Synthesis and Claisen rearrangement of bridged bicyclic enol ethers of relevance to the course of ketene s-*cis*-diene cycloaddition

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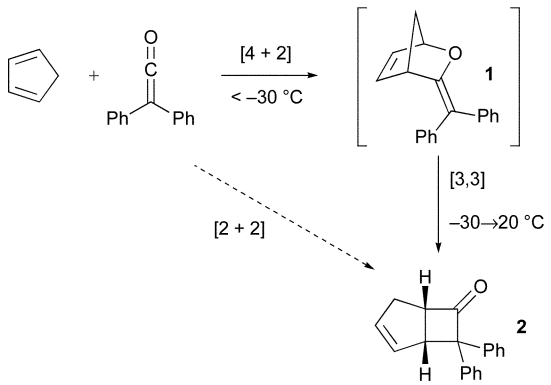
The synthesis is described of a range of 3-alkylidene-2-oxabicyclo[2.2.1]hept-5-ene and 3-alkylidene-2-oxabicyclo[2.2.2]oct-5-ene derivatives; Claisen rearrangement of these substrates either thermally or in the presence of an added Lewis acid results in the formation of bicyclic cyclobutanones with generally good conversions. These reactions may be performed in hydroxylic solvents, supporting a largely non-dissociative pathway for the rearrangement.

Introduction

Theoretical and experimental support for a preferred hetero-Diels–Alder/Claisen rearrangement pathway[1] (Scheme 1) for the overall [2 + 2]-cycloaddition of diphenylketene and cyclopentadiene contributed to a revision of the prevailing view[2] of the mechanism of this classical reaction.[3] Examples of this sense of periselectivity in related cycloadditions had been recorded[4] but the significance of these observations and their potential extent were perhaps under appreciated. In a later account,[5] Yamabe and Machiguchi noted that the course of ketene–diene cycloadditions is responsive to the nature of the diene. Thus, the *first-formed* products from acyclic dienes—largely s-*trans*—were reported to be mixtures of [2_{alkene} + 2_{alkene}] and [4_{diene} + $2_{carbonyl}$] cycloadducts whereas those from cyclic dienes—constrained to be s-*cis*—were reportedly just the [4 + 2] cycloadducts (such as enol ether **1**). The final, stable, products from these reactions were shown to be overall [4 + 2] and [2 + 2] adducts from acyclic and cyclic dienes respectively. Ghosez had reported a similar correlation of product with diene conformation in his study of the cycloadditions of dimethylketene dimethyliminium tetrafluoroborate; notably, [4 + 2] alkene–iminium cycloadducts were obtained with either cyclopentadiene or cyclohexadiene.[6]

Following the publication of Yamabe and Machiguchi's initial report we sought to address, by experiment,[7] some of the questions raised by their observations: is the formal [3,3]-rearrangement step an essentially concerted, intramolecular Claisen process, or is it highly asynchronous or even dissociative, proceeding, in the latter case, through the free ketene; could we prepare a range of examples of the bicyclic enol ethers (such as **1**) and allow them to progress to bicyclic cyclobutanones (such as **2**) that, for example, might not be available by formal [2 + 2]-cycloaddition; could we then prepare these intermediates enriched in one enantiomer as an alternative access to non-racemic cyclobutanones? In this paper we describe the results of our efforts to find reliable, flexible methods for the rational synthesis of the bicyclic enol ethers and detail the course of Claisen rearrangement of these enol ethers in the racemic series. We will present the preparation and rearrangement of enantiomerically-enriched substrates in a separate account in which we draw conclusions about the stereospecificity of the process, under various reaction conditions, and its potential application in enantioselective synthesis.



Scheme 1 Yamabe–Machiguchi mechanism for cyclic diene + ketene reaction.

Results and discussion

Because 2-oxabicyclo[2.2.1]heptan-3-one (**3**, Scheme 2) was expected[8] to be unstable at room temperature, we took the olefination of the analogous [2.2.2]-lactone **4**[9] as our starting point. Menger reported[10] that Tebbe methylenation of bicyclic lactones in the [3.3.1] and [3.2.1] series requires special care and, in our hands, treatment of lactone **4** with freshly-prepared Tebbe reagent afforded a product of ring-opening, cyclohexenol derivative **5**. Switching to a less Lewis acidic reagent mixture, we applied Chapleur's protocol[11] to give dichloromethylene bicycle **6** in moderate yield; a slightly higher yield could be obtained using the anion formed[12] by metal–halogen exchange of diethyl (trichloromethyl)phosphonate but this reaction proved unreliable. This compound (**6**) was stable at room temperature but complete rearrangement (→**7**[13]) could be achieved in toluene at reflux for 24 h. Clearly, under the traditional conditions for the generation of dichloroketene (*e.g.* trichloroacetyl chloride + Zn), and (cyclic) diene cycloaddition *in situ*, the so-formed Lewis acid ($ZnCl_2$) is able to catalyse rearrangement of the putative hetero-Diels–Alder adduct and that intermediate is simply not seen.

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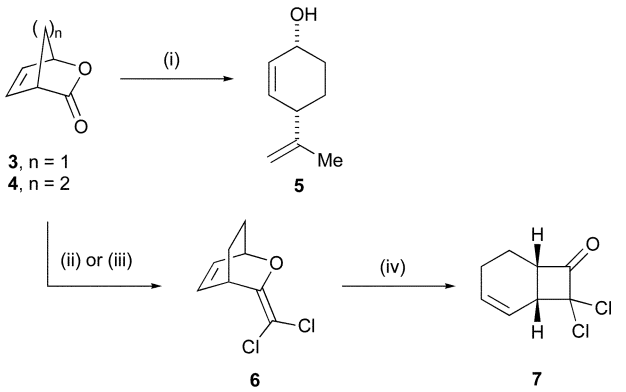


Scheme 2 Exploratory studies from lactone **4**. *Reagents and conditions*: (i) Tebbe reagent, pyridine, THF, PhMe, −48 → 20 °C, 1.5 h (72% from **4**); (ii) PPh_3, CCl_4, THF, reflux, 18 h (35%); (iii) $Cl_3CPO.(OEt)_2$, LiCl, BuLi, THF, −78 → 20 °C, 2 h (58%); (iv) PhMe, reflux, 24 h (89%).

Attempts to generalise this chemistry met with little success, largely through our inability to identify flexible conditions for the olefination; however, a Takai olefination[14] gave vinyl silane **8** (Fig. 1) in acceptable yield, but subsequent thermolysis gave slow conversion to a complex product mixture, the reaction presumably being complicated by desilylation or rearrangement of the predicted α-(trimethylsilyl)cyclobutanone. A totally different approach was needed and our attention turned to the selenoetherification[15] of cycloalkenyl trichloromethyl carbinols, an unprecedented[16] reaction that would allow flexibility in the order of formation of the two alkenes (Scheme 3).

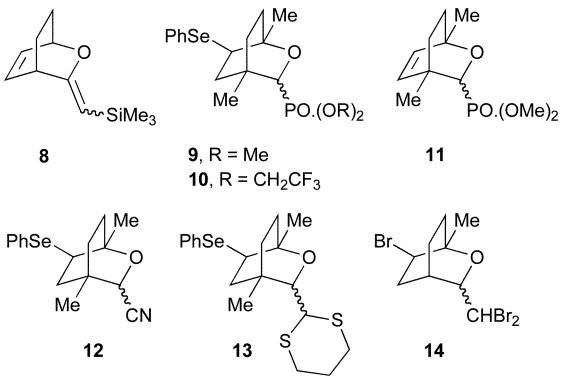
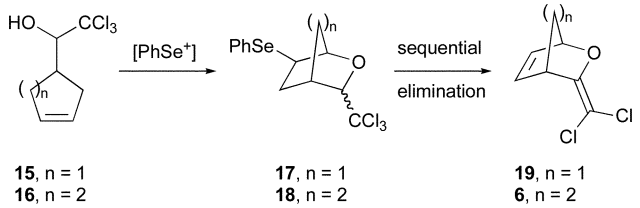
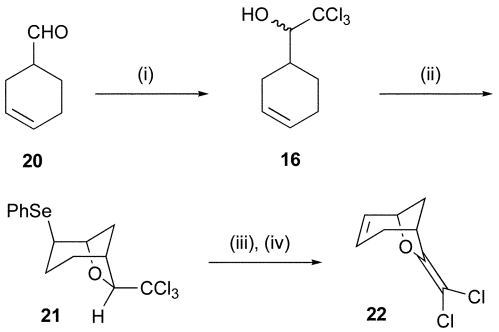


Fig. 1



Scheme 3 Trichloromethyl carbinol cyclisation and double elimination.

This idea was easily tested (Scheme 4) following trichloromethyl transfer[17] to commercially-available aldehyde **20**. Of the two diastereomers formed (**16**, 1 : 1 ratio) only one cyclised on treatment with NPSP–CSA to afford *exo*-trichloromethyl selenoether **21** as crystals of suitable quality for X-ray analysis (Fig. 2);[18]



Scheme 4 Synthesis of a bicyclo[3.2.1] substrate. *Reagents and conditions*: (i) $CHCl_3$, DBU, 20 °C, 16 h (82%); (ii) NPSP, CSA, CH_2Cl_2, 0 → 20 °C (33%; 66% of theoretical); (iii) aq. H_2O_2, THF, 0 °C, 0.5 h (79%); (iv) *t*-BuOK, THF, 0 °C, 2 h (81%).

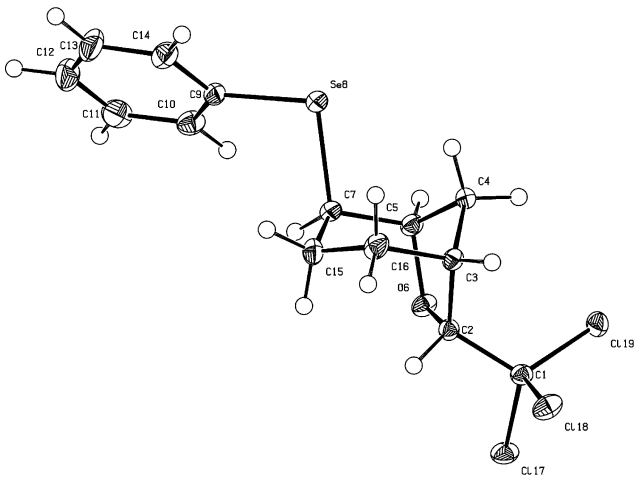
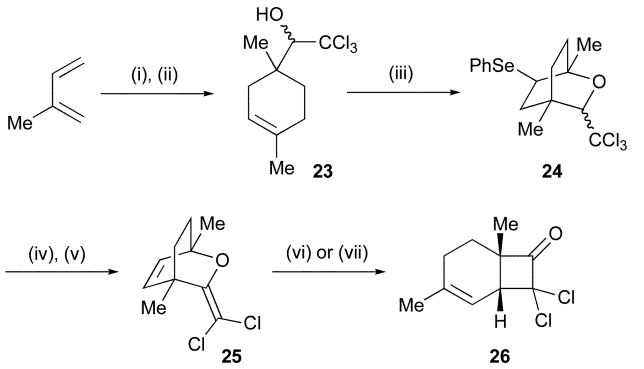


Fig. 2 ORTEP representation of bicyclic selenoether **21**.[18]

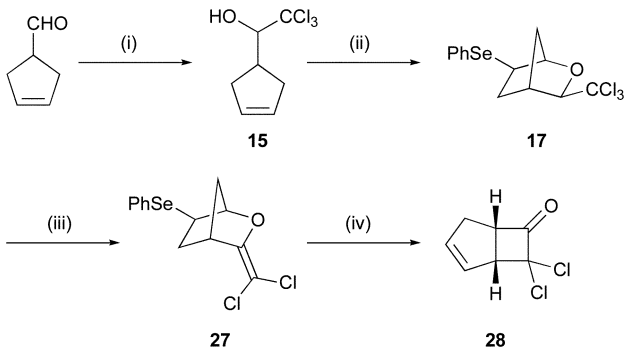
presumably, cyclisation of the second diastereomer (to give the *endo*-isomer) is hampered by crowding in the transition state between the sterically demanding trichloromethyl group and the three-carbon bridge. The sequential eliminations, of selenoxide and then HCl, proceeded without incident and bicyclic enol ether **22** was obtained in good yield. As expected,[10] this substrate required forcing conditions (benzene, 200 °C, sealed tube) to react and decomposition predominated; however, this sequence had established the viability of the proposal outlined in Scheme 3 and a substrate (**23**, Scheme 5) was targeted that was tailored to cyclise preferentially to a bicyclo[2.2.2] system.

The sequence from carbinol **23** worked well and substrate **25** rearranged cleanly at 80 °C to give the formal [2 + 2]-cycloadduct of dichloroketene and 1,4-dimethylcyclohexa-1,3-diene, **26**.[19] Anticipating an accelerating effect on the [3,3]-rearrangement of a protic solvent system,[20] enol ether **25** was warmed in an NMR tube in d_4-methanol–D_2O and, indeed, the reaction was found to be significantly more rapid, being largely complete within 16 h at 60 °C. Importantly, this result strongly supports an intramolecular, largely non-dissociative, pathway for the rearrangement since any dichloroketene, formed in a retro-[4 + 2] process, would be rapidly trapped by the solvent under these conditions.

