Pergamon

Tetrahedron, Vol. 53, No. 34, pp. 11669-11684, 1997

0040-4020/97 $17.00 + 0.00

PII: S0040-4020(97)00739-4

2-Functionalized Furans as Precursors of Versatile Cycloheptane Synthons

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Abstract: An study on the influence of steric and electronic effects of a function attached at C-2 of furans in the yield and diastereoselectivity of [4+3] cycloaddition reactions with oxyallyl cations is presented. In almost all studied furans a *cis* diastereospecificity and a high *endo* diastereoselectivity is observed. Increasing bulkyness of the function attached at C-2 of furans, the *endo* diastereoselectivity increases, but yield decreases. Increasing the electronic density of the furan system, by an electron donating group at C-2, both yield and diastereoselectivity increase. © 1997 Elsevier Science Ltd.

In relation with our interest in the preparation of polyfunctionalized cycloheptanes as synthetic precursors of biologically active natural products, in our research group we have carried out a systematic study of [4C(4π)+3C(2π)] cycloaddition reactions of C-2 functionalized furans as dienes with 1,3-dimethyl-oxyallyl cation as dienophile, (see fig. 1). Our primary interest in such study was to know the influence of the type of function attached at C-2 of furan in the yield and stereoselectivity of cycloaddition reactions.

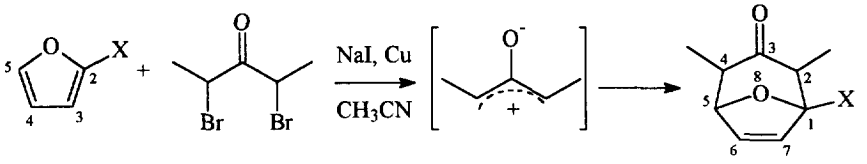


Figure 1. [4+3] Cycloaddition Reaction.

We have not found in the literature any reference regarding a similar systematic study. Only, there are a few examples[1] where furans substituted at C-2 by aryl or alkyl groups are used as dienes in such reactions, but none with a function linked to C-2 through an heteroatom which is of our major interest here.

From C-2 functionalized furans it is possible to obtain bicyclic cycloadducts having on C-1 an organic function which facilitates opening of the oxygen bridge. This methodology has some advantages with respect to other synthetic approaches because at least four different organic functions are introduced in the cycloadduct, since the beginning, maintaining at the same time the relative stereochemistry of substituents in the cycloheptane system. These features make the aforementioned cycloadducts very versatile and useful synthons, (see fig 2).

In this work we have carried out [4+3] cycloaddition reactions of seventeen different 2-substituted furans, (see table 1), we reacted the first four substrates, (entries 1 to 4), in order to evaluate mostly the

steric effects on the yield and diastereoselectivity in the cycloaddition reaction. Substrates from entries 5 to 9 were considered to study steric and electronic effects. Entries from 10 to 17 were evaluated to observe the

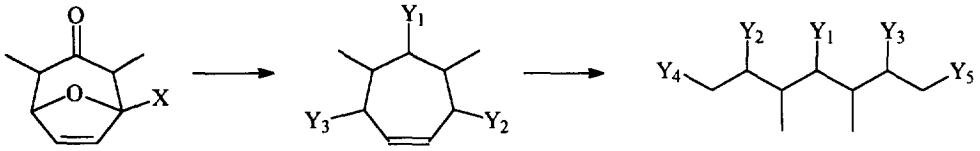


Figure 2. Synthetic Applications of Bicyclic Cycloadducts.

influence of the presence of an heteroatomic linkage, between the organic function and the C-2 atom of furan, in the outcome of these cycloaddition reactions, in order to get valuable information to conveniently develop the aforementioned synthetic methodology. In these experiments, 1,3-dimethyloxyallyl cation was used as dienophile. This cation is symmetric and it does not present regiochemistry problems, which considerably simplifies this study. It was generated *in situ* from 2,4-dibromo-3-pentanone by two alternative procedures: Hoffmann's method[2], (NaI, Cu, MeCN, 60°C), and Noyori's method[1a, 3], ($Fe_2(CO)_9$, C_6H_6, 80°C). The different electrophilic character of oxyallyl cations, generated by both methodologies, is quite important because it conditions the mechanism of cycloaddition reactions and their stereochemical results[1b, 2, 4].

From the evaluated furan substrates, four racemic diastereoisomeric cycloadducts are possible, depending on the relative position of substituents on C-1, C-2 and C-4 in the bicyclic system. As can be seen in figure 3, considering a concerted mechanism for the cycloaddition reaction 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 *endo/exo* and *cis/trans* cycloadducts respectively.

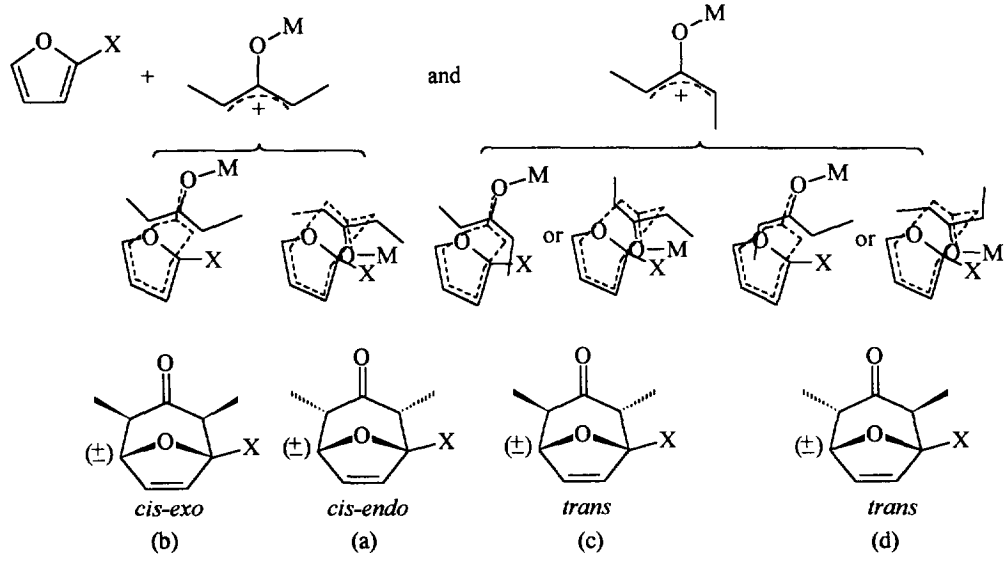


Figure 3. Possible Diastereomeric Cycloadducts.

In the present work we have studied both, reactivity of 2-functionalized furans evaluated by the parameters conversion and yield, and *cis-trans* as well as *endo-exo* diastereoselectivity in the cycloaddition reaction. These data have been obtained by ^{1}H-NMR and GC analysis and all experiments were carried out under the same standard conditions[2a, 3], in order to make results comparable. In Table 1, results from the evaluated 17 different furan models are shown. Furans were commercially available or synthesized according to the indicated bibliographic references.

From data quoted in Table 1 it is worth noting the *cis* diastereospecificity obtained in 15 of the 16 experiments carried out under Hoffmann's methodology. This fact is an indication that under Hoffmann's

Table 1. Results of [4+3] Cycloaddition Reactions.

Furan Substrate			Cycloaddition Results					
Entry	**X**	**Preparation (Reference)**	**Product**	**Synthetic Method***	**Yield**** **(%)**	**Conversion**** **(%)**	**Diastereoselectivity**	
							cis / trans (a,b/c,d)	***endo : exo a/b***
1	H	6	**18**	H	63	100	100	80:20
2	Me	6	**19**	H	77	93	100	92:8
3	^{t}Bu	7	**20**	H	9	60	100	67:33
4	Ph	8	**21**	H	60	66	100	97:3
5	COOEt	6	**22**	H	27	97	100	97:3
6	COOCh	9	**23**	H	22	63	100	100
7	CON^{i}Pr$_2$	9	**24**	H	0	0***	-	-
8	COH	6	**25**	H	25	10	68:14:14:5	
9	CH(OCH$_2$CH$_2$O)	10	**26**	H	54	100	100	60:40
10	OMe	6	**27**	H	84	96	100	67:33
10'	OMe	6	**27'**	N	80	82	88:12	91:9
11	OSiMe$_3$	6	**28**	H	86	100	100	95:5
12	OSiMe$_2$^{t}Bu	11	**29**	H	29	100	100	98:2
13	OCOPh	13	**30**	H	16	86	100	83:17
14	OCO^{t}Bu	13, 12	**31**	H	93	100	100	95:5
15	OCOOEt	12	**32**	H	100	37	100	100
16	OPO(NMe$_2$)$_2$	6	**33**	H	21	98	100	93:7
17	NO$_2$	6	**34**	N[14]	13	82	100	96:4

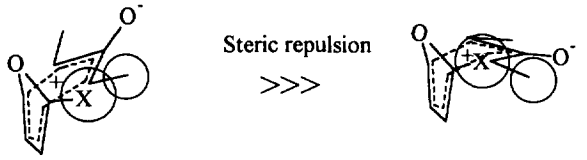
* Synthetic method used in the cycloadditon reactions: H = Hoffmann's method[2a]. N = Noyori's method[3].

** Conversions of furan substrates and yields of cycloadducts are not optimized. All reactions were carried out under the same standard conditions for comparative purposes. Conversion was evaluated by GC in front of a standard along 20h of reaction time, unless the reaction was complete before.

*** Unreactivity of furan 7 could be due to its low solubility in acetonitrile under the Hoffmann's conditions.

reaction conditions, the [4+3] cycloaddition, takes place *via* an oxyallyl cation having a "W" configuration[1b, 2, 4a]. This dienophile is trapped by the furane diene, through a concerted mechanism, affording exclusively the *cis* cycloadduct. Comparing entries 10 and 10' it is possible to appreciate how a change in the nature of dienophile, (and also of reaction mechanism), could modify diastereoselectivity.

