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Synthesis, Stereochemistry, and Chiroptical Spectra of Cyclopropyl Lactones and Thionolactones

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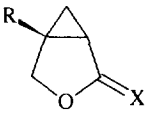
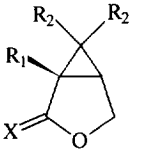
Abstract: Several optically active substituted 3-oxabicyclo[3.1.0]hexan-2-ones and their thiocarbonyl analogues were synthesized, and their circular dichroism spectra are reported. It was found that the n-π* Cotton effect sign is determined by the helicity of an inherently chiral chromophore formed by the lactone or thiolactone group and the cyclopropyl moiety. The π-π* Cotton effect of thiocarbonyl compounds shows opposite sign to that observed for the lowest energy transition. The crystal structures of two compounds were solved to establish their molecular geometries.

There is an increasing interest in optically active 3-oxabicyclo[3.1.0]hexan-2-ones as useful synthetic intermediates.[1,2] These lactones have found application in the synthesis of natural products,[3] substances with pharmacological activity,[4] and conformationally restricted analogues of naturally occuring amino acids.[5] Hence a simple method of determination of the absolute stereochemistry of the lactones with the 3-oxabicyclo[3.1.0]hexane skeleton is desirable. This problem can be solved by means of the circular dichroism (CD) spectroscopy using appropriate rules connecting the Cotton effect (CE) sign with the geometry of a molecule. Due to a very little conformational flexibility lactones with strained bicyclic skeletons are particularly well suited model compounds for chiroptical studies. The only absorption band of the ester chromophore accessible to commercial CD instruments is the weak n-π* transition at ca. 220 nm.[6] However, it is known that the substitution of sulfur for oxygen in the carbonyl group shifts the absorption maximum to the considerable longer wavelengths, which makes possible to observe the n-π* transition of thiocarbonyls near the visible region.[7] Though the chiroptical properties of lactones attracted a great deal of interest[6,8] there is no information available on the CD spectra of thionolactones.



1a R = H, X = O
1b R = H, X = S
2a R = Ph, X = O
2b R = Ph, X = S



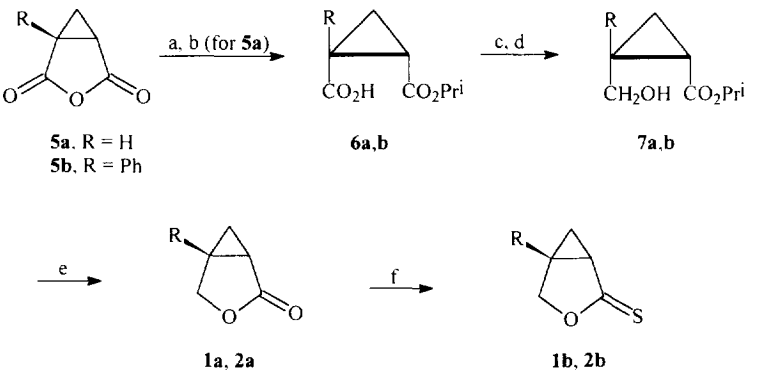
3a R_1 = H, R_2 = Me, X = O
3b R_1 = H, R_2 = Me, X = S
4a R_1 = Ph, R_2 = H, X = O
4b R_1 = Ph, R_2 = H, X = S

In the present work we describe the synthesis and the CD study of the bicyclic lactones **1a-4a** of the known absolute configuration and the corresponding thionolactones **1b-4b**. The molecular geometries were established by the X-ray crystallographic analysis of two model compounds.

Results and Discussion

Syntheses - The preparation of lactones **1a-4a** and thionolactones **1b-4b** is summarized in Scheme I.