In the bicyclo[2.2.1] series, cyclisation of trichloromethylcarbinol **15** (Scheme 6) proceeded stereoselectively to give the bicyclic ether **17** as a single diastereomer presumed to be that



Scheme 5 Synthesis and rearrangement of bicyclo[2.2.2] substrate **25**. *Reagents and conditions*: (i) methacrolein, $ZnCl_2$, CH_2Cl_2, 0 → 20 °C, 24 h (69%); (ii) LDA, $CHCl_3$, THF, −78 °C, 2 h (97%); (iii) NPSP, CSA, CH_2Cl_2, 0 → 20 °C (89%); (iv) aq. H_2O_2, THF, 0 °C, 0.5 h (90%); (v) *t*-BuOK, THF, 0 °C, 2 h (quant.); (vi) C_6D_6, reflux, 27 h (quant.); (vii) CD_3OD, 60 °C, 16 h.

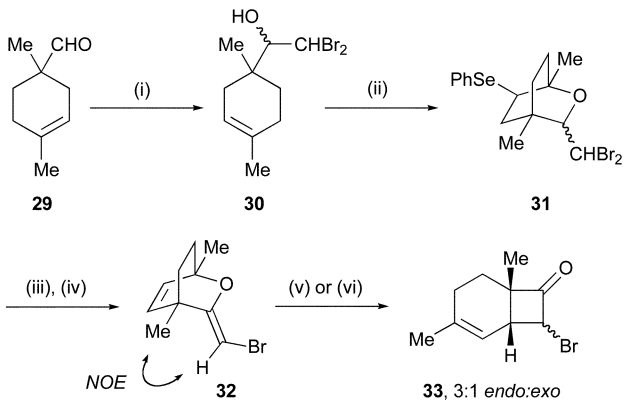


Scheme 6 Results in the bicyclo[2.2.1] series. *Reagents and conditions*: (i) LDA, $CHCl_3$, THF, −98 → −80 °C (53%); (ii) NPSP, CSA, CH_2Cl_2, reflux, 16 h (81%); (iii) *t*-BuOK, THF, 0 → 20 °C, 4.25 h (67%); (iv) aq. H_2O_2, pyridine, THF, 0 → 20 °C, 10 h (quant.).

shown. In this case the elimination steps had to be performed in the order: (1) loss of HCl; (2) selenoxide elimination. When the selenoxide elimination was attempted first, no isolable products could be obtained after standard work-up; it is probable that this 2-oxanorbornene system is unstable with respect to cycloreversion to cyclopentadiene and chloral.[21] Under the conditions of the selenoxide elimination, the expected bicyclic diene (**19**) was not obtained, the product immediately rearranging to the cyclobutanone (**28**)[22] in quantitative yield.

Next, we sought a modification to this chemistry that would allow flexibility in the range of enol ethers that could be generated, and a series of plausible olefin precursors (**9–13**, Fig. 1) was prepared by methods analogous to those used to prepare the trichloromethyl derivatives.[23] Ultimately, none of these proved useful; for example, whilst nitrile **12** could be deprotonated (with LDA) and alkylated α- to the cyano group with benzyl bromide, we were unable to achieve elimination of cyanide and, under basic conditions, ring-opening was observed instead.

However, selenocyclisation of dibromomethyl adduct **30** (Scheme 7) and consecutive eliminations led to vinyl bromide **32**, which was envisaged as a potential substrate for cross-coupling chemistry to give a range of substrates for a study of the influence of electronic effects on the course of the rearrangement step. The bromide (**32**) was produced as a single diastereomer (established



Scheme 7 *Reagents and conditions*: (i) LDA, CH_2Br_2, THF, −78 °C, 0.5 h (86%); (ii) NPSP, CSA, CH_2Cl_2, 0 → 20 °C (89%); (iii) *t*-BuOK, THF, 0 → 20 °C, 3 h (91%); (iv) $Na_2CO_3{\cdot}1.5H_2O_2$, aq. THF, 0 → 20 °C, 16 h (91%); (v) C_6D_6, 100 °C, 10 h (27%); (vi) Me_2AlCl, CH_2Cl_2, 0 °C, 10 min (72%).

by NOE as indicated). From the *exo*-situated dibromomethyl diastereomer, we ascribe this stereoselectivity to E2-elimination (reacting groups shown in blue) through a transition state deriving from conformation **II** (Fig. 3) above conformation **I** which suffers from a steric clash between the retained bromine atom and the proximal bridgehead methyl group (clashing groups shown in red); from the *endo*-diastereomer (that is differentiated from the *exo*-isomer solely by the location of the PhSe substituent) an equivalent interaction in conformation **III** (red groups) slows down elimination, favouring reaction through conformation **IV**. The influence of the bridgehead methyl group here is supported by the result of double elimination of HBr from substrate **14** (Fig. 1) in which both olefin diastereomers were obtained in almost equal proportion.

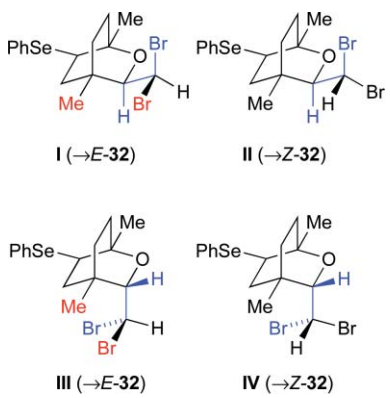
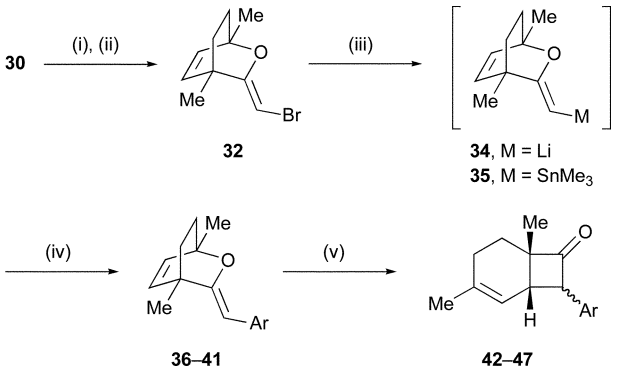


Fig. 3 Conformers in the elimination leading to vinyl bromide **32**.

We found that bromide **32** rearranged inefficiently in d_6-benzene at 100 °C, showing merely a 27% conversion to product after 10 h; prolonged heating led to significant decomposition. However, of importance to further work in this area, and of relevance to the more general observation of formal [2 + 2]-cycloadditions, the rearrangement could be effected cleanly at 0 °C with 0.2 equivalents of dimethylaluminium chloride in dichloromethane; under these conditions the product (**33**) was obtained as a 3 : 1 diastereomeric mixture at the carbonyl α-centre.

Two modifications to this route were made (Scheme 8): (1) the route was shortened and more easily effected on a large scale by



Scheme 8 Stille cross-coupling route to a variety of aryl-substituted cyclobutanones. *Reagents and conditions*: (i) NBS, CSA, CH_2Cl_2, 0 → 20 °C, 4 h (91%); (ii) *t*-BuOK, THF, 0 → 20 °C, 16 h (96%); (iii) *t*-BuLi, THF, Me_3SnCl, −78 → 20 °C, 1 h then (iv) ArI, $PdCl_2(PPh_3)_2$, DMF, 60 °C, 16 h; (v) C_6D_6, 100 °C (see Table 1).

employing bromoetherification to produce the bicyclic structure because both alkene functions could then be introduced in a single step by double elimination (→**32**); (2) because the vinyl bromide proved unreactive under conventional Stille-type cross-coupling conditions, stannyl substrate **35** was targeted, the electron rich enol ether being better suited as the nucleophilic component in the coupling chemistry. It proved most convenient to quench the derived vinyl lithium intermediate **34** with trimethyltin bromide and to simply concentrate the reaction mixture to give a residue that was taken directly into DMF for Stille cross-coupling.[24] In this way, we avoided exposure of the somewhat unstable stannane (**35**) to aqueous reagents and chromatography, with attendant gains in overall yield; furthermore, the co-formed LiCl/LiBr was automatically present in the cross-coupling reaction mixture, with the beneficial[25] result of lowering the temperature needed to achieve successful cross-coupling.

A series of electronically-differentiated *para*-substituted phenyl derivatives was prepared in this way (Table 1) and their rearrangement chemistry studied. Interestingly, we observed a general inverse correlation of rate of [3,3]-rearrangement with electron deficiency, the most electron rich substrate (**36**, entry 1) approaching completion[26] within 10 h at 100 °C whilst rearrangement of the most electron deficient substrate (**40**, entry 5) was incomplete after 100 h at this temperature. Epimerisation at the carbonyl α-centre became pronounced in the slower reactions (*e.g.* entries 4 and 5).

These qualitative rate effects are consistent with the trends observed in White's and Goering's classic studies in which the Claisen rearrangements of a variety of *para*-substituted allyl phenyl ethers were found to be well described by a Hammett relationship using σ_p^+ with a negative value of the reaction constant, ρ.[27]

Conclusions

This investigation has led to the development of general routes to functionalised methylene oxabicyclic compounds in the [2.2.1] and [2.2.2] series, permitting a study of their Claisen rearrangement under controlled conditions. A substrate in the [2.2.1] series rearranged spontaneously under the conditions (selenoxide elimination) used to form it; in the [2.2.2] series, in the absence of an added Lewis acid, thermolysis is necessary and there is evidence of competing cycloreversion over a period of hours at 100 °C.

Experimental

General procedure for selenocyclisation

To a stirred solution of the trichloromethyl- or dibromomethylcarbinol (0.15 M in dichloromethane) at 0 °C was added camphorsulfonic acid (CSA, 0.1 equivalents) and *N*-(phenylseleno)phthalimide (NPSP, 1.25 equivalents). After 30 min, the cooling bath was removed and stirring continued until TLC analysis showed complete consumption of the starting carbinol whereupon the mixture was concentrated *in vacuo* and purified by column chromatography.

General procedure for bromine–tin exchange and Stille cross-coupling

To a stirred solution of bromide **32** (0.1 M in THF) at −78 °C was added *tert*-butyllithium (2.2 equivalents of a 1.7 M solution in pentane). After 30 min, trimethyltin chloride (1.2 equivalents of a 1.0 M solution in hexanes) was added and, after a further 10 min, the mixture was allowed to warm to RT and concentrated *in vacuo* [Data for stannane **35**: δ_H (200 MHz, C_6D_6) 0.46 (9 H, s, $Sn(CH_3)_3$), 1.10–1.90 (4 H, m, 2 × CH_2) overlays 1.32 (3 H, s) and 1.41 (3 H, s, 2 × CH_3), 4.51 (1 H, s, =C*H*$SnMe_3$), 5.96 (1 H, d, *J* 8.0) and 6.05 (1 H, d, *J* 8.0, HC=CH)]. The residue was re-dissolved in DMF (to give a 0.3 M solution), treated with the appropriate aryl iodide (1.0 equivalent) and $PdCl_2(PPh_3)_4$ (5 mol%), and the resulting stirred solution heated to 60 °C for 16 h. The mixture was then allowed to cool to RT then stirred with sat. aq. KF (10 mL $mmol^{-1}$) for 10 min and extracted with ether (3 × 20 mL $mmol^{-1}$). The combined organic extracts were washed successively with sat. aq. KF (20 mL $mmol^{-1}$), 2.0 M aq. K_2CO_3 (2 × 20 mL $mmol^{-1}$), water (20 mL $mmol^{-1}$) and brine (20 mL $mmol^{-1}$), and were then dried over Na_2SO_4, concentrated *in vacuo* and the product isolated after column chromatography.

