A Convergent Construction of Quaternary Centres and Polycyclic Structures

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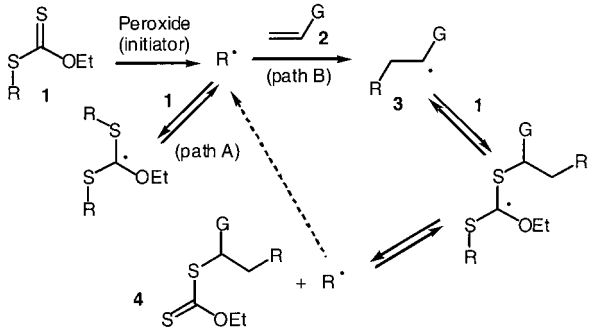
Abstract: Various xanthates, made by conjugate addition of xanthic acid to electrophilic olefins, add in a inter- or intra-molecular fashion to olefins allowing a direct introduction of a quaternary centres and the construction of polycyclic structures.

Key words: radical additions, xanthates, quaternary centres, polycycles, cycloalkenones

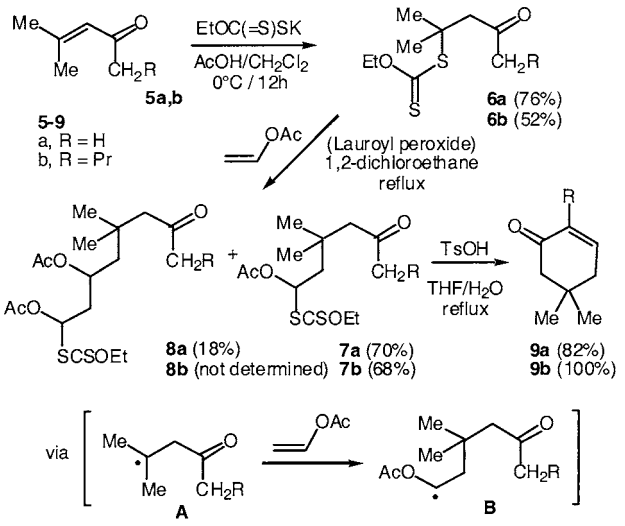
The intramolecular radical addition to unsaturated groups has emerged in recent times as a major tool for the construction of mono- and polycyclic structures.[1] In contrast, very few radical processes allow a clean intermolecular additions to unactivated olefins.[2] The main difficulty arises from the relative slowness of the addition step in comparison with unwanted competing reactions. This is typically the case with the popular stannane based chemistry, where premature hydrogen abstraction from the stannane is usually much faster than the intermolecular addition.[3] Many of these limitations can be lifted by exploiting the reversible addition-fragmentation to thiocarbonyl compounds. We have indeed shown, over the past few years, that xanthates **1** and related thiocarbonylsulfanyl derivatives undergo an efficient addition to a variety of olefins **2**, as outlined in Scheme 1.[4] The initial radical **R** is not irreversibly consumed by reaction with its xanthate precursor (path A) and therefore acquires enough lifetime to add to the olefin following path B. The resulting adduct, **4**, is also xanthate and lends itself to numerous subsequent radical and non-radical transformations.



Scheme 1

The utility of this process may be substantially increased by expanding the range of available starting xanthates. These are usually prepared by nucleophilic displacement of a leaving group with a xanthate salt, several of which are commercially available. Other interesting but less common routes rely on the reaction of bis-xanthates with carbanions[5] or with thermally labile diazo compounds.[6] Alternatively, the radical chain decomposition of (*S*)-acyl xanthates may be used in some special cases.[7] It has also been reported that xanthic acid can undergo a Michael-type addition to electrophilic olefins under certain conditions.[8] We have now found that this last reaction opens a cheap, flexible, and highly efficient approach for the creation of quaternary centers and for the construction of complex polycyclic structures.

