Competing β-scission and hydrogen transfer to the pinanyl radical in the addition of methyl thioglycolate to β-pinene derivatives

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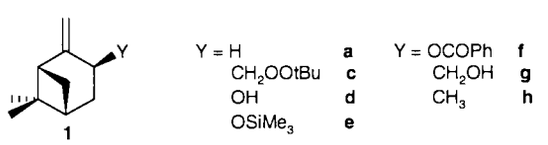
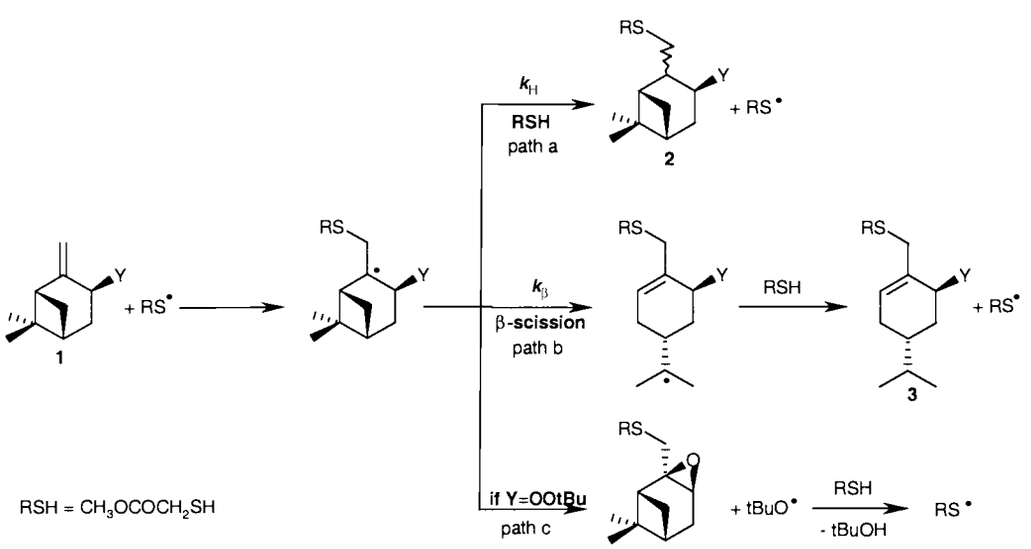
Despite previous reports to the contrary, addition of methyl thioglycolate to β-pinene always leads to both pinane and *p*-menthene adducts, the proportion of the latter increasing with the reaction temperature. This is attributable to the substantially higher activation entropy for β-scission than for hydrogen transfer, while the activation enthalpy is higher for the latter reaction. Any substituent at the 3-carbon of β-pinene, *trans* with respect to the *gem*-dimethyl bridge, increases the *p*-menthene yield: polar effects of the mainly electron-withdrawing substituents appear to disfavour hydrogen transfer to the tertiary pinanyl radical and favour β-scission. Analysis of the temperature dependence of the pinane : *p*-menthene ratio for the substituted β-pinenes indicates that variations in the activation entropy difference for the two reactions are at least as important as those of the activation enthalpy.

Introduction

There are conflicting reports as to the result of the addition of methyl thioglycolate to β-pinene, **1a** (Y = H). At room temperature the pinane adduct, **2a**, was reported as the sole product (Scheme 1, path a).[1] Refluxing at 160 °C gave only the *p*-menthene adduct, **3a**,[2] (path b) which was also obtained in the presence of acetic acid and methanol at 70 °C.[3] A further reaction of the tertiary pinanyl radical occurs when thiols are added to *tert*-butyl *trans*-pinocarveyl peroxide, **1b** (Y = OOtBu) at 60 or 80 °C. The adduct radical undergoes an intramolecular homolytic substitution (path c), to give a functionalized 2,3-epoxypinane,[4] to the exclusion of all other reactions; β-scission of the cyclobutane bridge (path b) or hydrogen transfer (path a), even though thiols are excellent hydrogen donors, is never observed. Preliminary experiments with *tert*-butyl *trans*-pinocarveylmethyl peroxide, **1c** (Y = CH_2OOtBu), at different temperatures showed that homolytic substitution leading to an oxetane is too slow to be observed and that both the pinane and the *p*-menthene adducts are formed simultaneously. The general case therefore would appear to be a competition between hydrogen transfer and β-scission.

In order to try to understand the behaviour of tertiary pinanyl radicals with thiols we have reexamined the reactions of β-pinene, then studied those of several derivatives with substituents at the 3-position, as indicated below.





Scheme 1

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Table 1 Temperature dependence of the pinane : *p*-menthene ratio in the addition of methyl thioglycolate to β-pinene : molar ratio 1.05 : 1

Run	*T*/°C	Conditions[a]	Yield (%)	**2a**[b,c]	**3a**[b]
1	−10		80	99	1
2	30		75	96	4
3	60		75	90	10
4	80		75	85	15
5	110		75	77	23
6	60	DEPC	—	90	10
7	160	DTBP	—	77	23
8	110	Open tube	57	55	45
9	160	Open tube	50	45	55
10	160	Open tube + DTBP[d]	50	32	68

[a] Standard for runs 1–5; initiator added for run 6 (diethyl percarbonate), 7 and 10 (di-*tert*-butyl peroxide); sample at atmospheric pressure for runs 8–10. [b] Relative yields of **2a** and **3a** determined by GC with internal standard. [c] Relative yields of *cis*-**2a** and *trans*-**2a** = 80 : 20 in all cases, determined by GC. [d] Literature conditions.[2]