Table 1 Results for Stille cross-coupling and [3,3]-rearrangement

Entry	ArI	Enol ether (% yield)	Time/h for rearrangement	Cyclobutanone (% yield)
1	*p*-$MeOC_6H_4I$	**36** (79)	10	**42** (78)
2	*p*-MeC_6H_4I	**37** (77)	16	**43** (89)
3	PhI	**38** (66)	30	**44** (73)
4	*p*-$F_3CC_6H_4I$	**39** (61)	100	**45** (51)
5	*p*-$O_2NC_6H_4I$	**40** (55)	100	**46** (36)
6	2-Iodofuran[28]	**41** (52)	22	**47** (67)

cis-4-(2-Propenyl)cyclohex-2-en-1-ol (5)[29]

To a stirred solution of lactone **4** (128 mg, 1.03 mmol) in a mixture of THF (0.5 mL), toluene (1.5 mL) and pyridine (10 μL) at −48 °C was added dropwise Tebbe reagent (4.1 mL of a 0.5 M solution in toluene, 2.05 mmol). The mixture was stirred for 30 min then allowed to warm to RT over 90 min before being re-cooled to −10 °C and quenched with NaOH (0.3 mL of a 4.0 M solution, 1.2 mmol). The mixture was allowed to warm to RT, diluted with ether, dried over Na_2SO_4 and concentrated *in vacuo*. Purification by column chromatography on basic alumina (ethyl acetate) afforded the product (**5**) as an oil (102 mg, 72%). R_f not recorded; ν_{max} (thin film)/cm^{-1} 3381s, br, 2938s, 1642m, 1451m, 1049m, 891m; δ_H (400 MHz, C_6D_6) 1.55–1.81 (4 H, m, 2 × CH_2) overlays 1.71 (3 H, s, CH_3), 2.56–2.59 (1 H, m, C*H*C(Me)=CH_2), 4.07–4.12 (1 H, m, C*H*OH), 4.93 (2 H, s, =CH_2), 5.73 (1 H, dd, *J* 10.1, 2.8, C*H*=CHCHOH) and 5.90 (1 H, app. dt, *J* 10.1, 3.0, =C*H*CHOH); δ_C (100 MHz, C_6D_6) 21.4, 24.0, 30.4, 43.4, 64.8, 111.5, 131.2, 132.8, 148.3; *m*/*z* (CI+) 138 (78%, $MNH_4^+ - H_2O$), 121 (100, $MH^+ - H_2O$); Accurate Mass: Found: 121.1018; C_9H_{13} ($MH^+ - H_2O$) requires 121.1017.

3-Dichloromethylene-2-oxabicyclo[2.2.2]oct-5-ene (6)

Method A. To a stirred solution of lactone **4**[9] (210 mg, 1.69 mmol) and triphenylphosphine (1.78 g, 6.76 mmol) in THF (30 mL), at reflux, was added over 2 h a solution of carbon tetrachloride (3.9 mL, 40.6 mmol) in THF (8 mL), *via* syringe pump. Reflux was maintained for a further 18 h. The mixture was then allowed to cool, poured onto a pH 7.5 buffer solution (30 mL) and extracted with dichloromethane (3 × 30 mL). The combined organic extracts were washed with sat. aq. $NaHCO_3$, dried over $MgSO_4$ and concentrated *in vacuo*. Column chromatography (4 : 1 petrol : ethyl acetate) gave recovered starting material (118 mg, 56%) and the product (**6**) (114 mg, 35%) as an oil. R_f 0.67 (1 : 1 petrol : ethyl acetate); ν_{max} (thin film)/cm^{-1} 2941m, 1650m, 1614w, 1458w, 1364m, 1345m, 1297m, 1213s, 1173w, 1154w, 1058m, 1028s; δ_H (400 MHz, $CDCl_3$) 1.41 (1 H, tdd, *J* 12.0, 4.6, 2.6), 1.51 (1 H, dddd, *J* 12.8, 12.0, 3.0, 1.8), 1.75 (1 H, dddd, *J* 12.4, 9.4, 3.0, 2.6) and 2.12 (1 H, dddd, *J* 12.8, 9.4, 4.6, 3.6, CH_2CH_2), 3.89 (1 H, app. dq, *J* 5.4, 2.6, CHC(OR)=), 5.05 (1 H, app. ddt, *J* 5.2, 3.6, 1.8, CH(OR)), 6.47–6.54 (2 H, m, HC=CH); δ_C (100 MHz, $CDCl_3$) 20.0, 25.4, 34.2, 72.1, 93.0, 132.3, 132.6, 150.5; *m*/*z* (CI+) 210 (50%, M($^{37}Cl^{35}Cl$)NH_4^+), 208 (71, M($^{35}Cl_2$)NH_4^+), 192 (34), 190 (59), 176 (28), 174 (100), 162 (31), 155 (30), 140 (81), 127 (50), 121 (46), 91 (83), 80 (52), 55 (95); Accurate Mass: Found: 208.0294; $C_8H_{12}NO^{35}Cl_2$ (MNH_4^+) requires: 208.0296.

Method B. To a stirred solution of (trichloromethyl)-diethylphosphonate[30] (893 mg, 3.5 mmol) and LiCl (135 mg, 3.18 mmol) in THF (10 mL) at −78 °C was added dropwise *n*-butyllithium (1.98 mL of a 1.6 M solution in hexanes, 3.2 mmol). After 10 min, a solution of lactone **4**[9] (197 mg, 1.59 mmol) in THF (5 mL) was added in a slow, dropwise fashion and the mixture allowed to warm to RT. The reaction mixture was then poured onto water (20 mL) and extracted with ether (3 × 20 mL). The combined organic extracts were dried over $MgSO_4$ and concentrated *in vacuo*. Purification by column chromatography (10 : 1 petrol : ethyl acetate) gave recovered starting material (20 mg, 10%) and the product (**6**) (174 mg, 58%); spectroscopic data as above.

8,8-Dichlorobicyclo[4.2.0]oct-2-en-7-one (7)[13]

Enol ether **6** (71 mg, 0.37 mmol) was heated under reflux in toluene (5 mL). After 24 h, the mixture was concentrated *in vacuo* and the residue purified by column chromatography (5 : 1 petrol : ethyl acetate) to afford the product (**7**) (63 mg, 89%) as an oil. R_f 0.66 (1 : 1 petrol : ethyl acetate); ν_{max} (thin film)/cm^{-1} 2930m, 1801s, 1436w, 1394w, 1343w, 1286w, 1129w, 1094w, 1051w; δ_H (400 MHz, $CDCl_3$) 1.65 (1 H, ddt, *J* 13.6, 10.4, 6.0, COCHC*H*H′), 2.01–2.22 (3 H, m, COCHCH*H*′C*H*H′), 3.44–3.49 (1 H, m, C*H*CCl_2), 4.12 (1 H, ddd, *J* 9.2, 6.0, 3.2, C*H*CO), 5.87–5.90 and 6.07–6.12 (2 H, m, *H*C=C*H*); δ_C (50 MHz, $CDCl_3$) 18.8, 20.8, 44.2, 53.3, 86.7, 123.0, 132.4, 196.7; *m*/*z* (EI+) 192 (4%, M($^{37}Cl^{35}Cl$)$^+$), 190 (8), 127 (12), 99 (12), 92 (15), 91 (95), 89 (16), 80 (64), 79 (100).

2,2,2-Trichloro-1-(cyclohex-3-enyl)ethanol (16)

To a stirred solution of 3-cyclohexene-1-carboxaldehyde (**20**) (0.59 mL, 5.03 mmol) in chloroform (0.80 mL, 10.1 mmol) was added dropwise DBU (0.75 mL, 5.03 mmol). Stirring was continued for a further 16 h before the mixture was diluted with ethyl acetate (30 mL), washed with hydrochloric acid (10 mL of a 1 M solution), then dried over $MgSO_4$ and concentrated *in vacuo*. Purification by column chromatography (5 : 1 petrol : ether) gave the product (**16**) as an oil and a *ca.* 1 : 1 mixture of diastereomers (942 mg, 82%) that were not separated. R_f 0.50/0.57 (1 : 1 petrol : ether); ν_{max} (thin film)/cm^{-1} 3436s, br, 2927s, 1665w, 1437m, 1390w, 1329w, 1243w, 1115m, 814s; δ_H (400 MHz, $CDCl_3$) 1.43–1.54 (1 H, m), 1.71–1.78 (2 H, m), 2.04–2.43 (4 H, m), 2.72–2.94 (1 H, app. s, OH), 3.93 (0.5 H, dd, *J* 6.3, 2.9) and 4.05 (0.5 H, dd, *J* 6.0, 2.7, C*H*OH), 5.66–5.73 (2 H, m, HC=CH); δ_C (50 MHz, $CDCl_3$) 22.1, 25.1, 25.2 (two peaks), 27.2, 31.6, 35.8, 36.3, 85.6, 86.3, 103.8, 104.2, 125.9, 126.1, 126.5, 127.4; *m*/*z* (FI+) 232 (31%, M($^{37}Cl_2{}^{35}Cl$)$^+$), 230 (98, M($^{37}Cl^{35}Cl_2$)$^+$), 228 (100, M($^{35}Cl_3$)$^+$); Accurate Mass: Found: 227.9872; $C_8H_{11}{}^{35}Cl_3O$ (M^+) requires 227.9875.

4-_exo_-Phenylseleno-7-_exo_-trichloromethyl-6-oxabicyclo[3.2.1]octane (21)

Following the general procedure for selenocyclisation, trichloromethyl alcohol **16** (636 mg, 2.77 mmol) gave after column chromatography (10 : 1 petrol : ether) selenide **21** (352 mg, 33%) as a yellow solid. [A small sample was crystallised from methanol by slow evaporation in order to obtain the structure shown in Fig. 2.] Mp 128–129 °C; R_f 0.60 (2 : 1 petrol : ether); ν_{max} (KBr disc)/cm^{-1} 2937s, 1573w, 1474m, 1365w, 1298w, 1194m, 1067s, 1021s, 933m, 876s; δ_H (400 MHz, $CDCl_3$) 1.67–1.72 (1 H, m, SeCHCH_2C*H*H′), 1.86–1.91 (2 H, m, SeCHC*H*H′CH*H*′), 2.06 (1 H, d, *J* 12.1, CH(OR)C*H*H′), 2.24–2.34 (1 H, m, SeCHCH*H*′), 2.46 (1 H, ddd, *J* 12.1, 7.5, 6.2, CH(OR)CH*H*′), 2.77 (1 H, app. s, Cl_3CHC*H*), 3.67–3.69 (1 H, m, SeC*H*), 4.43 (1 H, s, C*H*CCl_3), 4.70 (1 H, dd, *J* 6.2, 4.1, C*H*(OR)), 7.23–7.33 (3 H, m) and 7.48–7.59 (2 H, m, Ph); δ_C (100 MHz, $CDCl_3$) 23.7, 27.7, 30.4, 38.9, 43.8, 81.8, 91.9, 100.9, 127.6, 129.3, 129.4, 134.0; *m*/*z* (CI+) 385 (M($^{35}Cl_3{}^{80}Se$)H$^+$, 11%), 355 (12), 353 (56), 351 (100), 349 (45), 347 (13), 317 (34), 315 (65), 157 (32), 123 (30), 94 (32), 93 (36), 91 (35), 81 (83), 78 (74), 58 (29), 45 (28), 44 (37); Found; C 43.74, H 3.93 $C_{14}H_{15}Cl_3OSe$ requires C 43.76, H 3.94%.

7-Trichloromethyl-6-oxabicyclo[3.2.1]oct-3-ene

To a stirred solution of selenide **21** (143 mg, 0.37 mmol) in THF (2.5 mL) at 0 °C was added dropwise a solution of H_2O_2 (0.05 mL of a 35% w/v aq. solution) in THF (0.5 mL). After stirring for 2 h, the mixture was diluted with ether (50 mL), washed successively with water (20 mL) and brine (20 mL), dried over $MgSO_4$ and concentrated *in vacuo*. Purification by column chromatography (10 : 1 petrol : ether) afforded the title alkene as an oil (67 mg, 79%). R_f 0.60 (2 : 1 petrol : ether); ν_{max} (thin film)/cm^{-1} 2966s, 1632w, 1454m, 1434m, 1292m, 1263m, 1121w, 1082s; δ_H (400 MHz, $CDCl_3$) 1.80 (1 H, d, *J* 10.9, CH(OR)C*H*H′), 2.19–2.25 (1 H, m, CH=CHC*H*H), 2.35 (1 H, ddd, *J* 10.9, 5.9, 5.2, CH(OR)CH*H*′), 2.53 (1 H, ddd, *J* 18.2, 5.9, 2.4, CH=CHCH*H*′), 2.78–2.82 (1 H, app. s, C*H*CH(CCl_3)), 4.31 (1 H, s, C*H*CCl_3), 4.60 (1 H, app. t, *J* 5.2, CH(OR)), 5.72–5.79 (1 H, m) and 6.02–6.08 (1 H, m, HC=CH); δ_C (100 MHz, $CDCl_3$) 32.9, 35.0, 38.6, 74.3, 93.1, 100.3, 128.5, 130.0.

7-Dichloromethylene-6-oxabicyclo[3.2.1]oct-3-ene (22)

To a stirred solution of 7-trichloromethyl-6-oxabicyclo[3.2.1]oct-3-ene (46 mg, 0.20 mmol) in THF (2 mL) at 0 °C was added potassium *tert*-butoxide (45 mg, 0.40 mmol) in one portion. After 2 h, TLC analysis showed complete consumption of starting material. The mixture was poured onto water (10 mL) and extracted with ether (3 × 10 mL). The combined organic extracts were dried over $MgSO_4$ and concentrated *in vacuo* to afford the product (**22**) as an oil (31 mg, 81%). R_f 0.55 (2 : 1 petrol : ether); ν_{max} (thin film)/cm^{-1} 2983m, 1664s, 1632w, 1383m, 1192s, 1147s, 1119s, 1013s, 980s; δ_H (400 MHz, $CDCl_3$) 2.01 (1 H, d, *J* 10.8) and 2.22 (1 H, app. dt, *J* 10.8, 5.4, CH(OR)CH_2), 2.38–2.53 (2 H, m, CH_2CH=), 3.35 (1 H, app. s, CHC(CCl_2)), 4.76 (1 H, app. t, *J* 5.4, CH(OR)), 5.81–5.90 (1 H, m) and 6.04–6.11 (1 H, m, HC=CH); δ_C (100 MHz, $CDCl_3$) 31.3, 35.1, 38.6, 76.3, 95.7, 128.5, 130.2, 157.0.