Treatment of mesityl oxide **5a** with excess potassium *O*-ethylxanthate in a mixture of dichloromethane and acetic acid at 0 °C for 12 hours resulted in the clean formation of the Michael addition product **6a** (76%).[8] The addition of acetic acid is necessary to generate the xanthic acid in situ and to stabilise the product by inhibiting the otherwise facile reverse β-elimination process. Heating a mixture of **6a** with a 3.5-fold excess of vinyl acetate in refluxing 1,2-dichloroethane in the presence of a small amount of lauroyl peroxide gave the expected adduct **7a** in 70% yield (Scheme 2).



Scheme 2

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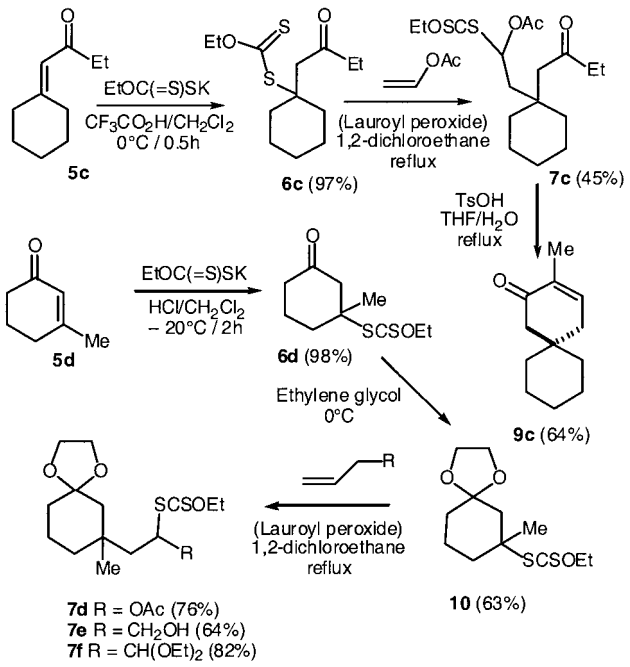
Two observations are worth underlining:
a) The radical addition and xanthate transfer could be performed without serious complications from the retro-Michael reaction, which would have liberated the unstable *O*-ethylxanthic acid, an inhibitor of the radical chain process. This further confirms the general mildness and neutrality of the experimental conditions and demonstrates the easy creation of a quaternary carbon atom by *intermolecular* radical addition.
b) It is implicit in the reaction manifold displayed in Scheme 1 that success of the radical addition hinges on the relative stability of radical **R** and adduct radical **3**. It is important that the former be more stable than the latter in order to drive the equilibrium forward. If the equilibrium favours adduct radical **3**, this radical will eventually start adding to olefin **2** resulting in telomer formation. In essentially all our previous studies, we insured that this was not the case by attaching a resonance stabilising group onto radical **R** In the present situation, where **R** = **A** and **3** = **B**, it was not obvious that the relative stability between a simple tertiary radical and an acetoxy substituted secondary radical would be sufficiently different to prevent extensive telomerisation of the vinyl acetate. Indeed, we could isolate a significant amount (18%) of double addition product **8a**. Presumably higher telomers were also formed but in smaller quantities.

The carbon bearing the acetoxy and xanthate groups in adduct **7a** has the oxidation level of an aldehyde. Heating with toluenesulfonic acid in aqueous THF caused cleavage into the aldehyde and ring closure via an internal aldol/crotonisation to give cyclohexenone **9a**. By a similar sequence, unsaturated enone **1b**[9] was converted into the corresponding cyclohexenone **6b** in good overall yield (Scheme 2).

We found that replacing the acetic acid by the stronger trifluoroacetic acid was beneficial when the xanthate was especially sensitive towards a retro-Michael reaction. Compound **6c** could thus be obtained in 96% yield; its fragility, however, translated into a lowered efficiency in the radical addition (Scheme 3). The corresponding adduct **7c** with vinyl acetate was obtained in a modest 45% yield. Exposure to toluenesulfonic acid finally afforded the spiroenone **9c** in 64% yield. Addition of the xanthate salt to methylcyclohexenone could be accomplished by using gaseous HCl in dichloromethane; however, the propensity of the resulting xanthate **6d** to undergo the retro-Michael reaction forced us to temporarily disguise the ketone group as the corresponding 1,3-dioxolane **10**. The xanthate transfer reaction could now be effected normally and smoothly to a number of olefins to give adducts **7d**–**f**, as shown by the examples depicted in the lower part of Scheme 3.