Scheme I



5a, R = H
5b, R = Ph

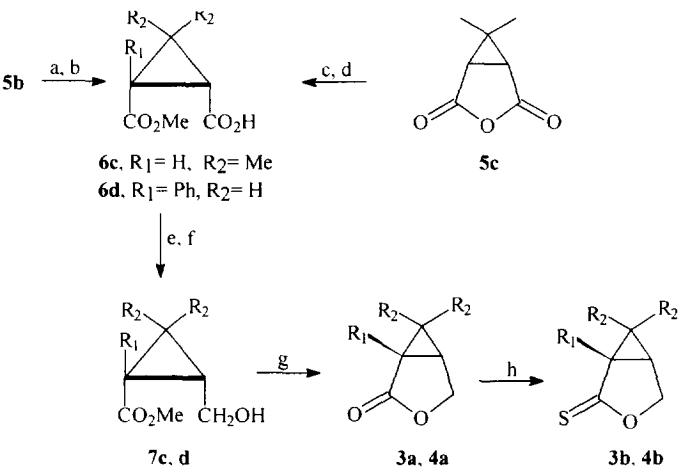
6a,b

7a,b

1a, 2a

1b, 2b

a) PriOH, pyridine; b) quinine; c) $(COCl)_2$; d) $NaBH_4$, THF;e) TosOH, C_6H_6, reflux12h; f) LR, PhMe, reflux 4h.



6c, R_1= H, R_2= Me
6d, R_1= Ph, R_2= H

5c

7c, d

3a, 4a

3b, 4b

a) MeOH, HCl, reflux; b) KOH, MeOH; c) MeOH, pyridine; d) d-ephedrine; e) $(COCl)_2$; f) $NaBH_4$, THF; g) TosOH, C_6H_6, reflux 12 h; h) LR, PhMe, reflux 4h.

The racemic half-esters **6a** and **6c** were obtained from the *meso*-anhydrides **5a** and **5c**, and resolved to enantiomers with quinine and ephedrine, respectively. The optically active monoesters **6b** and **6d** were prepared by a regioselective ring-opening of the anhydride **5b** and by a regioselective hydrolysis of the corresponding diester, respectively. The reduction of **6a-d** to the hydroxy esters **7a-d** followed by acid catalyzed cyclization in benzene afforded optically pure lactones **1a-4a**. Thionation of **1a-4a** with Lawesson's reagent[9] in boiling toluene gave thionolactones **1b-4b**.

Molecular Geometry. - Due to steric constraints imposed by a strained bicyclic structure, the bicyclo[3.1.0]hexane system and its heterocyclic analogues exhibit rather unusual stereochemistry. The six-membered ring in this kind of compounds prefers a boat-like conformation, because it leads to a staggered configuration about the C(1)-C(2) and C(4)-C(5) bonds, in contrast to a chair-like one, which leads to an eclipsed configuration about these bonds.[10] However, introduction of the sp^2 hybridized atoms into the five-membered ring part of the skeleton is expected to cause its flattening and result in a sofa-like geometry of the bicyclic system.[11] In fact, the X-ray crystallographic structures of the lactone **4a** and thionolactone **3b** (Fig 1, **4a** (left) and **3b** (right)) indicate only a very small folding of the five-membered rings: e.g., the O(3)-C(2)-C(1)-C(5) and O(3)-C(4)-C(5)-C(1) torsional angles in **4a** are of -3.7(2) and 9.5(2)°, and in **3b** they are of -3.5(2) and 5.5(2)°, respectively. An important feature of the above structures is a marked non-planarity of the ester and tioester groups manifested by the C-O-C=O and C-O-C=S torsional angles being of -170.0(2) and -172.9(1)° in **4a** and **3b**, respectively.[12] However, the observed distortions from planarity might be due to crystal packing forces, since geometries obtained from molecular modeling based on the semiempirical AM1 calculations[13] showed the five-membered rings and chromophores to be essentially planar.[14]

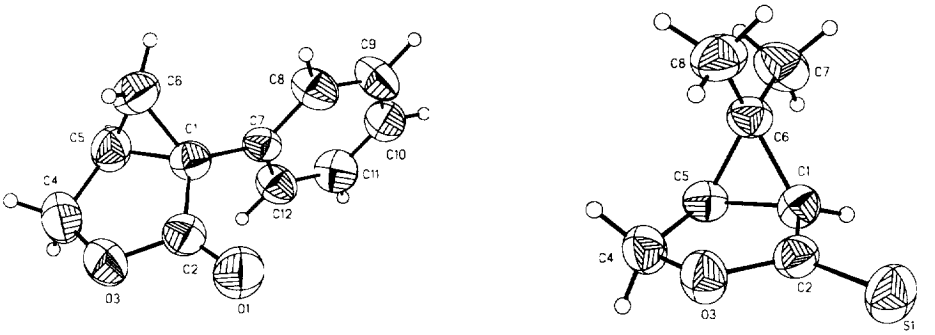


Figure 1. ORTEP draving of the crystal structure of **4a** (left) and **3b** (right). Thermal ellipsoids are drawn at the 50% probability level for heavy atoms.