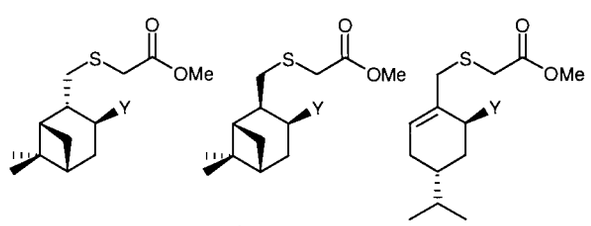
Results and discussion

Addition of methyl thioglycolate to β-pinene

Preliminary experiments showed that the conditions used in the previous work (equimolar methyl thioglycolate and β-pinene 2–3 days at room temperature with di-isopropyl percarbonate[1] or 8 h under reflux at 160 °C with di-*tert*-butyl peroxide[2]) needed to be adapted. An initiator is unnecessary since the reaction occurs even at −10 °C in the dark. It is clearly a radical reaction, as shown by tests run in the presence of radical traps such as hydroquinone. Hiatt and Bartlett[5] added the same thiol to styrene at 100 °C without initiation.

It was found to be preferable to work with a slight excess (5%) of thiol: with a lower ratio the alkene does not react completely; with a higher ratio significant amounts of disulfide are formed. The reaction was cleaner if the reactants were contained in screw-capped tubes rather than open to the atmosphere. The reaction time was adjusted according to the temperature (see Experimental section). Some runs were performed under different conditions in an attempt to simulate the earlier results.

Compounds likely to be formed are shown below (Y = H) and the results of the additions are presented in Table 1. Dimethyl 3,4-dithiaadipate arising from the dimerization of thiyl radicals may be present in the reaction medium, but it never exceeds 2%.



2 *cis* **2 *trans*** **3**

cis/*trans*: CH_2S with respect to the *gem*-dimethyl bridge

In all cases the two isomeric adducts **2a** and **3a** are formed at the same time. Their proportions do not vary with the duration of the reaction. Thus, at 80 °C (run 4) the ratio is 82 : 18 after 15 min, 85 : 15 after 30, 60 and 180 min for β-pinene conversions of 17, 23, 27 and 43%, respectively. While the *p*-menthene adduct **3a** is barely detectable at −10 °C, it increases with the temperature but always remains the minor product (runs 1–5).

Working at atmospheric pressure and not in screw-capped tubes leads to an increase in the amount of **3a** (runs 5 and 8 at 110 °C). When the sample is open to the air the amount of disulfide formed by dimerization of the thiyl radical becomes greater: 10% as against 2%. This leads to less clean reactions (coloured side-products), to lower yields and a lower effective concentration of thiol, disfavouring path a compared to path b (Scheme 1).

Table 2 Temperature dependence of the pinane : *p*-menthene ratio in the addition of methyl thioglycolate to β-pinene : molar ratio 10 : 1

Run	*T*/°C	[RSH][a]	**2a** : **3a**	**3a**[RSH]/**2a**
11	30	9.00	98 : 2	0.184
12	60	8.95	96 : 4	0.373
13	80	8.95	95 : 5	0.471
14	110	8.95	87 : 13	1.337
15	140	8.95	80 : 20	2.189
16	160	8.70	79 : 21	2.313

[a] Mean value, taking into account the initial and estimated final concentrations.

The presence of an initiator appropriate to the reaction temperature has no effect on the relative proportions of adducts **2a** and **3a** (runs 3 and 6). Finally, at 160 °C and atmospheric pressure in the presence of an initiator under the conditions of Gaiffe *et al.*[2] (run 10) the menthene adduct **3a** becomes the major product, but not the only product as claimed by these authors.

Relative magnitudes of the thermodynamic parameters

It was interesting to attempt a comparison of the thermodynamic parameters for the competing reactions of β-scission and hydrogen transfer responsible for the formation of **3a** and **2a**, respectively. This is easiest under conditions such that hydrogen transfer is a pseudo-first-order reaction. We have then:

$$v_\beta = k_\beta \text{ [pinanyl radical]}$$

and:

$$v_H = k_H \text{ [pinanyl radical][RSH]}$$

Then: $\mathbf{3a}/\mathbf{2a} = v_\beta/v_H = k_\beta/k_H$ [RSH], or $k_\beta/k_H = \mathbf{3a}[\text{RSH}]/\mathbf{2a}$ provided that [RSH] is large enough to be assumed constant throughout the reaction.

Under these conditions the differences in activation enthalpy and entropy for the β-scission and hydrogen transfer reactions can be therefore determined from the relative proportions of **3a** and **2a** measured at different temperatures. From the Eyring equation we can write:

$$k = (RT/Nh) * \exp(-\Delta G^\ddagger/RT), \text{ where } \Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$$

whence:

$$\text{Ln } \mathbf{3a}[\text{RSH}]/\mathbf{2a} = (\Delta S_\beta^\ddagger - \Delta S_H^\ddagger)/R - (\Delta H_\beta^\ddagger - \Delta H_H^\ddagger)/RT$$

The initial thiol : pinane molar ratio was therefore adjusted to 10 : 1, that is, an initial thiol concentration of 9.5 M. The final concentration varies slightly, depending on the amount of disulfide formed (1–7% on going from 30 to 110 °C), and this will lead to a small uncertainty in the entropy term. The results obtained are presented in Table 2. By plotting the logarithm of this ratio against $1/T$ we obtain: $\Delta H_\beta^\ddagger - \Delta H_H^\ddagger = 5.5 \pm 0.4$ kcal mol^{-1} and $\Delta S_\beta^\ddagger - \Delta S_H^\ddagger \approx 14.5 \pm 1.2$ cal mol^{-1} K^{-1}.†

That the activation entropy should be higher for β-scission than for hydrogen transfer is consistent with an increase in conformational freedom on going from a bicyclic to a monocyclic system. This, however, is compensated by the greater activation enthalpy associated with breaking a strong C–C bond as

† 1 cal = 4.184 J.

