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Synthesis, structure and chiroptical spectra of the bicyclic α -diketones, imides and dithioimides related to santenone

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Abstract

Isomeric α -diketones, imides and dithioimides related to santenone were prepared in a multistep synthesis from (+)-camphor and their CD spectra compared with those of analogous chromophoric systems related to camphor. In the case of conformationally rigid α -diketones the methyl substituents at C-7, lying on the symmetry plane of the chromophore, exert only a weak contribution to the $n-\pi^*$ Cotton effects. In contrast, the Cotton effect magnitudes of the anhydrides, imides and dithioimides are significantly affected by the substituents at C-8. The steric interaction of these chromophores with the *syn*-methyl group at C-8, leading to the chromophore distortion, was confirmed by X-ray crystallographic studies. © 2000 Elsevier Science Ltd. All rights reserved.

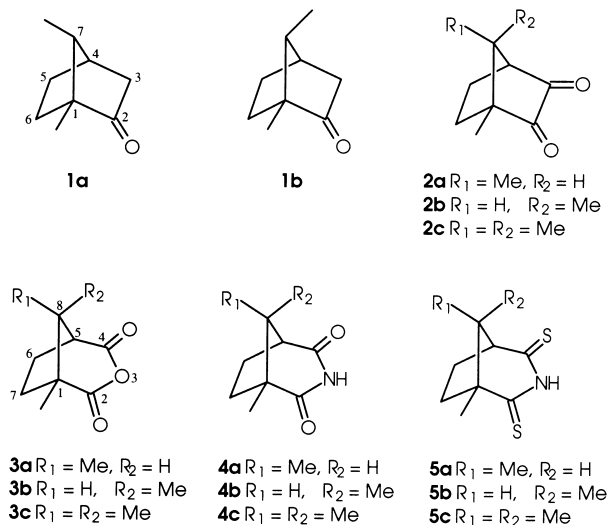
1. Introduction

Santenones **1a,b**, the isomeric ketones related to camphor, have been isolated from Indian sandalwood (*Santalum album*).¹ A close structural relationship between the α - and β -stereoisomers (**1a** and **1b**, respectively) results in serious difficulties in the preparation of their derivatives in a pure form. Furthermore, there are conflicting reports on their configuration at C-7.^{1–3} However, the optically active ketones **1a,b** can be considered as useful substrates for the synthesis of the model chromophoric systems suitable for spectroscopic studies.

Recently, we have been involved in the chiroptical studies of α -diketones,⁴ cyclic anhydrides, imides⁵ and dithioimides.⁶ In this paper we report the preparation and the CD spectra of santenone related compounds **2a,b–5a,b** containing the above chromophores. Our aim was to compare their chiroptical properties with those of the analogous compounds **2c–5c** derived from camphor. The systems **2a,b,c–5a,b,c** contain methyl substituents at C-7 or C-8 located on the symmetry plane of the chromophores.^{4–6} Because this plane is also a nodal surface in the corresponding sector rules,

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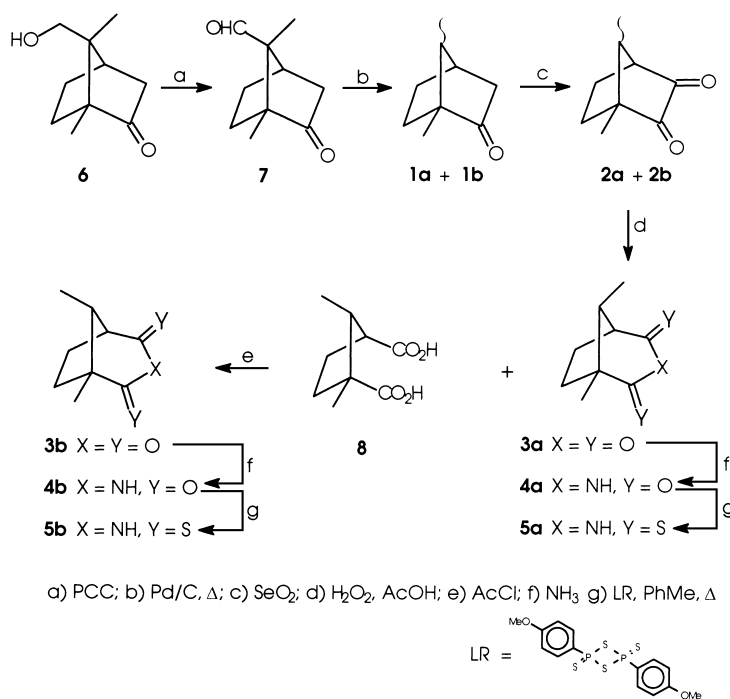
used for a prediction of the Cotton effect (CE) sign, the methyl substituents are expected to exert only a negligible contribution to the CE sign and magnitude of the conformationally rigid compounds. On the other hand, the steric effect of the substituents may influence geometry of the flexible chromophores and thus change not only the intensity of the CD bands but also their sign.