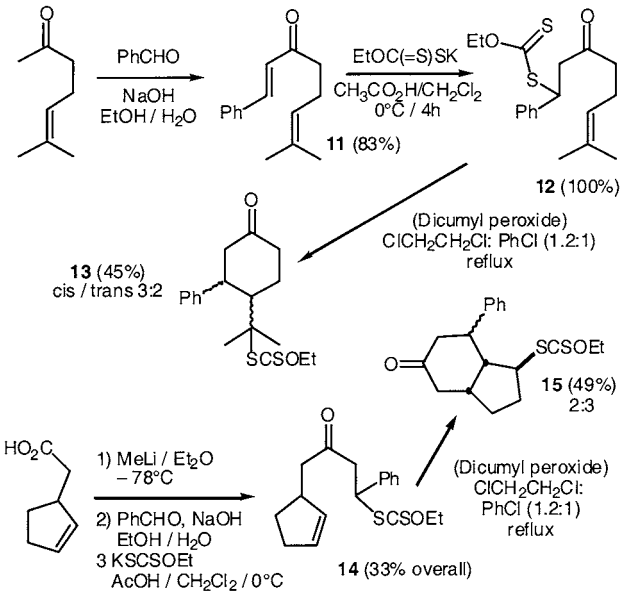
The intramolecular version of this methodology constitutes a convenient and powerful approach to polycyclic structures (Scheme 4). Thus, base induced aldol/crotonisation reaction of 6-methyl-hept-5-en-2-one with benzaldehyde provided enone **11** in 83% yield, which readily underwent conjugate addition with xanthic acid to give **12**



Scheme 3

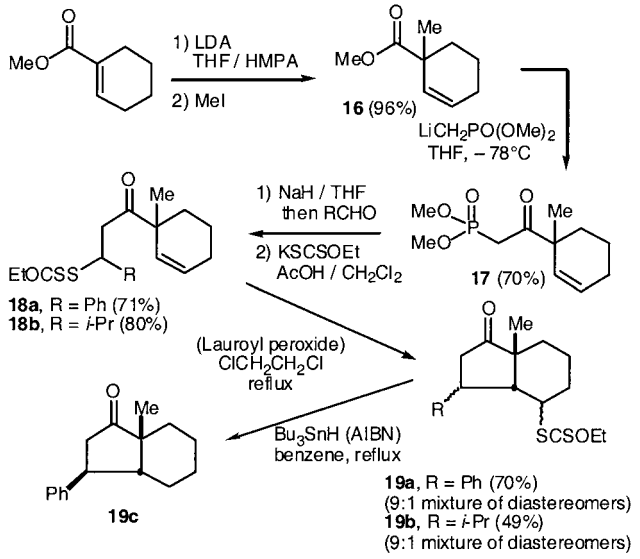
quantitatively. Exposure of the latter to dicumyl peroxide in a refluxing 1.2:1 mixture of 1,2-dichloroethane and chlorobenzene afforded substituted cyclohexanone **13** as a 3:2 mixture of two diastereoisomers in moderate yield. Using a similar sequence, bicyclic compound **15** was prepared with reasonable efficiency from xanthate **14**, the β-epimer being the major isomer in this case. Both examples highlight the accessibility of 6-membered rings by direct radical cyclisation.