1,4-Dimethyl-3-cyclohexene-1-carboxaldehyde (29)[31]

To a rapidly stirred mixture of isoprene (7.5 mL, 75.0 mmol), $ZnCl_2$ (2.56 g, 18.8 mmol) and hydroquinone (several crystals) in dichloromethane (75 mL) at 0 °C was added dropwise methacrolein (6.0 mL, 72.5 mmol). After 15 min the cooling bath was removed and stirring continued for a further 24 h. The mixture was then diluted with ether (100 mL), washed with sat. aq. $NaHCO_3$ (75 mL), dried over $MgSO_4$ and the solvent removed *in vacuo.* Reduced pressure distillation (86 °C @ 24 mmHg (lit.[31] 70–75 °C @ 30 mmHg)) afforded the product (**29**) as a colourless oil (6.95 g, 69%, contaminated with *ca.* 5% of the inseparable regioisomer); ν_{max} (thin film)/cm^{-1} 2916s, 1728s, 1438s, 1377m, 1017m, 911m; δ_H (400 MHz, $CDCl_3$) 0.96 (3 H, s, CH_3CCHO), 1.43 (1 H, dt, *J* 13.5, 7.0, CH_2C*H*H′CCHO), 1.56 (3 H, d, *J* 0.9, CH_3C=), 1.68–1.90 (2 H, m, CH_2CH*H*′CCHO overlays =CHC*H*H′), 1.85–1.89 (2 H, m, CH_2C(Me)=), 2.21–2.28 (1 H, m, =CHCH*H*′), 5.28–5.30 (1 H, m, CH=), 9.39 (1 H, s, C*H*O); δ_C (100 MHz, $CDCl_3$) 20.6, 23.3, 26.8, 28.9, 31.7, 44.2, 118.3, 133.5, 205.9; *m*/*z* (CI+) 156 (92%, MNH_4^+), 153 (20), 139 (58, MH^+), 138 (97), 123 (41), 110 (23), 109 (85), 95 (100), 94 (34), 91 (22), 81 (29), 58 (30), 50 (26), 44 (50).

2,2,2-Trichloro-1-(1,4-dimethylcyclohex-3-enyl)ethanol (23)

To a stirred solution of diisopropylamine (0.59 mL, 4.22 mmol) in THF (5 mL) at 0 °C was added dropwise butyllithium (2.6 mL of a 1.6 M solution in hexanes, 4.22 mmol). Stirring was continued for 30 min before this solution was added *via* cannula, in a slow dropwise fashion, to a stirred solution of aldehyde **29** (530 mg, 3.83 mmol) and chloroform (0.61 mL, 7.67 mmol) in THF (10 mL) at −78 °C. After 2 h the mixture was quenched with hydrochloric acid (5 mL of a 1 M solution), allowed to warm to RT, poured onto water (20 mL) and extracted with ether (3 × 20 mL). The combined organic extracts were dried over $MgSO_4$ and concentrated *in vacuo*. Purification by column chromatography (10 : 1 petrol : ether) afforded the product (**23**), a mobile oil, as a *ca.* 1 : 1 mixture of diastereomers (953 mg, 97%). R_f 0.50 (2 : 1 petrol : ether); ν_{max} (thin film)/cm^{-1} 3468s, br, 2966s, 1640w, 1446m, 1381, 1288w, 1226w, 1172w, 1058m, 818s; δ_H (400 MHz, $CDCl_3$) 1.17 and 1.18 (3 H, 2 × s, CH_3CCHOH), 1.64 and 1.67 (3 H, 2 × s, CH_3C=), 1.82–1.89 (2 H, m), 2.04–2.06 (3 H, m), 2.38 (0.5 H, d, *J* 16.9) and 2.61 (0.5 H, d, *J* 18.0, 3 × CH_2), 3.17 (0.5 H, d, *J* 6.0) and 3.22 (0.5 H, d, *J* 5.8, OH), 3.93 (0.5 H, d, *J* 6.0) and 3.95 (0.5 H, d, *J* 5.8, C*H*OH), 5.27–5.30 (1 H, m, C*H*=); δ_C (100 MHz, $CDCl_3$) 19.9, 20.3, 20.4, 23.2, 26.8, 27.0, 32.0, 32.6, 36.6 (two peaks), 38.9, 39.0, 86.4, 87.1, 103.9 (two peaks), 119.1 (two peaks), 132.1, 132.4; *m*/*z* (FI+) 258 (67%, M($^{37}Cl^{35}Cl_2$)$^+$), 256 (100, M($^{35}Cl_3$)$^+$); Accurate mass: Found: 256.0179; $C_{10}H_{15}{}^{35}Cl_3O$ (M^+) requires 256.0188.

1,4-Dimethyl-3-trichloromethyl-6-phenylseleno-2-oxabicyclo[2.2.2]octane (24)

Following the general procedure for selenocyclisation, trichloromethyl alcohol **23** (313 mg, 1.22 mmol) gave, after column chromatography (15 : 1 petrol : ether), selenide **24** (447 mg, 89%) as an oil and as a *ca.* 1 : 1 mix of diastereomers. R_f 0.68 (2 : 1 petrol : ether); ν_{max} (thin film)/cm^{-1} 2935s, 1579m, 1477s, 1437s, 1353w, 1201m, 1072s, 1021s; δ_H (400 MHz, $CDCl_3$) 1.18 (3 H, s, CH_3CCH(OR)), 1.29 (1.5 H, s) and 1.31 (1.5 H, s, CH_3C(OR)), 1.40–1.45 (1 H, m), 1.49–1.56 (1 H, m), 1.61–1.75 (1 H, m), 1.78–1.87 (0.5 H, m), 1.89–1.98 (0.5 H, m), 2.14 (0.5 H, ddd, *J* 14.0, 12.0, 2.8), 2.25–2.38 (1 H, m) and 3.01 (0.5 H, ddd, *J* 14.8, 10.8, 3.6, 3 × CH_2), 3.64 (0.5 H, ddd, *J* 10.8, 5.6, 2.8) and 3.76 (1 H, ddd, *J* 10.8, 6.8, 2.8, C*H*SePh), 4.14 (0.5 H, s) and 4.20 (0.5 H, s, CH(OR)), 7.26–7.34 (3 H, m) and 7.54–7.59 (2 H, m, Ph); δ_C (100 MHz, $CDCl_3$) 24.7, 25.0, 25.5, 25.8, 28.7, 29.1, 35.0, 35.1, 37.8, 39.1, 44.6, 45.2, 50.8, 51.0, 75.5, 76.0, 89.7, 90.1, 101.1, 101.2, 127.4, 127.5, 129.2 (two peaks), 130.1, 130.2, 133.8, 133.9; *m*/*z* (CI+) 417 (12%, M($^{37}Cl_2{}^{35}Cl^{80}Se$ and $^{37}Cl_3{}^{78}Se$)H$^+$), 415 (30, M($^{37}Cl^{35}Cl_2{}^{80}Se$ and $^{37}Cl_2{}^{35}Cl^{78}Se$)H$^+$), 413 (38, M($^{35}Cl_3{}^{80}Se$ and $^{37}Cl^{35}Cl_2{}^{78}Se$)H$^+$), 411 (15, M($^{35}Cl_3{}^{78}Se$)H$^+$), 381 (66), 379 (100), 377 (52), 375 (15), 345 (51), 343 (94), 341 (52), 309 (19); Accurate Mass: Found: 412.9757; $C_{16}H_{20}Cl_3O^{80}Se$ requires 412.9745.

1,4-Dimethyl-3-trichloromethyl-2-oxabicyclo[2.2.2]oct-5-ene

To a stirred solution of selenide **24** (445 mg, 1.08 mmol) in THF (7.5 mL) at 0 °C was added dropwise a solution of H_2O_2 (0.16 mL of a 35% w/v aq. solution, 1.62 mmol) in THF (1.6 mL). Stirring was continued for 4 h before the mixture was diluted with ether (50 mL), washed with water (2 × 20 mL), dried over $MgSO_4$ and concentrated *in vacuo.* Column chromatography (20 : 1

petrol : ether) gave the title alkene as an oil and as a *ca.* 1 : 1 mixture of diastereomers (249 mg, 90%). R_f 0.66 (2 : 1 petrol : ether); ν_{max} (thin film)/cm^{-1} 2934s, 1464m, 1380m, 1210w, 1116w, 1051s; δ_H (400 MHz, $CDCl_3$) 1.11 (0.5 H, dddd, *J* 12.8, 12.0, 5.8, 1.3) and 1.27 (0.5 H, td, *J* 12.0, 5.4, MeC(OR)CH_2C*H*H′), 1.38–1.49 (1 H, m, MeC(OR)C*H*H′) overlays 1.45 (2 × 1.5 H, 2 × s), 1.46 (1.5 H, s) and 1.47 (1.5 H, s, 2 × CH_3), 1.61–1.68 (0.5 H, m), 1.88 (0.5 H, ddd, *J* 12.8, 9.2, 5.4), 2.01 (0.5 H, ddd, *J* 13.2, 9.4, 5.8) and 2.40 (0.5 H, ddd, *J* 12.8, 9.4, 2.0, MeC(OR)CH*H*′CH*H*′), 3.77 (0.5 H, d, *J* 1.0) and 4.15 (0.5 H, d, *J* 1.3, $CHCCl_3$), 6.06 (0.5 H, d, *J* 9.0) and 6.16–6.21 (1.5 H, m, HC=CH); δ_C (100 MHz, $CDCl_3$) 22.9, 23.6, 23.7, 23.8, 26.6, 32.9 (two peaks), 35.0, 38.8, 40.0, 72.6, 72.9, 88.5, 90.1, 100.6, 101.0, 135.3, 136.0, 136.7, 142.4; *m*/*z* (CI+) 259 (27%, M($^{37}Cl_2{}^{35}Cl$)H$^+$), 257 (84, M($^{37}Cl{}^{35}Cl_2$)H$^+$), 255 (88, M($^{35}Cl_3$)H$^+$), 202 (25), 187 (34), 185 (100), 151 (80), 111 (80), 109 (80), 107 (31), 91 (20); Accurate Mass: Found: 255.0114; $C_{10}H_{14}{}^{35}Cl_3O$ (MH$^+$) requires 255.0110.

3-Dichloromethylene-1,4-dimethyl-2-oxabicyclo[2.2.2]oct-5-ene (25)

To a stirred solution of 1,4-dimethyl-3-trichloromethyl-2-oxabicyclo[2.2.2]oct-5-ene (185 mg, 0.72 mmol) in THF (7.5 mL) at 0 °C was added in one portion potassium *tert*-butoxide (326 mg, 2.90 mmol). After stirring for 15 min, the cooling bath was removed and stirring continued for 8 h whereupon TLC analysis showed complete consumption of starting material. The mixture was poured onto water (20 mL) and extracted with ether (3 × 20 mL). The combined organic extracts were dried over $MgSO_4$ and concentrated *in vacuo* to afford the enol ether (**25**), as an oil (158 mg, 100%) that required no further purification. R_f 0.54 (2 : 1 petrol : ether); ν_{max} (thin film)/cm^{-1} 2936s, 1613m, 1460m, 1383m, 1223m, 1100s, 1062m, 995s; δ_H (400 MHz, $CDCl_3$) 1.31 (1 H, td, *J* 11.6, 4.8, MeC(OR)CH_2C*H*H′), 1.56 (1 H, ddd, *J* 12.6, 11.6, 3.2, MeC(OR)C*H*H′) overlays 1.57 (3 H, s, CH_3CC(OR)=), 1.67 (3 H, s, CH_3CO), 1.76–1.82 (1 H, m, MeC(OR)CH_2CH*H*′), 1.92 (1 H, ddd, *J* 12.6, 9.6. 4.8, MeC(OR)CH*H*′), 6.11 (1 H, d, *J* 7.8) and 6.24 (1 H, d, *J* 7.8, HC=CH); δ_C (100 MHz, $CDCl_3$) 23.1, 23.4, 32.2, 33.6, 40.7, 76.8, 95.1, 135.9, 138.0, 152.5; *m*/*z* (CI+) 219 (11%, M($^{35}Cl_2$)H$^+$), 151 (100), 109 (74), 108 (52); Accurate Mass: Found: 219.0347; $C_{10}H_{13}{}^{35}Cl_2O$ (MH$^+$) requires: 219.0343.