Even though it is not possible to observe neat steric and/or electronic effects, because both act simultaneously, (stereoelectronic effects[5]), we have selected appropriate furane substrates in order to rationalize how the type of substituents at C-2 of furans can affect conversion, yield and stereoselectivity. Peering at data from Table 1 allows to draw certain important conclusions: increasing size of substituent X increases *endo* diastereoselectivity. This phenomenon is induced by the steric repulsion between the bulky substituent and a methyl group of the oxyallyl cation. Compare, for example, entries 1,2,3, also 5,6 and 11,12 or 13,14. Also, it is very common that rising bulkyness of the C-2 groups decreases conversion and/or yield, (see for example entries 2,3,4, also 5,6, and 11,12). This is due to the lower accesibility of furane diene by the oxyallyl cation, (see Fig. 4).



Extended Mode (*exo* approach) Compact Mode (*endo* approach)

Figura 4. Influence of the X Group Attached to C-2 of Furan in the Transition State of the Cycloaddition Reaction.

Looking at Table 1, we can make certain comparisons to illustrate how the electronic properties of the C-2 groups can determinate or modulate the yield and diastereoselectivity of the different families of studied furan substrates. The presence of electron-withdrawing groups at C-2, (see entries 5-8 and 16,17), weakens substituted furans as dienes affording low to moderate yields of cycloadducts.

If in position 2 of the furane ring alkyl groups, with slight electron-donating character, are anchored yields turn from moderate to good, (compare entries 1-4). Inserting groups with marked electron donating properties, (X=OR, OCOR, OSiRRR'), we obtain the best yields and conversions.

Finally, comparing entries 2 *versus* 10 and 5 *versus* 15, in which the only structural variation is the presence of an oxygen bridge, we can appreciate a clear increase of yield in the reaction, by insertion of that oxygen atom. The origin of these results could be interpreted on the basis of the electron-donating nature of the sp^3 oxygen bearing two pairs of non-shared electrons, and in the fact that the bulky groups are farther apart in 10 and 15 than in 2 and 5 respectively.

Assignment of stereochemistry in cycloadducts

In every cycloaddition experiment, the diastereoisomeric cycloadducts were isolated from the reaction mixture and purified by column chromatography, and spectroscopically characterized. In a few cases, we describe only one isomer, whether it is the unique diastereoisomer formed in the reaction or it is formed in such a small proportion that it is quite difficult to purify. The stereochemical assignment of diastereoisomeric cycloadducts was carried out in an unequivocal way by careful correlation of spectroscopic properties of both stereoisomers *endo* and *exo* , on the basis of 1D and 2D ^{1}H- and ^{13}C-NMR experiments: DEPT, COSY-45, COSY-90, DQFCOSY, HETCOR, HMBC, HMQC and NOESY. Next we exemplify our model of assignment for estereoisomers **27a** (*endo*) and **27b** (*exo*), whose relative stereochemistry was confirmed by X-Ray diffraction analysis of single crystals, (see Fig. 5). The experimental details as well as a selection of bond angles and legths for both compounds are quoted in the experimental part.

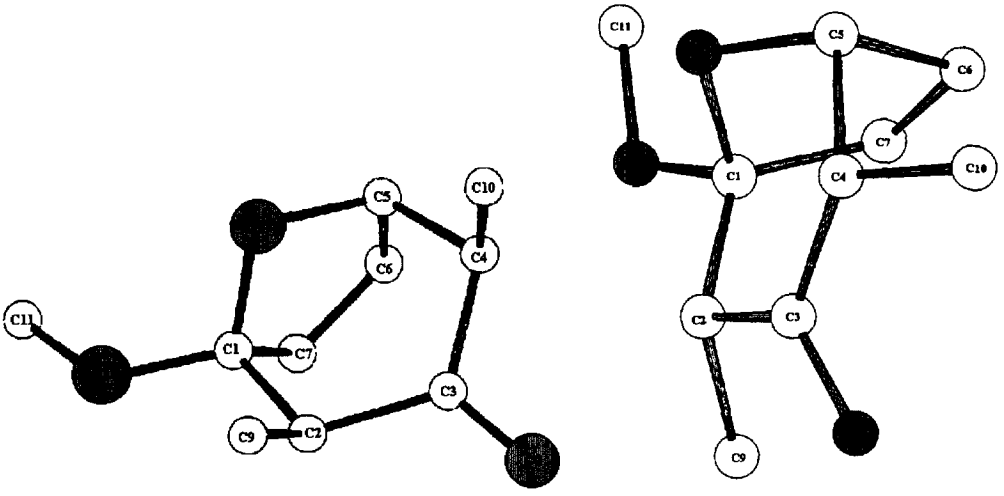


Figure 5. Structures of **27a** and **27b** Obtained from X-Ray Diffraction Analysis. Hydrogens are Omitted for Clarity.

Even though there is usually a difference between the conformations of molecules in an ordered crystal structure, as observed by X-Ray diffraction, and the average conformational disposition observed by NMR experiments in solution at room temperature, however, we obtained in our case a great similarity and internal coherence between both experimental analytical conditions.

As shown in Fig. 6 in solution we observed a different disposition for the methyl groups at C-2 and C-4 as well as a different conformation of the 1-oxan-4-one ring of the bicyclic system in **27a** and **27b.** In the *endo* diasteroisomer, the aforementioned ring adopts a half-chair conformation placing the methyl groups in a quasi-equatorial disposition, and directing H2 and H4 towards the bridging oxygen. In this particular structure the dihedral angle H4-C4-C5-H5 is close to 45°. In the *exo* diastereomer the 1-oxan-4-one ring adopts a boat conformation in order to decrease the 1,3-*cis*diaxial steric repulsion[15] between methyl groups attached to C2 and C4. In this case, protons H9 and H10 are directed to the bridging oxygen, meanwhile H2 and H4 are oriented to the double bond and are affected by its shielding anisotropy cone . In this last conformation, the dihedral angle H4-C4-C5-H5 is almost 90°.

These findings from the NMR experiments allowed us to assign the sterochemistry to diastereomeric cycloadducts on the basis of the values of chemical shifts and coupling constants for H2, H4, H9 and H10.

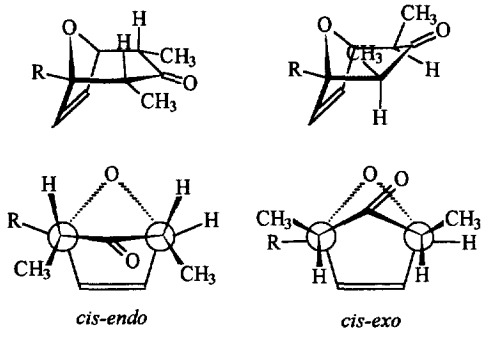


Figure 6. Different Conformation of the 1-Oxan-4-one Ring in Cycloadducts Depending on the Configuration at C2 and C4.

The oxabicyclic structure of cycloadducts has few degrees of conformational freedom and includes two polar groups: the bridging oxygen and the carbonyl group. On the other hand, the substituent attached to the bridge head (C1) has enough freedom to situate itself far away from the bicyclic system. For these reasons, the magnetic field arround the atoms of H and C in this structure will be affected in higher extent by the relative position with respect to these polar groups than by the function on C-1, (X). This phenomenon makes the following model of stereochemical assigment of general validity, and it could be applied to every pair of *endo/exo* diastereisomers , independently of the type of function X.

The *endo* or *exo* configuration could be established on the basis of chemical shifts and coupling constants of H4, H5, H9 and H10. In the *endo* isomer $J_{4,5}$= 4.5 - 5 Hz, while in the *exo* one, $J_{4,5} < 1.5$ Hz. On the other hand, in the *endo* isomers methyl groups on C2 and C4 appear at higher field than the ones of the *exo* isomer , due to a 1,3-dipolar deshielding interaction (of electrostatic character)[16] between methyl groups and the bridging oxygen. This interaction takes place in the *exo* diastereomer but not in the *endo* one in which methyl groups are oriented towards the double bond. An observation coherent with the previous one is that H2 and H4 are deshielded in the *endo* structures with respect to the *exo* ones because of the same deshielding electrostatic interaction with the bridging oxygen, (see experimental part for NMR data). According to these findings it is possible to deduce that *endo* and *exo* isomers have simultaneously opposite configurations at C2 and C4.

Also, stereochemical conclusions could be drawn by correlation of ^{13}C-NMR data, specially based on chemical shifts of C1, C3, C6, C7, C9 and C10 atoms. In first place, it is possible to observe that C6, C7, C9 and C10 in *endo* structures appear at higher fields than the homologous carbons in the *exo* isomers, due to C7 - C9 and also C6 - C10 γ-gauche interactions[17a]. This last phenomenon is not possible in the *exo* form. Moreover, there are shielding effects on C9 and C10 in *endo* isomers because of the anisotropy cone of carbonyl group[17b], which is not observed in the structure with *exo* configuration. The aforementioned interactions are only coherent with de assignment of the *cis-endo* configuration to cycloadduct **27a** and *cis-exo* configuration to **27b**.

In conclusion, we have submitted 17 different C-2 substituted furans to [4+3] cycloaddition reactions under Hoffmann's or Noyori's methodologies, obtaining a wide variety of C-1 functionalized 8-oxabicyclo[3.2.1]-6-octen-3-one systems, with yields from moderate to good, *cis* diastereospecificity in almost all cases, and very high *endo* diastereoselectivity. All furans and cycloadducts were properly purified and physically and spectroscopically characterized. At the moment we are applying these new properly fuctionalized bicyclic cycloadducts to the synthesis of bioactive natural products. Results from this work will be published in due course.