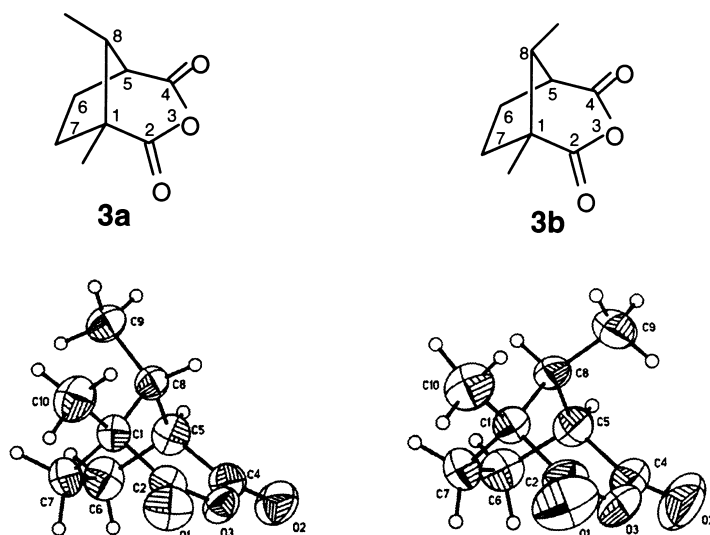
2. Results and discussion

The syntheses of the compounds **2a,b–5a,b** (Scheme 1) were based on π -hydroxycamphor **6** as a substrate, that can be prepared in several steps from (+)-camphor.⁷ A mixture of α - and β -santenones **1a,b** was obtained by decarbonylation of the corresponding aldehyde **7** in an inert atmosphere. This method gives much better yields than the autooxidation of **7** reported by Ishidate and Sano² and later by Nishimitsu.³ A significant steric effect of the C-7 *syn*-substituent facilitates differentiation of the α - and β -stereoisomers; the hydrogen peroxide oxidation of the α -diketone mixture **2** to anhydride **3** results finally in the acid **8** formed by immediate hydrolysis of the α -anhydride **3a**, whereas the β -anhydride **3b** remains unchanged in the reaction conditions. Imides **4a,b** were converted to dithioimides **5a,b** by reaction with Lawesson's reagent in boiling toluene. The configuration at C-8 was confirmed by the X-ray crystallographic structures of the anhydrides **3a** and **3b** (Fig. 1).

The chromophores studied are composed of two carbonyl or thiocarbonyl subunits and their interaction lifts degeneracy between two 'non-bonding' n_s and n_a levels being a combinations of the oxygen 2p or sulphur 3p atomic orbitals.^{4–6,8} In consequence, two $n-\pi^*$ electronic transitions can be observed in the visible or near UV region. Because of the opposite symmetry of the corresponding excited states, a sequence of the negative and positive Cotton effects (CEs) is expected in the CD spectra of these chromophoric systems (Table 1). According to our earlier studies^{4–6} the sign of the long-wavelength CE for the planar α -diketone, anhydride, imide and dithioimide chromophores can be predicted by the antiocant sector rule (the sector signs are opposite to those known for ketones). Since the only source of dissymmetry in the molecules **2a,b,c–5a,b,c** is the methyl group at C-1 and because the substituents at C-7 or C-8 are located on the nodal plane, the negative CE sign is predicted for the lowest energy $n-\pi^*$ band (Fig. 2).



Scheme 1.

Figure 1. Molecular structures of anhydrides **3a** and **3b**

Indeed, in the case of the α -diketones **2a–c** two oppositely signed CEs showing a pronounced fine structure are detected at ca. 480 and 290 nm (Fig. 3). The long-wavelength negative CD band is only slightly influenced by the substituents at C-7, whereas some differences observed in the magnitude of the second CE are apparently due to its overlap with the neighboring strong π - π^* transition.

