

New Terpenic Synthons: Methyl α - and γ -Dithiocyclogeranates

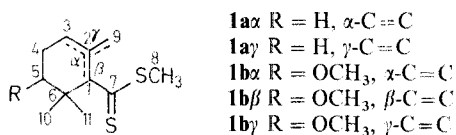
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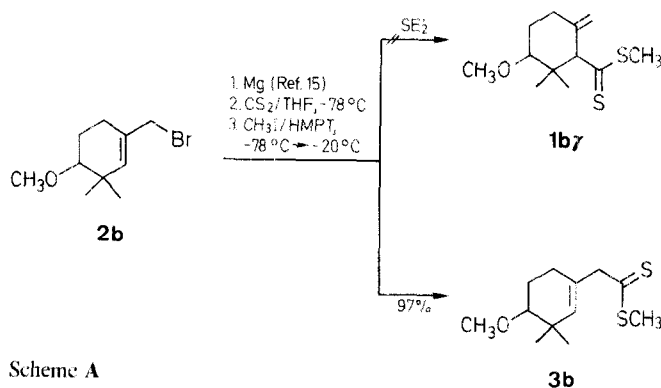
Methyl γ -dithiocyclogeranate, a new terpenic dithioester, was easily synthesized by the [2,3]-sigmatropic rearrangement of tosylhydrazone derivative **6a**. Treatment with acid gives methyl α -dithiocyclogeranate. Three methoxylated analogues are obtained in the same way.

Owing to their interesting ambident reactivity towards alkyl- and allyl-magnesium halides, dithioesters were previously used with success in the total synthesis of various natural products.¹

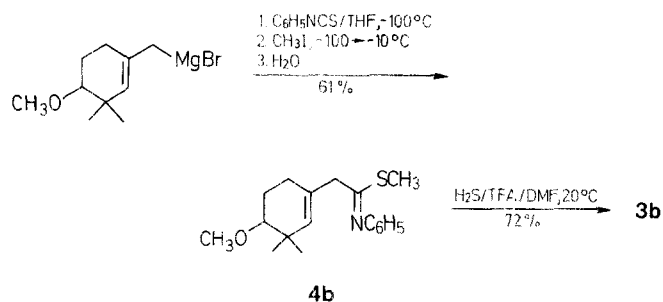
We describe herein the synthesis of five new terpenic dithioesters, namely methyl α - and γ -dithiocyclogeranates (**1a α** and **1a γ**) and methyl 5-methoxy- α -, β - and γ -dithiocyclogeranates (**1b α** , **1b β** and **1b γ**).



We first applied (Scheme A) the reported reaction of carbon disulfide with Grignard reagents^{2,3} in the case of the known bromide **2b**.⁴ As previously noted with other allylic bromides^{5,6} one could expect the addition of this Grignard reagent to carbon disulfide to occur with inversion of the allylic chain, affording, after methylation, the desired dithioester **1b γ** . However, we found that this reaction led exclusively to the unrearranged dithioester **3b**, irrespective of the reaction temperature (-78°C or 0°C) and of the order of addition of the reagents.⁶



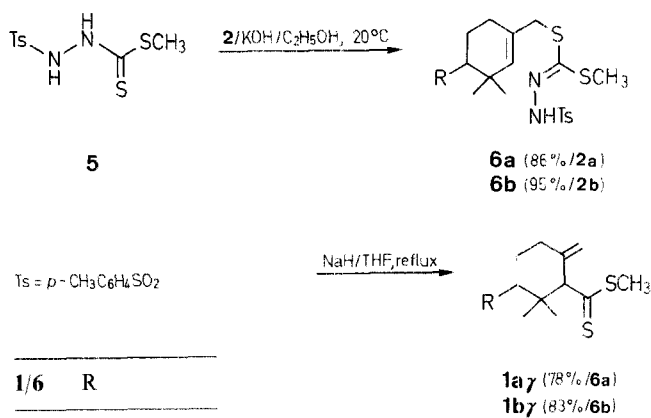
An alternative access to dithioester **1b γ** might consist of the reaction of phenylisothiocyanate with the same Grignard reagent.⁷ We found however that dithioester **3b** was obtained again after sulfhydrogenolysis of the intermediate thiocarboximide **4b** (Scheme B). Overall allylic inversion has not occurred, in contrast with previous results in the acyclic series.⁷



TFA = trifluoroacetic acid

Scheme B

We next examined the method of Baldwin and Walker⁸ who have shown that allylic carbazates, upon treatment with sodium hydride, undergo [2,3]-sigmatropic rearrangement to dithioesters (Scheme C).

