1-Thia-Cope Rearrangements during the Thionation of 2-*endo*-3-*endo*-Bis(aroyl)bicyclo[2.2.1]hept-5-enes

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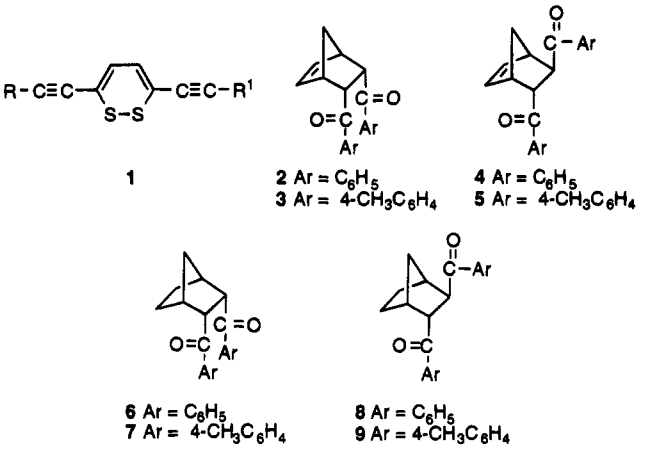
Owing to our interest in the synthesis and bioactivity of 1,2-dithiacyclohexa-3,5-dienes (1,2-dithiins, **1**),[1-3] we are investigating the reactions of various thionation reagents[4-7] with 1,4-diketones.[8] Efficient syntheses of a wide variety of natural and unnatural 1,2-dithiins and their derivatives[1-3,9-16] and a study of structure–activity relationships (SAR) will help to elucidate the mechanisms involved in the cleavage of DNA by 1,2-dithiins[11] and by enediyne antitumor agents,[17-21] and in the anti-HIV activity of 1,2-dithiins.[22] In order to evaluate the influence of bicyclic ring systems on the thionation of 1,4-diketones and the synthesis of 1,2-dithiins **1**, 2-*endo*-3-*endo*-dibenzoylbicyclo[2.2.1]hept-5-ene (**2**),[23-28] 2-*endo*-3-*endo*-bis(4-methylbenzoyl)bicyclo-[2.2.1]hept-5-ene (**3**), 2-*endo*-3-*exo*-dibenzoylbicyclo[2.2.1]hept-5-ene (**4**),[25,29] and 2-*endo*-3-*exo*-bis(4-methylbenzoyl)bicyclo[2.2.1]hept-5-ene (**5**) were prepared. Bicyclics **2**, **3**, and **4** were catalytically hydrogenated[30,31] to compounds **6**,[32] **7**, and **8**,[31] respectively, and compounds **6** and **7** were isomerized to **8** and **9**, respectively, during the thionation procedure.



1

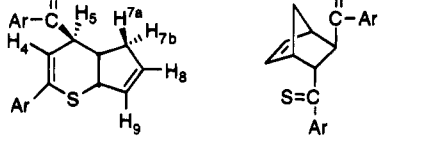
2 Ar = C_6H_5
3 Ar = 4-$CH_3C_6H_4$

4 Ar = C_6H_5
5 Ar = 4-$CH_3C_6H_4$

6 Ar = C_6H_5
7 Ar = 4-$CH_3C_6H_4$

8 Ar = C_6H_5
9 Ar = 4-$CH_3C_6H_4$

Thionation of the diketones would lead to dithiones (dienedithiols) with favorable molecular geometry which could be oxidized to substituted 1,2-dithiins **1**. Attempts to form the dithiones by the trimethylsilyl trifluoromethanesulfonate-promoted bis(trimethylsilyl) sulfide thionation[4] of **2** (1 h) and **3** (2 h) at room temperature led to the formation of 5-benzoyl-3-phenyl-2-thiabicyclo[4.3.0]-nona-3,8-diene (**10**) and 5-(4-methylbenzoyl)-3-(4-methylphenyl)-2-thiabicyclo[4.3.0]nona-3,8-diene (**11**), respectively. The structures of **10** and **11** were supported by elemental analyses and spectral data including 2D $^1H-^1H$ COSY spectra.