Table 3 Addition of methyl thioglycolate to 3-substituted (*trans*) β-pinenes: temperature dependence of the pinane : *p*-menthene ratio

Temperature[a]		−10 °C	30 °C	60 °C	80 °C	110 °C
Y	Compound	**2**[c] : **3**[b]	**2** : **3**	**2** : **3**	**2** : **3**	**2** : **3**
CH_2OOtBu	**1c**		75 : 25		36 : 64	
OH	**1d**	96 : 4	78 : 22	55 : 45	40 : 60	
$OSiMe_3$	**1e**	95 : 5		60 : 40	40 : 60	
OCOPh	**1f**	85 : 15	44 : 56	20 : 80	12 : 88	
CH_2OH	**1g**		78 : 22	57 : 43	40 : 60	24 : 76
CH_3	**1h**		80 : 20	61 : 39	53 : 47	30 : 70

[a] Standard conditions. [b] See Table 1. [c] Yield of *cis*-**2** is always much greater than yield of *trans*-**2** whatever the temperature; relative yields for **2d** and **2f**: 80 : 20, **2e**: 70 : 30 (determined by NMR of H-3); **2c** and **2g**: presence of *trans* (detected by ^1H and ^{13}C of 8- and 9-methyls); **2h**: presence of *trans* not determined.

Table 4 Semi-quantitative estimation of differences in activation entropies (cal mol^{-1} K^{-1}) and enthalpies (kcal mol^{-1}) for hydrogen transfer and β-scission in 3-substituted β-pinenes

Y	Compound	$\Delta S_\beta^\ddagger - \Delta S_H^\ddagger$	$\Delta H_\beta^\ddagger - \Delta H_H^\ddagger$
H[a]	**1a**	14.5 ± 1.2	5.5 ± 0.4
H[b]	**1a**	14.4 ± 0.4	6.0 ± 0.2
CH_2OOtBu[c]	**1c**	25.0	8.0
OH	**1d**	24.9 ± 0.1	8.1 ± 0.1
$OSiMe_3$	**1e**	22.7 ± 1.7	7.4 ± 0.5
OCOPh	**1f**	29.3 ± 0.5	8.4 ± 0.2
CH_2OH	**1g**	24.0 ± 0.6	7.8 ± 0.2
CH_3	**1h**	21.0 ± 1.8	7.0 ± 0.6

[a] Thiol 10 : 1. [b] Thiol 1.05 : 1. [c] Two points only.

opposed to a weak H–S bond. Consequently, hydrogen transfer is preferred but the difference in the activation energies for scission and hydrogen transfer falls as the temperature is raised, leading to an increased proportion of the *p*-menthene adduct. Rather similar results, but with even larger differences in the activation parameters, have been reported for the competition between ring-opening and hydrogen transfer in the reactions of radicals involving 1-norbornyl and 3-noradamantyl substituents.[6]

Addition of methyl thioglycolate to *trans*-3-substituted β-pinene derivatives

The derivatives **1c**–**1h** listed above were then subjected to the addition reaction, using only a small excess of thiol (1.05 : 1). Table 3 gives the proportions of the adducts obtained. As with **1a**, both adducts are obtained, but increasing the temperature always favours the *p*-menthene adduct, **3**.

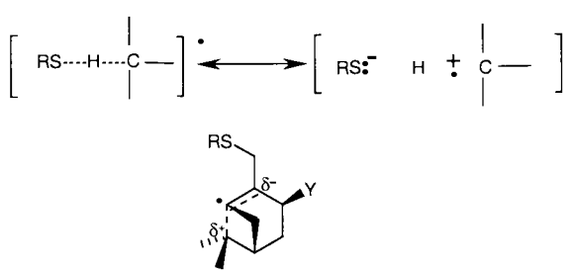
Compounds **1c**–**1h** were not studied with a large excess of thiol but by kinetic modelling,[7] assuming the reaction mechanism given in Scheme 1, it is possible to convert the product ratios to $k_\beta : k_H$ values and then to calculate the activation enthalpy and entropy differences as above (Table 4). In particular, given the change in experimental conditions on going from a ten-fold excess of thiol to a 5% excess, the values for β-pinene, **1a** ($\Delta H_\beta^\ddagger - \Delta H_H^\ddagger = 6.0 \pm 0.2$ kcal mol^{-1}, $\Delta S_\beta^\ddagger - \Delta S_H^\ddagger \approx 14.4 \pm 0.4$ cal mol^{-1} K^{-1}) can be considered in satisfactory agreement with those found by the simpler treatment (5.5 kcal mol^{-1} and 14.5 cal mol^{-1} K^{-1}, respectively).

Correlations for the other *trans*-3-substituted β-pinene derivatives give $\Delta H_\beta^\ddagger - \Delta H_H^\ddagger$ values which are systematically higher than for β-pinene itself, ranging from 7.0 ± 0.6 (**1h**) to 8.4 ± 0.2 kcal mol^{-1} (**1f**). The values for the entropy term range from 21 to 29 cal mol^{-1} K^{-1}. The calculated data, β-pinene included, give a $\Delta S_\beta^\ddagger - \Delta S_H^\ddagger$ *vs.* $\Delta H_\beta^\ddagger - \Delta H_H^\ddagger$ correlation, an isoselective relationship, with a correlation coefficient of 0.966 and an isoselective temperature of 170 ± 20 K; similar values of the latter can be obtained from two-temperature correlations.[8] This implies isokinetic relationships for the two competing reaction series. Simple isokinetic relationships are often the consequence of error compensation, but in the present case this is unlikely. The uncertainties on the parameters are considerably less than the range of values, particularly at the extremities of the correlation (compounds **1a** and **1f**).