EXPERIMENTAL SECTION

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 spectrophotometers as thin films or as solutions. NMR spectra were taken in deuterared chloroform and benzene on spectrometers at 200MHz (GEMINI-200), 300MHz (UNITY-300) and/or 500MHz (UNITY-500) for ^{1}H-NMR, and at 50MHz and 75.43MHz for ^{13}C-NMR. For ^{1}H-NMR tetramethylsilane was used as internal standard. ^{13}C NMR spectra were referenced to the δ 77.0 ppm 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 equipment. GC analyses were performed on HP-8790 gas chromatograph equipped with a HEWLETT-PACKARD-crosslinked MePhe-Silicone capillary column (l=25 m, ∅=0.2 mm, ε= o.25μm) using Hellium as carrier gas and a 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); 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 under Hoffmann's Conditions.

A two-neck flask, fitted with a magnetic stirring bar and a Dimroth condenser, under nitrogen, was charged with the furan derivative, with freshly actived copper powder and oven-dried (24 hours at 150°C) sodium iodide, in molar ratio 1:3:6 (furan:Cu:NaI), and acetonitrile as 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 was dependent on the reaction kinetics of each substrate, but varied from 4 to 20 hours. The reaction mixture was concentrated to dryness under vacuum at 0°C. Cold methylene chloride and ice water were added. The aqueous phase was extracted with cold methylene chloride 6 times. The organic phase was washed twice with cold aqueous 6% w/w ammonia followed by cold water, was dried over anhydrous $MgSO_4$, filtered through neutral alumina and concentrated to dryness under vacuum without heating. The product was purified by column chromatography on flash silica gel, using mixtures of hexane- ethyl acetate of increasing polarity.

General Procedure for the [4+3] Cycloadditions under Noyori's Conditions.

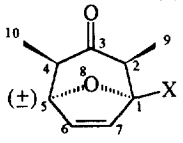
In a round bottomed flask fitted with magnetic stirring and a Dimroth condenser, under argon atmosphere, the C-2 functionalized furan was placed dissolved in benzene. Afterwards, the pyrophoric diironnonacarbonyl was added, (in a molar ratio of 1.75 : 1; Fe_2CO_9 : furan), as a solid in the reactor, (handled inside an ATMOSBAG® filled with argon). 2,4-Dibromo-3-pentanone, freshly filtered through neutral alumina, was added at room temperature ,(in a molar ratio of 1.05 : 1, dibromoketone : furan) . The reaction mixture was refluxed overnight. The reaction crude was filtered through neutral alumina eluting with benzene-ether (fraction 1), ethyl acetate (fraction 2) and methanol (fraction 3). The fractions which contain cycloadducts were treated with a small amount on cerium ammonium nitrate in acetone for one hour. The products were purified by column chromatography on flash silica gel.

Physical and Spectroscopic Characterization of Obtained Cycloadducts:

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

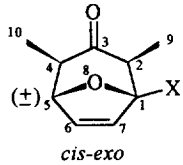
Table 2. Numbering and Substitution Patterns of Cycloadducts at C-1.

Diastereomer **(a)**



cis-endo

Diastereomer **(b)**



cis-exo

X= 18: H

19: CH_3

20: $C(CH_3)_3$

21: 

22: $COOCH_2CH_3$

23: $COOCHCH_2CH_2CH_2CH_2CH_2CH_2$

24: $CON(CH(CH_3)_2)_2$

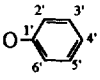
25: CHO

X= 26: $CH(OCH_2CH_2O)$

27: OCH_3

28: $OSi(CH_3)_3$

29: $OSi((CH_3)_2C(CH_3)_3$

30: 

31: $OCOC(CH_3)_3$

32: $OCOOCH_2CH_3$

33: $OPO(N(CH_3)_2)_2$

34: NO_2

2,4-Dimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one.
Cycloadduct **18a** : colourless oil. *IR [film, ν(cm^{-1})]:* 3080, 2974, 2950, 2885, 1715, 1590, 1460-1450, 1380, 1340, 1160, 1085, 920, 935, 860, 815, 730; *^{1}H NMR [300MHz, $CDCl_3$, δ(ppm)]:* 0.97 (6H; d; J=6.7 Hz; H9, H10), 2.80 (2H; dq; J_1=6.7 Hz, J_2=4.0 Hz; H2, H4), 4.85 (2H; d; J=4.0 Hz; H1, H5), 6.34 (2H; s; H6, H7); *^{13}C NMR [50 MHz, $CDCl_3$, δ(ppm)]:* 10.05 (C9,C10), 50.30 (C2,C4), 82.66 (C1,C5), 133.47(C6, C7), 208.95 (C3); *EM [DIP-EI, 70eV, 150°C, m/z(%)]:* 152 (21, M), 137 (26, M-CH_3), 95 (84, M-C_4H_9 or C_3H_5O), 81 (100, C_5H_5O); *GC(A):* RT = 7.4 min. *EA.* Found: C 71.12; H 8.02%. $C_9H_{12}O_2$ requires C 71.03; H 7.95%.

Cycloadduct **18b** : colourless oil.*IR [film, ν(cm^{-1})]:* 3080, 2960, 2925, 2885, 1703, 1630, 1450, 1375, 1320, 1240, 1175, 1085, 1040, 960, 930, 895, 815, 700; *^{1}H NMR [300MHz, $CDCl_3$, δ(ppm)]:* 1.36 (6H; d; J=7.5 Hz; H9, H10), 2.28 (2H; q; J=7.5 Hz; H2, H4), 4.65 (2H; s; H1, H5), 7.26 (2H; s; H6, H7); *^{13}C NMR [50 MHz, $CDCl_3$, δ(ppm)]:* 17.75 (C9, C10), 49.78 (C2, C4), 81.95 (C1, C5), 133.63 (C6, C7), 213.68 (C3); *EM [DIP-EI, 70eV, 150°C, m/z(%)]:* 152 (21, M), 137 (26, M-CH_3), 95 (84, M-C_4H_9 or C_3H_5O), 81 (100, C_5H_5O); *GC(A):* RT = 7.2 min. *EA.* Found: C 71.21; H 7.86%. $C_9H_{12}O_2$ requires C 71.03; H 7.95%.

1,2,4-Trimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one.
19a : yellowish oil. *IR [film, ν(cm^{-1})]:* 3400, 3000, 2950, 2875 , 1730, 1610, 1450, 1390, 1340, 1260, 1150, 1125, 1060, 1015, 990, 910, 900, 840, 750; *^{1}H NMR [300MHz, $CDCl_3$, δ(ppm)]:* 0.96 (3H; d; J=7.0 Hz; H9), 1.01 (3H; d; J=7.1 Hz; H10), 1.51 (3H; s; H11), 2.57 (1H; q; J=7.0 Hz; H2), 2.77 (1H; dq; J_1=7.2 Hz, J_2=4.6 Hz; H4), 4.84 (1H; dd; J_1=4.6 Hz, J_2=1.6 Hz; H5), 6.12 (1H; d; J=6.1 Hz; H7), 6.25 (1H; dd; J_1=6.0 Hz, J_2=1.7 Hz; H6); *^{13}C NMR [50 MHz, $CDCl_3$, δ(ppm)]:* 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); *EM [DIP-EI, 70eV, 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-$C_5H_{10}O$, 2-methylfuran); *GC(A):* RT = 11.4 min. *EA.* Found: C 72.30; H 8.12%. $C_{10}H_{14}O_2$ requires C 72.26; H 8.49%.

19b : yellowish oil. *IR [film, ν(cm^{-1})]:* 3400, 2950, 2925, 2865, 1700, 1650, 1450, 1390, 1270, 1225, 1200, 1190, 1110, 1100, 1080, 1030, 1000, 925, 750; *^{1}H NMR [300MHz, $CDCl_3$, δ(ppm)]:* 1.26 (3H; d; J=7.4 Hz; H9), 1.33 (3H; d; J=7.5 Hz; H10), 1.39 (3H; s; H11), 2.26 (1H; q; J=7.4 Hz; H4), 2.26 (1H; q; J=7.5 Hz; H2), 4.65 (1H; d; J=1.7 Hz; H5), 6.04 (1H; d; J=5.9 Hz; H7), 6.19 (1H; dd; J_1=6.0 Hz, J_2=2.0 Hz; H6); *^{13}C NMR [50 MHz, $CDCl_3$, δ(ppm)]:* 14.54 (C9), 17.53 (C10), 19.68 (C11), 48.93 (C2), 53.35 (C4), 82.24 (C5), 87.84 (C1), 133.29 (C7), 137.75 (C6), 209 (C3); *EM [DIP-EI, 70eV, 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-$C_5H_{10}O$, 2-methylfuran); *GC(A):* RT = 11.3 min. *EA.* Found: C 72.18; H 8.57%. $C_{10}H_{14}O_2$ requires C 72.26; H 8.49%.