8,8-Dichloro-3,6-dimethylbicyclo[4.2.0]oct-2-en-7-one (26)[19]

Method A. An NMR sample of enol ether **25** (28 mg, 0.13 mmol) in d_6-benzene (0.5 mL) was heated under reflux for 27 h whereupon analysis by ^{1}H NMR spectroscopy showed clean and complete conversion to cyclobutanone **26**. R_f 0.52 (2 : 1 petrol : ether); ν_{max} (thin film)/cm^{-1} 2931m, 1802s, 1446m, 870w, 804m; δ_H (400 MHz, C_6D_6) 1.09 (1 H, ddd, *J* 12.8, 7.2, 4.4, C*H*H′C(Me)CO), 1.14 (3 H, s, CH_3CCO), 1.35–1.49 (1 H, m, CH*H*′C(Me)CO), 1.57–1.58 (1 H, m, =C(Me)C*H*H′) overlays (3 H, s, CH_3C=), 1.79 (1 H, ddd, *J* 13.4, 7.0, 5.2, =C(Me)CH*H*′), 2.93 (1 H, d, *J* 1.9, $CHCCl_2$), 5.44 (1 H, d, *J* 1.9, CH=); δ_C (100 MHz, C_6D_6) 21.2, 23.4, 26.3, 29.2, 54.1, 58.3, 87.9, 117.3, 140.1, 201.1; *m*/*z* (CI+) 221 (62%, M($^{37}Cl{}^{35}Cl$)H$^+$), 219 (100, M($^{35}Cl_2$)H$^+$), 168 (27), 151 (22), 141 (25), 108 (22).

Method B. An NMR sample of enol ether **25** (21 mg, 0.10 mmol) in 4 : 1 CD_3OD : D_2O (0.5 mL) was heated to 60 °C for 16 h whereupon ^{1}H NMR analysis recorded *ca.* 90% conversion. δ_H (200 MHz, 4 : 1 CD_3OD : D_2O) key peaks only, sample not purified: 1.50 (3 H, s, CH_3CCO), 1.86 (3 H, s, CH_3C=), 3.22–3.30 (1 H, m, $CHCCl_2$), 5.15–5.22 (1 H, m, CH=).

2,2,2-Trichloro-1-(3-cyclopentenyl)ethanol (15)

To a stirred solution of diisopropylamine (0.68 mL, 4.88 mmol) in THF (10 mL) at 0 °C was added dropwise butyllithium (2.77 mL of a 1.6 M solution in hexanes, 4.43 mmol) and stirring continued for 30 min before cooling to −98 °C and slow addition of chloroform (0.39 mL, 4.88 mmol). After 15 min a solution of 3-cyclopentene-1-carboxaldehyde[32] (213 mg, 2.22 mmol) in THF (5 mL) was added and the mixture allowed to warm to −80 °C before quenching with hydrochloric acid (5 mL of a 1 M aqueous solution). The mixture was then allowed to warm to RT, poured onto water (20 mL) and extracted with ether (3 × 20 mL). The combined organic extracts were dried over $MgSO_4$ and concentrated *in vacuo*. Purification by column chromatography (10 : 1 petrol : ether) gave the product (**15**) as an oil (254 mg, 53%). R_f 0.45 (2 : 1 petrol : ether); ν_{max} (thin film)/cm^{-1} 3460brs, 2946s, 1614w, 1450w, 1380w, 1347w, 1120w, 1049w; δ_H (400 MHz, $CDCl_3$) 2.30–2.48 (2 H, m, 2 × C*H*H′), 2.57–2.64 (2 H, m, 2 × CH*H*′), 2.99 (1 H, app. quind, *J* 8.8, 4.0, C*H*CHOH), 3.21 (1 H, d, *J* 5.6, O*H*), 4.18 (1 H, dd, *J* 5.6, 4.0, C*H*OH), 5.61–5.72 (2 H, m, CH=CH); δ_C (100 MHz, $CDCl_3$) 33.1, 36.6, 39.9, 84.6, 104.0, 129.4, 130.1; *m*/*z* (FI+) 218 (31%, M($^{37}Cl_2{}^{35}Cl$)$^+$), 216 (100), 214 (90); Accurate mass: Found: 213.9716; $C_7H_9{}^{35}Cl_3O$ (M$^+$) requires: 213.9719.

6-Phenylseleno-3-trichloromethyl-2-oxabicyclo[2.2.1]heptane (17)

To a stirred solution of trichloromethyl alcohol **15** (152 mg, 0.71 mmol) and CSA (16 mg, 0.07 mmol) in dichloromethane (10 mL) at reflux was added over 2 h a solution of NPSP (426 mg, 1.41 mmol) in dichloromethane (5 mL). Reflux was maintained for a further 14 h before the mixture was concentrated *in vacuo*. Purification by column chromatography (15 : 1 petrol : ether) gave the product (**17**) as a solid (215 mg, 81%). R_f 0.63 (2 : 1 petrol : ether); mp 94–95 °C; ν_{max} (KBr disc)/cm^{-1} 2886m, 1442m, 1277m, 1151m, 1067m, 1044m, 896s, 808s, 705s; δ_H (400 MHz, $CDCl_3$) 1.62 (1 H, ddd, *J* 13.2, 5.6, 3.8, C*H*H′CHSe), 1.78 (1 H, dd, *J* 11.2, 3.0, apical-C*H*H′), 2.09 (1 H, ddd, *J* 13.2, 8.2, 2.4, CH*H*′CHSe), 2.45 (1 H, app. dquin, *J* 11.2, 2.4, apical-CH*H*′), 2.93 (1 H, d, *J* 3.8, CH(CCl_3)C*H*), 3.50 (1 H, ddd, *J* 8.2, 5.6, 2.4, CHSe), 4.00 (1 H, s, CHSeC*H*(OR)), 4.49 (1 H, d, *J* 3.0, $CHCCl_3$), 7.31–7.34 (3 H, m) and 7.52–7.55 (2 H, m, Ph); δ_C (100 MHz, $CDCl_3$) 31.9, 36.6, 41.1, 41.5, 82.5, 91.5, 99.4, 127.6, 129.3, 129.8, 133.2; *m*/*z* (CI+) 375 (30%, M($^{37}Cl_3{}^{78}Se$ and $^{37}Cl_2{}^{35}Cl{}^{80}Se$)H$^+$), 373 (82, M($^{37}Cl_2{}^{35}Cl{}^{78}Se$ and $^{37}Cl{}^{35}Cl_2{}^{80}Se$)H$^+$), 371 (98, M($^{37}Cl{}^{35}Cl_2{}^{78}Se$ and $^{35}Cl_3{}^{80}Se$)H$^+$), 369 (46, M($^{35}Cl_3{}^{78}Se$)H$^+$), 339 (65), 337 (100), 335 (50), 303 (290), 301 (67), 299 (32), 109 (27), 78 (68), 67 (34); Accurate mass: Found: 370.9280; $C_{13}H_{14}Cl_3O{}^{80}Se$ (MH$^+$) requires: 370.9275.

3-Dichloromethylene-6-phenylseleno-2-oxabicyclo[2.2.1]heptane (27)

To a stirred solution of bicycle **17** (319 mg, 0.86 mmol) in THF (9 mL) at 0 °C was added potassium *tert*-butoxide (386 mg, 3.44 mmol). After 15 min, the cooling bath was removed and stirring continued a further 4 h whereupon the mixture was poured

onto $NaHCO_3$ (20 mL of a sat. aq. solution) and extracted with ether (3 × 20 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated *in vacuo.* Purification by column chromatography (10 : 1 petrol : ether + 1% triethylamine) afforded the product (**27**) (192 mg, 67%) as a yellow oil; R_f 0.67 (2 : 1 petrol : ether); ν_{max} (thin film)/cm^{-1} 2959m, 1675s, 1578m, 1476s, 1438s, 1317s, 1271m, 1179s, 1100s, 1036w, 993s; δ_H (400 MHz, $CDCl_3$) 1.71 (1 H, ddd, *J* 13.2, 5.2, 4.0, SeCHC*H*H′), 1.98 (1 H app. dpent, *J* 11.0, 1.6) and 2.07 (1 H, dd, *J* 11.0, 1.4, apical-CH_2), 2.22 (1 H, ddd, *J* 13.2, 8.4, 1.6, CH*H*′CHSePh), 3.42 (1 H, d, *J* 2.4, CHC(OR)=), 3.56 (1 H, ddd, *J* 8.4, 5.2, 1.6, CHSe), 4.72 (1 H, app. s (unresolved m), CHOC=), 7.31–7.35 (3 H, m) and 7.51–7.57 (2 H, m, Ph); δ_C (100 MHz, $CDCl_3$) 33.5, 37.0, 40.6, 41.9, 85.6, 92.6, 127.8, 129.4 (two peaks), 133.6, 155.3; *m*/*z* (CI+) 339 (19%, M($^{37}Cl_2{}^{80}Se)H^+$), 337 (62, M($^{37}Cl_2{}^{78}Se$ and $^{35}Cl^{37}Cl^{80}Se)H^+$), 335 (100, M($^{35}Cl_2{}^{80}Se$ and $^{35}Cl^{37}Cl^{78}Se)H^+$), 333 (41, M($^{35}Cl_2{}^{78}Se)H^+$), 178 (14), 157 (13); Accurate Mass: Found: 334.9450; $C_{13}H_{12}{}^{35}Cl_2O^{80}Se$ requires: 334.9509.

7,7-Dichlorobicyclo[3.2.0]hept-2-en-6-one (28)[22]

To a stirred solution of selenide **27** (192 mg, 0.57 mmol) in THF (3.5 mL) at 0 °C was added sequentially pyridine (0.07 mL, 0.86 mmol) and a solution of H_2O_2 (0.09 mL of a 35% w/v aq. solution, 0.86 mmol) in THF (0.9 mL). After 10 min, the cooling bath was removed and stirring continued a further 10 h whereupon the mixture was poured onto water (15 mL) and extracted with ether (3 × 15 mL). The combined organic extracts were washed successively with sat. aq. $NaHCO_3$ (15 mL), 10% aq. $Na_2S_2O_3$ (15 mL), water (15 mL) and brine (15 mL) before drying over $MgSO_4$ and concentration *in vacuo*. Purification by column chromatography (20 : 1 petrol : ether) gave the product (**28**) (100 mg, 99%) as a colourless oil; R_f 0.59 (2 : 1 petrol : ether); δ_H (400 MHz, $CDCl_3$) 2.58 (1 H, app. ddq, *J* 17.6, 8.8, 2.1, C*H*H′), 2.83 (1 H, dm, *J* 17.6, CH*H*′), 4.06–4.10 (1 H, m, $CHCCl_2$), 4.27 (1 H, dddd, *J* 8.8, 7.3, 1.2, 0.4, CHCO), 5.79–5.83 (1 H, m) and 6.04–6.07 (1 H, m, HC=CH); δ_C (100 MHz, $CDCl_3$) 35.2, 58.6, 59.5, 88.0, 128.4, 136.8, 197.8.

2,2-Dibromo-1-(1,4-dimethylcyclohex-3-enyl)ethanol (30)

To a stirred solution of diisopropylamine (2.33 mL, 16.6 mmol) in THF (10 mL) at 0 °C was added butyllithium (9.4 mL of a 1.6 M solution in hexanes, 15.1 mmol). After 30 min this solution was added dropwise *via* cannula to a −78 °C stirred solution of aldehyde **29** (1.39 g, 10.1 mmol) and dibromomethane (2.12 mL, 30.2 mmol) in THF (20 mL) over *ca.* 30 min. After a further 5 min, the mixture was poured onto 1 M hydrochloric acid (75 mL) and extracted with ether (3 × 50 mL). The combined organic extracts were washed successively with water (50 mL) and brine (50 mL), dried over $MgSO_4$ and concentrated *in vacuo*. Purification by column chromatography (15 : 1 petrol : ether) gave the product (**30**) (2.71 g, 86%), a *ca.* 1 : 1 mixture of diastereomers, as a colourless oil; R_f 0.43 (4 : 1 petrol : ether); ν_{max} (thin film)/cm^{-1} 3463s, br, 2914s, 1446s, 1379s, 1206m, 1146m, 1082s, 1031m; δ_H (400 MHz, $CDCl_3$) 1.03 (3 H, s, CH_3CCH(OH)), 1.24–1.32 (0.5 H, m), 1.34–1.43 (0.5 H, m), 1.48–1.58 (1 H, m), 1.66–1.77 (1 H, m), 1.87–2.02 (2 H, m) and 2.17–2.23 (1 H, m, 3 × CH_2) overlays 1.64 (1.5 H, s) and 1.65 (1.5 H, s, CH_3C=), 2.54 (1 H, app. br s, OH), 3.81 (0.5 H, app. s) and 3.86 (0.5 H, app. s, C*H*OH), 5.26–5.29 (1 H, m, CH=), 6.10 (0.5 H, d, *J* 1.2) and 6.14 (0.5 H, d, *J* 1.2, $CHBr_2$); δ_C (100 MHz, $CDCl_3$) 19.1, 19.6, 23.2, 23.3, 26.7, 26.9, 30.7, 31.6, 34.6, 34.8, 37.6, 37.7, 48.8, 48.9, 82.7, 83.0, 118.2, 119.0, 132.2, 133.2; *m*/*z* (CI+) 313 (10%, M($^{81}Br^{79}Br)H^+$), 215 (13), 213 (12), 153 (32), 151 (59), 135 (58), 134 (19), 133 (31), 109 (100), 108 (46); Accurate Mass: Found: 310.9642; $C_{10}H_{17}{}^{79}Br_2O$ (MH$^+$) requires: 310.9646.