10 Ar = C_6H_5
11 Ar = 4-$CH_3C_6H_4$

12 Ar = C_6H_5
13 Ar = 4-$CH_3C_6H_4$

The configurations of compounds **10** and **11** were further established with $^1H-^1H$ NOE difference spectroscopy. In compound **10**, observation of a strong NOE from H6 to H1 (+7%) unambiguously establishes that these two protons are cis ($J = 6.0$ Hz) and a weak enhancement for H5 (+2%) when H6 was irradiated which indicates that H5 and H6 are trans ($J = 8.0$ Hz). In compound **11**, a large enhancement was observed at H1 (+8%) following the irradiation of H6, but a weak NOE was seen for H5 (+3%), which indicates that H1 and H6 are cis ($J = 1.7$ Hz) and that H5 and H6 are trans ($J = 8.2$ Hz).

The formation of **10** and **11** may result from a 1-thia-Cope rearrangement of the proposed respective thiocar-

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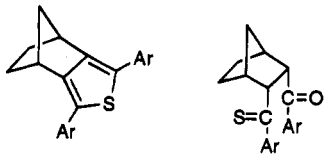
bonyl intermediates **12** and **13**. The [3,3]-sigmatropic mechanism probably involves a transition state with boatlike or twist-boatlike geometry. The ease of rearrangement, which may be catalyzed by trimethylsilyl trifluoromethanesulfonate, is facilitated by the favorable geometry which places the alkene and thione termini close to each other for facile 1,6-bond formation.

Under the same experimental conditions, the 2-*endo*-3-*exo*-isomers **4** (7 h) and **5** (4.5 h) reacted more slowly than **2** and **3** and gave the respective 1-thia-Cope rearrangement products **10** (26%) and **11** (32%) and recovered starting materials (approximately 70% conversion). Presumably, the thermodynamically more stable 2-*endo*-3-*exo*-isomers **4** and **5** were slowly isomerized to the less stable, but more reactive, 2-*endo*-3-*endo*-isomers **2** and **3** which underwent the thionation and rearrangement reactions. Although hetero-Cope rearrangement reactions are known,[33,34] there are only a few examples involving sulfur.[35-40] The reactions of **2** and **3**, which could be examples of a Lewis acid-accelerated sigmatropic rearrangement as well, show how substitution of a heteroatom (i.e., S) for carbon in the 1,5-diene system increases the synthetic utility of the hetero-Cope reactions and leads to the formation of derivatives **10** and **11** of the relatively rare 2-thiabicyclo[4.3.0]nonane system.[41]



14 Ar = C_6H_5 **16** Ar = C_6H_5
15 Ar = 4-$CH_3C_6H_4$ **17** Ar = 4-$CH_3C_6H_4$

In order to demonstrate the role of the carbon–carbon double bond in the mechanism, 2-*endo*-3-*endo*-**6**, 2-*endo*-3-*endo*-**7**, 2-*endo*-3-*exo*-**8**, and 2-*endo*-3-*exo*-**9** were subjected to the same mild thionation procedure. Thionation of compounds **6** (14 h) and **8** (48 h) afforded 1,3-diphenyl-4,5,6,7-tetrahydro-4,7-methanobenzo[*c*]thiophene (**14**),[42] presumably via monoketone monothione **16**.[8,39] In the absence of a double bond in the bicyclic system, **16** cyclizes to **14**. The structure of **14** was further established by single crystal X-ray analysis.[43] Compound **6** isomerized to **8** during the thionation procedure. Similarly, compounds **7** (48 h) and **9** (48 h) yielded 1,3-bis(4-methylphenyl)-4,5,6,7-tetrahydro-4,7-methanobenzo[*c*]thiophene (**15**) via **17**, and compound **7** was isomerized to **9** during the thionation procedure. Presumably, as with 2-*endo*-3-*exo*-**4** and 2-*endo*-3-*exo*-**5**, compounds **8** and **9** isomerize to the more reactive *endo,endo*-isomers (**6** and **7**). Formation of the intermediate monoketone monothiones **16** and **17** may occur before or after isomerization of **8** and **9**, respectively. None of the 2-*exo*-3-*exo*-isomers of **6**–**9** was detected.