2,4-Dimethyl-1-*tert*butyl-8-oxabicyclo[3.2.1]oct-6-en-3-one.
20a. *IR [film, ν(cm^{-1})]:* 3047, 2958, 2887, 1710, 1594, 1460, 1397, 1378, 1364, 1330, 1320, 1260, 1153, 1075, 1055, 1023, 982, 960, 951, 895, 806;*^{1}H-NMR [300MHz, $CDCl_3$, δ(ppm)]:* 0.99 (3H, d, J=7.2 Hz, H10), 1.07 (9H, s, H2'), 1.17 (3H, d, J=6.9 Hz, H9), 2.75 (1H, ddq, J1=7.2 Hz, J2=4.8 Hz, J3=0.6 Hz, H4), 2.84 (1H, dq, J1=7.2 Hz, J2=0.6 Hz, H2), 4.89 (1H, dd, J1=4.8 Hz, J2=1.8 Hz, H5), 6.23 (1H, dd, J1=6.3 Hz, J2=1.8 Hz, H6), 6.31 (1H, dd, J1=6.8 Hz, J2=0.3 Hz, H7);*^{13}C NMR [75 MHz, $CDCl_3$, δ(ppm)]:* 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);*EM [DIP-IC, NH_3, 70eV, 150°C, m/z(%)]:* 226 (23, N+NH4), 209 (46, M+H), 208 (3, M), 151 (2, M-C4H9), 136 (12, M-C5H12), 133 (19, M-C4H11O), 117 (30, C4H11O2), 116 (44, M-C4H12O2), 91 (100); GC(C): RT = 13.2 min. *EA.* Found: C 74.62; H 9.51%. $C_{13}H_{20}O_2$ requires C 74.96; H 9.68%.

20b. *IR [film, ν(cm^{-1})]:* 3047, 2958, 2887, 1710, 1594, 1460, 1397, 1378, 1364, 1330, 1320, 1260, 1153, 1075, 1055, 1023, 982, 960, 951, 895, 806; *^{1}H NMR [200MHz, CDCl$_3$, δ(ppm)]:* 1.07 (9H, s, H2'), 1.12 (3H, d, J=7.2 Hz), 1.32 (3H, d, J=7.2 Hz), 2.28 (1H, q, J=7.2 Hz), 2.87 (1H, q, J=7.2 Hz), 4.66 (1H, s, H5), 6.23 (1H, d, J=6.6 Hz, H6), 6.28 (1H, d, J=6.6 Hz, H7); *EM [DIP-IC, NH$_3$, 70eV, 150°C, m/z(%)]:* 226 (23, N+NH4), 209 (46, M+H), 208 (3, M), 151 (2, M-C4H9), 136 (12, M-C5H12), 133 (19, M-C4H11O), 117 (30, C4H11O2), 116 (44, M-C4H12O2), 91 (100); *GC(C):* RT = 13.7 min. *EA*. Found: C 74.80; H 9.62%. $C_{13}H_{20}O_2$ requires C 74.96; H 9.68%.

1-Phenyl-2,4-dimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one.

21a : white solid. *M.P.:* 62-63°C (CH_2Cl_2). *IR [KBr, ν(cm^{-1})]:* 3040, 2985, 2940, 1720, 1500, 1455, 1385, 1355, 1340, 1320, 1285, 1165, 1115, 1065, 1035, 1000, 975, 950, 935, 920, 900, 820, 770, 750, 710; *^{1}H NMR [200MHz, CDCl$_3$, δ(ppm)]:* 0.88 (3H; d; J=7.0 Hz; H10), 1.04 (3H; d; J=7.0 Hz; H9), 2.93 (1H; q; J=7.0 Hz; H4), 2.95 (1H; q; J=7.0 Hz; H2), 5.00 (1H; dd; J_1=4.6 Hz, J_2=1.8 Hz; H5), 6.43 (1H; dd; J_1=6.2 Hz, J_2=1.8 Hz; H6), 6.66 (1H; d; J=6.1 Hz; H7), 7.34-7.42 (4H; m; H2', H6', H3', H5'), 7.48 (1H; tt; J_1=6.6 Hz, J_2=2.0 Hz; H4'); *^{13}C NMR [50 MHz, CDCl$_3$, δ(ppm)]:* 10.05 (C9), 10.22 (C10), 49.54 (C4), 55.76 (C2), 82.71 (C5), 91.70 (C1), 126.10 (C4'), 127.99 (C3', C5'), 128.39 (C2', C6'), 133.70 (C6), 133.85 (C7), 139.04 (C1'); *EM [DIP-EI, 70eV, 150°C, m/z(%)]:* 229 (14, M+1), 228 (76, M), 213 (51, M-Me), 185 (10, M-C$_3$H$_7$ o C$_2$H$_3$O), 171 (100, M-C$_4$H$_9$ o C$_3$H$_5$O), 157 (94, M-C$_4$H$_5$O o C$_5$H$_{11}$), 144 (29, M-C$_5$H$_9$O), 128, 115, 95 (3, C$_5$H$_3$O$_2$), 55 (5, C$_4$H$_7$ or C$_3$H$_4$O).; GC(A): RT = 23.2 min. *EA*. Found: C 78.99; H 7.08%. $C_{15}H_{16}O_2$ requires C 78.92; H 7.06%.

21b : colourless oil. *IR [film, ν(cm^{-1})]:* 3145, 2990, 2950, 2900, 1720 (C=0, st), 1510, 1460, 1385, 1335, 1280, 1230, 1165, 1125, 1045, 1005, 970, 910, 890, 820, 745; *^{1}H NMR [200MHz, CDCl$_3$, δ(ppm)]:* 0.90 (3H; d; J=7.2 Hz; H9), 1.02 (3H; d; J=7.3 Hz; H10), 2.90 (1H; dq; J_1=7.2 Hz, J_2=4.8 Hz; H4), 3.21 (1H; q; J=7.3 Hz; H2), 4.99 (1H; d; J=4.8 Hz; H5), 6.41 (1H; d; J=0.4 Hz; H7), 6.45 (1H; d; J=0.4 Hz; H6), 7.34-7.42 (4H; m; H2', H6', H3', H5'), 7.48 (1H; tt; J_1=6.6 Hz, J_2=2.0 Hz; H4'); *^{13}C NMR [75 MHz, CDCl$_3$, δ(ppm)]:* 10.18 (C9), 10.34 (C10), 49.63 (C4), 53.18 (C2), 83.28 (C5), 92.34 (C1), 108.68 (C7), 110.39 (C6), 132.84 (C4'), 134.83 (C3', C5'), 143.11 (C2', C6'), 142.87 (C1'); *EM [DIP-EI, 70eV, 150°C, m/z(%)]:* 229 (14, M+1), 228 (76, M), 213 (51, M-Me), 185 (10, M-C$_3$H$_7$ o C$_2$H$_3$O), 171 (100, M-C$_4$H$_9$ o C$_3$H$_5$O), 157 (94, M-C$_4$H$_5$O or C$_5$H$_{11}$), 144 (29, M-C$_5$H$_9$O), 128, 115, 95 (3, C$_5$H$_3$O$_2$), 55 (5, C$_4$H$_7$ o C$_3$H$_4$O).; *GC(C):* RT = 18.0 min. *EA*. Found: C 78.89; H 7.07%. $C_{15}H_{16}O_2$ requires C 78.92; H 7.06%.

1-Ethoxycarbonyl-2,4-dimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one.

22a : white solid. *M.P.:* 46-47°C (CH_2Cl_2). *IR [film, ν(cm^{-1})]:* 3630, 3540, 3450, 3400, 3080, 2960, 2955, 2925, 2900, 1735 (C11=0, st), 1710 (C3=O, st), 1630, 1590, 1450, 1370, 1330, 1275, 1240, 1210, 1155, 1130, 1100, 1065, 1030, 980, 960, 890, 855, 810, 730; *^{1}H NMR [200MHz, CDCl$_3$, δ(ppm)]:* 0.90 (3H; d; J=7.0 Hz; H10), 0.93 (3H; d; J=7.0 Hz; H9), 1.27 (3H; t; J=7.1 Hz; H3'), 2.73 (1H; dq; J_1=7.0 Hz, J_2=5.0 Hz; H4), 2.82 (1H; q; J=7.0 Hz; H2), 4.24 (2H; q; J=7.2 Hz; H2'), 4.86 (1H; dd; J_1=5.0 Hz, J_2=2.0 Hz; H5), 6.30 (1H; dd; J_1=6.0 Hz, J_2=2.0 Hz; H6), 6.37 (1H; d; J=6.0 Hz; H7); *^{13}C NMR [50 MHz, CDCl$_3$, δ(ppm)]:* 9.44 (C9), 10.10 (C10), 13.99 (C3'), 49.47 (C4), 52.46 (C2), 61.67 (C2'), 83.15 (C5), 90.37 (C1), 132.15 (C7), 134.12 (C6), 168.10 (C1'), 206.71 (C3); *EM [DIP-EI, 70eV, 150°C, m/z(%)]:* 224 (6, M), 209 (0.7, M-CH3), 178 (18, M-EtOH), 168 (24, M-C$_3$H$_4$O), 150 (8, M-HCOOEt), 140 (30, M-C$_5$H$_9$O). *GC(A):* RT = 12.0 min. *EA*. Found: C 64.24; H 7.35%. $C_{12}H_{16}O_4$ requires C 64.27; H 7.19%.

22b : colourless oil.*IR [film, ν(cm^{-1})]:* 2979, 2941, 2362, 1717 (C=0, st), 1457, 1374, 1322, 1260, 1189, 1133, 1094, 1061, 959, 899, 861, 803, 720; *^{1}H NMR [200MHz, CDCl$_3$, δ(ppm)]:* 1.24 (3H; d; J=7.4 Hz; H9), 1.38 (3H; d; J=7.5 Hz; H10), 1.34 (3H; t; J=7.2 Hz; H3'), 2.32 (1H; q; J=7.5Hz; H2), 2.71 (1H; q; J=7.5 Hz; H4), 4.34 (2H; q; J=7.2 Hz; H2'), 4.85 (1H; d; J=1.5 Hz; H5), 6.27 (1H; d; J=5.7 Hz; H7), 6.33 (1H; dd; J_1=5.7 Hz, J_2=1.8 Hz; H6); *^{13}C NMR [50 MHz, CDCl$_3$, δ(ppm)]:* 17.75 (C9, C10), 49.78 (C2, C4), 81.95 (C1, C5), 133.63 (C6, C7), 213.68 (C3); *EM [DIP-EI, 70eV, 150°C,*

m/z(%)]: 224 (6, M), 209 (0.7, M-CH_3), 178 (18, M-EtOH), 168 (24, M-C_3H_4O), 150 (8, M-HCOOEt), 140 (30, M-C_5H_9O). *GC(A):* RT = 12.4 min. *EA.* Found: C 64.20; H 7.15%. $C_{12}H_{16}O_4$ requires C 64.27; H 7.19%.