Table 1
Circular dichroism data

compd	solvent ^a	λ , nm (10^{-3} $[\theta]$) ^b
2a	C	487(-1.48), 295(1.20)
2b	C	490(-1.91), 293(0.49)
2c	C	484(-1.40), 293(0.97)
3a	CD	237sh(-0.86), 223(-1.22)
3b	CD	239(-0.77)
3c	C	242sh(-0.43), 225(-1.06)
4a	CD	260(-0.27), 234(-0.94)
	M	280(-0.35), 236(-0.55)
4b	CD	261(-0.66), 225(0.13)
	M	260(-0.42), 225(0.10)
4c	C	268(-0.10), 230(-0.99)
	M	253(1.03), 227(-2.06)
5a	C	476(-1.80), 461(1.12), 417 (-1.05)
	M	480(-1.49), 443(0.34), 420 (-0.04)
5b	C	481(-0.50), 464(1.56), 419 (-0.53)
	M	488(-0.41), 463(1.18), 415 (-0.23)
5c	C	484(-0.52), 467(3.07), 421 (-1.89)
	M	497(-0.10), 467(3.04), 413(-1.40)

^a C – cyclohexane, CD – cyclohexane–dioxane (4:1),
M – methanol, ^bMolecular ellipticity in $\text{deg cm}^2 \text{dmol}^{-1}$

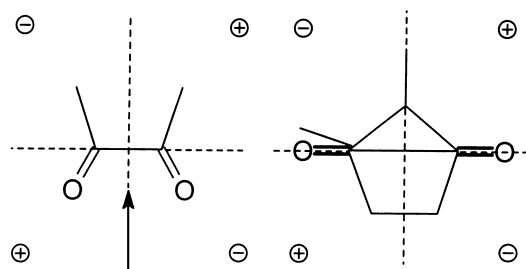


Figure 2. The octant projections of α -diketones **2a** and **2b**. The arrow shows direction of projection

Two well-resolved $n-\pi^*$ bands can also be detected in the dithioimide spectra near 470 and 420 nm. In contrast to α -diketones, the corresponding CEs in **5a–c** are strongly influenced by the substituents at C-8 (Fig. 4). The santenone related dithioimides **5a,b** exhibit much weaker CE magnitudes in the region of both $n-\pi^*$ transitions than those of the camphor related compound **5c**. However, the shape of the CD curves of all of three dithioimides **5a–c** is generally similar. Furthermore, these compounds show bisignate CEs in the region of the long-wavelength absorption band and their intensities are influenced by the solvent polarity. Two overlapping $n-\pi^*$ CEs in the CD spectra of the parent imides **4a–c** are shifted to much shorter wavelengths, i.e. 260

