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PAPER

A flexible, unified radical-based approach to polycyclic structures†‡

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Cis- and *trans*-decalins, *trans*-perhydroazulenes, and [5.3.1]-bicyclo-undecanone scaffolds can be readily constructed starting from unsaturated ketones and using the degenerative xanthate transfer technology to accomplish unusual and otherwise difficult radical cyclisations.

Introduction

Terpenes exhibit an astonishing diversity of structures. The intricate polycyclic carbon framework decorated with various oxygen-based functional groups found in many members of this large family of natural products has attracted much attention from synthetic organic chemists.[1] Some examples are displayed in Fig. 1. Essentially all the techniques for ring construction have been employed in the course of these synthetic endeavours. While the advent of efficient and practical metathesis catalysts has all but solved most of the difficulties associated with the formation of rings of nearly all sizes,[2] it still seemed worthwhile exploring other routes to polycyclic scaffolds containing six-, seven-, and eight-membered rings, since these arrangements are quite frequent in terpenes. The possibility of introducing different substitution patterns in comparison with previous approaches could in some cases simplify the synthetic planning.

Radical reactions have had a strong impact on the synthesis of terpenes, especially as regards the formation of five-membered rings. In this respect, the spectacular and pioneering synthesis of hirsutene, a linear triquinane, by Curran and co-workers,[3] may be considered as an important milestone. The efficiency of radical-based methods for the formation of polyquinanes and other terpenes containing cyclopentane motifs derives from the fast rate of the 5-*exo* ring closure, allowing the cyclisation step, under judicious experimental conditions, to compete successfully with premature capture of the uncyclised radical.

This can be seen in Scheme 1 for the case of the now classical stannane mediated processes.[4] In the case of the parent 5-hexen-1-yl radical **1**, the 5-*exo* ring closure leading to **3** is sufficiently rapid to overtake undesired bimolecular reduction by the stannane to give **2**, as long as medium is dilute or the stannane is added slowly, either drop-wise or by the use of a syringe pump, so as to keep its concentration low. Furthermore, the 5-*exo* cyclisation is fifty times faster than the corresponding 6-*endo* cyclisation, so that competition from the latter mode is generally minimal. In contrast, the formation of a 6-membered ring **6** (n = 1) from **4** (n = 1) by a 6-*exo* closure is hampered by the intrinsically sluggish rate of cyclisation favouring premature reduction to give **5** (n = 1), and by a serious competition both from the 7-*endo* mode leading to **7** (n = 1) and from an allylic hydrogen abstraction leading to **8** (n = 1).[5] Clearly, access to six-membered rings by either a 6-*endo*

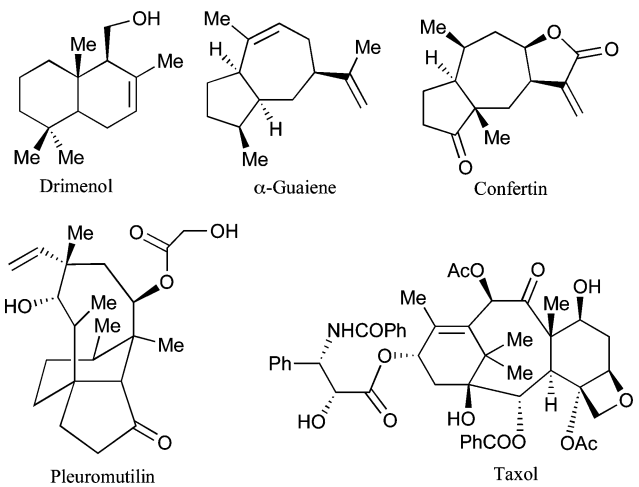
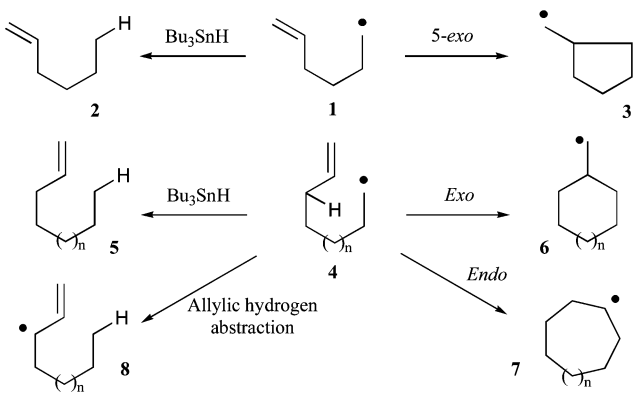


Fig. 1 Examples of polycyclic terpenes.



Scheme 1 General outline of radical cyclisations.

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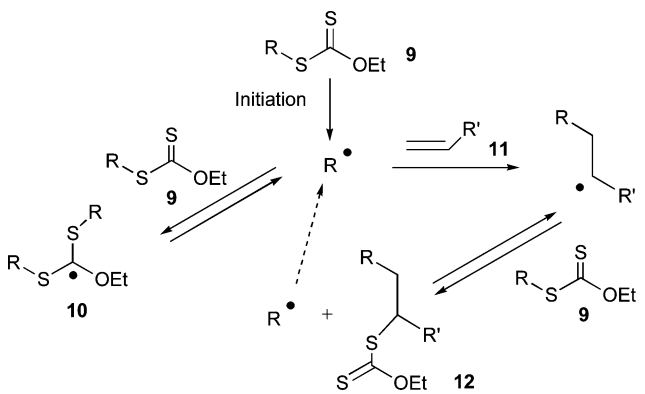
‡ This paper is dedicated with respect to the memory of our dear friend, Professor Athel L. J. Beckwith.

or a 6-*exo* radical ring closure is a much more risky strategy. The situation for the construction of seven-membered and especially eight-membered rings (**6**, **7**, n = 2, 3) is even more difficult and problematic. Consequently, successful examples in this category are far less frequent.[5,6]

We now report what appears to be a reasonably general approach to polycyclic structures featuring the direct formation of six-, seven-, and eight-membered rings. It hinges on providing the radical with sufficient lifetime to undergo slow cyclisation processes and on using stabilised acetonyl radicals to limit the untoward competing allylic hydrogen abstraction.

Results and discussion

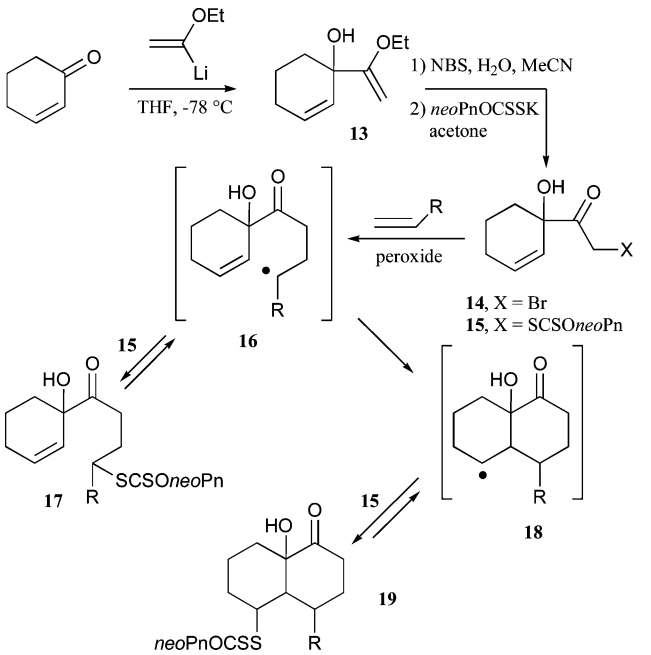
We have developed over the past years the reversible addition-fragmentation-transfer of xanthates and related derivatives.[7] In this system, depicted in simplified form in Scheme 2, the reaction of radicals R$^{\bullet}$ with their xanthate precursor **9** is a degenerate process that not only does not consume radicals R$^{\bullet}$, but the adducts, **10**, are rather un-reactive species and act as a convenient reservoir for radicals R$^{\bullet}$. This eliminates a major competing pathway and provides the radicals with a much longer effective lifetime, even under concentrated conditions. This is in stark contrast to most other radical methods, and especially those based on triorganotin hydrides. It becomes now possible to contemplate accomplishing more difficult radical transformations, such as an *intermolecular* addition to an un-activated alkene **11** to give a new xanthate **12**, as shown on Scheme 2.



Scheme 2 Simplified mechanism for the xanthate transfer process.