UV-vis and CD Spectra. - The UV spectra of the lactones **1a** and **3a** show weak absorption near 220 nm (ε 65), typical for this class of compounds and originating from the n-π* electronic excitation.[6b] The lowest energy transition of the corresponding thionolactones **1b** and **3b** appears as a low intensity band at about 390 nm in cyclohexane solution. It manifests the n-π* origin through its prominent blue shift of ca. 20 nm upon changing the solvent to methanol. A higher intensity strong absorption at 250 nm can be identified as the π-π* excitation on the basis of a small red shift (3 nm) on going from non-polar (cyclohexane) to polar (methanol) solvent. Available information regarding the electronic spectra of thioesters is scant. Janssen observed a weak band at 377 nm (ε 40) and a strong one at 241 nm (ε 10000 - 15000) in hydrocarbon solvent for ethyl thionoacetate and assigned them to n-π* and π-π* excitations, respectively.[15] More recent semiempirical MO calculations confirmed these assignments.[16]

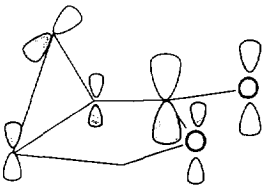
Table 1. CD Data of Lactones **1a** - **4a** and Thionolactones **1b** - **4b**.

Compd.	Solv.[a]	λ, nm (10^{-3}[θ])[b]	Compd.	Solv.[a]	λ, nm (10^{-3}[θ])[b]
1a	C	222 (-16.3)	**1b**	C	393 (-11.8), 250 (38.4)
	M	217 (-24.7)			
2a	C	227 (-45.8), 267 (0.09)	**2b**	C	392 (-21.2), 252 (26.2)
	M	225 (-58.1)			
3a	C	226 (10.4)	**3b**	C	394 (14.0), 254 (-40.0)
	M	217 (16.7)			
4a	C	222 (16.1), 266 (0.38)	**4b**	C	395 (11.3), 248 (-24.0)
	M	220 (16.2), 260 (0.31)			

[a] C - cyclohexane, M - methanol [b] Molar ellipticity in deg cm^2 $dmol^{-1}$

A characteristic feature of the CD spectra of the lactones **1a-4a** and their thiocarbonyl analogues **1b-4b** (Table 1) is the unusually strong magnitude of the Cotton effects (CEs) corresponding to the n-π* transition. It is noteworthy, that both classes of compounds show the same CE signs. The close correlation between the long-wavelength CEs of the related lactones and thionolactones results from similarities in their molecular geometries and confirms essentially the same character of their n-π* electronic transitions. However, the existing lactone sector rules[6, 17] cannot be used for correlation of the CE sign with the molecular chirality, since they predict the cyclopropyl ring contribution to the CE of opposite sign to that observed (e.g., **1a** and **3a**). By analogy with α,β-cyclopropyl ketones,[18] which do not obey the octant rule, the chiroptical properties of the title compounds can be explained assuming inherent chirality of their chromophores.[19] They are

formed by the ester or thionoester group "conjugated" with the cyclopropyl moiety.[20] It is confirmed by the CNDO/S-CI calculations[21] revealing effective delocalization of the π^* molecular orbital (shown below), involved in the lowest energy excitation, to the cyclopropyl moiety.