3-Dibromomethyl-1,4-dimethyl-6-phenylseleno-2-oxabicyclo[2.2.2]octane (31)

Following the general procedure for selenocyclisation, halocarbinol **30** (1.87 g, 6.0 mmol), gave, after column chromatography (50 : 1 petrol : ether), selenide **31** (2.49 g, 89%), a *ca.* 1 : 1 mixture of diastereomers, as a yellow oil; R_f 0.54 (4 : 1 petrol : ether); ν_{max} (thin film)/cm^{-1} 2931s, 1578m, 1464s, 1380m, 1350w, 1300w, 1231m, 1145s, 1073s, 1022s; δ_H (400 MHz, $CDCl_3$) 0.92 (1.5 H, s) and 0.96 (1.5 H, s, CH_3CCH(OR)), 1.29 (3 H, s, CH_3C(OR)), 1.35–1.58 (2.5 H, m), 1.65 (0.5 H, dd, *J* 13.8, 5.7), 1.81–1.89 (1 H, m), 2.04–2.20 (1 H, m), 2.25 (0.5 H, ddd, *J* 14.4, 11.0, 3.8) and 2.87 (0.5 H, ddd *J* 14.8, 10.9, 3.6, 3 × CH_2), 3.65 (0.5 H, ddd, *J* 10.6, 5.7, 2.6) and 3.81 (0.5 H, ddd, *J* 10.9, 6.2, 2.8, CHSe), 4.06 (0.5 H, d, *J* 3.2) and 4.11 (0.5 H, d, *J* 1.6, CH(OR)), 5.84–5.85 (1 H, m, $CHBr_2$), 7.26–7.30 (3 H, m) and 7.51–7.61 (2 H, m, Ph); δ_C (100 MHz, $CDCl_3$) 22.3, 23.4, 25.7, 25.8, 26.7, 28.4, 29.4, 34.1, 34.7, 36.6, 38.5, 45.1, 45.2, 45.4, 45.9, 47.1, 74.6, 75.0, 85.2, 85.5, 127.3, 127.4, 129.1 (two peaks), 130.1, 130.3, 133.7, 133.8; *m*/*z* (CI+) 467 (8%, M($^{79}Br_2{}^{80}Se$ and $^{79}Br^{81}Br^{78}Se)H^+$), 224 (14), 207 (10), 131 (27), 70 (100); Accurate Mass: Found: 466.9113; $C_{16}H_{21}{}^{79}Br_2O^{80}Se$ (MH$^+$) requires: 466.9124.

3-(*Z*)-Bromomethylene-1,4-dimethyl-6-phenylseleno-2-oxabicyclo[2.2.2]octane

To a stirred solution of dibromide **31** (225 mg, 0.48 mmol) in THF (5 mL) at 0 °C was added potassium *tert*-butoxide (216 mg, 1.93 mmol). After 15 min, the cooling bath was removed and stirring continued a further 3 h whereupon the mixture was poured onto water (20 mL) and extracted with ether (3 × 20 mL). The combined organic extracts were washed with water (20 mL) and brine (20 mL), dried over $MgSO_4$ and concentrated *in vacuo.* Purification by column chromatography (15 : 1 petrol : ether) gave the title compound as a yellow oil (168 mg, 91%); R_f 0.55 (4 : 1 petrol : ether); ν_{max} (thin film)/cm^{-1} 2931s, 1578s, 1465s, 1380s, 1350m, 1300w, 1231m, 1145s, 1073s, 1022s; δ_H (400 MHz, C_6D_6) 0.67 (3 H, s, CH_3CC(OR)), 1.26–1.31 (2 H, m, MeC(OR)C*H*H′C*H*H′), 1.40 (3 H, s, CH_3C(OR)), 1.48–1.60 (2 H, m, MeC(OR)CH_2C*H*′ overlays SeCHC*H*H′), 1.90 (1 H, app. tdd, *J* 12.6, 2.0, 1.0, SeCHCH*H*′), 2.06–2.13 (1 H, m, MeC(OR)CH*H*′), 3.47 (1 H, ddd, *J* 12.6, 6.0, 2.8, C*H*Se), 4.87 (1 H, s, C*H*Br), 7.02–7.09 (3 H, m) and 7.37–7.45 (2 H, m, Ph); δ_C (100 MHz, C_6D_6) 22.2, 25.6, 29.3, 32.3, 36.0, 43.0, 46.7, 73.6, 79.2, 127.8, 129.6, 130.6, 134.1, 161.8; *m*/*z* (CI+) 389 (32%, M($^{81}Br^{80}Se)H^+$), 387 (41, M($^{81}Br^{78}Se$ and $^{79}Br^{80}Se)H^+$), 385 (21, M($^{79}Br^{78}Se)H^+$), 307 (11), 231 (15), 153 (53), 151 (100), 148 (60), 122 (31), 109 (43), 107 (40), 93 (31), 78 (57), 70 (42); Accurate Mass: Found: 386.9865; $C_{16}H_{20}{}^{79}BrO^{80}Se$ (MH$^+$) requires: 386.9863.

3-(*Z*)-Bromomethylene-1,4-dimethyl-2-oxabicyclo[2.2.2]oct-5-ene (32)

Method A. To a stirred solution of 3-(*Z*)-bromomethylene-1,4-dimethyl-6-phenylseleno-2-oxabicyclo[2.2.2]octane (306 mg, 0.79 mmol) in THF (5 mL) and water (2 mL) at 0 °C was added $Na_2CO_3{\cdot}1.5H_2O_2$ (248 mg, 1.58 mmol). After 15 min, the cooling bath was removed and stirring continued 16 h, whereupon the mixture was poured onto water (20 mL) and extracted with ether (3 × 20 mL). The combined organic extracts were washed with water (20 mL) and brine (20 mL), dried over $MgSO_4$ and concentrated *in vacuo.* Purification by column chromatography (50 : 1 petrol : ether) gave the product (**32**) (164 mg, 91%) as an oil; R_f 0.55 (4 : 1 petrol : ether); ν_{max} (thin film)/cm^{-1} 2961s, 1641s, 1454m, 1380m, 1367m, 1325m, 1272m, 1245m, 1107s, 1084s, 940s; δ_H (400 MHz, C_6D_6) 0.93–1.06 (1 H, m, MeC(OR)CH_2C*H*H′) obscured by 1.00 (3 H, s, CH_3CC(OR)), 1.15 (1 H, ddd, *J* 12.6, 12.0, 3.0, MeC(OR)C*H*H′), 1.31 (1 H, ddd, *J* 12.0, 9.4, 3.0, MeC(OR)CH_2CH*H*′), 1.41 (3 H, s, CH_3CO), 1.67 (1 H, ddd, *J* 12.6, 9.4, 5.0, MeC(OR)CH*H*′), 4.88 (1 H, s, =CHBr), 5.84 (1 H, d, *J* 7.9) and 5.93 (1 H, d, *J* 7.9, HC=CH); δ_C (100 MHz, C_6D_6) 20.2, 23.2, 31.7, 33.8, 40.6, 72.0, 76.6, 135.5, 137.4, 159.9; *m*/*z* (CI+) 248 (22%, M(^{81}Br)NH_4^+), 246 (20), 231 (41), 229 (40), 168 (25), 108 (100), 93 (22); Accurate Mass: Found: 229.0230; $C_{10}H_{14}{}^{79}BrO$ (MH^+) requires: 229.0228.

Method B. To a stirred solution of 3-dibromomethyl-6-bromo-1,4-dimethyl-2-oxabicyclo[2.2.2]octane (prepared from halocarbinol **30** as detailed below) (163 mg, 0.42 mmol) in THF (4 mL) at 0 °C was added potassium *tert*-butoxide (374 mg, 3.34 mmol). After 15 min, the cooling bath was removed and stirring continued for 16 h. The mixture was then poured onto water (10 mL) and extracted with ether (3 × 10 mL), The combined organic extracts were washed with water (10 mL) and brine (10 mL), dried over $MgSO_4$ and concentrated *in vacuo.* Purification, as above, gave the product (**32**) (93 mg, 96%); data as above.

Method C (variant of Method B). Following the individually detailed procedures with no intermediate purification aldehyde **29** (5.35 g, 38.8 mmol) afforded bromoenol ether **32** (5.4 g, 61% over three steps).

3-Dibromomethyl-6-bromo-1,4-dimethyl-2-oxabicyclo[2.2.2]octane

To a stirred solution of halocarbinol **30** (402 mg, 1.29 mmol) in dichloromethane (10 mL) at 0 °C was added CSA (30 mg, 0.129 mmol) and NBS (287 mg, 1.61 mmol). After 15 min, the cooling bath was removed and stirring continued for 4 h, whereupon the mixture was poured onto water (50 mL) and extracted with ether (3 × 50 mL). The combined organic extracts were washed successively with sat. aq. $NaHCO_3$ (50 mL), 10% aq. $Na_2S_2O_3$ (50 mL), water (50 mL) and brine (50 mL), dried over $MgSO_4$ and concentrated *in vacuo.* Purification by column chromatography (50 : 1 petrol : ether) afforded the title compound (459 mg, 91%), a *ca.* 1 : 1 mixture of, as a colourless oil; R_f 0.60 (4 : 1 petrol : ether); ν_{max} (thin film)/cm^{-1} 2934s, 1465s, 1381s, 1145m, 1074s, 1041s, 877m; δ_H (400 MHz, $CDCl_3$) 0.92 (1.5 H, s) and 1.00 (1.5 H, s, CH_3CCH(OR)), 1.34 (1.5 H, s) and 1.37 (1.5 H, s, CH_3C(OR)), 1.45–1.60 (1 H, m), 1.76–1.92 (2 H, m), 1.93–2.06 (1 H, m), 2.18–2.27 (0.5 H, m), 2.30–2.40 (1 H, m) and 3.10 (0.5 H, ddd, *J* 15.2, 10.2, 3.2, 3 × CH_2), 3.99 (0.5 H, d, *J* 4.0) and 4.09 (0.5 H, s, CH(OR)), 4.07–4.15 (0.5 H, m) and 4.29 (0.5 H, ddd, *J* 10.2, 4.6, 1.8, CHBr), 5.80–5.81 (1 H, $CHBr_2$); δ_C (100 MHz, $CDCl_3$) 21.7, 23.7, 24.9, 25.0, 26.0, 26.9, 27.7, 34.2, 35.1, 36.0, 41.4, 44.5, 44.9, 49.2, 51.0, 51.2, 72.1, 73.5, 84.9, 85.5 (two peaks); *m*/*z* (CI+) 391 (10%, M(^{81}Br^{79}Br_2)H^+), 389 (12), 313 (31), 311 (74), 309 (33), 266 (22), 264 (17), 249 (43), 247 (44), 233 (67), 231 (77), 219 (37), 217 (36), 186 (17), 169 (100), 151 (66), 141 (32), 125 (22); Accurate Mass: Found: 387.8619; $C_{10}H_{15}{}^{79}Br_3O$ (M^+) requires: 387.8673.

8-Bromo-3,6-dimethylbicyclo[4.2.0]oct-2-en-7-one (33)

To a stirred solution of enol ether **32** (165 mg, 0.72 mmol) in dichloromethane (2 mL) at 0 °C was added dropwise dimethylaluminium chloride (0.14 mL of a 1 M solution in dichloromethane, 0.14 mmol). After 10 min the mixture was poured onto sat. aq. $NaHCO_3$ (10 mL) and extracted with ether (3 × 10 mL). The combined organic extracts were washed successively with 1 M hydrochloric acid (10 mL) and brine (10 mL), dried over $MgSO_4$ and concentrated *in vacuo*. Purification by column chromatography (30 : 1 petrol : ether) afforded the product (**33**), as an oil and as a 3 : 1 mixture of *endo* : *exo* diastereomers (119 mg, 72%); R_f 0.38 (4 : 1 petrol : ether); ν_{max} (thin film)/cm^{-1} 2927s, 1784s, 1445m, 1379m, 1265m, 1037m, 1003s; Data for *exo*-bromide: δ_H (400 MHz, $CDCl_3$) 1.33 (3 H, s, CH_3CC=O), 1.56 (1 H, app. dt, *J* 13.5, 4.9, =C(Me)CH_2C*H*H′), 1.71–1.80 (1 H, m, =C(Me)C*H*H′) overlays 1.77 (3 H, s, CH_3C=), 1.84–2.01 (2 H, m, CH*H*′CH*H*′), 2.61 (1 H, app. s, C*H*CHBr), 4.62 (1 H, d, *J* 6.6, C*H*Br), 5.75–5.80 (1 H, m, =CH); δ_C (100 MHz, $CDCl_3$) 21.1, 24.0, 25.4, 25.8, 44.3, 53.2, 58.0, 118.9, 137.7, 206.2; Data for *endo*-bromide: δ_H (400 MHz, $CDCl_3$) 1.32–1.42 (1 H, m, =C(Me)CH_2C*H*H′) overlays 1.37 (3 H, s, CH_3CC=O), 1.74 (3 H, s, CH_3C=), 1.81–2.05 (3 H, m, =C(Me)CH_2CH*H*′), 2.89 (1 H, app. ddd, *J* 8.4, 4.5, 1.3, C*H*CHBr), 5.28 (1 H, d, *J* 8.4, CHBr), 5.37–5.40 (1 H, m, =CH); δ_C (100 MHz, $CDCl_3$) 23.2, 24.0, 26.8, 28.7, 37.7, 53.8, 58.9, 119.3, 138.3, 207.3; *m*/*z* (CI+) 248 (12%, M(^{81}Br)NH_4^+), 246 (12, M(^{79}Br)NH_4^+), 151 (37), 121 (21), 108 (100), 93 (20), 91 (16), 69 (35); Accurate Mass: Found: 246.0506; $C_{10}H_{17}{}^{79}BrNO$ (MNH_4^+) requires: 246.0494.