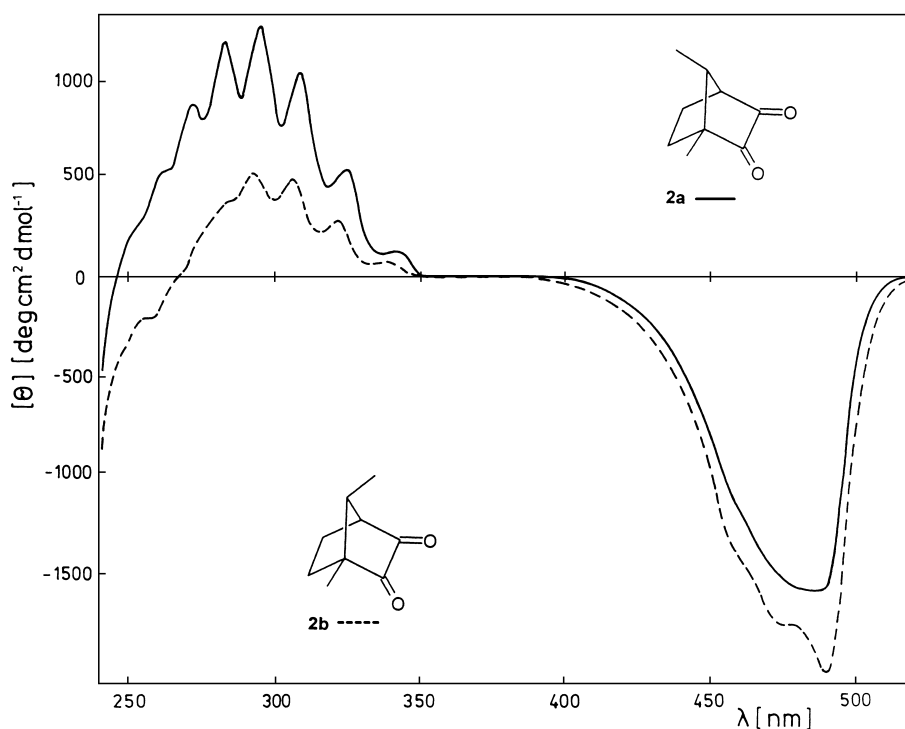


Figure 3. Circular dichroism (CD) spectra of α -diketones **2a** and **2b** in cyclohexane

and 230 nm but their magnitudes are also strongly dependent on the substituents at C-8 and the solvent changes. Such behavior is usually indicative of conformational equilibria in solution as shown by a temperature dependence of the spectra of **5c**.⁹ Obviously, the shifts in conformational equilibria caused by substituents and solvents may influence the CE magnitude and sign.

The above results prove that in the case of rigid systems like α -diketones **2a–c** the substituents located on the nodal surface give only a weak contribution to the CE. Similar results have been reported by Lightner and Toan for substituted adamantanones.¹⁰ However, in the case of compounds with flexible chromophores like **3a,b,c–5a,b,c** the substituents may indirectly affect the CE magnitude or sign by steric interactions with the imide or dithioimide moieties; particularly, the *syn*-methyl group at C-8 may interfere with the chromophores changing their geometry. It is known that even a slight deformation of a chromophore may cause its inherent chirality that considerably affects the CE magnitude.¹¹ The flexibility of the anhydride, imide and dithioimide functions has been already evidenced^{4–6} and was further confirmed by the X-ray crystallographic structures of **3a,b** and **5a,b** (Figs. 1 and 5). Owing to a steric interaction between the *syn*-methyl group at C-8 in **3b** and the anhydride chromophore, the oxygen atom is located 0.101(2) Å below the plane formed by the carbonyl groups. A very similar geometry has been also reported for camphoric anhydride^{12a} and *N*-substituted camphorimide.^{12b} On the other hand, in the absence of this kind of interaction in **3a**, the anhydride group is nearly planar in this compound [the oxygen atom is deviated only by 0.012(2) Å from the plane formed by the neighboring carbonyls]. Though crystal structures of **5a,b** reveal only small distortions of the dithioimide chromophore, however, the MNDO calculations, reported earlier,⁶ suggest a possibility of much stronger deviations of this chromophore in a solution. In addition, it has been shown that a specific

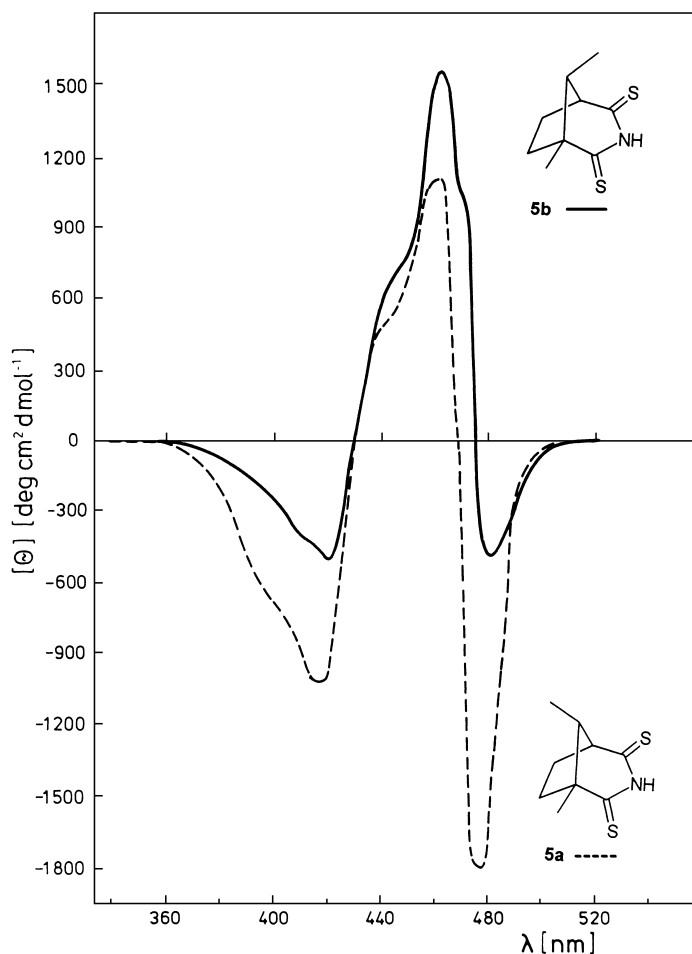
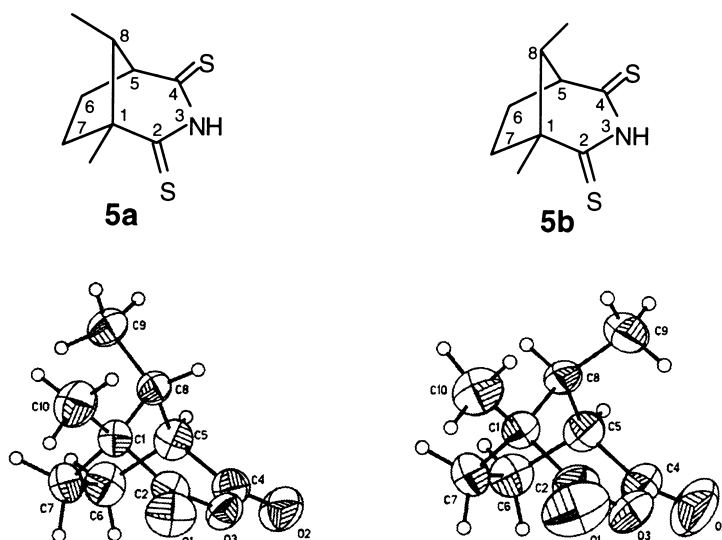