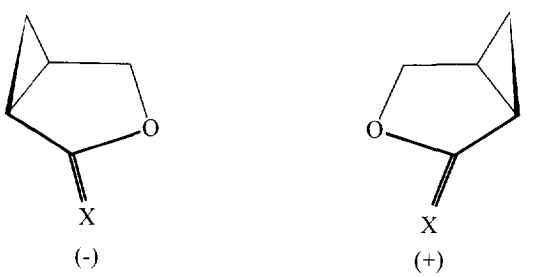


Thus the n-π^* CE sign should be determined by the helicity of the dissymmetric chromophore (Scheme II), which remains in agreement with the experiment. This contribution (chiral first sphere following Snatzke's hypothesis of spheres)[22] overweighs that made by the ring substituents (chiral first sphere). The role of the phenyl substituents in **2a,b** and **4a,b** seems to be more complex than that of of the alkyl groups, because they also may be treated as "conjugated" with the three-membered ring.[23] This may explain the enhanced absorption of **2b** [λ_{max} 393 nm (ε 100)] and extremely strong CE exhibited by **2a,b**, since their chromophores should be extended to the phenyl ring. Furthermore, in the case of **4a,b** the situation becomes even more complicated, due to a homoconjugation of the phenyl group with the carbonyl or thiocarbonyl functions. Obviously, the above interactions depend on the mutual orientation of the phenyl ring and the remaining part of the molecule.

The influence of the small deviations of the ester and thionoester groups from planarity observed in the X-ray structures seems to be less important, since the literature examples of some severely distorted tricyclic lactone systems show much weaker CEs than the cyclopropyl lactones.[24]

The additional weak and highly structured CD bands at 265 nm exhibited by the compounds **2a** and **4a** unequivocally can be attributed to the ^1L_b transition of the phenyl group.

Scheme II



X = O, S

The π-π^* absorption of thionolactones **1b-4b** occuring in near UV makes possible to observe the corresponding CEs. Their sign is opposite to that observed for the lowest energy transition and also might be useful for stereochemical predictions. However, the small value of the dissymmetry factor[25] ($g = \Delta\varepsilon/\varepsilon$ of ca. 0.001) of this allowed electric dipole transition makes measurements in that region slightly more difficult.

Experimental

CD spectra were recorded on a JASCO J-20 spectropolarimeter. UV-vis measurements were performed on a Beckman 3600 spectrophotometer. ^1H and ^{13}C NMR spectra were obtained with Bruker MSL-300 and WP-200 spectrometers operating at 300 and 50 MHz, respectively. IR absorptions were taken with a Zeiss UR-10 spectrometer. Specific rotations were measured on a Rudolph Autopol II digital polarimeter.

1,2-Cyclopropanedicarboxylic Anhydride (5a). 1,2-Cyclopropanedicarboxylic acid (5.0 g), a mixture of *cis* and *trans* isomers prepared according to the McCoys procedure,[26] was boiled with acetic anhydride (5 ml) for 0.5 h. Then the acetic anhydride was distilled off, the bath temperature was rised up to 250 °C and the product began to distill; yield 3.9 g (91%); m.p. 58-59 °C (toluene) (lit.[26] m.p. 58-60 °C).

(1*R*,2*S*)-2-(1-Methylethoxycarbonyl)-1-cyclopropanecarboxylic Acid (6a). Anhydride **5a** (5.0 g, 45 mmol) was dissolved in a mixture of 2-propanol (10 ml) and pyridine (6 ml) and heated at 100 °C for 1 h. Then the solvents were evaporated at reduced pressure, the residue was dissolved in AcOEt (30 ml) and washed with diluted hydrochloric acid. The organic layer was dried ($MgSO_4$), evaporated to dryness and the product was crystallized from toluene-hexane to obtain 6.9 g (90%) of the racemic monoester **6a**; m.p. 48 °C; ^1H NMR ($CDCl_3$) δ 9.55 (br, 1 H), 5.03 (sep, J = 6.2 Hz, 1 H), 2.07 (m, 2 H), 1.66 (m, 1 H), 1.31 (m, 1H), 1.22 (d, J = 6.2 Hz, 3 H), 1.21 (d, J = 6.2 Hz, 3 H).

Anal. Calcd. for $C_8H_{12}O_4$ (172): C, 55.81; H, 7.02. Found: C, 55.92; H, 7.00.