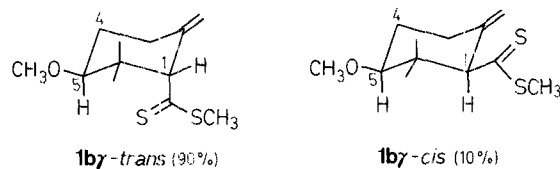
Ts = $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2$

1/6	R
a	H
b	OCH_3

Scheme C

Methyl 3-*p*-toluenesulfonyldithiocarbamate **5** (obtained in two steps from *p*-toluenesulfonylhydrazide⁹) was alkylated with bromides **2** in the presence of potassium hydroxide to the *p*-toluenesulfonylhydrazone derivatives **6**. On refluxing in tetrahydrofuran, the sodium salts of **6** induced the [2,3]-sigmatropic rearrangement to the desired dithioesters **1**_y (Scheme C).

Stereoselectivity of [2,3]-sigmatropic rearrangements¹⁰ is confirmed here: dithioester **1b**_y is obtained as a 9:1 mixture¹¹ of *trans/cis* **1b**_y isomers, easily separated by gas-chromatography.¹²



The *trans* stereochemistry was assigned for the most abundant isomer on the basis of ¹H-NMR spectra analysis (Table 1). For both isomers, the ¹H-NMR spectra exhibit a doublet of doublet ($J_1 = \sim 9 \text{ Hz}$, $J_2 = \sim 3 \text{ Hz}$) for the C-5 methine hydrogens coupled with the C-4 methylene. These values are consistent with an axial position for these hydrogens and equatorial methoxy groups. Chemical shifts of these methine hydrogens are very different; located at $\delta = 2.95 \text{ ppm}$ with the minor isomer, the doublet of doublet is found at $\delta = 4.04 \text{ ppm}$ with the major one. Such a deshielding effect can be interpreted¹³ as resulting from the influence of an axial thiocarbonyl at C-1 in the major isomer which thus has a *trans*-stereochemistry.

According to the described procedure,⁷ isomerization of these dithioesters to the conjugated β -isomers was attempted using 5 mol % of triethylamine. This was however unsuccessful with dithioester **1a**_y which was recovered after 5 h refluxing in ether.

Table 1. ¹H-NMR Spectra of Dithioesters **1**: (CDCl_3/TMS), δ (ppm)^a

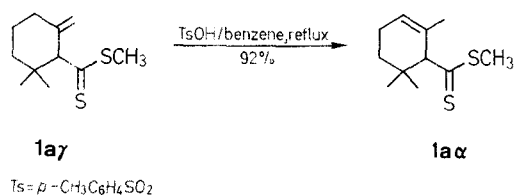
Compound No.	H-1	H-3	H-4	H-5	H-8	H-9	H10/11	OCH_3
1a α	3.62 (s)	5.70 (br s)	1.15 (1H), 2.15 (3H) (2 \times m)		2.65 (s)	1.63 (br s)	0.92, 1.01 (2 \times s)	
1a γ	3.93 (s)	1.07–1.87 (m, 3H); 2.03–2.49 (m, 2H); 2.72–3.17 (m, 1H)			2.55 (s)	4.93 (br s)	0.99 (s)	
1b α - <i>trans</i>	3.72 (s)	5.61 (br s)	2.01 (m)	4.01 dd, $J = 6, 10 \text{ Hz}$	2.67 (s)	1.62 (s)	1.01 (s)	3.39 (s)
1b β		1.75–2.43 (m)		3.11 dd, $J = 4, 9 \text{ Hz}$	2.66 (s)	1.63 (s)	1.17 (s)	3.45 (s)
1b γ - <i>cis</i>	3.88 (s)	1.3–2.4 (m)		2.95 dd, $J = 3, 9 \text{ Hz}$	2.60 (s)	5.03 (br s)	1.05, 1.14 (2 \times s)	3.40 (s)
1b γ - <i>trans</i>	4.08 (s)	1.33–2.48 (m, 3H); 2.73–3.17 (m, 1H)		4.04 dd ^b , $J = 3, 9 \text{ Hz}$	2.56 (s)	4.95 (br s)	0.96, 1.06 (2 \times s)	3.38 (s)