Figure 4. Circular dichroism (CD) spectra of dithioimides **5a** and **5b** in cyclohexane

solvent-solute interaction is possible for ketones containing axially oriented β -substituents.¹³ Assuming that the *syn*-methyl group at C-8 has an analogous orientation to the carbonyl or thiocarbonyl units in **3b–5b** its effect may also be responsible for a strong solvent dependence of their CD spectra.

3. Experimental

CD spectra were recorded on a JASCO J-715 dichrograph. 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 at 300 and 50 MHz, respectively. The deuteriated solvents were used as an internal lock for ^1H and ^{13}C NMR. FT-IR absorptions were taken with a Bruker IFS66 spectrometer. Specific rotations were measured on a Rudolph Autopol II digital polarimeter.

Figure 5. Molecular structures of dithioimides **5a** and **5b**

3.1. (1*R*,4*R*,7*R*)-7-Formyl-1,7-dimethylbicyclo[2.2.1]heptan-2-one **7**

Pyridinium chlorochromate (PCC) (12.9 g, 60 mmol) was added to a stirred solution of π -hydroxycamphor **6**⁷ (5.0 g, 30 mmol) in methylene chloride (100 mL). After stirring for 2 h at room temperature pentane (100 mL) was added to the reaction mixture. The organic layer was decolorized with silica gel, evaporated to dryness to obtain of 4.2 g of the crude product that was used for the next step. An analytically pure sample of the aldehyde was prepared by column chromatography on silica gel using benzene as the eluent; monosemicarbazone m.p. 198°C (lit.¹⁴ m.p. 202°C); $[\alpha]_D^{21} +40$ (*c* 1, CHCl₃); IR (KBr): 2877, 2819, 1747, 1721 cm⁻¹; ¹H NMR (CDCl₃) δ 9.73 (s, 1H), 2.61 (t, *J*=4.4 Hz, 1H), 2.39 (dt, *J*=19.6 and 3.9 Hz, 1H), 1.98 (m, 3H), 1.84 (m, 1H), 1.52 (m, 2H), 1.18 (s, 3H), 1.00 (s, 3H); ¹³C NMR (CDCl₃) δ 215.5, 202.4, 60.2, 57.2, 42.2, 39.3, 29.2, 26.4, 11.7, 9.7.