The racemate was resolved to enantiomers with quinine (three crystallizations of the salt from acetone-hexane). The laevorotatory product **6a** solidified upon refrigeration and had $[\alpha]^{22}_D$ -9.7 (*c* 10, $CHCl_3$), ee 97%.[27]

(1*R*,2*S*)-2-(1-Methylethoxycarbonyl)-1-phenyl-1-cyclopropanecarboxylic Acid (6b). The half ester **6b** was obtained from (1*R*,2*S*)-1-phenyl-1,2-cyclopropanedicarboxylic anhydride[28] (**5b**) in a manner similar to that of compound **6a** and had m.p. 84-85 °C (toluene-hexane); $[\alpha]^{20}_D$ +162 (*c* 1, MeOH); ^1H

NMR ($CDCl_3$) δ 7.42 (m, 2 H), 7.31 (m, 3 H), 5.02 (sep, J = 6.3 Hz, 1 H), 2.26 (dd, J = 5.0 and 8.6 Hz, 1 H), 2.10 (dd, J = 4.9 and 6.6 Hz, 1 H), 1.53 (dd, J = 5.0 and 8.6 Hz, 1 H), 1.22 (d, J = 6.3 Hz, 3 H), 1.21 (d, J = 6.3 Hz, 3 H).

Anal. Calcd. for $C_{14}H_{16}O_4$ (248): C, 67.73; H, 6.50. Found: C, 67.52; H, 6.55.

3,3-Dimethyl-1,2-cyclopropanedicarboxylic Anhydride (5c). Powdered $KMnO_4$ (40g, 0.25 mol) was added in small portions to a stirred solution of ethyl chrysanthemate (Aldrich, a mixture of *cis* and *trans* isomers) (15 ml, 0.14 mol) in acetone (50 ml) over a period of 3 h. Stirring was continued for further 2 h. The precipitate was filtered, washed with acetone, mixed with Na_2SO_3 (30 g, 0.24 mol) and carefully added in small portions to 80 ml 30% H_2SO_4 with striring and cooling. The reaction mixture was extracted two times with portions of 50 ml AcOEt. The combined extracts were dried (Na_2SO_4) and the solvent was removed in vacuo. The residue was dissolved in 20 ml of 40% aqueous NaOH and refluxed for 10 min., acidified with 30% H_2SO_4 and extracted with three portions of 50 ml AcOEt. The combined extracts were dried (Na_2SO_4), evaporated to dryness and the resulted dicarboxylic acid was boiled with acetic anhydride (20 ml) for 20 min. Then the acetic anhydride was distilled off, bath temperature was raised up to 250 °C and the anhydride began to distill; yield 6.5 g (61%); m. p. 54-55 °C (toluene-hexane) (lit.[29] m.p. 56 °C).

(1*R*,2*S*)-2-(Methoxycarbonyl)-3,3-dimethyl-1-cyclopropanecarboxylic Acid (6c). Anhydride **5c** (6.5 g, 46 mmol) was dissolved in a mixture of methanol (30 ml) and pyridine (10 ml) and allowed to stand at room temperature for 12 h. Then the solvents were removed, the residue was dissolved in AcOEt (50 ml) and washed with dilute HCl. The organic layer was dried (Na_2SO_4) and AcOEt was evaporated at reduced pressure. The racemic half-ester was crystallized from toluene hexane; yield 5.9 g (74%); m. p. 105-107 °C (lit.[30] m.p. 107-109 °C); ^{1}H NMR ($CDCl_3$) δ 9.8 (br s, 1H), 3.72 (s, 3 H), 1.96 (AB system, J = 8.9 Hz, 2 H), 1.38 (s, 3 H), 1.27 (s, 3 H).

The racemic monoester was resolved to enantiomers by crystallization of the d-ephedrine salt from acetone-hexane. The laevorotatory product **6c** had m.p. 54-55 °C (toluene-hexane); $[\alpha]^{22}_D$ -19.0 (*c* 4, MeOH) {lit.[31a] enantiomer $[\alpha]^{20}_D$ +29.95 (wet EtOH); lit.[31b] $[\alpha]^{22}_D$ -17.5 (*c* 1, MeOH), ee 90% }.

