Acta Chemica Scandinavica, 1998: 52: 453–460
Printed in UK – all rights reserved

ACTA
CHEMICA SCANDINAVICA
ISSN 0904–213X

α-Hetero-substituted Furans as Dienes in [4+3] Cycloadditions with 1,3-Dimethyloxyallyl Cation for the Preparation of New Versatile Cycloheptane Synthons: A Study of the Factors Controlling the Diastereoselectivity

Angel M. Montaña,* Sandra Ribes, Pedro M. Grima and Francisca García

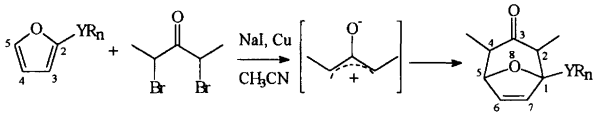
Departamento de Química Orgánica, Universidad de Barcelona, Martí i Franqués 1–11, 08028 Barcelona, Spain

Montaña, A. M., Ribes, S., Grima, P. M. and García, F., 1998. α-Hetero-substituted Furans as Dienes in [4+3] Cycloadditions with 1,3-Dimethyloxyallyl Cation for the Preparation of New Versatile Cycloheptane Synthons: A Study of the Factors Controlling the Diastereoselectivity. – Acta Chem. Scand. 52: 453–460. © Acta Chemica Scandinavica 1998.

[4+3] Cycloaddition reactions of 2-functionalized furans with 1,3-dimethyloxyallyl cation, afford versatile polyfunctionalized cycloheptane synthons. Increasing electron-donating properties and/or decreasing size of the substituent at C-2 of furan improves yield but decreases stereoselectivity. The opposite effect is also observed, so, by designing a bulky enough α-substituent it is possible to obtain *endo* stereospecificity. *cis* Stereospecificity is observed in all studied cases and it is probably determined by the type of reaction mechanism.

We present here the results of our work on the [4+3] cycloaddition reactions of 2-functionalized furans with oxyallyl cations (Fig. 1). This work is related to our research efforts oriented towards the synthesis of polyfunctionalized cycloheptanes as versatile synthons and precursors of biologically active natural products.[1] We have focused our attention on furans as dienes having a function attached at C-2 through a heteroatom (in particular atoms from groups IVA and VIA of the periodic table).

The resulting functionalization on C-1 of cycloadducts, together with the wide variety of heteroatomic linkers, (Y=O, S, Se, Si, Ge, Sn), and their different reactivity, give these products high versatility regarding modification of their structures: interconversion of functional groups, cleavage of the oxygen bridge, etc. (Fig. 2). Starting from these bicyclic cycloadducts it is possible to prepare polyfunctionalized cycloheptanes or linear heptane synthons having five different organic functions and up to five stereocenters.



Y=C, Si, Ge, Sn; O, S, Se

Fig. 1. [4+3] Cycloaddition reaction.

In the present work, fifteen different furan substrates were subjected to cycloaddition. In these reactions, a 1,3-dimethyloxyallyl cation model was used as the dienophile, owing to its symmetry, to avoid regiochemistry problems which would complicate the interpretation of results of this study. This cation was generated *in situ*[2] by reaction of 2,4-dibromo-3-pentanone with NaI and Cu, in MeCN at 60 °C.

According to the mechanism proposed by Hoffmann[1] for this type of [4+3] cycloaddition reaction, four possible racemic diastereoisomers could be formed (Fig. 3A), depending on the relative positions of substituents on C-1, C-2 and C-4 in the cycloadduct. Considering a concerted mechanism for the [4+3] cycloaddition reactions and depending on both the type of coupling (extended or compact) and the configuration of oxyallyl cation (*ZZ* or *ZE*), it is possible to obtain *cis* or *trans* as well as *endo* or *exo* cycloadducts, respectively.

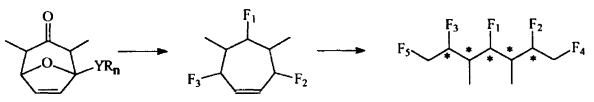


Fig. 2. Synthetic applications of bicyclic cycloadducts.

* To whom correspondence should be addressed.

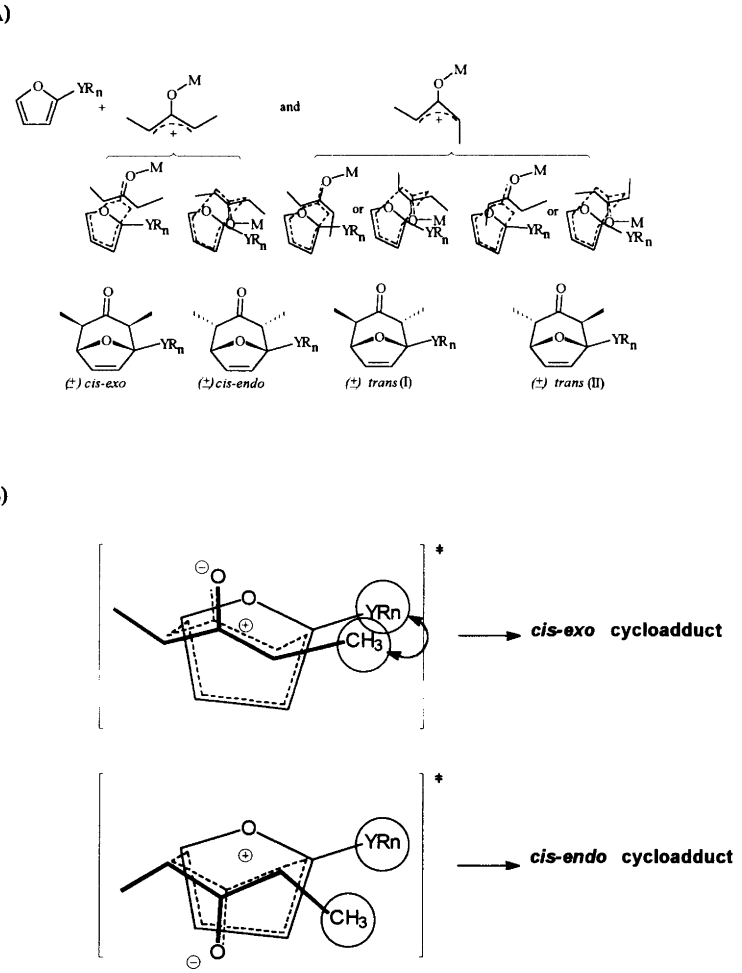


Fig. 3. (A) Possible diastereomeric cycloadducts. (B) *Cis–endo* and *cis–exo* approaches in the transition state of [4+3] cycloadditions.

Results and discussion

In this work we have analyzed both the reactivity of furans in front of the oxyallyl cation (conversion and yield), and the stereoselectivity of cycloaddition: *cis–trans* and *endo–exo* diastereoselectivity. In Table 1, results obtained from the cycloaddition reactions of 15 furan models are listed. Furans were commercially available or synthesized according to the references indicated.

By careful analysis of the experimental data in Table 1, it is possible to establish a relationship between conversion-yield and diastereoselectivity and the stereoelectronic properties of groups (YR_n) attached at C-2 of furans or their heteroatomic linkers (Y).

First of all, it is worth noting that *cis* stereospecificity was obtained in all 15 studied models. This fact might indicate that, under the reaction conditions used, the [4+3] cycloadditions take place via a concerted mechanism where the oxyallyl cation preferentially has a 'W' configuration.[2]

For substituents of type YMe_3 (Y=C, Si, Ge, Sn), (see entries 2–5), it is possible to appreciate in all cases, apart from the *cis* stereospecificity, a moderate yield of cycloaddition product (due to the volume of YMe_3 and its close proximity to reactive carbons of furan) and an increase in *endo* diastereoselectivity on going down the group, reaching *endo* stereospecificity in systems 3 and 4.

