.3, 136.8, 136.9, 138.0.

13b: δ 20.1 (q), 20.3 (q), 21.0 (q), 29.2 (t), 29.9 (t), 33.0 (t), 40.2 (d), 43.1 (d), 44.2 (d), 51.2 (d), 60.8 (d), 122.9, 124.7, 125.7, 126.6, 127.4, 128.0, 128.2, 130.6, 133.4, 133.9, 135.3, 136.9, 137.3, 137.6, 138.1.

15: δ 29.0 (t), 29.9 (t), 34.0 (t), 40.6 (d), 42.5 (d), 42.9 (d), 47.3 (d), 59.0 (d), 121.6, 122.9, 124.3, 125.2, 126.0, 126.7, 126.9, 128.7, 128.8, 130.1, 130.6, 131.6 (d), 134.0 (s).

16b: δ 20.1 (q), 20.3 (q), 21.1 (q), 42.3 (t), 45.1 (d), 45.8 (d), 47.5 (d), 50.8 (d), 58.7 (d), 123.0, 124.6, 125.8, 126.8, 127.5, 128.1, 128.3, 130.3, 133.5, 134.9, 135.1, 137.0, 137.1, 138.0, 138.1, 139.5, 140.0.

19b: δ 19.8 (q), 19.9 (q), 21.0 (q), 42.9 (t), 43.3 (d), 44.2 (d), 45.2 (d), 47.4 (d), 58.3 (d), 119.5, 123.0, 123.6, 127.9, 128.2, 132.4, 135.0, 136.5, 136.6, 136.9, 137.8, 139.5.

21: δ 43.2 (t), 43.5 (d), 45.2 (d), 45.6 (d), 47.9 (d), 57.4 (d), 121.7, 122.9, 124.4, 125.2, 126.1, 126.7, 127.1, 128.6, 128.8, 130.0, 131.1, 131.3, 132.7, 136.5 (d), 139.4 (d), 149.6.

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