(1*S*,2*R*)-2-(Methoxycarbonyl)-2-phenyl-1-cyclopropanecarboxylic Acid (6d). Thionyl chloride (0.5 ml) was carefully added to a stirred solution of (1*R*,2*S*)-1-phenyl-1,2-cyclopropanedicarboxylic anhydride[28] (**5b**) (9.4 g, 50 mmol) in methanol (50 ml) and the mixture was refluxed for 12 h. After removal of the methanol the residue was dissolved in benzene and washed with saturated aqueous $NaHCO_3$. The

organic layer was dried ($MgSO_4$) and the solvent was evaporated at reduced pressure. The resulted diester was hydrolyzed with KOH (2.9 g) in methanol (20 ml) for 8 h at room temperature. Then the solvent was removed in vacuo and the resulted solid was dissolved in water (20 m l), acidified weith dilute HCl and extracted with AcOEt (30 ml). The extract was dried ($MgSO_4$) and the solvent was evaporated to obtain the oily half-ester **6d** (9.5 g); ^{1}H NMR ($CDCl_3$) δ 7.46 (m, 2 H), 7.30 (m, 3 H), 3.67 (s, 3 H), 2.27 (dd, J = 4.9 and 8.5 Hz, 1 H), 2.14 (dd, J = 4.9 and 6.2 Hz, 1 H), 1.61 (dd, J = 4.9 and 8.5 Hz, 1 H); **the cyclohexylammonium salt** m.p. 145-147 °C (benzene- hexane); $[\alpha]^{20}_D$ +101 (*c* 2, C_6H_6).

Anal. Calcd. for $C_{18}H_{25}NO_4$ (319): C, 67.69; H, 7.89; N, 4.39. Found: C, 67.52; H, 7.95; N, 4.28.

(1*S*,5*R*)-3-Oxabicyclo[3.1.0]hexan-2-one (1a). Oxalyl chloride (2.0 ml) was added to a solution of the half-ester **6a** (1.7 g, 10 mmol) in benzene (1.5 ml). After vigorous reaction ceased (ca. 1 h) the solvents were evaporated and the resulted acid chloride was taken into THF (20 ml) and powdered $NaBH_4$ (1.0 g) was added with stirring. After cooling the reaction mixture to 0 °C, 10 ml of water was added dropwise with stirring. The stirring was continued for 0.5 h and the reaction mixture was extracted with three portions of 30 ml AcOEt. The combined extracts were dried (Na_2SO_4) and the solvent was evaporated in vacuo. The resulted sirrup was dissolved in C_6H_6 (15 ml) containing 4-toluenesulphonic acid (100 mg) and refluxed for 12 h. After removal of the benzene the residue was chromatographed on silica-gel (elution with benzene) to obtain 0.82 g (84%) of the product as an oil; $[\alpha]^{20}_D$ -60.0 (*c* 2.8, $CHCl_3$) {lit.[1a] $[\alpha]^{25}_D$ -61.8 (*c* 6, $CHCl_3$)}; IR (film) 1760 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.31 (dd, J = 4.9 and 9.3 Hz, 1 H), 4.19 (d, J = 9.2 Hz, 1 H), 2.21 (m, 1 H), 2.02 (dddd, J = 1.0, 3.3, 5.8 and 9.0 Hz, 1 H), 1.23 (ddd, J = 4.8, 7.5 and 9.0 Hz, 1 H), 0.82 (dt, J = 3.3 and 4.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 176.5, 69.4, 17.4, 17.2, 12.1; UV (cyclohexane) λ_{max} 220 nm (ε 64).

(1*S*,5*S*)-5-Phenyl-3-oxabicyclo[3.1.0]hexan-2-one (2a). The lactone **2a** was obtained from the half-ester **6b** in a manner similar to that of compound **1a** and had m.p. 41-42 °C (toluene-hexane); $[\alpha]^{22}_D$ -13.0 (*c* 2, C_6H_6); IR (KBr) 1765 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.38-7.25 (complex m, 5 H), 4.50 (dd, J = 0.9 and 9.2 Hz, 1 H), 4.48 (dd, J =0.9 and 9.2 Hz, 1 H), 2.31 (ddd, J = 0.9, 3.5 and 9.2 Hz, 1 H), 1.70 (ddd, J = 0.9, 4.7 and 7.5 Hz, 1 H), 1.37 (dd, J = 3.5 and 4.7 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 175.5, 136.4, 128.7, 127.8, 127.7, 73.3, 33.5, 24.5, 18.9.

Anal. Calcd. for $C_{11}H_{10}O_2$ (174): C, 75.84; H, 5.79. Found: C, 75.79; H, 5.83.