^a Measured at 90 MHz on a Varian EM 390 spectrometer.^b Partially masked.Table 2. ¹³C-NMR Spectra^a of Dithioesters **1**^b: (CDCl_3/TMS), δ (ppm)

Compound	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	OCH_3
1a α	71.87 (d)	132.17 (s)	123.72 (d)	22.71 (t)	29.85 (t)	33.00 (s)	241.33 (s)	20.33 (q)	22.71 (q)	28.09 (2 \times q)		
1a γ	73.98 (d)	146.12 (s)	31.49 (t)	22.64 (t)	34.89 (t)	35.77 (s)	237.82 (s)	19.79 (q)	111.97 (t)	28.32, 26.62 (2 \times q)		
1b α - <i>trans</i>	74.15 (d)	132.50 (s)	122.39 (d)	28.40 (t)	78.49 (d)	37.65 (s)	240.52 (s)	20.56 (q)		22.09, 22.28, 23.39 (3 \times q)		57.65 (q)
1b β	146.46 (s)	128.85 (s)	29.63 (t)	29.60 (t)	84.66 (d)	38.51 (s)	236.58 (s)	17.24 (q)		22.90, 20.73, 20.52 (3 \times q)		57.45 (q)
1b γ - <i>trans</i>	74.15 (d)	145.08 (s)	30.50 (t)	26.05 (t)	81.63 (d)	40.11 (s)	237.69 (s)	20.06 (q)	112.66 (t)	21.99, 23.29 (2 \times q)		57.43 (q)

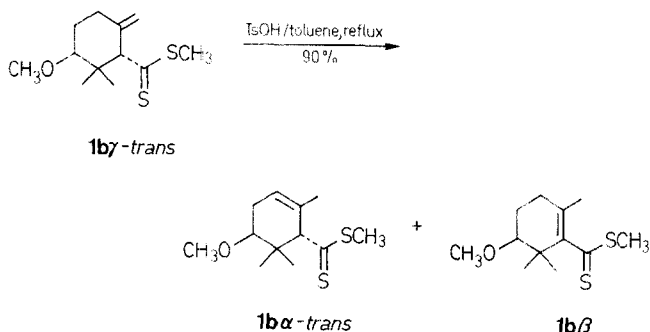
^a Measured at 20 MHz on a Varian FT-80A Spectrometer.^b The numbering is the same as given in Table 1.

Under acidic conditions (*p*-toluenesulfonic acid), dithioester **1ay** was converted into the α isomer **1a α** in 92% yield after 2 h refluxing in benzene (Scheme D).



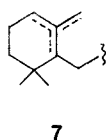
Scheme D

This isomerization was selective, no β -isomer being detected by GC or by ^1H - and ^{13}C -NMR (Table 2). However, this selectivity was not observed in the reaction of the methoxy-dithioester **1by-trans** with *p*-toluenesulfonic acid: dithioesters **1b α -trans** and **1b β** were obtained in 90% crude yield as a 71:29 mixture¹¹ (Scheme E).



Scheme E

In summary, we believe these new terpenic synthons will prove to be of value for the synthesis of sesquiterpenes possessing the 1,3,3-trimethyl-2-cyclohexenyl (cyclocitral) system **7**, which is also common to the retinoids and carotenoids.¹⁴



A magnesium-free stock-solution of the Grignard derived from the known bromide **2b**⁴ was prepared according to the described procedure.¹⁵ After the reaction was completed, the warm solution was decanted from excess magnesium by passing through a glasswool pad under an argon atmosphere. Yields ranging from 80 to 90% were determined through backtitration with acid according to Gilman.¹⁶

Methyl 2-(4-Methoxy-3,3-dimethyl-1-cyclohexenyl)dithioacetate (**3b**):