Experimental Section

EIMS were obtained at an ionization potential of 70 eV, and CIMS (NH_3 or 2-methylpropane) were obtained at 50, 70 , or 100 eV. ^1H NMR (300 and 500 MHz) and ^{13}C NMR (75.4 and 125.7 MHZ) spectra were recorded in $CDCl_3$. Analytical TLC was performed on Analtech Uniplate 10 × 20 cm (250 μm thick) silica gel GF prescored glass plates, which were developed with hexanes or 10:1 hexanes/ethyl acetate. The plates were visualized by UV. Flash column chromatography was performed on 40 g of 225–400-mesh silica gel.

(*E*)-1,4-Diphenylbut-2-ene-1,4-dione was obtained as previously described:[23-25] yellow crystals, 75%, mp 109–110 °C (lit.[24] mp 109–110 °C); HREIMS *m/z* 236.0821, calcd 236.0837 for $C_{16}H_{12}O_2$; IR (CCl_4, cm^{-1}) 3064 w, 2981 w, 1727 m, 1659 vs, 1596 m, 1448 m, 1321 vs, 1296 vs, 1193 s, 1119 w, 1017 m; UV (CH_3CN) λ_{max} (log ϵ) = 261 (3.62).

(*Z*)-1,4-Diphenylbut-2-ene-1,4-dione was obtained from (*E*)-1,4-diphenylbut-2-ene-1,4-dione:[25] white crystals, 90%, mp 133–134 °C (lit.[25] mp 136 °C); HREIMS *m/z* 236.0826, calcd 236.0837 for $C_{16}H_{12}O_2$; IR (CCl_4, cm^{-1}) 3064 w, 1670 vs, 1599 w, 1449 w, 1391 w, 1321 m, 1295 s, 1230 s, 1194 w, 1012 w; ^1H NMR δ 7.17 (s, 2 H), 7.43 (t, J = 7 Hz, 4 H), 7.55 (t, J = 7 Hz, 2 H), 7.91 (d, J = 7 Hz, 4 H); ^{13}C NMR δ 128.5, 128.6, 133.4, 135.5, 135.9, 192.3 (**C**=O); UV (CH_3CN) λ_{max} (log ϵ) = 256 (3.67).

(*E*)-1,4-Bis(4-Methylphenyl)but-2-ene-1,4-dione was obtained as previously described:[23-25] yellow crystals, mp 147–148 °C (lit.[28] mp 148 °C); ^1H NMR δ 2.43 (s, 6 H), 7.31 (d, J = 8 Hz, 4 H), 7,96 (d, J = 8 Hz, 4 H), 7.99 (s, 2 H); ^{13}C NMR δ 21.6, 128.9, 129.5, 134.4, 134.8, 144.7, 189.3 (**C**=O).

(*Z*)-1,4-Bis(4-methylphenyl)but-2-ene-1,4-dione was obtained from (*E*)-1,4-bis(4-methylphenyl)but-2-ene-1,4-dione:[25,26] white crystals, mp 123–124 °C (lit.[23] mp 123 °C); TLC 10:1 hexanes/ethyl acetate, R_f = 0.2; ^1H NMR δ 2.46 (s, 6 H), 7.14 (s, 2 H), 7.30 (d, 4 H), 7.86 (d, 4 H); ^{13}C NMR δ 21.52, 128.54, 129.21, 133.49, 135.17, 144.21, 191.87.

2-*endo*-3-*endo*-Dibenzoylbicyclo[2.2.1]hept-5-ene (Bicyclo[2.2.1]hept-2-ene-2,3-diylbis(phenylmethanone), 2) was obtained from (*Z*)-1,4-diphenylbut-2-ene-1,4-dione and cyclopentadiene:[25] white crystals, 88%, mp 161–162 °C (lit.[25] mp 161 °C); HREIMS *m/z* 302.1316, calcd 302.1306 for $C_{21}H_{18}O_2$; IR (CCl_4, cm^{-1}) 3063 w, 2978 w, 1689 vs, 1595 w, 1447 w, 1323 w, 1213 vs, 1015 w; ^1H NMR δ 1.55–1.61 (m, 2 H), 3.33 (s, 2 H), 4.35 (s, 2 H), 6.24 (s, 2 H), 7.32–7.46 (m, 6 H), 7.62–7.64 (m, 4 H); ^{13}C NMR δ 48.0, 48.3, 53.5, 127.5, 128.4, 132.3, 134.6, 137.6, 198.0 (**C**=O); UV (CH_3CN) λ_{max} (log ϵ) = 240 (3.54).