***endo*-1-Cyclohexyloxycarbonyl-2,4-dimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one, 23a.** Cycloadduct was obtained as an oil. No *exo* diastereomer was detected. *IR [film, ν(cm^{-1})]:* 2939, 2862, 1715 (C=0, st), 1451, 1380, 1335, 1281, 1248, 1214, 1162, 1137, 1121, 1071, 1038, 1013, 990, 965, 930, 895, 814, 731; *^{1}H NMR [200MHz, $CDCl_3$, δ(ppm)]:* 0.98 (3H; d; J=7.0 Hz; H10), 1.00 (3H; d; J=7.0 Hz; H9), 1.2-2.0 (11H, m; H2', H3', H4', H5', H6', H7'), 2.88 (1H; q; J=7.0 Hz; H2), 2.94 (1H; q; J=7.0 Hz; H4), 4.95 (1H; dd; J_1=4.8 Hz, J_2=1.6 Hz; H5), [4.79 (1H; s; H2' ax.)], 6.36 (1H; dd; J_1=6.0 Hz, J_2=1.6 Hz; H6), 6.46 (1H; d;J=6.0 Hz; H7); *^{13}C NMR [50 MHz, $CDCl_3$, δ(ppm)]:* 9.58 (C9), 10.26 (C10), 23.66, 23.62 (C4', C6'), 25.19 (C5'), 31.37, 31.44 (C3', C7'), 49.64 (C4), 52.73 (C2), 74.38 (C2'), 83.29 (C5), 90.66 (C1), 132.43 (C7), 134.17 (C6), 168 (C1'), 207 (C3); *EM [DIP-EI, 70eV, 150°C, m/z(%)]:* 182 (9, M), 167 (6, M-Me), 149 (19, M-SH), 111 (9, M-C_5H_7O), 100 (55, M-Ch), 83 (6, C_5H_7O or Ch), 55 (100, C_3H_4O); *GC(E):* RT = 33.3 min. *EA.* Found: C 68.74; H 8.12%. $C_{16}H_{22}O_4$ requires C 69.04; H 7.97%.

1-Formyl-2,4-dimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one. Cycloadducts were obtained as a 1.5:1 non-separable mixture of diastereomers **25a** and **25b**. *IR [film, ν(cm^{-1})]:* 3120, 2980, 2940, 2890, 1765 (CH=0, st), 1720 (C3=O, st);*^{1}H NMR [200MHz, $CDCl_3$, δ(ppm)]: inter allia,* 1.42 (6H; d; J=7.0 Hz; H9 y H10), 3.72 (1H; q; J=7.0 Hz; H2), 4.34 (1H; q; J=7.0 Hz; H4), 5.16 (1H; d; J_1=3.3 Hz; H5), 6.39-6.35-6.21 (1H; d; J=3.3 Hz; H6), 7.45-7.41-7.35 (1H; s; H7), 9.03 (1H; s; H11); *GC(C):* RT = 15.1; 14.9; 14.3; 13.6 min.

1-[1-(2,5-Dioxolanyl)]-2,4-dimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one.
26a : colourless oil. *IR [film, ν(cm^{-1})]:* 3600, 3070, 2960, 2920, 2870, 1710 (C=0, st), 1450, 1370, 1230, 1200, 950; *^{1}H NMR [300MHz, $CDCl_3$, δ(ppm)]:* 0.94 (3H; d; J=7.0 Hz; H10), 1.03 (3H; d; J=7.0 Hz; H9), 2.78 (1H; dq; J_1=7.0 Hz, J_2=4.5 Hz; H4), 2.88 (1H; q; J=7.0 Hz; H2), 3.93 (2H; m; H3'), 4.08 (2H; m; H4'), 4.91 (1H; dd; J_1=4.5 Hz, J_2=1.5 Hz; H5), 5.15 (1H; s; H1'), 6.23 (1H; d; J=6.0 Hz; H7), 6.35 (1H; dd; J_1=6.0 Hz, J_2=2.0 Hz; H6); *^{13}C NMR [75 MHz, $CDCl_3$, δ(ppm)]:* 9.89 (C9), 10.81 (C10), 50.00 (C2), 51.53 (C4), 65.62, 66.26 (C3', C4'), 83.38 (C5), 90.37 (C1), 102.99 (C1'), 133.11 (C7), 134.65 (C6), 209.21 (C3); *EM [DIP-CI, NH3, 70eV, 150°C, m/z(%)]:* 314, 259(11, M+N_2H_7), 242 (100, M+NH_4), 229 (7, M), 168 (2, M-C_4H_7 or C_3H_4O), 163 (3, M-$C_2H_5O_2$); *GC(F):* RT = 14.2 min. *EA.* Found: C 64.34; H 7.20%. $C_{12}H_{16}O_4$ requires C 64.27; H 7.19%.

26b : colourless oil.*IR [film, ν(cm^{-1})]:* 3600, 3070, 2960, 2920, 2870, 1710 (C=0, st), 1450, 1370, 1230, 1200, 950; *^{1}H- NMR [300MHz, $CDCl_3$, δ(ppm)]:* 1.02 (3H; d; J=7.0 Hz; H10), 1.3 (3H; d; J=7.0 Hz; H9), 2.30 (1H; q; J=7.0 Hz; H4), 2.95 (1H; q; J=7.0 Hz; H2), 3.93 (2H; m; H3'), 4.08 (2H; m; H4'), 4.73 (1H; d; J=2.0 Hz; H5), 5.13 (1H; s; H1'), 6.20 (1H; d; J=6.0 Hz; H7), 6.32 (1H; dd; J_1=6.0 Hz, J_2=2.0 Hz; H6); *^{13}C NMR [75 MHz, $CDCl_3$, δ(ppm)]:* 9.89 (C9), 16.65 (C10), 49.26 (C2), 49.94 (C4), 65.54, 66.79 (C3', C4'), 83.83 (C5), 89.9 (C1), 103.27 (C1'), 131.72 (C7), 136,29 (C6), 209.10 (C3); *EM [DIP-CI, NH3, 70eV, 150°C, m/z(%)]:* 314, 259(11, M+N_2H_7), 242 (100, M+NH_4), 229 (7, M), 168 (2, M-C_4H_7 o C_3H_4O)., 163 (3, M-$C_2H_5O_2$); *GC(F):* RT = 13.7 min. *EA.* Found: C 64.18; H 7.25%. $C_{12}H_{16}O_4$ requires C 64.27; H 7.19%.

2,4-Dimethyl-1-methoxy-8-oxabicyclo[3.2.1]oct-6-en-3-one.
27a (***cis-endo***): white solid. *M.P.:* 60-61°C (ether). *IR [film, ν(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; *^{1}H NMR [500MHz, $CDCl_3$, δ(ppm)]:* 0.84 (3H; d; J=7.0 Hz; H10), 0.91 (3H; d; J=7.0 Hz; H9), 2.60 (1H; q; J=7.0 Hz; H2), 2.62.(1H; dq; J_1=7.0 Hz, J_2=4.8 Hz; H4), 3.28 (3H; s; OMe), 4.73 (1H; dd; J_1=4.8 Hz, J_2=1.9 Hz; H5), 6.06 (1H; d; J=6.1 Hz; H7), 6.28 (1H; dd; J_1=6.1 Hz, J_2=1.9 Hz; H6); *^{13}C NMR [50 MHz, $CDCl_3$, δ(ppm)]:* 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); *EM [DIP-CI, NH3, 70eV, 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):* RT = 9.1 min. *EA.* Found: C 65.67; H 7.49%. $C_{10}H_{14}O_3$ requires C 65.92; H 7.74%.

27b (***cis-exo***): white solid. *M.P.*= 61-62°C (ether). *IR [film, v(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; *^{1}H NMR [500MHz, $CDCl_3$, δ(ppm)]:* 1.27 (3H; d; J=7.5 Hz; H9), 1.36 (3H; d; J=7.5 Hz; H10), 2.23 (1H, brdq; J_1=7.5 Hz; J_2<1.0 Hz; H4), 2.54 (1H; dq; J_1=7.5 Hz, J_2<1 Hz; H2), 3.42 (3H; s; OMe), 4.67 (1H; d; J=1.9 Hz; H5), 6.09 (1H; d; J=6.0 Hz;H7), 6.33 (1H, dd; J_1=6.0 Hz, J_2=1.9 Hz; H6); *^{13}C NMR [50 MHz, $CDCl_3$, δ(ppm)]:*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); *EM [DIP-CI, NH3, 70eV, 150°C, m/z(%)]:* 182 (3, M), 167 (8, M-CH_3), 153 (6, M-CHO), 125 (37, M-C_4H_9 o C_3H_5O), 111 (100, M-C_5H_{11} o 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):* RT = 8.9 min. *EA.* Found: C 65.82; H 7.61%. $C_{10}H_{14}O_3$ requires C 65.92; H 7.74%.