A: "Normal" Addition.^{2,3}

A solution of carbon disulfide (1 ml, 16.6 mmol) in tetrahydrofuran (4 ml) is slowly added (~1 h) to a stirred solution of 0.47 molar Grignard reagent in tetrahydrofuran (20 ml, 9.4 mmol) under a slight positive pressure of argon, at -78°C . After stirring for 3 h at -78°C , a solution of methyl iodide (1 ml, 16.1 mmol) in anhydrous ethanol (3 ml) is added over a 15 min period. Stirring is continued for 5 h during which time temperature is allowed to reach -20°C . The mixture is then hydrolysed with saturated ammonium chloride solution (20 ml) and extracted with ether (3×20 ml). The combined ether extract is washed with saturated ammonium chloride solution (3×15 ml) and saturated brine (2×15 ml). The organic layer is dried with magnesium sulfate and concentrated *in vacuo* to give **3b** as an orange liquid; yield: 2.22 g (97%).

IR (Film): $\nu = 2815, 1368, 1355, 1180, 1099, 1015\text{ cm}^{-1}$.

^1H -NMR (CDCl_3/TMS): $\delta = 1.00, 1.07$ (2 s, 6 H, $2 \times \text{CH}_3$); 1.53–2.33 (m, 4 H, CH_2); 2.63 (s, 3 H, SCH_3); 3.07 (dd, $J = 9, 3\text{ Hz}$, 1 H, CHOCH_3); 3.41 (s, 3 H, OCH_3); 3.73 [s, 2 H, $\text{CH}_2\text{C}(\text{S})\text{SCH}_3$]; 5.43 ppm (br s, 1 H, $\text{CH} =$).

B: Reverse Addition.⁶

A 0.47 molar solution of the Grignard reagent in tetrahydrofuran (14 ml, 6.58 mmol) is added over 45 min to a stirred solution of carbon disulfide (1.5 ml, 25 mmol) in tetrahydrofuran (15 ml) under a slight positive pressure of argon at -78°C . After 1.2 h stirring at -78°C , a solution of methyl iodide (1.58 g, 11 mmol) in tetrahydrofuran (3.5 ml) is added and stirring continued overnight while the temperature is allowed to rise slowly to 0°C . Hydrolysis and extraction as in A affords dithioester **3b**; yield: 1.3 g (81%).

Methyl N-Phenyl-2-(4-methoxy-3,3-dimethyl-1-cyclohexenyl)-thioacetimidate (**4b**):⁷

A solution of phenylisothiocyanate (0.945 g, 7 mmol) in tetrahydrofuran (5 ml) is added over 1 h to a stirred 0.44 molar solution of the Grignard of the bromide **2b** in tetrahydrofuran (18 ml, 7.92 mmol, 1.13 equiv) under a slight positive pressure of argon, at -100°C (pentane/liquid nitrogen). Stirring is continued for 1.5 h, then methyl iodide (1 ml, 16.1 mmol, 2.3 equiv) is added. While stirring overnight, the temperature is allowed to slowly rise to 10°C . The mixture is then hydrolysed with saturated ammonium chloride solution (15 ml) and extracted with ether (3×20 ml). The combined ether extract is washed with saturated ammonium chloride solution (4×20 ml) and dried with magnesium sulfate. Concentration *in vacuo* gives **4b** as a greenish oil; yield: 1.3 g (61%).

IR (Film): $\nu = 2070, 1620, 1590, 1180, 1090\text{ cm}^{-1}$.

^1H -NMR (CDCl_3/TMS): $\delta = 0.93$ (s, 3 H); 1.00 (s, 3 H); 1.5–2.2 (m, 4 H, $2 \times \text{CH}_2$); 2.38 (s, 3 H, SCH_3); 2.87–3.23 (m, 3 H, $\text{CHOCH}_3 + \text{CH}_2\text{C}(\text{NC}_6\text{H}_5)\text{SCH}_3$); 3.40 (s, 3 H, OCH_3); 5.17 (m, 1 H, $\text{CH} =$); 6.70–7.57 ppm (m, 5 H_{arom}).