2-*endo*-3-*endo*-Bis(4-Methylbenzoyl)bicyclo[2.2.1]hept-5-ene (3) was obtained from (*Z*)-1,4-bis(4-methylphenyl)but-2-ene-1,4-dione and cyclopentadiene:[25] white crystals, mp 175–176 °C; HRCIMS *m/z* [M + H]$^+$ 331.1709, calcd 331.1698 for [$C_{23}H_{22}O_2$ + H]$^+$; ^1H NMR δ 1.53–1.63 (m, 2 H), 2.32 (s, 6 H), 3.31 (s, 2 H), 4.30 (s, 2 H), 6.22 (s, 2 H), 7.14 (d, J = 8 Hz, 4 H), 7.74 (d, J = 8 Hz, 4 H); ^{13}C NMR δ 21.4, 48.0, 48.2, 53.3, 127.6, 129.1, 134.5, 135.1, 142.9, 197.6 (**C**=O). Anal. Calcd for $C_{23}H_{22}O_2$: C, 83.60; H, 6.72. Found: C, 83.45; H, 6.45.

2-*endo*-3-*exo*-Dibenzoylbicyclo[2.2.1]hept-5-ene (4) was obtained from (*E*)-1,4-diphenylbut-2-ene-1,4-dione and cyclopentadiene:[25] 84%, mp 80–81 °C (lit.[29] mp 80 °C); HREIMS *m/z* 302.1318, calcd 302.1306 for $C_{21}H_{18}O_2$; ^1H NMR δ 1.48 (d, J = 8.0 Hz, 1 H), 1.88 (d, J = 8.0 Hz, 1 H), 3.15 (s, 1 H), 3.35 (s, 1 H),

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3.97 (d, J = 4.3 Hz, 1 H), 4.51 (t, J = 3.9 Hz, 1 H), 5.94 (q, J = 2.7 Hz, 1 H), 6.43 (q, J = 3.2 Hz, 1 H), 7.45–8.03 (m, 10 H); ^{13}C NMR δ 47.16, 47.78, 48.51, 128.17, 128.39, 132.77, 132.92, 134.39, 136.94, 199.34, 200.61.

2-*endo*-3-*exo*-5,6-Bis(4-Methylbenzoyl)bicyclo[2.2.1]hept-5-ene (5) was obtained during the thionation of compound **3** (41%): mp 112–113 °C; TLC 10:1 hexanes/ethyl acetate, R_f = 0.38; HREIMS m/z 330.1610 calcd 330.1619 for $C_{23}H_{22}O_2$; IR (KBr, cm^{-1}) 2961 m, 2871 m, 1679 s, 1604 s, 1451 w, 1406 w, 1291 m, 1179 m, 1011 w, 824 m; ^{1}H NMR δ 1.22–1.31 (m, 2 H), 1.58–1.66 (m, 2 H), 1.78–1.80 (d, J = 9.8 Hz, 2 H), 2.39 (s, 3 H), 2.42 (s, 3 H), 2.53 (s, 1 H), 2.74 (s, 1 H), 4.07 (d, J = 5.0 Hz, 1 H), 4.44 (t, 4.5 Hz, 1 H), 7.25 (t, J = 7.5 Hz, 4 H), 7.93 (t, J = 8.0 Hz, 4 H); ^{13}C NMR δ 22.22, 24.72, 29.62, 38.98, 42.57, 43.77, 50.18, 51.48, 129.23, 129.27, 129.40, 129.83, 134.38, 135.22, 144.13, 144.23, 200.54, 201.03. Anal. Calcd for $C_{23}H_{22}O_2$: C, 83.60; H, 6.72. Found: C, 83.16; H, 6.35.