Formation of six-membered rings

For our first approach to decalin structures, we exploited this property and considered the general route outlined in Scheme 3. Thus, starting from a cyclohexenone, addition of 1-ethoxy-vinyllithium would give enol ether **13**, which should be easily brominated to afford bromoketone **14**. Displacement of the bromine with readily available sodium *O*-neopentyl xanthate would lead to the required precursor **15**, which, hopefully, would undergo the desired *exo* cyclisation to give decalin **19**. The choice of the *O*-neopentyl xanthate over the more ubiquitous *O*-ethyl derivative was dictated by its simpler NMR signature and consequently easier determination of isomeric ratios. The advantages of this strategy are numerous: (a) It is highly flexible and convergent, and diversity can be easily introduced by simply modifying the alkene partner or

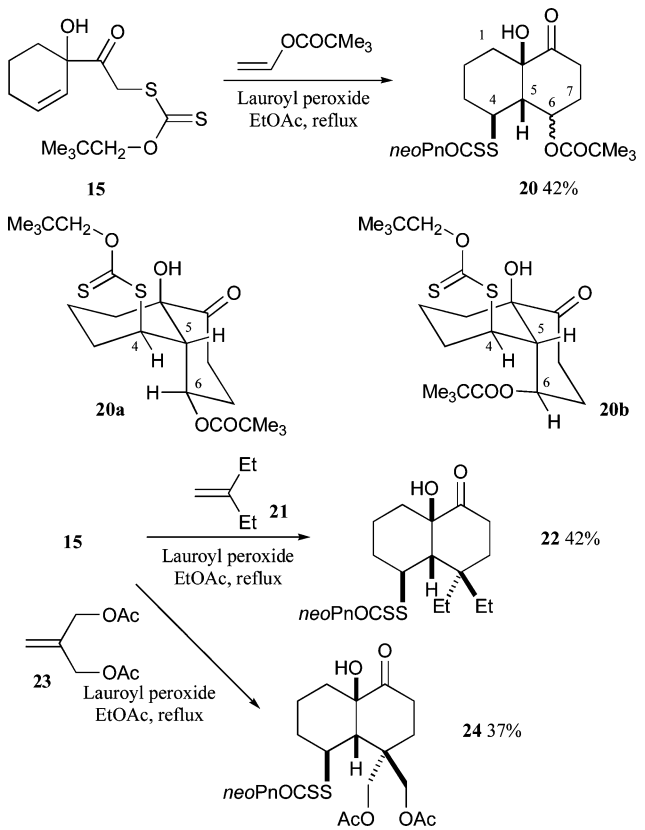


Scheme 3 A convergent access to decalins.

eventually the substituents on the cyclohexenone ring (including its size). (b) In the likely event the intermediate adduct radical **16** reacts faster with the xanthate precursor **15** than undergo the desired cyclisation, this will be of no consequence, since the xanthate exchange process is reversible and it is always possible to go back to radical **16** under conditions more propitious for ring closure. (c) There are no readily accessible allylic hydrogens that can cause radical translocation, and competition from a 7-*endo* pathway is very unlikely because of the unacceptable strain in attaining the transition state. (d) The presence of the xanthate in the final product is a very valuable synthetic asset, since it can be modified in almost infinite ways through the exceedingly rich chemistry of sulfur-based functional groups.[8] (e) Finally, no heavy metals are involved, and the reagents and starting materials are readily available.

The synthesis of xanthate **15** could be accomplished readily in 79% overall yield from 2-cyclohexenone. Its addition to vinyl pivalate and concomitant cyclisation proceeded reasonably efficiently, considering the number of discrete steps involved, to give adduct **20** as a mixture of epimers **20a** and **20b** (85 : 15) in 42% yield (Scheme 4). Both had the *cis*-decalin framework and differed only in the stereochemistry of the carbon bearing the pivaloyloxy group. The *cis*-junction could be ascertained from the small coupling constant of the hydrogen atom at the junction with that on the carbon bearing the xanthate group, indicating an equatorial disposition for both. The formation of a *cis*-decalin is in line with earlier observations.[9] NMR analysis also indicated that in the major product, the pivaloyloxy group occupies an *exo*-equatorial position, and in both compounds the xanthate group stood in what appears to be the less hindered *exo*-axial position. In an equatorial orientation, the bulky *O*-neopentyl xanthate would come into conflict with the axial substituent (hydrogen or pivalate) on the adjacent ring on C-6 (Scheme 4).

By using a symmetrical 1,1-disubstituted alkenes **21** and **23** as the olefinic trap, only one isomer of the corresponding cyclised

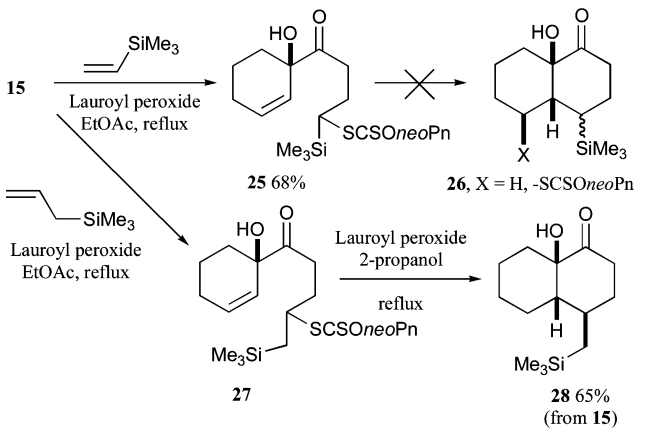


Scheme 4 Examples of *cis*-decalin syntheses.

products **22** and **24** were observed, albeit in modest yields. This nevertheless simplified parts of the NMR spectra and allowed us to confirm that the xanthate group occupies the axial position and that the ring junction is indeed of the *cis*-type. For convenience, the liquid 2-ethyl-butene **21** was used instead of the more volatile but more interesting isobutene, which would have required the use of pressure resistant sealed tubes. Isobutene would have furnished decalins with a *geminal* dimethyl motifs frequently found in terpenes.[1]

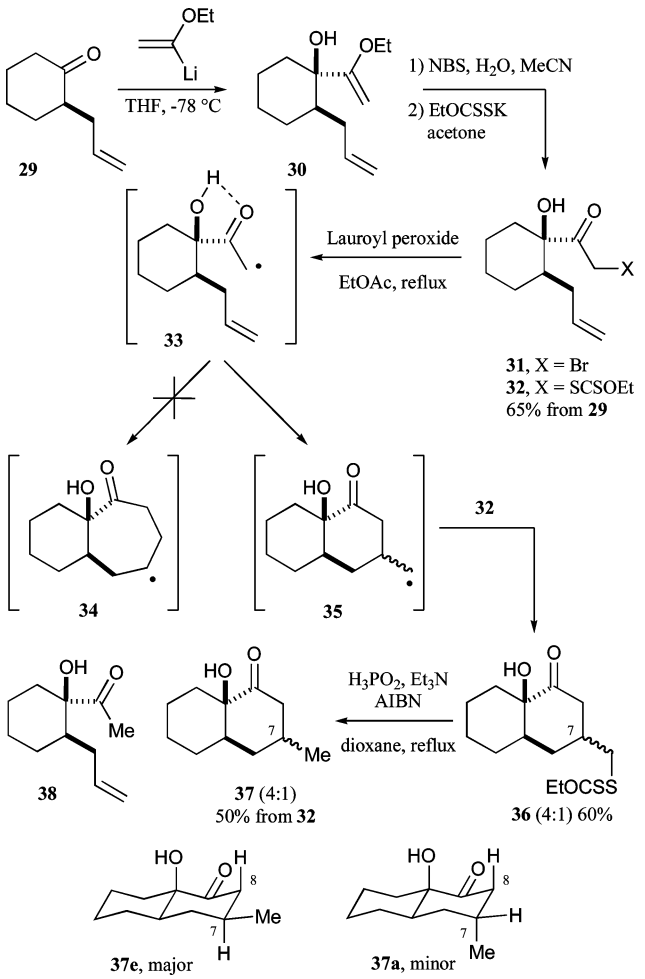
No attempts were made to improve the yields, but it is nonetheless noteworthy that quaternary centres could be so easily introduced. The limits of this strategy were however uncovered when the addition-cyclisation was attempted using trimethyl vinylsilane as the olefinic component (Scheme 5). While the first addition proceeded efficiently to give the expected adduct **25** in 68% yield, no conditions could be found to induce a clean ring-closure into **26**, either with transfer of the xanthate group or with concomitant reduction. This is in contrast to the sequence involving the homologous allyl trimethylsilane, where addition and reductive cyclisation could be accomplished in an overall yield of 65% by treatment of the crude product **27** from the addition step with a stoichiometric amount of peroxide in refluxing 2-propanol.[10]

Another limitation of the present approach is the difficulty in introducing a substituent in position-7. With a few notable exceptions, 1,2-substituted alkenes tend to be poor partners in *intermolecular* radical additions. The placement of a substituent on position-7 has therefore to be done at a later stage. An alternative



Scheme 5 Silicon substituted *cis*-decalins.