Competition between hydrogen transfer and β-scission

For the *trans*-3-substituted derivatives the ratio of **2** to **3** differs significantly from the values observed for β-pinene. In particular, the *p*-menthene adduct becomes the major component as of about 80 °C, even at 30 °C for **1f**. The rate constant ratio $k_\beta : k_H$ is higher if the 3-carbon is substituted. There are then three possibilities: (i) the rate of β-scission is increased more than that of hydrogen transfer by electron-withdrawal; (ii) the first is increased while the second is reduced; (iii) both are reduced but the second more than the first. The 3-substituent could be considered to modify the geometry of the radical and the orientation of the orbital of the unpaired electron and, consequently, affect the rate of β-scission, but it is not possible to quantify any effect of this sort. On the other hand, one can reason on the basis of substituent polarity.

There is no information in the literature concerning hydrogen transfer from thiols to alkyl radicals with different β-substituents. However, it is known that hydrogen transfer is sensitive to polar effects:[9] the presence of electron-attracting substituents on the radical disfavours the reaction by raising the level of the transition state (Scheme 2). Conversely, steric hindrance would



Scheme 2

not appear to be important, given the small size of the extremity of the thiol attacking the radical frontally and colinearly. The ease of transfer should therefore decrease in the order: Me ~ H > CH_2OH, CH_2OOtBu > $OSiMe_3$, OH ⩾ OCOPh.

No work has been published on the rate of β-scission of tertiary pinanyl radicals. On the other hand, that of cyclopropylmethyl and cyclobutylmethyl radicals has been much studied.[10–12] It has been shown[10] that k_β varies by a factor of 1700 depending on the number and the position of methyl substituents in the latter, the most important effect being a marked acceleration of the reaction by substituents in the γ-position, corresponding to the 6-carbon in our system. The nature of the transition state and the interpretation of these effects remain controversial. Whereas Beckwith[10] maintains that the transition state for ring opening is reactant-like, other workers[11,12]

argue on the basis of an activation energy–reaction enthalpy correlation that it is product-like. If the polar effect of the methyl group is to stabilize a partial positive charge and to destabilize a partial negative charge, then the conflicting results on the opening of *trans*-methyl-cyclopropylmethyl[13] and cyclobutylmethyl radicals require opposite dipolar character in the transition state, the positive charge being on the α-carbon or the γ-carbon, respectively. The charge-polarized transition state for cyclobutylmethyl radical opening was rejected on the grounds that the substituents at the α- or γ-carbons should have rate effects of opposite sign, which they do, but similar magnitude, which they do not. However, this argument neglects the importance of steric effects at the γ-carbon, which enhance the rate much more than polar effects at the α-carbon decrease it. If we accept a charge-polarized transition state for tertiary pinanyl radical opening (Scheme 2), then the 3-substituent will be close to the partially negatively charged carbon, though separated by the 3-carbon, and would be expected to favour β-scission when it is electron-attracting: OCOPh ⩾ OH, $OSiMe_3$ > CH_2OOtBu, CH_2OH > H ~ Me.

The increase in the **3**:**2** ratio when the hydrogen in the 3-position is replaced by more polar groups would be explained by a lower rate of hydrogen transfer and a higher rate of β-scission. The differences between the various substrates are mainly entropic, a variation in the relative activation entropy of 10 cal mol^{-1} K^{-1} at 80 °C representing a contribution of 3.5 kcal mol^{-1} to the activation energy, which is greater than the entire span of activation enthalpy differences. In view of the difficulty of interpreting the variation in the **3**:**2** ratio, related to the activation energy differences, there is no question of discussing the "interaction mechanisms"[14] responsible for the parallel variation of the activation enthalpy and entropy differences.

cis and *trans* pinane adducts

The presence and the *cis*:*trans* distribution of the pinane adducts, **2**, not always detectable by GC, were determined where possible by NMR. The distribution does not vary with the temperature. The pinane adduct **2a** is present as the *cis* and *trans* diastereoisomers, in a ratio of 80:20. Davies found a similar ratio (75:25) at room temperature.[1] This author concludes that the *gem*-dimethyl bridge does not therefore greatly hinder the approach of the thiol to the radical site.

For pinocarveol, **1d**, and its derivatives **1e** and **1f**, observation of the 3-hydrogen signal, which is different for the two isomers, indicates a *cis*:*trans* ratio of 80:20 in **2d** and **2f**, 70:30 for **2e**. For **1c** and **1g** the ^1H and ^{13}C NMR spectra reveal the 8- and 9-methyls of the two isomers, the *cis* being very much the more important, but the ratio cannot be determined with precision. For **1h** it is not possible to establish that the *trans* isomer is formed.

The agreement between our results on β-pinene and those on its derivatives shows that the introduction of a *trans* substituent at the 3-position does not affect the relative ease of hydrogen transfer from thiol to either face of the radical. The substituent Y apparently introduces no significant steric hindrance. Further to the explanation given by Davies[1] concerning the small size of the thiol there is the question of the geometry of the radical: this would appear to adopt a flattened conformation in which the substituent occupies a non-hindering quasi-equatorial position, as has been shown by Teisseire *et al*. for pinocampheols[15] and confirmed by Jefford *et al*. for norpinols.[16]

Conclusion

This study demonstrates that the addition of methyl thioglycolate to β-pinene is never simple but leads to a mixture of pinane and *p*-menthene isomers in which the former are always the most important regardless of the temperature.

The introduction of a substituent at the 3-position of β-pinene, *trans* with respect to the *gem*-dimethyl bridge, always increases the *p*-menthene isomer fraction which can become predominant at high temperature. It is the polar electron-attracting effect of the substituent which is the most important, reducing the rate of hydrogen transfer and increasing that of β-scission. Its steric requirements would appear to have little or no impact on either the relative proportions of pinane and *p*-menthene or on the distribution of the *cis* and *trans* pinane isomers.