2-*endo*-3-*endo*-Dibenzoylbicyclo[2.2.1]heptane (Bicyclo-[2.2.1]heptane-2,3-diyl-bis(phenylmethanone), 6). Compound **2** was hydrogenated,[30,31] by the procedure described below for **8**, to give **6** (97%): mp 172–173 °C (lit.[32] mp 144–146 °C); HREIMS m/z 304.1473, calcd 304.1463 for $C_{21}H_{20}O_2$; IR (KBr, cm^{-1}) 3058, 2960, 2873, 1676, 1596, 1580; ^{1}H NMR δ 1.44–1.73 (m, 6 H), 2.78 (s, 2 H), 3.99 (s, 2 H), 7.26–7.79 (m, 10 H); ^{13}C NMR δ 23.87, 39.74, 41.63, 52.14, 127.40, 127.62, 128.42, 132.21, 137.94, 198.91. Anal. Calcd for $C_{21}H_{20}O_2$: C, 82.86; H, 6.62. Found: C, 82.65; H, 6.55.

2-*endo*-3-*endo*-Bis(4-Methylbenzoyl)bicyclo[2.2.1]-heptane (Bicyclo[2.2.1]heptane-2,3-diylbis[(4-methylphenyl)methanone], 7) was obtained (79%) by reduction of compound **3** using the procedure described below for the preparation of compound **8**.[30,31] Compound **7**: mp 179–180 °C; TLC 10:1 hexanes/ethyl acetate, R_f = 0.25; HREIMS m/z 332.1781, calcd 332.1776 for $C_{23}H_{24}O_2$; ^{1}H NMR δ 1.42 (d, 2 H), 1.54 (d, 2 H), 1.69 (d, 2 H), 2.31 (s, 6 H), 2.75 (s, 2 H), 3.93 (s, 2 H), 7.11 (d, 4 H), 7.67 (d, 4 H); ^{13}C NMR δ 21.29, 23.70, 38.17, 39.49, 41.50, 42.96, 49.37, 50.68, 51.83, 127.36, 128.46, 128.58, 128.91, 129.03, 135.20, 142.60, 143.53, 198.37, 200.24. Anal. Calcd for $C_{23}H_{24}O_2$: C, 83.09; H, 7.28. Found: C, 82.80; H, 7.06.

2-*endo*-3-*exo*-Dibenzoylbicyclo[2.2.1]heptane (8). To a solution of compound **4** (300 mg, 1.0 mmol) in 10 mL of acetone was added 20 mg of Pd/C (5%) in one portion. The mixture was stirred under H_2 at rt for 2 h, diethyl ether (50 mL) was added, and the Pd/C catalyst was removed by filtration. The filtrate was washed with H_2O (2 × 100 mL), dried ($MgSO_4$), and filtered, and the solvent was evaporated *in vacuo*. Chromatography (10:1 hexanes/ethyl acetate) gave **8** (98%); mp 97–98 °C (lit.[31] mp 105–106 °C); HREIMS m/z 304.1466, calcd 304.1463 for $C_{21}H_{20}O_2$; IR (KBr, cm^{-1}) 3060, 2944, 2868, 1674, 1596, 1579; ^{1}H NMR δ 1.24–1.35 (m, 3 H), 1.63–1.69 (m, 2 H), 1.78–1.82 (d, 1 H, J = 10.85 Hz), 2.55 (s, 1 H), 2.76 (s, 1 H), 4.12 (d, 1 H, J = 4.88 Hz), 4.48–4.51 (m, 1 H), 7.43–8.05 (m, 10 H); ^{13}C NMR δ 24.04, 28.99, 38.28, 41.83, 43.06, 49.69, 50.88, 128.44, 128.50, 128.59, 132.89, 136.16, 137.02, 200.25, 200.53. Anal. Calcd for $C_{21}H_{20}O_2$: C, 82.86; H, 6.62. Found: C, 82.55; H, 6.46.