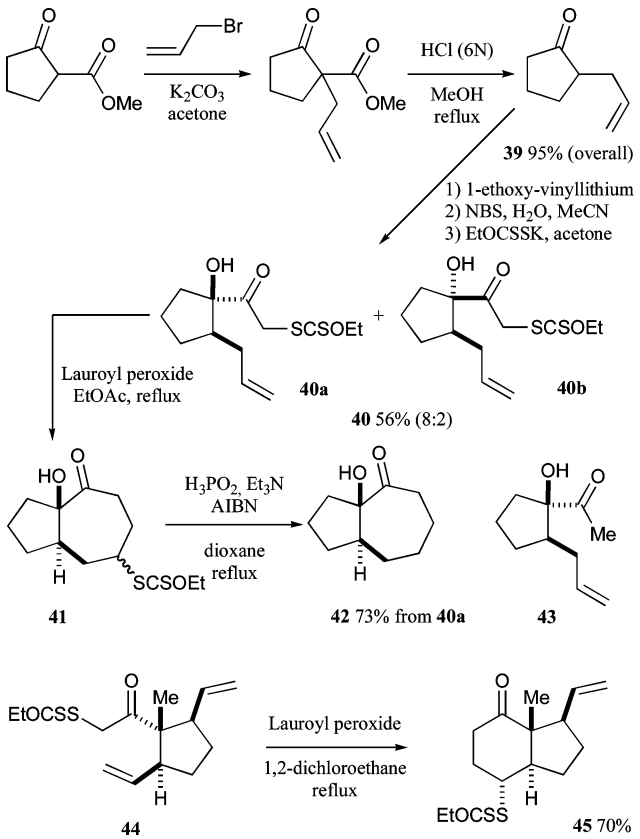
strategy is to modify the structure of the starting material and to rely on an *intramolecular* process, as pictured in Scheme 6.



Scheme 6 Synthesis of *trans*-decalins.

Addition of 1-ethoxy-vinyllithium to 2-allylcyclohexanone **29** took place from the least hindered side to give the *cis*-alcohol **30**. Bromination furnished bromoketone **31** and displacement with potassium *O*-ethyl xanthate provided the desired precursor **32** in 65% overall yield. Because of the relative *trans*-disposition of the allyl side-chain and the radical bearing acetyl unit, as well

as the existence of a somewhat rigidifying hydrogen bonding between the hydroxy and ketone groups, it was not obvious from the outset if the ring closure of radical **33** would proceed by a 7-*endo* mode to **34** or by a 6-*exo* route to **35**, or both. In the event, only the 6-*exo*-derived product **36** was observed upon exposure of xanthate **32** to the action of the peroxide. It was obtained in 60% yield as a 4 : 1 mixture of epimers. The relative configuration was established by repeating the lauroyl mediated cyclisation of xanthate **32** and reducing the crude product with triethylammonium hypophosphite to give the same 4 : 1 ratio of methyldecalinone **37** in 54% overall yield (Scheme 6).[11] Examination of the NMR spectra revealed for the major epimer a large 12–13 Hz coupling constant between the hydrogen on C-7 and the axial H on C-8, indicating an *axial* disposition for the former. The methyl group must therefore be *equatorial*, as in **37e**. For the minor epimer, a 6–7 Hz coupling constant was observed between the hydrogen on C-7 and the axial H on C-8, indicating an *equatorial* disposition for the former, as in **37a**. Interestingly, when xanthate **32** was exposed to triethylammonium hypophosphite and AIBN in refluxing dioxane, the cyclised-reduced material **37** was obtained directly in 50% yield along with reduced, but uncyclised product **38** (observed by NMR but not quantified). The yield of compound **37** was higher (66%) when the slower reducing combination of 2-propanol and stoichiometric amounts of lauroyl peroxide was used for the simultaneous cyclisation and reductive dexanthylation.



Scheme 7 Synthesis of a perhydroazulene.

Formation of seven-membered rings

In the light of these observations, it became interesting to see if a *trans*-hydrindane could be made by the same approach. To this end, 2-allylcyclopentanone **39** was prepared from 2-methoxycarbonyl-cyclopentanone, as shown in Scheme 7, and subjected to the usual sequence leading to xanthate **40a,b** in 56% overall yield without purification of the intermediates. In this case, the addition of the 1-ethoxy-vinyllithium did not proceed with high stereoselectivity and significant amounts of the *trans*-isomer **40b** were observed. Exposure of xanthate **40a** to lauroyl peroxide in refluxing ethyl acetate did not afford any hydrindane product but gave instead perhydroazulenone **41**, which, without purification, was reduced with hypophosphite into ketone **42** in 73% overall yield. In this system, clearly, the 7-*endo* ring-closure mode is favoured over the 6-*exo* pathway. The perhydroazulene system is a central architecture in numerous terpene families: guainolides, pseudoguainolides, carotanes, aromadendranes, *etc.*, with hundreds of members (*e.g.* α-guaiene and confertin in Fig. 1). The present approach to this motif is straightforward and very concise.

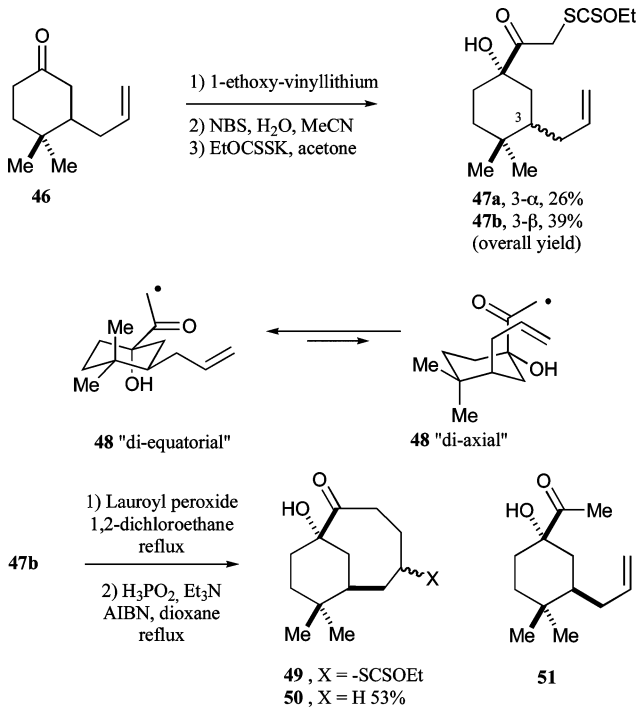
In order to have a feel for the rate of the 7-*endo* cyclisation, we subjected xanthate **40a** to the action of triethylammonium hypophosphite. Under these conditions, a 1 : 2 mixture of perhydroazulenone **42** and reduced but uncyclised material **43** was obtained in 95% combined yield. By using the slower reducing 2-propanol/lauroyl peroxide, an improved ratio of 1 : 1 of **42**:**43** was produced in equally good combined yield (87%). The application of the xanthate transfer process prior to performing the reduction is clearly a superior tactic, for it ensures that little or no premature reduction takes place. This example highlights the unique and decisive advantages of the xanthate technology when dealing with sluggish radical transformations, such as the 7-*endo* cyclisation.

As our study was in progress, Ollivier, Santelli, and their co-workers reported the 6-*endo* cyclisation of xanthate **44** into *trans*-hydrindane **45** in good yield, as part of their synthetic work on steroids.[12] This gratifying result clearly demonstrates that the same strategy may be employed to access both hydrindanes and perhydroazulenes.

B Formation of eight-membered rings

We finally considered the more difficult case of constructing eight-membered rings, which are also common in terpenes (*e.g.* basmanes, taxanes, fusicoccanes *etc.*). In a model study, we had found that it was possible using the xanthate transfer to form the eight-membered ring present in pleuromutilin (Fig. 1),[13] but we had built on a fairly rigid template, which made the ring-closure easier. It was not therefore obvious that success could be attained on a more flexible framework, such as **47b**, prepared in the usual manner from well-known ketone **46**. The directing effect of the allyl group was less effective in this case, and an almost equal yield of epimers **47a** and **47b** were obtained from the ionic sequence (Scheme 8).