Experimental

General methods

NMR spectra were measured on a Bruker AC 250 spectrometer operating at 250 MHz (proton) or 62.9 MHz (carbon). Chemical shifts are given in ppm and *J* values in Hz. ^1H shifts are referenced to residual $CHCl_3$ (δ 7.26) as internal standard. ^{13}C shifts are relative to internal standard $CDCl_3$ (δ 77.0). Mass spectra were recorded on a Fisons Autospec-EQ instrument either with electron impact (70 eV) or chemical ionization (ammonia). Where possible, the exact molecular weight was determined by high resolution analysis. Capillary GC analyses were run on a Delsi Di200 with a CP Sil-8 column (length 25 m, id 0.25 mm, film thickness 0.25 μm).

Starting materials

tert-Butyl *trans*-pinocarveylmethyl peroxide, **1c**, *trans*-pinocarveol, **1d**, *trans*-pinocarveyl benzoate, **1f**, *trans*-3-(hydroxymethyl)-β-pinene, **1g**, and *trans*-3-methyl-β-pinene, **1h**, were prepared as described.[17–21]

trans-3-Trimethylsiloxy-β-pinene, **1e**, is obtained by the reaction of hexamethyldisilazane with *trans*-pinocarveol. *trans*-Pinocarveol, **1d** (2.89 g, 0.019 mol) and hexamethyldisilazane (6.13 g, 0.046 mol) were heated in an inert atmosphere at 110 °C for 24 h, and the silyl ether purified by distillation. Yield 87%; bp 117 °C/25 mm; δ_H: 4.89 and 4.79 (2H, 2m, H-10), 4.38 (1H, d, *J* 7.5, H-3), 2.6–1.7 (6H, m, H-1,4,5,7), 1.25 (3H, s, H-8), 0.65 (3H, s, H-9) and 0.14 (9H, s, $SiMe_3$); δ_C: 154.4 (C-2), 111.6 (C-10), 66.9 (C-3), 51.0 (C-1), 40.6 (C-6), 40.0 (C-5), 36.8 (C-4), 27.8 (C-7), 26.0 (C-8), 22.1 (C-9) and 0.5 ($SiMe_3$).

Addition of methyl thioglycolate

The reaction mixture (1 mmol of the pinane substrate and 1.05 mmol of methyl thioglycolate for the analytical studies, 3–4 times these amounts for identifications) is introduced into a screw-topped tube placed in a thermostatted bath or in the freezing compartment of a refrigerator (−10 °C). The reaction times are as follows: 7 days at −10 °C, 3 days at 30 °C, 24 h at 60 °C, 16 h at 80 and 110 °C, 8 h at 160 °C. After removal of the unreacted starting materials by distillation at reduced pressure, the addition products are identified after purification or enrichment by silica gel chromatography. Yields where given (Table 1) are those of the distilled material. It was generally not possible to separate the pinane and *p*-menthene adducts completely; the purity of a given adduct or *cis*–*trans* adduct mixture described below is given as a percentage (%) and was determined by GC. For the analytical studies the adducts are determined directly on the crude product mixture by GC, using the internal standard method. Experimental conditions for the substituted derivatives were those used for β-pinene and were not optimized; yields are therefore somewhat lower than for β-pinene.

Characteristics of addition products

(i) From β-pinene, 1a. *Methyl 4-(6,6-dimethylbicyclo[3.1.1]-hept-2-yl)-3-thiabutanoate,*[1] ***2a*** *cis and trans.* (100%, *cis*–*trans* mixture). δ_H (*cis* isomer): 3.71 (3H, s, OCH_3), 3.17 (2H, s, SCH_2CO), 2.70 and 2.65 (2H, ABX, J_{AB} 12.5, J_{AX} 7.5, J_{BX} 8.0, CH_2S), 2.4–1.2 (m, H-1,2,3,4,5,7s), 1.16 (3H, s, H-8), 0.97 (3H,

Table 5 ^{13}C NMR spectra of pinane adducts, **2**

		C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	CH_2S	SCH_2	COO	OCH_3	Y
2a	*cis*	45.0	40.9 or 40.0	21.6	25.8	40.0 or 40.9	38.2	32.9 or 33.1	27.6	22.8	39.4	33.1 or 32.9	170.3	51.7	
	trans	44.5	34.1	21.7	22.8	40.5	23.9	23.8	26.3	19.8	38.8	33.3	170.3	52.0	
2c	*cis*	44.9	43.6	33.7	31.3 or 32.4	41.3	38.8	32.4 or 31.3	27.7	23.0	38.7	34.0	171.0	52.4	82.2, 80.4, 26.6
	trans								26.5						76.6, 80.4, 26.6
2d[a]	*cis*	45.6	51.9	69.2	37.7	41.4	37.9	33.3	27.3	23.8	38.0	33.5	171.1	52.5	
	trans	45.8	40.2	63.8	35.7			24.5	26.3	20.2	34.4	34.0	171.1	52.5	
2e	*cis*	44.3	51.7	70.0	37.3	41.9	38.3	33.6 or 33.4	27.5	23.9	39.7	33.4 or 33.6	171.0	52.4	0.5
	trans	44.2	41.1	65.3	34.4 or 34.1	40.4	39.5	24.4	26.6	20.3	34.1 or 34.4		171.0	52.0	0.6
2f	*cis*	44.1	47.9	72.5	33.8	41.1	34.8	32.9	27.1	23.8	37.2	33.3	170.9	52.3	166.2, 130.6, 129.6, 128.3, 132.8
2g[a]	*cis*	44.1	43.6	37.4	30.7	41.1		32.2	27.5	22.9	38.7	33.4	171.3	52.4	70.0
	trans								26.8	20.6					66.6
2h[a]	*cis*	49.8	44.4	30.0	36.6	41.9		33.4 or 33.6	27.8	22.8	38.3	33.6 or 33.4	171.0	52.3	26.4

[a] $^1H/^{13}C$ correlation.