2-*endo*-3-*exo*-Bis(4-Methylbenzoyl)bicyclo[2.2.1]-heptane (9) was obtained (41%) during the thionation of compound **7** (*vide infra*). Compound **9**: mp 112–113 °C; TLC 10:1 hexanes/ethyl acetate, R_f = 0.38; HRCIMS m/z [M + H]$^+$ 333.1866, calcd for [$C_{23}H_{24}O_2$ + H]$^+$ 333.1854; IR (KBr, cm^{-1}) 2961 m, 2871 m, 1679 s, 1604 s, 1451 w, 1406 w, 1291 m, 1179 m, 1011 w, 824 m; ^{1}H NMR δ 1.22–1.31 (m, 2 H), 1.58–1.66 (m, 2 H), 1.78–1.80 (d, J = 9.8 Hz, 2 H), 2.39 (s, 3 H), 2.42 (s, 3 H), 2.53 (s, 1 H), 2.74 (s, 1 H), 4.07 (d, J = 5.0 Hz, 1 H), 4.44 (t, 4.5 Hz, 1 H), 7.25 (t, J = 7.5 Hz, 4 H), 7.93 (t, J = 8.0 Hz, 4 H); ^{13}C NMR δ 22.22, 24.72, 29.62, 38.98, 42.57, 43.77, 50.18, 51.48, 129.23, 129.27, 129.40, 129.83, 134.38, 135.22, 144.13, 144.23, 200.54, 201.03. Anal. Calcd for $C_{23}H_{24}O_2$: C, 83.09; H, 7.28. Found: C, 82.80; H, 6.93.

5-Benzoyl-3-phenyl-2-thiabicyclo[4.3.0]nona-3,8-diene (10). A flask equipped with a magnetic stirbar, a rubber septum port, a solid addition funnel, a water condenser topped with a T-tube leading to a source of dry N_2 was charged with a mixture of bis(trimethylsilyl) sulfide (238 mg, 1.32 mmol)[3] and trimethylsilyl trifluoromethansulfonate (29 mg, 0.13 mmol) in CH_3CN (6 mL). Compound **2** (200 mg, 0.66 mmol) was added slowly in small portions *via* the solid addition funnel. After the addition the reaction mixture was stirred at rt for 2 h. TLC analysis (99:1 hexanes/ethyl acetate) showed the absence of **2**. Ether (50 mL) was added to the reaction mixture and this reaction mixture was poured to a mixture of ice (15 g) and 10% aqueous $NaHCO_3$ (15 mL). The organic layer was washed with saturated NaCl solution (25 mL) and dried (4 Å molecular sieves, 10 h), the volatile materials were removed *via* in vacuo, and the residue was chromatographed (silica gel, 40 g, 225–400 mesh, 99:1 hexanes/ethyl acetate, R_f = 0.09). Recrystallization from methanol gave white crystals (**10**, 140 mg, 66%, mp 107–108 °C): HREIMS m/z 318.1071, calcd 318.1078 for $C_{21}H_{18}OS$; IR (CCl_4, cm^{-1}) 3060 s, 3029 m, 2925 m, 2850 m, 1689 vs, 1597 s, 1580 m, 1489 s, 1446 vs, 1345 s, 1270 s, 1231 vs, 1202 s, 1181 s, 1074 w, 1029 m, 988 m, 948 m, 909 s, 839 m; ^{1}H NMR δ 2.29 (ddd, $J_{H7b-H7a}$ = 17.0 Hz, J_{H7b-H8} = 2.0 Hz, J_{H7b-H6} = 5.0 Hz, H7b), 2.70 (dd, $J_{H7a-H7b}$ = 17.0 Hz, J_{H7a-H8} = 8.4 Hz, H7b), 3.42 (m, J_{H6-H7b} = 5.3 Hz, J_{H6-H1} = 6.0 Hz, J_{H6-H5} = 8.0 Hz, H6), 4.11 (dd, J_{H5-H6} = 8.0 Hz, J_{H5-H4} = 6.0 Hz, H5), 4.36 (d, J = 9.0 Hz, H1), 5.74 (m, J_{H8-H7b} = 2.0 Hz, J_{H8-H7a} = 7.8 Hz, J_{H8-H9} = 2.0 Hz, H8), 5.86 (m, J_{H9-H8} = 2.0 Hz, J_{H9-H1} = 6.0 Hz, H9), 6.44 (d, J_{H4-H5} = 6 Hz, H4), 7.23 (m, aromatic 3 H), 7.45 (m, aromatic 5 H), 7.99 (d, J = 8.0 Hz, aromatic 2 H); ^{13}C NMR δ 36.1, 44.1, 52.7, 53.5, 124.9, 126.3, 128.2, 128.5, 128.8, 130.1, 133.1, 126.5, 138.6, 141.4, 200.0; UV (CH_3CN) λ_{max} (log ϵ) = 241 (4.64). Anal. Calcd for $C_{21}H_{18}OS$: C, 79.22; H, 5.70. Found: C, 78.86; H, 5.41.