Radical **48** derived from xanthate **47b** exists mostly in the chair conformation, where the two bulkiest substituents are in the less congested equatorial orientation. In this disposition, the radical is too far from the alkene and cannot undergo the desired addition. For cyclisation to occur, the radical has to adopt the less stable conformation with the reacting partners in a 1,3-diaxial



Scheme 8 Example of an 8-*endo* cyclisation.

arrangement that is propitious for interaction, but also more crowded (Scheme 8). This adds a further constraint to an already sluggish transformation. We were therefore relieved to find that despite the unfavourable equilibrium, the ring closure did take place in acceptable yield. Thus treatment of **47b** with lauroyl peroxide followed by reductive dexanthylation with hypophosphite afforded [5.3.1]-bicyclo-undecanone **50** in 53% overall yield. It is interesting to note that direct reductive cyclisation using 2-propanol/lauroyl peroxide furnished only a small yield (24%) of bicylic ketone **50**; the major product was methyl ketone 51 (63%) arising from premature hydrogen atom abstraction by radical **48**. This illustrates another instance where proceeding by way of the xanthate transfer product, **49** in this case, circumvents premature reduction and allows the desired radical cyclisation to take place satisfactorily.

Conclusions

This preliminary study provides the outlines of what appears to be a very powerful, yet concise and highly flexible, approach to both fused and bridged polycyclic structures, with various combinations of five-, six-, seven-, and eight-membered rings. The relatively long lifetime of radicals generated through the degenerative xanthate transfer process provides a convenient and experimentally very practical method for overcoming the limitations imposed by intrinsically slow radical transformations, and opens thus numerous synthetic opportunities. In the examples shown, the xanthate group was reductively removed to simplify characterisation, but its presence in the cyclised product, in addition to the very useful vicinal hydroxy-ketone moiety, constitutes a tremendous springboard for the introduction of further substituents and functional groups.

Experimental

General details

Anhydrous THF was obtained by distillation from sodium-benzophenone under nitrogen. Infrared spectra were recorded as solutions in CCl_4 using CaF_2 cells, on a Perkin–Elmer FT 1600. Absorption maxima (vmax) are reported in wavenumbers (cm^1) and only selected peaks are reported. Magnetic resonance spectra were recorded at ambient temperature on a Bruker AMX 400 instrument. Proton magnetic resonance spectra (^{1}H NMR) were recorded at 400 MHz and coupling constants (*J*) are reported to ± 0.5 Hz. Carbon magnetic resonance spectra (^{13}C NMR) were recorded at 100.6 MHz. Chemical shifts (δ_H, δ_C) are quoted in parts per million (ppm) and are referenced to the residual solvent peak. High-resolution mass spectra were recorded by positive electron impact ionization (EI +) at 70 eV on a JEOL JMS-GCmate II mass spectrometer. The quoted masses are accurate to ± 5 ppm.

General procedure A for the synthesis of the xanthates

To a stirred solution of ethyl vinyl ether (5 n mmol) in freshly distilled THF (2 n ml) under nitrogen and at – 78 °C, was added drop-wise over 10 min *tert*-butyl lithium (~1.35 M in pentane, 2 n mmol). After 15 more minutes, the acetone/dry ice bath was replaced by a water/ice bath, and stirring was kept for 15 min. The flask was cooled back to – 78 °C, and a solution of the cycloalkanone (n mmol) in distilled THF (2 n ml) was added drop-wise over 10 min. The mixture was allowed to warm up to room temperature, and stirred for an additional 2 h. Saturated ammonium chloride and diethyl ether were added to quench the reaction. The aqueous layer was then extracted with diethyl ether, and the combined organic layers were washed with brine, dried, and then concentrated under reduced pressure, yielding pure ethyl vinyl ether adduct.

The ethyl vinyl ether adduct (n mmol) was then dissolved in a mixture of acetonitrile/water (9 : 1) (2 n mL) under nitrogen in an ice water bath, and a solution of *N*-bromosuccinimide (1.1 n mmol) in acetonitrile/water (9 : 1) (2 n mL) was then added. Stirring was kept for 20 more minutes, and the mixture was then partitioned between diethyl ether and water. The organic layer was then washed with brine, and dried over anhydrous $MgSO_4$. Filtration and removal of the solvent under reduced pressure, gave the α-bromoketone.

The crude bromoketone (n mmol) was then stirred in acetone (1.5 n mL) under nitrogen at 0 °C, and sodium *O*-neopentyl xanthate or potassium *O*-ethyl xanthate (1.2 n mmol) was then added. After one hour at 0 °C, the mixture was partitioned between diethyl ether and water. Brine was added to the aqueous layer, which was then extracted twice with diethyl ether. The combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, filtered, and the solvent removed *in vacuo* to afford the crude xanthate, which was purified by chromatography.

O-(2,2-Dimethyl-propyl)-*S*-[2-(1-hydroxy-cyclohex-2-enyl)-2-oxo-ethyl] dithiocarbonate 15

Following general procedure A, the sequence was carried out using 2-cyclohexenone (1.5 mL, 15 mmol) and sodium *O*-neopentyl

xanthate. The crude xanthate was purified by column chromatography using petroleum ether/ethyl acetate (9/1) as the eluent to give pure xanthate **15** in 79% yield, δ_H (400 MHz, $CDCl_3$) 6.20 (ddd, J = 2.7 Hz, J = 4.9 Hz, J = 9.8 Hz, 1H, C*H*═CHC(OH)), 5.67 (td, J = 2.7 Hz, J = 9.8 Hz, 1H, CH═C*H*C(OSi)), 4.40 (d, J = 17.6 Hz, 1H, OCH_2), 4.31 (d, J = 17.6 Hz, 1H, OCH_2), 4.26 (s, 2H, SCH_2), 3.47 (s, 1H, O*H*), 1.9–2.3 (m, 3H), 1.7–1.9 (m, 3H), 1.02 (s, 9H, $CH_2C(CH_3)_3$); δ_C (100.6 MHz, $CDCl_3$) 213.5 (*C*═S), 205.9 (*C*═O), 134.5 (*C*H═CH), 125.7 (CH═*C*H), 84.1 (O*C*H$_2$), 76.5 (C_qOH), 41.6 (S*C*H$_2$), 33.6 ($CH_2CH_2CH_2$), 31.8 ($CH_2C(CH_3)_3$), 26.5 (C(*C*H$_3$)$_3$), 24.7, 18.0 ($CH_2CH_2CH_2$); ν_{max} (CCl_4)/cm^{-1} 3494, 1722, 1227, 1068. HRMS (EI +), Found: M$^+$, 302.1009. $C_{14}H_{22}O_3S_2$ requires M$^+$, 302.1010.

General procedure B for the intermolecular addition and cyclisation

A solution of the xanthate (n mmol) and olefin (generally 3n or 4n mmol), in ethyl acetate (n mL), was refluxed under nitrogen for 15 min. Dilauroyl peroxide (DLP) was then added in portions of 5% every 90 min, until the reaction was over. The excess olefin and the solvent were then removed *in vacuo*, giving crude adduct compound. The crude was then diluted in ethyl acetate (10n mL), and after being refluxed for 15 min under nitrogen, dilauroyl peroxide was added in portions of 5% every 90 min, until complete consumption of the starting material. Evaporation of the solvent gave the crude cyclised compound.

8-(2,2-Dimethyl-propoxythiocarbonylsulfanyl)-4a-hydroxy-4-oxo-decahydro-naphthalen-1-yl 2,2-dimethyl-propionate 20

Following general procedure B, the reaction was carried out using xanthate **15** (106 mg, 0.35 mmol), vinylpivalate (77 μL, 0.52 mmol) as the olefin, and DLP (15 mol% at first, then 30 mol%). The crude product was purified by column chromatography using toluene/diethyl ether (97.5/2.5) as eluent to give bicyclic product **20** in 42% yield (mixed with 15% of axial pivalate), δ_H (400 MHz, $CDCl_3$) 5.37 (dt, J = 4.4 Hz, J = 11.2 Hz, 1H, CH_{ax}OPiv), 4.35 (m, 1H, CH_{eq}S), 4.19–4.28 (m, 2H, OCH_2), 3.98 (s, 1H, O*H*), 2.74 (dt, J = 4.6 Hz, J = 14.9 Hz, 1H, COC$H_{(ax)2}$), 2.54 (ddd, J = 2.6 Hz, J = 6.1 Hz, J = 14.9 Hz, 1H, COC$H_{(eq)2}$), 2.25–2.42 (m, 2H), 2.0–2.15 (m, 2H), 1.88–1.98 (m, 1H), 1.78–1.88 (m, 1H), 1.62–1.72 (m, 1H), 1.27–1.30 (m, 1H), 1.25 (s, 9H, C(CH_3)$_3$), 1.00 (s, 9H, C(CH_3)$_3$); δ_C (100.6 MHz, $CDCl_3$) 217.3, 210.6 (*C*═O, *C*═S), 178.1 (*O*-*C*═O), 83.2 (O*C*H$_2$), 76.2 (*C*OH), 68.3, 52.5, 44.9 (*C*H- *C*H- *C*H), 38.9 (CO*C*(CH$_3$)$_3$), 33.7, 32.7, 30.4 (*C*H$_2$), 31.7 ($CH_2C(CH_3)_3$), 27.3 (*C*H$_2$), 26.5 ($CH_2C(CH_3)_3$), 25.8, 16.8 (*C*H$_2$); ν_{max} (CCl_4)/cm^{-1} 3482, 1725, 1215, 1067, 1150. HRMS (EI +), Found: M$^+$, 430.1851. $C_{21}H_{34}O_5S_2$ requires: M$^+$, 430.1848.