Sulphydrogenolysis of **4b** to Dithioester **3b**:¹⁷

A solution of trifluoroacetic acid (0.25 g, 2.2 mmol) in dry dimethylformamide (2 ml) is added dropwise to a stirred solution of thioacetimidate **4b** (0.6 g, 2 mmol) in dry dimethylformamide (3 ml) at 20°C . After stirring for 15 min, gaseous hydrogen sulfide (Caution: highly toxic, use only in a well-ventilated hood) is blown in just above the stirred solution. After 1.5 h, the introduction of hydrogen sulfide is stopped and the solution is poured onto ice-water (15 ml), extracted with ether (3×10 ml), washed with saturated brine (3×10 ml) and dried with magnesium sulfate. The solvent is removed *in vacuo* to give the dithioester **3b**; yield: 0.35 g (72%).

p-Toluenesulfonylhydrazone-S-methylcarbazate (**6a**):

Under nitrogen, a solution of methyl 3-*p*-toluene sulfonyldithiocarbazate **5**⁹ (8.2 g, 29.7 mmol) in anhydrous ethanol (60 ml) is added to a stirred solution of potassium hydroxide (1.67 g, 29.7 mmol) in anhydrous ethanol (60 ml). After stirring for 10 min, a solution of distilled bromide **2a**¹⁸ (6.03 g, 29.7 mmol) in anhydrous ethanol (15 ml) is added and stirring continued for 3 h at 20°C . The solvent is removed *in vacuo*, leaving a residue which is extracted with ether (120 ml) and washed with saturated brine (3×100 ml). The organic layer is dried with magnesium sulfate and concentrated *in vacuo* to give an oil which crystallises on standing. Recrystallization from acetone/pentane affords **6a** as colourless crystals; yield: 10.2 g (86%). m.p. $81\text{--}82^\circ\text{C}$.

$\text{C}_{18}\text{H}_{26}\text{N}_2\text{O}_2\text{S}_3$ calc. C 54.23 H 6.59 N 7.03 O 8.03 S 24.13 (398.6) found 54.45 6.30 7.12 7.92 24.06

IR (Film): $\nu = 3210, 1168, 814\text{ cm}^{-1}$.

MS (EI): $m/e = 398$ (4.9%, M^+); 351 (5.9); 243 (11.4); 213 (13.7); 123 (100); 91 (44); 81 (46).

MS (CI, NH_3): $m/e = 399$ (100%, MH^+); 215 (30.6); 174 (25.1); 139 (15.2); 123 (26.6).

^1H -NMR (CDCl_3/TMS): $\delta = 0.89$ (s, 6 H, $2 \times \text{CH}_3$); 1.23–2.08 (m, 6 H, $3 \times \text{CH}_2$); 2.32 (s, 3 H, SCH_3); 2.45 (s, 3 H, CH_3Ar); 3.47 (s, 2 H, CH_2S); 5.41 (s, 1 H, $\text{CH} =$); 7.45–7.97 (2d, 4 H_{arom}); 8.22 ppm (s, 1 H, NH).

p-Toluenesulfonylhydrazone-S-methylcarbazate (**6b**):

Using the same procedure, bromide **2b**⁴ is converted to **6b**; yield: 95%. m.p. $74.5\text{--}78^\circ\text{C}$ (acetone/pentane).

$\text{C}_{19}\text{H}_{28}\text{N}_2\text{O}_3\text{S}_3$ calc. C 53.24 H 6.58 N 6.54 O 11.20 S 22.44 (428.6) found 53.37 6.48 6.50 11.12 22.73

IR (Film): $\nu = 3177, 1384, 1372, 1358, 1338, 1169, 1100, 1035, 1019, 864, 814, 706, 669\text{ cm}^{-1}$.

MS (EI): $m/e = 428$ (5.6%, M^+); 381 (13.0); 258 (13.1); 243.1 (36.5); 153 (100); 144 (61.4); 123 (34.4); 121 (100); 107 (43); 91 (100); 81 (30); 79 (77.8); 59 (100).

MS (CI, NH_3): $m/e = 431$ [(MH + 2)⁺; 16.5%]; 430 [(MH + 1)⁺; 23.6]; 429 (MH⁺, 100); 245 (94.1); 189 (84); 174 (39.6); 139 (40.1); 121 (35.7); 108 (23.1); 91 (17.6).