3-(*Z*)-(*p*-Methoxyphenyl)methylene-1,4-dimethyl-2-oxabicyclo[2.2.2]oct-5-ene (36)

Following the general procedure for cross coupling, bromide **32** (228 mg, 1.0 mmol) gave, after column chromatography (50 : 1 petrol : ether), enol ether **36** as a colourless oil (202 mg, 79%); R_f 0.47 (4 : 1 petrol : ether); ν_{max} (thin film)/cm^{-1} 2933m, 1654s, 1609m, 1509s, 1460m, 1381m, 1349m, 1244s, 1177m, 1106s, 1036m, 950m, 836m; δ_H (400 MHz, C_6D_6) 1.22 (1 H, app. td, *J* 11.4, 4.7, MeC(OR)CH_2C*H*H′), 1.25–1.32 (1 H, m, MeC(OR)C*H*H′) overlays 1.29 (3 H, s, CH_3CC(OR)=), 1.46–1.45 (1 H, m, MeC(OR)CH_2CH*H*′) overlays 1.50 (3 H, s, CH_3CO), 1.80 (1 H, app. ddd, *J* 12.1, 9.6, 4.7, MeC(OR)CH*H*′), 3.45 (3 H, s, OCH_3), 5.36 (1 H, s, ArC*H*=), 6.03 (2 H, app. s, HC=CH), 7.02 (2 H, d, *J* 9.0) and 7.93 (2 H, d, *J* 9.0, Ar); δ_C (100 MHz, C_6D_6) 21.2, 23.6, 32.3, 34.2, 39.9, 54.9, 75.8, 94.9, 114.1, 129.4, 131.2,

134.7, 138.3, 157.1, 157.6; *m/z* (CI+) 274 (MNH_4^+, 24%), 257 (MH^+, 62), 224 (31), 131 (100), 94 (24); Accurate Mass: Found: 257.1537; $C_{17}H_{21}O_2$ requires: 257.1542.

3-(*Z*)-(*p*-Methylphenyl)methylene-1,4-dimethyl-2-oxabicyclo[2.2.2]oct-5-ene (37)

Following the general procedure for cross coupling, bromide **32** (228 mg, 1.0 mmol) gave, after column chromatography (50 : 1 petrol : ether), enol ether **37** as an oil (185 mg, 77%); R_f 0.63 (4 : 1 petrol : ether); ν_{max} (thin film)/cm^{-1} 2932s, 1652s, 1512m, 1455m, 1076m, 948m; δ_H (400 MHz, C_6D_6) 1.17–1.31 (2 H, m, MeC(OR)C*H*H′C*H*H′) overlays 1.26 (3 H, s, CH_3CO), 1.42–1.55 (1 H, m, MeC(OR)CH_2CH*H*′) overlays 1.50 (3 H, s, CH_3CC(OR)=), 1.79 (1 H, app. ddd, *J* 12.1, 9.6, 4.7, MeC(OR)CH*H*′), 2.28 (3 H, s, Ar-CH_3), 5.38 (1 H, s, ArC*H*=), 6.01 (2 H, app. s, HC=CH), 7.23 (2 H, d, *J* 7.9) and 7.90 (2 H, d, *J* 7.9, Ar); δ_C (100 MHz, C_6D_6) 21.2, 21.4, 23.6, 32.3, 34.1, 40.0, 76.0, 95.4, 128.6, 129.8, 134.0, 134.7, 135.6, 138.2, 158.1; *m/z* (CI+) 242 (25%), 241 (100, MH^+), 131 (56); Accurate Mass: Found: 241.1592; $C_{17}H_{21}O$ (MH^+) requires: 241.1592.

3-(*Z*)-Benzylidene-1,4-dimethyl-2-oxabicyclo[2.2.2]oct-5-ene (38)

Following the general procedure for cross coupling, bromide **32** (230 mg, 1.0 mmol) gave, after chromatography (50 : 1 petrol : ether), enol ether **38** (150 mg, 66%) as a colourless oil; R_f 0.57 (4 : 1 petrol : ether); ν_{max} (thin film)/cm^{-1} 2933s, 1651s, 1600w, 1448m, 1381m, 1245w, 1079s, 949s; δ_H (400 MHz, C_6D_6) 1.16–1.33 (2 H, m, MeC(OR)C*H*H′C*H*H′) overlays 1.27 (3 H, s, CH_3CC(OR)=), 1.47–1.54 (1 H, m, MeC(OR)CH_2CH*H*′) overlays 1.48 (3 H, s, CH_3CO), 1.74–1.80 (1 H, m, MeC(OR)CH*H*′), 5.39 (1 H, s, PhC*H*=), 6.01 (2 H, app. s, HC=CH), 7.16 (1 H, app. td, *J* 7.3, 1.1), 7.47 (2 H, app. t, *J* 7.3) and 7.98 (2 H, app. dd, *J* 7.3, 1.1, Ph); δ_C (100 MHz, C_6D_6) 21.1, 23.5, 32.2, 34.1, 40.0, 76.1, 95.5, 125.0, 128.7, 128.9, 134.8, 138.1, 138.4, 159.0; *m/z* (CI+) 227 (10%, MH^+), 131 (15), 87 (22), 70 (100), 55 (22); Accurate Mass: Found: 227.1443; $C_{16}H_{19}O$ (MH^+) requires: 227.1436.

3-(*Z*)-(*p*-Trifluoromethylphenyl)methylene-1,4-dimethyl-2-oxabicyclo[2.2.2]oct-5-ene (39)

Following the general procedure for cross coupling, bromide **32** (228 mg, 1.0 mmol) gave, after column chromatography (50 : 1 petrol : ether), enol ether **39** as a colourless oil (179 mg, 61%); R_f 0.62 (4 : 1 petrol : ether); ν_{max} (thin film)/cm^{-1} 2937s, 1648s, 1611s, 1459m, 1415m, 1324s, 1245m, 1211s, 1163s, 1113s, 1069s, 1017s, 951s, 849s; δ_H (400 MHz, C_6D_6) 1.15 (1 H, ddd, *J* 11.5, 11.4, 4.7, MeC(OR)CH_2C*H*H′), 1.22–1.28 (1 H, m, MeC(OR)C*H*H′) overlays 1.24 (3 H, s, CH_3CC(OR)=), 1.43–1.48 (1 H, m, MeC(OR)CCH_2CH*H*′) overlays 1.45 (3 H, s, CH_3CO), 1.69 (1 H, app. ddd, *J* 12.2, 9.6, 4.7, MeC(OR)CH*H*′), 5.23 (1 H, s, ArC*H*=), 5.90–6.00 (2 H, m, HC=CH), 7.56 (2 H, d, *J* 8.1) and 7.76 (2 H, d, *J* 8.1, Ar); δ_C (100 MHz, C_6D_6) 21.3, 23.2, 32.6, 33.9, 40.2, 76.8, 94.2, 125.4 (q, *J* 4.0), 125.8 (q, *J* 269.0), 126.0 (q, *J* 32.0), 126.8, 134.8, 137.8, 142.0, 161.6; δ_F (376.5 MHz, C_6D_6) −61.41; *m/z* (CI+) 296 (22%), 295 (100, MH^+); Accurate Mass: Found: 295.1296; $C_{17}H_{18}F_3O$ (MH^+) requires: 295.1310.

3-(*Z*)-(*p*-Nitrophenyl)methylene-1,4-dimethyl-2-oxabicyclo[2.2.2]oct-5-ene (40)

Following the general procedure for cross coupling, bromide **32** (228 mg, 1.0 mmol) gave, after column chromatography (30 : 1 petrol : ether), enol ether **40** as a yellow oil (149 mg, 55%); R_f 0.47 (4 : 1 petrol : ether); ν_{max} (thin film)/cm^{-1} 2934w, 1636m, 1585m, 1506s, 1335s, 1245w, 1183w, 1109m, 1081s, 1057m, 949m, 858m; δ_H (400 MHz, C_6D_6) 1.11–1.18 (1 H, m) and 1.19–1.25 (1 H, m, MeC(OR)C*H*H′C*H*H′) overlays 1.20 (3 H, s, CH_3CC(OR)=), 1.30–1.38 (1 H, m, MeC(OR)CH_2CH*H*′), 1.44 (3 H, s, CH_3CO), 1.59–1.66 (1 H, m, MeC(OR)CH*H*′), 5.17 (1 H, s, ArC*H*=), 5.91 (1 H, d, *J* 7.9) and 5.95 (1 H, d, *J* 7.9, CH=CH), 7.59 (2 H, d, *J* 7.2) and 8.13 (2 H, d, *J* 7.2, Ar); δ_C (100 MHz, C_6D_6) 20.7, 22.7, 31.7, 33.7, 40.6, 77.5, 94.2, 123.9, 127.8, 134.9, 137.5, 144.8, 145.0, 163.7; *m/z* (CI+) 272 (5%, MH^+), 225 (12), 224 (48), 149 (100), 132 (15), 131 (62), 87 (21), 70 (23); Accurate Mass: Found: 272.1287; $C_{16}H_{18}NO_3$ (MH^+) requires: 272.1287.

3-(*Z*)-(2-Furyl)methylene-1,4-dimethyl-2-oxabicyclo[2.2.2]oct-5-ene (41)

Following the general procedure for cross coupling, bromide **32** (228 mg, 1.0 mmol) gave, after column chromatography (50 : 1 petrol : ether), enol ether **41** as a colourless oil (112 mg, 52%); R_f 0.63 (4 : 1 petrol : ether); ν_{max} (thin film)/cm^{-1} 2934s, 1658s, 1615s, 1495m, 1458m, 1381s, 1337s, 1220m, 1085s, 1058m, 955s, 936s; δ_H (400 MHz, C_6D_6) 1.09–1.13 (1 H, m, MeC(OR)CH_2C*H*H′) overlays 1.13 (3 H, s, CH_3CC(OR)=), 1.23 (1 H, ddd, *J* 12.6, 11.0, 2.8, MeC(OR)C*H*H′), 1.39 (1 H, ddd, *J* 11.4, 9.5, 2.8, MeC(OR)CH_2CH*H*′), 1.46 (3 H, s, CH_3C(OR), 1.71 (1 H, ddd, *J* 12.6, 9.5, 4.6, MeC(OR)CH*H*′), 5.57 (1 H, s, furan-C*H*=), 5.88–6.02 (2 H, m, CH=CH), 6.46 (1 H, app. s), 6.89 (1 H, app. s) and 7.29 (1 H, app. s, Fu); δ_C (100 MHz, C_6D_6) 20.4, 23.3, 32.0, 34.0, 39.6, 76.4, 86.6, 106.1, 111.8, 134.9, 137.8, 139.1, 153.7, 158.2; *m/z* (CI+) 217 (21%, MH^+), 70 (100); Accurate Mass: Found: 217.1228; $C_{14}H_{17}O_2$ (MH^+) requires: 217.1229.

endo-8-*p*-Methoxyphenyl-3,6-dimethylbicyclo[4.2.0]oct-2-en-7-one (42)