S-(8,8-Diethyl-4a-hydroxy-5-oxo-decahydronaphthalen-1-yl)-*O*-(2,2-dimethyl-propyl) dithiocarbonate 22

Following general procedure B, the reaction was carried out using xanthate **15** (302 mg, 1.0 mmol), 2-ethyl-but-1-ene (490 μL, 4.0 mmol) as the olefin, and DLP (first 25 mol%, then 15 mol%). The crude product was purified by column chromatography using petroleum ether/diethyl ether (9/1) as eluent to give bicyclic product **22** in 43% yield, δ_H (400 MHz, $CDCl_3$) 4.39 (m, 1H, SCH_{eq}), 4.24 (m, 2H, OCH_2), 3.83 (s, 1H, O*H*), 2.61 (dt, J = 4.7 Hz, J = 14.5 Hz, 1H, C(O)CH_{2ax}), 2.38 (dt, J = 14.2 Hz, J = 3.4 Hz, 1H, C(O)CH_{2eq}), 2.18 (s, 1H, SCHCH_{eq}), 1.90–2.15 (m, 3H, CH_2-CH_2-CH_2, C(Et)$_2$-CH_2), 1.75–1.90 (m, 2H, CH_2-CH_2-CH_2, C(Et)$_2$-CH_2), 1.50–1.65 (m, 4H, 2 × CH_2-CH$_3$), 1.35–1.45 (m, 1H, CH_2-CH_2-CH_2, C(Et)$_2$-CH_2), 1.17–1.32 (m, 2H, CH_2-CH_2-CH_2, C(Et)$_2$-CH_2), 1.00 (s, 9H, C(CH_3)$_3$), 0.94 (t, J = 7.4 Hz, 3H, CH$_2$CH_3), 0.76 (t, J = 7.5 Hz, 3H, CH$_2$CH_3); δ_C (100.6 MHz, $CDCl_3$) 217.1, 213.5 (*C*═O, *C*═S), 83.0 (*C*OH), 76.5 (O*C*H$_2$), 52.1 (S*C*H), 44.4 (SCH*C*H), 40.9 (*C*(Et)$_2$), 33.9, 33.6, 30.3, 29.9, 29.1, 28.0, 15.9 (*C*H$_2$*C*H$_2$C═O, *C*H$_2$*C*H$_2$*C*H$_2$, 2 × *C*H$_2$CH$_3$), 31.7 (*C*(CH$_3$)$_3$), 26.5 (C(*C*H$_3$)$_3$), 8.2, 8.0 (2 × CH$_2$*C*H$_3$); ν_{max} (CCl_4)/cm^{-1} 3485, 1714, 1208, 1069. HRMS (EI +), Found: M$^+$, 386.1957. $C_{20}H_{34}O_3S_2$ requires, M$^+$, 386.1949.

1-Acetoxymethyl-8-(2,2-dimethyl-propoxythiocar-bonylsulfanyl)-4a-hydroxy-4-oxo-decahydro-naphthalen-1-ylmethyl acetate 24

Following general procedure B, the reaction was carried out using xanthate **15** (76 mg, 0.25 mmol), acetic acid 2-acetoxymethyl-allyl ester (172 mg, 1 mmol) as the olefin, and DLP (total of 75 mol%). The crude product was purified by column chromatography using petroleum ether/ethyl acetate (7/3) as eluent to give bicyclic product **24** in 37% yield, δ_H (400 MHz, $CDCl_3$) 4.70 (d, J = 11.5 Hz, 1H, CH_2OAc), 4.64 (m, 1H, SC*H*), 4.1–4.3 (m, 5H, 2 × CH_2OAc, SC(S)OCH_2), 2.76 (dt, J = 5.1 Hz, J = 14.8 Hz, 1H, CH$_2$-CH_{2ax}), 2.4–2.5 (m, 2H, SCH-C*H*, CH$_2$-CH_{2eq}), 2.14 (s, 3H, CH_3CO), 2.05 (s, 3H, CH_3CO), 2.2 (m, 1H) + 1.7 (m, 1H) (SCHCH_2), 2.0–2.1 (m, 2H, CH_2), 1.6 (m, 1H) + 1.45 (m, 1H) (CH_2), 1.2–1.3 (m, 2H, CH_2), 1.00 (s, 9H, C(CH_3)$_3$); δ_C (100.6 MHz, $CDCl_3$) 216.6, 211.9 (*C*═O, *C*═S), 170.7, 170.5 (2 × O–*C*═O), 83.3 (O*C*H$_2$), 75.8 (*C*OH), 67.5, 63.2 (2 × O*C*H$_2$), 51.6 (SCH-*C*H), 44.3 (S*C*H), 42.3 ($C_q(CH_2OAc)_2$), 34.1, 32.8, 29.6, 28.9 (2 × *C*H$_2$-*C*H$_2$), 31.8 ($CH_2C(CH_3)_3$), 26.5 (C(*C*H$_3$)$_3$), 20.85, 20.81 (2 × *C*H$_3$CO), 15.8 (*C*H$_2$CHS); ν_{max} (CCl_4)/cm^{-1} 3480, 1749, 1718, 1223, 1069. HRMS (EI +), Found: M$^+$, 474.1761. $C_{22}H_{34}O_7S_2$ requires, M$^+$, 474.1746.

O-(2,2-Dimethyl-propyl)-*S*-[4-(1-hydroxy-cyclohex-2-enyl)-4-oxo-1-trimethylsilanyl-butyl] dithiocarbonate 25

Following the first part of general procedure B, the reaction was carried out using xanthate **15** (302 mg, 1 mmol), DLP (30 mol%), and vinyltrimethylsilane (1.5 mL, 10 mmol) as the olefin. The crude product was purified by column chromatography using petroleum ether/ethyl acetate (9/1) as eluent to give bicyclic product **25** in 68% yield as a 1 : 1 mixture of two diastereoisomers, δ_H (400 MHz, $CDCl_3$) 6.09 (ddd, J = 2.5 Hz, J = 5.2 Hz, J = 9.9 Hz, 1H, CH═C*H*-CH$_2$, isomers 1/2), 5.45 (m, J = 9.9 Hz (d), 1H, C*H*═CH-CH$_2$, isomers 1/2), 4.20–4.34 (m, 2H, SCSOCH_2, isomers 1/2), 3.91, 3.89 (s, 1H, O*H*, isomers 1/2), 3.17 (dt, J = 3.8 Hz, J = 10.9 Hz, 1H, C*H*Si, isomers 1/2), 2.65–2.80 (m, 2H, CH_2C═O, isomers 1/2), 2.10–2.20, 1.95–2.08, 1.56–1.82 (m, 8H, CH_2-CH_2-CH_2, CH_2CHSi, isomers 1/2), 1.00 (s, 9H, C(*C*H$_3$)$_3$, isomers 1/2), 0.10 (s, 9H, Si(CH_3)$_3$, isomers 1/2). δ_C (100.6 MHz, $CDCl_3$) 216.7, 213.2 (*C*═O, *C*═S, isomers 1/2), 133.6,133.5, (*C*═C, isomers 1/2), 126.13, 126.08 (*C*═C, isomers 1/2), 83.6 (O*C*H$_2$, isomers 1/2), 75.9 (*C*OH, isomers 1/2), 36.2, 36.1 (*C*HSi, isomers 1/2), 34.9, 34.7 (*C*H$_2$C═O, isomers 1/2), 33.4, 33.3 (*C*H$_2$, isomers 1/2), 31.9 (*C*(CH$_3$)$_3$, isomers 1/2), 26.5 (C(*C*H$_3$)$_3$, isomers 1/2), 24.8, 24.9 (*C*H$_2$, isomers 1/2), 24.70, 24.69 (*C*H$_2$, isomers 1/2), 18.1 (*C*H$_2$, isomers 1/2), – 2.70, – 2.73 (Si(*C*H$_3$)$_3$), isomers 1/2); IR

ν_{max} (CCl_4)/cm^{-1} 3479, 1708, 1213, 1067. HRMS (EI +), Found: M^+, 402.1719. $C_{19}H_{34}O_3S_2Si$ requires: M^+, 402.1719.