A similar effect was noted in the model system YMe (Y=O, S, Se): on progressing down group VIA an improvement in the *endo–exo* diastereoselectivity and a decrease in yield are observed. This last fact could be interpreted by taking into account that when the volume of atom Y in YMe increases it is more difficult for the cation to approximate the furan diene system, making cycloaddition less feasible (Fig. 3B). According to these experimental data, the steric effect of atom Y of groups YMe_3 and YMe should be of larger magnitude than the concomitant electronic effect, when optimising the cycloaddition outcome. This could explain how, when descending group IVA or VIA (even though the electronegativity of atom Y decreases and consequently the attached diene becomes richer in electron density), the tendency to undergo cycloaddition decreases, affording lower yields.

On the other hand, comparing functional groups with

Table 1. Yield, conversion and diastereoselectivity in [4+3] cycloadditions.

Furan substrate			Cycloaddition results			
					Diastereoselectivity	
Entry	YR_n	Preparation (Ref.)	Yield (%)	Conversion (%)	*cis*:*trans*	*endo*:*exo*
1	Me	[a]	77	93	100:0	92:8
2	CMe_3	3	9	60	100:0	67:33
3	$SiMe_3$	4	32	100	100:0	100:0
4	$GeMe_3$	5	30	100	100:0	100:0
5	$SnMe_3$	6	30	96	100:0	94:6
6	$SnBu_3$	5	67	31	100:0	100:0
7	$OSiMe_3$	[a]	86	100	100:0	95:5
8	OMe	[a]	84	96	100:0	67:33
9	SMe	6	37	65	100:0	93:7
10	SCh	6	27	63	100:0	100:0
11	SPh	7	79	60	100:0	93:7
12	SOMe	8	5	84	100:0	100:0
13	SOTol	9	28	47	100:0	88:12
14	SeMe	10	31	62	100:0	97:3
15	$SeCH_2Ph$	10	25	57	100:0	100:0

[a]Commercially available.

the same heteroatom linker, Y, it is possible to observe the stereoelectronic effects of anchored R groups. So, looking at entries 9–11 (Y=S), entries 5 and 6 (Y=Sn), or entries 14 and 15 (Y=Se), we can appreciate how the nature of group R affects the yield and stereoselectivity of the cycloadducts obtained. In all cases we noted a greater influence of the steric effect than of the inductive effect on the cycloaddition results.

Comparing entries 9 and 10 in Table 1, we observed how the larger volume of the cyclohexyl group with respect to the methyl group affords a lower yield and higher diastereoselectivity. Entries 10 and 11 (cyclohexyl and phenyl groups) show how the steric effect exerted by the cyclohexyl group overwhelms the negative inductive effect of the phenyl group. In tin derivatives, entries 5 and 6, we noted how changing the R group from Me to *n*-Bu caused the *endo* diastereoselectivity to rise and the overall yield to decrease. The same basic interpretation could be applied to the behaviour of models 14 and 15 in which subtitution of a methyl group by a phenyl group leads to a lower yield and a higher stereoselectivity.

Insertion of an oxygen atom as a 'linker' (Y=O) greatly improves the yield and slightly decreases the *endo* diastereoselectivity (compare entries 1 versus 8 and 3 versus 7). These results could be interpreted on the basis of the electron-donating nature of the sp^3 oxygen which bears two pairs of non-shared electrons (in spite of its electronegativity value), and considering that the bulky groups are farther apart in 7 and 8 than in 3 and 2, respectively.

Conclusions

Following this systematic study it is possible to establish structure–reactivity and structure–diastereoselectivity relationships in the [4+3] cycloaddition reactions of 2-functionalized furans with 1,3-dimethyloxyallyl cation. First of all it is possible to conclude that *cis–trans* diastereoselectivity does not depend on the nature of the function on C-2 of the furan substrate but on the reaction conditions (mechanism). Secondly, we note that both yield and *endo–exo* diastereoselectivity of [4+3] cycloaddition reactions of furans with 1,3-dimethyloxyallyl cation are highly affected by the pattern of substitution at C-2 of the furan diene. Bulky and/or electron-withdrawing functional groups on C-2 afford moderate to low yields. Small and/or electron-donating groups improve considerably the conversion of reagents and yield of cycloadducts. Regarding *endo–exo* diastereoselectivity it is quite clear from these experiments that increasing the size of the function attached at C-2 of the furan increases *endo* diastereoselectivity of the cycloaddition, becoming stereospecific when the substituent is bulky enough. Thirdly, it is possible to design an appropriate model with the optimum function groups at C-2 of the furan to obtain good yields and very high *endo* diastereoselectivities. For this purpose, it is necessary to insert a 'spacer', for example an oxygen atom (Y=O), which activates the furan diene through an electron-donating effect, and to put sterically demanding R groups (YR_n) away from the reactive centers of furan, but without compromising its steric discriminating effect when the furan approaches the oxyallyl cation.

Experimental

General procedures. Unless otherwise noted, all reactions were conducted under an atmosphere of dry nitrogen or argon in oven-dried glassware. Raw materials were obtained from commercial suppliers and used without further purification. All solvents were purified before use: ether, tetrahydrofuran, benzene, hexane and pentane

were distilled under nitrogen from sodium–benzophenone. Methylene chloride and acetonitrile were distilled under nitrogen from CaH_2. Infrared spectra were recorded on a FT-IR Nicolet 510 and a Perkin–Elmer 681 spectrophotometer as thin films or as solutions. NMR spectra were taken for samples in deuteriated chloroform and benzene on spectrometers at 200 MHz (Gemini-200), 300 MHz (Unity-300) and/or 500 MHz (Unity-500) for ^1H NMR, and at 50 MHz and 75.43 MHz for ^{13}C NMR. For ^1H NMR tetramethylsilane was used as an internal standard. ^{13}C NMR spectra were referenced to the δ 77.0 resonance of chloroform. Mass spectra were measured on a Hewlett–Packard 5890 mass spectrometer using electron impact and/or chemical ionization. Melting points were measured on a Gallenkamp melting point apparatus. GC analyses were performed on an HP-8790 gas chromatograph equipped with a Hewlett–Packard cross-linked MePhe–Silicone capillary column ($l=25$ m, $\varnothing=0.2$ mm, $\varepsilon=0.25$ μm) using helium as the carrier gas and an FID detector ($T=250$ °C, H_2, 4.2 psi; air, 2.1 psi). GC analyses were carried out under different temperature–time conditions as follows: [code; initial temperature (°C); initial time (min); rate (°C min^{-1}); final temperature (°C); final time (min)]: [A: 100; 1; 10; 200; 15], [B: 100; 1; 5; 200; 15], [C: 50; 1; 10; 200; 15], [D: 50; 1; 5; 200; 15], [E: 50; 1; 10; 200; 25], [F: 50; 1; 10; 100; 15], [G: 50; 1; 5; 100; 15]. Elemental analyses were obtained with a Fisons Na-1500 apparatus, analysing combustion gases by chromatography and using a thermal conductivity detector.