3.2. (1*R*,4*S*,7*R*)-1,7-Dimethylbicyclo[2.2.1]heptan-2,3-dione **2a**

Aldehyde **7** (4.0 g, 24 mmol) and 10% palladium on charcoal (0.3 g) were heated at 180°C for 12 h under nitrogen. The product was dissolved in pentane, filtered and the filtrate was evaporated to dryness. The resulted mixture of santenones **1a,b** (3.1 g) was mixed with selenium dioxide (2.8 g, 25 mmol), dissolved in acetic acid (10 mL) and refluxed for 18 h. After cooling the reaction mixture was filtered and evaporated to dryness. The residue was dissolved in toluene and washed with water. The organic layer was dried (MgSO₄), the solvent evaporated at reduced pressure and the residue was crystallized from hexane to obtain 0.85 g of α -diketone **2a**; m.p. 97–99°C (lit.³ m.p. 97–98°C); $[\alpha]_D^{22} -111$ (*c* 1.3, CCl₄) [lit.³ $[\alpha]_D^{15} -38.5$ (*c* 1, EtOH) which, according to Nishimitsu, rose to +10 after 50 h and remained constant thereafter^{3,15}]; IR (KBr): 1777, 1757 cm⁻¹; ¹H NMR (CDCl₃) δ 2.73 (d, *J*=5.1 Hz, 1H), 2.18 (m, 1H), 2.01 (q, *J*=6.6 Hz, 1H), 1.81 (m, 1H), 1.68 (m, 1H), 1.55 (m, 1H), 1.16 (s, 3H), 1.06 (d, *J*=6.6 Hz, 3H); ¹³C NMR (CDCl₃) δ 203.9, 201.9, 56.0, 52.7, 39.9, 27.4, 22.5, 11.2, 8.3.

3.3. (1R,4S,7S)-1,7-Dimethylbicyclo[2.2.1]heptan-2,3-dione **2b**

α -Diketone **2b** crystallizes upon concentration and cooling of the mother liquor from the above; m.p. 62.5–63°C (lit.³ m.p. 59–60°C); $[\alpha]_D^{22}$ –155 (*c* 2, CCl₄) [lit.³ $[\alpha]_D^{15}$ –110.3 (*c* 1, EtOH) which, according to Nishimitsu, changes to –9.5 after 60 h and remained constant thereafter^{3,15}]; IR (KBr): 1770, 1756 cm⁻¹; ¹H NMR (CDCl₃) δ 2.90 (dd, *J* = 5.2 and 1.5 Hz, 1H), 2.27 (dq, *J* = 7.3 and 1.6 Hz, 1H), 2.15 (m, 1H), 1.88 (m, 1H), 1.68 (m, 2H), 1.20 (s, 3H), 0.93 (d, *J* = 7.3 Hz, 3H); ¹³C NMR (CDCl₃) δ 205.4, 203.5, 56.7, 54.4, 43.7, 31.5, 23.5, 12.2.

3.4. (1R,4S,8RS)-1,8-Dimethyl-3-oxabicyclo[3.2.1]octan-2,4-dione **3b**

The mixture of santenones **1a,b** (3.1 g) was mixed with selenium dioxide (2.8 g, 25 mmol), dissolved in acetic acid (10 mL) and refluxed for 18 h. The reaction mixture was filtered, concentrated to ca. 3 mL and 30% hydrogen peroxide (1.5 mL) was added. After cooling to 0°C the product was filtered, dried and crystallized from toluene–hexane; yield 0.65 g; m.p. 109–111°C (lit.³ m.p. 110°C); $[\alpha]_D^{21}$ +6.4 (*c* 1.8, C₆H₆) [lit.³ $[\alpha]_D^{15}$ +10.3 (*c* 1, EtOH)]; IR (KBr): 1806, 1769 cm⁻¹; ¹H NMR (CDCl₃) δ 3.11 (dd, *J* = 6.8 and 4.0 Hz, 1H), 2.25–2.10 (complex m, 2H), 2.00–1.85 (complex m, 2H), 1.34 (s, 3H), 1.06 (d, *J* = 7.1 Hz, 3H); ¹³C NMR (CDCl₃) δ 171.8, 170.0, 50.3, 49.2, 43.8, 34.9, 25.4, 18.3, 11.3.