General procedure C for the reductive cyclisation in isopropanol

A solution of the xanthate (n mmol) in isopropanol (10 n ml) was refluxed under nitrogen for 15 min. Dilauroyl peroxide was then added in portion of 20% every 60 min, until the reaction was complete. The solvent was then removed *in vacuo*, giving the crude cyclic compound.

8a-Hydroxy-4-trimethylsilanylmethyl-octahydronaphthalen-1-one 28

Following the first part of general procedure B, the addition reaction was carried out using xanthate **15** (135 mg, 0.45 mmol), allyltrimethylsilane (572 μL, 3.6 mmol) as the olefin, and DLP (15 mol%), giving crude adduct **27**. Without purification, this adduct was then transformed following general procedure C. The crude product was purified by column chromatography using petroleum ether/ethyl acetate (97.5/2.5) as eluent to give bicyclic product **22** in 65% overall yield, δ_H (400 MHz, $CDCl_3$) 3.93 (s, 1H, OH), 2.66 (dt, J = 6.0 Hz, J = 14.4 Hz, 1H, CH_2C═O), 2.43 (ddd, J = 2.4 Hz, J = 4.2 Hz, J = 14.1 Hz, 1H, CH_2C═O), 2.13–2.20 (m, 1H, CH_2), 2.06–2.13 (m, 1H, CHCH$_2$Si), 1.90 (dt, J = 4.4 Hz, J = 13.0 Hz, 1H, CH_2C(OH)), 1.57–1.84 (m, 4H, 2 × CH_2), 1.46–1.54 (m, 1H, CH_2), 1.40–1.44 (m, 1H, CHC(OH)), 1.34–1.40 (m, 1H, CH_2), 1.25–1.34 (m, 2H, CH_2), 0.91 (dd, J = 2.6 Hz, J = 14.9 Hz, 1H, CH_2Si), 0.23 (dd, J = 10.2 Hz, J = 14.9 Hz, 1H, CH_2Si), 0.06 (s, 9H, Si(CH_3)$_3$); δ_C (100.6 MHz, $CDCl_3$) 214.3 (C═O), 77.7 (C-OH), 52.0 (CH-COH), 37.1, 35.2, 32.2 (3 × CH$_2$), 32.0 (CHCH$_2$Si), 22.6, 21.2, 20.4, 19.7 (4 × CH$_2$), − 0.45 (Si(CH$_3$)$_3$); ν_{max} (CCl_4)/cm^{-1} 3486, 1711. HRMS (EI +), Found: M^+, 254.1706. $C_{14}H_{26}O_2Si$ requires: M^+, 254.1702.

***S*-[2-(2-allyl-1-hydroxy-cyclohexyl)-2-oxo-ethyl]-*O*-ethyl Dithiocarbonate 32**

Following general procedure A for the formation of xanthate, the reaction was carried out using 2-allyl-cyclohexanone (1.38 g, 10 mmol), and potassium *O*-ethyl xanthate, to give crude xanthate **32**. This compound was purified by column chromatography using petroleum ether/diethyl ether (9/1) as eluent to give pure xanthate **32** in 65% overall yield, δ_H (400 MHz, $CDCl_3$) 5.71 (m, 1H, CH═CH$_2$), 4.97–5.01 (m, 2H, CH═CH_2), 4.65 (q, J = 7.1 Hz, 2H, OCH_2CH$_3$), 4.41 (d, J = 17.7 Hz, 1H, SCH_2), 4.33 (d, J = 17.7 Hz, 1H, SCH_2), 3.21 (s, 1H, OH), 1.85–1.95, 1.62–1.82, 1.28–1.36 (m, 11H, CH_2-CH_2-CH_2-CH_2-CH-CH_2), 1.42 (t, J = 7.1 Hz, 3H, CH$_2$CH_3); δ_C (100.6 MHz, $CDCl_3$) 213.3 (C═S), 207.6 (C═O), 136.3 (CH═CH$_2$), 116.8 (CH═CH_2), 81.5 (COH), 70.8 (OCH_2), 42.3 (SCH_2), 42.1 (CH-COH), 36.3, 35.5, 26.7, 25.4, 20.7 (5 × CH_2), 13.7 (CH$_2$CH3); ν_{max} (CCl_4)/cm^{-1} 3490, 1717, 1229, 1054. HRMS (EI +), Found: M^+, 302.1001. $C_{14}H_{22}O_3S_2$ requires: M^+, 302.1011.

General procedure D for the radical cyclisation

A solution of xanthate (n mmol) in ethyl acetate (10 n ml) was refluxed under nitrogen for 15 min. Dilauroyl peroxide was then added in portions of 5 mol% every 90 min, until the reaction was complete. The solvent was then removed *in vacuo*, giving crude cyclic compound.

***O*-Ethyl-*S*-(4a-hydroxy-4-oxo-decahydro-naphthalen-2-ylmethyl) dithiocarbonate 36**

Following general procedure D, the reaction was carried out using xanthate **32** (150 mg, 0.5 mmol), and DLP (15 mol%), to give crude cyclic compound **36**. This crude material was purified by column chromatography using petroleum ether/diethyl ether (8/2) as eluent to give bicyclic product **36** in 60% overall yield as a 4 : 1 mixture of two diastereoisomers, δ_H (400 MHz, $CDCl_3$) 4.63 (q, J = 7.1 Hz, 1H, OCH_2, *isomers 1*/2), 3.29 (dd, J = 6.7 Hz, J = 13.4 Hz, 1H, COCH_{ax}, *isomer 2*), 3.14 (d, J = 6.6 Hz, 2H, CH_2S, *isomer 1*), 3.06 (dd, J = 1.3 Hz, J = 7.8 Hz, 2H, CH_2S, *isomer 2*), 2.8 (t, J = 12.9 Hz, 1H, COCH_{ax}, *isomer 1*), 2.47–2.56 (m, 1H, COCH_{eq}, *isomer 2*), 2.32–2.39 (m, 1H, COCH_{eq}, *isomer 1*), 1.92–2.22 (m, 2H, OH, CHCH$_2$CH(CH$_2$)$_4$, *isomers 1*/2), 1.43–1.74 (m, 10H, CHCH$_2$CH(CH$_2$)$_4$, *isomers 1*/2), 1.40 (t, J = 7.1 Hz, 3H, OCH$_2$CH_3,*isomers 1*/2), 1.16–1.26 (m, 1H, CHCH$_2$CH(CH$_2$)$_4$, *isomers 1*/2); δ_C (100.6 MHz, $CDCl_3$) 214.3, 211.3 (C═O, C═S), 76.0 (COH, *isomer 2*), 65.2 (COH, *isomer 1*), 70.1 (OCH$_2$, *isomers 1*/2), 44.6 (CHCOH, *isomer 1*), 42.7 (COCH$_2$CHCH$_2$, *isomer 1*), 41.8 (COCH$_2$CHCH$_2$, *isomer 1*), 41.2 (COCH$_2$CHCH$_2$, *isomer 2*), 41.1 (CHCOH, *isomer 2*), 38.9 (COCH$_2$CHCH$_2$, *isomer 2*), 37.9 (CHCH$_2$S, *isomer 1*), 35.4 (CHCH$_2$S, *isomer 2*), 33.0 ((CH$_2$)$_4$CHCH$_2$, *isomer 1*), 31.03 ((CH$_2$)$_4$CHCH$_2$, *isomer 1*), 30.97 ((CH$_2$)$_4$CHCH$_2$, *isomer 2*), 30.4 ((CH$_2$)$_4$CHCH$_2$, *isomer 2*), 27.22 ((CH$_2$)$_4$CHCH$_2$, *isomer 1*), 27.18 ((CH$_2$)$_4$CHCH$_2$, *isomer 2*), 25.35 ((CH$_2$)$_4$CHCH$_2$, *isomers 1*/2), 20.8 ((CH$_2$)$_4$CHCH$_2$, *isomers 1*/2), 13.7 (OCH$_2$$CH_3$, *isomers 1*/2); ν_{max} (CCl_4)/cm^{-1} 3603, 1720, 1220, 1051. HRMS (EI +), Found: M^+, 302.1022. $C_{14}H_{22}O_3S_2$requires: M^+, 302.1011,.