General procedure for the [4+3] cycloaddition reactions. A two-necked flask, fitted with a magnetic stirring bar and a Dimroth condenser, under nitrogen, was charged with the furan derivative, freshly actived copper powder and oven-dried (24 h at 150 °C) sodium iodide, in molar ratio 1:3:6 (furan:Cu:NaI), with acetonitrile as the solvent. To the resulting suspension heated to 30 °C, one equivalent of 2,4-dibromo-3-pentanone, freshly passed through a small column of activated neutral alumina, was added dropwise. The reaction was maintained under reflux and controlled by GC. The reaction time depended on the reaction kinetics of each substrate, but varied from 4 to 20 h. The reaction mixture was concentrated to dryness under vacuum at 0 °C, after which cold methylene chloride and ice–water were added. The aqueous phase was extracted six times with cold methylene chloride, and the organic phase was washed twice with cold aqueous 6% w/w ammonia followed by cold water and dried over anhydrous $MgSO_4$. The dried solution was filtered through neutral alumina and concentrated to dryness under vacuum without heating. The product was purified by flash column chromatography on silica gel, using mixtures of hexane–ethyl acetate of increasing polarity. Diastereoisomers (**a**) and (**b**) were separated under the aforementioned chromatographic conditions. All cycloaddition reactions were carried out on a 200 mg scale (for 2,4-dibromo-3-pentanone).

Physical and spectroscopic characterization of cycloadducts obtained. The determination of the relative stereochemistry of *cis/trans* and *endo/exo* diastereoisomers was established by a careful comparative study and correlation of ^1H and ^{13}C NMR spectra of cycloadducts, and by means of DEPT, COSY-90, HETCOR, PS-NOESY, HMBC and HMQC NMR experiments.

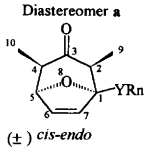
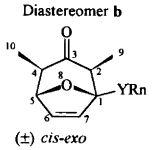
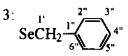
The numbering of carbons in cycloadducts is indicated in Table 2.

1,2,4-Trimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (**1**). Cycloadducts were obtained as a separable 11:1 mixture of *endo/exo* diastereoisomers **1a** and **1b**, respectively.

1a : pale yellow oil. IR (film): ν_{max} (cm^{-1}) 3400, 3000, 2950, 2875, 1730, 1610, 1450, 1390, 1340, 1260, 1150, 1125, 1060, 1015, 990, 910, 900, 840, 750. ^1H NMR (300 MHz, $CDCl_3$): δ 0.96 (3 H, d, $J=7.0$ Hz, H9), 1.01 (3 H, d, $J=7.1$ Hz, H10), 1.51 (3 H, s, H11), 2.57 (1 H, q, $J=7.0$ Hz, H2), 2.77 (1 H, dq, $J_1=7.2$ Hz, $J_2=4.6$ Hz, H4), 4.84 (1 H, dd, $J_1=4.6$ Hz, $J_2=1.6$ Hz, H5), 6.12 (1 H, d, $J=6.1$ Hz, H7), 6.25 (1 H, dd, $J_1=6.0$ Hz, $J_2=1.7$ Hz, H6). ^{13}C NMR (50 MHz, $CDCl_3$): δ 9.75 (C9), 10.11 (C10), 21.33 (C11), 49.27 (C2), 55.36 (C4), 82.24 (C5), 87.54 (C1), 132.89 (C7), 136.31 (C6), 208.79 (C3). MS (DIP-EI, 70 eV, 150 °C): *m/z* (%) 166 (16, *M*), 151 (21, $M-CH_3$), 137 (3, $M-CHO$), 110 (22, $M-C_3H_4O$), 109 (47, $M-C_3H_5O$), 95 (100, $M-C_4H_7O$, $C_5H_3O_2$), 81 (10, $M-C_5H_{10}O$). GC (A): $t_R=11.4$ min. Elemental analysis: calc. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49: Found: C, 72.31; H, 8.46%.

1b: pale yellow oil. IR (film): ν_{max} (cm^{-1}) 3400, 2950, 2925, 2865, 1700, 1650, 1450, 1390, 1270, 1225, 1200, 1190, 1110, 1100, 1080, 1030, 1000, 925, 750. ^1H NMR (300 MHz, $CDCl_3$) δ 1.26 (3 H, d, $J=7.4$ Hz, H9), 1.33 (3 H, d, $J=7.5$ Hz, H10), 1.39 (3 H, s, H11), 2.26 (1 H, q, $J=7.4$ Hz, H4), 2.26 (1 H, q, $J=7.5$ Hz, H2), 4.65 (1 H, d, $J=1.7$ Hz, H5), 6.04 (1 H, d, $J=5.9$ Hz, H7), 6.19 (1 H, dd, $J_1=6.0$ Hz, $J_2=2.0$ Hz, H6). ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.54 (C9), 17.53 (C10), 19.68

Table 2. Numbering and substitution patterns of cycloadducts at C-1.

	YR_n	YR_n
Diastereomer **a**  (±) *cis-endo*	1: CH_3	9: SCH_3
	2: $C(CH_3)_3$	10: S-$CHCH_2CH_2CH_2CH_2CH_2$
	3: $Si(CH_3)_3$	11: 
	4: $Ge(CH_3)_3$	
	5: $Sn(CH_3)_3$	12: $SeCH_3$
Diastereomer **b**  (±) *cis-exo*	6: $Sn(CH_2CH_2CH_2CH_3)_3$	
	7: $OSi(CH_3)_3$	
	8: OCH_3	13: 

(C11), 48.93 (C2), 53.35 (C4), 82.24 (C5), 87.84 (C1), 133.29 (C7), 137.75 (C6), 209 (C3). MS [DIP-EI, 70 eV, 150 °C, *m/z* (%)]: 166 (16, *M*), 151 (21, $M-CH_3$), 137 (3, $M-CHO$), 110 (22, $M-C_3H_4O$), 109 (47, $M-C_3H_5O$), 95 (100, $M-C_4H_7O$, $C_5H_3O_2$), 81 (10, $M-C_5H_{10}O$). GC (A): $t_R=11.3$ min. Elemental analysis: calc. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.28; H, 8.51%.

*2,4-Dimethyl-1-*tert*-butyl-8-oxabicyclo[3.2.1]oct-6-en-3-one* (**2**).

2a: colourless oil. IR (film): ν_{max} (cm^{-1}) 3047, 2958, 2887, 1710, 1594, 1460, 1397, 1378, 1364, 1330, 1320, 1260, 1153, 1075, 1055, 1023, 982, 960, 951, 895, 806. ^1H NMR (300 MHz, $CDCl_3$): δ 0.99 (3 H, d, $J=7.2$ Hz, H10), 1.07 (9 H, s, H2), 1.17 (3 H, d, $J=6.9$ Hz, H9), 2.75 (1 H, ddq, $J_1=7.2$ Hz, $J_2=4.8$ Hz, $J_3=0.6$ Hz, H4), 2.84 (1 H, dq, $J_1=7.2$ Hz, $J_2=0.6$ Hz, H2), 4.89 (1 H, dd, $J_1=4.8$ Hz, $J_2=1.8$ Hz, H5), 6.23 (1 H, dd, $J_1=6.3$ Hz, $J_2=1.8$ Hz, H6), 6.31 (1 H, dd, $J_1=6.8$ Hz, $J_2=0.3$ Hz, H7). ^{13}C NMR (75 MHz, $CDCl_3$): δ 11.05 (C10), 12.37 (C9), 27.30 (C2), 36.15 (C1), 50.08 (C4), 53.67 (C2), 82.77 (C5), 95.36 (C1), 132.95 (C7), 134.29 (C6), 211.08 (C3). MS (DIP-CI, NH_3, 70 eV, 150 °C): *m/z* (%) 226 (20, $M+NH_4$), 209 (42, $M+H$), 208 (13, *M*), 151 (8, $M-C_4H_9$), 136 (15, $M-C_5H_{12}$), 133 (25, $M-C_4H_{11}O$), 117 (38, $C_4H_{11}O_2$), 116 (49, $M-C_4H_{12}O_2$), 91 (100). GC (C): $t_R=13.2$ min. Elemental analysis: calc. for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.62; H, 9.51%.