¹H-NMR (CDCl_3/TMS): $\delta = 0.89$ (s, 3 H, CH_3); 0.97 (s, 3 H, CH_3); 1.47–2.25 (m, 4 H, 2 CH_2); 2.37 (s, 3 H, SCH_3); 2.42 (s, 3 H, CH_3Ar); 3.02 (dd, $J = 3$ and 9 Hz, 1 H, CHOCH_3); 3.40 (s, 3 H, OCH_3); 3.44 (s, 2 H, CH_2S); 5.30 (s, 1 H, $\text{CH}=\text{}$); 7.47–7.93 (2d, 4 H_{arom}); 8.20 ppm (s, 1 H, NH).

Methyl 2-Methylene-6,6-dimethylcyclohexene Dithiocarboxylate (1a γ ; Methyl γ -dithiocyclogeranate):

A solution of hydrazone **6a** (11.7 g, 29.4 mmol) in anhydrous tetrahydrofuran (30 ml) is added dropwise, under argon, to a stirred suspension of sodium hydride (1.412 g, 60% dispersion in mineral oil, 35.3 mmol, 1.2 equiv) in anhydrous tetrahydrofuran (350 ml). After stirring for 45 min at 20°C, the brown mixture is filtered under argon, diluted with tetrahydrofuran (500 ml) and refluxed for 6 h under a slight positive pressure of argon. After solvent removal *in vacuo*, the residue is taken up in ether (250 ml), washed with water (2 \times 100 ml) and saturated brine (2 \times 100 ml). The organic layer is dried with magnesium sulfate and concentrated *in vacuo* to leave on oil which is chromatographed on silica gel (230 g) with cyclohexane (300 ml) as eluent. Removal of the solvent on a rotary evaporator affords **1a γ** as an orange oil, homogeneous by TLC and GC; yield: 4.9 g (78%).

$\text{C}_{11}\text{H}_{18}\text{S}_2$ calc. C 61.63 H 8.46 S 29.91
(214.4) found 61.85 8.47 29.61

IR (Film): $\nu = 3071, 1639, 1386, 1364, 1170, 895 \text{ cm}^{-1}$.

MS (EI): $m/e = 216$ [5.0%, (M + 2)⁺]; 215 [8.0, (M + 1)⁺]; 214 (64.6, M⁺); 199 (14.2); 157 (70.5); 144 (100); 143 (34.1); 91 (26.2); 81 (30.4); 69 (36.3).

MS (CI, NH_3): $m/e = 215$ (100.0, MH⁺); 201 (13.0); 148 (33.7); 144 (11.5); 59 (10.1); 58 (16.5).

Methyl 5-Methoxy-2-methylene-6,6-dimethylcyclohexene Dithiocarboxylate (1b γ ; Methyl 5-Methoxy- γ -dithiocyclogeranate):

By the same procedure, dithioester **1b γ -trans** and **-cis** are obtained from hydrazone **6b**¹², yield: 83%. The following microanalyses, infra-red and mass spectra were recorded with the *trans*-isomer of **1b γ** .

$\text{C}_{12}\text{H}_{20}\text{OS}_2$ calc. C 58.97 H 8.25 O 6.55 S 26.23
(244.4) found 58.60 8.18 7.01 26.37

IR (Film): $\nu = 3070, 2818, 1644, 1385, 1362, 1177, 1100, 898 \text{ cm}^{-1}$.

MS (EI): $m/e = 244$ (7.6%, M⁺); 229 (6.6); 212 (10.6); 197 (14.3); 157 (16.7); 146 (10.6); 145 (15.1); 144 (100); 143 (23.3); 131 (35.1); 129 (23.4); 121 (10.4); 67 (22.6).

MS (CI, NH_3): $m/e = 245$ (100%, MH⁺); 231 (5.3); 229 (3.5); 213 (16.9); 197 (16.0); 144 (15.8).

Attempted Isomerisation of 1a γ to 1a β :

Triethylamine (15 μl , 0.05 equiv) is added *via* syringe to a stirred solution of dithioester **1a γ** (0.454 g, 2.12 mmol) in ether (3 ml). After refluxing for 1.25 h, GC monitoring does not show any isomerization and hence a second portion of triethylamine (15 μl) is added. After refluxing for 5 h, the solution is cooled, diluted with ether (10 ml), washed first with 5% hydrochloric acid (2 \times 10 ml), then with saturated brine (2 \times 10 ml) and dried with magnesium sulfate. Solvent removal *in vacuo* gives an orange liquid which is shown (GC, ¹H-NMR) to be identical with the starting material **1a γ** .