Table 6 ^{13}C NMR spectra of *p*-menthene adducts, **3**

	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8 and C-9	CH_2S	SCH_2	COO	OCH_3	Y
3a	132.4	126.5	27.4	40.0	26.3	29.1	32.3	20.0 and 19.7	39.6	31.9	171.2	52.4	
3c	132.5	129.1	29.2 or 29.1	35.2 or 34.3	29.1 or 29.2	34.3 or 35.2	32.5	20.1 and 19.7	37.8	32.2	171.0	52.4	77.1, 80.3, 26.5
3d[a]	133.2	130.9	29.2	33.9	35.1	66.0	32.0	20.0 and 19.6	37.0	32.1	171.2	52.6	
3e	133.5	130.0				64.3		20.2 and 19.7			169.8		1.0
3f	130.2	133.1	28.9	34.8	32.5	68.0	31.7	19.9 and 19.4	36.1	32.1	170.9	52.2	166.2, 130.7, 129.6, 128.4, 132.9
3g	132.3	129.4	28.8 or 29.0	38.3	29.0 or 28.8	35.0	32.1	20.1 and 19.4	37.8	32.1	171.2	52.4	64.8
3h	136.7	126.4	33.7 or 33.8		33.8 or 33.7		32.1	20.0 and 19.5	37.4	32.0	171.0	52.3	19.6

[a] $^1H/^{13}C$ correlation.

s, H-9) and 0.89 (1H, d, *J* 9.7, H-7a); δ_H (*trans* isomer): 2.55 and 2.52 (2H, ABX, J_{AB} 12.2, J_{AX} 7.8, J_{BX} 6.8, CH_2S), 1.18 (3H, s, H-8), 0.79 (3H, s, H-9); δ_C: see Table 5; MS-CI *m*/*z*: 260 (MNH_4^+); MS-EI *m*/*z* (%): 242 ($M^{+\bullet}$, 3), 169 (98), 136 (25), 123 (53), 121 (25), 95 (20), 93 (74), 91 (22), 82 (51), 81 (73), 79 (38), 69 (100), 67 (69), 55 (38), 43 (25) and 41 (85).

Methyl 4-(4-isopropylcyclohex-1-en-1-yl)-3-thiabutanoate, ***3a****.* (80%). δ_H: 5.55 (1H, m, H-2), 3.70 (3H, s, OCH_3), 3.13 (2H, m, CH_2S), 3.10 (2H, s, SCH_2CO), 2.4–1.2 (8H, m, H-3,4,5,6,7), 0.86 and 0.85 (6H, 2d, *J* 6.7, H-8,9); δ_C: see Table 6; MS-CI *m*/*z*: 260 (MNH_4^+); MS-EI *m*/*z* (%): 242 ($M^{+\bullet}$, 9), 169 (37), 136 (58), 135 (25), 93 (100), 81 (55), 79 (41), 69 (34), 37 (26), 43 (29) and 41 (37) (Found: (MS) 242.133846. $C_{13}H_{22}O_2S$ requires 242.134052).

(ii) From *tert*-butyl *trans*-pinocarveylmethyl peroxide, 1c. *Methyl 4-[6,6-dimethyl-3-(tert-butylperoxy)methylbicyclo-[3.1.1]hept-2-yl]-3-thiabutanoate,* ***2c*** *cis and trans.* (80%, *cis–trans* mixture). δ_H (*cis* isomer): 3.98–3.82 (2H, m, CH_2OO), 3.69 (3H, s, OCH_3), 3.19 and 3.18 (2H, AB, $J \sim 0$, SCH_2CO), 2.80 and 2.67 (2H, ABX, J_{AB} 12.8, J_{AX} 10.1, J_{BX} 5.2, CH_2S), 2.3–1.3 (7H, m, H-1,2,3,4,5,7s), 1.22 (9H, s, *t*-Bu), 1.18 (3H, s, H-8), 0.95 (3H, s, H-9) and 0.78 (1H, d, *J* 9.7, H-7a); δ_H (*trans* isomer): 1.11 (3H, s, H-8) and 0.79 (3H, s, H-9); δ_C: see Table 5; MS-CI *m*/*z*: 362 (MNH_4^+).

Methyl 4-[4-isopropyl-6-(tert-butylperoxy)methylcyclohex-1-en-1-yl]-3-thiabutanoate, ***3c****.* (60%). δ_H: 5.66 (1H, m, H-2), 3.98–3.82 (2H, m, CH_2OO), 3.69 (3H, s, OCH_3), 3.25–3.02 (4H, m, CH_2SCH_2CO), 2.3–1.3 (7H, m, H-3,4,5,6,7), 1.21 (9H, s, *t*-Bu), 0.88 and 0.86 (6H, 2d, *J* 6.3, H-8,9); δ_C: see Table 6; MS-CI *m*/*z*: 362 (MNH_4^+).