An NMR tube charged with a solution of enol ether **36** (116 mg, 0.45 mmol) in C_6D_6 (0.5 mL) was heated to 100 °C for 10 h. The mixture was concentrated *in vacuo* and purified by column chromatography (50 : 1 petrol : ether) to afford the product (**42**) (90 mg, 78%) as a colourless oil (dr = 8 : 1); R_f 0.53 (4 : 1 petrol : ether); ν_{max} (thin film)/cm^{-1} 2973s, 1765s, 1601s, 1513s, 1458s, 1421m, 1381m, 1255s, 1173s, 1113s, 1030s, 835s; δ_H (400 MHz, $CDCl_3$) 1.39–1.47 (1 H, m, =C(Me)CH_2C*H*H′) overlays 1.45 (3 H, s, CH_3CCO), 1.63 (3 H, s, CH_3C=), 1.85–1.91 (1 H, m, =C(Me)C*H*H′), 2.04–2.09 (2 H, m, =C(Me)CH*H*′CH*H*′), 2.90–2.95 (1 H, m, C*H*CH=), 3.78 (3 H, s, OCH_3), 4.80 (1 H, d, *J* 10.0, CHCO), 5.07–5.08 (1 H, m, CH=), 6.81 (2 H, d, *J* 8.8) and 6.98 (2 H, d, *J* 8.8, Ar); δ_C (100 MHz, $CDCl_3$) 24.0, 24.2, 27.4, 27.9, 38.7, 55.2, 58.6, 63.3, 113.5, 120.7, 126.8, 130.0, 137.0, 158.5, 214.9; *m/z* (CI+) 257 (11%, MH^+), 71 (41), 70 (100); Accurate Mass: Found: 257.1543; $C_{17}H_{21}O_2$ (MH^+) requires: 257.1542.

endo-8-_p_-Methylphenyl-3,6-dimethylbicyclo[4.2.0]oct-2-en-7-one (43)

An NMR tube charged with a solution of enol ether **37** (114 mg, 0.48 mmol) in C_6D_6 (0.5 mL) was heated to 100 °C for 16 h. The mixture was concentrated *in vacuo* and purified by column chromatography (50 : 1 petrol : ether) to afford the product (**43**) (102 mg, 89%) as a colourless oil (dr = 28 : 1); R_f 0.53 (4 : 1 petrol : ether); ν_{max} (thin film)/cm^{-1} 2922s, 1771s, 1516m, 1450m, 1378w, 1291w, 1123w, 1014m; δ_H (400 MHz, $CDCl_3$) 1.40–1.48 (1 H, m, =C(Me)CH$_2$C*H*H′) overlays 1.47 (3 H, s, CH_3CCO), 1.64 (3 H, s, CH_3C=), 1.87–1.93 (1 H, m, =C(Me)C*H*H′), 2.05–2.11 (2 H, m, =C(Me)CH*H*′C*H*H′), 2.33 (3 H, s, C*H*$_3$Ar), 2.93–2.98 (1 H, m, C*H*CH=), 4.83 (1 H, d, *J* 10.1, CHCO), 5.10–5.11 (1 H, m, CH=), 6.97 (2 H, d, *J* 7.8) and 7.09 (2 H, d, *J* 7.8, Ar); δ_C (100 MHz, $CDCl_3$) 21.2, 24.0, 24.2, 27.9, 28.2, 38.6, 58.7, 63.6, 120.5, 128.8, 128.9, 136.1, 136.5, 137.0, 214.8; *m*/*z* (CI+) 241 (15%, MH$^+$), 132 (12), 131 (21), 87 (19), 71 (24), 70 (100), 55 (23); Accurate Mass: Found: 241.1596; $C_{17}H_{21}O$ (MH$^+$) requires: 241.1592.

endo-8-Phenyl-3,6-dimethylbicyclo[4.2.0]oct-2-en-7-one (44)

An NMR tube charged with a solution of enol ether **38** (93 mg, 0.41 mmol) in C_6D_6 (0.5 mL) was heated to 100 °C for 30 h whereupon analysis by ^{1}H NMR spectroscopy indicated complete consumption of the starting material. The mixture was concentrated *in vacuo* and purified by column chromatography (50 : 1 petrol : ether) to afford the product (**44**) (68 mg, 73%), a 10.5 : 1 mixture of *endo* : *exo* isomers, as a colourless oil; R_f 0.52 (4 : 1 petrol : ether); ν_{max} (thin film)/cm^{-1} 2929s, 1770s, 1597m, 1497s, 1449m, 1219m, 1016m; δ_H (400 MHz, $CDCl_3$) Data for *endo* isomer: 1.40–1.48 (1 H, m), 1.48 (3 H, s, CH_3CCO), 1.63 (3 H, s, CH_3C=), 1.85–1.92 (1 H, m), 2.06–2.17 (2 H, m), 2.98 (1 H, dddt, *J* 10.0, 5.6, 2.8, 1.4, C*H*CH=), 4.87 (1 H, d, *J* 10.0, C*H*Ph), 5.06–5.10 (1 H, m, CH=), 7.06–7.09 (2 H, m) and 7.20–7.37 (3 H, m, Ph); Data for *exo* isomer: 1.21 (3 H, s, CH_3CCO), 1.40–1.48 (1 H, m), 1.62–1.70 (1 H, m), 1.79 (3 H, s, CH_3C=), 2.06–2.17 (2 H, m), 2.55–2.59 (1 H, m, C*H*CH=), 4.26 (1 H, d, *J* 8.1, C*H*Ph), 5.82 (1 H, app. s, CH=), 7.06–7.09 (2 H, m) and 7.20–7.37 (3 H, m, Ph); δ_C (100 MHz, $CDCl_3$) Data for *endo* isomer: 24.0, 24.2, 27.3, 27.9, 38.6, 58.8, 63.8, 120.5, 126.9, 128.0, 128.9, 134.7, 137.1, 214.6; Data for *exo* isomer: 18.9, 24.0, 25.3, 28.2, 40.7, 56.9, 68.1, 121.3, 127.1, 128.1, 128.7, 134.7, 136.2, 212.6; *m*/*z* (CI+) 227 (12%, MH$^+$), 131 (25), 87 (26), 71 (53), 70 (100), 58 (13); Accurate Mass: Found: 227.1447; $C_{16}H_{19}O$ (MH$^+$) requires: 227.1436.

8-_p_-Trifluoromethylphenyl-3,6-dimethylbicyclo[4.2.0]oct-2-en-7-one (45)

An NMR tube charged with a solution of enol ether **39** (106 mg, 0.36 mmol) in C_6D_6 (0.5 mL) was heated to 100 °C for 100 h. The mixture was then concentrated *in vacuo* and purified by column chromatography (50 : 1 petrol : ether) to afford the product (**45**) (54 mg, 51%), a 1.4 : 1 mixture of *exo* : *endo* diastereomers, as a colourless oil; R_f 0.43 (4 : 1 petrol : ether); ν_{max} (thin film)/cm^{-1} 2926m, 1774s, 1619m, 1448w, 1415w, 1378w, 1327s, 1165s, 1124s, 1069s, 1019m; δ_H (400 MHz, $CDCl_3$; resonances attributable solely to the minor isomer are marked with an asterisk) 1.22 (3 H, s) and 1.48* (3 H, s, CH_3CCO), 1.43–1.45* (1 H, m, =C(Me)CH$_2$C*H*H′), 1.61* (3 H, s) and 1.80 (3 H, s, CH_3C=), 1.69 (1 H, app. dt, *J* 13.2, 4.2, =C(Me)CH$_2$C*H*H′), 1.84–2.10 (3 H, m, =C(Me)C*H*$_2$CH*H*′), 2.55–2.58 (1 H, m) and 2.98–3.04* (1 H, m, C*H*CHAr), 4.30 (1 H, d, *J* 8.0) and 4.89* (1 H, d, *J* 10.0, C*H*Ar), 5.05–5.06* (1 H, m) and 5.79–5.80 (1 H, m, C*H*=), 7.21* (2 H, app. d, *J* 8.4), 7.34 (2 H, app. d, *J* 8.0), 7.53* (2 H, app. d, *J* 8.4) and 7.60 (2 H, app. d, *J* 8.0, Ar); δ_C (100 MHz, $CDCl_3$, unable to resolve ^{13}C–^{19}F coupling in this spectrum) 18.9, 23.9, 24.0 (two peaks), 25.2, 27.3, 27.8, 28.0, 38.5, 40.4, 57.2, 59.2, 63.1, 67.5, 119.9, 120.8, 122.8, 122.9, 124.9, 125.0, 125.3, 125.5, 127.4, 129.0, 136.8, 137.8, 138.7, 140.6, 211.2, 213.2; δ_F (376.5 MHz, $CDCl_3$) −62.49; *m*/*z* (CI+) 296 (14%, MH$^+$), 295 (100), 131 (63), 87 (28); Accurate Mass: Found: 295.1313; $C_{17}H_{18}F_3O$ (MH$^+$) requires: 295.1310.

8-_p_-Nitrophenyl-3,6-dimethylbicyclo[4.2.0]oct-2-en-7-one (46)

An NMR tube charged with a solution of enol ether **40** (108 mg, 0.40 mmol) in C_6D_6 (0.5 mL) was heated to 100 °C for 100 h. The mixture was then concentrated *in vacuo* and purified by column chromatography (50 : 1 petrol : ether) to afford the product (**46**) (39 mg, 36%), a 3.3 : 1 *exo* : *endo* mixture of diastereomers, as a colourless oil; R_f 0.31 (4 : 1 petrol : ether); ν_{max} (thin film)/cm^{-1} 2925m, 1771s, 1599m, 1519s, 1448w, 1346s, 1109w, 1018w; δ_H (400 MHz, $CDCl_3$; resonances attributable solely to the minor isomer are marked with an asterisk) 1.22 (3 H, s) and 1.49* (3 H, s, CH_3CCO), 1.40–1.48* (1 H, m, =C(Me)CH$_2$C*H*H′), 1.60* (3 H, s) and 1.81 (3 H, s, CH_3C=), 1.70 (1 H, app. dt, *J* 13.6, 4.4, =C(Me)CH$_2$C*H*H′), 1.85–2.10 (3 H, m, =C(Me)C*H*$_2$CH*H*′), 2.57–2.60 (1 H, m) and 3.02–3.08* (1 H, m, C*H*CHAr), 4.34 (1 H, d, *J* 8.3) and 4.94* (1 H, d, *J* 10.0, C*H*Ar), 4.95–5.04* (1 H, m) and 5.80–5.81 (1 H, m, C*H*=), 7.27* (2 H, app. d, *J* 9.2), 7.43 (2 H, app. d, *J* 8.8), 8.14* (2 H, app. d, *J* 9.2) and 8.20 (2 H, app. d, *J* 8.8, Ar); δ_C (100 MHz, $CDCl_3$) 18.9, 24.0 (two peaks), 25.2, 27.3, 27.8, 28.0, 38.6, 40.3, 57.5, 59.4, 65.8, 67.4, 119.6, 120.4, 123.3, 123.6, 123.9, 127.8, 128.7, 129.5, 137.2, 138.3, 142.4, 143.9, 210.2, 212.3; *m*/*z* (CI+) 272 (6%, MH$^+$), 218 (100), 201 (12), 131 (82), 70 (30); Accurate Mass: Found: 272.1287; $C_{16}H_{18}NO_3$ (MH$^+$) requires: 272.1287.

8-(2-Furyl)-3,6-dimethylbicyclo[4.2.0]oct-2-en-7-one (47)

An NMR tube charged with a solution of enol ether **41** (87 mg, 0.40 mmol) in C_6D_6 (0.5 mL) was heated to 100 °C for 22 h whereupon analysis by ^{1}H NMR spectroscopy indicated complete consumption of the starting material. The mixture was concentrated *in vacuo* and purified by column chromatography (50 : 1 petrol : ether) to afford the product (**47**) (58 mg, 67%), a 2.9 : 1 mixture of *endo* : *exo* diastereomers, as a colourless oil; R_f 0.48 (4 : 1 petrol : ether); ν_{max} (thin film)/cm^{-1} 2925m, 1777s, 1446m, 1009s; δ_H (400 MHz, $CDCl_3$; resonances attributable solely to the minor isomer are marked with an asterisk) 1.27* (3 H, s, CH_3CCO), 1.37–1.46 (1 H, m) overlays 1.42 (3 H, CH_3CCO), 1.56–1.65* (1 H, m), 1.66 (3 H, s) and 1.78* (3 H, s, CH_3C=), 1.80–2.10 (3 H, m), 2.63–2.68* (1 H, m) and 2.92–2.98 (1 H, m, CH=), 4.21* (1 H, d, *J* 7.6) and 4.87 (1 H, d, *J* 9.6, C*H*Fu), 5.22–5.23 (1 H, m) and 5.74–5.76* (1 H, m, C*H*=), 6.07–6.08 (1 H, m) and 6.15–6.16* (1 H, m, 3-Fu), 6.28–6.29 (1 H, m) and 6.33* (1 H, app. td, *J* 2.2, 0.8, 4-Fu), 7.31 (1 H, dd, *J* 1.8, 0.6) and 7.36* (1 H, dd, *J* 2.2,

1.0, 5-Fu); δ_C (100 MHz, $CDCl_3$) 19.2, 23.4, 24.0, 25.4, 25.6, 27.0, 27.8, 27.9, 38.0, 39.4, 57.8 (two peaks), 59.5, 62.0, 106.7, 108.1, 110.2, 110.3, 119.6, 120.9, 136.4, 137.5, 141.5, 142.1, 148.5, 149.9, 210.1, 211.4; *m/z* (CI+) 217 (15%, MH^+), 131 (22), 108 (27), 87 (23), 71 (52), 70 (100), 55 (32); Accurate Mass: Found: 217.1237; $C_{14}H_{17}O_2$ (MH^+) requires: 217.1229.

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