Methyl 2,6,6-Trimethyl-2-cyclohexene Dithiocarboxylate (1a α ; Methyl α -Dithiocyclogeranate):

p-Toluenesulfonic acid (40 mg, 0.21 mmol, 0.1 equiv) is added to a stirred solution of dithioester **1a γ** (0.45 g, 2.1 mmol) in benzene (50 ml). After refluxing for 24 h, the solution is cooled, washed first with saturated aqueous sodium hydrogen carbonate (2 \times 25 ml) and then with saturated brine (2 \times 25 ml). The organic layer is dried with magnesium sulfate and concentrated *in vacuo* to give dithioester **1a α** as an orange liquid, homogeneous by TLC and GC; yield: 0.416 g (92%).

HRMS: $m/e = \text{calc. for } \text{C}_{11}\text{H}_{18}\text{S}_2: 214.0849$; found: 214.08446.

IR (Film): $\nu = 3029, 1385, 1363, 1187, 826 \text{ cm}^{-1}$.

MS (EI): $m/e = 216$ [6.4%, (M + 2)⁺]; 215 [7.0%, (M + 1)⁺]; 214 [61.3, M⁺]; 157 (72.2); 124 (29.4); 123 (47.4); 91 (63.7); 81 (34.6); 58 (100); 55 (30.0).

Using toluene as solvent, the same procedure as above is applied to dithioester **1b γ -trans**. Analytical samples of the resulting dithioesters **1b α -trans** and **1b β** were obtained through preparative GC on the

following column: 10% Carbowax 20M on Chromosorb WAW 80/100, 2 m \times 1/4 in. helium as carrier gas (80 ml/min), 185°C, thermal conductivity detection.

Methyl *trans*-5-Methoxy-2,6,6-trimethyl-2-cyclohexene Dithiocarboxylate (1b α -*trans*):

HRMS: $m/e = \text{calc. for } \text{C}_{12}\text{H}_{20}\text{OS}_2: 244.0955$; found: 244.09543.

IR (Film): $\nu = 3030, 2817, 1384, 1363, 1181, 1102, 825 \text{ cm}^{-1}$.

MS (EI): $m/e = 244$ (22.9%, M⁺); 229 (12.9); 212 (13.7); 211 (15.1); 197 (24.3); 145 (20.5); 144 (61.2); 131 (29.4); 121 (100); 111 (27.5); 99 (52.8); 91 (39.1); 67 (40.2); 59 (45.0); 58 (93.8).

Methyl 5-Methoxy-2,6,6-trimethyl-1-cyclohexene Dithiocarboxylate (1b β):

HRMS: $m/e = \text{calc. for } \text{C}_{12}\text{H}_{20}\text{OS}_2: 244.0955$; found: 244.09543.

IR (Film): $\nu = 3026, 2821, 1360, 1181, 1103 \text{ cm}^{-1}$.

MS (EI): $m/e = 246$ [1.5%, (M + 2)⁺]; 245 [2.0, (M + 1)⁺]; 244 (13.4, M⁺); 229 (19.4); 212 (39.2); 197 (24.4); 171 (54.4); 165 (40.9); 153 (42.8); 121 (100); 91 (20.4).

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- Ratios were determined by integration (Minigrator, Intersmat Instruments) of the GC chromatograms obtained from the following columns (Thermal Conductivity Detection):
– 10% Carbowax 20M on Chromosorb WAW 80/100, 2 m \times 1/8 inch, helium as carrier gas (30 ml/min), 150°C;
– 5% SE 30 on Chromosorb WAW 80/100, 2 m \times 1/8 inch, helium as carrier gas (30 ml/min), 150°C.
- Although pure analytical samples of these isomers could be obtained through preparative GC (10% Carbowax 20M, 185°C), dithioester **1b γ -trans**, first eluted, was the sole isomer to be obtained in a pure form through preparative liquid chromatography (silica gel, cyclohexane/ethyl acetate (95:5)). The more polar isomer **1b γ -cis** was obtained as a mixture with the *trans*-isomer.
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