2b: colourless oil. IR (film): ν_{max} (cm^{-1}) 3047, 2958, 2887, 1710, 1594, 1460, 1397, 1378, 1364, 1330, 1320, 1260, 1153, 1075, 1055, 1023, 982, 960, 951, 895, 806. ^1H NMR (200 MHz, $CDCl_3$): δ 1.07 (9 H, s, H2), 1.12 (3 H, d, $J=7.2$ Hz), 1.32 (3 H, d, $J=7.2$ Hz), 2.28 (1 H, q, $J=7.2$ Hz), 2.87 (1 H, q, $J=7.2$ Hz), 4.66 (1 H, s, H5), 6.23 (1 H, d, $J=6.6$ Hz, H6), 6.28 (1 H, d, $J=6.6$ Hz, H7). MS (DIP-CI, NH_3, 70 eV, 150 °C): *m/z* (%) 226 (23, $M+NH_4$), 209 (46, $M+H$), 208 (3, *M*), 151 (2, $M-C_4H_9$), 136 (12, $M-C_5H_{12}$), 133 (19, $M-C_4H_{11}O$), 117 (30, $C_4H_{11}O_2$), 116 (44, $M-C_4H_{12}O_2$), 91 (100). GC (C): $t_R=13.7$ min. Elemental analysis: calc. for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.80; H, 9.62%.

endo-*2,4-Dimethyl-1-trimethylsilyl-8-oxabicyclo[3.2.1]-oct-6-en-3-one* (**3**). Cycloadduct **3** was obtained as a unique diastereoisomer **3a**. No *exo* diastereoisomer was detected. Colourless oil. IR (film): ν_{max} (cm^{-1}) 2971, 1710 (C=O, st), 1588, 1449, 1378, 1337, 1250, 1154, 1042, 1000, 944, 890, 841, 753, 727. ^1H NMR (200 MHz, $CDCl_3$): δ 0.08 (9 H, s, $SiMe_3$), 0.87 (3 H, d, $J=7.0$ Hz, H9), 0.91 (3 H, d, $J=7.0$ Hz, H10), 2.69 (1 H, dq, $J_1=7.0$ Hz, $J_2=1.0$ Hz, H4), 2.70 (1 H, q, $J=7.0$ Hz, H2), 4.76 (1 H, dd, $J_1=5.0$ Hz, $J_2=1.5$ Hz, H5), 6.18 (2 H, s, H6, H7). ^{13}C NMR (75 MHz, $CDCl_3$): δ 3.18 ($SiMe_3$), 10.02 (C10), 10.66 (C9), 51.26 (C4), 52.35 (C2), 84.20 (C5), 84.87 (C1), 132.14 (C6), 134.79 (C7), 209.96 (C3). MS (DIP-EI, 70 eV, 150 °C): *m/z* (%) 224 (1, *M*), 207 (8), 195 (4, $M-C_2H_5$), 189, 159, 151 (7, $M-SiMe_3$), 121 (15, $M-SiMe_3-2Me$), 83 (51, C_5H_7O), 57 (100, C_4H_9 or C_3H_5O). GC (A): $t_R=10.4$ min. Elemental analysis: calc. for $C_{12}H_{20}O_2Si$: C, 64.24; H, 8.98. Found: C, 63.98; H, 9.05%.

endo-*2,4-Dimethyl-1-trimethylgermanyl-8-oxabicyclo-[3.2.1]oct-6-en-3-one* (**4**). Cycloadduct **4** was obtained as a unique diastereoisomer **4a**. No *exo* diastereoisomer was detected. White solid. M.p. 59–61 °C ($CHCl_3$). IR (film): ν_{max} (cm^{-1}) 3085, 2988, 2933, 2883, 1702 (C=O, st), 1650, 1458, 1420, 1379, 1342, 1304, 1250, 1167,1067,1042, 950, 892, 821, 810. ^1H NMR (500 MHz, $CDCl_3$): δ 0.25 (9 H, s, $GeMe_3$), 0.92 (3 H, d, $J=7.0$ Hz, H9), 0.93 (3 H, d, $J=7.0$ Hz, H10), 2.75 (1 H, ddq, $J_1=7.0$ Hz, $J_2=4.5$ Hz, $J_3=0.5$ Hz, H4), 2.80 (1 H, dq, $J_1=7.0$ Hz, $J_2=0.5$ Hz, H2), 4.81 (1 H, d, $J=5.0$ Hz, H5), 6.24 (2 H, d, $J=0.5$ Hz, H6, H7). ^{13}C NMR (75 MHz, $CDCl_3$): δ 3.48 ($GeMe_3$), 10.06 (C9), 10.64 (C10), 51.26 (C4), 53.13 (C2), 84.13 (C5), 86.88 (C1), 131.98 (C7), 135.33 (C6), 210.09 (C3). MS (DIP-EI, 70 eV, 150 °C): *m/z* (%) 268 (6, *M*), 255 (16, $M-CH$), 253 (12, $M-CH_3$), 251 (9, $M-OH$), 238 (1, $M-C_2H_6$), 227 (5, $M-C_3H_5$), 225 (4, $M-C_3H_7$ or C_2H_3O), 223 (4, $M-C_3H_9$), 151 (4, $M-GeMe_3$), 119 (100, $GeMe_3$), 118 (24), 117 (71), 115 (54), 109 (11), 95 (32), 91 (39). GC (A): $t_R=10.03$ min. Elemental analysis: calc. for $C_{12}H_{20}GeO_2$: C, 53.61; H, 7.50. Found: C, 54.01; H, 7.38%.

2,4-Dimethyl-1-trimethylstannyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (**5**). The cycloadducts were obtained as a separable 17:1 mixture of diastereomers **5a** and **5b**.

5a: colourless oil. IR (film): ν_{max} (cm^{-1}) 2968, 1700 (C=O, st), 1459, 1376, 1301, 1158, 1030, 947, 884, 768, 735, 619, 531, 442. ^1H NMR (200 MHz, $CDCl_3$): δ 0.19 (9 H, s, $SnMe_3$), 0.91 (3 H, d, $J=7.0$ Hz, H9), 0.92 (3 H, d, $J=7.0$ Hz, H10), 2.75 (1 H, dq, $J_1=7.0$ Hz, $J_2=3.4$ Hz, H4), 2.89 (1 H, q, $J=7.0$ Hz, H2), 4.79 (1 H, dd, $J_1=3.4$ Hz, $J_2=1.1$ Hz, H5), 6.21 (1 H, dd, $J_1=5.9$ Hz, $J_2=1.1$ Hz, H6), 6.32 (1 H, d, $J=5.9$ Hz, H7). ^{13}C NMR (50 MHz, $CDCl_3$): δ −10.33 ($SnMe_3$), 9.93 (C10), 11.16 (C9), 16.39 (C1), 51.59 (C2), 54.44 (C4), 84.10 (C5), 130.85 (C7), 137.02 (C6). MS (DIP-EI, 70 eV, 150 °C): *m/z* (%) 315 (2, *M*), 301 (5, $M-CH_2$), 273 (9, $M-C_3H_7$), 164 (60, $M-HSnMe_3$), 151 (11, $M-SnMe_3$), 149 (95, $M-SnMe_3$), 83 (84, C_5H_7O), 69 (31, C_4H_5O), 57 (100, C_4H_9 or C_4H_5O), GC (A): $t_R=17.8$ min. Elemental analysis: calc. for $C_{12}H_{20}O_2Sn$: C, 45.76; H, 6.40: Found: C, 45.82; H, 7.03%.