More interesting, in the context of natural product synthesis, is the conversion of commercially available methyl



Scheme 4

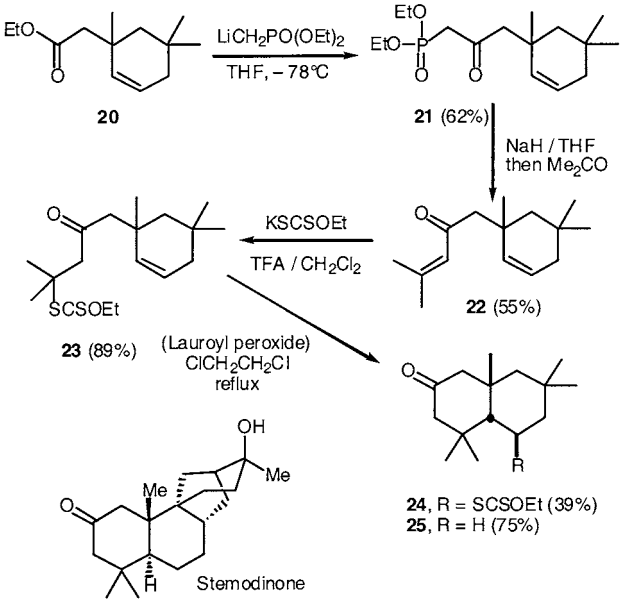
cyclohexenecarboxylate into bicyclic structures **19a** and **19b** by the sequence shown in Scheme 5. Methylation of the extended anion followed by exposure to lithiated diethyl methylphosphonate provided the key Wittig–Horner reagent **17**. Condensation with both benzaldehyde and isobutyraldehyde led to the corresponding conjugated enones, which were treated with the xanthate salt in acetic acid to furnish xanthates **18a** and **18b** in 71% and 80% yield respectively. Refluxing a 1,2-dichloroethane solution in the presence of a small amount of lauroyl peroxide triggered the ring closure into bicyclic derivatives **19a** (70%) and **19b** (49%). In both cases an approximately 9:1 mixture of diasteriomers was produced. Reductive removal of the xanthate from the major isomer in the case of **19a** gave compound **19c**, whose relative stereochemistry was determined by a NOESY NMR experiment. Compound **19b**, with a pendant isopropyl group, possesses the core structure of many terpenes.[10]



Scheme 5

Starting from known ester **20** derived from isophorol,[11] xanthate **23** (Scheme 6) was prepared using a similar sequence. The more difficult six-membered ring closure leading to **24** could be accomplished, albeit in a modest 39% yield. Reductive removal of the xanthate group with tributyltin hydride gave **25** in 75% yield. Both **24** and **25** were obtained as single isomers, although the stereochemistry could not be determined with certainty. The xanthate group in **25** occupies a pseudo-axial position since the NMR signal for the hydrogen on C-6 (steroid numbering) does not exhibit a large coupling typical of an axial disposition. The ring junction is assumed to be *cis*- by analogy with the rare examples in the literature of a 6-*exo*-ring-closure on a cyclohexene.[1] Cyclohexane rings with geminal dimethyl substituents are ubiquitous in terpenes. Our example was in fact designed as a model for the projected synthesis of the more elaborate stemodinone.

None of the yields in the present preliminary work has been optimised and room for improvement certainly exists; nevertheless, this study provides a glimpse of the synthetic possibilities arising from the conjugate addition of xanthates to electrophilic olefins. Complex structures and quaternary centres can be readily assembled starting from easily available starting materials and reagents.



Scheme 6

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(9) **Typical Experimental Procedures: 5,5-Dimethyl-2-cyclohexenone 9a.** A degassed solution of **6a**[8] (186 mg; 0.84 mmol) and vinyl acetate (0.35 mL; 3.87 mmol) in