27c [***trans,***(1S*,2S*)]: colourless oil. *IR [film, v(cm^{-1})]:* 3095, 2977, 2950, 2883, 2837, 1713 (C=O, st), 1650, 1457, 1375, 1337, 1283, 1177, 1098, 1050, 1040, 982, 905, 821, 767; *^{1}H NMR [300MHz, $CDCl_3$, δ(ppm)]:* 1.04 (3H; d; J=6.9 Hz; H9), 1.36 (3H; d; J=7.2 Hz; H10), 2.27 (1H; q; J=7.2 Hz; H4), 2.82 (1H; q; J=6.9 Hz; H2), 3.42 (3H; s; OMe), 4.68 (1H; d; J=2.1 Hz; H5), 6.14 (1H; d; J=6.0 Hz; H7), 6.39 (1H; dd; J_1=6.0 Hz, J_2=2.1 Hz; H6); *^{13}C NMR [50 MHz, $CDCl_3$, δ(ppm)]:* 9.30 (C9), 16.87 (C10), 48.17 (C4), 52.10 (OMe), 54.21 (C2), 80.39 (C5), 120.84 (C1), 131.60 (C7), 138.46 (C6), 214.40 (C3); *EM [DIP-CI, CH4, 70eV, 150°C, m/z(%)]:* 211 (10, M+C_2H_5), 183 (100, M+H), 182 (9, M), 167(2, M-CH_3), 151 (6, M-CH_3O), 127 (2, M-C_4H_7 or C_3H_4O), 95 (7, $C_5H_{11}O$, $C_4H_7O_2$); *GC(C):* RT = 13.6 min. *EA.* Found: C 65.90; H 7.68%. $C_{10}H_{14}O_3$ requires C 65.92; H 7.74%.

2,4-Dimethyl-1-trimethylsilyloxy-8-oxabicyclo[3.2.1]oct-6-en-3-one.

28a : colourless oil. *IR [film, v(cm^{-1})]:* 2960, 1715 (C=0, st), 1450, 1370, 1325, 1300, 1250, 1220, 1195, 1155, 1115, 1090, 1040, 965, 910, 880, 840, 820, 760; *^{1}H NMR [300MHz, $CDCl_3$, δ(ppm)]:* 0.16 (9H; s; OSiMe3), 0.91 (3H; d; J=7.0 Hz; H9), 1.03 (3H; d; J=7.0 Hz; H10), 2.65 (1H; q; J=7.0 Hz; H2), 2.70 (1H; dq; J_1=7.0 Hz, J_2=4.5 Hz; H4), 4.80 (1H; ddd; J_1=4.5 Hz, J_2=2.0 Hz, J_3=0.5 Hz; H5), 6.10 (1H; dd; J_1=6.0 Hz, J_2=1.0 Hz; H7), 6.23 (1H; 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(ppm)]:* 1.50 (OSiMe3), 8.97 (C9), 10.28 (C10), 48.11 (C4), 57.42 (C2), 79.36 (C5), 133.67 (C7), 135.83 (C6), 208.75 (C3); *EM [GC-MS(EI), 70eV, 150°C, m/z(%)]:* 238 (6, M), 163 (M-SiMe3), 149 (16, M-OSiMe3), 91 (16, H_2OSiMe3), 73 (100, SiMe3); *GC(E)*: RT = 18.4 min. *EA.* Found: C 59.94; H 8.63%. $C_{12}H_{20}O_3$ Si requires C 59.96; H 8.39%.

28b : colourless oil.*IR [film, v(cm^{-1})]:* 2960, 1715 (C=0, st), 1457, 1328, 1252, 1219, 1194, 1115, 1084,, 1017, 967, 888; ^{1}H NMR [300MHz, $CDCl_3$, δ(ppm)]: 0.10 (9H; s; OSiMe3), 1.25 (3H; d; J=7.5 Hz; H9), 1.34 (3H; d; J=7.4 Hz; H10), 1.34 (3H; d; J=7.4 Hz; H10), 2.18 (1H; q; J=7.6 Hz; H2), 2.51 (1H; q; J=7.3Hz; H4), 4.63 (1H; d; J=1.8 Hz; H5), 6.06 (1H; d; J=5.9 Hz; H7), 6.22 (1H; dd; J_1=5.9 Hz, J_2=1.9 Hz; H6); *^{13}C NMR [50 MHz, $CDCl_3$, δ(ppm)]:* 1.50 (OSiMe3), 13.23 (C10), 17.89 (C9), 47.73 (C4), 55.39 (C2), 79.91 (C5), 134.36 (C7), 136.74 (C6), 214.31 (C3); *EM [GC-MS(EI), 70eV, 150°C, m/z(%)]:* 238 (6, M), 163 (M-SiMe3), 149 (16, M-OSiMe3), 91 (16, H_2OSiMe3), 73 (100, SiMe3); *GC(E):* RT = 18.2 min. *EA.* Found: C 59.92; H 8.41%. $C_{12}H_{20}O_3$ Si requires C 59.96; H 8.39%.

1-*tert*-Butyldimethylsilyloxy-2,4-dimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one.

29a :colourless oil. *IR [film, v(cm^{-1})]:* 2956, 2933, 2887, 2860, 2362, 2339, 1717 (C=0, st), 1654, 1465, 1362, 1328, 1258, 1225, 1196, 1158, 1115, 1090, 1042, 1007, 967, 938, 913, 874, 839, 816, 749, 679; *^{1}H NMR [200MHz, $CDCl_3$, δ(ppm)]:* 0.07 (3H; s; Me, OSiMe2), 0.18 (3H; s; Me, OSiMe2), 0.61 (3H; d;

J=7.0 Hz; H10), 0.91 (9H; s; OSi^{t}Bu), 1.10 (3H; d; J=7.0 Hz; H9), 2.18 (1H; dq; J_1=7.0 Hz, J_2=4.7 Hz; H4), 2.51 (1H; q; J=7.0 Hz; H2), 4.17 (1H; dd; J_1=4.7 Hz, J_2=1.9 Hz; H5), 5.53 (1H; dd; J_1=5.9 Hz, J_2=1.9Hz; H6), 5.68 (1H; d; J=5.9 Hz; H7); *^{13}C NMR [75 MHz, $CDCl_3$, δ(ppm)]:* -3.12 (Me, OSiMe2),, -2.87 (Me, OSiMe2), 9.06 (C9), 10.30 (C10), 25.65(3 Me, OSi^{t}Bu), 26.24 (C4^{io},OSi^{t}Bu), 48.22 (C4), 57.66 (C2), 79.44 (C5), 114.66 (C1), 133.69 (C6), 136.00 (C7), 209.10 (C3); *EM [DIP-CI, NH3, 70eV, 150°C, m/z(%)]:* 283 (100, M+1), 225 (2, M-^{t}Bu), 198 (2, M-$C_5H_{10}O$), 132 (2, HOSiMe2^{t}Bu); *GC(A):* RT = 13.2 min. *EA.* Found: C 64.01; H 9.21%. $C_{15}H_{26}O_3$ Si requires C 63.79; H 9.28%.
29b. GC(A): RT = 13.4 min.

1-Benzoyloxy-2,4-dimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one.
30a: white solid. *M.P.:* 92-93°C (CH_2Cl_2). *IR [KBr, ν(cm^{-1})]:* 2979, 1737 (C=0, st), 1602, 1455, 1260, 1150, 1117, 1057, 1000, 899, 751, 708; *^{1}H NMR [200MHz, $CDCl_3$, δ(ppm)]:* 1.02 (3H; d; J=7.1 Hz; H10), 1.18 (3H; d; J=7.0 Hz; H9), 2.87 (1H; dq; J_1=7.0 Hz, J_2=4.8 Hz; H4), 3.27 (1H; q; J=7.0 Hz; H2), 5.05 (1H; dd; J_1=4.7 Hz, J_2=1.9 Hz; H5), 6.38 (1H; dd; J_1=6.1 Hz, J_2=1.9 Hz; H6), 6.53 (1H; d; J=6.1 Hz; H7), 7.47 (2H; t; J=7.6 Hz; H4', H6'), 7.61 (1H; tt; J_1=7.6 Hz, J_2=1.4 Hz; H5'), 8.07 (2H; td; J_1=7 Hz, J_2=1.2 Hz; H3', H7'); *^{13}C NMR [50 MHz, $CDCl_3$, δ(ppm)]:* 9.05 (C9), 10.29 (C10), 48.34 (C4), 54.49 (C2), 80.72 (C5), 110.19 (C1), 128.50 (C6), 129.88 (C7), 131.78 (C5'), 133.60 (C4', C6'), 133.84 (C3', C7'), 160.22 (C1'), 207.27 (C3); *EM [DIP-CI, NH3, 70eV, 150°C, m/z(%)]:* 290 (100, M+NH_4+2H), 270 (2, M), 150 (2, M-OCOPh), 95 (11, $C_5H_3O_2$); *GC(C):* RT = 20.5 min. *EA* Found: C 70.47; H 6.24%. $C_{16}H_{16}O_4$ requires C 70.57; H 5.92%.

30b : colourless oil.*IR [film, ν(cm^{-1})]:* 2979, 1723 (C=0, st), 1602, 1453, 1378, 1266, 1177, 1065, 1023, 710; *^{1}H- NMR [200MHz, $CDCl_3$, δ(ppm)]:* 1.34 (3H; d; J=7.5 Hz; H10), 1.42 (3H; d; J=7.6 Hz; H9), 2.32 (1H; q; J=7.5 Hz; H4), 3.48 (1H; q; J=7.6 Hz; H2), 5.30 (1H; d; J=1.9 Hz; H5), 6.40 (1H; dd; J_1=5.6 Hz, J_2=1.9 Hz; H6), 6.70 (1H; d; J=5.6 Hz; H7), 7.49 (2H; q; J=9.0 Hz; H4', H6'), 7.60 (1H; d; J=9.0 Hz; H5'), 8.07 (2H; td; J_1=9 Hz, J_2=2.5 Hz; H3', H7')); *^{13}C NMR [50 MHz, $CDCl_3$, δ(ppm)]:* 13.56 (C9), 17.99 (C10), 47.80 (C4), 53.45 (C2), 80.69 (C5), 111.00 (C1), 128.53 (C6), 129.87 (C7), 133.51 (C5'), 133.64 (C4', C6'), 134.71 (C3', C7'), 164 (C1'), 212.14 (C3); *EM [DIP-CI, NH3, 70eV, 150°C, m/z(%)]:* 290 (100, M+NH_4+2H), 270 (2, M), 150 (2, M-OCOPh), 95 (11, $C_5H_3O_2$); *CG(C):* TR = 18.7 min. *EA* Found: C 70.45; H 6.02%. $C_{16}H_{16}O_4$ requires C 70.57; H 5.92%.