5b: colourless oil. IR (film): ν_{max} (cm^{-1}) 2937, 1713 (C=O, st), 1378, 1297, 1262, 1156, 1054, 934, 814. ^1H NMR (300 MHz, $CDCl_3$): δ −0.06 (9 H, s, $SnMe_3$), 0.91 (3 H, d, $J=7.1$ Hz, H9), 0.95 (3 H, d, $J=7.1$ Hz, H10), 2.74 (2 H, q, $J_1=7.1$ Hz, H2, H4), 4.78 (1 H, d, $J=4.8$ Hz, H5), 6.27 (H6, s, 2 H, H7). ^{13}C NMR (75 MHz, $CDCl_3$): δ 1.01 ($SnMe_3$), 10.11 (C9, C10),

29.70 (C1), 50.37 (C2, C4), 82.71 (C5), 133.50 (C6, C7). MS (DIP-EI, 70 eV, 150 °C): *m/z* (%) 315 (2, *M*), 301 (5, $M-CH_2$), 273 (9, $M-C_3H_7$), 164 (60, $M-HSnMe_3$), 151 (11, $M-SnMe_3$), 149 (95, $M-SnMe_3$), 83 (84, C_5H_7O), 69 (31, C_4H_5O), 57 (100, C_4H_9 or C_4H_5O). GC (A): $t_R=11.8$ min. Elemental analysis: calc. for $C_{12}H_{20}O_2Sn$: C, 45.76; H, 6.40. Found: C, 45.91; H, 6.98%.

endo-*2,4-Dimethyl-1-tributilstannyl-8-oxabicyclo[3.2.1]-oct-6-en-3-one* (**6a**). Cycloadduct **6a** was obtained as a yellowish oil. No *exo* cycloadduct was found. IR (film): ν_{max} (cm^{-1}) 3095, 2967, 2931, 2896, 2866, 1721 (C=O, st), 1677, 1458,1425, 1375, 1338, 1295, 1153, 1085, 1030, 937, 883, 818. ^1H NMR (300 MHz, $CDCl_3$): δ 0.87 (3 H, d, $J=7.5$ Hz, H10), 0.89 (9 H, t, $J=7.8$ Hz, H4′), 0.92 (3 H, d, $J=7.2$ Hz, H9), 0.97 (6 H, m, H1′), 1.31 (6 H, q, $J=7.5$ Hz, H3′), 1.50 (6 H, m, $W_{1/2}=19.1$ Hz, H2′), 2.75 (1 H, ddq, $J_1=7.2$ Hz, $J_2=4.5$ Hz, $J_3=0.6$ Hz, H4), 2.88 (1 H, q, $J=7.2$ Hz, H2), 4.76 (1 H, dd, $J_1=4.5$ Hz, $J_2=0.9$ Hz, H5), 6.17 (1 H, ddd, $J_1=6.3$ Hz, $J_2=0.9$ Hz, $J_3=0.6$ Hz, H6), 6.32 (1 H, d, $J=6.0$ Hz, H7). ^{13}C NMR (50 MHz, $CDCl_3$): δ 9.82 (C1′), 10.37 (C10), 11.84 (C9), 14.14 (C4′), 27.91 (C3′), 29.51 (C2′), 52.17 (C4), 55.32 (C2), 84.32 (C5), 90.02 (C1), 130.56 (C6), 138.28 (C7), 210.61 (C3). MS (DIP-EI, 70 eV, 150 °C): *m/z* (%) 413 (1, $M-C_2H_5$ or CHO), 385 (9, $M-C_4H_9$), 329 (27, $M-C_8H_{19}$), 328 (10, $M-C_8H_{18}$), 291 (9, $SnBu_3$), 271 (16, $M-C_{12}H_{27}$), 231 (26), 232 (18), 233 (40), 234 (25), 235 (52) ($SnBu_2$), 175 (59), 176 (31), 177 (88), 178 (28), 179 (88) (SnBu), 151 (3, $M-SnBu_3$), 116 (5), 117 (18), 118 (16), 119 (34), 120 (22) (Sn), 95 (100). GC (H): $t_R=20.51$ min. Elemental analysis: calc. for $C_{21}H_{38}O_2Sn$: C, 56.99; H, 8.66. Found: C, 57.01; H, 8.56%.

2,4-Dimethyl-1-trimethylsilyloxy-8-oxabicyclo[3.2.1]oct-6-en-3-one (**7**). The cycloadducts were obtained under Hoffmann's conditions as a separable 20:1 mixture of diastereoisomers **7a** and **7b**.

7a: colourless oil. IR (film): ν_{max} (cm^{-1}) 2960, 1715 (C=O, st), 1450, 1370, 1325, 1300, 1250, 1220, 1195, 1155, 1115, 1090, 1040, 965, 910, 880, 840, 820, 760. ^1H NMR (300 MHz, $CDCl_3$): δ 0.16 (9 H, s, $OSiMe_3$), 0.91 (3 H, d, $J=7.0$ Hz, H9), 1.03 (3 H, d, $J=7.0$ Hz, H10), 2.65 (1 H, q, $J=7.0$ Hz, H2), 2.70 (1 H, dq, $J_1=7.0$ Hz, $J_2=4.5$ Hz, H4), 4.80 (1 H, ddd, $J_1=4.5$ Hz, $J_2=2.0$ Hz, $J_3=0.5$ Hz, H5), 6.10 (1 H, dd, $J_1=6.0$ Hz, $J_2=1.0$ Hz, H7), 6.23 (1 H, ddd, $J_1=5.0$ Hz, $J_2=2.0$ Hz, $J_3=0.5$ Hz, H6). ^{13}C NMR (50 MHz, $CDCl_3$): δ 1.50 ($OSiMe_3$), 8.97 (C9), 10.28 (C10), 48.11 (C4), 57.42 (C2), 79.36 (C5), 133.67 (C7), 135.83 (C6), 208.75 (C3). MS [GC-MS (EI), 70 eV, 150 °C]: *m/z* (%) 238 (6, *M*), 163 ($M-SiMe_3$), 149 (16, $M-OSiMe_3$), 91 (16, H_2OSiMe_3), 73 (100, $SiMe_3$). GC (E): $t_R=18.4$ min. Elemental analysis: calc. for $C_{12}H_{20}O_3Si$: C, 59.96; H, 8.39. Found: C, 59.94; H, 8.63%.

7b: colourless oil. IR (film): ν_{max} (cm^{-1}) 2960, 1715 (C=O, st), 1457, 1328, 1252, 1219, 1194, 1115, 1084, 1017, 967, 888. ^1H NMR (300 MHz, $CDCl_3$): δ 0.10 (9 H, s, $OSiMe_3$), 1.25 (3 H, d, $J=7.5$ Hz, H9), 1.34 (3 H, d, $J=7.4$ Hz, H10), 1.34 (3 H, d, $J=7.4$ Hz, H10), 2.18 (1 H, q, $J=7.6$ Hz, H2), 2.51 (1 H, q, $J=7.3$ Hz, H4), 4.63 (1 H, d, $J=1.8$ Hz, H5), 6.06 (1 H, d, $J=5.9$ Hz, H7), 6.22 (1 H, dd, $J_1=5.9$ Hz, $J_2=1.9$ Hz, H6). ^{13}C NMR (50 MHz, $CDCl_3$): δ 1.50 ($OSiMe_3$), 13.23 (C10), 17.89 (C9), 47.73 (C4), 55.39 (C2), 79.91 (C5), 134.36 (C7), 136.74 (C6), 214.31 (C3). MS [GC-MS (EI, 70 eV, 150 °C]: *m/z* (%) 238 (6, *M*), 163 ($M-SiMe_3$), 149 (16, $M-OSiMe_3$), 91 (16, H_2OSiMe_3), 73 (100, $SiMe_3$). GC (E): $t_R=18.2$ min. Elemental analysis: calc. for $C_{12}H_{20}O_3Si$: C, 59.96; H, 8.39. Found: C, 59.92; H, 8.41%.