$ClCH_2CH_2Cl$ (1.2 mL), was heated to reflux under an inert atmosphere. After a few minutes of refluxing, solid lauroyl peroxide (5 mol%) was added and heating was continued for 1.5 h. Another small amount of lauroyl peroxide (2 mol%) was added followed by further similar lots every hour until TLC indicated completion of the reaction (13 mol% in total). After cooling to r.t., the solvent was removed under reduced pressure and the residue purified by silica gel chromatography (EtOAc–petroleum ether, 5:95) to afford **7a** as a yellowish oil (180 mg; 70%). IR (film): 2957, 1751, 1715, 1367, 1218, 1051, 488 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) = 6.68 (dd, J_1 = 5.1, J_2 = 7.6 Hz, 1 H), 4.65 (q, J = 7.1 Hz, 2 H), 2.46 (s, 2 H), 2.20–2.04 (m, 8 H), 1.42 (t, J = 6.1 Hz, 3 H), 1.08 (s, 3 H), 1.07 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 212.7, 207.5, 170.3, 78.3, 70.4, 53.0, 44.9, 32.8, 31.7, 27.5, 27.4, 28.0, 13.3. MS (IC, NH_3): m/z = 324 [M + NH_3]. Anal. Calcd for $C_{13}H_{22}O_4S_2$: C, 50.95; H, 7.24. Found: C, 50.92; H, 7.31. A solution of ketone **7a** (100 mg; 0.4 mmol), *p*-TsOH (30 mg) and H_2O (0.1 mL) in THF (4 mL) was refluxed for 48 h. The reaction mixture was cooled to r.t. and neutralised with a sat. solution of $NaHCO_3$. The organic layer was extracted with Et_2O, washed with brine, dried over Na_2SO_4, filtered, and the solvent removed in vacuo. The residue was purified by silica gel chromatography (elution by diethyl ether–pentane, 0.5:9.5) to afford the known enone[12] **9a** (39 mg, 82%). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) = 6.86 (dt, J_1 = 4.1, J_2 = 10.1 Hz, 1 H), 6.02 (dt, J_1 = 2.0, J_2 = 10.1 Hz, 1 H), 2.27 (s, 2 H), 2.24 (dd, J_1 = 2.0, J_2 = 4.1 Hz, 2 H), 1.04 (s, 6 H): ^{13}C NMR (100 MHz; $CDCl_3$): δ (ppm) = 199.7 (C=O), 148.1 (CH), 128.6 (CH), 51.4 (CH_2), 39.5 ($C_{quat.}$), 29.3 (CH_2), 28.9 (2 CH_3). MS (IC, NH_3) m/z = 125 [M + H], 142 [M + NH_4].

Methyl 1-Methyl-2-cyclohexenecarboxylate 16. To a stirred solution of freshly distilled diisopropylamine (1.31 mL, 9.3 mmol, 1.4 equiv) in of THF (8 mL) maintained at 0 °C under argon were added dropwise *n*-BuLi (5.53 mL, 1.56 M in hexanes, 8.6 mmol, 1.3 equiv). After 15 min the solution was cooled down to –78 °C and dry HMPA (1.50 mL, 8.6 mmol, 1.3 equiv) was added. The mixture was stirred for 30 min at the same temperature and commercial 1-cyclohexenylmethyl-carboxylate (0.93 g, 6.6 mmol, 1.0 equiv) was then added followed after 10 min by (0.62 mL, 10.0 mmol, 1.5 equiv) of methyl iodide. The solution was then allowed to warm to –5 °C over 2 h when a sat. aq solution of NH_4Cl was poured into the orange mixture. After dilution with petroleum ether and washing with brine, the organic layer was dried over $NaSO_4$ and carefully concentrated in vacuo to give ester **16** as a yellow liquid, which was used as such in the next step (0.98 g, crude yield: 96%). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) = 1.27 (s, 3 H, CH_3C), 1.45 (ddd, $^2J_{HH}$ = 13.1 Hz, $^3J_{HH}$ = 9.7 Hz and $^3J_{HH}$ = 3.4 Hz1 H), 1.56–1.71 (m, 2 H), 1.96–2.02 (m, 2 H), 2.13–2.19 (m, 1 H), 3.69 (s, 3 H, CH_3O), 5.68 (dm, $^3J_{HH}$ = 10.1 Hz, 1 H), 5.78 (dt, $^3J_{HH}$ = 10.1 Hz and $^3J_{HH}$ = 3.6 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 19.3 (CH_3), 24.4 (CH_2), 26.1 (CH_2), 32.7 (CH_2), 42.8 ($C_{quat.}$), 51.6 (CH_3O), 127.6 (CH), 130.3 (CH), 177.2 (C=O).