(iii) From *trans*-pinocarveol, 1d. *Methyl 4-(6,6-dimethyl-3-hydroxybicyclo[3.1.1]hept-2-yl)-3-thiabutanoate,* ***2d*** *cis and trans.* δ_H (100%, *cis* isomer): 4.10–4.02 (1H, m, H-3), 3.62 (3H, s, OCH_3), 3.20 and 3.13 (2H, AB, *J* 14.7, SCH_2CO), 2.95 (1H, br, OH), 2.65 and 2.55 (2H, ABX, J_{AB} 13.2, J_{AX} 9.5, J_{BX} 6.6, CH_2S), 2.5–1.6 (6H, m, H-1,2,4,5,7s), 1.10 (3H, s, H-8), 1.01 (1H, d, *J* 9.8, H-7a), 0.77 (3H, s, H-9); δ_H (*trans* isomer): 3.61 (3H, s, OCH_3), 4.31–4.21 (1H, m, H-3), 1.11 (3H, s, H-8) and 0.65 (3H, s, H-9); δ_C: see Table 5; MS-CI *m*/*z* 276 (MNH_4^+); MS-EI *m*/*z* (%): 258 ($M^{+\bullet}$, 3), 185 (26), 135 (22), 124 (48), 121 (52), 119 (22), 107 (48), 93 (37), 91 (32), 83 (29), 82 (100), 81 (38), 79 (37), 69 (42), 67 (41), 55 (39), 53 (22), 45 (34), 43 (49) and 41 (78) (Found (MS) 258.128906, $C_{13}H_{22}O_3S$ requires 258.128967).

Methyl 4-(4-isopropyl-6-hydroxycyclohex-1-en-1-yl)-3-thiabutanoate, ***3d****.* (100%). δ_H: 5.74 (1H, m, H-2), 4.31 (1H, m, H-6), 3.70 (3H, s, OCH_3), 3.37 and 3.25 (2H, AB, *J* 13.5, CH_2S), 3.14 (2H, s, SCH_2CO), 2.30 (1H, br, OH), 2.2–1.1 (6H, m, H-3,4,5,7), 0.89 and 0.87 (6H, 2d, *J* 6.4, H-8,9); δ_C: see Table 6; MS-CI *m*/*z*: 276 (MNH_4^+); MS-EI *m*/*z* (%): 258 ($M^{+\bullet}$, 6), 240 (24), 197 (23), 153 (78), 152 (30), 135 (20), 109 (42), 95 (25), 93 (33), 92 (27), 91 (100), 83 (20), 82 (34), 81 (38), 79 (31), 69 (22),

55 (28), 45 (20), 43 (36) and 41 (35) (Found (MS) 258.128897, $C_{13}H_{22}O_3S$ requires 258.128967).

(iv) From 3-trimethylsiloxy-β-pinene, 1e. *Methyl 4-(6,6-dimethyl-3-trimethylsiloxybicyclo[3.1.1]hept-2-yl)-3-thiabutanoate,* ***2e*** *cis and trans.* (100%, *cis–trans* mixture). δ_H (*cis* isomer): 4.10–4.00 (1H, m, H-3), 3.70 (3H, s, OCH_3), 3.28–3.15 (2H, m, SCH_2CO), 2.9–1.7 (8H, m, H-1,2,4,5,7s, CH_2S), 1.19 (3H, s, H-8), 1.09 (1H, d, *J* 9.7, H-7a), 0.88 (3H, s, H-9) and 0.10 (9H, s, $SiMe_3$); δ_H (*trans* isomer): 4.20–4.12 (1H, m, H-3), 3.72 (3H, s, OCH_3), 1.20 (3H, s, H-8), 0.74 (3H, s, H-9) and 0.08 (9H, s, $SiMe_3$); δ_C: see Table 5; MS-EI *m*/*z* (%): 258 (4), 185 (42), 135 (24), 134 (39), 121 (30), 119 (23), 107 (49), 93 (40), 91 (24), 83 (24), 82 (91), 81 (33), 79 (39), 69 (41), 67 (52), 61 (20), 55 (37), 53 (19), 45 (39), 43 (50) and 41 (100).

Methyl 4-(4-isopropyl-6-trimethylsiloxycyclohex-1-en-1-yl)-3-thiabutanoate, ***3e****.* (50%). δ_H: 5.70 (1H, m, H-2), 0.87 (6H, d, *J* 6.3, H-8,9) and 0.13 (9H, s, $SiMe_3$); δ_C: see Table 6; MS-EI *m*/*z* (%): 258 (6), 240 (24), 197 (27), 153 (100), 152 (35), 135 (39), 109 (51), 107 (24), 95 (37), 93 (32), 92 (21), 91 (61), 83 (36), 81 (54), 79 (37), 77 (24), 69 (23), 67 (17), 55 (31), 53 (21), 45 (27), 43 (57) and 41 (72).

(v) From *trans*-pinocarveol benzoate, 1f. *6,6-Dimethyl-2-(2-thia-5-oxa-4-oxohexyl)bicyclo[3.1.1]hept-3-yl benzoate,* ***2f*** *cis and trans. (60%, cis–trans mixture).* δ_H (*cis* isomer): 8.09–7.98 (2H, m, H-2′,6′), 7.56–7.49 (1H, m, H-4′), 7.44–7.38 (2H, m, H-3′,5′), 5.38–5.30 (1H, m, H-3), 3.63 (3H, s, OCH_3), 3.16–3.13 (2H, m, SCH_2CO), 2.88 and 2.79 (2H, ABX, J_{AB} 12.8, J_{AX} 8.3, J_{BX} 7.6, CH_2S), 2.5–1.3 (6H, m, H-1,2,4,5,7s), 1.24 (3H, s, H-8), 1.18 (1H, d, *J* 10.0, H-7a) and 0.98 (3H, s, H-9); δ_H (*trans* isomer): 5.49–5.40 (1H, m, H-3) and 1.26 (3H, s, H-8); δ_C: see Table 5; MS-CI *m*/*z*: 380 (MNH_4^+); MS-EI *m*/*z* (%): 167 (13), 135 (13), 134 (41), 121 (25), 119 (10), 105 (100), 93 (14), 91 (25), 79 (12), 77 (36), 43 (10) and 41 (11).