3.5. (1R,4S,8R)-1,8-Dimethyl-3-oxabicyclo[3.2.1]octan-2,4-dione **3a**

The reaction mixture from the above was evaporated to dryness. The residue was dissolved in acetic anhydride (5 mL), refluxed for 10 min and the solvent was evaporated at reduced pressure. The product was crystallized from toluene–hexane; yield 0.87 g; m.p. 127°C (lit.³ m.p. 126–127°C); $[\alpha]_D^{21}$ –17.5 (*c* 2, C₆H₆) [lit.³ $[\alpha]_D^{15}$ –16.7 (*c* 1, EtOH)]; IR (KBr): 1815, 1769 cm⁻¹; ¹H NMR (CDCl₃) δ 2.95 (d, *J* = 7.2 Hz, 1H), 2.35–2.25 (complex m, 2H), 2.10–1.90 (complex m, 3H), 1.35 (s, 3H), 0.98 (d, *J* = 7.0 Hz, 3H); ¹³C NMR (CDCl₃) δ 172.8, 170.0, 50.9, 49.2, 40.8, 31.8, 25.2, 16.4, 12.4.

3.6. (1R,4S,8R)-1,8-Dimethyl-3-azabicyclo[3.2.1]octan-2,4-dione **4a**

Anhydride **3a** (0.34 g, 2 mmol) was dissolved in 25% aqueous ammonia (3 mL) and evaporated to dryness. The residue was heated at 180°C for 0.5 h, dissolved in chloroform, decolorized with silica gel, filtered and the solvent was evaporated. The product was crystallized from toluene–hexane; yield 0.27 g; m.p. 156–158°C; $[\alpha]_D^{21}$ –8.7 (*c* 3.3, CHCl₃); IR (KBr): 3204 (br), 3088, 1719, 1705 cm⁻¹; ¹H NMR (CDCl₃) δ 7.78 (br s, 1H), 2.76 (dd, *J* = 7.2 and 1.5 Hz, 1H), 2.32 (m, 1H), 2.26 (q, *J* = 7.0 Hz, 1H), 1.90 (m, 3H), 1.28 (s, 3H), 0.96 (d, *J* = 7.0 Hz, 3H); ¹³C NMR (CDCl₃) δ 178.9, 176.9, 51.4, 42.8, 32.5, 25.9, 15.5, 13.2. Anal. calcd for C₉H₁₃NO₂ (167): C, 64.65; H, 7.83; N, 8.38. Found: C, 64.58; H, 7.86; N, 8.31.

3.7. (1R,4S,8S)-1,8-Dimethyl-3-azabicyclo[3.2.1]octan-2,4-dione **4b**

Imide **3b** was obtained from anhydride **3b** as above; m.p. 147–148°C (from toluene–hexane); $[\alpha]_D^{23}$ +12.5 (*c* 2, CHCl₃); IR (KBr): 3209 (br), 3091, 1722, 1698 cm⁻¹; ¹H NMR (CDCl₃) δ 8.06 (br s, 1H), 2.91 (dd, *J* = 4.4 and 2.1 Hz, 1H), 2.20–1.75 (complex m, 5H), 1.26 (s, 3H), 1.02 (d, *J* = 7.0

Hz, 3H); ^{13}C NMR (CDCl_3) δ 177.5, 176.4, 50.6, 50.4, 45.5, 35.7, 26.2, 17.5, 10.7. Anal. calcd for $\text{C}_9\text{H}_{13}\text{NO}_2$ (167): C, 64.65; H, 7.83; N, 8.38. Found: C, 64.68; H, 7.68; N, 8.22.

3.8. (1*R*,4*S*,8*R*)-1,8-Dimethyl-3-azabicyclo[3.2.1]octan-2,4-dithione **5a**

A mixture of imide **4a** (0.25 g, 1.5 mmol) and Lawesson's reagent (0.70 g, 1.7 mmol) in toluene (5 mL) was refluxed for 12 h. The toluene was evaporated at reduced pressure and the residue was chromatographed on silica gel using toluene as the eluent. After collection of the yellow fraction and evaporation of the solvent, the product was crystallized from heptane; yield 0.25 g; m.p. 69°C; $[\alpha]_{\text{D}}^{22}$ -45.4 (*c* 1.4, C_6H_6); IR (KBr): 3161 (br), 1488, 1313, 1119, 1044 cm^{-1} ; ^1H NMR (CDCl_3) δ 10.54 (br s, 1H), 3.40 (dd, $J=7.2$ and 1.2 Hz, 1H), 2.38 (m, 1H), 2.26 (q, $J=7.0$ Hz, 1H), 1.96 (m, 3H), 1.45 (s, 3H), 1.00 (d, $J=7.0$ Hz, 3H); ^{13}C NMR (CDCl_3) δ 215.5, 210.8, 61.0, 57.7, 43.8, 36.4, 29.8, 20.6, 14.4. Anal. calcd for $\text{C}_9\text{H}_{13}\text{NS}_2$ (199): C, 54.23; H, 6.57; N, 7.03; S, 32.17. Found: C, 54.18; H, 6.65; N, 6.91; S, 32.25.