8a-Hydroxy-3-methyl-octahydro-naphthalen-1-one 37e and 37a

Following general procedure C for the reductive intramolecular cyclisation in isopropanol, the reaction was carried out using xanthate **32** (90 mg, 0.30 mmol). This crude material was purified by column chromatography using petroleum ether/diethyl ether (85/15) as eluent to give epimers **37e** and **37a**.

Epimer **37e** (53% yield), δ_H (400 MHz, $CDCl_3$) 2.77 (t, J = 12.8 Hz, 1H, C$H_{2(ax)}$C═O), 2.23 (ddd, J = 1.6 Hz, J = 4.1 Hz, J = 12.7 Hz, 1H, C$H_{2(eq)}$C═O), 1.4–1.9, 1.24 (m, 13H), 1.01 (d, J = 6.5 Hz, 3H, CH_3); δ_C (100.6 MHz, $CDCl_3$) 212.4 (C═O), 75.3 (C-OH), 45.7 (CH$_2$), 45.3 (CH-COH), 36.0 (CH$_2$), 34.1 (CH-CH$_3$), 31.2, 27.4, 25.5 (3 × CH$_2$), 22.3 (CH$_3$), 20.9 (CH$_2$); ν_{max} (CCl_4)/cm^{-1} 3604, 1719. HRMS (EI +), Found: M^+, 182.1315. $C_{11}H_{18}O_2$ requires: M^+, 182.1307.

Epimer **37a** (13% yield), δ_H (400 MHz, $CDCl_3$) 3.27 (dd, J = 6.5 Hz, J = 12.8 Hz, 1H, C$H_{2(ax)}$C═O), 2.34–2.45 (m, 2H), 1.96–2.04 (m, 2H), 1.35–1.75 (m, 8H), 1.15–1.35 (m, 2H), 0.97 (d, J = 7.3 Hz, 3H, CH_3); δ_C (100.6 MHz, $CDCl_3$) 77.2 (C-OH), 43.7 (CH$_2$), 40.8 (CH-COH), 33.3, 31.2 (2 × CH$_2$), 30.5 (CH-CH$_3$), 27.4, 25.5, 21.0 (3 × CH$_2$), 19.3 (CH$_3$); ν_{max} (CCl_4)/cm^{-1} 3604, 1719. HRMS (EI +), Found: M^+, 182.1315. $C_{11}H_{18}O_2$requires: M^+, 182.1307.

2-Allylcyclopentanone 39

Methyl-2-oxocyclopentane carboxylate (2.6 mL, 20 mmol), was stirred in acetone (50 mL) with dry potassium carbonate (11 g, 80 mmol) and allyl bromide (9 mL, 100 mmol). The mixture was

heated under reflux for 4 h. After filtration of the excess of salt, water was added, and the mixture was extracted several times with ethyl acetate. The organic layers were then washed with water, brine, dried, and the solvent was removed under reduced pressure, giving allylated cyclopentanone of sufficient purity for the next step. This material was heated under reflux for 150 min in methanol (48 mL) with a solution of hydrochloric acid (6N; 24 mL). Once the reaction was complete, the mixture was partitioned between diethyl ether and water. The organic layer was then washed with water and brine, dried over anhydrous magnesium sulfate, and the solvent removed under reduced pressure, giving previously described,[14] pure 2-allylcyclopentanone **39** in 95% yield.

S-[2-(2-allyl-1-hydroxy-cyclopentyl)-2-oxo-ethyl]-*O*-ethyl dithiocarbonate 40a and 40b

Following general procedure A, the reaction was carried out using cyclopentanone **39** (980 mg, 5 mmol), potassium *O*-ethyl xanthate and NCS (instead of NBS), to give crude xanthate **40**. This compound was purified by column chromatography using petroleum ether/diethyl ether (9/1) as eluent to give pure xanthates **40a** and **40b**.

Xanthate **40a** (45% yield), δ_H (400 MHz, $CDCl_3$) 5.69 (tdd, J = 7.1 Hz, J = 10.1 Hz, J = 17.2 Hz, 1H, C*H*═CH_2), 5.02 (dd, J = 1.5 Hz, J = 17.1 Hz, 1H, CH═C$H_{(cis)2}$), 4.94 (dd, J = 1.1 Hz, J = 10.1 Hz, 1H, CH═C$H_{(trans)2}$), 4.63 (q, J = 7.1 Hz, 2H, OCH_2CH$_3$), 4.31 (s, 2H, SCH_2), 3.02 (s, 1H, O*H*), 2.35 (ddd, J = 7.6 Hz, J = 11.0 Hz, J = 14. 6 Hz, 1H), 2.12–2.26 (m, 1H), 2.05–2.15 (m, 2H), 1.87–2.05 (m, 2H), 1.67–1.86 (m, 2H), 1.50–1.62 (m, 1H), 1.41 (t, J = 7.1 Hz, 3H, CH$_2$CH_3); δ_C (100.6 MHz, $CDCl_3$) 213.3 (*C*═S), 207.1 (*C*═O), 136.8 (*C*H═CH_2), 116.2 (CH═*C*H$_2$), 88.0 (*C*OH), 70.8 (O*C*H$_2$), 48.6 (*C*HC(OH)), 41.9 (S*C*H$_2$), 39.8, 33.1, 30.4, 22.7 (4 × *C*H$_2$), 13.7 (CH$_2$*C*H3); ν_{max} (CCl_4)/cm^{-1} 3504, 1714, 1227, 1052. HRMS (EI +), Found: M$^+$, 288.0854. $C_{13}H_{20}O_3S_2$requires: M$^+$, 288.0854.

Xanthate **40b** (11% yield), δ_H (400 MHz, $CDCl_3$) 5.71 (tdd, J = 6.7 Hz, J = 10.2 Hz, J = 17.0 Hz, 1H, C*H*═CH_2), 4.95–5.04 (m, 2H, CH═CH_2), 4.63 (q, J = 7.1 Hz, 2H, OCH_2CH$_3$), 4.51 (d, J = 17.6 Hz, 1H, SCH_2), 4.23 (d, J = 17.6 Hz, 1H, SCH_2), 2.7–3.0, (1H, O*H*), 2.2–2.3 (m, 1H), 1.97–2.17 (m, 3H), 1.72–1.90 (m, 4H), 1.47–1.60 (m, 1H), 1.40 (t, J = 7.1 Hz, 3H, CH$_2$CH_3); δ_C (100.6 MHz, $CDCl_3$) 213.7 (*C*═S), 206.9 (*C*═O), 136.7 (*C*H═CH_2), 116.3 (CH═*C*H$_2$), 89.5 (*C*OH), 70.7 (O*C*H$_2$), 52.2 (*C*HC(OH)), 44.0 (S*C*H$_2$), 38.5, 34.5, 30.5, 21.7 (4 × *C*H$_2$), 13.7 (CH$_2$*C*H3); ν_{max} (CCl_4)/cm^{-1} 3504, 1714, 1227, 1052. HRMS (EI +),Found: M$^+$, 288.0854. $C_{13}H_{20}O_3S_2$ requires: M$^+$, 288.0854.

General procedure E for the reduction of the xanthates with H_3PO_2

A solution of the xanthate (n mmol), triethylamine (5.5 n mmol), and hypophosphorous acid (50% in water; 5 n mmol) in dioxane (12.5 n mL) was refluxed under nitrogen for 15 min. AIBN (0.15 n mmol) in dioxane (0.4 n mL) was then added to the solution, and reflux was kept for an additional one hour under nitrogen. The resulting mixture was partitioned between ethyl acetate and water. The organic layer was then washed with brine, dried over anhydrous $MgSO_4$, filtered, and the solvent was removed *in vacuo*, giving the crude reduced product.