Thionation of 2-*endo*-3-*exo*-Dibenzoylbicyclo[2.2.1]hept-5-ene (4). Following the procedure described above (7 h) for **2**, compound **4** gave **10** (26%, 70% conversion).

5-(4-Methylbenzoyl)-3-(4-methylphenyl)-2-thiabicyclo-[4.3.0]nona-3,8-diene (11) was obtained from compound **3** using the procedure described above for the preparation of **10**. The residue was chromatographed (R_f = 0.10) to give a yellowish liquid (150 mg, 71%): HREIMS m/z 346.1383, calcd 346.1392 for $C_{23}H_{22}OS$; IR (CCl_4, cm^{-1}) 3028 w, 2923 m, 2853 w, 1683 vs, 1607 s, 1508 m, 1442 w, 1408 w, 1342 w, 1276 m, 1233 m, 1180 s, 1118 w, 1037 w, 1016 w, 912 m; ^{1}H NMR δ 2.22 (m, $J_{H7b-H7a}$ = 17.0 Hz, H7b), 2.29 (s, CH_3), 2.39 (s, CH_3), 2.68 (dd, $J_{H7a-H7b}$ = 17.0 Hz, J_{H7a-H8} = 8.0 Hz, H7a), 3.33 (m, J_{H6-H5} = 8.5 Hz, J_{H6-H7b} = 5.5 Hz, H6), 4.07 (dd, J_{H5-H4} = 5.4 Hz, J_{H5-H6} = 8.2 Hz, H5), 4.33 (dd, J_{H1-H9} = 8.2 Hz, J_{H1-H6} = 1.7 Hz, H1), 5.74 (m, J_{H8-H9} = 2.2 Hz, J_{H8-H7a} = 8.0 Hz, H8), 5.88 (m, J_{H9-H1} = 8.2 Hz, H9), 6.39 (d, J_{H4-H5} = 5.4 Hz, H4), 7.07 (d, J = 8.0 Hz, aromatic 2 H), 7.26 (d, J = 8.0 Hz, aromatic 2 H), 7.42 (d, J = 8.0 Hz, aromatic 2 H), 7.90 (d, J = 8.0 Hz, aromatic 2 H); ^{13}C NMR δ 21.0, 21.5, 36.1, 44.2, 52.5, 53.4, 124.3, 126.2, 128.3, 128.9, 129.2, 129.9, 133.1, 124.0, 135.7, 138.1, 141.0, 143.6, 199.7; UV (CH_3CN) λ_{max} (log ϵ) = 251 (4.37). Anal. Calcd for $C_{23}H_{22}OS$: C, 79.74; H, 6.41. Found: C, 79.44; H, 6.50.

Thionation of 2-*endo*-3-*exo*-Bis(4-Methylbenzoyl)bicyclo-[2.2.1]hept-5-ene (5). Following the procedure described above (4.5 h) for **2**, compound **5** gave **11** (32%, 70% conversion).