Dimethyl [2-(1-Methyl-cyclohex-2-enyl)-2-oxo-ethyl]-phosphonate 17. *n*-BuLi (1.56 M in hexanes, 7.8 mL, 12.2 mmol, 2.1 equiv) was added at –78 °C under argon to a stirred solution of commercial dimethyl methylphosphonate (1.55 mL,14.3 mmol, 2.5 equiv) in THF (20 mL). After 30 min at –78 °C, ester **16** was added with a syringe over 10 min and the mixture was stirred for 6 h at the same temperature. At this point a sat. aq solution of NH_4Cl was poured into the flask and the mixture was diluted with EtOAc. The organic layer was washed successively with sat. aq solutions of NH_4Cl and NaCl then dried over $NaSO_4$. Concentration under reduced pressure afforded a yellowish oil which was purified by flash column chromatography in petroleum ether–EtOAc (40% to 100%) to yield **17** as a colourless oil (0.99 g, 70%). IR (film): 2937, 1707, 1458, 1257, 1036 cm^{-1}. MS (IC, NH_3) m/z = 264 [M + NH_4]$^+$, 247 [M + H]$^+$. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) = 1.21 (s, 3 H, CH_3C), 1.41 (ddd, $^2J_{HH}$ = 12.5 Hz, $^3J_{HH}$ = 8.6 Hz and $^3J_{HH}$ = 3.5 Hz, 1 H), 1.52–1.66 (m, 2 H), 2.00–2.08 (m, 3 H), 3.18 (dd, $^2J_{HP}$ = 21.6 Hz and $^2J_{HH}$ = 15.4 Hz, 1 H), 3.24 (dd, $^2J_{HP}$ = 21.1 Hz and $^2J_{HH}$ = 15.4 Hz, 1 H), 3.78 (d, $^3J_{HP}$ = 2.1 Hz, 3 H), 3.81 (d, $^3J_{HP}$ = 2.1 Hz, 3 H), 5.66 (dt, $^3J_{HH}$ = 10.1 Hz and $^4J_{HH}$ = 2.1 Hz, 1 H), 5.90 (dt, $^3J_{HH}$ = 10.1 Hz and $^3J_{HH}$ = 3.7 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 18.8 (CH_3), 23.9 (CH_2), 24.5 (CH_2), 31.4 (CH_2), 35.9 (d, $^1J_{CP}$ = 136 Hz, 1 C, CH_2P), 49.9 ($C_{quat.}$), 52.6 (CH_3O), 129.2 (CH), 129.8 (CH), 205.3 (d, $^1J_{CP}$ = 7 Hz, 1 C, C=O).