3a-Hydroxy-octahydroazulen-4-one 42

Following general procedure D, the reaction was carried out using xanthate **40a** (58 mg, 0.2 mmol), and DLP (15 mol%), giving crude cyclic compound **41**. Without purification, this compound was reduced following general procedure E. The crude product was purified by column chromatography using petroleum ether/ethyl acetate (85/15) as eluent to give pure title compound **42** in 73% overall yield, δ_H (400 MHz, $CDCl_3$) 2.74 (td, J = 4.8 Hz, J = 14.6 Hz, 1H, COCH_2), 2.55 (m, 1H, COCH_2), 2.27 (ddd, J = 8.0 Hz, J = 10.6 Hz, J = 13.9 Hz, 1H, CH_2C-OH), 2.11 (s, 1H, O*H*), 1.5–1.9/1.20–1.36 (m, 12H); δ_C (100.6 MHz, $CDCl_3$) 214.6 (*C*═O), 87.8 (*C*-OH), 48.1 (*C*H), 41.4 (*C*H$_2$CO), 37.3, 30.8, 28.3, 27.9, 23.4, 20.8 (6 × *C*H$_2$); ν_{max} (CCl_4)/cm^{-1} 3618, 1702. HRMS (EI +),Found: M$^+$, 168.1146. $C_{10}H_{16}O_2$requires: M$^+$, 168.1150.

S-[2-(3-Allyl-1-hydroxy-4,4-dimethylcyclohexyl)-2-oxoethyl]-*O*-ethyl dithiocarbonate 47a and 47b

Following general procedure A, the reaction was carried out using 3-allyl-4,4-dimethylcyclohexanone (830 mg, 5 mmol), and potassium *O*-ethyl xanthate, to give crude xanthate **47a** and **47b** as a 3 to 2 mixture of two diastereoisomers, which could be separated by column chromatography using petroleum ether/diethyl ether (8/2) as the eluent.

Xanthate **47a**, 26% yield, δ_H (400 MHz, $CDCl_3$) 5.65–5.80 (m, 1H, C*H*═CH_2), 4.90–4.94 (m, 2H, CH═CH_2), 4.56 (q, J = 7.2 Hz, 2H, OCH_2CH$_3$), 4.31 (s, 2H, SCH_2), 3.12 (s, 1H, O*H*), 2.32 (m, 1H), 1.88 (dt, J = 4.1 Hz, J = 13.8 Hz, 1H), 1.51–1.69, 1.40–1.50 (m, 6H), 1.34 (t, J = 7.2 Hz, 3H, CH$_2$CH_3), 1.27 (td, J = 3.3 Hz, J = 13.5 Hz, 1H), 0.95 (s, 3H, C(CH_3)$_2$), 0.80 (s, 3H, C(CH_3)$_2$); δ_C (100.6 MHz, $CDCl_3$) 214.1 (*C*═S), 204.7 (*C*═O), 138.0 (*C*H═CH_2), 116.1 (CH═*C*H$_2$), 78.6 (*C*OH), 70.7 (O*C*H$_2$), 41.6 (S*C*H$_2$), 42.2 (*C*H), 36.1, 34.9 (3 × *C*H$_2$), 32.2 (*C*(CH$_3$)$_2$), 31.8 (*C*H$_2$), 29.1, 18.4 (C(*C*H$_3$)$_2$), 13.8 (CH$_2$*C*H3); ν_{max} (CCl_4)/cm^{-1} 3490, 1719, 1228, 1053. HRMS (EI +), Found: M$^+$, 330.1321. $C_{16}H_{26}O_3S_2$ requires: M$^+$, 330.1324.

Xanthate **47b**, 39% yield, δ_H (400 MHz, $CDCl_3$) 5.65–5.80 (m, 1H, C*H*═CH_2), 4.90–4.94 (m, 2H, CH═CH_2), 4.56 (q, J = 7.2 Hz, 2H, OCH_2CH$_3$), 4.40 (d, J = 17.7 Hz, 1H, SCH_2), 4.34 (d, J = 17.7 Hz, 1H, SCH_2), 3.12 (s, 1H, O*H*), 2.14 (ddd, J = 2.4 Hz, J = 3.6 Hz, J = 13.6 Hz, 1H), 2.05 (dtd, J = 2.4 Hz, J = 4.1 Hz, J = 13.3 Hz, 1H), 1.51–1.69, 1.40–1.50 (m, 6H), 1.42 (t, J = 7.1 Hz, 3H, CH$_2$CH_3), 1.27 (td, J = 3.3 Hz, J = 13.5 Hz, 1H, CH_2-CH_2/CH_2-C*H*-CH_2), 0.95 (s, 3H, C(CH_3)$_2$), 0.86 (s, 3H, C(CH_3)$_2$); δ_C (100.6 MHz, $CDCl_3$) 213.0 (*C*═S), 207.4 (*C*═O), 137.6 (*C*H═CH_2), 115.8 (CH═*C*H$_2$), 79.3 (*C*OH), 70.4 (O*C*H$_2$), 41.5 (S*C*H$_2$), 40.0 (*C*H), 35.8, 35.0, 34.3 (3 × *C*H$_2$), 32.3 (*C*(CH$_3$)$_2$), 30.1 (*C*H$_2$), 29.7, 18.2 (C(*C*H$_3$)$_2$), 13.5 (CH$_2$*C*H3); ν_{max} (CCl_4)/cm^{-1} 3490, 1719, 1228, 1053. HRMS (EI +), Found: M$^+$, 330.1321. $C_{16}H_{26}O_3S_2$ requires: M$^+$, 330.1324.

1-Hydroxy-8,8-dimethylbicyclo[5.3.1]undecan-2-one 50

Following general procedure D, the reaction was carried out using xanthate **47b** (30 mg, 0.09 mmol), and DLP (15 mol%), giving crude bicyclic xanthate **49**, which was then reduced following general procedure E into bicyclic **50**. Purification by column chromatography using petroleum ether/diethyl ether (8/2) as eluent gave compound **50** in 53% overall yield, δ_H (400 MHz,

$CDCl_3$) 3.12 (ddd, J = 3.9 Hz, J = 11.5 Hz, J = 13.7 Hz, 1H, CH_2C═O), 2.43 (td, J = 2.8 Hz, J = 14.2 Hz, 1H, CH_2C═O), 2.18–2.25 (m, 2H), 1.94–2.08 (m, 2H), 1.82–1.94 (m, 2H), 1.6–1.8 (m, 2H), 1.52–1.60 (m, 1H), 1.25–1.50 (m, 3H), 1.18–1.25 (m, 1H), 1.12 (s, 3H, CH_3), 0.84 (s, 3H, CH_3), 0.64–0.76 (m, 1H); δ_C (100.6 MHz, $CDCl_3$) 212.8 (*C*═O), 74.5 (*C*-OH), 42.4 (*C*H), 36.4 (*C*H_2), 32.6 (*C*$(CH_3)_2$), 31.8, 31.4, 31.1, 29.1 (4 × *C*H_2), 28.3 (*C*H_3), 27.4 (*C*H_2), 27.3 (*C*H_3), 24.2 (*C*H_2); ν_{max} (CCl_4)/cm^{-1} 3589, 1709. HRMS (EI +), Found: M^+, 210.1625. $C_{13}H_{22}O_2$ requires: M^+, 210.1620.

1-(3-Allyl-1-hydroxy-4,4-dimethyl-cyclohexyl)-ethanone (51)

Following general procedure C, the reaction was carried out using xanthate **47b** (100 mg, 0.3 mmol), to give **51** mixed with bicyclic compound **50**. Purification of the crude mixture by column chromatography using petroleum ether/diethyl ether (8/2) as eluent gave compound **51** in 63%, overall yield, δ_H (400 MHz, $CDCl_3$) 5.69 (dddd, J = 5.3 Hz, J = 8.4 Hz, J = 9.4 Hz, J = 13.8 Hz, C*H*═CH_2), 4.93–5.00 (m, 2H, CH═CH_2), 2.36–2.44 (m, 1H), 2.34 (t, J = 7.5 Hz, 1H), 1.88 (dt, J = 4.2 Hz, J = 13.4 Hz, 1H), 1.68–1.77 (m, 1H), 1.58–1.68 (m, 2H), 1.42–1.48 (m, 2H), 1.28–1.37 (m, 2H), 1.01 (s, 3H, CH_3), 0.87 (s, 3H, CH_3); δ_C (100.6 MHz, $CDCl_3$) 212.6 (*C*═O), 138.0 (*C*H═CH_2), 115.8 (CH═*C*H_2), 78.6 (*C*OH), 40.2 (*C*HC$(Me)_2$), 36.2 (C(OH)*C*H_2CH), 34.9 (*C*$H_2C_qCHCH_2$), 34.6 (CH_2C_qCH*C*H_2), 32.5 (*C*$(CH_3)_2$), 29.98 (CH_2*C*H_2C(OH), 29.92, 23.7, 18.5 (*C*H_3CO, C(*C*$H_3)_2$); ν_{max} (CCl_4)/cm^{-1} 1712. HRMS (EI +), Found: M^+, 210.1614. $C_{13}H_{22}O_2$ requires: M^+, 210.1620.

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