(1*S*,5*R*)-6,6-Dimethyl-3-oxabicyclo[3.1.0]hexan-2-one (3a). The lactone **3a** was obtained from the half-ester **6c**, in a manner similar to that of compound **1a**, as an oil and had $[\alpha]^{21}_{D}$ +82 (*c* 1, $CHCl_3$) {lit.[2e] $[\alpha]^{23}_{D}$ +85.0 (*c* 1.96, $CHCl_3$)}; IR (film) 1760 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.32 (dd, J = 5.5 and 9.9 Hz, 1 H), 4.10 (dt, J = 1.1 and 9.9 Hz, 1 H), 2.02 (ddd, J = 1.1, 5.5 and 6.4 Hz, 1 H), 1.90 (dd, J = 1.0 and 6.4 Hz, 1 H), 1.13 (s, 3 H), 1.12 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 174.9, 66.5, 30.4, 29.9, 25.1, 22.9, 14.3; UV (cyclohexane) λ_{max} 218 nm (ε 68).

(1*R*,5*S*)-1-Phenyl-3-oxabicyclo[3.1.0]hexan-2-one (4a). The lactone **4a** was obtained from the half-ester **6d**, in a manner similar to that of compound **1a**, as colorless crystalls and had m.p. 59-60 °C (toluene-hexane) (lit.[4a] m.p. 56-57 °C); $[\alpha]^{22}_{D}$ +85 (*c* 1.6, MeOH) {lit. enantiomer $[\alpha]^{20}_{D}$ -78.5 (*c* 1.42, MeOH)}; IR (KBr) 1750 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.44-7.30 (complex m, 5 H), 4.47 (dd, J = 4.6 and 9.3 Hz, 1 H), 4.30 (d, J = 9.3 Hz, 1 H), 2.56 (dt, J = 4.6 and 7.8 Hz, 1 H), 1.65 (dd, J = 4.8 and 7.8 Hz, 1 H), 1.37 (t, J = 4.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 176.0, 134.0, 128.4, 128.2, 127.4, 68.0, 31.5, 24.9, 20.0.

(1*S*,5*R*)-3-Oxabicyclo[3.1.0]hexan-2-thione (1b). The lactone **1a** (1.28 g, 13 mmol) and Lawesson's reagent (2.83 g, 7 mmol) were refluxed in toluene (6 ml) for 4h. After removal of toluene the residue was chromatographed on silica-gel (elution with benzene-hexane, 2:1) to obtain 0.65 g (44%) of the product as a yellow oil; $[\alpha]^{20}_{D}$ -383 (*c* 2, C_6H_6); IR (film) 1350, 1245, 1185 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.68 (dd, J = 4.8 and 9.9 Hz, 1 H), 4.60 (dt, J = 1.1 and 9.9 Hz, 1 H), 2.82 (dddd, J = 1.1, 3.2, 5.6 and 9.0 Hz, 1 H), 2.32 (dddt, J = 1.1, 4.9, 5.6 and 7.5 Hz, 1 H), 1.42 (ddd, J = 4.9, 7.6 and 9.0 Hz, 1 H), 0.88 (dt, J = 3.2 and 4.9 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 221.2, 78.5, 34.5, 21.1, 16.1; UV (cyclohexane) λ_{max} 391 (ε 36), 250 nm (11300); UV (MeOH) λ_{max} 370 (ε 46) and 252 nm (12700).

Anal. Calcd. for C_5H_6OS (114): C, 52.60; H, 5.30; S, 28.09. Found: C, 52.35; H, 5.32; S, 27.82.

(1*S*,5*S*)-5-Phenyl-3-oxabicyclo[3.1.0]hexan-2-thione (2b). The thionolactone **2b** was obtained in a manner similar to that of compound **1b** and had m.p. 41 °C (hexane); $[\alpha]^{20}_{D}$ -374.5 (*c* 2, C_6H_6); IR (KBr) 1370, 1330, 1200 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.40-7.25 (complex m, 5 H), 4.87 (dd, J = 0.9 and 9.9 Hz, 1 H), 4.82 (dd, J = 0.9 and 9.9 Hz, 1 H), 3.01 (ddd, J = 1.1, 3.4 and 9.2 Hz, 1 H), 1.87 (ddd, J = 0.9, 4.8 and 9.2 Hz, 1 H), 1.41 (dd, J = 3.4 and 4.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 220.3, 136.0, 129.0, 128.2, 127.9, 82.2, 41.7, 37.6, 22.9; UV (cyclohexane) λ_{max} 393 (ε 100) and 252 nm (19900).