***O*-Ethyl-*S*-[3-(1-methyl-cyclohex-2-enyl)-3-oxo-1-phenyl-propyl] Dithiocarbonate 18a.** To a suspension of NaH (60% in mineral oil; 16 mg, 0.40 mmol) in THF (1 mL) maintained at 0 °C under argon was added drop wise a solution of **17** (82 mg, 0.33 mmol) in THF (0.5 mL). The resulting mixture was stirred for 30 min before adding benzaldehyde (41 μL, 0.40 mmol) slowly, leading rapidly to a yellow solution. After 2 h at 0 °C, a TLC analysis showed no more starting material. A sat. aq solution of NH_4Cl was poured into the flask and the mixture diluted with Et_2O. The organic layer was washed successively with sat.aq solutions of NH_4Cl and NaCl then dried over Na_2SO_4. Removal of solvent under reduced pressure afforded crude 1-(1-methyl-cyclohex-2-enyl)-1-oxo-3-phenyl-prop-2-ene as a yellow oil. This compound was dissolved in a (3:2) mixture of CH_2Cl_2 and HOAc (2.5 mL) and the solution was cooled down to 0 °C. Commercial potassium *O*-ethyl xanthate (0.26 g, 1.64 mmol) was added portion-wise over 2 h, followed by one more hour of stirring. After addition of water and dilution with Et_2O, the organic layer was washed successively with H_2O and brine and dried over Na_2SO_4. After concentration in vacuo the resulting yellow oil was submitted to flash column chromatography using petroleum ether–EtOAc (5%) as eluent to give **18a** as a viscous pale yellow oil (81 mg, 71%) and as a (2:1) mixture of diastereoisomers. IR (film): 3062, 3025, 2935, 2868, 1707, 1602, 1453, 1221, 1111, 1048 cm^{-1}. MS (IC, NH_3) m/z = 349 [M + H]$^+$, 229 {M – [(SC(*S*)OEt] + H}$^+$. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) = 0.98 (s, 2 H, CH_3C), 1.10 (s, 1 H, CH_3C), 1.18–1.32 (m, 2 H), 1.35 (t, $^3J_{HH}$ = 7.1 Hz, 1.5 H, CH_3CH$_2$O), 1.37 (t, $^3J_{HH}$ = 7.1 Hz, 1.5 H, CH_3CH$_2$O), 1.38–1.43 (m, 1 H), 1.49–1.58 (m, 1 H,), 1.92–1.99 (m 4 H), 3.22 (d, $^3J_{HH}$ = 7.2 Hz, 2 H), 4.59 (q, $^3J_{HH}$ = 7.1 Hz, 2 H, CH_2O), 5.28 (t, $^3J_{HH}$ = 7.2 Hz, 1 H, C*H*-Ph), 5.51 (dt, $^3J_{HH}$ = 10.1 Hz and $^4J_{HH}$ = 1.9 Hz, 2/3 H), 5.60 (dt, $^3J_{HH}$ = 10.1 Hz and $^4J_{HH}$ = 1.9 Hz, 1/3 H), 5.78–5.84 (m, 1 H), 7.11 (d, $^3J_{HH}$ = 15.7 Hz, 1 H), 7.18–7.31 (m, 3 H, $H_{arom.}$), 7.34–7.36 (m, 2 H, $H_{arom.}$). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 13.3 (CH_3), 18.9 and 19.0 (CH_2), 24.2 (CH_3), 24.5 (CH_2), 31.4 and 31.6 (CH_2), 43.8 ($C_{quat.}$), 47.0 (CH_2), 48.7 (CH), 69.6 (CH_2), 127.3 (CH), 127.7 and 127.8 (CH), 128.2 (CH), 129.2 (CH), 129.5 (CH), 139.6 and 139.7 ($C_{quat.\ arom.}$), 209.8 and 209.9 (C=O), 212.0 (C=S).

***O*-Ethyl-*S*-(7a-methyl-1-oxo-3-phenyl-octahydro-inden-4-yl) Dithiocarbonate 19a.** A solution of **18a** (81 mg, 0.23 mmol) in $ClCH_2CH_2Cl$ (2.3 mL) was heated to reflux under argon for 15 min then solid lauroyl peroxide (7 mg, 0.02 mmol) was added from the top of the condenser. The reflux was continued for 7 h during which time a further four smaller portions of peroxide were added every 90 min (total:

12 mg). Cooling and removal of the solvent in vacuo gave a pale yellow solid which was purified by flash column chromatography in petroleum ether–EtOAc (5%) to yield **19a** as colourless needles (57 mg, 70%) and as a (9:1) mixture of diastereoisomers. IR (film): 2935, 1742, 1452, 1216, 1112, 1050 cm^{-1}; MS (IC, NH_3) *m*/*z* = 366 [M + NH_4]$^+$, 349 [M + H]$^+$. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm, major isomer): 1.37 (t, $^3J_{HH}$ = 7.2 Hz, 3 H, C*H*$_3$CH$_2$O), 1.30 (s, 3 H), 1.31–1.38 (m, 1 H), 1.51 (dt, $^2J_{HH}$ = 12.4 Hz and $^3J_{HH}$ = 4.8 Hz, 1 H), 1.61–1.72 (m, 2 H), 1.58–1.77 (m, 2 H), 1.94 (dm, $^2J_{HH}$ = 14.5 Hz, 1 H, C*H*-CH-S), 2.04 (ddt, $^2J_{HH}$ = 14.5 Hz, $^3J_{HH}$ = 11.8 Hz and $^3J_{HH}$ = 4.4 Hz, 1 H, C*H*-CH-S), 2.33 (dm, $^3J_{HH}$ = 11.4 Hz, 1 H, C*H*-CHPh), 2.51 (dd, $^2J_{HH}$ = 19.2 Hz and $^3J_{HH}$ = 11.2 Hz, 1 H), 2.92 (dd, $^2J_{HH}$ = 19.2 Hz and $^3J_{HH}$ = 8.2 Hz, 1 H), 3.40 (ddd, $^3J_{HH}$ = 11.4 Hz, $^3J_{HH}$ = 11.2 Hz and $^3J_{HH}$ = 8.2 Hz, 1 H, C*H*Ph), 3.97–4.01 (m, 1 H, C*H*-S), 4.45–4.57 (m, 2 H, C*H*$_2$O), 7.24–7.33 (m, 3 H, $H_{arom.}$), 7.36–7.40 (m, 2 H, $H_{arom.}$). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm, for major isomer) = 13.4 (CH_3), 17.3 (CH_2), 20.8 (CH_3), 26.0 (CH_2), 28.4 (CH_2), 42.0 (CH), 44.2 (CH_2), 44.3 (CH), 47.9 ($C_{quat.}$), 54.6 (*C*H-S), 69.3 (*C*H$_2$O), 127.0 (CH), 127.3 (CH), 128.5 (CH), 140.7 ($C_{quat.\ arom.}$), 212.8 (C=O), 218.7 (C=S). Anal. Calcd for $C_{19}H_{24}O_2S_2$ (%): C, 65.48; H, 6.94. Found (%): C, 65.77; H, 7.13.

7a-Methyl-3-phenyl-octahydro-inden-1-one 19c. To a refluxing solution of **19a** (23 mg, 0.066 mmol) in benzene (0.7 mL) were added Bu_3SnH (20 μL, 0.073 mmol), followed by AIBN (1 mg, 6.6 μmol). After 30 min the mixture was cooled to r.t. and concentrated under reduced pressure. The residue was purified by flash column chromatography in petroleum ether–EtOAc (0% to 5%) to give **19c** as a white solid (9 mg, 60%) and as a single diastereoisomer (spatial structure assigned by NOE experiment). IR (CCl_4): 2933, 2860, 1739, 1455 cm^{-1}. MS (IC, NH_3) *m*/*z* = 246 [M + NH_4]$^+$, 229 [M + H]$^+$. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 1.21 (s, 3 H, C*H*$_3$-), 1.26–1.33 (m, 2 H), 1.40–1.59 (m, 4 H), 1.64–1.73 (m, 2 H), 2.00 (m, 1 H, -C*H*-CHPh), 2.42 (dd, $^2J_{HH}$ = 19.2 Hz and $^3J_{HH}$ = 11.2 Hz, 1 H), 2.88 (dd, $^2J_{HH}$ = 19.2 Hz and $^3J_{HH}$ = 8.1 Hz, 1 H), 3.43 (ddd, $^3J_{HH}$ = 11.6 Hz, $^3J_{HH}$ = 11.2 Hz and $^3J_{HH}$ = 8.1 Hz, 1 H, -C*H*-Ph), 7.23–7.27 (m, 3 H, $H_{arom.}$) 7.32–7.36 (m, 2 H, $H_{arom.}$). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 18.9 (CH_3), 20.1, 20.6, 20.8 (CH_2), 28.2 (CH_2), 40.4 (CH), 44.7 (CH_2), 48.0 ($C_{quat.}$), 49.8 (CH), 126.4, 127.2, 128.3 ($CH_{arom.}$), 142.2 ($C_{quat.\ arom.}$), 220.7 (C=O). Anal. Calcd for $C_{19}H_{24}O_2S_2$ (%): C, 84.16; H, 8.83. Found (%):C, 83.95; H, 8.97.

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