1,3-Diphenyl-4,5,6,7-tetrahydro-4,7-methanobenzo[*c*]-thiophene (14). Trimethylsilyl trifluoromethansulfonate (87 mg, 0.39 mmol) was slowly added to a solution of compound **6** (200 mg, 0.66 mmol) and bis(trimethylsilyl) sulfide (240 mg, 1.32 mmol) in CH_3CN (10 mL). The mixture was stirred at rt under N_2 for 14 h. Diethyl ether (50 mL) was added to the reaction solution, which was then poured to a mixture of ice (15 g) and 10% $NaHCO_3$ (15 mL). The organic phase was washed with saturated NaCl solution (30 mL), and was dried over molecular sieves. The solution was concentrated *in vacuo*, and the residue was chromatographed (10:1 hexanes/ethyl acetate). Fractions (15 mL) were collected and concentrated *in vacuo*. Two components were isolated. Fractions 4–9 gave compound **14** (60 mg, 30%): mp 145–146 °C (lit.[39] mp 146–147 °C); TLC 10:1 hexanes/ethyl acetate, R_f = 0.73; HRCIMS m/z [M + H]$^+$ 303.1194, calcd for [$C_{21}H_{18}S$ + H]$^+$ 303.1207; IR (CCl_4, cm^{-1}) 3060 s, 3029 m, 2925 m, 2850 m, 1689 vs, 1597 s, 1580 m, 1489 s, 1446 vs, 1345 s, 1270 s, 1231 vs, 1202 s, 1181 s, 1074 w, 1029 m, 988 m, 948 m, 909 s, 839 m; ^{1}H NMR δ 1.21 (m, 2 H), 1.56 (t, 2 H), 2.04 (t, 2 H), 3.58 (s, 2 H), 7.25–7.58 (m, 10 H); ^{13}C NMR δ 27.75, 29.50, 31.06, 39.67, 42.11, 125.40, 127.46, 127.54, 129.59, 129.69, 148.14. Anal. Calcd for $C_{21}H_{18}S$: C, 83.41; H, 6.00. Found: C, 83.25; H, 6.05. Fractions 15–20 gave the 2-*endo*-3-*exo*-isomer **8** (90 mg, 45%).

Thionation of 2-*endo*-3-*exo*-Dibenzoylbicyclo[2.2.1]-heptane (8). Compound **8** was thionated (48 h) by the procedure described above for **6**. Chromatography afforded starting material (**8**, 60% conversion) and the thiophene derivative **14** (15%).

1,3-Bis-(4-Methylphenyl)-4,5,6,7-tetrahydro-4,7-methanobenzo[c]thiophene (15). Trimethylsilyl trifluoromethansulfonate (90 mg, 0.4 mmol) was slowly added to a solution of 2-*endo*-3-*endo*-bis(4-methylbenzoyl)bicyclo[2.2.1]heptane (**7**, 219 mg, 0.66 mmol) and bis(trimethylsilyl) sulfide (240 mg, 1.32 mmol) in CH_3CN (10 mL). The mixture was stirred under N_2 at rt for 48 h. Diethyl ether (50 mL) was added to the reaction solution, which was then poured onto a mixture of ice (15 g) and 10% $NaHCO_3$ (15 mL). The organic phase was washed with saturated NaCl solution (30 mL), dried ($MgSO_4$), and concentrated *in vacuo*, and the residue was chromatographed (10:1 hexanes/ethyl acetate). The first fraction was the thiophene derivative **15** (18%), mp 184–185 °C; TLC 10:1 hexanes/ethyl acetate, $R_f = 0.65$; HREIMS m/z 330.1437, calcd 330.1442 for $C_{23}H_{22}S$; IR (KBr, cm^{-1}) 3019 w, 2967 m, 2865 w, 1636 w, 1503 s, 1116 w, 816 s; ^1H NMR δ 1.53 (m, 3 H), 1.55 (m, 1 H), 2.03 (d, 2 H), 2.36 (s, 6 H), 3.55 (s, 2 H), 7.18–7.47 (m, 8 H); ^{13}C NMR δ 21.01, 27.29, 40.67, 49.59, 126.39, 126.82, 129.26, 131.68, 136.29, 147.55. Anal. Calcd for $C_{23}H_{22}S$: C, 83.60; H, 6.72. Found: C, 83.37; H, 6.47. The second fraction was the 2-*endo*-3-*exo*-isomer (**9**, 41%).

Thionation of 2-*endo*-3-*exo*-Bis(4-Methylbenzoyl)bicyclo-[2.2.1]heptane (9). Compound **9** was thionated at rt (48 h) by the procedure described above for **7**. Chromatography afforded starting material **9** (60% conversion) and the thiophene derivative **17** (17%).

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Supplementary Material Available: The ^1H NMR spectra of **3**, **5–10**, **13**, and **14**, the 2D $^1H-^1H$ COSY spectra of **9–11**, and the ^1H NOE spectrum of **10** (13 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.