2,4-Dimethyl-1-methoxy-8-oxabicyclo[3.2.1]oct-6-en-3-one (**8**). Diastereoisomers **8a** and **8b** were formed as a 2:1 mixture, separable by column chromatography.

8a: white solid. M.p.: 60–61 °C (diethyl ether). IR (film): ν_{max} (cm^{-1}) 3105, 3005, 2960, 2920, 2860, 1710 (C=O, st), 1615, 1460, 1450, 1390, 1380, 1360, 1340, 1310, 1280, 1200, 1170, 1130, 1110, 1010, 1000, 990, 910, 830, 820, 770, 660. ^1H NMR (500 MHz, $CDCl_3$): δ 0.84 (3 H, d, $J=7.0$ Hz, H10), 0.91 (3 H, d, $J=7.0$ Hz, H9), 2.60 (1 H, q, $J=7.0$ Hz, H2), 2.62 (1 H, dq, $J_1=7.0$ Hz, $J_2=4.8$ Hz, H4), 3.28 (3 H, s, OMe), 4.73 (1 H, dd, $J_1=4.8$ Hz, $J_2=1.9$ Hz, H5), 6.06 (1 H, d, $J=6.1$ Hz, H7), 6.28 (1 H, dd, $J_1=6.1$ Hz, $J_2=1.9$ Hz, H6), ^{13}C NMR (50 MHz, $CDCl_3$): δ 8.64 (C10), 10.18 (C9), 48.01 (C4), 51.14 (OMe), 54.68 (C2), 79.00 (C5), 112.16 (C1), 132.42 (C7), 136.10 (C6), 208.11 (C3). MS (DIP-CI, NH_3, 70 eV, 150 °C): *m/z* (%) 182 (3, *M*), 167 (8, $M-CH_3$), 153 (6, $M-CHO$), 125 (37, $M-C_4H_9$ or C_3H_5O), 111 (100, $M-C_5H_{11}$ or C_4H_7O), 95 (37, $C_5H_{11}O$ or $C_4H_7O_2$), 83 (22, C_5H_7O), 67 (38, C_4H_4O). GC (B): $t_R=9.1$ min. Elemental analysis: calc. for $C_{10}H_{14}O_3$: C, 65.92; H, 7.74. Found: C, 65.67; H, 7.49%.

8b: white solid. M.p. = 61–62 °C (ethyl ether). IR (film): ν_{max} (cm^{-1}) 3100, 3000, 2970, 2895, 2850, 1730, 1715 (C=O, st), 1615, 1470, 1340, 1310, 1300, 1280, 1200, 1130, 1100, 970, 910, 820, 740. ^1H NMR (500 MHz, $CDCl_3$): δ 1.27 (3 H, d, $J=7.5$ Hz, H9), 1.36 (3 H, d, $J=7.5$ Hz, H10), 2.23 (1 H, br dq, $J_1=7.5$ Hz, $J_2<1.0$ Hz, H4), 2.54 (1 H, dq, $J_1=7.5$ Hz, $J_2<1$ Hz, H2), 3.42 (3 H, s, OMe), 4.67 (1 H, d, $J=1.9$ Hz, H5), 6.09 (1 H, d, $J=6.0$ Hz,H7), 6.33 (1 H, dd, $J_1=6.0$ Hz, $J_2=1.9$ Hz, H6), ^{13}C NMR (50 MHz, $CDCl_3$): δ 13.14 (C9), 17.83 (C10), 47.82 (C4), 51.39 (OMe), 54.05 (C2), 79.72 (C5), 110.27 (C1), 133.39 (C7), 137.01 (C6), 213.74 (C3), MS (DIP-CI, NH_3, 70 eV, 150 °C): *m/z* (%) 182 (3, *M*), 167 (8, $M-CH_3$), 153 (6, $M-CHO$), 125 (37, $M-C_4H_9$ or C_3H_5O), 111 (100, $M-C_5H_{11}$ or C_4H_7O), 95 (37, $C_5H_{11}O$, $C_4H_7O_2$), 83 (22, C_5H_7O), 67 (38, C_4H_4O). GC (B): $t_R=8.9$ min. Elemental analysis: calc. for $C_{10}H_{14}O_3$: C, 65.92; H, 7.74. Found: C, 65.82; H, 7.61%.

2,4-Dimethyl-1-methylthio-8-oxabicyclo[3.2.1]oct-6-en-3-one (**9**). Hoffmann's reaction conditions afforded a separable 13:1 mixture of diastereoisomers **9a** and **9b**.

9a: colourless oil. IR (film): ν_{max} (cm^{-1}) 3408, 3085, 2977, 2937, 2877, 2362, 1715 (C=O, st), 1592, 1457, 1378, 1339, 1295, 1262, 1192, 1156, 1086, 1034, 998, 945, 890, 812, 745, 724, 668, 625. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.98 (3 H, d, J=7.1 Hz, H10), 1.11 (3 H, d, J=7.0 Hz, H9), 2.12 (3 H, s, SMe), 2.79 (1 H, dq, J=7.2 Hz, H2), 2.81 (1 H, q, J=7.0 Hz, H4), 4.89 (1 H, dd, J_1=4.8 Hz, J_2=2.0 Hz, H5), 6.15 (1 H, d, J=6.0 Hz, H7), 6.33 (1 H, dd, J_1=5.9 Hz, J_2=1.8 Hz, H6), ^{13}C NMR (50 MHz, $CDCl_3$): δ 10.33 (C10), 10.62 (C9), 10.71 (SMe), 49.65 (C4), 54.98 (C2), 82.65 (C5), 115.60 (C1), 134.78 (C7), 135.30 (C6). MS (DIP-CI, NH_3, 70 eV, 150 °C): *m/z* (%) 199 (100, M+1), 167 (1, $M-OCH_3$), 134 (24, $M-C_5H_{10}O$). GC (C): t_R=16.1 min. Elemental analysis: calc. for $C_{10}H_{14}O_2S$: C, 60.58; H, 7.12. Found: C, 61.02; H, 7.23%.