2,4-Dimethyl-1-pivaloyloxy-8-oxabicyclo[3.2.1]oct-6-en-3-one.
31a : white solid. *M.P.:* 80-81°C (CH_2Cl_2) *IR [KBr, ν(cm^{-1})]:* 2975, 2930, 2870, 1740 (C11=O, st), 1710 (C3=0, st), 1475, 1450, 1370, 1335, 1275, 1130, 1075, 1050, 1000, 975, 900, 875, 830, 815, 740; *^{1}H NMR [200MHz, $CDCl_3$, δ(ppm)]:* 0.98 (3H; d; J=7.0 Hz; H10), 1.07 (3H; d; J=7.0 Hz; H9), 1.26 (9H; s; H3', H4', H5'), 2.68 (1H; dq; J_1=7.0 Hz, J_2=4.7 Hz; H4), 2.98 (1H; q; J=7.0 Hz; H2), 4.85 (1H; dd; J_1=4.7 Hz, J_2=1.9 Hz; H5), 6.18 (1H; dd; J_1=6.1 Hz, J_2=1.8 Hz; H6), 6.28 (1H; d; J=6.1 Hz; H7); *^{13}C NMR [50 MHz, $CDCl_3$, δ(ppm)]:* 8.56 (C9), 9.91 (C10), 26.56 (C3', C4', C5'), 39.06 (C2'), 47.92 (C4), 53.94 (C2), 80.20 (C5), 109.25 (C1), 131.09 (C6), 133.57 (C7), 175.72 (C1'), 206.75 (C3); *EM [DIP-EI, 70eV, 150°C, m/z(%)]:* 252 (1, M), 196 (6, M-^{t}Bu), 168 (100, M-CO^{t}Bu), 153 (12, M-OCO^{t}Bu),, 151 (4, M-OCO^{t}Bu), 123, 122, 113, 112, 111, 101 (OCO^{t}Bu); *GC(E):* RT = 17.9 min. *EA* Found: C 66.67; H 8.02%. $C_{14}H_{20}O_4$ requires C 66.65; H 7.99%.

31b : colourless oil.*IR [film, ν(cm^{-1})]:* 2975, 2930, 2870, 1740 (C11=O, st), 1710 (C3=0, st), 1475, 1450, 1370, 1335, 1275, 1130, 1075, 1050, 1000, 975, 900, 875, 830, 815, 740; *^{1}H NMR [200MHz, $CDCl_3$, δ(ppm)]:* 0.99 (3H; d; J=7.1 Hz; H10), 1.07 (3H; d; J=7.0 Hz; H9), 1.26 (9H; s; H3', H4', H5'), 2.79 (1H; dq; J_1=7.3Hz, J_2=5.1 Hz; H4), 3.09 (1H; q; J=7.0 Hz; H2), 4.96 (1H; dd; J_1=4.7 Hz, J_2=1.9 Hz; H5), 6.27 (1H; dd; J_1=6.1 Hz, J_2=1.9 Hz; H6), 6.38 (1H; d; J=6.1 Hz; H7); *^{13}C NMR [50 MHz, $CDCl_3$, δ(ppm)]:* 9.36 (C9), 10.73 (C10), 27.43 (C3', C4', C5'), 39.92 (C2'), 48.78 (C4), 54.79 (C2), 81.06 (C5), 110.06 (C1), 131.85 (C6), 134.42 (C7), 176.02 (C1'), 207.81 (C3); *EM [DIP-EI, 70eV, 150°C, m/z(%)]:* 252 (1, M), 196 (6, M-^{t}Bu), 168 (100, M-CO^{t}Bu), 153 (12, M-

OCO^tBu),, 151 (4, M-OCO^tBu), 123, 122, 113, 112, 111, 101 (OCO^tBu); *GC(A):* RT = 17.6 min. *EA* Found: C 66.60; H 8.11%. $C_{14}H_{20}O_4$ requires C 66.65; H 7.99%.

***endo*-1-Ethoxycarbonyloxy-2,4-dimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one, 32a** . Cycloadduct obtained as a colourless oil. No *exo* diastereomer was detected. *IR [film, $\nu(cm^{-1})$]:* 3514, 3100, 2983, 2941, 2881, 1766 (C11=O, st), 1719 (C3=0, st), 1602, 1457, 1372, 1339, 1245, 1160, 1117, 1090, 1036, 1003, 899, 834, 816, 789, 756, 726, 629; *^1H NMR [300MHz, $CDCl_3$, δ(ppm)]:* 0.98 (3H; d; J=7.2 Hz; H10), 1.09 (3H; d; J=7.0 Hz; H9), 1.32 (3H; t; J=7.2 Hz; H3'), 2.80 (1H; dq; J_1=7.0 Hz, J_2=4.8 Hz; H4), 3.07 (1H; q; J=7.1 Hz; H2), 4.22 (2H; q; J=7.0 Hz; H2'), 4.98 (1H; dd; J_1=4.7 Hz, J_2=1.8 Hz; H5), 6.32 (1H; dd; J_1=6.1 Hz, J_2=1.8Hz; H6), 6.39 (1H; d; J=6.1 Hz; H7); *^{13}C NMR [50 MHz, $CDCl_3$, δ(ppm)]:* 8.79 (C9), 10.23 (C10), 14.01 (C3'), 48.06 (C4), 54.14 (C2), 64.28 (C2'), 80.57 (C5), 110.81 (C1), 133.14 (C6), 133.90 (C7), 151.97 (C1'), 206.93 (C3); *EM [DIP-CI, NH_3, 70eV, 150°C, m/z(%)]:* 258 (100, M+NH_4, 241 (10, M+1), 240 (1, M), 190 (5, M-EtOH-4H), 168 (3, M-COOEt), 151 (1, M-OCOOEt), 95 (3, C_5H_6O), 52 (14, C_4H_4); *GC(A):* RT = 13.6 min. *EA* Found: C 60.20; H 6.74%. $C_{12}H_{16}O5$ requires C 59.99; H 6.71%.

2,4-dimethyl-1-[bis-(*N,N*-dimethylamine)phosphoryloxy]-8-oxabicyclo[3.2.1]oct-6-en-3-one.
33a : white solid. *M.P.:* 81-82°C (CH_2Cl_2). *IR [KBr, $\nu(cm^{-1})$]:* 2937, 1711 (C=0, st), 1461, 1302, 1229, 1158, 1117, 1081, 1000, 924, 882, 822, 760, 683, 511, 471; *^1H NMR [500MHz, $CDCl_3$, δ(ppm)]:* 0.93 (3H; d; J=7.0 Hz; H10), 1.01 (3H; d; J=7.1 Hz; H9), [2.57 (3H; s; Me), 2.59 (3H; s; Me), 2.61 (3H, s; Me), 2.63 (3H; s; Me), OPO(NMe2)2], 2.75 (1H; dq; J_1=7.0 Hz, J_2=5.5 Hz; H4), 2.94 (1H; q; J=7.0 Hz; H2), 4.87 (1H; dd; J_1=5.5 Hz, J_2=2.5 Hz; H5), 6.27 (1H; dd; J_1=6.0 Hz, J_2=2.5Hz; H6), 6.47 (1H; d; J=6 Hz; H7); *^{13}C NMR [75 MHz, $CDCl_3$, δ(ppm)]:* 9.06 (C9), 10.39 (C10), 36.51 (OPO(NMe2)2), 48.03 (C4), 56.07 (C2), 56.16 (C1), 79.98 (C5), 132.99 (C6), 134.27 (C7), 207.82 (C3); *EM [DIP-CI, NH_3, 70eV, 150°C, m/z(%)]:* 320 (1, M+NH_4), 303 (100, M+1), 219 (1, M-C_5H_7OH), 153 (1, M-OPO(NMe2)2), 152 (, M-HOPO(NMe2)2); *GC(A):* RT = 12.9 min. *EA* Found: C 51.74; H 7.42; N 9.32%. $C_{13}H_{23}O_4N_2P$ requires C 51.65; H 7.67; N 9.27%.