Anal. Calcd. for $C_{11}H_{10}OS$ (190): C, 69.41; H, 5.30; S, 16.85. Found: C, 69.49; H, 5.33; S; 16.71.

(1*S*,5*R*)-6,6-Dimethyl-3-oxabicyclo[3.1.0]hexan-2-thione (3b). The thionolactone **3b** was obtained in a manner similar to that of compound **1b** and had m.p. 46-47 °C (hexane); $[\alpha]^{20}_{D}$ +465 (*c* 1.1, C_6H_6); IR (KBr) 1350, 1230, 1190 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.68(dd, J = 5.7 and 10.5 Hz, 1 H), 4.49(dt, J = 1.3 and 10.5 Hz, 1 H), 2.70 (dd, J = 1.3 and 6.0 Hz, 1 H), 2.12 (td, J = 1.4 and 5.9 Hz, 1 H), 1.19 (s, 3 H), 1.11 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 219.0, 75.5, 47.4, 33.0, 26.1, 25.0, 13.1; UV (cyclohexane) λ_{max} 395 (ε 44), 254 nm (15000); UV (MeOH) λ_{max} 370 (ε 62) and 257 nm (16600) .

Anal. Calcd. for $C_7H_{10}OS$ (142): C, 59.12; H, 7.09; S, 22.55. Found: C, 59.18; H, 7.10; S, 22.40.

(1*R*,5*S*)-1-Phenyl-3-oxabicyclo[3.1,0]hexan-2-thione (4b). The thionolactone **4b** was obtained in a manner similar to that of compound **1b** and had m.p. 121-122 °C (toluene-hexane): $[\alpha]^{20}_{D}$ +133 (*c* 2, C_6H_6); IR (KBr) 1340, 1290, 1240 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.42-33 (complex m, 5 H), 4.83 (dd, J = 4.7 and 9.9 Hz, 1 H), 4.65 (d, J = 9.9 Hz, 1 H), 2.55 (ddt, J = 0.9, 4.8 and 7.8 Hz, 1 H), 1.88 (dd, J = 4.8 and 7.8 Hz, 1 H), 1.32 (t, J = 4.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 221.7, 135.9, 130.1, 128.3, 127.9, 76.7, 48.0, 27.9, 21.7; UV (cyclohexane) λ_{max} (ε 32) and 254 nm (9900).

Anal. Calcd. for $C_{11}H_{10}OS$ (190): C, 69.41; H, 5.30; S, 16.85. Found: C, 69.37; H, 5.29; S, 17.10.

X-Ray Crystal Structure Analysis.[32] Diffraction data were obtained on a Kuma KM-4 diffractometer with graphite monochromated MoKα radiation for a crystal of **4a** with dimensions 0.4x0.35x0.1 mm and a crystal of racemic **3b** with dimensions 0.7x0.4x0.2 mm. The structures were solved by direct methods with the program SHELXS-86.[33] Full matrix least-squares refinement was carried out with SHELXL-93.[34]

Crystal data for $C_{11}H_{10}O_2$ (**4a**): orthorhombic, space group $P2_12_12_1$, a = 5.344(1) A, b = 8.891(2) A, c = 18.854 A, V = 895.8(3) A^3, Z = 4, D_{calcd} = 1.292 g cm^{-3}, λ(Mo Kα) = 0.71073 A, T = 293 K, R_1 = 0.033, wR_2 = 0.089 for 1601 independent reflections of which 1194 had $I > 2\sigma(I)$.

Crystal data for $C_7H_{10}OS$ (**3b**): monoclinic, space group $P2_1/c$, a = 8.776(2) A, b = 7.453(1) A, c = 11.836(2) A, β = 100.19(2)°, V = 762.0(2) A^3, Z = 4, D_{calcd} = 1.240 g cm^{-3}, λ(Mo Kα) = 0.71073 A, T = 293 K, R_1 = 0.029, wR_2 = 0.079 for 1349 independent reflections of which 1022 had $I > 2\sigma(I)$.

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