4-Isopropyl-1-(2-thia-5-oxa-4-oxohexyl)cyclohex-1-en-6-yl benzoate, ***3f****.* (100%). δ_H: 8.09–7.98 (2H, m, H-2′,6′), 7.56–7.49 (1H, m, H-4′), 7.44–7.38 (2H, m, H-3′,5′), 5.99 (1H, m, H-2), 5.82 (1H, m, H-6), 3.66 (3H, s, OCH_3), 3.36–3.21 (2H, m, CH_2S), 3.10 (2H, s, SCH_2CO), 2.3–1.3 (6H, m, H-3,4,5,7) and 0.86 (6H, d, *J* 6.3, H-8,9); δ_C: see Table 6; MS-CI *m*/*z*: 380 (MNH_4^+); MS-EI *m*/*z* (%): 240 (33), 197 (26), 137 (10), 135 (12), 134 (23), 123 (11), 122 (15), 105 (64), 93 (14), 92 (24), 91 (100), 79 (13), 77 (37), 43 (11) and 41(10).

(vi) From *trans*-3-(hydroxymethyl)-β-pinene, 1g. *Methyl 4-[3-(hydroxymethyl)-6,6-dimethylbicyclo[3.1.1]hept-2-yl]-3-thiabutanoate,* ***2g*** *cis and trans.* (100%, *cis–trans* mixture). δ_H (*cis* isomer): 3.66 (3H, s, OCH_3), 3.59–3.40 (2H, m, CH_2O), 3.18 and 3.12 (2H, AB, *J* 14.4, SCH_2CO), 2.80–2.57 (3H, m, CH_2S, OH), 2.30–2.21 (1H, m, H-7s), 2.1–1.4 (6H, m, H-1,2,3,4,5), 1.14 (3H, s, H-8), 0.92 (3H, s, H-9) and 0.73 (1H, d, *J* 9.7, H-7a); δ_H (*trans* isomer): 1.18 (3H, s, H-8) and 0.78 (3H, s, H-9); δ_C: see Table 5; MS-EI *m*/*z* (%): 272 ($M^{+\bullet}$, 5), 254 (M − H_2O, 3), 199 (100), 149 (28), 107 (26), 105 (21), 95 (22), 93 (28), 69 (22) and 41 (43) (Found (MS) 272.144646, $C_{14}H_{24}O_3S$ requires 272.144617).

Methyl 4-[6-(hydroxymethyl)-4-isopropylcyclohex-1-en-1-yl]-3-thiabutanoate, ***3g****.* (30%). δ_H: 5.64 (1H, m, H-2), 0.84 and 0.81 (6H, 2d, *J* 6.4, H-8,9); δ_C: see Table 6; MS-EI *m*/*z* (%): 272 ($M^{+\bullet}$, 3), 254 (−H_2O), 242 (49), 166 (33), 149 (29), 148 (20), 136 (67), 135 (64), 107 (51), 105 (57), 93 (100), 92 (20), 81 (23), 79 (45), 77 (32), 45 (22), 43 (41) and 41 (73) (Found (MS) 272.144582, $C_{14}H_{24}O_3S$ requires 272.144617).

(vii) From *trans*-3-methyl-β-pinene, 1h. *Methyl 4-(3,6,6-trimethylbicyclo[3.1.1]hept-2-yl)-3-thiabutanoate,* ***2h*** *cis.* (80%). δ_H: 3.70 (3H, s, OCH_3), 3.18 and 3.14 (2H, AB, *J* 14.4, SCH_2CO), 2.72 and 2.61 (2H, ABX, J_{AB} 12.5, J_{AX} 9.6, J_{BX} 5.7, CH_2S), 2.4–1.1 (7H, m, H-1,2,3,4,5,7s), 1.17 (3H, s, H-8), 1.06 (3H, d, *J* 7.6, CH_3), 0.95 (3H, s, H-9) and 0.77 (1H, d, *J* 9.6, H-7a); δ_C: see Table 5; MS-EI *m*/*z* (%): 256 ($M^{+\bullet}$, 9), 183 (100), 137 (21), 107 (25), 96 (24), 95 (27), 93 (20), 81 (55), 79 (20), 69 (61), 67 (26), 55 (29), 45 (25) and 41 (61) (Found (MS) 256.151751, $C_{14}H_{24}O_2S$ requires 256.149702).

Methyl 4-(4-isopropyl-6-methylcyclohex-1-en-1-yl)-3-thiabutanoate, ***3h****.* (40%) δ_H: 5.53 (1H, m, H-2), 3.69 (3H, s, OCH_3), 3.22–3.07 (4H, m, CH_2SCH_2CO), 2.4–1.2 (7H, m, H-3,4,5,6,7), 0.99 (3H, d, *J* 7.1, CH_3), 0.86 and 0.85 (6H, 2d, *J* 6.4, H-8,9); δ_C: see Table 6; MS-EI *m*/*z* (%): 256 ($M^{+\bullet}$, 9), 183 (23), 150 (47), 107 (100), 95 (54), 93 (39), 91 (25), 81 (26), 79 (28), 69 (22), 43 (27) and 41 (40) (Found (MS) 256.150813, $C_{14}H_{24}O_2S$ requires 256.149702).

Kinetic modeling

The product ratios for runs with only a small excess of thiol were converted to rate constant ratios by simulation of the reaction using the KINAL programme associated with a Simplex routine.[7] Initial concentrations were calculated on the assumption that all substrates have the same density : molecular weight ratio as β-pinene. This is clearly an approximation, but tests over a range of plausible values showed that there is no effect upon the enthalpy term and not more than 0.1 cal mol^{-1} K^{-1} on the entropy term. The rate constant for ring-opening was set at an arbitrary value and that for transfer optimized with respect to the final product ratio, the rate constants for the other steps and the time scale being set at values compatible with completion of the reaction. These have no effect upon the transfer rate constant. No attempt was made to include side-reactions, such as dimerization of the thiyl radical, in the reaction model, it being assumed that the reaction proceeds with 100% yield of the identified products.

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