33b : colourless oil. *IR [film, $\nu(cm^{-1})$]:* 2937, 2362, 2341, 1715 (C=0, st), 1457, 13302, 1235, 1079, 996, 884, 822, 760, 668; *^1H NMR [200MHz, $CDCl_3$, δ(ppm)]:* 1.34 (3H; d; J=7.5 Hz; H10), 1.37 (3H; d; J=7.5 Hz; H9), 2.22 (1H; dq; J= 7.5 Hz; H4), 2.51 (1H; q; J= 7.5 Hz; H2), [2.58 (3H; s; Me), 2.63 (3H; s; Me), 2.63 (3H, s; Me), 2.68 (3H; s; Me), OPO(NMe2)2], 4.71 (1H; d; J=1.8 Hz; H5), 6.28 (1H; dd; J_1=6.0 Hz, J_2=1.9 Hz; H6), 6.49 (1H; d; J=6 Hz; H7); *^{13}C NMR [75 MHz, $CDCl_3$, δ(ppm)]:* 13.47 (C9), 17.86 (C10), 36.45 (OPO(NMe2)2), 47.55 (C4), 54.80 (C2), 54.89 (C1), 80.26 (C5), 133.92 (C6), 134.56 (C7), 212.72 (C3); EM [DIP-CI, NH_3, 70eV, 150°C, m/z(%)]: 320 (1, M+NH_4), 303 (100, M+1), 219 (1, M-C_5H_7OH), 153 (1, M-OPO(NMe2)2), 152 (, M-HOPO(NMe2)2); *GC(A):* RT = 10.8 min. *EA* Found: C 51.60; H 7.52; N 9.19%. $C_{13}H_{23}O_4N_2P$ requires C 51.65; H 7.67; N 9.27%.

2,4-dimethyl-1-nitro-8-oxabicyclo[3.2.1]oct-6-en-3-one.
34a : colourless oil. *IR [film, $\nu(cm^{-1})$]:* 2937, 2811, 1712 (C=0, st), 1607, 1459, 1372, 988, 924, 880, 822, 760, 680; *^1H NMR [200MHz, $CDCl_3$, δ(ppm)]:* 1.04 (3H; d; J=7.0 Hz; H10), 1.10 (3H; d; J=7.2 Hz; H9), 2.94 (1H; dq; J_1=7.0 Hz, J_2=5.1 Hz; H4), 3.20 (1H; q; J=7.2 Hz; H2), 5.13 (1H; dd; J_1=4.8 Hz, J_2=1.4 Hz; H5), 6.08 (1H; dd; J_1=6.2 Hz, J_2=1.5Hz; H6), 6.63 (1H; d; J=6.1 Hz; H7); *^{13}C NMR [50 MHz, $CDCl_3$, δ(ppm)]:* 8.89 (C10), 10.38 (C9), 48.41 (C4), 54.34 (C2), (C1), 83.42 (C5), 129.81 (C6), 137.18 (C7), (C3); EM [DIP-EI, 70eV, 150°C, m/z(%)]: 197 (1, M), 167 (12, M-NO), 151 (5, M-NO_2), 95 (85, $C_5H_6O_2$), 83 (100, C_5H_7O), 55 (48, C_4H_7 o C_3H_4O); *GC(A):* RT = 15.7 min. *EA* Found: C 54.74; H 5.58; N 7.02%. $C_9H_{11}O_4N$ requires C 54.82; H 5.62; N 7.10%.

34b. GC(A): RT = 14.5 min.

X-Ray structure determination for 27a and 27b:

Diffraction analysis of single crystals of 27a: Six crystals were used for data collection, which are not stable at room temperature. The crystal size alters from (0.1x0.1x0.2) to (0.3x0.3x0.6 mm). Crystals were mounted on a ENRAF-NONIUS CAD4 four-circle diffractometer. Unit cells parameters were determined from automatic centering of 25 reflections ($12 < \Theta < 21°$) and refined by least-squares method. Intensities were collected with graphite monochromatized MoKα radiation, using $\omega/2\Theta$ scan technique. 3437 reflections were measured in the range $1.79 < \Theta < 29.95$; 1786 of which were independent. In the merge process the intensity measured with the crystal less altered was selected. 409 reflections were omited in the refinement process because the high difference between the measured and the calculated intensities, so only 1377 reflections were used in the refinement process, Three reflections were measures every two hours as orientation and intensity control. Lorentz polarization and intensity decay corrections were made.

Diffraction analysis of single crystals of 27b: A prismatic crystal (0.2x0.3x0.4 mm) was selected and mounted on the diffractometer. 2976 reflections were measured in the range $2.58 \leq \Theta \leq 31.03$. 2811 of wich were non- equivalent by symmetry (Rint on I = 0.044). 2372 reflections were assumed as observed applying the condition $I > 2\sigma$ (I). Three reflections were measures every two hours as orientation and intensity control, significant intensity decay was not observed. Lorentz polarization but not absortion corrections were made.

The structures of **27a** and **27b** were solved by direct methods, using SHELXS computer program[18a] and refined by full-matrix least-squares method with SHELX93 computer program[18b] using 943 (**27a**) and 2761 (**27b**) reflections , (very negative intensities were not assumed). The function minimized was $\Sigma\ w\ |\ |Fo|^2 - |Fc|^2\ |^2$. The parameters f, f' and f'' were taken from International Tables of X-Ray Crystallography[18c] . The chirality of structures was defined from the Flack coefficient[18d] . All hydrogen atoms were computed and refined with an overall isotropic temperature factor using a riding model. The experimental parameters for X-ray diffraction analysis of **27a** and **27b** as well as a selection of bond lenghts and angles are quoted respectively in Tables 3 and 4.

Table 3. Crystal Data and Structure Refinement for **27a** and **27b**

Parameters	**Cycloadduct 27a**	**Cycloadduct 27b**
Empirical formula	$C_{10}H_{14}O_3$	$C_{10}H_{14}O_3$
Formula weight	182.21	182.21
Temperature	293(2)°K	225(2)°K
Wavelenght	0.71069 Å	0.71069 Å
Crystal system	Orthorrhombic	monoclinic
Space group	$Pc2_1b$	$P2_1/n$
Unit Cell Dimensions	a= 6.580(4) Å, α = 90°	a= 8.966(4) Å, α = 90°
	b= 22.720(3) Å, β = 90°	b= 10.47(2) Å, β = 109.47(5)°
	c= 12.904(2) Å, γ = 90°	c= 10.612(7) Å, γ = 90°
Volume	1929.1(12) $Å^3$	939(2) $Å^3$
Z	8	4
Density (calculated)	1.255 Mg/m^3	1.289 Mg/m^3
Absorption coefficient	0.092 mm^{-1}	0.094 mm^{-1}
F(000)	784	392
Crystal size	0.1 x 0.1 x 0.2 mm	0.2 x 0.3 x 0.4 mm
Theta range for data collection	1.79 to 29.95°	2.58 to 31.03°
Index ranges	$0 \leq h \leq 9, -1 \leq k \leq 31, 0 \leq l \leq 13$	$-12 \leq h \leq 11, 0 \leq k \leq 15, 0 \leq l \leq 14$
Reflections collected	3437	2976
Independent reflections	1786	2811 (R_{int} = 0.0443)
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2

Table 3. Continuation

Parameters	**Cycloadduct 27a**	**Cycloadduct 27b**
Data/ refined parameters	1377 / 237	2761 / 175
Goodness-of-fit on F^2	0.786	0.894
Final R indices	R1= 0.053, WR2=0.141	R1= 0.0594, WR2=0.1716
Extinction coefficient	0.000(2)	0.20(2)
Largest difference peak and hole	0.115 and -0.093 e. $Å^{-3}$	0.446 and -0.322 e. $Å^{-3}$

Table 4. Selected Bond Lenghts (Å) and Angles (°) for **27a** and **27b**[19]

Bond Lenghts (Å)	**27a**	**27b**	**Bond Angles** (°)	**27a**	**27b**
O2-C3	1.27(2)	1.20(2)	C11-O3-C1	117.7(11)	115.9 (11)
O3-C11	1.36(2)	1.42(2)	C5-O1-C1	106.1(9)	103.2(9)
O3-C1	1.37(2)	1.39(2)	O2-C3-C2	122.8(12)	121.9(14)
O1-C5	1.48(1)	1.44(2)	O2-C3-C4	111.8(12)	118.8(14)
O1-C1	1.53(1)	1.39(2)	C2-C3-C4	124.8(10)	119.3(10)
C2-C3	1.50(2)	1.53(2)	C1-C2-C3	108.6(10)	110.5(11)
C3-C4	1.54(2)	1.48(3)	C1-C2-C9	113.9(10)	113.3(11)
C1-C2	1.49(2)	1.52(2)	C3-C2-C9	109.3(10)	109.3(12)
C2-C9	1.50(2)	1.54(2)	O3-C1-C7	115.5(11)	117.6(11)
C1-C7	1.38(2)	1.52(2)	O3-C1-C2	109.3(11)	109.6(10)
C6-C7	1.42(2)	1.30(2)	C7-C1-C2	118.6(13)	110.3(10)
C5-C6	1.56(2)	1.50(2)	O3-C1-O1	108.0(11)	109.9(9)
C4-C5	1.58(2)	1.53(2)	C7-C1-O1	99.7(10)	102.8(10)
C4-C10	1.48(2)	1.53(3)	C2-C1-O1	104.2(10)	105.9(12)
			C1-C7-C6	114.1(13)	108.5(13)
			C7-C6-C5	104.9(11)	107.1(13)
			O1-C5-C6	100.3(9)	103.4(12)
			O1-C5-C4	105.6(9)	107.8(11)
			C6-C5-C4	103.0(8)	111.3(13)
			C10-C4-C3	124.4(12)	109.7(14)
			C10-C4-C5	110.4(11)	113.3(14)
			C3-C4-C5	110.6(9)	108.2(11)

Acknowledgements. We would like to acknowledge the Spanish Ministry of Education and Science for finantial support, (Grant MEC PB93-0754 and MEC Acciones Concertadas 03.5.08.418.3V.680.15). Also fellowships to P.M.G. from the Catalonian Research Council (CIRIT) and to F.G. from the Spanish Ministry of Education and Science are gratefully acknowledged.

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19. Supplementary material available. Complete crystal data, list of refined coordinates and a complete list of bond distances are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this work. See *Tetrahedron* **40**(2), ii, (1984).

(*Received in UK* 18 *April* 1997; *revised* 20 *June* 1997; *accepted* 26 *June* 1997)