3.9. (1*R*,4*S*,8*S*)-1,8-Dimethyl-3-azabicyclo[3.2.1]octan-2,4-dithione **5b**

Compound **5b** was obtained from imide **4b** as above; m.p. 82°C (from heptane); $[\alpha]_{\text{D}}^{23}$ +31 (*c* 1, C_6H_6); IR (KBr): 3191 (br), 1478, 1346, 1118, 1055 cm^{-1} ; ^1H NMR (CDCl_3) δ 10.48 (br s, 1H), 3.56 (m, 1H), 2.30–1.90 (complex m, 5H), 1.44 (s, 3H), 0.98 (d, $J=7.0$ Hz, 3H); ^{13}C NMR (CDCl_3) δ 213.3, 209.3, 59.9, 56.2, 46.6, 39.7, 30.2, 23.1, 10.2. Anal. calcd for $\text{C}_9\text{H}_{13}\text{NS}_2$ (199): C, 54.23; H, 6.57; N, 7.03; S, 32.17. Found: C, 54.32; H, 6.57; N, 6.93; S, 32.30.

3.10. X-Ray crystal structure analysis

Diffraction data were obtained on a Kuma KM-4 diffractometer with graphite monochromated Cu K α radiation ($\lambda=1.54178$ Å). The structures were solved by direct methods with the program SHELXS-86.¹⁶ Full matrix least-squares refinement was carried out with SHELXL-97.¹⁷

Crystal data for $\text{C}_9\text{H}_{12}\text{O}_3$ **3a**: monoclinic, $P2_1$, $a=7.414(2)$, $b=6.455(1)$, $c=8.996(2)$ Å, $\beta=97.99(2)^\circ$, $V=426.4(2)$ Å³, $Z=2$, $D_{\text{calcd}}=1.310$ g cm⁻³, $T=293(2)$ K, $R_1=0.0377$, $wR_2=0.1106$ for 1408 reflections with $I>2\sigma(I)$ [$R_1=0.0403$, $wR_2=0.1126$ for all 1469 independent reflections].

Crystal data for $\text{C}_9\text{H}_{12}\text{O}_3$ **3b**: monoclinic, $P2_1$, $a=6.773(1)$, $b=7.334(1)$, $c=8.741(2)$ Å, $\beta=97.91(3)^\circ$, $V=430.1(1)$ Å³, $Z=2$, $D_{\text{calcd}}=1.299$ g cm⁻³, $T=293(2)$ K, $R_1=0.0352$, $wR_2=0.1006$ for 1588 reflections with $I>2\sigma(I)$ [$R_1=0.0364$, $wR_2=0.1023$ for all 1631 independent reflections].

Crystal data for $\text{C}_9\text{H}_{13}\text{NS}_2$ **5a**: monoclinic, $P2_1$, $a=12.306(2)$, $b=8.6780(9)$, $c=9.9470(7)$ Å, $\beta=105.600(8)^\circ$, $V=1023.1(2)$ Å³, $Z=4$, $D_{\text{calcd}}=1.294$ g cm⁻³, $T=293(2)$ K, $R_1=0.0559$, $wR_2=0.1476$ for 2984 reflections with $I>2\sigma(I)$ [$R_1=0.0616$, $wR_2=0.1511$ for all 3221 independent reflections].

Crystal data for $\text{C}_9\text{H}_{13}\text{NS}_2$ **5b**: monoclinic, $P2_12_12_1$, $a=7.805(2)$, $b=10.782(2)$, $c=28.899(5)$ Å, $V=2011.2(8)$ Å³, $Z=8$, $D_{\text{calcd}}=1.317$ g cm⁻³, $T=293(2)$ K, $R_1=0.0492$, $wR_2=0.1260$ for 3062 reflections with $I>2\sigma(I)$ [$R_1=0.0554$, $wR_2=0.1289$ for all 3336 independent reflections].

The atomic coordinates for the reported crystal structures are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory,

Lensfield Road, Cambridge CB2 1EW, UK. Any request should be accompanied by a full literature citation.

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