9b: oily product. IR (film): ν_{max} (cm^{-1}) 3408, 3085, 2977, 2937, 2877, 2362, 1715 (C=O, st), 1592, 1457, 1378, 1339, 1295, 1262, 1192, 1156, 1086, 1034, 998, 945, 890, 812, 745, 724, 668, 625. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.31 (3 H, d, J=7.5 Hz, H10), 1.34 (3 H, d, J=7.5 Hz, H9),, 2.12 (3 H, s, SMe), 2.28 (1 H, q, J=7.5 Hz, H2), 2.52 (1 H, q, J=7.5 Hz, H4), 4.72 (1 H, d, J=1.5 Hz, H5), 6.08 (1 H, d, J=6.0 Hz, H7), 6.29 (1 H, dd, J_1=5.5 Hz, J_2=1.5 Hz, H6). ^{13}C NMR (50 MHz, $CDCl_3$): δ 14.85 (C9), 17.68 (C10), 19.68 (SMe), 49.08 (C4), 54.03 (C2), 82.97 (C5), 115.60 (C1), 135.18 (C7), 136.57 (C6). MS (DIP-CI, NH_3, 70 eV, 150 °C): *m/z* (%) 199 (100, M+1), 167 (1, $M-OCH_3$), 134 (24, $M-C_5H_{10}O$). GC (C): t_R=16.7 min. Elemental analysis: calc. for $C_{10}H_{14}O_2S$: C, 60.58; H, 7.12. Found: C, 60.95; H, 7.18%.

endo-*2,4-Dimethyl-1-cyclohexylthio-8-oxabicyclo[3.2.1]-oct-6-en-3-one* (**10a**). The cycloaddition reaction afforded **10a** as the only diastereoisomer. No *exo* diastereomer was detected. Colourless oil. IR (film): ν_{max} (cm^{-1}) 2925, 2850, 1710 (C=O, st), 1590, 1450, 1375, 1290, 1235, 1245, 1205, 1150, 1100, 1060, 1030, 995, 960, 940, 885, 810, 740. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.97 (3 H, d, J=7.0 Hz, H10), 1.11 (3 H, d, J=7.0 Hz, H9), 1.31, 1.37, 1.42, 1.68 (10 H, m, H2′, H3′, H4′, H5′, H6′), 1.98 (1 H, s, H1′), 2.79 (1 H, q, J=7.1 Hz, H2), 2.82 (1 H, dq, J_1=7.0 Hz, J_2=4.8 Hz, H4), 4.90 (1 H, dd, J_1=4.8 Hz, J_2=1.6 Hz, H5), 6.19 (1 H, d, J=6.0 Hz, H7), 6.31 (1 H, dd, J_1=5.9 Hz, J_2=1.6 Hz, H6). ^{13}C NMR (50 MHz, $CDCl_3$): δ 10.35 (C9), 10.96 (C10), 25.50 (C4′), 26.01 (C3′, C5′), 35.09, 35.21 (C2′, C6′), 41.72 (C1′), 49.72 (C4), 55.67 (C2), 82.52 (C5), 97.36 (C1), 133.88 (C7), 136.10 (C6), 207, 74 (C3). MS (DIP-EI, 70 eV, 150 °C): *m/z* (%) 266 (20, M), 251 (1, M−Me), 209 (7, $M-C_3H_5O$), 184 (53, $M-C_6H_{10}$), 169 (28, $M-C_6H_9O$ or C_7H_{13}), 151 (15, M−ChSH), 95 (100, $C_5H_3O_2$). GC (C): t_R=31.9 min. Elemental analysis: calc. for $C_{15}H_{22}O_2S$: C, 67.63; H, 8.32. Found: C, 67.01; H, 8.15%.

2,4-Dimethyl-1-phenylthio-8-oxabicyclo[3.2.1]oct-6-en-3-one (**11**). The reaction resulted in a 97:3 mixture of diastereomers **11a** and **11b**, which were separated by flash column chromatography.

11a: oily product. IR (film): ν_{max} (cm^{-1}) 3062, 2977, 1717 (C=O, st), 1457, 1376, 1337, 1154, 1032, 810, 749, 693. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.94 (3 H, d, J=7.1 Hz, H10), 1.16 (3 H, d, J=7.1 Hz, H9), 2.79 (1 H, q, J=7.1 Hz, H4), 2.81 (1 H, q, J=7.1 Hz, H2), 4.94 (1 H, dd, J_1=4.8 Hz, J_2=1.6 Hz, H5), 6.12 (1 H, d, J=6.0 Hz, H7), 6.25 (1 H, dd, J_1=5.9 Hz, J_2=1.7 Hz, H6), 7.62 (2 H, dd, J_1=9.6 Hz, J_2=2.2 Hz, H2′, H6′), 7.33 (2 H, d, J=2.3 Hz, H3′, H5′), 7.31 (1 H, d, J=1.2 Hz, H4′). ^{13}C NMR (50 MHz, $CDCl_3$): δ 10.30 (C9), 10.96 (C10), 49.48 (C4), 54.79 (C2), 82.81 (C5), 98.57 (C1), 128.50 (C7), 128.67 (C6), 134.16 (C3′, C5′), 134.94 (C2′, C6′), 135.06 (C4′), 135.22 (C1′). MS (DIP-EI, 70 eV, 150 °C): *m/z* (%) 260 (33, M), 245 (7, $M-CH_3$), 203 (32, $M-C_4H_9$ or C_3H_5O), 151 (4, M−SPh), 95 (100, $C_5H_3O_2$), 83 (6, C_5H_7O), 67 (41, C_4H_3O). GC (C): t_R=16.1 min. Elemental analysis: calc. for $C_{15}H_{16}O_2S$: C, 69.20; H, 6.19. Found: C, 69.35; H, 6.11%.

11b: colourless oil. IR (film): ν_{max} (cm^{-1}) 3062, 2977, 1717 (C=O, st), 1457, 1376, 1337, 1154, 1032, 810, 749, 693. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.06 (3 H, d, J=7.5 Hz, H10), 1.14 (3 H, d, J=7.5 Hz, H9), 2.78 (2 H, m, H2, H4), 4.74 (1 H, dd, J_1=4.8 Hz, J_2=1.7 Hz, H5), 5.85 (1 H, d, J=6.0 Hz, H7), 6.05 (1 H, dd, J_1=5.9 Hz, J_2=2.0 Hz, H6), 7.32 (2 H, dd, J_1=5.5 Hz, J_2=3.0 Hz, H3′, H5′), 7.62 (2 H, dd, J_1=6.0 Hz, J_2<1.0 Hz, H2′, H6′), 7.68 (1 H, dd, J_1=3.0 Hz, J_2<1.0 Hz, H4′). ^{13}C NMR (50 MHz, $CDCl_3$): δ 10.86 (C9), 11.51 (C10), 50.06 (C4), 55.38 (C2), 83.39 (C5), 100.28 (C1), 129.24 (C7), 129.37 (C6), 134.71 (C3′, C5′), 135.81 (C2′, C6′), 137.01 (C4′), 139.01 (C1′). MS (DIP-EI, 70 eV, 150 °C): *m/z* (%) 260 (33, M), 245 (7, $M-CH_3$), 203 (32, $M-C_4H_9$ or C_3H_5O), 151 (4, M−SPh), 95 (100, $C_5H_3O_2$), 83 (6, C_5H_7O), 67 (41, C_4H_3O). Elemental analysis: calc. for $C_{15}H_{16}O_2S$: C, 69.20; H, 6.19. Found: C, 69.01; H, 6.33%.

2,4-Dimethyl-1-methylseleno-8-oxabicyclo[3.2.1]oct-6-en-3-one (**12**). Cycloadducts were obtained as a separable 34:1 mixture of diastereoisomers **12a** and **12b**.

12a: colourless oil. IR (film): ν_{max} (cm^{-1}) 3090, 2980, 2940, 2880, 1700 (C=O, st), 1570, 1430, 1350, 1305, 1260, 1240, 1210, 1180, 1115, 985, 940, 920, 895, 880, 760, 690. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.98 (3 H, d, J=7.0 Hz, H10), 1.12 (3 H, d, J=7.0 Hz, H9), 2.03 (3 H, s, SeMe), 2.86 (1 H, q, J=7.0 Hz, H2), 2.87 (1 H, q, J=7.0 Hz, H4), 4.91 (1 H, dd, J_1=4.7 Hz, J_2=1.4 Hz, H5), 6.26 (1 H, d, J=5.9 Hz, H7), 6.32 (1 H, dd, J_1=5.9 Hz, J_2=1.5 Hz, H6). ^{13}C NMR (50 MHz, $CDCl_3$): δ 2.17 (SeMe), 10.25 (C9), 11.45 (C10), 50.03 (C4), 56.13 (C2), 83.37 (C5), 91.43 (C1), 134.05 (C7), 136.67 (C6), 207.37

(C3). MS (DIP-EI, 70 eV, 150 °C): *m/z* (%) 246 (9, *M*), 231 (2, *M*−Me), 167 (1, *M*−Se), 152 (6, *M*−SeMe), 95 (100, HSeMe or $C_5H_3O_2$), 85, 83 (84, C_5H_7O), 67 (67, C_4H_3O), 55 (40, C_4H_7 or C_3H_4O). GC (E): t_R = 17.4 min. Elemental analysis: calc. for $C_{10}H_{14}O_2Se$: C, 48.99; H, 5.76. Found: C, 49.12; H, 5.74%.

12b: oily product. IR (film): ν_{max} (cm^{-1}) 2935, 1713 (C=O, st), 1455, 1376, 1154, 1032, 988, 965, 812, 741. ^1H NMR (200 MHz, $CDCl_3$): δ 1.12 (3 H, d, J=7.2 Hz, H9), 1.37 (3 H, d, J=7.2 Hz, H10), 2.04 (3 H, s, SeMe), 2.91 (3 H, q, J=7.2 Hz, H2), 2.99 (1 H, q, J=7.2 Hz, H4), 4.73 (1 H, s, H5), 6.26 (1 H, d, J=5.9 Hz, H7), 6.31 (1 H, dd, J_1=5.9 Hz, J_2=1.7 Hz, H6). ^{13}C NMR (75 MHz, $CDCl_3$): δ 1.2 (SeMe), 10.31 (C9), 11.35 (C10), 49.37 (C4), 564.72 (C2), 83.96 (C5), 91.50 (C1), 135.36 (C7), 135.65 (C6), 209.71 (C3). MS (DIP-EI, 70 eV, 150 °C): *m/z* (%) 246 (9, *M*), 231 (2, *M*−Me), 167 (1, *M*−Se), 152 (6, *M*−SeMe), 95 (100, HSeMe or $C_5H_3O_2$), 85, 83 (84, C_5H_7O), 67 (67, C_4H_3O), 55 (40, C_4H_7 or C_3H_4O). GC (E): t_R = 16.5 min. Elemental analysis: calc. for $C_{10}H_{14}O_2Se$: C, 48.99; H, 5.76. Found: C, 48.75; H, 5.65%.

endo-*2,4-Dimethyl-1-benzylseleno-8-oxabicyclo[3.2.1]-oct-6-en-3-one* (**13a**). Cycloadduct **13a** was formed in the reaction as the sole product. No *exo* diastereoisomer was detected by GC. Yellow solid. MP: 75–77 °C ($CHCl_3$). IR (film): ν_{max} (cm^{-1}) 3050, 3029, 2971, 2935, 2875, 1711 (C=O, st), 1601, 1580, 1495, 1453, 1378, 1335, 1295, 1248, 1154, 1028, 984, 963, 940, 812. ^1H NMR (200 MHz, $CDCl_3$): δ 0.99 (3 H, d, J=7.0 Hz, H10), 1.10 (3 H, d, J=7.1 Hz, H9), 2.87 (1 H, dq, J_1=7.0 Hz, J_2=5.0 Hz, H4), 2.93 (1 H, q, J=7.0 Hz, H2), 3.94 (2 H, d, J=5.1 Hz, H1′), 4.96 (1 H, dd, J_1=4.8 Hz, J_2=1.5 Hz, H5), 6.31 (1 H, s, H7), 6.32 (1 H, d, J=1.5 Hz, H6), 7.28 (5 H, m, $W_{1/2}$=15.7 Hz, H2″, H3″, H4″, H5″, H6″). ^{13}C NMR (75 MHz, $CDCl_3$): δ 10.29 (C10), 11.47 (C9), 26.51 (C1′), 50.12 (C4), 56.43 (C2), 83.46 (C5), 92.73 (C1), 126.80 (C4″), 128.49 (C3, C5), 129.13 (C2, C6), 133.85 (C6), 137.17 (C7), 138.30 (C1), 207.19 (C3). MS (DIP-CI, NH3, 70 eV, 150 °C): *m/z* (%) 337 (20), 338 (49), 339 (10), 340 (100), 341 (18), 342 (19) (M+NH_4), 319 (12), 320 (13), 321 (31), 322 (10), 323 (61), 324 (11) (*M*), 170 (1, C_7H_7Se), 91 (6, C_7H_7). GC (B): t_R = 24.7 min. Elemental analysis: calc. $C_{16}H_{18}O_2Se$: C, 59.82; H, 5.65. Found: C, 59.75; H, 5.97%.

Acknowledgements. We would like to acknowledge the Spanish Ministry of Education for financial support, (Grant MEC PB93-0754 and MEC *Acciones Concertadas* 1992). Also fellowships to P.M.G. from the Catalonian Research Council (CIRIT) and to F.G. from the Spanish Ministry of Education are gratefully acknowledged.

References

1. (a) Hoffmann, H. M. R. *Angew Chem. 20* (1973) 877; (b) Hoffmann, H. M. R. *Angew Chem., Int. Ed. Engl. 23* (1984) 1; (c) Mann, J. *Tetrahedron 42* (1986) 4611; (d) Hosomi, A. and Tominaga, Y. In: Trost, B. and Fleming, I., Eds., *Comprehensive Organic Chemistry*, Pergamon, Oxford 1991, Vol. 5, pp. 593–615; (e) Noyori, R. and Hayakawa, Y. *Tetrahedron 41* (1985) 5879.
2. Ashcroft, M. R. and Hoffmann, H. M. R. *Org. Synth. 58* (1978) 17.
3. (a) Lukevits, E. Y., Ignatovich, L. M. and Goldberg, Y. Sh. *J. Heterocycl. Chem.* (1986) 678; (b) Fitzpatrick, J. E., Milner, D. J. and White, P. *Synth. Commun. 2* (1982) 489.
4. Burkenser, K. A. and Currie, R. B. *J. Am. Chem. Soc. 70* (1947) 1780.
5. (a) Liebeskind, L. S. and Wang, J. *J. Org. Chem. 58* (1993) 3550; (b) Bailey, J. R. *Tetrahedron Lett. 27* (1986) 4407; (c) Yamamoto, M., Munakata, H., Kishikawa, K., Kohmoto, S. and Yamada, K. *Bull. Chem. Soc. Jpn. 65* (1992) 2366.
6. (a) Stutz, P. and Stadler, P. A. *Org. Synth. 56* (1988) 109; (b) Lumbroso, H., Bertin, D. M., Fringuelli, F. and Tattichi, A. *J. Chem. Soc., Perkin Trans. 2* (1977) 776.
7. (a) Adams, R., Reifchneider, W. and Nair, M. D. *Croat. Chem. Acta 29* (1957) 279; (b) Adams, R. and Ferretti, A. *J. Org. Chem. 81* (1959) 4927.
8. Benassi, R., Folli, U., Iarossi, D., Mucci, A., Mussatti, A., Nardelli, M., Schenetti, M. and Taddei, F. *J. Mol. Struct. 246* (1991) 81.
9. Girordier, L., Maignan, C. and Rouessac, F. *Tetrahedron Asymmetry 3* (1992) 857.
10. Niwa, L., Aoki, H., Tanaka, H., Munakata, K. and Namiki, M. *Chem. Ber. 99* (1966) 3215.

Received June 11, 1997.